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REPORT OF THE OECD/UNEP WORKSHOP ON THE USE OF MULTIMEDIA MODELS FOR ESTIMATING OVERALL ENVIRONMENTAL PERSISTENCE AND LONG-RANGE TRANSPORT IN THE CONTEXT OF PBTS/POPS ASSESSMENT

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No. 36

Report of the OECD/UNEP Workshop on the Use of Multimedia Models for Estimating Overall Environmental Persistence and Long Range Transport in the Context of PBTS/POPS Assessment

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The work of the OECD related to chemical safety is carried out in the Environment, Health and Safety Programme. As part of its work on chemical testing, the OECD has issued several Council Decisions and Recommendations (the former legally binding on Member countries), as well as numerous Guidance Documents and technical reports. The best known of these publications, the OECD Test Guidelines, is a collection of methods used to assess the hazards of chemicals and of chemical preparations. These methods cover tests for physical and chemical properties, effects on human health and wildlife, and accumulation and degradation in the environment. The OECD Test Guidelines are recognised world-wide as the standard reference tool for chemical testing.

More information about the Environment, Health and Safety Programme and its publications (including the Test Guidelines) is available on the OECD's World Wide Web site http://www.oecd.org/ehs/.

The Environment, Health and Safety Programme co-operates closely with other international organisations. This document was produced within the framework of the Inter-Organisation Programme for the Sound Management of Chemicals (IOMC).

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FOREWORD

This document contains the report from the OECD/UNEP Workshop on the Use of Multimedia Models for Estimating Overall Persistence and Long-range Transport in the Context of PBTs/POPs Assessment, held on 29-31 October 2001 in Ottawa, Canada, together with background papers, presentation summaries, and reports from the three subgroups. The workshop was co-hosted by Environment Canada and the US Environmental Protection Agency.

At the 33rd Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology in February 2002, it was agreed to establish an expert group to follow up on the recommendations from the workshop described in this report, including the development of further guidance on the use of multimedia models.

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1. EXECUTIVE SUMMARY

1. Background and overview

The OECD/UNEP Workshop on the Use of Multimedia Models for Estimating Overall Environmental Persistence and Long-range Transport in the Context of POPs/PBTs Assessment was held in Ottawa, Canada on 29-31 October 2001. The workshop, jointly hosted by Environment Canada and the United States Environment Protection Agency, was attended by 64 experts from 14 OECD Member Countries, the European Commission, the North American Commission for Environmental Co-operation, the United Nations Economic Commission for Europe, the United Nations Environment Programme (UNEP), Business and Industry Advisory Committee, two non-governmental organisations, and OECD Secretariat. Mr. John Buccini (Canada) chaired the workshop.

The purpose of the workshop was to explore the use of multimedia models in chemical screening and assessment for environmental persistence and long-range transport, where single medium approaches are dominant at present. Particular focus was on assessment of persistent, bioaccumulating and toxic (PBT) substances and persistent organic pollutants (POPs). This workshop was one of the activities on environmental exposure assessment under the OECD Chemicals Programme. It was also a part of the UNEP activities toward developing technical tools for implementing the Stockholm Convention on POPs.

At the first plenary session, four experts made keynote speeches on the state of the art of multimedia modelling. These were followed by seven speeches on the views of the users of multimedia models from the policy/user community. Then the workshop broke into three subgroups: (1) application of multimedia models; (2) model design; and (3) data needs. After three subgroup discussion sessions and two feed-back plenary sessions, the final plenary session arrived at a set of overall conclusions and recommendations, including research needs.

2. Summary conclusions

The first objective of the workshop was to summarise the needs for multimedia models in POPs/PBTs assessment. At the opening plenary session, presentations were made about the needs from various international and national initiatives for effective tools to identify, prioritise and assess substances of concern. Regarding long-range transport, it was agreed that multimedia models were the most reasonable way to calculate its potential. Other models that include realistic variation in climatic and geographical variables also provide useful information on long-range transport. Overall persistence can be calculated from a multimedia model based on the environmental release pattern, fate and transport and summing the degradation rates in specific media. It was noted that, for assessment purposes, multimedia estimates of overall persistence could bring additional insight compared to solely basing the assessment on single-media half-lives. Lack of basic knowledge on certain factors influencing environmental fate, including degradation, implies that results relating to overall persistence and the potential for long-range environmental transport should be used with care. This is also implied because

validation of screening-level models of overall persistence and long-range environmental transport can hardly be validated. It was also noted that the distribution of a substance among the environmental media, as calculated using a multimedia model, could be used to determine which media would contain a "realistic presence" of the substance, and therefore which single media half-lives were important in an assessment.

The second objective was to summarise currently available methods/approaches based on multimedia models for estimating overall persistence and long-range transport. The background paper "Introduction to multimedia models" (Annex 3) provides a good summary of such methods and approaches. The report from the subgroup 2 (Annex 6-1) refers to other available models such as more complex transport models. It was concluded that, currently, generic multimedia models could be applied at the screening-level assessment of persistence and long-range transport, especially if these two parameters are evaluated using relative methods (e.g. ranking) rather than absolute values.

The third objective was to evaluate the validity, uncertainty and reliability of multimedia models in estimating overall persistence and long-range transport. It was concluded that sensitivity analysis should be performed to focus on the key variables that would exert the greatest influence on the output. For example, persistence is most sensitive to degradation rates, which at the same time are the most uncertain input parameters. It is important to understand the amount of uncertainty that results from including or not including a parameter, process, mode of entry (i.e. into which environmental media the substance is initially introduced) etc. Regarding validity of multimedia models, it was out of the scope of this workshop to evaluate individual models. Moreover, direct validation of screening-level models for overall persistence and long-range transport potential is difficult if not impossible, since these parameters cannot easily be measured. However, it is possible to evaluate higher-tier models against environmental monitoring data, to learn from that experience, and to feed that information back to the screening-level models to increase confidence in them.

The fourth objective was to summarise and evaluate available methods/approaches that could be used for developing criteria to identify substances of concern. The workshop discussed the possibility of using the parameters of overall persistence and long-range transport potential. There was no agreement on whether these parameters could be used on their own in screening chemicals. It was concluded that if chemical screening is based on overall persistence and long-range transport potential, it should be performed using a ranking approach or an approach that assigns chemicals to classes. Such approaches would incorporate comparing the estimates of overall persistence and long-range transport potential of the chemical of interest with those of "benchmark chemicals".

The fifth objective was to examine and recommend ways in which assessors could identify and obtain the critical data needed to run the models. Specific data needs and their sources were identified in the report from subgroup 3 (Annex 7-1). It was emphasised that data quality should be taken into account in interpreting model results. A data hierarchy scheme should be employed when choosing input data for multimedia models, the highest priority being given to measured data derived using OECD test guidelines.

3. Recommendations

The sixth objective was to discuss how the estimates of overall persistence and long-range transport potential could be incorporated into and enhance ongoing and future risk assessment activities. The workshop made the following six recommendations for future activities.

(i) 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.

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

(iii) 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.

(iv) 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.

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

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

2. RESUME DES CONCLUSIONS DE L'ATELIER

1. Contexte et recapitulatif

L'Atelier OCDE/PNUE sur l'utilisation des modèles multimedia destinés à évaluer la persistance globale dans l'environnement et le transport à grande distance des substances chimiques, dans le cadre de l'évaluation des substances toxiques persistantes bio-accumulables et des polluants organiques persistants (POP), s'est tenu à Ottawa, au Canada, du 29 au 31 octobre 2001. Organisé conjointement par Environnement Canada et l'Agence des Etats-Unis pour la protection de l'environnement, il a accueilli 64 experts venus de 14 pays Membres de l'OCDE, de la Commission européenne, de la Commission nord-américaine de coopération environnementale, de la Commission économique des Nations Unies pour l'Europe, du Programme des Nations Unies pour l'environnement (PNUE), du Comité consultatif économique et industriel (BIAC), de deux organisations non gouvernementales et du Secrétariat de l'OCDE. Il était présidé par M. John Buccini (Canada).

L'objectif de cet atelier était de réfléchir à l'utilisation des modèles multimedia dans l'étude et l'évaluation de la persistance dans l'environnement et du transport à longue distance des substances chimiques, qui obéissent pour l'instant, principalement, à des méthodes ne concernant qu'un milieu à la fois. L'accent a été mis sur l'évaluation des substances toxiques persistantes bio-accumulables et sur les polluants organiques persistants (POP). Cet atelier faisait partie des activités sur l'évaluation de l'exposition de l'environnement, conduites dans le cadre du Programme de l'OCDE sur les produits chimiques. Il relevait en outre des activités du PNUE visant à mettre au point des outils techniques pour mettre en œuvre la Convention de Stockholm sur les POP.

Lors de la première réunion plénière, quatre experts ont dressé le bilan des connaissances acquises à ce jour dans le domaine de la modélisation multimedia. Ensuite, sept exposés ont présenté les points de vue des utilisateurs des modèles multimedia (responsables de l'action des pouvoirs publics et des activités d'évaluation), après quoi l'atelier a été scindé en trois sous-groupes : (1) application des modèles multimedia, (2) conception des modèles et (3) données requises. Au terme de trois sessions de débats en sous-groupes et de deux sessions plénières de synthèse, la réunion plénière finale a abouti à la formulation d'une série de conclusions et de recommandations générales, y compris sur les recherches à entreprendre.

2. Resume des conclusions de l'atelier

Le premier objectif de l'atelier était de faire le point sur les besoins en matière de modèles multimedia dans le domaine de l'évaluation des substances toxiques persistantes bio-accumulables et des POP. Lors de la réunion plénière inaugurale, plusieurs exposés ont été consacrés à la nécessité, dans le cadre de diverses initiatives nationales et internationales, de mettre au point des outils efficaces pour déterminer, hiérarchiser et évaluer les substances concernées. S'agissant du transport à grande distance, il a été convenu que les modèles multimedia constituaient le meilleur moyen de calculer son potentiel. La

persistance globale peut être calculée à l'aide d'un modèle multimediamultimedia en prenant en compte la distribution prévue et en totalisant les taux de dégradation dans des milieux particuliers. Il a été signalé que, dans l'optique d'une évaluation, les estimations de la persistance fondées sur la demi-vie dans un seul milieu ne permettaient pas d'obtenir un résultat aussi proche de la réalité environnementale que les estimations multimedia de la persistance globale. Néanmoins, il a également été noté que la distribution d'une substance dans les différents milieux, telle qu'elle est calculée à l'aide d'un modèle multimedia, pouvait être utilisée pour déterminer "de manière réaliste" ceux d'entre eux où ladite substance serait présente, ce qui permet de dire dans quels milieux il importe d'évaluer les demi-vies.

Le deuxième objectif était de faire le point sur les méthodes/approches fondées sur les modèles multimedia disponibles actuellement pour estimer la persistance globale et le transport à grande distance. Dans le cadre des préparatifs de l'atelier, ces méthodes et approches ont été synthétisées dans un document d'information intitulé "Introduction to multimedia models" (annexe 3). Il a été conclu que, à l'heure actuelle, les modèles multimedia génériques pouvaient être appliqués à l'évaluation de la persistance et du transport à grande distance des substances chimiques au stade du tri, notamment dès lors que ces deux phénomènes sont étudiés au moyen d'une méthode relative (classement, pas exemple) et non pas sur la base de valeurs absolues.

Le troisième objectif était d'évaluer la validité, les lacunes et la fiabilité des modèles multimedia appliqués à l'évaluation de la persistance globale et du transport à grande distance des substances chimiques. Il a été convenu qu'il était nécessaire de réaliser des analyses de sensibilité pour mettre en évidence les variables clés qui exerceraient la plus forte incidence sur les résultats. Par exemple, la persistance est sensible avant tout aux taux de dégradation, qui constituent eux-mêmes les paramètres de départ les plus incertains. Il importe de mesurer le degré d'incertitude qui résulte de la prise en compte ou de l'exclusion d'un paramètre, d'un processus ou d'un mode de pénétration (dans quel milieu la substance concernée est rejeté en premier lieu), etc. S'agissant de la validité des modèles multimedia, il n'était pas question, dans le cadre de cet atelier, d'évaluer chacun d'entre eux. Qui plus est, la validation directe des modèles d'évaluation du potentiel de persistance et de transport à grande distance des substances chimiques, au stade du tri, est difficile voire impossible, dans la mesure où ces phénomènes peuvent difficilement être mesurés. Cependant, il importe d'évaluer les modèles utilisés aux stades suivants en s'appuyant sur des données d'observation de l'environnement, afin d'en tirer des enseignements et d'en tenir compte dans les modèles employés au stade du tri.

Le quatrième objectif était de récapituler et d'évaluer les méthodes/approches disponibles pouvant être utilisées pour définir des critères d'identification des substances à étudier. Les participants se sont penchés sur la possibilité d'employer les paramètres du potentiel de persistance globale et de transport à grande distance. Aucun accord ne s'est dégagé quant à la question de savoir si ces paramètres pouvaient être utilisés seuls dans la sélection des substances chimiques. Il a été conclu que, si la sélection des substances chimiques s'appuie sur le potentiel de persistance globale et de transport à grande distance, elle doit être effectuée à partir d'une méthode de classement ou d'une approche permettant d'affecter les substances chimiques à des catégories. Ces approches comprendraient une comparaison des estimations relatives au potentiel de persistance globale et de transport à grande distance des substances à étudier d'une part et de "substances de référence" d'autre part.

Le cinquième objectif était de se demander et de recommander comment les évaluateurs pourraient définir et obtenir les principales données nécessaires pour faire tourner les modèles. Les données requises et leurs sources sont mises en évidence dans le rapport du sous-groupe numéro trois (annexe 7-1). Il a été souligné que la qualité des données devait être prise en considération dans l'interprétation des résultats. Un système de hiérarchisation des données devrait être employé dans le choix des données à introduire dans les modèles multimedia, la priorité étant accordée en premier lieu aux données mesurées conformément aux lignes directrices de l'OCDE sur les essais.

3. Recommandations generales

Le sixième objectif était de débattre de la façon dont les estimations du potentiel de persistance globale et de transport à grande distance pouvaient être prises en compte dans les activités en cours et futures d'évaluation des risques et les renforcer. Les participants à l'atelier ont formulé les six recommandations suivantes au sujet des activités futures :

(i) L'OCDE devrait étudier les approches utilisées actuellement pour évaluer le potentiel de persistance et de transport à grande distance des substances chimiques, et réfléchir aux moyens qui permettraient de les harmoniser davantage. Afin d'évaluer l'utilité de l'estimation de la persistance globale, des travaux supplémentaires devraient être consacrés à l'évaluation de l'incertitude caractérisant la valeur de la persistance globale en tant que paramètre de conception et d'utilisation des modèles multimilieux.

(ii) L'OCDE devrait entreprendre des activités visant à mettre au point un processus à plusieurs niveaux de classement ou de classification des substances.

(iii) L'OCDE, en coopération avec le PNUE, devrait énoncer à l'intention des utilisateurs des lignes directrices relatives à l'applicabilité et à l'utilité des modèles, axées notamment sur la précision, la disponibilité des données et les adaptations des modèles.

(iv) Les organisations intergouvernementales, les administrations nationales et l'industrie devraient effectuer des comparaisons de leurs modèles multimilieux et de leurs données de surveillance, afin de mesurer les lacunes des modèles, de mettre en évidence les principaux aspects qu'il convient de perfectionner et d'accroître la cohérence entre les différents niveaux de complexité des modèles.

(v) Un ensemble fondamental de modèles multimilieux devrait être mis à la disposition du public et accessible gratuitement.

(vi) Les modèles et les processus d'évaluation devraient être totalement transparents de manière à ce que tous les acteurs concernés puissent pleinement juger des mécanismes du processus de prise de décision.

3. BACKGROUND

1. PBTs/POPs and multimedia models

In recent years chemical assessment activities world-wide have witnessed a strong emphasis on reducing risk from substances that are persistent, bio-accumulative and toxic (PBT). Especially prominent is the subset of PBT substances called persistent organic pollutants (POPs), which are prone to long-range transport (LRT) and subsequent deposition at locations far removed from the sources. A wide range of programs aimed at identification, assessment and control of risks from exposure to POPs/PBTs have emerged at the national and regional and global levels. Prominent examples include the North American Agreement on Environmental Co-operation (NAAEC)'s Sound Management of Chemicals (SMOC) initiative; the new EU White Paper on Chemicals Policy, the strategies on hazardous substances under the Oslo-Paris Convention for the Protection of the Marine Environment of the North-east Atlantic (OSPAR), POPs Protocol under UNECE Convention on Long-range Trans-boundary Air Pollution; and most recently the signing of the Stockholm Convention on POPs under the United Nations Environment Programme (UNEP). Presentations by experts in these programmes are included as Annex 4.

The issue of PBTs/POPs is one of the priority areas in the OECD Chemicals Programme. The OECD Environmental Strategy for the first decade of the 21st Century, adopted in May 2001, calls for national actions to "phase-out the use of slowly degradable and bio-accumulative toxic chemicals in products", and proposes a further OECD work for "developing criteria for identifying inherently unsafe chemicals (e.g. for persistence, bioaccumulation, toxicity)".

Simultaneously, there has been major growth in the range of applications and prominence of multimedia mass-balance models in chemical assessment. The OECD Workshop on the Application of Simple Models for Environmental Exposure Assessment (Berlin, December 1991) discussed the use of multimedia models, and its outcomes were incorporated into the manual for OECD High Production Volume Chemicals Programme (OECD 1993). Multimedia models have been the focus of or played a prominent role in numerous technical workshops, including: Society of Environmental Toxicology and Chemistry (SETAC) workshops on the strengths and limitations of multimedia models, held in 1994 in Leuven, Belgium and Denver, USA (Cowan et al. 1995); and the OECD Workshop on Improving the Use of Monitoring Data in the Exposure Assessment of Industrial Chemicals, held in 1998 in Berlin (OECD 2000). Among the many applications of multimedia models, their use in estimating overall environmental persistence and transport potential has been strongly endorsed by the scientific community, as reflected in the conclusions of experts who participated in the 1998 SETAC Workshop on Evaluation of Persistence and Long-range Transport of Organic Chemicals in the Environment in Fairmont Hot Springs, British Columbia (Klecka et al, 2000). This latter workshop sparked a major research effort to further develop and refine methods for estimating persistence and transport potential, the benefits of which will continue to appear for years to come.

Despite the popularity of these tools and models, outside of the research community POPs/PBTs assessment has continued to rely almost exclusively on the single-medium approach and criteria. If POPs/PBTs activities are to benefit from these tools, it was first necessary to develop a broad consensus on what is the proper role of multimedia models in screening and prioritising new and existing chemicals with respect to PBT characteristics and in assessment of risk, and then to capture this as technical guidance in a form that is clear, specific and practical.

2. Objectives of the workshop

With this as a background, OECD and UNEP co-organised this workshop to bridge the gap between the science of multimedia models and the POPs/PBTs assessment in the real world. Its specific objectives are as follows:

(i) Summarise the user needs of stakeholders in both OECD and non-OECD countries for multimedia models.

(ii) Summarise currently available methods/approaches based on multimedia models for estimating overall environmental persistence and LRT potential.

(iii) Evaluate the validity, uncertainty and reliability of the multimedia model methods for estimating overall environmental persistence and LRT potential.

(iv) Summarise and evaluate available methods/approaches that could be used for developing criteria to identify substances having overall persistence and LRT potential sufficient to warrant concern, in the context of POPs/PBTs assessment.

(v) Examine and recommend ways in which assessors can identify and obtain the critical data needed to run the models.

(vi) Discuss ways in which these estimates of overall environmental persistence and LRT potential can be incorporated into and enhance ongoing and future risk assessment activities.

The workshop focused on how measures of overall environmental persistence and LRT potential, estimated using multimedia fate models, can be integrated into risk assessment. Certain ancillary issues, especially the shortage of substance-specific data needed for modelling and how this problem can be solved, were also addressed. The intent was not to address specific policy or recommend specific numerical criteria for identifying substances as POPs/PBTs, but it was aimed to arrive at recommendations on the most important technical issues, which were expressed in a way that would facilitate implementation.

3. Organisation of the workshop

At OECD, the plan for this workshop was first proposed by the United States Environmental Protection Agency (USEPA) at the 8th meeting of the Task Force on Environmental Exposure Assessment (Solna, Sweden, September 2000), and after the endorsement by the Task Force, at the 31st Joint Meeting of the Chemicals Committee and the Working Party on Chemicals (Paris, November 2000).

UNEP is interested in developing scientific tools for implementing the Stockholm Convention on POPs, especially for evaluating persistence and long-range transport in the process of addition to the list of POPs. Therefore, it agreed to co-organise the workshop with OECD.

The Steering Group for the workshop was established with members nominated by OECD Member countries and observer organisations. The list of its members is attached as Annex 1-3.

In preparation for the workshop, the Steering Group, together with invited experts, developed a set of documents that were distributed in advance. Mackay et al. wrote a background paper (Annex 3), which provided a good introduction to multimedia models and was written to be understandable by non-experts. Bonnell, Mackay et al. and Harner developed issue papers on the use of models (Annex 5-2), modelling (Annex 6-2) and data needs (Annex 7-2) respectively.

4. Workshop structure

The workshop was organised around a series of plenary and subgroup discussion sessions. The opening plenary reviewed the objectives and offered the views of a selected number of experts on the state of the art of multimedia models followed by the views of the users. After the opening plenary the participants broke into three subgroups to address the specific issues listed below and to present their discussion ideas in plenary. The workshop ended with a closing plenary session where the workshop's conclusions and recommendations were agreed.

Subgroup 1: Application of models for overall persistence and long-range transport

Issue 1: Estimating overall environmental persistence and LRT Potential – When? How? Why?

Under what circumstances is it appropriate or necessary to calculate overall persistence and LRT potential using a multimedia model? What are the various descriptors used to represent overall persistence and long-range transport potential? What methods are available for calculating the various descriptors of overall persistence? What methods are available for estimating a chemical's propensity to be transported long distances via the atmosphere? When should LRT via water be considered and what methods/measures are available? Detailed guidance is needed on where, when and how to use multimedia models and which information from them, and how that information can be used by assessors.

Issue 2: How to use the estimates of overall persistence and LRT potential from these models

There are two fundamental approaches for using the estimates of overall persistence and LRT potential of substances, e.g., to identify PBTs/POPs. These are relative or ranking methods and absolute (e.g., fenceline) approaches. Given that it has been observed that while the absolute values of overall persistence and LRT distance differ between models, the relative ranking of substances is often similar (Wania and Mackay, 2000), when would relative or absolute approaches be most suitable? In the relative approach recognised benchmark substances could be used as criteria to identify PBT/POPs. In this case, if the calculated overall persistence or LRT potential of a substance is greater than that of the benchmark substance, it would be designated as sufficiently persistent or having sufficient LRT for assessment purposes. In the absolute approach, temporal and spatial criteria are used so as not to exceed residence times and travel distances of concern. What are the advantages and disadvantages of this approach, considering the wide range of POPs/PBTs assessment activities referred to above? What are currently available approaches/methods for determining absolute criteria and their strengths and limitations? What combinations of relative and absolute approaches might be used in a tiered or stepwise assessment of either overall persistence and/or LRT potential?

Subgroup 2: Model design

Issue 3: Design aspects of models for estimating overall persistence and LRT potential

There are aspects of model design that may be closely linked with the policy or regulatory context within which the model will be used and with the differences in the estimates of overall persistence and LRT potential produced by them. The objective of this discussion is to identify key aspects of, and provide recommendations for, model design. Some important aspects of these multimedia models to be discussed include: 1) number of media included; 2) the advantages/disadvantages of linked multimedia models versus a single multimedia model; 3) size, volume or relative proportion of environmental media; 4) how variations in environmental conditions (e.g. temperature) and chemical properties are handled; and 5) what constitutes a valid loss process (e.g., burial in sediment and soil, transformation, advection). Another critical design consideration is if, how and when characteristics of the modelled environment should be tailored to specific model applications. Guidance on these issues is needed if models are to be integrated into the assessment process.

Issue 4: Reliability, sensitivity, uncertainty and robustness of models for estimating overall persistence and LRT potential

Models for estimating the overall persistence and LRT potential should be evaluated before using them in the identification of PBT/POP substances. Understanding the sensitivity and robustness of the relative ranking of substances produced by the various multimedia models is important especially for those rankings near any potential benchmark substance or absolute rank criteria. The quality of the underlying multimedia model should be assured in terms of its external and internal validity before it is used in regulatory applications. Monitoring data and results from more sophisticated models could be compared to the ranking of substances to evaluate validity. The outcome of this session is a guidance on how users can judge the suitability for a specific application of existing models based on their respective strengths and limitations with regard to each of these topics. Statements about each of the representative models regarding their current status, strengths, and limitations on each of these topics are included.

Subgroup 3: Data needs

Issue 5: Data needs for models for estimating overall persistence and LRT potential

Multimedia models need a variety of input data. First, the various data needs are summarised and the most critical ones identified, based on sensitivity analysis and experience. The focus of subsequent discussion is on which of these data needs can be met with available methods and which data needs are not adequately met by existing methods. In each case any available methods and databases for meeting these needs are identified and the strengths and limitations of each method or database are described. In those cases where existing methods or data are considered inadequate, recommendations for research are identified. Currently recognised critical needs are for reaction half-lives for the individual environmental media and the emissions patterns or mode of entry of the substance into the environment.

4. OVERVIEW OF THE WORKSHOP

1. Participants and bureau members

The workshop was attended by 64 participants from 14 Member Countries, the European Commission, the North American Commission for Environmental Co-operation, the UN Economic Commission for Europe, the UNEP, Business and Industry Advisory Committee (BIAC), non-governmental organisations, and OECD Secretariat. The list of participants is attached as Annex 1-1.

The workshop was designed so that the plenary and each subgroup would consist of a balanced mix of expertise, especially between:

- Assessors–individuals responsible for assessment of chemical substances for PBT properties, i.e., in the actual implementation of national, regional and global programs; and

- Model developers and users–primarily individuals in the research community or closely allied with it, who are the technical experts in modelling of overall persistence and LRT potential.

Mr. John Buccini (Canada) chaired the workshop, and Mr. Eisaku Toda of OECD and Mr. Bo Wahlström of UNEP served as rapporteurs. Together with them the chairpersons and rapporteurs for the subgroups and other members of the Steering Committee and authors of the issue papers composed the bureau for the workshop, which met from time to time during the workshop to plan and manage the progress of the workshop.

2. Opening

The chairman opened the meeting and welcomed the participants to Ottawa. He noted the timeliness of the meeting in view of the recently adopted Stockholm Convention on POPs and several ongoing national and regional programmes within the OECD to address the issue of persistent, bio-accumulating and toxic substances.

Ms. Libby Harrison, OECD Secretariat, presented the objectives of the workshop within the OECD Chemicals Programme. She also noted that this was a joint OECD-UNEP workshop and expressed her pleasure in having non-OECD countries represented at the workshop. She underlined the importance of the subject in the OECD programme and pointed to the fact that activities on less degradable bio-accumulating substances were specifically addressed in the OECD Environmental Strategy.

Mr. Gunnar Bengtsson, Chairman of the Joint Meeting, addressed the participants and noted that chemicals manufacturing was shifting to non-OECD countries, therefore the opening up of workshops such as this one to non-OECD participants was very appropriate. He also noted that as tariffs to trade were decreasing, non-tariff barriers would become more important and that this would lead to an

increased demand for standardised methods for assessing and managing chemicals across the globe. He also noted that the subject of this workshop was linked to and underpinned almost all the sub-programmes under the OECD Chemicals Programme.

3. Plenary presentations 1: state of the art of the science

The opening plenary session was divided in two parts. The first session was intended to set the stage for the discussions in the working groups and bring all participants up to speed on the state of the art of the science on multimedia models for estimating overall persistence and long range transport, while the second was devoted to the views of the users of the results of the modelling. All the summary texts provided by the speakers are attached as Annex 4.

The first speaker, Mr. Don Mackay of Trent University, Canada, gave an overview of the multimedia models, their features and application. He noted that multi-compartment models although they needed more data also had a higher degree of fidelity. The essential compartments to include were air, water, soil and sediment while others; e.g. vegetation might be included as needed. He described in some detail the characteristics of single and multiple compartment models and the information that could be derived from them. He stressed that modelling is only as accurate as the data put into the models, that the models should be able to describe their accuracy and be transparent.

Mr. Frank Wania, University of Toronto, presented a comparative study of different models based on a common set of data for 26 chemicals. These data were distributed to research groups working on multimedia models, which were asked to calculate overall persistence and long range transport as absolute values and relative ranking. The results clearly showed that agreement of absolute values could not be achieved, while the different models gave better agreement on relative ranking, suggesting that benchmark substances might be used. He then presented a further study comparing two multimedia models for predicted LRT potentials of PCBs. He also introduced the concept of Arctic Accumulation Potential as a parameter for designating POPs and noted that with time oceanic transport might become relatively more important than air transport.

Mr. Michael Matthies, University of Osnabrück, Germany described the concept of Characteristic Travel Distance (CTD) and its relationship to overall persistence. He noted that stickiness was an important factor in determining CTD e.g. for dioxins and furans. He described the sensitivity of the CTD determination to various factors and stressed the importance of sensitivity and uncertainty analysis in evaluating data from multimedia models. He noted that temperature changes could affect CTD either way depending on how much half-life and volatility was altered. In concluding, he noted that the ranking of substances was robust if the variability was similar and those uncertainties were particularly important in the fail-pass region, but not for very persistent or little persistent substances.

Mr. Dick Sijm, National Institute of Public Health and the Environment, the Netherlands, presented a thought starter on the risk dimension of PBT classification. He reminded the participants of the need to include the risk dimension, e.g. effects and emission rates. He underscored the need to look at specific emission scenarios and those properties that contributed most to persistence. He also suggested that chemicals should be ranked not only on intrinsic properties, but also on extrinsic properties e.g. patterns of use and sources of emissions.

4. Plenary presentations 2: views of the users

Mr. David Stone, representing UN Economic Commission for Europe (UNECE), gave a short background on the POPs protocol of the UNECE Convention on Long-range Transbounday Air Pollution and the procedure for adding substances to the protocol. He noted that although multimedia

models would not replace existing processes for identifying new substances, they could play a supportive role in it.

Mr. Bo Wahlstrom, UNEP, described the recently adopted Stockholm Convention on POPs and the stepwise procedure for adding new POPs to the convention. He noted that the use of models was actually mentioned in the Convention text under the screening criteria for long-range transport, but that they could also be of use in estimating persistence for chemicals with few data. The results from models could drive generation of measured data for the later stages of in depth assessment.

Mr. Jack de Bruijn, European Chemicals Bureau, and Mr. Ulrich Claussen, German Federal Environmental Agency, presented the European perspectives for POPs/PBTs assessment. Mr. Bruijn explained the strategies of the European Union on POPs, PBTs and very persistent/very bioaccumulating substances in the new White Paper on Chemicals Policy. He also explained the common EU/OSPAR approaches on risk assessment for marine environment. He stressed the need for measured data in screening and assessment of POPs/PBTs. Mr. Claussen described the selection and prioritisation procedures for hazardous substances under OSPAR Convention.

Mr. Sam Sasnett, USEPA, gave the North American view on the usefulness of multimedia models in assessment of chemicals. He saw some promise in these methods, particularly in supporting risk management and prevention, but also expressed concern as to their added value in determining persistence and informing the risk assessment.

Ms. Kay Fox, BIAC, presented industry's view and noted that although these models can contribute to the regulatory process they need to be based on sound scientific principles and appropriately validated. She cautioned against using data from models as measures of risk and the need for management of the chemicals. She also stressed that actual emission patterns and quantities should be used whenever available. Monitoring and measured data should be prepared according to international guidelines and used as much as possible.

Finally, Mr. Romeo Quijano, IPEN, gave a personal perspective on the importance of a precautionary approach in addressing chemicals assessment. He noted some aspects that were important to the NGO community, e.g. the need to be preventive, reverse onus of proof, elimination as a goal, transparency and openness and a need-based assessment process.

5. Subgroup sessions

Ms. Christina Cowan-Ellsberry, BIAC, presented a briefing on the objectives of the subgroups and process for reporting from the subgroups. Then the workshop broke into three subgroups, which met in the afternoon of Day 1, after the plenary session on Day 2, and before the plenary session on Day 3.

The leaders of the subgroups are as follows. The list of members of the subgroups is attached as Annex 1-2.

Subgroup 1: Application of multimedia models for overall persistence and LRT potential
Chairperson: Mr. Michael Matthies, University of Osnabrück, Germany
Rapporteurs: Mr. Bob Boethling, USEPA
Mr. Martin Scheringer, ETH Zürich, Switzerland

Subgroup 2: Model design
Chairperson: Mr. Don Mackay, Trent University, Canada
Rapporteurs: Ms. Christina Cowan-Ellsberry, BIAC

Mr. Andreas Beyer, University of Osnabrück, Germany
Ms. Deborah Bennett, Harvard School of Public Health, US

Subgroup 3: Data needs for use in multimedia models
Chairperson: Mr. Burkhard Wagner, Federal Environment Agency, Germany
Rapporteurs: Mr. Tom Harner, Environment Canada
Mr. Pat Kennedy, Environmental Protection Agency, US
Ms. Kathrin Fenner, ETH Zurich, Switzerland

6. Interim reports from the subgroups (Day 2)

The plenary session in the morning of Day 2 reviewed the progress of the subgroups. A representative of each subgroup made a brief presentation on their work so far. This was followed by a time for comments and questions first by the members of the same subgroup, and then by those from other subgroups. Mr. Bob Boethling, Mr. Don Mackay and Mr. Pat Kennedy presented the progress of subgroups 1, 2 and 3 respectively.

One of the cross-cutting issues that emerged from the discussion in this session is the issue of validation of generic multimedia models. A question was raised about if and how a generic model could be validated for parameters that could not be measured easily, such as overall persistence or LRT potential. It was suggested that while direct validation was difficult, a "feed-back validation" may be possible by validating more detailed models against measured data, and using that information to increase the credibility of generic models.

At the end of this session, it was agreed to task the bureau to identify the core elements from the subgroup conclusions and draft the overall conclusions and recommendations to be discussed at the end of the workshop.

7. Final reports from the subgroups (Day 3)

On Day 3, all the subgroup discussion finished before the coffee break, and the subsequent plenary session reviewed the conclusions and recommendations from the subgroups. The participants agreed that presentations by subgroup leaders should take place in the following order: Subgroup 2 (modelling), Subgroup 3 (data needs) and then Subgroup 1 (application).

Ms. Chris Cowan-Ellsberry presented the work by Subgroup 2. The most important conclusion from the groups was that multimedia models could currently be used with confidence at the screening-level assessment of overall persistence and LRT especially if these two parameters are evaluated via ranking and not absolute values, for non-polar, non-ionising substances and polar non-ionising substances. LRT potential should not be expressed in terms of kilometres as this could result in users assuming that this represented a real distance. The group recommended that tiered approaches should be used for evaluating overall persistence and LRT potential, that a core set of models for screening evaluation should be developed, that guidance be written for users on model applicability and fitness for purposes, and that intercomparison of multimedia models with varying complexity should be carried out. The research needs identified include, among others, expanding model application beyond non-polar, non-ionising substances and polar non-ionising substances, and clarifying how and when the vegetation compartment should be included.

Mr. Pat Kennedy presented the outcomes from Subgroup 3. Some of the important conclusions from the group are that persistence is most sensitive to degradation rates, which are at the same time the most uncertain model input parameters; that a concerted international effort for using multimedia models for screening persistence and LRT is lacking; and that there is a considerable uncertainty in the absolute estimation of overall persistence and LRT potential. The group recommended to use a data hierarchy

scheme for choosing input data starting from the measured data using OECD test guidelines, then measured data from other acceptable methods, QSAR estimation and expert judgement/default values; and that OECD should encourage the incorporation of multimedia model-based screening of persistence and LRT in international programmes based on agreed guidelines. The group also identified a number of research needs.

Mr. Bob Boethling presented the conclusions from Subgroup 1. Whereas the utility of LRT potential was not questioned, the added value of using the actual estimate of overall persistence in regulatory assessment schemes was less clear. Overall persistence and LRT potential might be most effectively used in a ranking approach rather than with absolute criteria, and in a multi-tiered approach that proceeds from simple to more complex models. The group recommended that inter-model comparison exercises should be conducted to improve consistency of predictions obtained from different models, and to give guidance for regulatory purposes. The group also identified research needs such as investigation of degradation rates and the uncertainty that can be generated by using environmental properties for different climatic zones.

At the end of the morning session, Ms. Libby Harrison explained the process and the timing for the drafting, commenting and publishing the report of the workshop.

8. Closing plenary session

In this closing session, the participants reviewed and discussed paragraph by paragraph the draft overall conclusions and recommendations from the workshop, which had been prepared during the lunchtime bureau meeting. The paragraphs were reworded and new sentences were inserted on the spot, reflecting the discussions and agreements during this session.

A number of important arguments were raised here. These include: what added value the estimate of overall persistence had, and how variable the absolute values and ranking were depending on the model parameters and choice of models. Conclusions of the plenary discussion on these issues are reflected in the overall conclusions and recommendations.

After this review process, the workshop adopted the overall conclusions and recommendations as proposed and amended.

At the end of the session, Jeanette Southwood made a statement that she requested to be recorded. Her statement was as follows: "NGOs are concerned that substances can be nominated only by the signatories under the Stockholm Convention. It is possible that harmful substances will not be nominated because no individual government is interested in doing so. Provision should be made for nominations by other parties such as NGOs. NGOs are also concerned that bureaucratic inertia may slow the decision-making process. For example, dossiers prepared by industry on High Production Volume (HPV) chemicals may undergo prolonged review by OECD prior to public release. All such documents should be released on the Internet for public comment as the documents become available and prior to final evaluations by OECD."

9. Closing

The participants thanked Mr. John Buccini for his excellent chairmanship, the members of the workshop bureau and the steering group for their leadership and preparatory works, OECD and UNEP for the efficient secretariat support, Canada and USA for hosting the workshop, and the staff of Environment Canada for their hospitality. The chairman closed the workshop by thanking all the participants for their active contribution.

5. OVERALL CONCLUSIONS

1. What are the needs for multimedia models in assessment of POPs/PBTs?

A considerable number of global, regional and national activities for reducing risks by POPs/PBTs require effective tools for identifying, prioritising and assessing substances of concern either individually (e.g. Stockholm Convention on POPs, new chemicals, pesticides) or from among thousands of chemicals.

It is agreed that multimedia models are the most reasonable way to calculate the long-range transport potential. (This parameter is referred to as LRTP hereinafter.)[1]

For persistence, the single-medium half-life approach is largely used especially at a screening level. However, for more realistic assessment, there is a need to consider partitioning, which is ignored in the single-medium approach. The distribution of the substance among the compartments (as calculated using a multimedia model) and the "significance" of the compartment in the calculation of overall persistence can be used to indicate which media-specific half-lives should be used to indicate persistence for chemical screening.

Overall persistence in the environment is dependent on the mode of entry, the degradation rates in various environmental media and the distribution of the chemical in the environment. A measure of overall persistence (P_{OV}) can be calculated from a multimedia model, incorporating the predicted distribution and degradation rates.

2. What methods/approaches are currently available?

The methods and approaches currently available for estimating P_{OV} and LRTP are summarised in the background paper by Mackay et al. A core set of models that can be used in the screening evaluation should be developed, rather than aiming at one model to be used for all classes of chemicals. Subgroup 2 gave recommendations on the desirable characteristics of such screening level models.

It is concluded that generic multimedia models, currently, can be applied at the screening-level assessment of persistence and LRTP, especially if these two parameters are evaluated via ranking and not absolute values.[2] Multimedia models are primarily adequate for non-polar non-ionising substances,

1. After the workshop, Henrik Soren Larsen proposed an additional sentence: “Other models that include realistic variation in climatic and geographical variables also provide useful information on long-range transport.”

2. After the workshop, Henrik Soren Larsen proposed an additional sentence: “Lack of basic knowledge on certain factors influencing environmental fate, including degradation, implies that results relating to overall persistence and the potential for long-range environmental transport should be used with care.”

and polar non-ionising substances. The applicability of models to polar non-ionising substances is limited by the general lack of availability of inputs. (See section 6.)

Tiered approaches should be used for evaluating overall persistence and LRTP. These approaches build from limited data to more reliable and/or complex data, and from simple generic models to more detailed models.

3. Sensitivity, uncertainty and validity

Sensitivity of multimedia models needs to be analysed for all input parameters, because the model output can only be as good as the data used in the model. The sensitivity of parameters may vary with the chemical. Highest quality data should be used especially for sensitive parameters.

Sensitivity analysis should be performed to focus on the key variables which exert the greatest influence on the output. For example, persistence is most sensitive to degradation rates, which at the same time are the most uncertain input parameters.

It is important to understand the amount of uncertainty that results from including or not including a parameter, process, compartment, mode of entry or scenario in the screening level model.

It is recommended that evaluation of higher tier models against environmental monitoring data be conducted in order to learn from experience, and use this information to increase the confidence in screening level models.

4. Use of multimedia models in POPs/PBTs identification

Some participants considered that P_{OV} and LRTP could be used on their own when screening chemicals, while others thought they must be combined with other properties such as bioaccumulation and toxicity.

If chemical screening is based on P_{OV} and LRTP, it should be performed using a ranking approach or an approach involving assigning chemicals to classes. These should incorporate “benchmark chemicals” (i.e. a defined set of chemicals with which to compare the estimates of P_{OV} and LRTP) as a means to relate these characteristics of known persistent and mobile substances. It was concluded that determining absolute or “cut-off” criteria for P_{OV} and LRTP was difficult, if not impossible, because of the uncertainty of what these thresholds should be, how they may be determined (e.g. the choice of model, etc. can determine the value of P_{OV} or LRTP), what they mean or how they could be used.

It was strongly noted that ranking is also dependent on choice of model, choice of parameters and mode of entry. However, if the number and the relative size of the model compartments and the mode of entry are kept equal, various level III models (i.e. steady-state conditions but non-equilibrium between compartments) will give similar rankings with respect to P_{OV} and LRTP.

5. Use of multimedia models in risk assessment

Multimedia models, P_{OV} and LRTP provide useful information for use in risk assessment and should be incorporated into these activities by both governments and industry. For example, multimedia models can be used in exposure assessment to indicate the media most likely to be affected and resulting exposure pathways, the geographic location of affected areas, and the time scale of exposure.

6. Availability and quality of data for multimedia models

Typically more data are available to run multimedia models for pesticides than for industrial chemicals.

Whereas multimedia models can be applied to all climate zones, data are lacking for some zones and some models may require refinement.

A data hierarchy scheme should be employed when choosing input data for multimedia models. Priority is given to:

- Measured data derived using OECD test guidelines
- Measured data derived from other acceptable methods
- Extrapolation/Interpolation from measured data on structurally similar chemicals (i.e. closest analogues)
- Reliable QSAR estimation
- Expert judgement/Default values

Data quality should be taken into account in interpreting model results. If further investigations are warranted input data should be replaced by more reliable data, e.g. experimental data, particularly for degradation.

6. RECOMMENDATIONS

It is recommended that OECD should:

- Review the current approaches used for assessment of persistence and LRTP, and identify opportunities for more harmonised approaches;
- Undertake activities to develop a tiered process for ranking or classification of substances; and
- Develop, in co-operation with UNEP, guidance for users on model applicability and fitness for purposes including information on accuracy, data availability and model adaptations.

With regard to the first point above, in order to explore the certitude of using P_{OV} in the context of global decision making, further work should be carried out to evaluate the uncertainty in the value of P_{OV}, depending upon the:

- mode of entry;
- characteristics of compartments (including volume and temperature);
- number and type of compartments;
- processes included in the compartments; and
- intrinsic fate related properties.

It is recommended that intergovernmental organisations, national governments and industry should undertake inter-comparison of geo-referenced models and other multimedia models of varying levels of complexity as well as comparison to monitoring data to understand the model uncertainty and identify key needs for refinement as well as adding consistency across the various complexity of models.

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

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. RESEARCH NEEDS

Further research is needed particularly in the following areas.[3]

- Improve model applicability to chemicals beyond the non-polar non-ionising substances and polar non-ionising substances for which we have the most confidence with the existing screening level tools.

- Examine novel means for deriving degradation rates in the environment by exploiting existing historical monitoring data.

- Develop empirical relationships that can be used to characterise the multimedia partitioning of non-polar non-ionising chemicals and polar non-ionising chemicals.

- Examine better description of input data such as deposition rate to surfaces, and partitioning/degradation related to vegetation.

- Examine temperature dependence for key physical/chemical properties, degradation rates and partition coefficients.

- Assessing the importance of the OH-radical degradation pathway for chemicals that are associated with aerosols or particles.

- Investigate and/or collect degradation rates and geographical/environmental parameters for different climatic zones.

- Attempt to develop an estimate of uncertainty and variability of input parameters.

3 . After the workshop, Henrik Soren Larsen proposed an additional research need: "Investigate the importance of mass transport in water and air of substances adsorbed on particles and on aerosols, in that regard including degradation rates of substances adsorbed and investigate the relative importance of LRT by the hydrosphere including transport on the water surface."

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ANNEX 1-2: SUBGROUP MEMBERS

Subgroup #1: Application of models for overall persistence and LRT	Subgroup #2: Model design and sensitivity	Subgroup #3: Data needs for use in multimedia models
Michael Matthies (Chair) Bob Boethling (rappo) Martin Scheringer (rappo) Mark Bonnell (author) Gunnar Bengtsson Mike Collins Ian Cousins Jack De Bruijin Sergey Dutchak Kay Fox Ted Kuchniki Henril Soren Larsen Chris Lee-Steere Jean-Marie Libre Pong-gyun Park Romeo Quijano Sam Sassnet Jeanette Southwood David Stone Noriyuki Suzuki Bo Wahlström	Don Mackay (chair/author) Andreas Beyer (rappo) Chris Cowan-Ellsberry (rappo) Bill Adams Debbie Bennet Ray Beauchamp Sylvain Bintein Ulrich Claussen Maria Doa John Gannon John Harman Alan Irving Kevin Jones Gerhard Lammel Dong-soo Lee Clemens Mensink John Panagopoulos Bruce Rodan Victor Shatalov Dick Sijm Peter Borgen Sorensen	Burkhard Wagner (chair) Tom Harner (rappo/author) Pat Kennedy (rappo) Dave Brooke James Cowles Régis Farret Kathrin Fenner Todd Gouin Diana Graham André Lecloux Hiroshi Matsumoto Paul Miller David Niemi Velu Senthil Heather Simmons Pieter van de Most Frank Wania Takashi Watanabe

Note: John Buccini, Don Gutzman, Libby Harrison and Eisaku Toda do not belong to subgroups.

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ANNEX 2: WORKSHOP AGENDA

Monday 29th October 2001

08h30 **1. Opening**

Mr. John BUCCINI, Environment Canada, will make a welcoming address.
Ms. Libby HARRISON, OECD, will remind the participants of the background and the objectives of the Workshop.

08h50 **Opening plenary session**

Chairperson: Mr. John BUCCINI, Environment Canada, Canada
Rapporteurs: Mr. Eisaku TODA, OECD
Mr. Bo WAHLSTRÖM, UNEP

2. Keynote speeches (15 minutes each)

2-1 An introduction to multi-media models: their features and applications
by Mr. Don MACKAY, Trent University, Canada

2-2 Comparison and evaluation of several LRT assessment models
by Mr. Frank WANIA, University of Toronto, Canada

2-3 Sensitivity, uncertainty and reliability of overall persistence and LRT potential
by Mr. Michael MATTHIES, University of Osnabrück, Germany

2-4 Risk dimension of PBT classification
by Mr. Dick SIJM, National Institute of Public Health and the Environment, the Netherlands

10h30 COFFEE BREAK

10h50 **3. Presentations on the views of users** (10 minutes each)

POPs Protocol of the LRTAP Convention
By Mr. David STONE, UNECE

Stockholm Convention and the future POPs Review Committee
By Mr. Bo WAHLSTRÖM, UNEP

European policies on POPs/PBTs
By Mr. Jack DE BRUIJN, European Chemical Bureau, EU and Mr. Ulrich CLAUSSEN, Federal Environment Agency, Germany

A co-ordinated North American governmental perspective

By Mr. Sam SASNETT, Environmental Protection Agency, US

An industry perspective
By Ms. Kay FOX and Mr. Bill ADAMS, BIAC

Precaution and the assessment of POPs under the Stockholm Convention
By Mr. Romeo QUIJANO, University of the Philippines Manila

12h30 LUNCH BREAK

14h00 **4. Briefing on the objectives and procedures of subgroups**
By Ms. Chris COWAN-ELLSBERRY, BIAC

14h20 **5. Subgroup session**

Workshop participants will break into three subgroups. Subgroup discussion should be directed to arriving at conclusions and recommendations on the questions raised in the issue papers and the subgroup agenda (attached).

Subgroup 1: application of models for overall persistence and LRT potential
Chairperson: Mr. Michael MATTHIES, University of Osnabrück, Germany
Rapporteurs: Mr. Bob BOETHLING, Environmental Protection Agency, US
Mr. Martin SCHERINGER, Federal Institute of Technology, Switzerland
Discussion issues:
- Estimating overall environmental persistence and LRT potential – when, how and why
- How to use the estimates of overall persistence and LRT potential from these models

Subgroup 2: model design and sensitivity
Chairperson: Mr. Don MACKAY, Trent University, Canada
Rapporteurs: Ms. Chris COWAN-ELLSBERRY, BIAC
Mr. Andreas BEYER, University of Osnabrück, Germany
Discussion issues:
- Design aspects of models for estimating overall persistence and LRT potential
- Reliability, sensitivity, uncertainty and robustness of models for estimating overall persistence and LRT potential

Subgroup 3: data needs
Chairperson: Mr. Burkhard WAGNER, Federal Environment Agency, Germany
Rapporteurs: Mr. Tom HARNER, Environment Canada, Canada
Mr. Pat KENNEDY, Environmental Protection Agency, US
Discussion issues:
- Data needs for models for estimating overall persistence and LRT potential

15h30 COFFEE BREAK

15h50 **5. Subgroup session (continued)**
The discussion on the first day should be reported back to the Tuesday morning plenary session. (10 min presentation) Each subgroup should be prepared for this.

18h00 **Adjourn for the day**

Tuesday 30th October 2001

08h30 **6. Plenary: review of subgroup discussion**

Chairpersons/rapporteurs of the three subgroups will make 10-minute presentations on their discussions on the previous day. Issues to be further explored in the following subgroup session will be identified.

09h30 COFFEE BREAK

09h50 **7. Subgroup session**

12h30 LUNCH BREAK

14h00 **7. Subgroup session (continued)**

15h30 COFFEE BREAK

15h50 **7. Subgroup session (continued)**

Subgroup should present their reports, including a brief record of discussion, conclusions and recommendations, at the Wednesday morning plenary session (10-15 min presentation). For this, subgroups should finish all the substantial discussion on Tuesday.

18h00 **Adjourn for the day**

Wednesday 31st October 2001

08h30 **8. Subgroup session: review of draft subgroup reports**

Discussion at this session is limited to comments on the accuracy of draft report. No substantial points should be re-opened here.

09h30 COFFEE BREAK

09h50 **9. Plenary: review of subgroup reports**

Chairpersons/rapporteurs of the three subgroups will make 10-15 minute presentations on their conclusions. The participants will discuss the elements of the conclusions and recommendations from the Workshop.

12h00 LUNCH BREAK

14h00 **10. Plenary: Conclusions, recommendations and further actions**

The participants will agree on conclusions, recommendations and further actions.

16h00 **Close**

Subgroup 1: Application of Models for Overall Persistence and LRT Potential Agenda

Chairperson: Michael MATTHIES, University of Osnabrück, Germany
Rapporteurs: Bob BOETHLING, Environmental Protection Agency, USA
Martin SCHERINGER, ETH Zürich, Switzerland

Brief Introduction of working group participants (background, expertise, expectations, interests)

Objectives of Subgroup 1

- Summarise the user needs of stakeholders in both the OECD and non-OECD countries for multimedia models,
- Summarise currently available methods/approaches based on multimedia models for estimating overall persistence and LRT potential,
- Evaluate possible approaches to establishing pass/fail criteria, including uncertainties of model outcomes and criteria,
- Discuss ways in which these estimates of overall persistence and LRT potential can be incorporated into and enhance ongoing and future risk assessment activities.

Agreement on Agenda (additions, deletions, time allocations, priorities)

Discussion Questions

1. What is the potential role of MM models in POPs/PBTs assessment in both OECD and non-OECD countries?

- Participants should briefly present tools and approaches in national/international organization to identify POPs/PBTs.
- Brief explanation of the terminology and definitions.
- Under what circumstances is it appropriate or necessary to calculate some measure of overall persistence and LRT potential?

2. What methods/models are currently available to estimate overall persistence and LRT potential?

- Why use multimedia models to estimate persistence and LRT potential?
- What are the various descriptors used to represent overall persistence and LRT potential?
- What methods are available for calculating the various descriptors of overall persistence?
- What methods are available for estimating a chemical's propensity to be transported long distances via the atmosphere?
- When should LRT via water be considered and what methods/measures are available?
- Are multimedia models equally applicable to all climates (e.g. moderate vs. tropical vs. polar)?

3. How to use the estimates of overall persistence and LRT potential from these models for chemical screening?

- What does it mean when a substance has a high LRT potential in chemical screening?
- If a substance is not expected to have a significant presence in a medium, do half-life criteria for that medium need to be considered for determining persistence?

- Can a similar idea be used for determining when estimates of LRT potential should used in chemical screening? If not, when should LRT estimates be used in chemical screening?
- When should estimates of overall persistence vs. estimates of single media half-lives be used to screen substances for persistence?

4. What approaches are developed to using overall persistence and LRT potential in chemical screening?

- What methods/approaches for developing fail/pass criteria are available that can be used to identify substances having overall persistence and LRT potential sufficient to warrant concern?
- When would a relative vs. absolute approach be more appropriate to screening chemicals for LRT potential and $P_{OVERALL}$?
- When can a combination of approaches be used?
- If a relative approach is to be used to screen substances for LRT and $P_{OVERALL}$, how might this be done?
- Is it reasonable to establish absolute criteria for LRT and $P_{OVERALL}$ for chemical screening and how might this be done?
- What is the validity/sensitivity/robustness of the screening process when applying relative or absolute fail/pass criteria?

5. How to use the estimates of overall persistence and LRT potential from these models in human and ecological risk assessment?

- How can estimates of LRT and $P_{OVERALL}$ be used to assess potential for human exposure?
- How can estimates of LRT be used in human and ecological risk assessment?
- How can estimates of $P_{OVERALL}$ be used to help assess potential for risk?
- Participants should be encouraged to share their own experiences (briefly!) in assessing exposure and risk for POPs/PBTs.

6. Are there any other issues for using LRTP and $P_{OVERALL}$?

- What scale of assessment should these models be able to address?
- How should estimates of LRTP and persistence from more than one model be considered?
- What is the relative importance of using a generic model vs. a model that can be adapted or modified for specific circumstances?

Tentative Time Schedule

- Complete questions 1 and 2 by end of Monday
- Complete questions 3 and 4 by noon of Tuesday
- Complete questions 5 and 6 by end of Tuesday
- Final report discussion and approval completed on Wednesday morning

Expected Outcomes

- Short presentations of discussions from Monday and Tuesday
- Summary on workshop discussions
- Recommendations for using overall persistence and LRT potential in chemical screening of POP/PTBs
- Recommendations for using overall persistence and LRT potential in human and ecological risk assessment
- Recommendations for further research

Subgroup 2: Model design and sensitivity Agenda

Chairperson: Don MACKAY, Trent University, Canada
Rapporteurs: Chris COWAN-ELLSBERRY, BIAC
Andreas BEYER, University of Osnabrück, Germany

Brief Introduction of working group participants (background, expertise, expectations, interests)

Objective
To summarise the current status and provide perspective on the design aspects of multi-media models and on the reliability, sensitivity, uncertainty and robustness of these models for estimating overall persistence and long-range transport potential within anticipated regulatory applications. Based on this information develop a list of research needs and recommendations that will improve the reliability and suitability of these models within the anticipated regulatory applications.

Agreement on Agenda (additions, deletions, time allocations, priorities)

Discussion Questions

1. What classes of chemicals can be evaluated?

   - Current limitations of models with regard to application to specific classes of chemicals
   - Recommendations on how to expand this range of applicability to other classes of chemicals
   - Research needs that must be addressed before models can be applied to additional classes of chemicals

2. What media should be included?

   - Assuming that air, water and soil /sediment are the basic media, when should other media be included?
   - How best do we treat dispersed particles in air and water?
   - When should vegetation be added, if ever?
   - Segmentation of air and/or soil into layers or sub-media? Use a substance specific soil depth?
   - Guidance on when to consider adding or sub-dividing media

3. What loss processes should be included in the estimation of overall persistence?

   - Should loss processes include reversible loss processes and/or inter-media transfer processes?
   - Inclusion of advection, transport to stratosphere, sediment burial?

4. Should we recommend models for estimation of overall persistence?

   - Do we need Level II or III models, single or multiple unit world models, dynamic or steady-state models?
   - Are the recommendations dependent on the regulatory application's needs?
   - What are the recommended dimensions, characteristics of the environment and generic versus spatially explicit environment?
   - Do we need to consider temperature correction?
   - Does the model use of accept mode-of-entry data?

5. Which genre of LRT model should be used and when?

- When could each of the three approaches for estimating LRT be most applicable (e.g., connected multi-media, langrangian and expanded box approaches)?
- What measure should be used to represent LRT?
- When should a generic versus specific environment be used?
- How should variations in environmental conditions during transport (e.g., temperature) be handled?

6. LRT in air and/or water?

- Typically the LRT in air over land has been considered, under what conditions and for which type of chemicals should LRT in water be evaluated?
- What special considerations are needed for evaluating LRT in fresh and/or sea water?

7. What about model reliability, sensitivity, uncertainty and robustness when estimating overall persistence and LRT for a chemical?

- Difference between sensitivity and uncertainty?
- How much uncertainty in the estimates of overall persistence and LRT can be expected for a given model? What is acceptable?
- Will this level of uncertainty impact the reliability and robustness of the model for regulatory application?
- How can the uncertainty be reduced? Better estimates of environmental conditions? Better estimates or algorithms for inter-media transfer? Or better estimates of chemical properties? What is priority and how is this determined for a specific chemical?

8. What approach (tiered or not) can be used in the assessment of overall persistence and LRT based on the genre of model used and the availability and reliability of chemical data? This overlaps with Working Group 1 and thus will be primarily comments on their recommendations from a model design perspective.

Tentative Time Schedule

- Compete Questions 1 to 4 by end of Monday
- Complete Questions 5 to 7 by noon of Tuesday
- Complete remaining questions by end of Tuesday with final report discussions and approval completed on Wednesday AM.

Note: This agenda is not meant to preclude a alternative of faster initial review of all questions to gain an impression of overall scope, then to return to address specific issues in more detail. We anticipate that the agenda will evolve somewhat during the discussions.

Expected Outcomes

- Short presentations of discussions from Monday and Tuesday
- Summary of working group discussions on each question including identified research needs and recommendations. We will seek to write, preview, revise and generally approve a document addressing all the issues. Any differences of opinion will be included in the document.

Subgroup 3: Data needs for use in multimedia models
Agenda

Chairperson: Burkhard WAGNER, Federal Environment Agency, Germany
Rapporteurs: Tom HARNER, Environment Canada, Canada
Pat KENNEDY, Environmental Protection Agency, US

Brief Introduction of participants (background, expertise, expectations, interests)

Objectives of Subgroup 3

The objectives of Subgroup 3 are to identify the data needs, availability, sources, and quality indicators of data for:

- Screening models for overall persistence and long-range transport potential
- Chemical substance characteristics
- Environment characteristics
- Mode of entry and emission rates

Agreement on Agenda (Additions, deletions, time allocations, priorities)

Discussion Questions

1. Data Needs (industrial chemicals, pesticides)

   - What are the critical chemical characteristics that must be specified for multimedia models? These may include physical chemical properties, abiotic and biotic degradation rates, partitioning constants, deposition rates, other removal rates, etc; which OECD Test Guidelines can be used, interpretation of test data for use in model.
   - To the characterise the mode of entry and emission rates for a chemical sufficiently for use in a multimedia model, what information must one have about chemical loading (frequency, amount, averaging time) and the media to which release occurs? When are default assumptions about mode of entry and emission rates appropriate and when are they not appropriate?
   - What are the data needs for environmental characteristics (i.e. meteorological parameters and characteristics of the physical environment) that are needed when using multimedia models? Some multimedia models provide defaults for environmental characteristics data. Are these defaults generally acceptable for purposes of screening chemicals as potential PBTs/POPs?

2. Data Availability and Data Sources

   - What data for chemical characteristics are typically the easiest to obtain and what are the sources of this data? What data for chemical characteristics are typically the most difficult to

obtain and what are the options for obtaining this data? What can be done to make it easier to obtain data on chemical characteristics? Can/should QSARs be used, when experimental data are lacking? Temperature dependence of test data

- What data for mode of entry and emission rates is easiest to obtain? What data is most difficult to obtain? What can be done to make it easier to obtain data on modes of entry and emission rates?
- What data for environmental characteristics is easy to obtain and what are the sources of this data? What data for environmental characteristics are difficult to obtain and what are the options for obtaining this data? What can be done to make it easier to obtain data on environmental characteristics?

3. Guidance for Characterising the Quality of Multimedia Model Input Data and Outputs for Regulatory Use

- Are there key data elements that should always be included in a characterisation of input data quality? Is there a simple way to identify key data elements?
- When characterising the quality of input data, what characteristics of the data should be addressed?
- Which data are most uncertain and lead to uncertainty in results?
- What are the characteristics of monitoring data that make it useful for evaluating the validity of multimedia model estimates of overall environmental persistence and long-range transport?

4. Conclusions and Recommendations

- What does the Subgroup conclude?
- What does the Subgroup recommend?
- Which research needs can be identified?

Tentative Time Schedule

- Complete agenda items 1 by end of Monday
- Complete agenda items 2 and 3 by the afternoon coffee break on Tuesday
- Complete agenda item 4 and start subgroup report by end of Tuesday
- Review and amend subgroup report Wednesday morning

Note: This agenda is not meant to preclude an alternative or faster review of all questions to gain an impression of the overall scope.

Expected Outcomes

- Short presentations of discussions from Monday and Tuesday in plenary
- Summary of working group discussions on each agenda item including conclusions, recommendations, identified research needs. We shall seek to write, preview, revise and generally approve a document addressing all issues. Any differences of opinion will be included in the document.

ANNEX 3: INTRODUCTION TO MULTIMEDIA MODELS

Final Report Prepared As A

Background paper for OECD Workshop

Ottawa, October 2001

including

A LIST OF DEFINITIONS RELATING TO PERSISTENCE

AND LONG-RANGE TRANSPORT

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July 2001

CEMC Report No. 200102

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- 3.4 Extension to multiple compartments
- 3.5 Connected multimedia models

4 Concentration, fugacity and Levels I to IV

5 Evaluation of persistence

6 Evaluation of long-range transport

7 Intensive and Extensive quantities: the road from hazard to risk

8 Conclusions

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APPENDIX 1 A List of Definitions Relating to Persistence and Long-range Transport

APPENDIX 2 Relevant Websites

EXECUTIVE SUMMARY

This report is designed to introduce the reader to multimedia mass balance models, especially their use for estimating persistence and long-range transport. The incentives for using models are discussed. The nature and structure of real and evaluative compartmental or box models is described for single and multiple box systems, including the various methods by which individual multimedia models are linked linearly, in a circular configuration, nested one within another, or as a network. The use of concentration and fugacity is outlined, as is the concept of increasingly complex Level I, II, III, and IV models.

Approaches for evaluating persistence are described and it is suggested that the most useful expression of persistence is the reaction residence time deduced from Level II or Level III models. Approaches for evaluating long-range transport are discussed including the use of spatial range and a characteristic travel distance. These quantities can be calculated using multimedia box models or Lagrangian models. A brief account is given of the differing data requirements for assessing hazard and risk.

Appendix 1 lists generally accepted definitions of a number of terms used in this context. Appendix 2 gives relevant website addresses.

1 INTRODUCTION

This report is designed to provide background information on multimedia models (MMMs) and in particular show how they may be used to estimate persistence (P) and potential for long-range transport (LRT). Such estimations are components of the assessment process for persistent, bioaccumulative and toxic (PBT) substances, which are also referred to as persistent organic pollutants (POPs). This document is designed to set out the fundamental principles underlying MMMs and bring all participants to a common level of understanding. A supplementary list of definitions is appended.

2 WHY ARE MODELS NEEDED?

It is well established that certain chemicals, when discharged to the environment, can persist for a sufficiently long period of time (months and years), can travel considerable distances (1000s of km) and can migrate between the available media of air, fresh and marine waters, soils, sediments, vegetation and other biota, including humans. The environment is complex in nature and is continually changing, thus chemical fate is correspondingly complex. It is impossible to describe, or even know, the fate of chemicals accurately, but it is believed that the broad features of chemical fate can be understood and even predicted, provided that sufficient information is available on certain key chemical and environmental properties. Notable among these properties are partitioning properties, which control how the chemical is distributed at equilibrium between media, such as air and water and reactive properties, that govern how fast the chemical reacts or degrades (usually expressed for convenience as a half-life in each environmental medium). An essential point is that these properties vary enormously in magnitude from chemical to chemical, i.e. by a factor of a million or more, thus chemical behaviour is correspondingly different by such a factor. Environmental conditions such as temperature, sunlight intensity, rainfall and soil and vegetation types also vary greatly.

The combination of variability between chemicals and between environments creates such complexity that the human mind cannot readily survey the set of properties and forecast how a specific chemical is likely to behave.

Certain attributes of chemicals in the environment can be measured directly, notably concentrations. Other attributes cannot be measured directly, notably fluxes such as evaporation rates, persistence and distance travelled. They can only be estimated by using models. We thus need the assistance of a calculating tool that will accept the available input data, process them and give relevant output. This is the role of the MMM. Its predictions are not likely to be highly accurate (i.e. rarely better than a factor of two in accuracy), but they can be consistent, repeatable, transparent and they can be validated to some extent by comparing predictions with observations.

It is difficult to conceive how assessments of P and LRT can be done consistently and openly without the use of such models.

The problem is to identify which models are best suited to addressing the various tasks, how they should be tested and applied, and how their accuracy can be assessed. In recent years, these models have been used to address the following diverse tasks:

- Comparison of relative fates of different chemicals.
- Identification of important fate processes.
- Estimation of overall persistence and residence times.
- Estimation of potential for LRT.
- Estimation of environmental concentrations and exposures.
- Determination of bioaccumulation in organisms and food webs.
- Evaluation of likely recovery times of contaminated environments.
- Checking the consistency of monitoring data.
- Screening and prioritising chemicals.
- In general, as a decision support tool documenting the sources and nature of contamination and feasible remedial strategies.

Clearly, since a range of models is available, guidance is required on which model to use, or develop for which purpose.

3 MODEL STRUCTURES

3.1 Eulerian, Lagrangian and diffusion systems

Modellers set up their equations in several formats depending on the objective. Most common in this context are compartment, box or Eulerian models in which the environment is divided or segmented into a number of volumes or boxes, which are fixed in space and are usually treated as being homogeneous, i.e. well-mixed, in chemical composition. This has the advantage that only one concentration need be defined per box. Another (Lagrangian) approach that is widely used in atmospheric and river modelling, is to define a parcel of air or water and follow it, and the chemical in it, in time as the parcel moves from place to place. There are also situations where there is marked heterogeneity in concentration, and it is preferable to set up diffusion/advection/reaction differential equations and solve them either numerically or analytically. This is often done when describing chemical migration in sediments and soils, but it can also be applied to atmospheric dispersion, aquatic and oceanic systems. *In principle, all approaches should give the same, or similar results.* Here we focus primarily on compartmental models because it is likely that they will be most commonly applied in the regulatory context. For some purposes Lagrangian models may be used when evaluating LRT in air or water. Diffusion models can be valuable when seeking a general picture of chemical fate in the global atmosphere or oceans, or when estimating the near-source dispersion of emitted chemicals.

3.2 Models of "real" and "evaluative" systems

When there are data on chemical properties, inputs and concentrations in a well-identified region, it is possible to set up a model describing this site-specific situation. Models are routinely applied in rivers, lakes, soils, biota and air pollution studies. Validation is possible by comparing the model output with observations. MMMs have been set up for regions, nations, continents and even the global system. These can be referred to as models of *"real"* systems.

Another family of models is the *"evaluative"* models in which the environment is fictitious i.e. it does not correspond to a particular area, but it is realistic. The fate of a variety of chemicals can be evaluated in such models. The same equations are used in real and evaluative models; only the environmental parameters are different. This approach is particularly attractive for international regulation purposes because the assessment is not in a specific region; it is general. Examples are the EQC model of Mackay et al. (1996) CalTox by McKone et al. (1993) and the SimpleBox model included in the European Union System for the Evaluation of Substances (EUSES) model used in the European Union (EC, 1996). Table 1: lists a number of available models used to predict persistence and long-range transport.

Table 1: Models used to predict contaminant persistence and long-range transport.

Model	Reference	Description
BENNX	Bennett et al., 1998, 1999	Persistence and long-range transport models
CalTox	McKone, 1993	Level III evaluative model developed in California, includes exposure
ChemCAN	Mackay et al., 1991	Level III regional model with a database of Canadian regional environments
Chemrange and SCHE	Scheringer et al., 1996 and 1997	Circular multi-box model for calculating persistence and long-range transport
CoZMo-POP	Wania et al., 2000a	Regional model specifically for large drainage basins or coastal environments
ELPOS	Beyer and Matthies, 2001a	Modified EUSES/SimpleBox to calculate overall persistence, CTD in air and water
EQC	Mackay et al., 1996	Level I, II and III calculations in a single model, fixed environment
GloboPOP	Wania et al., 1993, 1999a and 1999b	Global model
HELD	Held (in press)	3D version of the SCHE model
Level II	Mackay, 2001	Level II model with a user-defined environment
Level III	Mackay, 2001	Level III model with a user-defined environment
PENX	Pennington and Ralston, 1999, Pennington (in press)	PEN1: Steady-state concentration based model, has been used by the EPA PEN2: Heuristic-based approach
SimpleBox	Van de Meent, 1993	Level III regional model that is used in EUSES
TAPL3	Beyer et al., 2000 Webster et al., 1998	Transport and persistence Level III model with user-defined environment, fixed emissions
VDMX	Brandes et al., 1996 Van de Meent, 1993	Persistence and LRT models based on SimpleBox
WANIA	Wania, 1998	Three compartment (air, water, soil) Level III fugacity model.
WANX	Wania, 1998	WAN1:Includes global scale advective loss processes WAN2: Does not include advection

3.3 The single compartmental mass balance

The first step in model development is to divide the environment into a number of compartments of defined volume that are fixed in space. Considering first a single compartment as shown in Figure 1, it is possible to set out the input and output processes. Included can be discharge or emission, advective inflow in air or water (and the corresponding advective outflow), diffusion to and from adjacent compartments, formation from other chemical species and degrading reactions to form other chemical species. The mass balance principle first enunciated by Lavoisier states that the rate of inventory change of the mass of chemical in the volume must equal the total rate of chemical input minus the total rate of output. Mathematically this is expressed by the differential equation

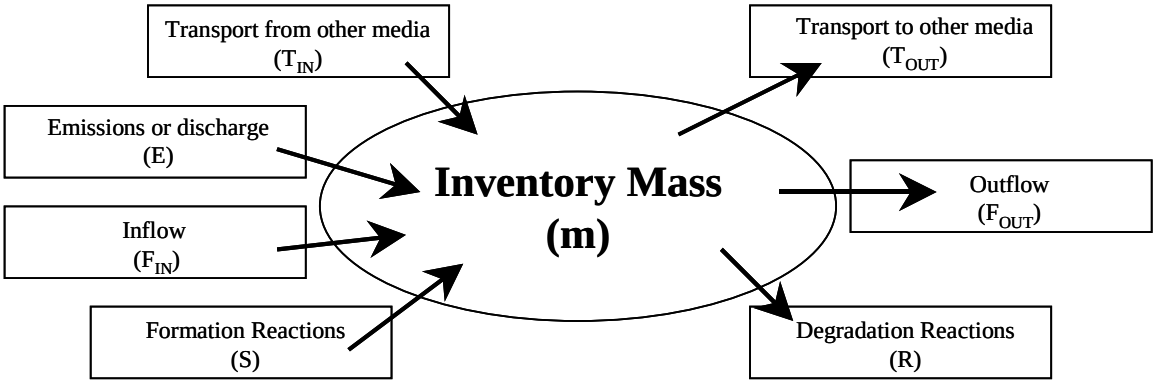
$dm/dt = d(VC)/dt$ = input rate - output rate (with units such as g/h)

where m is mass in the compartment (e.g. g), V is volume (e.g. m^3) and C is concentration (e.g. g/m^3). This is the same equation as applies to cash in a bank account, i.e. change in funds per month equals monthly income less monthly expenditure. A particularly useful and simple version applies when the inventory is fairly constant with time, and thus the derivative on the left side is small or zero. Input rates then equal output rates under steady-state conditions. The advantage of making this steady-state assumption is that the mathematics become algebra rather than calculus.

The next task is to predict the various output process rates as a function of the chemical's concentration. If the input rates are known and all output rates can be expressed as a function of concentration, then the mass balance equation can be used to calculate the chemical concentration and hence the mass of chemical in the box and the rates of the various loss processes. This is also illustrated in Figure 1.

An important quantity is the persistence of the chemical. This can be expressed as the ***residence time*** of the chemical in the box, which is best calculated at steady-state. This is the mass of chemical in the box divided by the total rate of output (or input when steady-state applies). Under unsteady-state, or dynamic conditions, a ***characteristic time*** can be calculated similarly as the mass divided by the output rate. This is the average time that the chemical spends in the single compartment or box and is a first indication of persistence. It is possible to calculate a residence time attributable to reaction and other loss processes such as outflow both individually and collectively. Here we use the word persistence as generally expressing the longevity of the chemical in the environment. Residence time, characteristic time and half-life have specific mathematical definitions.

When calculating persistence, not all loss processes are relevant. Outflow by advection is not a permanent environmental loss process. It only transports a chemical from one environmental location to another. On the other hand, reaction eliminates a chemical from the environment permanently and completely. If the only loss is by reaction with a half-life $t_{1/2}$, then the rate of reaction is VCk_R where k_R is $0.693/ t_{1/2}$ and is the rate constant. The residence time τ is then $(VC)/(VCk_R)$ or $1/k_R$ and equals $t_{1/2}$ /0.693. In this case $t_{1/2}$ is 69% of τ. Some models consider loss processes other than reactions as irreversible losses, e.g. sediment burial or transport to the stratosphere.



$$\frac{dm}{dt} = T_{IN} + E + F_{IN} + S - (T_{OUT} + F_{OUT} + R)$$

Where $m = VC$

V = volume

C = concentration

If :

$T_{OUT} = VCk_T$ NOTE : All rates can be calculated from VCk

$F_{OUT} = VCk_F$ Where k is the rate constant

$R = VCk_R$

Then :

$$\frac{dVC}{dt} = T_{IN} + E + F_{IN} + S - VC(k_T + k_F + k_R)$$

$$\text{at steady state } \frac{dm}{dt} = \frac{dVC}{dt} = 0$$

Thus :

$$C = \frac{T_{IN} + E + F_{IN} + S}{V(k_T + k_F + k_R)}$$

$$\text{Residence Time} = \frac{\text{Inventory}}{\text{Output Rate}} = \frac{m}{VC(k_T + k_F + k_R)} = \frac{1}{k_T + k_F + k_R}$$

Figure 1 Derivation of expressions for compartmental concentrations at steady-state using rate constants.

3.4 Extension to multiple compartments

If the model consists of two connected boxes as in Figure 2, the same approach can be applied twice, once to each box, and to the combination of the two boxes, i.e. the system as a whole. The residence time in each box or in the system of two boxes is a simple extension of the single box approach. Overall persistence in a multimedia system can be expressed using the residence time in the system without considering advective losses:

$$\tau_{OR} = m_{total} / R_{total} = m_{total} / (m_1k_1 + m_2k_2 + \ldots) = (\Sigma f_i \cdot k_{Ri})^{-1} \qquad (1)$$

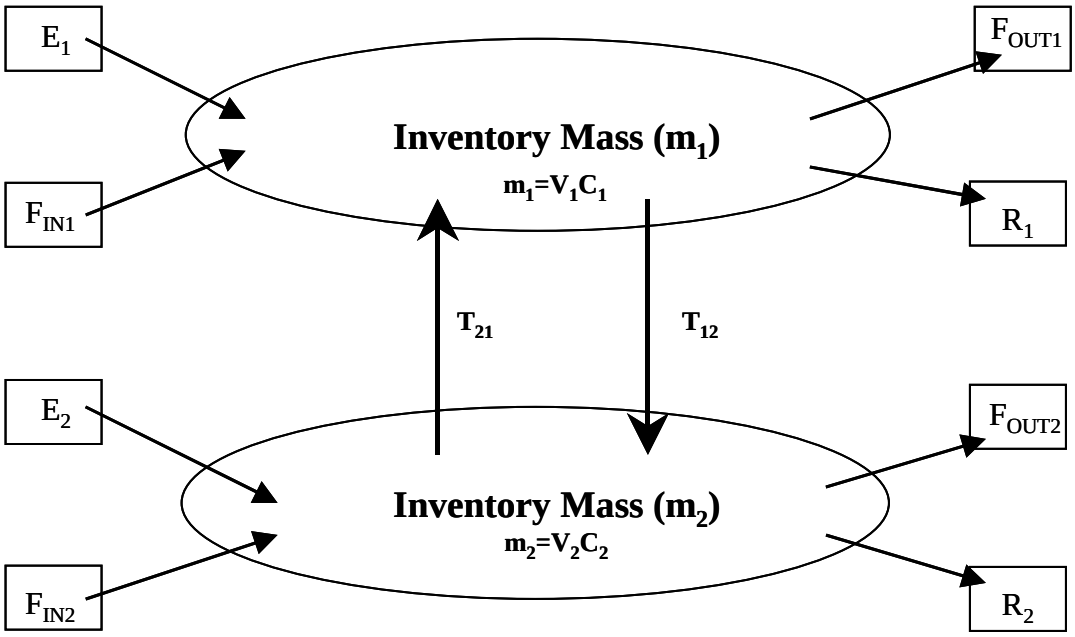
where $f_i = m_i / m_{tot}$ = mass fraction in compartment i and R_{total} is the total rate of reaction.

Other compartments can be added. As an illustration, Figure 3 shows a typical output of the EQC model that has four compartments (air, water, soil and sediment) (Mackay et al. 1996a). Klecka et al. (2001) have suggested a minimum of three compartments (air, water and soil plus sediment) but there is a general consensus that four are required to adequately represent the environmental fate of a chemical and by extension, its overall persistence.

Figures 4, 5 and 6 show the EQC output for the constant emission of 1000 kg/h into one compartment only, i.e. air, water or soil. In Figure 3, the same emission goes into all three compartments for a total emission of 3000 kg/h. It can be noted that if the masses, fluxes, concentrations and fugacities in Figures 4, 5 and 6 are added, they equal the corresponding quantity in Figure 3. Considering for example, the mass of benzo(a)pyrene in soil, the masses in Figure 4, 5 and 6 are 1.42×10^7 kg (air emission), 14948 kg (water emission) and 2.45×10^7 kg (soil emission) which sum to the 3.87×10^7 kg in Figure 3. This is a consequence of the linear equations used in the model. This property enables the concentration in a compartment to be apportioned to each of the three sources.

The residence times, however, do not add. The residence times in each compartment individually are the same in all four figures, however, the overall residence times attributable to reaction, advection or both are not equal because they depend on how the chemical enters the environment, i.e. its “mode-of-entry”. For example, the system reaction residence times in Figures 3 to 6 are 1110, 900, 1805 and 1023 days respectively. (Note that only the overall, i.e. reaction plus advection, residence times are shown on each figure.) Often these differences are much greater.

The key conclusion is that persistence is best expressed as a residence time attributable to reaction only. For a single compartment this is the half-life divided by 0.693. For multiple compartments the overall residence time is a weighted average of the individual residence times, and the weighting depends on the mode-of-entry and the partitioning characteristics of the chemical.



Individual Media Residence Times

$$\tau_1 = \frac{m_1}{F_{OUT1} + R_1 + T_{12}} = \frac{1}{k_{F1} + k_{R1} + k_{12}}$$

$$\tau_2 = \frac{m_2}{F_{OUT2} + R_2 + T_{21}} = \frac{1}{k_{F2} + k_{R2} + k_{21}}$$

Overall Residence Time Attributable to Reactions and Advection

$$\tau_0 = \frac{(m_1 + m_2)}{F_{OUT1} + F_{OUT2} + R_1 + R_2}$$

Overall Residence Time Attributable only to Reactions

$$\tau_{OR} = \frac{(m_1 + m_2)}{R_1 + R_2} = \frac{(m_1 + m_2)}{m_1 k_{R1} + m_2 k_{R2}} = \frac{1}{f_1 k_{R1} + f_2 k_{R2}}$$

Where f_i is the fraction of the mass in compartment i

Figure 2 Expressions for calculating the individual and overall media residence times of a chemical in a steady-state multiple compartment system using rate constants.

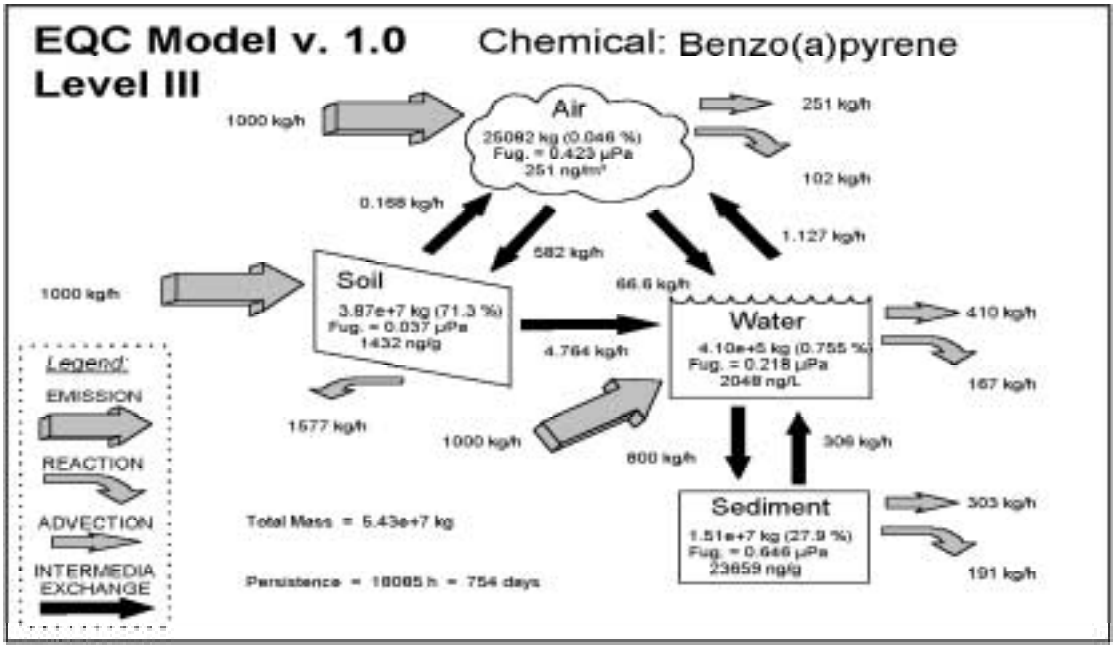


Figure 3 Graphical output from Level III EQC Benzo(a)pyrene Here, persistence is total mass divided by total rates of loss (advection and n).
i.e. 5.43× 10⁷ kg / (3000 kg/h) = 18100 h or 754
The reaction persistence is ×10⁷ kg / 2037 kg/h = 26700 h or 1110
The advection persistence is ×10⁷ kg / 964 kg/h = 56300 h or 2350

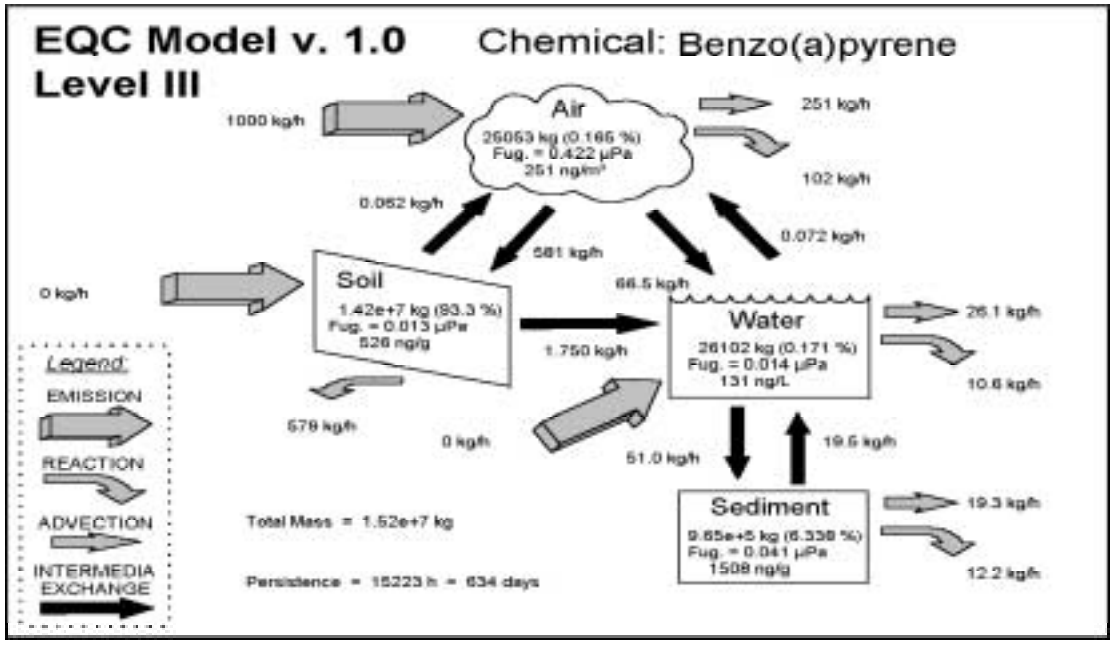


Figure 4 Graphical output from Level III EQC with an emission of h into the air compartment

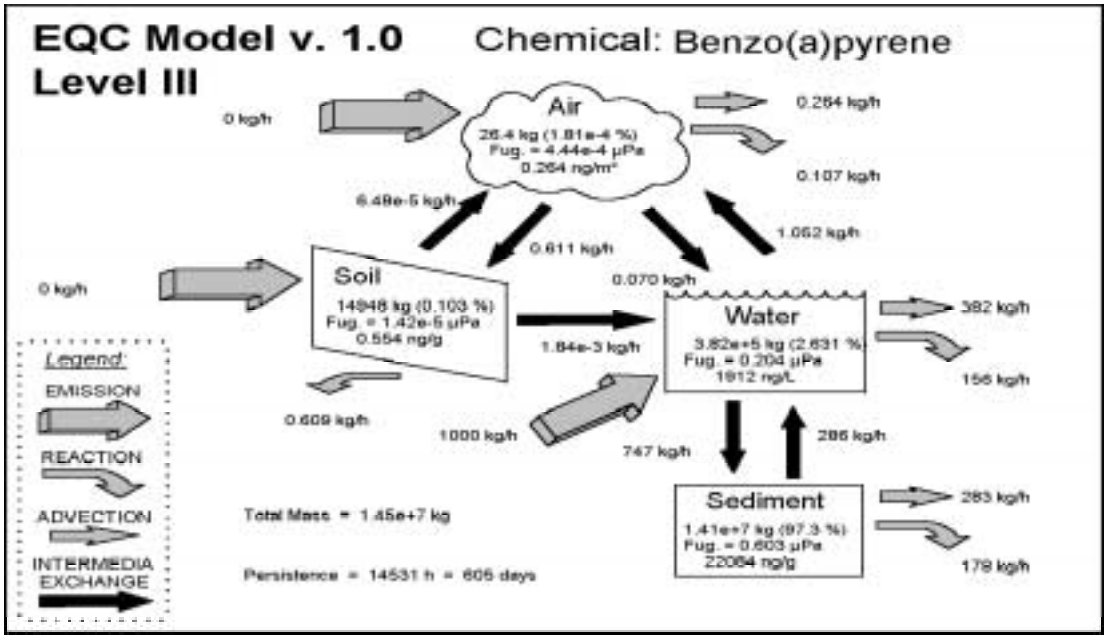


Figure 5 Graphical output from Level III EQC with an emission of 1000 kg/h into the water compartment.

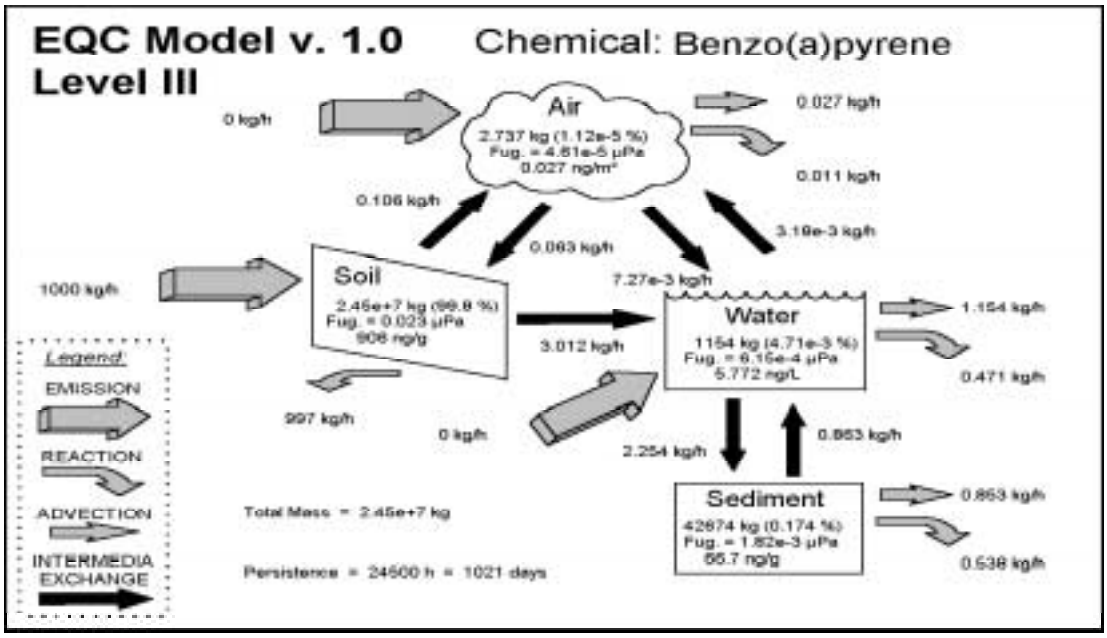


Figure 6 Graphical output from Level III EQC with an emission of 1000 kg/h into the soil compartment.

Other compartments can be added without appreciably increasing complexity, especially if it is assumed that they are in chemical equilibrium with an existing compartment. Examples are aerosol particles added to the air, or suspended solids and biota to water. This equilibrium assumption avoids the necessity of writing a separate mass balance for the added phase because the concentration is related by a known partition coefficient to that of its companion compartment. More problematic is vegetation that is not readily assigned to either air or soil and may deserve separate treatment. It may be desirable to treat air, water or soil as multiple compartments or layers depending on the circumstances.

In general, if it is known that concentrations differ significantly between two locations, then these locations may deserve to be treated as separate compartments. Compartments that are not at equilibrium are essentially independent and expressions for transfer to and from them must be compiled and a mass balance equation set up. The number of mass balance equations is thus the number of such independent compartments.

3.5 Connected multimedia models

It is also possible to connect a number of multimedia models of the type illustrated in Figures 3 to 6. In the global model depicted in Figure 7, Wania et al. (1993, 1999a, 1999b) set up a series of nine such connected models representing meridional segments of the planet with appropriate volumes and temperatures. Scheringer (1996) has suggested a circular set of connected models as shown in Figure 8 (and more recently a variable number of linearly connected models (Scheringer et al., 2000)). In the EUSES system a local model is nested in a regional model that, in turn, is nested in a continental model as shown in Figure 9 (EC, 1996). In the ChemCAN model rewritten as a linked version and the BETR (Berkeley-Trent) models the segments are linked in a two dimensional network as shown in Figure 10, and allow exchanges of contaminant in air and water with typically three surrounding segments (MacLeod et al., 2001, Woodfine et al., 2001).

It is thus possible to build assemblies of multimedia models with a variety of configurations to meet specitfi requirements.

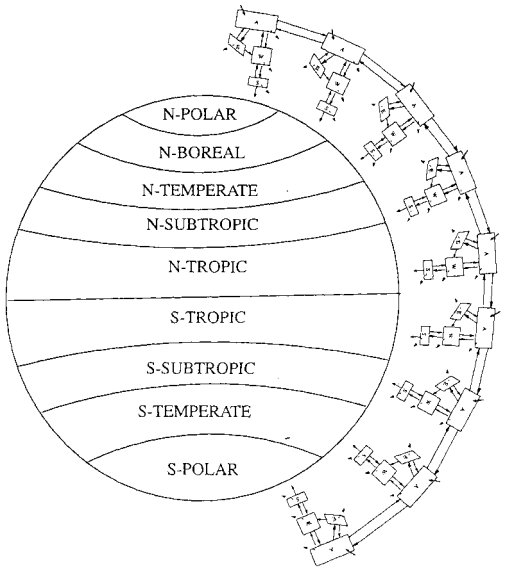


Figure 7 Global model by Wania et al. (1993, 1999a, 1999b) in which "unit worlds" represent meridional segments arranged linearly.

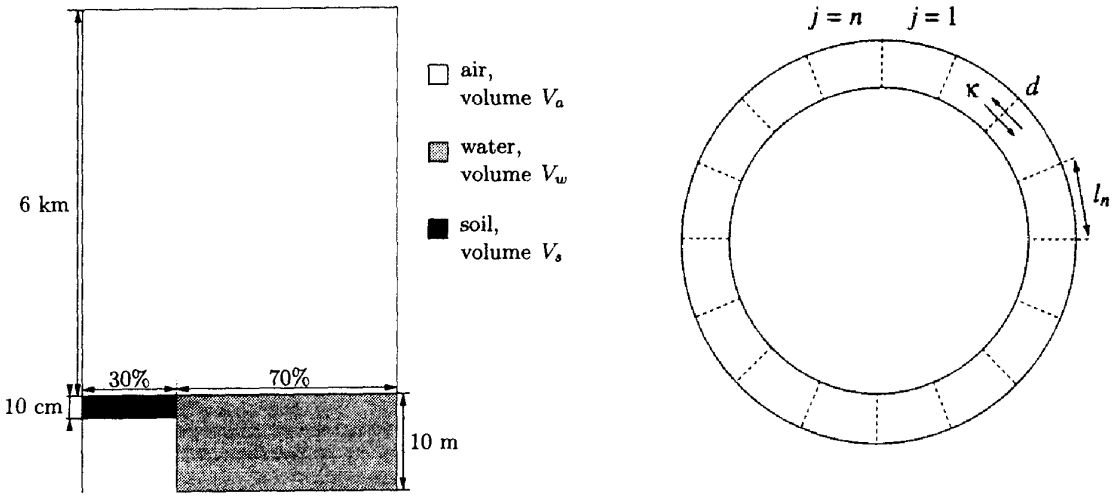


Figure 8 **Global model by Scheringer (1996) in which three-compartment "unit worlds" are arranged in a circular configuration.**

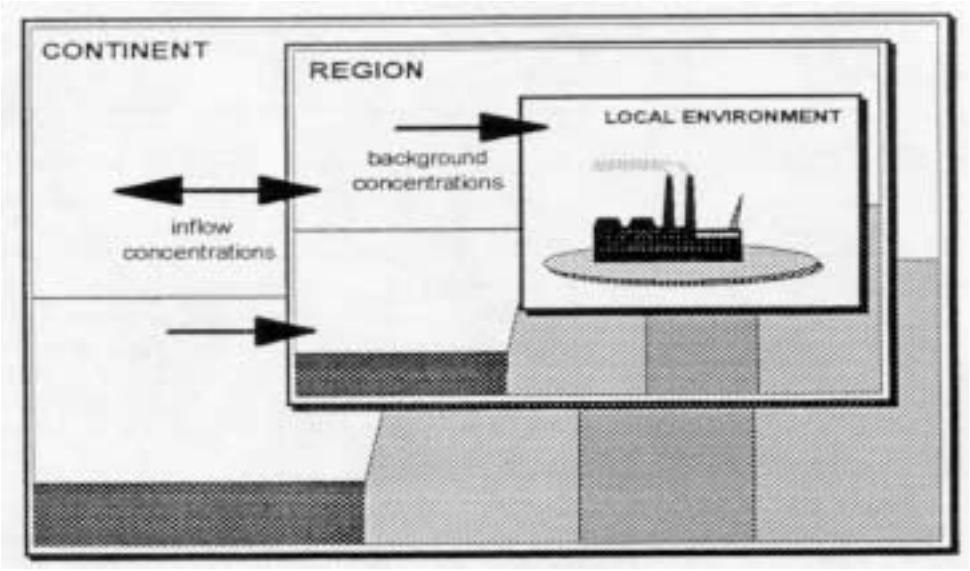


Figure 9 **Nested continental model used in EUSES (EC, 1996) in which a local "unit world" is contained in a regional one, which in turn is contained in a continental one.**

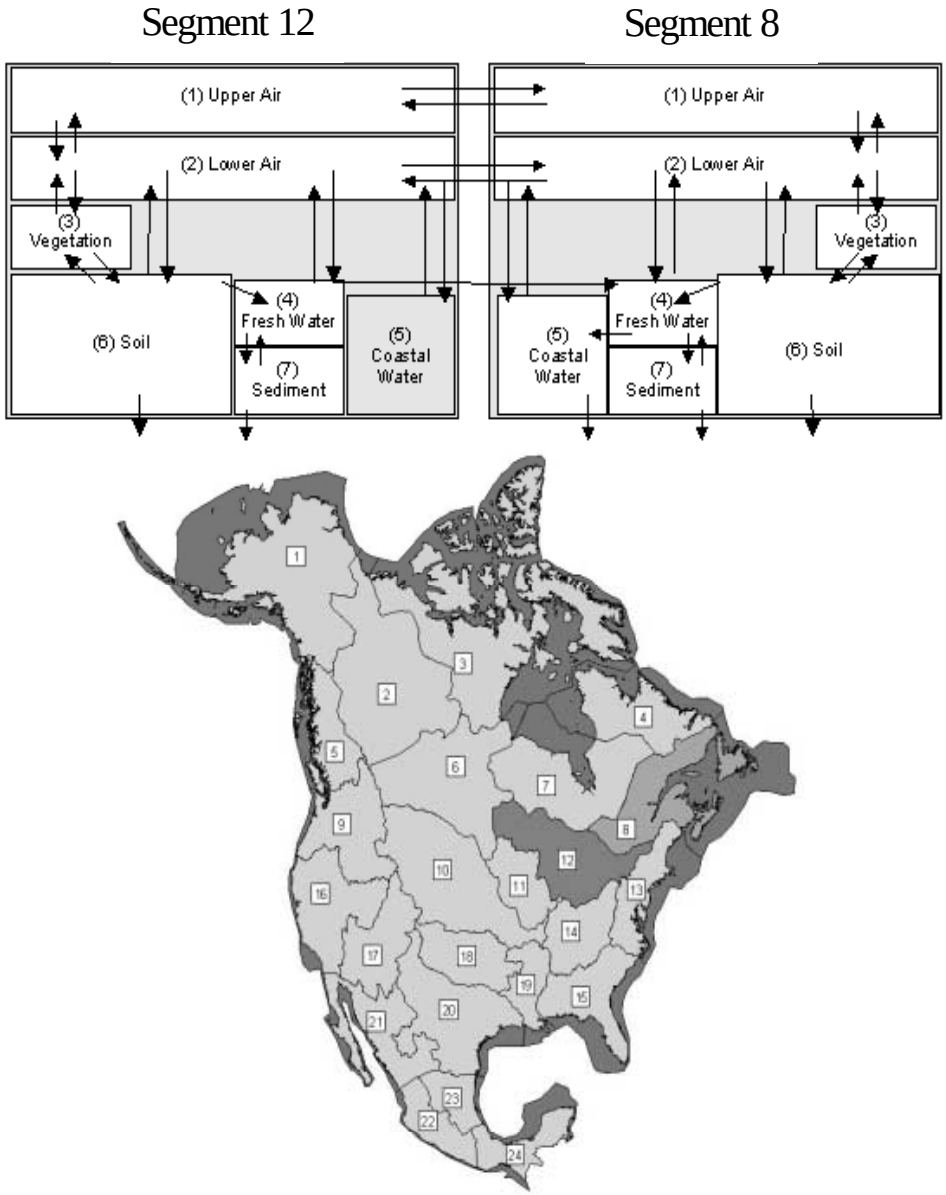


Figure 10 Two dimensionally linked North America BETR model showing only the linkage of two adjacent models, segments 12 and 8 (MacLeod et al., 2001, Woodfine et al., 2001). There are 24 connected segments and the remainder of the world is segment 25.

4 CONCENTRATION, FUGACITY AND LEVELS I TO IV

When writing mass balance equations, the conventional approach is to use concentrations and a variety of rate constants. Another approach, that is ultimately algebraically identical, is to use fugacity as a surrogate for concentration. 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. The concentrations are, of course, different for each medium. The number of mass balance equations equals the number of fugacities. A series of fugacity models has been devised with levels of increasing complexity as follows.

Level I models merely show the relative equilibrium partitioning of a conserved (i.e. non-reacting) chemical in a multimedia setting. They assume equilibrium and steady-state to apply in this closed system.

Level II models include degrading reactions and advective loss but assume all media are at equilibrium, so only one fugacity and one mass balance equation applies. They assume equilibrium and steady-state to apply in an open system with inputs and outputs. Mode-of-entry is irrelevant because the chemical immediately establishes equilibrium upon introduction to the system.

Level III models assume steady-state i.e. conditions are constant with time but compartments are not at equilibrium and different fugacities apply to each medium. Rates of intermedia transport are calculated. Typically there are four compartments and four fugacities. Figure 3 is such a model. Mode-of-entry information is needed.

Level IV models are dynamic or unsteady-state in nature. They are most often used to determine how long it will take for concentrations to change as a result of changing rates of emission.

In the EQC model there are four compartments and Level I, II and III calculations are included. In EUSES/SimpleBox there are six compartments (air, fresh water, sediment and three soils) and Level III conditions apply. The global model of Wania is Level IV in nature. It is possible to set up a four-compartment system in which sediment and water are assumed to be in equilibrium yielding three mass balance equations. The usual selection is between Level II and Level III calculations each with four compartments.

5 EVALUATION OF PERSISTENCE

For an individual medium, persistence can be expressed as the residence time attributable to reaction or as the half-life. These quantities are numerically related. For a multimedia system, the concept of half-life cannot be applied because some compartments experience faster reactions than others and overall behaviour is not first-order. It is then essential to express persistence as an overall residence time attributable to reaction.

When calculating reaction residence time, a value can be calculated for each compartment individually or for the entire set of compartments for which mass balance equations exist. There is thus only one overall residence time for Level II models but there are potentially five for four compartment Level III models, i.e. 4 individual values and one overall value. The individual media residence times are the reciprocal of the reaction rate constants k_{Ri}. The overall residence time under steady-state conditions is the reciprocal of a weighted mean rate constant in which each individual rate constant is multiplied by

the mass fraction in compartment i. Individual residence times are of limited use because they express only part of the picture. It is the overall persistence that is of most interest.

An important property of these models is that once the expressions have been set up and parameters defined, the individual residence times for each compartment are fixed.

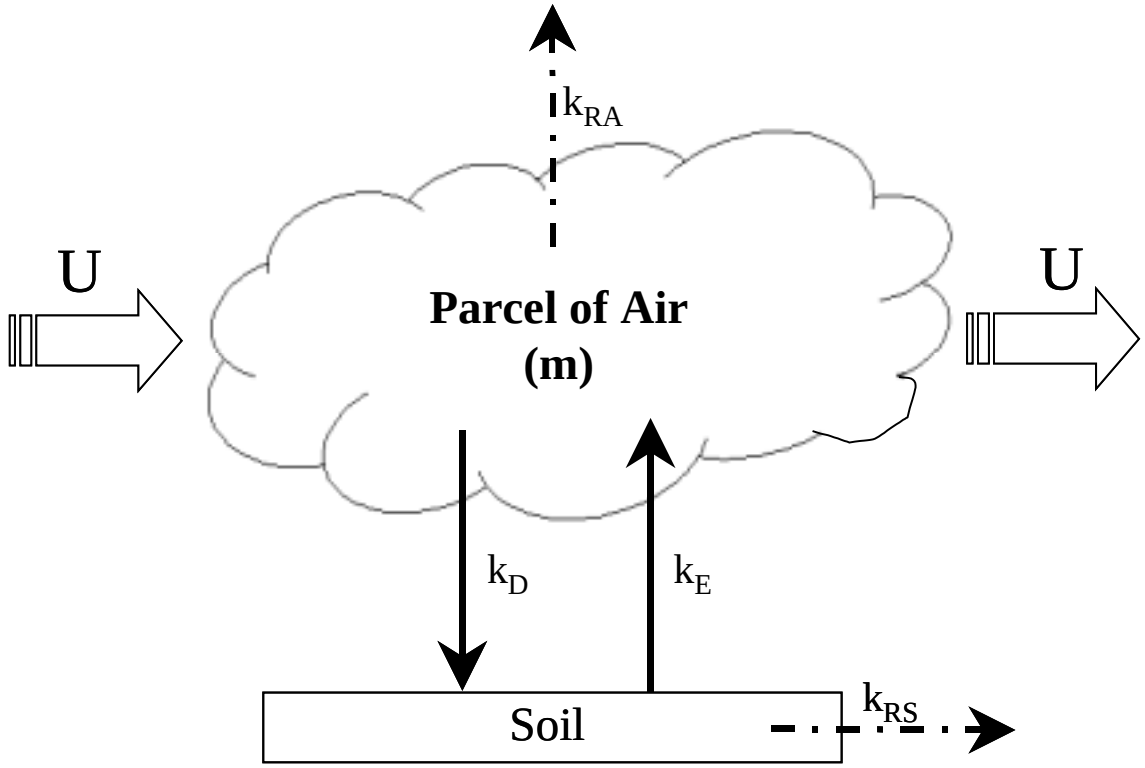
In Level II models, no intermedia mass exchange rates are deduced, i.e. all resistances are neglected, and equilibrium is achieved instantaneously. Thus, the mass fractions in each medium are independent of the chemical mode-of-entry and there is only one overall residence time for Level II models. In Level III models, intermedia mass transfer resistances are no longer zero and the mass fractions depend on the mode-of-entry. The overall persistence is thus a function of how the mass enters the system. It is quite difficult to calculate a residence time for an unsteady-state or Level IV model.

The important implications are that persistence is best expressed as a residence time, and that for Level III models overall persistence depends on mode-of-entry. If no mode-of-entry information is available the only options are to assume one or more modes-of-entry, or use a Level II model in which persistence is independent of mode-of-entry.

In summary, an individual reaction residence time or persistence can be calculated for each compartment or box for which a mass balance equation applies. Values can also be deduced for the system of boxes as a whole. If the boxes are at the same fugacity (i.e. equilibrium applies, as in Level II) mode-of-entry is not important. If they are at different fugacities (i.e. not at equilibrium, as in Level III and IV) mode-of-entry influences overall system residence time, but not the individual compartmental residence times. Gouin et al. (2000) have described how persistence can be evaluated using a Level II model. Webster et al. (1998) have used a Level III model for this purpose.

6 EVALUATION OF LONG-RANGE TRANSPORT

The most readily appreciated and easily visualized description of LRT is to use a Lagrangian system and follow a parcel of air (or water) containing chemical as it is transported. This is illustrated in Figure 11. Another approach, which pre-dates the Lagrangian model, is to treat the global environment as a series of connected multimedia environments, possibly circular in configuration, then calculate the spatial concentration distribution and express it as a distance within which most of the chemical resides. This has been developed and advocated in a series of papers by Scheringer and colleagues as cited in the references.



Where : U = velocity

k_{RA} = reaction rate constant in air

k_D = deposition rate constant

k_E = evaporation rate constant

k_{RS} = reaction rate constant in soil

Stickiness or the fraction retained is $S = k_{RS} / (k_{RS} + k_E)$

thus net deposition = $k_D S$

$$\text{Characteristic Travel Distance (CTD)} = \frac{U}{k_R + k_D S}$$

$$\text{However residence time in air } \tau_A = \frac{1}{k_R + k_D S}$$

also $CTD = \tau_o U f_A$

τ_o is overall residence time, f_A is fraction in air, since τ_A is $\tau_o f_A$

Figure 11 Long-range transport calculations in Lagrangian coordinates in which the changing concentration in a parcel of air is followed as it travels over soil. A similar approach can be used for water.

Using the Lagrangian approach, a half-distance was suggested by Van Pul et al. (1998) as the distance travelled at which half the chemical mass remains. Bennett et al. (1998) defined an analogous characteristic travel distance (CTD) at which $1/e^{th}$ remains, i.e. 37%. They showed that the CTD is

given by the velocity of the mobile medium (here wind velocity) divided by an effective rate constant k_{eff}, which includes all exchange processes with, and degradation processes within, the other compartments. The half-distance is 0.693 times the CTD. Beyer et al. (2000) expanded on this and showed that k_{eff} is $(k_R + k_D S)$ where k_R is the reaction rate constant, k_D is the rate constant for transfer to other media (e.g. air to soil) and S is the "stickiness" of the receiving media, i.e. the fraction which is permanently retained. It can be shown that "stickiness" of soil is controlled by the rate constants for degradation and evaporation. Beyer et al. (2000) also showed that the characteristic travel distance CTD is the product of the overall reaction residence time, the assumed velocity and the mass fraction in the mobile medium.

A key point is that the CTD is $U\tau f_i$ obtained from a steady-state box model where U is velocity, τ is overall reaction residence time calculated for mode-of-entry into the mobile medium, and f_i is the mass fraction of chemical in the mobile medium. Essentially the chemical resides for τ hours thus it can travel $U\tau$ km (if U has units of km/h), but only a fraction f_i can proceed at this velocity, so on the average the substance will travel $U\tau f_i$ km.

It should be noted that CTD must be evaluated for a chemical that is discharged into the mobile medium of interest. Since persistence and mass distribution are both affected by mode-of-entry in a Level III model, the apparent CTD is also affected and the results can be difficult to interpret. A practical case is the CTD of a pesticide in air when the pesticide is discharged to soil. In such cases it is best to use the model to calculate the fraction of the applied pesticide that evaporates, then estimate the CTD for this fraction. In such cases an Effective Travel Distance (ETD) can be defined by a statement of the type "2% of the chemical discharged to soil may travel over 100 km in air as a result of evaporation".

The CTD can also be calculated from the assumption that the advective loss equals the reactive loss under steady-state conditions (all other loss processes being neglected). The equilibrium distance is identical to the CTD (Hertwich 1999, van de Meent, 2000). In summary, LRT can be deduced from a Lagrangian (moving parcel) or a Eulerian (box) model or using a flow equilibrium approach. An advantage of the box model is that it is this type of model that is already needed to evaluate persistence. Wania and Mackay (2000b) has compared several LRT models and has concluded that they give generally similar results.

The key conclusion is that LRT can be calculated and expressed in a variety of ways. It can be regarded as an average distance a chemical moves in air or water. It can also be considered as the distance within which most of the chemical is retained when the chemical is distributed at steady-state within the environment. A single model or connected models can be used. The connected models can be set up as a series, a circular set, a two-dimensional network or using a nested configuration.

In principle, when estimating persistence or LRT potential, it seems desirable that the model used be as simple as possible, yet consistent with generating reliable results. It must be transparent, user-friendly and user-understandable. It should be capable of a degree of validation. It should be applicable to as many classes of chemicals as possible including those which speciate. There is also an incentive to use, if possible, the same model for persistence and long-range transport.

7 INTENSIVE AND EXTENSIVE QUANTITIES: THE ROAD FROM HAZARD TO RISK

If a multimedia model is set up with defined volumes and a quantity of chemical is introduced to assess its fate, then the P and LRT results obtained are independent of the quantity of chemical introduced. Doubling the discharge rate merely doubles the quantity of chemical, so the residence time and

persistence are unaffected. Likewise LRT distance is unaffected. On reflection this is intuitively obvious because unless a substance reacts with itself or saturates available reaction sites, its lifetime is independent of how many molecules are released. P and LRT are thus ***intensive*** properties of the chemical and the environment and are independent of quantity used or emitted.

On the other hand, concentrations and amounts of substance in media are extensive because they do depend on quantity used or emitted. Risk of toxic effects is also extensive because it depends on exposure, which in turn depends on concentration. Toxicity, when expressed as a LC50 or LD50 is intensive because it is actually a ratio of two extensive quantities, a concentration and a specified effect. The reader is referred to Mackay et al. (2001) for a more detailed discussion of this issue.

The key point is that the hazard of a chemical is intensive in nature and can be evaluated from partitioning and reactivity properties and measurements of toxicity. No quantity of release information is needed. If risk, which is extensive in nature, is to be evaluated, quantity of release and probably mode-of-entry information are also needed.

The risk from a high production volume substance that is not very toxic and has a low hazard may be greater than that of a low volume, highly toxic and hazardous substance. It is thus essential that there be a clear regulatory policy on whether it is hazard or risk that is being evaluated since they require different data. One approach is to estimate hazard as a first tier, then if necessary estimate risk in a second tier.

8 CONCLUSIONS

A large and growing volume of literature exists on multimedia models. They serve an essential role as tools for bringing together information on chemical and environmental properties with a view to estimating chemical fate. They can be configured in various ways and can range greatly in complexity, but in principle it is preferable to use the simplest model that can generate the desired result.

Persistence is usually expressed as a half-life or the related reaction residence time. Both can be readily calculated for each environmental compartment e.g. air, water etc., but only residence time can be calculated for a group of connected compartments. Only degrading reactions should be considered when evaluating persistence. Other loss processes, which merely transport the chemical to other locations, should not be considered as influencing persistence.

Long-range transport potential can be calculated in a variety of ways but it is likely that all approaches will give similar results. This potential can be expressed as a distance that a specified fraction of the discharged chemical may travel i.e. as a half-distance or a characteristic travel distance. It can also be expressed as a distance within which most of the emitted chemical will be contained.

Both persistence and LRT potential depend on the properties of the chemical and those of the environment in which its fate is evaluated. Multimedia models play an essential role in bringing together these chemical and environmental properties in a logical and transparent manner to produce numerical expressions of persistence and LRT. A number of approaches can be adopted yielding somewhat different results, however, differences between model results usually reflect differences in input data and the underlying assumptions and structure of the assumed model.

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APPENDIX 1:
A List of Definitions Relating to Persistence and Long-Range Transport

Compiled by Andreas Beyer and Michael Matthies

1. Multimedia Models

Multimedia fate model (van Leeuwen and Hermens, 1995): In multimedia models, the total environment is represented as a set of spatially homogeneous boxes; one box for each environmental compartment in which the chemical is assumed to be evenly distributed. The number, size, properties etc of boxes can vary.

Level I to IV (Mackay 1991, Cowan et al. 1995, Trapp and Matthies, 1998): A *Level I model* is a closed system mass balance of a defined quantity of chemical as it partitions at equilibrium between compartments. There is no reaction. A *Level II model* is a steady-state open system description of chemical fate at equilibrium with constant chemical emission rate. It includes reaction and advection as loss processes. It can also be written in unsteady-state form. A *Level III model* is a steady-state description of chemical fate between a number of well-mixed compartments which are not at equilibrium. This level thus includes inter-media mass transport expressions. A *Level IV model* is an unsteady-state version of *Level III*.

2. Persistence

Temporal scale (Scheringer and Berg 1994, Beyer et al. 2001): The *temporal scale* of a chemical describes the duration of the exposure or the time required for the degradation of the chemical to a certain degree. The temporal scale is usually quantified by the overall residence time or half-life of a chemical.

Overall residence time or overall persistence (Scheringer 1996, Webster et al. 1998, Gouin et al. 2000): The overall residence time is the mean time that a molecule resides in the system, taking into account all intra-media and transfer processes. It is calculated using a multimedia model. In addition an advective residence time can be calculated in which the only losses are by advection, i.e. no reactions and other processes. Finally a *reaction* residence time can be calculated in which there are no *advective* and no other losses: this is the definition of *overall environmental persistence* which is most relevant in this context. The model used can be level II or level III. The level III requires mode of entry information. The level II does not.

3. Long-range Environmental Transport

Spatial scale (Scheringer, Berg 1994, Beyer et al. 2001): The *spatial scale* of a chemical is referred to as the tendency of a chemical to distribute in space, thus it is a measure for the area or region that might be affected by a certain chemical. Both the temporal and spatial scales do not consider actual amounts of emission, but are based on intensive properties of the chemical and the properties of the environment in which it is being transported, for example wind speed and landscape type.

Characteristic travel distance (Bennett et al. 1998, Beyer et al. 2000, Beyer and Matthies, 2001): The *characteristic travel distance* (CTD) describes the effective loss of a chemical from a mobile phase (e.g. air) and weighs it with the advective transport (e.g. wind). It is the distance from the source where the initial mass in the mobile medium (air or water) drops to 1/e, i.e. approx. 37%. CTD is determined by the balance between competitive rates of transport and loss in a mobile medium, e.g. air. The CTD is independent from the mode of entry.

Half-distance (van Pul et al., 1998): The *half-distance* X is the distance from the source where the initial mass in the air drops to 50%. This approach is comparable to the CTD .

Effective travel distance (Beyer et al, 2000): The *effective travel distance* (ETD) extends consistently the idea of the characteristic travel distance for the case of different input patterns. It takes into account the fraction f of the totally emitted mass which is initially present in the mobile medium is calculated. The mass in the mobile medium will decrease according to the same profile as the CTD, since constant physical conditions are assumed.

Spatial range (Scheringer 1996): The *spatial range* describes the distance that contains 95% of the total spatial distribution of exposure without specific assumptions on the transport and degradation processes determining the shape of that distribution.

Transport distance (Rodan et al. 1999): A fixed emission of 3,000 kg/h into each medium is assumed for all chemicals and a multimedia model is used to calculate the initial concentration of the chemical in the air of the source area. The distance at which the initial concentration drops to 10^{-11} g/m^3 is defined as the chemical's *transport distance* TD.

4. Further useful definitions

Extensive and intensive properties (Scheringer and Berg 1994): Following the thermodynamic definition of these terms *extensive* properties depend on the size of the system (e.g. mass or volume) while *intensive* properties are size independent (e.g. temperature or density). The concentration of a certain organic chemical that can be measured in remote areas (i.e. the *exposure*) will depend on three quantities: the amount released (extensive), its persistence (intensive), and its long-range transport potential (intensive). Thus, a high concentration in remote areas can be *mass-dominated*, i.e. caused by large emissions, or *range-dominated*, i.e. persistence and long-range transport cause a distant exposure. Hence, by using intensive criteria based on properties of the substance it is possible to compare chemicals separated from emissions.

Stickiness (Beyer et al. 2000): The *stickiness* describes the ability of surface media (soil, water, sediment, vegetation) to retain a chemical after deposition. Stickiness is defined as the fraction of the substance that remains in the surface compartments after deposition. It is calculated as the chemical's net flux from air to the surface divided by the gross flux.

Penetration depth and scale height (Brandes et al. 1996, Bennett et al., 1998, Hertwich and McKone 2001): *Penetration depth and scale height* describe the vertical chemical transport in soil and air respectively. Both of them define heights (depths) for well mixed compartments that contain the same amount of chemical as compartments of infinite depth. Hence, they follow the same idea as the characteristic travel distance (Beyer et al. 2000).

The (soil) penetration depth is the depth at which, at steady-state, the rate of chemical reaction is equal to its rate of movement into the soil by diffusive and advective processes. It considers diffusion, convection due to water transport, and first-order chemical transformation.

The (atmospheric) scale height can be interpreted as the height of a uniformly mixed air compartment with a constant partial pressure p_0 that contains the same amount of substance as is present in the actual atmosphere, having variable concentrations as a function of height, i.e. there is a concentration gradient or profile. The scale height considers dispersion, gravity, and first-order chemical transformation.

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Appendix 2:
Relevant Websites

Model	Organization and URL
BENNX	Exposure and Risk Assessment Group http://eande.lbl.gov/IEP/ERA/people/bennett.html
CalTox	Department of Toxic Substance Control http://www.dtsc.ca.gov/sppt/herd/
Chemrange	Eidgenössische Technische Hochschule Zürich http://ltcmail.ethz.ch/hungerb/research/product/chemrange.html
ELPOS	Institut für Umweltsystemforschung http://www.usf.uos.de/
EQC, Level II, Level III, ChemCAN, TAPL3	Canadian Environmental Modelling Centre, Trent University http://www.trentu.ca/academic/aminss/envmodel/
EUSES	European Chemicals Bureau http://ecb.ei.jrc.it/existing-chemicals/
PENX	Life Cycle Group for Sustainable Development http://dgrwww.epfl.ch/GECOS/DD/
SCHE	Safety and Environmental Technology Group Laboratory of Technical Chemistry http://ltcmail.ethz.ch/scheri/
VDMX	Utrecht University http://www.geo.uu.nl/Research/Geochemistry/D_vdMeent.html
WANIA, WANX, CoZMo-POP, GloboPOP	The Wania Group, University of Toronto http://www.scar.utoronto.ca/~wania/

ANNEX 4: PRESENTATION SUMMARIES AND OTHER PAPERS

Don Mackay: An introduction to multimedia models: their features and applications
Frank Wania: Comparing Predictions of the Long Range Transport Behaviour of Organic Chemicals from Various Multi-Media Fate Models
Michael Matthies: Sensitivity, uncertainty and reliability of overall persistence and long-range transport potential
Dik van de Meent and Dick Sijm: Risk dimension of PBT-classification
David Stone: POPs Protocol of the Convention on Long-range Transboundary Air Pollution
Bo Wahlström: Stockholm Convention and the future POPs Review Committee
Jack de Bruijn: PBT-criteria in the European Union: Recent developments
Heinz-Jochen Poremski and Ulrich Claussen: Selection and Prioritisation Procedure for Hazardous Substances within the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic
Sam Sasnett: North American government perspective on multi media persistence modeling
Kay Fox and Bill Adams: An industry perspective for the OECD/UNEP Workshop on the use of multimedia models
Kay Fox et. al.: An industry perspective for the OECD/UNEP Workshop on the use of multimedia models (detailed paper)
Darryl Luscombe and Romeo Quijano: Precaution and the Assessment of POPs under the Stockholm Convention
André Lecloux : Statistical Analysis of Local Monitoring Data to Assess Regional Exposure and to Validate Multi-Media Models
Noriyuki Suzuki: Assessment of long-term exposure with persistence consideration in the last evaluation task for dioxin risk assessment in Japan
Sergey Dutchak et.al.: Usage of POP multimedia models under UN ECE CLRTAP
Sergey Duchak et.al.: Application of EMEP transport models to assessment of long-range transport potential and overall persistence

Don Mackay: An introduction to multimedia models: their features and applications

Trent University

As an introduction to the Workshop, a brief description is provided of the nature of multimedia models and the incentives for applying them as part of the regulatory process. The mass balance principles underlying single and multiple compartment, steady-state and dynamic mass balances are described, especially as a method of determining persistence, either as a half-life or as a residence or characteristic time. A variety of modelling approaches is described, including multi-compartmental or "unit world" models, various configurations by which these "unit worlds" can be combined and Lagrangian and diffusion/dispersion techniques. Applications of these models to describe the potential for long range transport are also discussed. Several topics are raised for possible discussion including issues relating to definition of the model environment and the needs for reliable input data, simplicity, transparency, expression of uncertainty and the quest for a degree of validation.

Frank Wania: Comparing Predictions of the Long Range Transport Behaviour of Organic Chemicals from Various Multi-Media Fate Models

University of Toronto at Scarborough

Results from three different studies related to the use of multimedia fate and transport models for estimating the long range transport potential of organic chemicals will be discussed:

In the first study several research groups were asked to calculate parameters characterising overall persistence and long-range transport potential for a set of 26 diverse chemicals using their respective multimedia modelling approaches (12 for persistence and 8 for LRT). Absolute values for P and LRT potential differed substantially among models, suggesting that these characteristics can not be defined independently of the model used to generate the estimate. However, all persistence models based on Level III multimedia calculations which include a sediment compartment and all long-range transport potential models produced similar relative P and LRT potential rankings. This suggests that the use of specific chemicals as benchmarks for persistence and long-range transport appears to be a viable option in assessments of LRT and P.

To explore this possibility further we looked in greater detail at the prediction of the LRT potential of selected congeners of the polychlorinated biphenyls (PCBs) using two publicly available multimedia models. This group of compounds was selected because it includes a variety of substances with a divergent and fairly well established LRT behaviour. In contrast to the first study results from the two models resulted in significantly different rankings according to LRT potential. The results also revealed that only a very small number of model input parameters had a significant influence on the parameters characterising LRT potential.

Current modelling approaches indicate a high LRT potential for every substance with high volatility and high persistence in the atmosphere. A modelling approach is introduced that quantifies not only the potential of a chemical to travel long distances, but additionally its potential to accumulate in remote regions. Based on a zonally averaged global distribution model, this approach identifies combination of properties that make a substance subject to accumulation in polar regions – with sometimes unexpected results.

Michael Matthies: Sensitivity, uncertainty and reliability of overall persistence and long-range transport potential

Institute of Environmental Systems Research, University of Osnabrück

The overall residence time, τ_{ov} and the characteristic travel distance (CTD) in air, L_{air} are calculated for 109 organic chemicals (pesticides, POPs, industrial chemicals) with the multimedia model ELPOS (Environmental Long-range transport potential and Persistence of Organic Substances). It is a modified version of the SimpleBox model used for estimating regional background concentrations in EUSES (European Union System for the Evaluation of Substances). The sensitivity analysis shows that the parameter sensitivity strongly depends on the characteristics of the chemicals as well as assumptions with respect to environmental conditions. The ranking of the chemicals can be affected if uncertainty of the parameters is taken into account, e.g. by using 90^{th}-percentiles instead of mean values. Gas-particle partitioning, photo-oxidative degradability in air, degradation in water and soil (both field and laboratory measurements), rain rate and degradation on foliage are studied on their influence on τ_{ov} and CTD. The model accounts for temperature variations within the range of 5° to 30° C. While the overall persistence always increases with lower temperature, L_{air} can increase or decrease depending on the opposing processes of atmospheric degradation and deposition. The CTD is compared to a measured PCB-concentration gradient in the North Sea and to pesticides in rain. Both revealed a qualitative agreement supporting the ranking and screening properties of τ_{ov} and L_{air}.

Dik van de Meent and Dick Sijm: Risk dimension of PBT-classification

RIVM, Bilthoven, The Netherlands.

The focus of international discussions about risk management for POPs has shifted almost completely towards the so-called PBT criteria, putting weight predominantly on intensive substance characteristics: Persistence (and transport potential) in the environment, Bioaccumulation, and Toxicity. Hardly any attention is paid to the extensive entities: volumes/emissions, concentrations, risk. The risk dimension seems to be disregarded in classifying chemicals for international regulatory action. We believe that this is neither correct nor necessary.

By far the most important factor that drove this shift has been the complexity of the risk assessment process. Risk assessment has proven to be a difficult and time consuming process, and has resulted in little progress in risk management so far. Some argue that safe levels for POPs cannot be defined, and that, therefore, risk assessment is not possible at all. Indeed, lack of simple and robust assessment and ranking procedures has rendered the risk approach to POPs selection very difficult.

The international POPs discussion would be assisted greatly by linking environmental fate modeling with ecotoxicology, and deriving simple algorithms for ranking POPs according to either extensive (risk-based) characteristics or to intensive (intrinsic properties only) characteristics. We believe that this can be done.
We propose calculated toxic pressure on ecosystems as a surrogate for "risk", and to use this for ranking POP-candidates. Emissions need to be estimated on the basis of production volumes and roughly estimated emission factors. Having estimated the emission rates, multimedia models can be used for calculating concentrations in regional, continental and global environments. Toxic pressure on these scales can then be calculated from ecotoxicological species sensitivity distributions. We believe that calculated toxic pressures for a large series of well-documented chemicals will provide the basis for deriving simple log-linear relationships, so that eventually risk scores can be obtained directly as a function of production volumes, physical chemical properties and toxicities.

Thus-calculated risk scores are extensive attributes of chemicals and their actual use, and are indicative of the ecological consequences of societal use of toxic chemicals. As extensive damage scores, these could help to quantify the risk dimension of the POPs issue.

David Stone: POPs Protocol of the Convention on Long-range Transboundary Air Pollution

Northern Science and Contaminants Research

Brief history of the LRTAP POPs Protocol:

At the end of the 1980's, several countries were aware that some POPs were occurring in remote ecosystems at levels similar to those associated with adverse effects in species close to source regions. In the Arctic, some of the most important traditional dietary items carried the highest pollutant loadings. In most cases, this could not be due to local sources. Long-range transboundary movement through natural vectors (e.g. the atmosphere and ocean currents) provided the only explanation. At the same time it was generally realized that national or sub-regional controls cannot alone prevent ecosystem accumulation of those POPs capable of long-range transport. Clearly international action was needed to control POPs at their source.

In1989, several international organizations were approached, including the Convention on Long-range Transboundary Air Pollution (LRTAP). The Executive Body to the Convention asked for a synopsis delineating the issue which was provided in 1991. It then established a Task Force to prepare an assessment on the need for, and the possible modalities of, action. The Task Force presented its assessment in 1994, and by December 1995, a working group was established to prepare a draft Protocol which was finally adopted as the 1998 Aarhus Protocol on POPs.

How the substance list was derived for the LRTAP POPs Protocol.

Substances were selected following a 4-stage approach originally proposed by the former LRTAP Task Force, and which was applied to an initial list of 107 substances. The first two stages were based upon criteria.
Stage 1 - Screening for LRTAP potential: Determined by cut-off criteria for vapour pressure, atmospheric lifetime, and biodegredation potential in water and soil or monitoring evidence of LRTAP.
Stage 2 - Setting priorities for risk characterisation: Determined by a numerical scoring procedure with criteria for bioaccumulation and mammalian and aquatic toxicity. It was applied to 87 substances which passed Stage 1.
Stage 3 - Risk characterisation: 32 substances “passed” stage 2, but by combining groups of PCBs and PAHs, existing national and international risk assessments were reviewed for only 17 substances.
Stage 4 - Risk management considerations: This was an open negotiation process.

How new substances are to be selected

This is to be achieved following the amendment procedure set out in paragraph 6 of Article 14 and its accompanying Executive Body Decision1998/2.

Under paragraph 1 of the later, any Party wishing to propose a new substance, must provide a risk profile demonstrating characteristics in relation to “indicative numerical values” (the word criteria was deliberately avoided). The characteristics identified are: potential for long-range atmospheric transport; toxicity; persistence; and, bioaccumulation. However, for each of the above, a surrogate is permitted. For example, as an alternative to concordance with the prescribed numerical values, it is permitted 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 which would include information on socio-economic factors and information on "production / uses / emissions, measured environmental levels in areas distant from sources, abiotic and biotic degradation processes and rates, degradation products, bioavailability ....." [4]

Under paragraph 2, the Executive Body will ensure technical reviews of the proposal to " evaluate inter alia: a) the 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".

The Executive Body has available several mechanisms for receiving advice and information, including EMEP (sources and levels), the Meteorological Synthesizing Centre-East (modeling) and the joint WHO / LRTAP Convention Task Force on Health. In 2000, it also established an ad hoc Experts Group on POPs to review and assess data put forward, (including risk profiles) pursuant to the procedure to add substances. However, since the Protocol has yet to enter into force, it is too early to comment on operational aspects.

The possible role of multi-media models in the substance selection process.

In theory, there are two ways in which multimedia models could be used in the context of the LRTAP POPs Protocol.

1) Replace (or become an alternative to) the existing substance identification process described in Executive Body Decision 1998/2. The procedure was placed as an Executive Body Decision (rather than being embedded in the Protocol) in order to make such amendments possible while avoiding the complication of opening the entire Protocol for revision. However, in my view, significant revisions to Executive Body Decision 1998/2 are very unlikely to occur in the foreseeable future. The procedure for adding substances was one of the most challenging tasks of the negotiations and this was also true of the Stockholm Convention[5]. This is because it is a component of a process to undertake a significant change in the legal obligations of Parties to the Protocol. Parties are therefore always likely to favor simple clear-cut criteria or characteristics about which there can be limited scientific and legal interpretation, rather than the complexities of multi-media models.

2) Be supportive of the existing architecture of the Protocol which provides at least three potentially complementary opportunities. They are:

a) Article 7 (Strategies, policies, programmes, measures, and information). This is a difficult Article to summarize but basically it requires Parties to put into place measures to undertake their Protocol obligations. One section is particularly interesting. It concerns national programmes for substance evaluation and states that each Party shall "Take into consideration in its programmes for evaluating substances, the characteristics specified in paragraph 1 of Executive Body decision 1998/2 ...." If "the

[4] The use of italics here and in the following paragraph is not to denote a quotation but to draw attention to opportunities discussed in the section below on the possible role of Multi-Media models in the LRTAP POPs Protocol.

[5] It is interesting that negotiators of the global Stockholm Convention decided to embed their equivalent of Executive Body Decision 1998/2 into the body of the Convention.

characteristics" include the surrogates mentioned above, and especially if the Convention begins to use multi-media models in this context, then some may argue that Parties consider utilizing this methodology in their national evaluation activities.

b) Article 8 (Research, development and monitoring). This encourages Parties to undertake and cooperate on an extensive compendium of research and monitoring topics. Multi-media models would certainly fit. However, to be really relevant, it would be preferable to seek a link to a more operational part of the Protocol (as indicated in the final sentence of this Article: "Priority should be given to research on substances considered to be the most likely to be submitted under the procedures specified in article 14, paragraph 6"). This neatly brings us to the next opportunity.

c) Article 14, paragraph 6 and Executive Body decision 1998/2. As described above, this deals with the procedure for amending the Protocol for the purpose of adding new substances. In the section above on the possible role of multi-media models in the substance selection process, I expressed doubt that Parties would wish in the near future to replace a "criteria-characteristics" approach with a multi-media model approach. However, in the section describing how new substances are to be selected, I drew attention in italicized text to the surrogate options which exists for the criteria-characteristics and also to other opportunities provided in Executive Body decision 1998/2 for the presentation of information in support of a proposal to add a substance to the Protocol. These provide ample scope for Parties to include perspectives derived from multi-media models into any proposals that they may wish to make and for Parties to include such information in their review of any proposals.

Conclusions.

One of the most attractive possibilities to be explored would be how much the multi-media models are able to develop a potential to integrate information in a way which captures the confidence of national decision makers and international negotiators. The surrogate information characteristics included in the present LRTAP Protocol suggests that this could be developed in a phased fashion alongside the traditional criteria approach.

Bo Wahlström: Stockholm Convention and the future POPs Review Committee

Senior Scientific Advisor, UNEP Chemicals

OECD/UNEP Workshop on the Use of Multimedia Models for Estimating Overall Persistence and Long-Range Transport in the Context of PBTs/POPs Assessment, 29 October 2001.

On 22 May 2001, 127 countries adopted the Stockholm Convention on POPs. The main objective of this convention is to protect human health and the environment from persistent organic pollutants. This shall be done in a precautionary manner through reducing and eliminating the production and use of nine pesticides (aldrin, chlordane, dieldrin, DDT, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene) and 2 industrial chemicals (PCBs and hexachlorobenzene) and by reducing with the goal of their continuing minimization and, where feasible, ultimate elimination of unintentionally produced POPs (polychlorinated dibenzo-p-dioxins and furans, PCBs and hexachlorobenzene).

The convention contains provisions for the addition of further substances by nominations from Parties to the Convention. The proposed candidate substances will be assessed in several steps by a subsidiary body, the POPs Review Committee, starting with a screening assessment against specified criteria e.g. for persistence, bioaccumulation, long-range transport and toxicity. In later stages a fully comprehensive assessment, including options for risk management, will be undertaken. The outcome of

the assessment will be a risk profile and recommendations to the Conference of the Parties on the inclusion of the proposed substance.

The criteria for persistence in Annex D of the convention are expressed as single-media criteria as follows:
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
Evidence that the chemical is otherwise sufficiently persistent to justify its consideration within the scope of this Convention.

In certain situations, e.g lack of data according to (i), the POPs Review Committee will need take into consideration other evidence. Such evidence would include estimates from multimedia models for overall persistence.

The criteria for long-range transport (LRT) are not expressed as numerical values. The potential for LRT should be assessed from:

- measured levels in locations distant form the source;
- monitoring data indicating LRT has occurred; or
- fate properties and/or model results demonstrating potential for LRT.

For many substances data on measured levels or monitoring data will be sparse, scattered or non-existing. In such cases, greater reliance must be put on estimates of LRT from models. The outcome of this workshop will therefore be of great use to the future POPs Review Committee and for other assessment related activities within UNEP.

Jack de Bruijn: PBT-criteria in the European Union: Recent developments

European Chemicals Bureau, Joint Research Centre, CEC

Recently the EU and OSPAR have agreed on a framework for a Common EC/OSPAR Approach on Risk Assessment Methodology for the Marine Environment. This framework outlines the general approach that should be taken when the risks to the marine environment of a chemical are to be assessed and specifically addresses the additional protection goals for this compartment compared to the protection goals for the inland assessment. These protection goals are:

- the concern that hazardous substances may accumulate in parts of the marine environment and that:
- the effects of such accumulation are unpredictable in the long-term;
- that such accumulation would be practically difficult to reverse;
- the concern that remote areas of the oceans should remain untouched by hazardous substances resulting from human activity, and that the intrinsic value of pristine environments should be protected.

Of these additional concerns (a) above can be seen as the principle concern that is characterised by a spatial and temporal scale not covered by the inland risk assessment approach. It is a concern that chemical substances which can be shown both to persist for long periods and bioaccumulate in biota, can give rise to toxic effects after a greater time and at a greater distance than chemicals without these properties. These properties specifically lead to a substantially increased uncertainty in the estimation of an acceptable risk to human health and the environment. As a matter of precaution and consistent with the Commission Communication on the Precautionary Principle, it is proposed to adopt for these PBT

(Persistent, Bioaccumulative and Toxic) and VPVB (Very Persistent, Very Bioaccumulative) substances a risk avoidance approach which is hazard based rather than risk based.

In the context of the EU White Paper on the Future Chemicals Policy the question if PBT and VPVB substances should be treated differently has also come up and a discussion on criteria to select these substances has started.

This paper will shortly highlight the most recent developments within the EU with emphasis on the way the PBT-assessment has been implemented in detail in the revised EU Technical Guidance Documents on Risk Assessment for New Substances, Existing Substances and Biocides. It will also identify the major scientific questions that remain and for which additional work is needed.

Heinz-Jochen Poremski and Ulrich Claussen: Selection and Prioritisation Procedure for Hazardous Substances within the OSPAR Convention for the Protection of the Marine

Federal Environmental Agency, Germany

Summary

In 1998, the contracting parties to the OSPAR Convention agreed on a "Strategy with regard to Hazardous Substances": [..] the prevention of pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances thereby moving towards the target of their cessation within one generation (25 years, year 2020) [..]. In OSPAR, an Ad hoc working group on the development of a dynamic selection and prioritisation mechanism for hazardous substances (called DYNAMEC) has developed a dynamic selection and prioritization scheme for the marine environment.

Strategy

The key elements of the strategy itself comprise:

- a dynamic selection and prioritisation mechanism
- the establishment of a list for Priority Action
- the development of assessment tools for the evaluation of risks in the marine environment
- the development of criteria and methods which could be used for identification and development of less hazardous, or preferably non-hazardous substances which could be used as substitutes for hazardous substances
- the aspects of feasibility for the implementation of measures
- the close co-operation with all relevant parties and international organisations
- implementation of measures on national basis
- assessment of implementation.

Dynamic Selection and Prioritization Scheme

The selection and prioritisation mechanism should include the following three steps:

- Step 1: initial selection (i.e. the identification of substances of possible concern for the marine environment);
- Step 2: ranking (i.e. the application of a ranking algorithm to the initially-selected substances to produce ranking of relative risk);
- Step 3: selection of substances for priority action; for example by the means of an assessment of risks (DYNAMEC, 1998)

Initial Selection and Ranking

A selection and prioritization procedure needed to be developed. The European Union Risk Ranking Method and the so-called COMMPS (Combined Monitoring-based and Modelling-based Procedure) approach were taken as the basis for further development. It comprises the following 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 procedure
- Step 3: Elaboration of a priority list based on predicted exposure data modelled from production vol- ume, 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 modelling-based list by additional expert judgement and consideration of additional information
- Step 5: Further detailed consideration by expert judgement on the highest risk-ranking substances and establishing finally a priority list

Exposure Assessment for Monitoring-based Ranking
Measured concentrations are used as input for the monitoring-based ranking. The 90^{th} and 50^{th} percentiles and the arithmetic means plus standard deviation are considered for further evaluation. The aggregated concentrations are scored (max. score = 10). They are logarithmically scaled as an exposure index for each substance:

$$I_{exp} = A \times \log (C/C_{min}) / \log (C_{max}/C_{min}); A = 10$$

Exposure Assessment for Modelling-based Ranking
The scale of the model is at an European level which corresponds to the "continental scale" defined in the EU-Technical Guidance Document (EU Council Regulation No. 793/93).
The Emissions, Distribution and Degradation (EEXV) is estimated by:

1. Emission: production volume x main use category and fractions of release (e.g. closed system, wide dispersive use)
2. Distribution: using the Mackay Level 1 model
3. Degradation (DEG): taking the results of biodegradability testing, e.g. Ready Biodegradability: 0.1 DEG, Inherent Biodegradability: 0.5 DEG, Persistent: 1.0 DEG, Default: 1.0 DEG

The EURAM aquatic exposure score is calculated as follows:

$$I_{exp} = 1.37 [\log (EEXV) + 1.301] ; EEXV = Emission \times DIST \times DEG$$

Effects Assessment of Organic Substances
The direct and indirect effects on aquatic organisms are considered as well as selected endpoints for effects on humans. PNECs (Predicted No-Effect Concentrations) for direct aquatic effects are estimated by using specific test results by considering the number of taxonomic groups and by applying extrapolation/assessment factors.

The indirect aquatic effects are calculated from the log P_{OW} as a measure for the bioaccumulation potential. They are scaled from log $P_{OW} < 3$ until log $P_{OW} > 5$ and respective scores are allocated.

Indirect effects on humans are assessed by considering CMT properties (carcinogencity, mutagenicity, teratogenicity) as well as chronic effects. These properties are also scored and all effec-related scores lead to:

Direct ecological effects:
$EFS_d = B \times \log (PNEC/PNEC_{max}) / \log (PNEC_{min}/PNEC_{max})$ B = 5
Indirect effects: EFS_i = (0 .... 3) derived from log P_{OW}
Human toxicity: EFS_h = (0 .... 2) derived from R-phrases, CMT-properties
$I_{eff} = EFS_d + EFS_i + EFS_h$
The final index for combining exposure and effects will lead to: $I_{fin} = I_{exp} \times I_{eff}$

Outcome of the ranking exercise were 4 lists, i.e. a ranking list for

- **water** based on measured environmental concentration and the properties of the substances;
- **water** based on modelled exposure scores (based on calculation from production volumes and use patterns);
- **sediments** based on measured environmental concentration and the properties of the substances; and
- **sediments** based on modelled exposure scores (based on calculation from production volume and use pattern).

However, not all of the initially selected substances could be ranked, only those for which information on production and use and/or monitoring data were available (203 out of 400).

Selection of Priority Substances
To facilitate the decision which substances to tackle first to update the current OSPAR List of Chemicals for Priority Action, it was agreed that a "selection box" of 80 substances should be extracted from the four ranking lists in a pragmatic way by (i) combining a selection of the 48 top-ranked substances from each of the 4 ranked lists, (ii) excluding from this selection substances already on Annex 2 of the strategy and (iii) adding all those initially selected substances which fulfilled the selection criteria I (POP-like Substances)or which were flagged as endocrine disruptors.

Keywords: OSPAR, DYNAMEC, hazardous substances, prioritisation, selection, PBT criteria

Sam Sasnett: North American government perspective on multi media persistence modeling

U.S. Environmental Protection Agency

North American governments, both collectively and individually have to deal with some fundamental responsibilities relating to PBT substances. We have both an identification responsibility and a risk management responsibility. And reality dictates that - regardless of the relative "wealth" of a nation - we have to prioritize and act based upon the best methods and data available.
This conference focuses on "overall" expression of chemical persistence in the environment as being technically superior to single media values. In canvassing some of my government colleagues I find mixed reactions - interest and support for further progress coupled with concern that the "best not become the enemy of the better".

North American governments are - like any other government - a customer looking for the best tools for the job. But the U.S., Canada and Mexico have already established individual and collective PBT programs (NARAPs, the Great Lakes Binational Toxics Strategy, U.S. PBT Program) using single media values as the sufficient basis for the P of the those priority PBTs selected. When looking at additional PBT pollutants the determination of persistence (however it is done) may actually be even less that 1/3 of the equation. Beyond these three hazard properties (measured or estimated) there are other important screening factors such as volume produced or released, evidence of presence in the

environment, and production/use patterns of the substance that can determine whether it will receive our governments attention.

On a more positive note, North American governments recognize the practical value of the multimedia persistence determination. For example the U.S. EPA is now finalizing and will soon release a tool called the PBT Profiler. It is a web-based tool that will allow anyone to evaluate the relative PBTness of a substance by inputting that chemical's CAS number. It is built on EPA's new chemical evaluation experience where little if any hazard data is submitted for evaluation. The PBT Profiler uses a multi-media modeling approach to generate the persistence value. Many companies that have tested the Profiler have indicated that it can be a great pollution prevention tool. In addition, the ability of multimedia modeling to help predict how substances will move in the environment and where they are most likely to contribute to exposure is obviously a significant advancement in estimating both long range transport and the potential risk of a substance or class of substances. One challenge for the improvement and practical application by our governments of such models is the widely varying climate conditions across North America - from tropical rainforests to the Arctic.

Therefore the perspective of North American governments is that multimedia persistence modeling can and, to a degree, already is contributing to PBT substance identification and risk management. We encourage the scientific community to pursue the development of improved scientific methods for persistence determination. But the work of government is not going to stop until the perfect model is available. Government regulators and others responsible for promoting pollution prevention and risk reduction are going to look for the value added. During this conference you may hear some of us say "That's nice, but so what?" So keep us as your "customer" in mind.

Kay Fox and Bill Adams: An industry perspective for the OECD/UNEP Workshop on the use of multimedia models

Business and Industry Advisory Committee

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Industry believes that MFTMs can provide a valuable contribution to the regulatory process. However, further work is needed to ensure that these models - and the interpretation of the model results - are based on sound scientific principles and appropriately validated. Industry is currently funding several research projects to help meet these needs.

It is our belief that substance evaluation for the purpose of regulatory management should be based upon appropriate risk assessment methodology which assures that proper exposure assessment is incorporated in the evaluation. Whilst screening for persistence and long-range transport (LRT) potential is a useful pragmatic step, it should only be considered as an intermediate step towards more detailed risk assessment and not as an end in itself. Concepts such as characteristic travel distance (CTD) and overall persistence ($P_{overall}$) are useful parameters for screening but should not be thought of as measures of risk. Importantly, they should not be considered or used in isolation as they are but one element in the overall dossier for a chemical. When other data are available, such as actual emission quantities, these should be utilised as early as possible in the screening process.

In Summary, Industry believes that:

- MFTMs can provide valuable insight into the fate and distribution of chemicals in the environment, and recognises that such models are increasingly useful in a regulatory context. However, further work is needed to ensure that these models - and the interpretation of the model results - are based on sound scientific principles.
- CTD and $P_{overall}$ are useful parameters for screening, but they should not be considered or used in isolation even in the screening tier of an assessment. They should only point the way, together with other necessary information, for more detailed risk assessment. As well as CTD and $P_{overall}$, emission data should be considered early in the screening process.
- A relative approach is more likely to be successful at screening level in a regulatory framework than an absolute approach.
- Uncertainty in model outputs should be characterised, and should always be reported along with model results.
- All measured data used for model input or for model evaluation should be collected and reported according to established guidelines.
- The models are only an estimate of reality, and potentially contain many scientific uncertainties. Hence appropriate and relevant monitoring data should be used to evaluate model predictions.

Kay Fox, Bill Adams, Chris Cowan, John Gannon, Diana Graham, Andre Lecloux, and Richard Murray-Smith: An industry perspective for the OECD/UNEP Workshop on the use of multimedia models (detailed paper)

Business and Industry Advisory Committee

Over the past 30 years Multimedia Fate and Transport Models (MFTMs) have had an important role in shaping our understanding of how chemicals behave in the environment. More than anything, they provide a tool to help us think, by allowing us to visualise overall fate and distribution in a way we cannot readily perceive if we simply attempt to evaluate isolated measured concentrations or look at individual processes such as biodegradation or volatilisation alone.

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Industry Activities

Industry is keen to contribute to the improved understanding of MFTMs and the nature of persistence, particularly in a regulatory context, and as a result industry has funded several ongoing activities.

In Europe, CEFIC has launched 27 major projects under its 'Long-Range Research Initiative' (LRI)[6], two of which specifically address the areas of MFTMs and persistence. One project concerns the application and validation of a MFTM to the Baltic Sea region. This project will attempt to assess the strengths and limitations of MFTMs given the different spatial and temporal resolutions for which data may be available, and the various uncertainties or variability that may be associated with the data and model predictions. Several other LRI projects are also closely related - for example there is one project on emission estimation, several on persistence and bioaccumulation, and one on atmospheric deposition modelling.
As chemical persistence is a central factor in long-range transport, ECETOC (the Industry-sponsored European Centre for Ecotoxicology and Toxicology of Chemicals) has a taskforce working to critically review methods for predicting persistence.

In the US, the American Chemistry Council (ACC) sponsored Long-Range Research Initiative recently funded two research projects which evolved from an LRI Workshop on atmospheric transport. The Atmospheric Reactivity Task Group of the Solvents Council of the ACC has funded projects on urban-scale environmental fate modelling and its impact on ozone formation. In Japan, a workshop on the application of multimedia modelling has recently been sponsored by the Japanese Chemical Industry Association.

Industry associations have also sponsored relevant studies. For example, EUROCHLOR has developed methods for interpreting aggregated local monitoring data at a regional scale, which are useful for model validation. EUROCHLOR also have extensive monitoring data for several chlorinated compounds which show temporal as well as spatial trends, illustrating that dynamic aspects of modelling may need to be considered for some compounds. In Canada, the Chlorine Council has funded projects which have summarised data on atmospheric emission sources for various chlorinated compounds, and also projects on urban and oceanic emissions. The Chlorine Council has also funded projects on the influence of elevation and temperature upon atmospheric deposition in Canada, long-term trends in organochlorine levels in the Great Lakes, and use of multimedia models in screening for POPs. Industry associations and individual companies have further contributed to the development and dissemination of multimedia models through their support of the Canadian Environmental Modelling Centre at Trent University.

$P_{overall}$ and CTD concepts

In the context of POPs, parameters such as $P_{overall}$ and CTD have potential to assist in screening and identifying substances that might persist or travel long distances in the environment. The concept of $P_{overall}$ is useful in terms of moving beyond simple single-media half-lives. It is clearly inappropriate to 'penalise' a chemical for being persistent in a compartment in which it is never found and the concept of overall persistence goes some way towards addressing this. The CTD concept is also useful since it highlights the potential for long-range transport. There is a simple relationship between $P_{overall}$ and CTD, but the CTD provides additional information about LRT potential that is not obvious from the $P_{overall}$ alone. Hence, both $P_{overall}$ and CTD are potentially useful and complementary concepts. Although both $P_{overall}$ and CTD are simple to calculate, their interpretation, especially in a regulatory context, is difficult. There are two main reasons for this: Firstly, there is considerable scientific uncertainty surrounding model predictions and, secondly, even if accurate values of $P_{overall}$ and CTD can be determined, it is not at all obvious how these should be used in the regulatory process.

[6]See http://www.cefic.be/lri for further information. Projects of interest include: Identification and evaluation of emission databases in Europe; Evaluating Multimedia Fate and Transport Models; Atmospheric Deposition; Understanding and measurement of persistence in the marine and terrestrial compartments.

Regulatory Interpretation (Screening versus Risk Assessment)

In a regulatory framework, the ultimate interest is to manage the risk of substances based upon the actual risk presented to the environment or to humans. This requires an understanding of both hazard and exposure. Since $P_{overall}$ or CTD give no information about actual exposure, any chemical screening using these parameters should only be used as a starting point to help decide, together with other necessary information, whether risk assessment is required.

Persistence and LRT are not inherently bad. The use of risk assessment techniques also requires consideration of toxic effects and whether or not predicted environmental concentrations are sufficiently high to warrant a concern. This requires knowledge of the quantity of chemical released, and of the environmental compartments to which the release occurs. These factors are absent in the calculation of $P_{overall}$ and CTD, and they should be taken into account as part of the initial screening assessment. The assessment would also benefit from the release data being incorporated into the screening process as early as possible. Indeed, to quote a recent paper;

.....'To adequately assess the risk of toxic effects, both the toxic hazard and the degree of exposure must be characterised. Since exposure cannot be estimated without knowledge of the emission rate of chemicals to the environment, a compelling case can be made that screening to identify P, B, T and LRT substances should be expanded to include quantity released to the environment as an additional factor'.....[7]
Hence, since the ultimate goal is risk assessment, it makes sense to incorporate a release factor, and some assessment of effect, as early as possible in the screening process.

Relative versus Absolute Approaches

Another important consideration in using $P_{overall}$ and CTD is the strengths and limitations of applying these results in relative versus absolute evaluations.

Relative evaluations are generally used to provide a ranking of chemicals based on a given characteristic -- in this case, $P_{overall}$ or CTD. This approach can be useful in the screening assessment for prioritising substances for further, more detailed evaluation.

An absolute approach, by contrast, involves comparing the results to absolute cut-off values that represent, for example, a specific overall environmental half-life or long-range transport distance. Therefore, the models must be able to provide valid and reliable estimates of $P_{overall}$ and CTD for chemicals. However, there is no way to validate these parameters directly as there is no method for measuring them in the laboratory or field. Thus, the use of $P_{overall}$ and CTD in an absolute evaluation is problematic.

Somewhere between these two approaches is the use of benchmark substances. In this situation, the approach is to evaluate substances on a given characteristic (e.g. $P_{overall}$ or CTD) and state whether it is 'better' or 'worse' than a given benchmark substance. This approach gives an absolute determination (i.e., it meets the criteria or not) but in a relative way. The results of such a benchmark comparison

[7] Don Mackay, Lynn McCarty and Matthew Macleod. On the validity of classifying chemicals for persistence, bioaccumulation, toxicity, and potential for long range transport. Env Tox & Chem. **(** 7) pp1491-1498, 2001.

could then be used to determine whether a full risk assessment is required. They should never be used in isolation or confused as measures of risk in themselves.

Scientific Uncertainty

An important principle in the application of MFTMs is that uncertainty should be considered in any evaluation of a substance's $P_{overall}$ and LRT potential. This is especially important when considering the appropriate role of these models (i.e. screening versus higher tier evaluations) and the ability to distinguish between different substances in a statistically significant way.

Uncertainty results from a variety of sources. For example, it is inherent in the chemical characteristics data, in the mathematical equations used to describe the fate processes and in the environmental characteristics. As scientific understanding and experimental methods improve, these uncertainties can be better quantified. Hence, there is a need to up-date models when scientific understanding increases.

In addition, even when ostensibly the same model is being used, different results can be obtained because of differences in the ways that different users interpret and enter the same data[8]. For example, different interpretation of specifications and units (e.g. wet weight versus dry weight based concentrations) can cause the results to be different, or to be interpreted differently. This type of error is very likely to occur in practice. Thus the use of these models must be based on careful and unambiguous definition of all parameters. This type of uncertainty was clearly demonstrated in the preliminary work to the 1991 OECD modelling workshop[9], in which different OECD Member Countries were asked to apply MFTMs to 10 different chemicals. Although in many cases the same model was used for the same chemical, very different predictions were obtained by different practitioners.

Techniques are available which allow for the calculation of the uncertainty in the model results, and these are useful in understanding the reliability and utility of the model results. However, some sources of uncertainty such as that due to the mathematical equations and user variability are less well defined and thus harder to quantify. A cross comparison of the model results for ten chemicals with four MFTMs (Cowan et al. 1995) showed that these sources of uncertainty can be substantial. In several cases, the differences were greater than one order of magnitude and in one case (i.e. lead in soil) greater than 2 orders of magnitude. Hence absolute quantification of the uncertainty in the $P_{overall}$ and CTD can be extremely difficult.

The $P_{overall}$ and CTD estimates may be less sensitive to choice of model or compartment sizes, which makes them potentially more useful in a regulatory context than predicted environmental concentrations. However, considerable uncertainty may still exist in the chemical specific data. Further work is needed to define appropriate methods of measuring or estimating these data, particularly with respect to degradation rates in different environmental media and how these affect the $P_{overall}$ and CTD estimates.

As the regulatory application of models is developed, all of the above factors will need to be considered and this is likely to result in both quantitative and qualitative estimates of uncertainty. Of course the challenge is not only to define methods for estimating uncertainty, but also to define what range of

[8] Cowan, C.E. D. Mackay, T.C.J. Feijtel, D. van de Meent, A. DiGuardo, J. Davies, N. Mackay. 1995. The Multi-Media Fate Model: A vital tool for predicting the fate of chemicals. SETAC, Pensacola, FL

[9] OECD (1994). Report of the OECD Workshop on the Application of Simple Models for Exposure Assessment. Environmental Monograph # 69. Paris.

uncertainty model predictions is acceptable at the different stages of the regulatory process. For example, at a screening level stage of the regulatory process, should models used be expected to predict to an accuracy of better than a factor of 10, or not?

Data Requirements, and the Use of Monitoring data

Data needs fall into two categories, data needed for input into the models and monitoring data needed for validation of the model output. Development of both types of data should be addressed in a systematic way, so that information generated in one area is comparable to that generated in another.

Data needed for model input may be either data concerning the inherent properties of the chemical, such as half-life values in various media, or data of a temporal nature such as emission levels to different environmental compartments. Model outputs will improve when accurate data for both of these categories are available. When many of the inputs are estimates based on similarities to other molecules or on estimates of emission levels, there will always be a large uncertainty in the output. Where possible any new data generation should follow accepted international guidelines (e.g. OECD, ASTM, ISO.)

To validate MFTMs, comparison of measured and calculated exposure levels is essential. Ideally, for risk assessment, we would like to have measured concentrations everywhere, but this is clearly unrealistic. Indeed the role of models is ultimately to provide Predicted Environmental Concentrations (PECs) where monitoring data are not available. However, in order to interpret PECs confidently in a regulatory context, it is essential that comparison with appropriate monitoring data is undertaken, whenever possible. If sufficient data are available, it may be preferable to use spatially or even temporally resolved GIS[10]-based modelling systems to predict environmental concentrations at specific places and times, which can be verified by environmental measurements. These models can then be used to calculate an average concentration covering selected, appropriate sites, to correspond to a PEC which is acceptable in a regulatory context. Industry is currently contributing to the development of suitable modelling tools, which can be used for this purpose.

Criteria for monitoring data generation have already been specified by OECD in their report on the Berlin Monitoring Workshop[11], and discussed at a recent SETAC Workshop [12] (Klecka et al, 2000). These criteria need to be considered in the planning of any data collection. However, the use of monitoring data for model validation is a complex subject in itself (for example, how much data do you need?). It seems there should be no hard and fast rules since different types and quantities of data are available for different substances. However, it is clear that modelling and monitoring complement each other. One without the other is much less convincing than having both together.

It is important that data needs are recognised and that a systematic approach is taken to filling current gaps in understanding about inherent chemical properties and the actual occurrence of chemicals in the environment. Monitoring data must also be developed that will allow validation of Multi-Media Models so that improvements can be made in our predictive capabilities.

[10] GIS is geographical information system

[11] OECD (2000). Report of the OECD Workshop on Improving the Use of Monitoring Data in the Exposure Assessment of Industrial Chemicals. OECD Environmental Health and Safety Publications, Series on Testing and Assessment No. 18. Paris.

[12] Klecka, G. et al., editors. (2000) Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment. SETAC Press, Pensacola, Florida.

Summary

- Industry believes that MFTMs can provide valuable insight into the fate and distribution of chemicals in the environment, and recognises that such models are increasingly useful in a regulatory context. However, further work is needed to ensure that these models - and the interpretation of the model results - are based on sound scientific principles.

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- The models are only an estimate of reality and there are potentially many scientific uncertainties. Hence monitoring data should be used whenever possible to support model predictions.

Darryl Luscombe and Romeo Quijano: Precaution and the Assessment of POPs under the Stockholm Convention

D. Luscombe – Greenpeace International[13] and R. Quijano[14] – University of the Philippines Manila

The Stockholm Convention on Persistent Organic Pollutants (POPs) was adopted by over one hundred nations on 21st May 2001. The Convention initially targets nine pesticides and two industrial chemicals (aldrin, chlordane, dieldrin, DDT, endrin, heptachlor, hexachlorobenzene, mirex, PCBs and toxaphene) for international action aimed at eliminating the use and production of these chemicals. It also requires action to reduce, and where feasible, eliminate the unintentional production of POPs in industrial processes - initially the polychlorinated dibenzo-p-dioxins and furans, hexachlorobenzene and PCBs.

The Convention also provides for including additional existing substances to the list of POPs requiring international action. However, in many respects the true significance of the Stockholm Convention relates not to the initial list of 12 substances, but the broader commitment to prevent the production and use of all new substances with the characteristics of POPs.

The objective of the Convention is to protect human health and the environment from POPs in the context of the precautionary approach set out under Principle 15 of the Rio Declaration on Environment

[13] Participating Organisation of the International POPs Elimination Network (IPEN)

[14] International Co-Chair of the International POPs Elimination Network (IPEN)

and Development. The use of the precautionary principle is operationalized in a number of the provisions of the Convention and is integral to its application.

The precautionary principle as set out in the Rio Declaration states; Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation. Other variations and formulations of the principle exist, yet the basic premise remains the same – the threat of permanent or irreversible damage should be avoided, even in the case of scientific uncertainty.

The Principle of Precautionary Action arising under German Federal law clarifies some of the aims of precautionary principle. Namely, that (a) harm should be avoided before it occurs; (b) high quality scientific research should act to provide early warnings of the potential for damage; (c) action not merely can, but MUST, be taken on the basis of available information as necessary to avoid threats, even when evidence of causality remains limited; and (d) all technical, social and economic developments should tend towards a progressive reduction in overall environmental burden.

The criteria for assessing new and additional POPs under the terms of the Convention relate to the potential for persistence, bio-accumulation, long-range transport and adverse effects. Unfortunately, for many of the thousands of chemicals in wide-spread use in commerce, existing data on these properties is severely limited or non-existent. The challenge therefore, is to assess these and newly developed substances in a manner which will identify those which have the potential characteristics of POPs based on limited and incomplete information.

In the circumstance where science and policy decisions are made on limited evidence, the demarcation between the two is not necessarily unambiguous. The development and application of scientific methods is crucial to this task, as is the acknowledgment of the inherent limitations and uncertainties of those methods. The application of the precautionary principle therefore provides an essential tool in the assessment of new and additional POPs.

André Lecloux : Statistical Analysis of Local Monitoring Data to Assess Regional Exposure and to Validate Multi-Media Models

Euro Chlor Science Director

One of the key issue in modelling is to reach a good balance between practicability and reliability, in other words to develop models which are simple to understand, easy to use and robust enough to represent the real world. Before being used in regulatory applications, simple models should be validated by comparison either to more sophisticated approaches or to reliable monitoring data.

Multi-media models to estimate the overall persistence and the Long-Range-Transport (LRT) potential of chemicals should be applied at least at a regional scale while the monitoring data are always measured at well defined locations. To overcome the difficulty of comparing local measurements to regional estimates, a statistical methodology has been developed to determine exposure level distribution, representative of a region. This experimental distribution of concentrations can then be compared to the distribution of modelling results, obtained by varying the parameter values of the model. This methodology, based on a statistical aggregation of local monitoring data, can be adapted to various scales and provide a tool for assessing the spatial variations in global modelling.

A similar statistical approach has been developed and applied to define reliable regional, temporal trends starting from monitoring data obtained at various locations at different times. These regional trends can also be used to assess the temporal variations in global modelling.

In this paper, the principles of these statistical analyses will be shortly described and illustrated by several regional exposure distributions of persistent chemicals and their regional temporal trends. A proposal will also be made on how to use this approach in multi-media model validation.

Noriyuki Suzuki: Assessment of long-term exposure with persistence consideration in the last evaluation task for dioxin risk assessment in Japan

National Institute for Environmental Studies

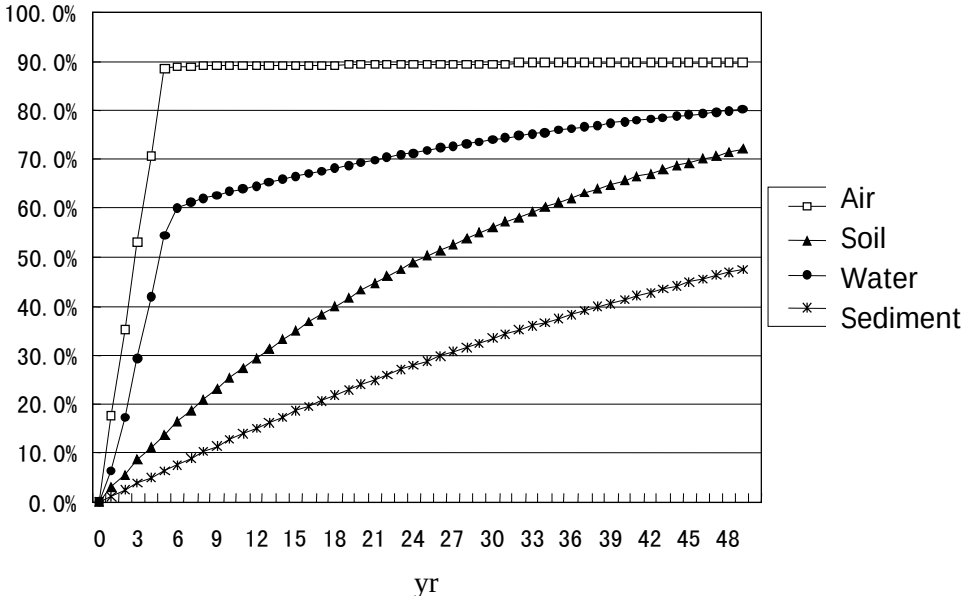
Environment Agency, Japan (Ministry of Environment from year 2000), made major effort of risk assessment of dioxin based on the Law concerning Special Measures against Dioxins established in July 1999. The 90% reduction of dioxin emission by the end of March 2003 compared to the emission in 1998 was declared in the Basic Guidelines for the Promotion of Measures against Dioxins established by the Ministerial Council on Dioxin Policy in March 1999.

As a part of the assessment process, persistence of dioxins in the environmental media after the 90% reduction scenario was evaluated based on the multimedia fate model with air, water, soil and sediment with particulate/soluble phases. Part of the results is shown in the Figure 1 below.

From the information in Figure 1, persistence of dioxin exposure from various media was discussed. Some of the discussions were performed on whether the concentration in fish was determined by water or sediment concentration. This point should be important because the persistence in the water and sediment may be very different. The results of this effort also imply the importance of remediation of soil and sediment.

Although this effort is not directly intend to assess overall persistence in the context of POPs/PBT identification, it has some similarity in the consideration of full multimedia persistence in the assessment process using the dynamic multimedia fate model. I think this is one of the experiences of Ministry of Environment for the use of multimedia models in the POPs/PBT assessment.

Figure 1 Reduction of dioxins in the multimedia environment after the 90% reduction scenario in 5 years. Percentage means the model result of reduction in the media from the start point, year 0.



Sergey Dutchak, A. Malanichev, V. Shatalov, and N. Vulykh : Usage of POP multimedia models under UN ECE CLRTAP

Introduction

At present a lot of international organizations (UNEP, EMEP, HELCOM, OSPAR, AMAP and others) have included the investigation of POP environmental pollution in their working programmes. Due to its complexity, this problem needs the widest cooperation of scientists on the international level. Here we present a brief description of EMEP activities in this field.

The main goals of EMEP are:
In good time before each annual session of the Executive Body, EMEP shall provide information on the long-range transport and deposition of persistent organic pollutants.
EMEP should assist Working Group on Effects in elaborating effect-oriented approach for POPs (risk assessment).
EMEP plans to contribute to the work of Ad hoc expert group on evaluation of new substances.
For solving these goals a complex monitoring/modeling approach to assessment of POP contamination should be developed. In particular, the aim of this paper is to present the information on EMEP activities in assessment of POP contamination by means of the multi-compartment POP transport model (MSCE-POP) and to consider the possibilities of usage of this model in the frame of environmental protection on all the three above mentioned stages. Below we present short description of the model and possibilities of its application to the assessment of environmental pollution both on the stage of primary consideration of a chemical to be included into international POP activities and on the stage of its more detailed examination, and give a short description of model validation by comparison obtained calculation results with available measurements.

Progress in investigations of POP environmental pollution

Table 1 presents the EMEP activity on the field of investigation of POP environmental pollution. It includes collection of physical-chemical properties, emission data, monitoring information and model assessment of substances under question. The extent of advance in corresponding directions marked by intensity of background. The more saturated color of background, the more detailed elaboration of respective direction.

There are presented two groups of substances. The first contains substances, which are included into Protocol. Great attention has been paying to lindane (γ-HCH), benzo[a]pyrene, (B[a]P), polychlorinated biphenyls (PCBs). For these substances noticeable progress has achieved actually in all direction. For dioxines/furanes (D&F) and hexachlorobenzene (HCB) certain information on physical-chemical properties, emission data, monitoring data has been collected and pilot calculations have been carried out. Such substances as DDT, and Heptachlor are on the stage of preliminary collection and processing of information.

The second group contains the substances, which are not included into Protocol. They are dicofol, hexachlorobutadiene (HCBD), pentachlorobenzene, polichlorinated naphtalenes (PCNs) and pentachlorophenol (PCP). Collection of physical-chemical, emission and monitoring information of these substances are on the first stage and only for pentachlorobenzene and PCP preliminary model estimates of overall persistence and long range transport potential have made. The last will be discussed some later. For proper interpretation of modeling result the next part includes brief description of MSCE-POP transport model, as well input and output information.

Table 1. Progress in EMEP activity on pollutants in question

pollutant	physical-chemical properties	Emission data	monitoring information	model assessment
substances already included in the protocol				
pesticides				
Lindane				
HCB				
DDT				
Heptachlor				
industrial pollutants				
PAHs (B[a]P)				
PCBs				
PCDD/F				
substances not currently included in the Protocol				
Dicofol				
HCBD				
Pentachlorobenzene				
PCNs				
PCP				

intensity of background reflects an extent of advance in respective direction:

Initial	Intermediate	Advanced

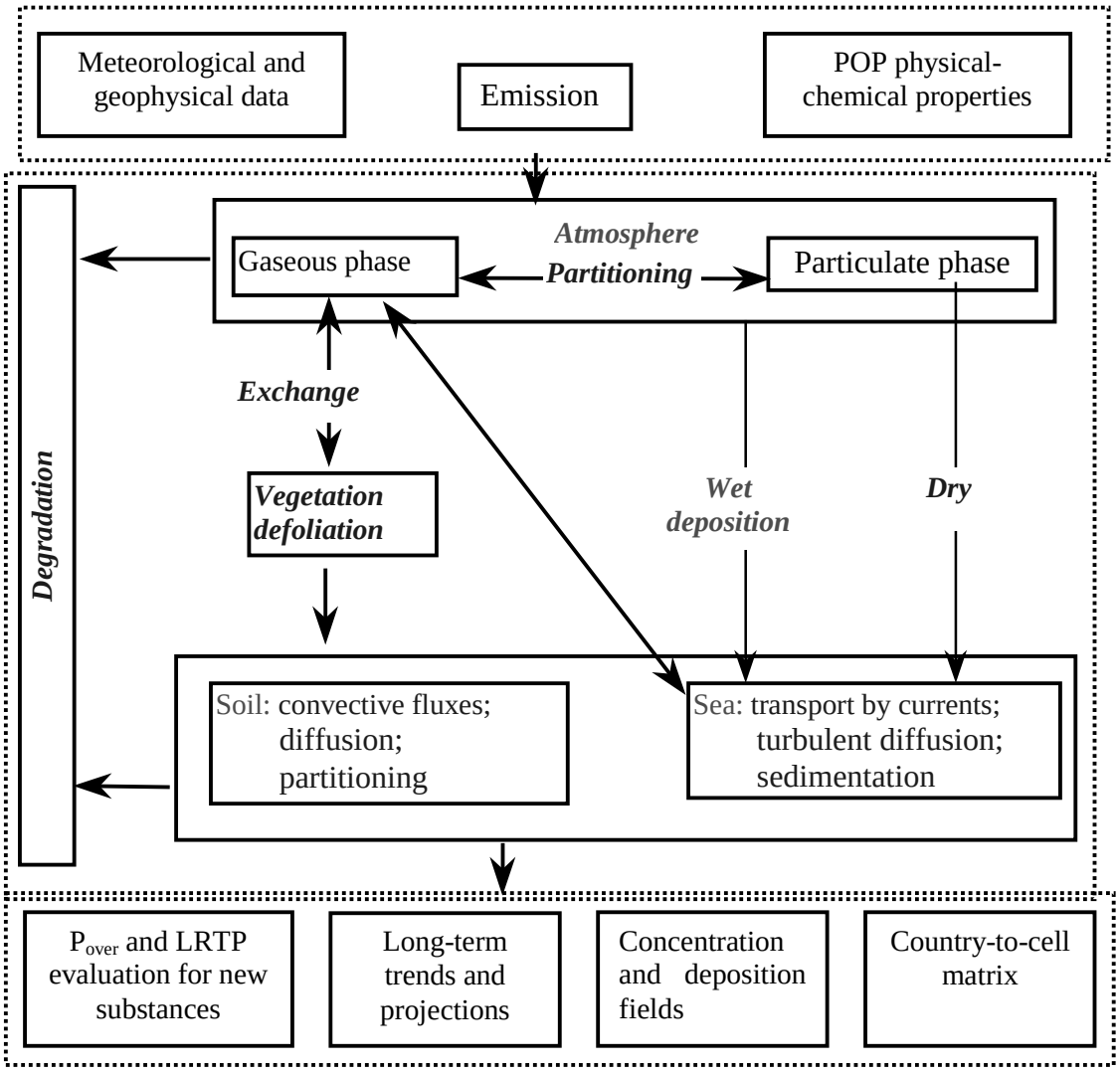
Model description

Here we present a short description of MSCE-POP model being under development in MSC-E since 1998. This model is a multi-compartment one describing exchange processes between basic environmental compartments. Figure 1 presents the structure of the model showing environmental media (marked red) and processes (marked blue) included. Sets of input and output data are also indicated in the figure.

As seen from Figure 1, the model includes such environmental media as atmosphere, soil, seawater, and vegetation. Vegetation is taken into account since it can play a role in the pollutant transport from atmosphere to soil for some pollutants (to describe such a transport we have introduced forest litter as an intermediate media between vegetation and soil).

The model was elaborated for the EMEP domain on the basis of Eulerian transport atmospheric model with spatial resolution 150x150 km. The description of exchange processes with underlying surface was primarily done on the basis of Jacobs and A.van Pul [1996] and the box model by A. Strand and Ø Hov [1993]. Model parameterizations are elaborated for PAHs (B[a]P), HCHs, PCBs, HCB, and PCDD/Fs. At present there exists a modification of the model for B[a]P with resolution 50x50km. The model version on hemispheric scale with $2.5x2.5^0$ resolution is under development.

Figure 1. The scheme of the multicompartment transport model MSCE-POP



In the model, such media as atmosphere, soil, and sea are separated vertically into a number of layers to describe the vertical transport of a pollutant in question. Variability of soil and vegetation properties in the horizontal direction is taken into account with the help of the corresponding land-use and leaf area index information.

Calculation time required for modeling is not too large. Thus, calculations of transport inside the EMEP region within one year with 150 x 150 km resolution takes about 40 minutes. For hemispherical version with $2.5x2.5^0$ resolution this time equals about 6 hours.

Below we illustrate some results obtained by our model to show its possibilities.

Calculation results

Complex chemical mixtures

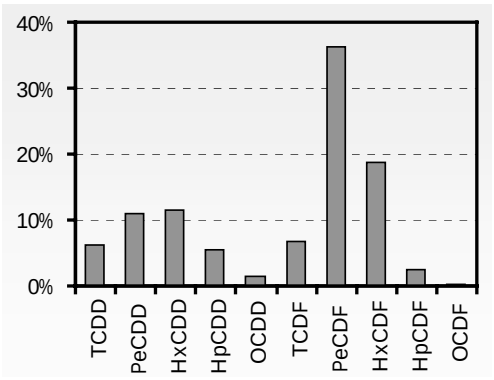
Here we describe the application of the model for solving the problem of complex chemical mixtures. Such a problem arises when considering a group of chemicals consisting of a lot of particular chemicals possessing different physical-chemical properties such as PAHs, PCBs, or dioxins/furans, etc. The matter is that modelling of all chemicals from such a group takes a lot of calculation time and is not reasonable since usually not all of them contribute considerably to the pollution of the environment. So, on the first step of investigation of such a group there arises a problem of determining the list of chemicals covering noticeable part of pollution of the environment by the chemical group in question. Further, in some cases it is possible to select a particular chemical from the group "indicator chemical" such that modelling the transport of the mixture of all chemicals from the group with properties of the selected chemical leads to the result acceptable with reasonable accuracy.

We shall illustrate the problem by the example of dioxins/furans (for details see [Vulykh and Shatalov, 2001]). This group of chemicals consists of 210 congeners with different physical-chemical properties. It can be split into 10 homologous groups: TCDDs, PeCDDs, HxCdDDs, HpCDDs, OCDDs, TCDFs, PeCDFs, HxCdDFs, HpCDFs, and OCDFs depending on their chemical structure. On the first stage the contributions of each group to the total toxicity of dioxins/furans mixture in various environmental compartments was performed with the help of measurement data obtained from literature sources (to assess the toxicity we used NATO system of toxicity equivalents). The results for air and vegetation are presented in Figure 2.

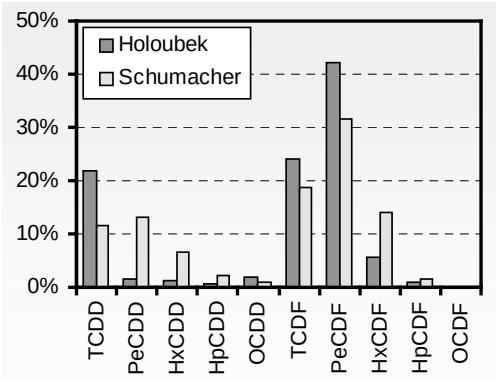
Further, it was found that the contributions of homologous groups to emission toxicity are similar to that in the air. On the basis of these results four homologous groups were selected for the consideration on the first stage : PeCDDs, HxCDDs, PeCDFs, and HxCDFs. On next stages of investigations TCDDs and TCDFs are to be included into consideration due to their considerable contributions to the toxicity of environmental media other than air.

More detailed analysis of measurement and emission data allowed us to select particular congeners for modeling on first and second stages of investigations (see [Vulykh and Shatalov, 2001]). The results are summarized in Table 2.

Figure 2. Relative contributions of PCDD/Fs homologous groups to the overall dioxins/furans toxicity in air and vegetation



Air
[*Pacyna et al.,* 1999]
[*Lohmann and Jones,* 1998], …



Vegetation
[*Holoubek et al.,* 2000]
[*Schumacher et al.*, 2000]

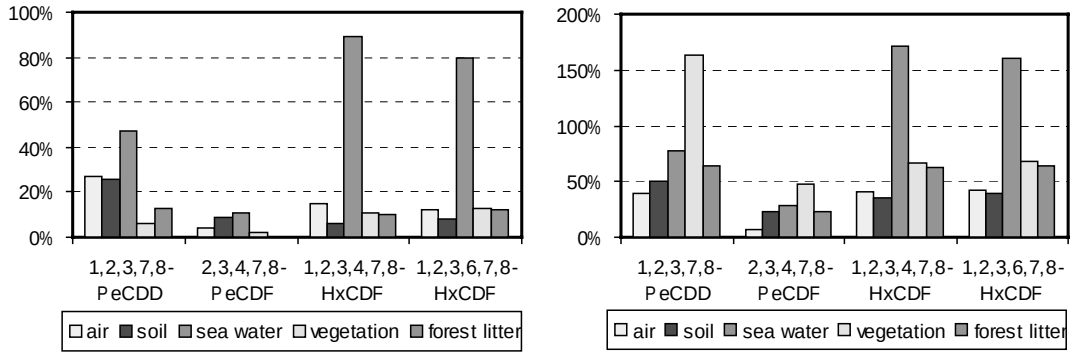
Table 2. List of priority congeners

Congener	Stage	Reasons for inclusion
1,2,3,7,8-PeCDD	I	Essential contribution to the toxicity of dioxins/furans mixture in environmental compartments
2,3,4,7,8-PeCDF		
1,2,3,4,7,8-HxCDF		
1,2,3,6,7,8-HxCDF		
2,3,7,8-TCDD	II	Noticeable contribution to the toxicity of dioxins/furans mixture in soil, vegetation, and sea water
2,3,7,8-TCDF		
1,2,3,6,7,8-HxCDD		Noticeable contribution to the toxicity of dioxins/furans mixture in soil and sea water. Long life-time in soil
1,2,3,7,8,9-HxCDD		

The next goal of investigation of dioxins/furans group was to select an "indicator congener" out of four congeners of the first priority. To do this five model runs were performed:

Four mono-congener runs: in each properties of one of the congeners are assigned to the whole mixture.
Multi-congener run: all four congeners are transported simultaneously each with its own properties.
The calculation results of each of mono-congener runs were compared with that for multi-congener run.
Figure 3 illustrates the results of comparison both for balance values and spatial distributions.

Figure 3. Relative differences between results of multi-congener and mono-congener runs from the viewpoint of balance values and spatial distributions



Balance values Spatial distribution

From the left diagram it is seen that contents in all considered environmental media calculated with properties of 2,3,4,7,8-PeCDF differ from corresponding contents calculated in the course of multi-congener run at most by 10%. The discrepancies between media content obtained by other mono-congener runs and by multi-congener run are essentially larger. This shows that from the viewpoint of balance values properties of 2,3,4,7,8-PeCDF can be use with the accuracy of 10%.

However, the discrepancies between concentration levels in different environmental media within particular grid cells can be much larger. Therefore, to select 2,3,4,7,8-PeCDF as an "indicator congener" it is necessary to calculate maximum differences between concentration levels obtained by other mono-congener runs and by multi-congener run over all grid cells. The results of such calculations are shown on the right diagram in Figure 3. It is seen that the discrepancies for concentration in vegetation can reach 50% in some grid cells whereas in other media these discrepancies are not more than 30% over the whole grid. This is exactly an estimate of the accuracy of usage 2,3,4,7,8-PeCDF as an indicator congener.

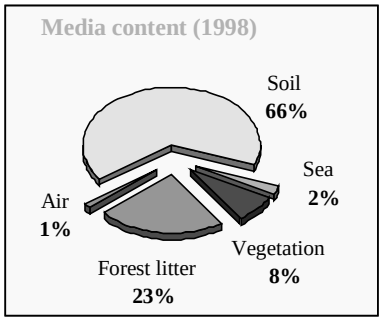
So, the multimedia model can be a tool for selection "indicator chemicals" from large chemical groups.

Mass balance

One of important outputs of the MSCE-POP model is mass balance that is relative accumulation in various environmental compartments. Here by accumulation of the given compartment we mean simply the amount of a pollutant contained in the compartment by the end of the calculation period.

Figure 4 shows the distribution of dioxins/furans between environmental compartments obtained up to the end of 29-year calculation period (from 1970 to 1998).

Figure 4. Mass balance for dioxins/furans as a result of model run from 1970 to 1998



The analysis of the calculated mass balance allows one to assess the relative importance of accumulation in various environmental compartments for the pollutant in question.

These results can be also used for the comparison with the results obtained by box models.

Long-term trends

To analyze the dynamics of long-term accumulation of various POPs in various environmental compartments model runs for sufficiently long time period were performed. This is possible due to emission inventories by [Pacyna et al., 1999] for the period from 1970 to 1995 obtained in the framework of the POPCYCLING-Baltic project. The model allows one to calculate long-term trends of depositions and concentrations in various environmental media for various European countries and regions. Figures 5 and 6 show the results of such calculations exemplified by comparison of emission and deposition dynamics in two European countries (Germany and Slovakia) in comparison with total European emission.

Figure 5. Total European emission of dioxins/furans for 1995 [Pacyna et al., 1999*]*

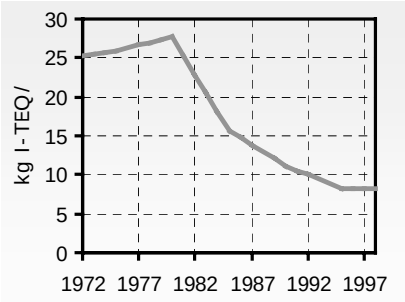
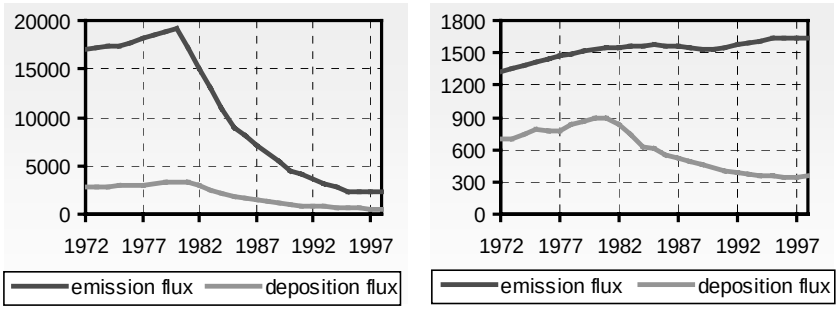


Figure 6. Emission and deposition fluxes in Germany (left) and Slovakia (right) for 1995, pg I-TEQ/m^2/y



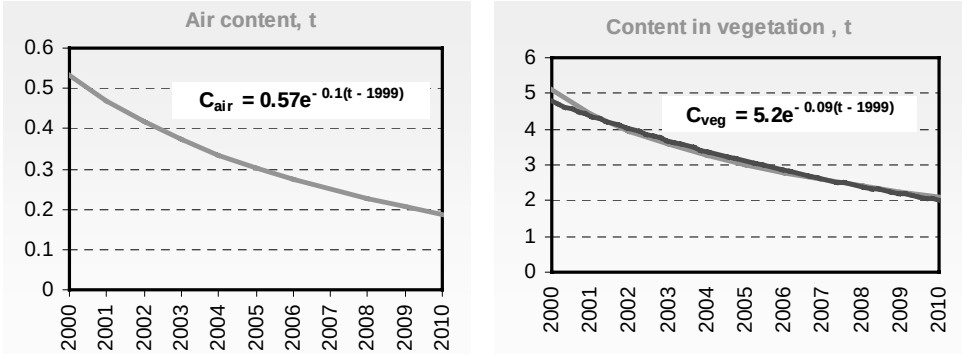
From the plots presented in Figures 5 and 6 it is clear, in particular, that the dynamics of deposition flux in a country is determined rather by dynamics of the total European emissions than by emission of the country itself. This shows that the role of transboundary transport for dioxins/furans is essential.

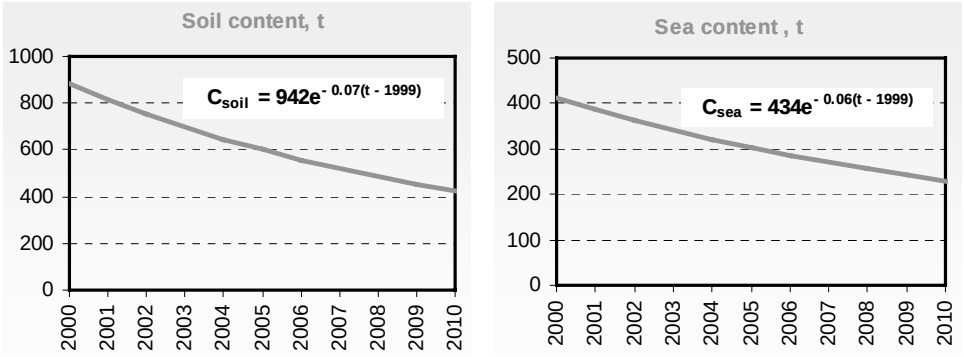
The investigation of long-term trends of contamination in various environmental compartments can be useful for evaluation of results of realized emission reduction strategy from the viewpoint of environmental pollution.

Media responses to emission reductions

One of possible applications of the model is the evaluation of environmental media response to possible emission reduction. To exemplify such a possibility a model run for PCBs from 1970 to 2010 was performed under the assumption that no emissions in Europe take place since 1999 (zero emission scenario). Figure 7 presents plots of PCB pollution in main environmental media and re-emission flux together with their exponential approximation. The curves of exponential approximations are omitted in those cases when they essentially coincide with the approximated curve.

Figure 7. Trends of PCB content in air, vegetation, soil, and seawater over the EMEP domain under the assumption that no emissions take place since 1999

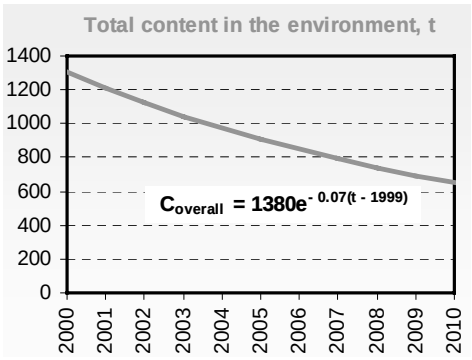




From the exponential approximation coefficients it can be calculated that the time of half-clearance of the atmosphere with allowance of multimedia exchange (multimedia clearance period) is about 7 years even at full emission cessation. For soil and sea the multimedia clearance periods are about 9 and 12 years, respectively. Here the content in forest litter is included to soil content since forest litter can be viewed as an upper soil layer; for soil itself the multimedia clearance period equals 16 years. For all the shown period the air concentrations are supported by the re-emission flux (both from soil and sea). The obtained results are in accordance with observations over Great Britain (see [Sweetman and Jones, 2000]).

The multimedia clearance periods in various environmental media can be used as estimates for persistence of the pollutant in question in these media. For assessment of the overall persistence it is possible to use exponential approximation for the content in the whole environment shown on Figure 8.

Figure 8. Trend of PCB content in the environment over the EMEP domain



The corresponding clearance period equals 10 years. The corresponding clearance rate $R_{overall}$ can be obtained by averaging clearance rates R_i of all media considered with weights proportional to media contents C_i:

$$R_{overall} = \frac{\sum R_i C_i}{\sum C_i}$$

However, it has to be taken into account that the value of multimedia clearance period for the overall environment depends on the period considered and on the emission scenario used. The reason for his phenomenon is that exponential approximation describes well trends not for all environmental media. For example, trend for content in vegetation (Figure 7) is not well described by exponential approximation.

Construction of projections for contamination levels under different emission reduction scenarios can be useful for elaboration of reasonable scenarios for chemicals scheduled for restriction of use. Projections for zero emission scenario (full cessation of emissions beginning from some moment) can

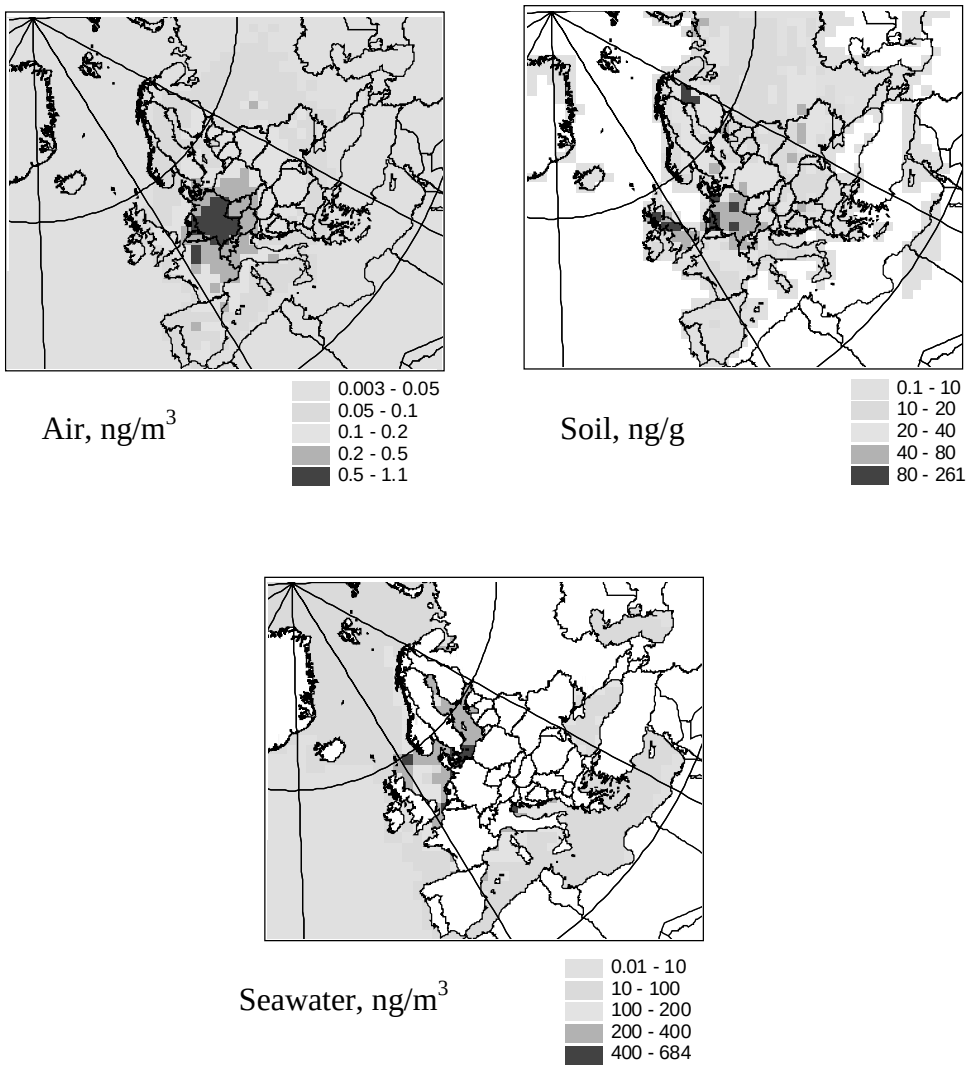
be used for evaluation of persistence of the given pollutant in various environmental media and of overall persistence in the environment.

Spatial distributions

One more important model output is spatial distributions of concentrations and deposition over the calculation domain.

Figure 9 exemplifies calculated spatial distributions by PCB concentrations in air, soil, and seawater in 1998 obtained as a result of model run for the period from 1970 to 1998. Maps of this type can be used for localization of hot spots in POP contamination formed both by long-range transport and accumulation. For example, from maps of Figure 9 it is clear that spatial distributions of air and soil concentrations are not similar. Soil concentration map shows domains with relatively high levels obtained due to accumulation during the all calculation period. One of such domains is in Scandinavian Peninsula being possibly explained by high deposition velocities to forests. Maps of spatial distributions for POP concentrations in various media can also point out peculiarities of the long-range transport process. For instance, spatial distribution map for seawater concentrations show the results of marine transport of PCBs. Relatively high concentrations near the North boundary of the Scandinavian Peninsula can be explained by transport with sea currents from more contaminated marine regions.

Figure 9. Calculated spatial distributions of PCBs in 1998 in various environmental compartments



Examination of spatial distribution for POP concentrations in the atmosphere can also serve as a tool for evaluating the long-range transport potential for this or that pollutant. To carry out such an evaluation one can use model runs for conventional emission sources concentrated in some characteristic points in Europe. One of the characteristics of the long-range transport – spatial range – is then defined as the distance containing 95% of the total spatial content of the pollutant (definitions of different characteristics of persistence and long-range transport see [Mackay et al., 2001]). It is worth mentioning that spatial range may depend on the period covered by calculations due to accumulation in the media other than atmosphere.

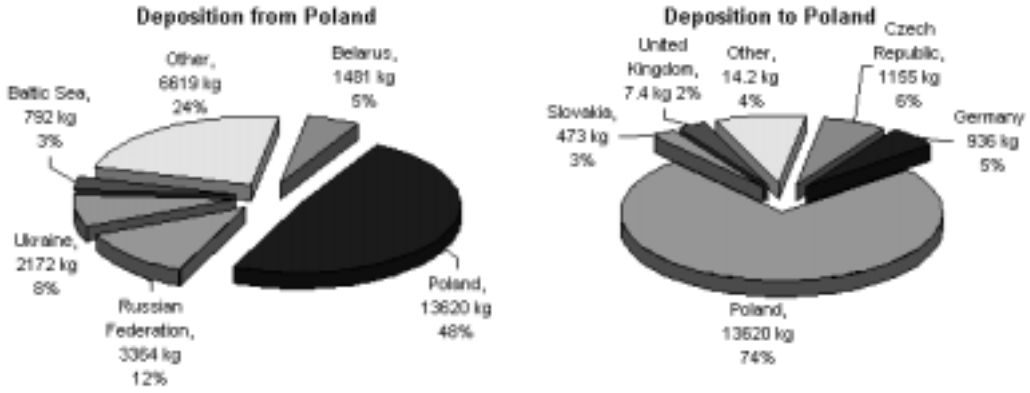
So, calculation of spatial distributions of contamination in various environmental compartments can be used for localization of hot spots for subsequent risk assessment. Such calculations can serve as a tool of evaluation of long-range transport potential even in the case when emissions are unknown.

Evaluation of transboundary transport

At present a model modification for calculating country-to-region matrices is performed for B[a]P. This modification allows one to analyze relative contributions of emission sources from different countries to formation of depositions and concentration levels in a given country (import) and to evaluate fractions

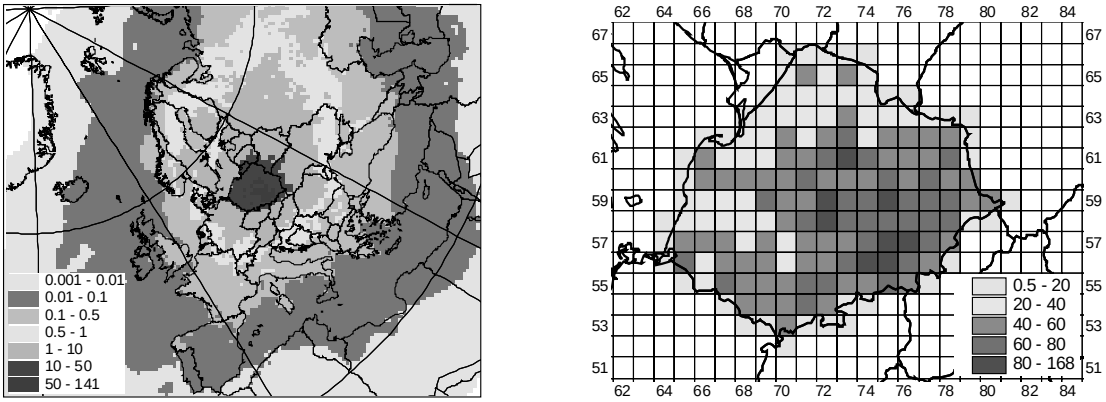
of emissions from a given country transported to other countries and regions (export). The calculation of transboundary transport was performed for 1998. As an example, Figure 10 demonstrates pie charts of B[a]P import and export for Poland in 1998.

Figure 10. Export and import of B[a]P for Poland in 1998



Further, the modified model gives a possibility to assess spatial distributions of concentrations/depositions originated by emissions from a given country (export). The example is given in Figure 11a where the map of deposition from Poland emission sources in 1998 is presented.

Figure 11. Spatial distributions of depositions from Poland (a) and to Poland (b) in 1998, g/km^2/y



(a) (b)

Similarly, the model assesses spatial distribution of depositions/concentrations in a given country originated by all European emission sources. The example is given in Figure 11b where the spatial distribution of pollution due to all European sources in Poland is presented. It is possible also to calculate such a chart excluding emission sources of the country under consideration. These charts can be used as a background information for national (more detailed) modeling.

As it was already mentioned, the model calculates import and export not only for depositions (traditional approach) but also for concentrations in the atmosphere. It is conditioned by the fact that in some countries limit values for B[a]P atmospheric concentration are used.

Thus, for such (mostly particle-bound) pollutants as B[a]P it is possible to assess transboundary fluxes which can be useful both in the stage of working out abatement strategies and on the stage of the control of compliance. Apart from direct assessment of transboundary transport, the calculated matrices can be used for evaluation of model sensitivity with respect to total emissions from various European countries and for assessment of responses of B[a]P air concentrations and depositions to emission reductions in a (group of) European country.

Model validation

Model validation was performed both by comparison of calculation and measurement data and by investigation of model sensitivity to model parameters. Here we shall describe the results of the comparison between calculation results obtained on the basis of the model and available measurement data. More detailed description of model validation can be found in MSC-E reports [Pekar et al., 1998; Pekar et al., 1999; Shatalov et al., 2000].

The description of the comparison results will be performed on the basis of measurement to calculation factor (MCF). This factor is defined as a ratio of calculated value to the measured one if the latter is less than the former and as a ratio of measured value to the calculated one in the opposite case:

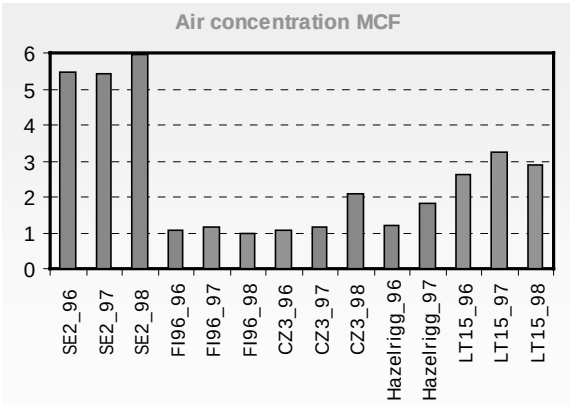
$$\mathrm{MCF} = \max\left(\frac{meas}{calc}, \frac{calc}{meas}\right)$$

Below we present the values of MCF for various pollutants and their characteristics.

Benzo*[a]*pyrene

Figure 12 presents the diagram of MCFs obtained in the period from 1996 to 1998 at different locations in Europe. Here by SE2_96, … the comparison result obtained at the EMEP station SE2 in 1996 is marked, by Hazelrigg__96, … – the results using measurement data obtained at Hazelrigg in 1996 (see [Coleman et al., 1998]).

Figure 12. Comparison of calculated and observed air concentrations for B[a]P.

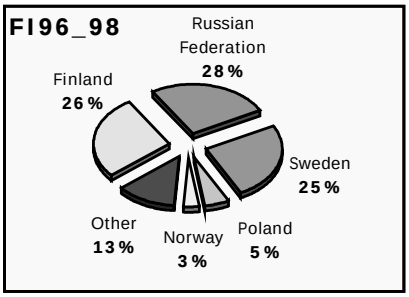


– calculated value exceeds measured one,
– measured value exceeds calculated one.

It can be seen that at the Sweden station SE2 the model overestimates air concentrations within the factor of 6, at Lithuanian station LT15 model underestimates air concentrations within the factor of 4. At the rest of the stations the discrepancy between measured and calculated air concentrations is in essence within a factor of 2. The results of the comparison shows that the model essentially correct describes main processes of B[a]P long-range transport in the environment taking into account that measured concentrations vary in wide range (from 0.02 to 1.5 ng/m^3).

Source-receptor method worked out for B[a]P allows one to determine main sources of B[a]P contributing to the formation of concentration levels at the measurement site. For example, Figure 13 shows the formation of air pollution levels at the Finnish station FI96 in 1998.

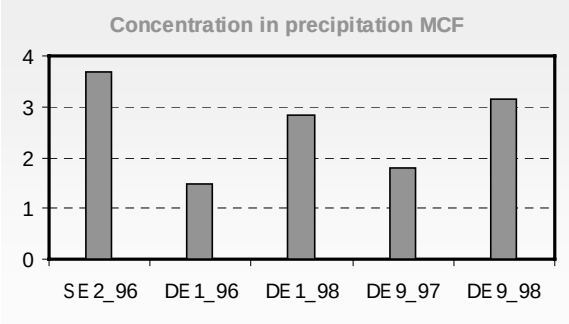
Figure 13. Formation of air pollution levels at the Finnish station FI96 in 1998.



This approach can help in the analysis of main emission sources which uncertainties cause the discrepancies between measurement and calculation data.

In Figure 14 the plot of MCFs for B[a]P concentrations in precipitation is presented; the notation is the same as for Figure 10.

Figure 14. Comparison of calculated and observed concentrations in precipitation for B[a]P.

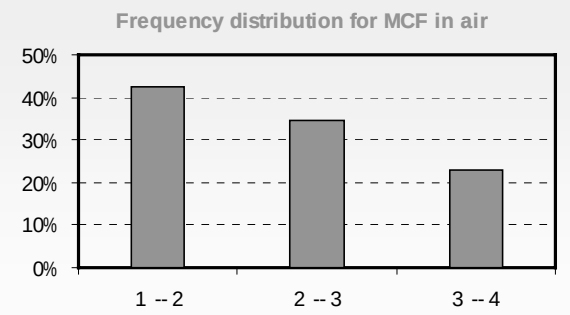


One can see that the model underestimates concentrations in precipitation within a factor of 4. We do not present the results of comparison of B[a]P concentrations in other media since for calculations of country-to-country matrices the simplified version of the model was used where exchange processes between atmosphere and underlying surface were not taken into account.

Polychlorinated biphenils

For PCBs the comparison of measured and calculated results was performed on the basis of PCB-153 as an indicator congener. The frequency distribution of MCF for atmospheric concentrations constructed on the basis of 26 measurements obtained in the period from 1991 to 1998 at different locations in Europe is presented in Figure 15.

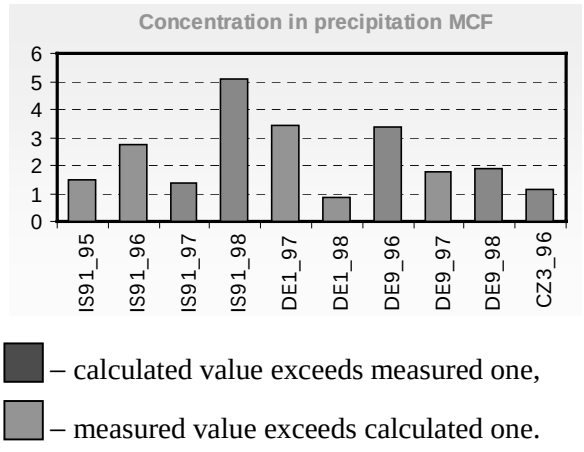
Figure 15. Frequency distribution of MCF for PCB-153 air concentrations.



One can see that for almost all measurements the discrepancy between measured and calculated values is within a factor of 4 (in fact, only in one case MCF = 6). Moreover, for about 80% of MCF values this discrepancy is within a factor of 3. Again, the range of the measured air concentrations of PCB-153 used is rather wide – from 0.3 to 50 ng/m^3.

The comparison of measured and calculated values for concentrations in precipitation is illustrated by Figure 16, where the same notation as for Figure 12 is used.

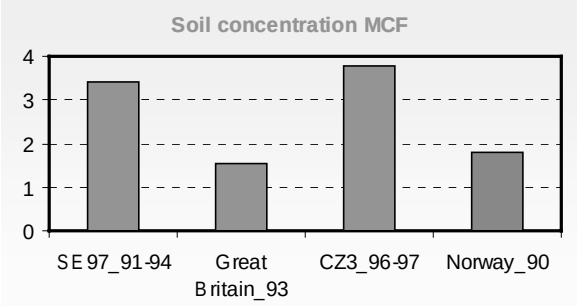
Figure 16. Comparison of calculated and observed concentrations in precipitation for PCB-153



As seen from the diagram in Figure 16, model may overestimate concentrations in precipitation within the factor of 5 and underestimate within a factor of 4.

Figure 17 shows the result of the comparison of calculated and measured soil concentrations. As seen from the diagram presented in Figure 17 the model may overestimate soil concentrations within the factor of 2 and underestimate within a factor of 4.

Figure 17. Comparison of calculated and observed soil.



– calculated value exceeds measured one,

– measured value exceeds calculated one.

The results of the comparison of calculated and measured values of concentrations in vegetation and seawater, the discrepancies between measured and calculated values of these concentrations are within the order of magnitude.

Dioxins/furans, hexachlorobenzene, and hexaclorohexanes

We do not present here the comparison results for these pollutants (the details can be found in the EMEP reports [Pekar et al., 1998; Pekar et al., 1999; Shatalov et al., 2000]. We only mention that the discrepancies between measured and calculated values for these pollutants are essentially within an order of magnitude.

As it is seen from the presented results on comparison between calculated and measurement data, the model describes the long-range transport within an order of magnitude for all pollutants considered. For B[a]P and PCBs the results are even better.
So, the model can be a tool for filling gaps in measurement data for POPs in the regions not covered by monitoring networks and national campaigns within the mentioned accuracy.

Conclusions

The above described investigations show that further development and refinement of POP transport Eulerian models could allow one to use them for solving the following:

evaluation of POP long-range transport and accumulation in different environmental compartments;
analysis of long-term trends of content in various media;
projection scenarios of contamination levels in various environmental compartments;
determination of hot spots for risk assessment;
evaluation of POP transboundary and transcontinental transport for some substances;
selection of new substances for inclusion in international agreements on the basis of evaluation of P_{over} and LRTP.

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Sergey Duchak, A. Malanichev, V. Shatalov, and N. Vulykh : Application of EMEP transport models to assessment of long-range transport potential and overall persistence

The aim of this paper is to illustrate possibilities and framework of usage of spatially resolved models for evaluating long-range transport potential (LRTP) and overall persistence (P_{over}) in the environment. To this end we have considered Pentachlorophenol (PCP) as an example of a substance not currently included in the Protocol. This substance was considered on the first meeting of Ad Hoc Expert Group. Below we present the evaluation of long-range transport potential and overall environmental persistence for PCP on the basis of preliminary modelling for this pollutant.

Physical-chemical properties of PCP

Basic physical-chemical properties of PCP are summarized in Table 1.

On one hand, the above properties show that:
Due to high value of vapor pressure, PCP will exist in the atmosphere mainly in the gaseous phase.
This pollutant is persistent in the atmosphere (atmospheric half-life is 19 days on the average).

- These factors lead to high enough long-range transport potential.

On the other hand:

- ♦ PCP is rapidly degraded in soil and, especially, water.
- ♦ The value of washout ratio for gaseous phase (calculated on the basis of Henry coefficient) shows that the wet deposition velocity for PCP is quite significant.

These factors diminish the characteristic length of the atmospheric transport.

Further, large difference between half-life times in basic environmental compartments (19 days in the atmosphere, 1.5 months in soil, and only 2 days in sea water) makes assessment of overall environmental persistence difficult since it is strongly dependent on relative media content (see formula (2) below).
To encounter the influence of these “opposite-directed” factors on overall persistence and long-range transport potential application of model assessment seems to be reasonable.
To assess long-range transport potential and overall environmental persistence, three model runs by MSCE-POP model were made.

Table 1. *Physical-chemical parameters of PCP*

Parameter		**Value**	**Reference**
Henry coefficient H at 10^0C, Pa*m^3/mol		0.62	[*EPA*, 1982, cited by NIST Chemistry Webbook]
Temperature dependence constant for Henry coefficient: d(– lnH)/d(1/T), K		1300	
Vapor pressure over the overcooled liquid at 25^0C, Pa		0.12	[*Mackay D. et al.*, vol. V, 1997]
Temperature dependence constant for P_L: d(– lnP_L)/d(1/T), K		8300	[*Stephenson R.M. and Malanovski S.*, 1987]
Octanol/water partition coefficient (dimensionless)		131826	[*Howard and Meylan*, 1997]
Organic carbon/water partition coefficient, m^3/kg		5370	[*Mackay D. et al.*, vol. V, 1997]
Molar volume, cm^3/mol		162.4	[*Jaw et al.*, 1999]
Molecular diffusion coefficients	Air	6.27E-6	Calculated by the equation from [*Schwarzenbach et al.*, 1993]
	Water	7.52E-10	
Half-lives in the atmosphere (days)	Winter	193	Calculated by the results from [*Yu Lu and Khall*, 1991] and [*Howard and Meylan*, 1997]
	Spring/fall	22	
	Summer	9	
Half-life in soil (days)		48	[*Hazardous Substances Databank*]
Half-life in water (days)		2	

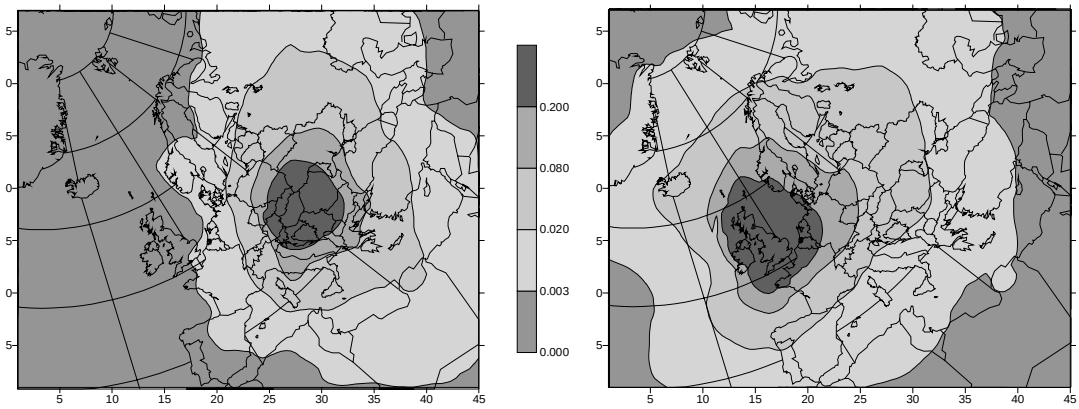
The first two runs (covering two-year period each) calculated long-range transport from emission sources located in Hungary and United Kingdom separately (Figures 1 a and b). The third run was done under the assumption that all emissions in Europe are ceased with initial concentrations in all the environmental media taken from the results of first run (using Hungarian emissions only). This run was used for the assessment of environmental persistence of PCP.

Below the results of all three runs are described.

Long-range transport potential

Here we present the evaluation of PCP long-range transport potential on the basis of modelling results. As mentioned above, two model runs for two-year period each were performed for assessment of long-range transport. Both runs use PCP physical-chemical properties described above (see Table 3) and meteodata for 1990 and 1991. The difference between the two runs is in emission data. For the first run we assumed that emissions take place in Hungary only, and the total annual emission equals to 340 tonnes (according to UBA emission inventory for 1990, see [Berdowski et al., 1997]) being uniformly distributed over the country. For the second run emission from the United Kingdom only (554 tonnes according to the same inventory) was used. Spatial distributions of air concentrations in the end of 1991 for each of two runs is presented in Figure 1.

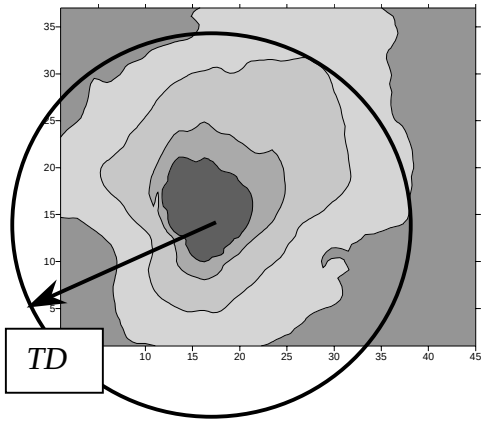
Figure 1. Spatial distribution of air concentrations (ng/m^3) obtained to the end of two-year calculation period: a) from Hungarian sources; b) from the United Kingdom sources



a) b)

One of possible measures of the long-range transport potential is the transport distance TD (see [Mackay et al., 2001]). We recall that this distance is defined as the distance between an emission source of 3000 kg/day (or 1095 tonnes/year) and the place where air concentrations decrease up to 0.01 ng/m^3. To evaluate transport distance air concentrations shown in Figure 1 were rescaled to bring the power of emission sources to the given value. Further, evidently the transport distance depends on the direction, and for obtaining a single figure transport distances in various directions were averaged. As the average TD the radius of the circle with area $S_{0.01}$ equal to that covered by concentrations exceeding 0.01 ng/m^3 (after rescaling) was used (see Figure 2):

Figure 2. Definition of the average transport distance



$$TD = \sqrt{\frac{S_{0.01}}{\pi}}, \qquad (1)$$

We remark that the value of TD obtained by such an averaging shows not only the average length of the atmospheric transport but also the area polluted.

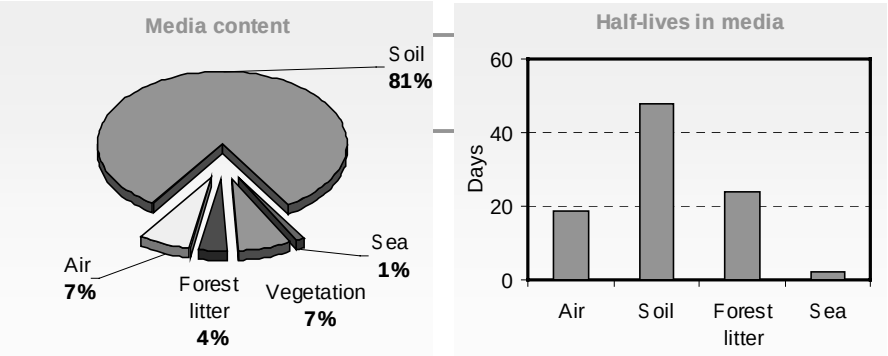
The values of the transport distance calculated on the basis of results of the two above runs occur to be very close: 2516 km for the first and 2728 km for the second run. Depending on the transport direction the particular values of transport distance can vary between approximately 1500 and 3000 and more kilometers.

The above considerations show that the application of MSCE-POP model allows estimating TDs for different locations of emission sources. Additional calculations show that if the emission sources used for calculations are located over sea, the values of transport distance can be essentially less (approximately by an order of magnitude) than the above estimated. Hence, in estimating long-range transport potential spatial distribution of contamination may be essential.

Overall persistence in the environment

To evaluate overall environmental persistence, a one-year model run was performed with zero emissions and initial data obtained in the course of the above described two-year run with emissions located in Hungary. Since the distribution of a pollutant between environmental media is of crucial importance for the value of overall persistence, we present the pie chart of media content assumed as initial values for the run (Figure 3).

Figure 3. Distribution of PCP in the environment taken as initial value for the model run and degradation half-lives in various media



As it was mentioned above, this distribution was obtained during the model run for two-year period with emissions located in Hungary. As it was checked by additional model calculations, this distribution is rather close to a steady-state one for the given location of emission sources.

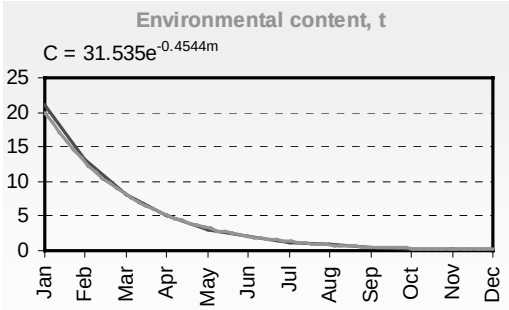
There exists a simplified method of evaluating of the overall persistence in the environment by steady-state fractions and particular clearance rates of a pollutant in environmental compartments (see [Mackay et al., 2001]). The corresponding estimate is as follows:

$$r_{overall} = \sum r_i \cdot f_i \,, \qquad (2)$$

where $r_{overall}$ is the overall environmental clearance rate, r_i are degradation rates (the corresponding half-lives are shown in Figure 3) and f_i are fractions of the pollutant in the environmental compartments. Calculations by this formula using data from Table 1 for degradation rates and from Figure 3 for fractions gives the value 2.25×10^{-7} s^{-1} of overall environmental clearance rate, which corresponds to half-life of 36 days.

Application of the model allows one to refine the value of environmental half-life. Figure 4 shows the plot of calculated dependence of PCP content in the entire European environment during the year with emissions equal to zero (clearance).

Figure 4. Annual dynamics of environmental clearance during a year with no emissions and estimation of overall persistence; C is the value of environmental content.



This plot contains also the exponential approximation of dependence of the content value C on the month number m:

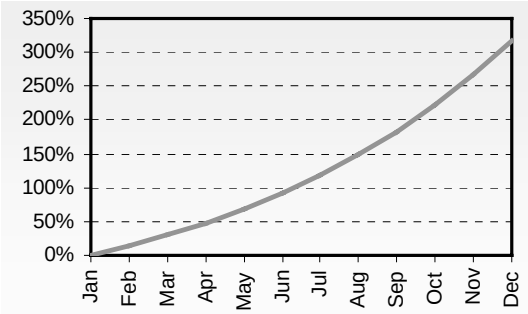
$$C = C_0 e^{-km}, \qquad (3)$$

where C_0 is the pollutant content in the environment in the beginning of the clearance period ng/m^3, k is the model estimate of the environmental clearance rate, month^{-1}.

For PCP we have obtained C_0 = 31.5, k = 0.45 (see Figure 4). From the coefficient in the exponent one can easily calculate the overall half-life time of PCP in the environment during the considered one-year period. This half-life equals 46 days, which is obviously in between values of half-lives in particular environmental compartments (about 19 days on the average in the atmosphere, 48 days in soil, and 2 days in sea). The obtained value of half-life in the environment differs from that obtained by steady-state approximation by 25%.

As seen from the above considerations, estimate of environmental half-life obtained by MSCE-POP model agrees well with steady-state approximation. However, in some cases the half-life period obtained by the model can be essentially different. For instance, the difference of predictions of the environmental content made by exponential approximation (3) with one and the same initial values C_0 and clearance rates k taken from model run and steady-state approximation can be significant. Figure 5 shows the plot of differences (in percentage) caused by difference in clearance rates during a one-year period.

Figure 5. Differences between predicted environmental contents obtained with model evaluated and steady-state clearance rates



As seen from this figure, the difference between two predictions is small enough in the beginning of the period and can become high enough by its end. This fact is explained by the change of PCP fractions in the environment during the clearance process. In particular, the fraction of PCP containing in the terrestrial environmental compartments (soil, vegetation, and forest litter) increased during the calculation period. Since PCP is more persistent in these compartments, this have led to the increase of overall persistence in the environment compared with that calculated for the initial stage of calculations.

We remark also that if the emission sources used for calculation of steady-state distribution of PCP between environmental compartments are located over sea, the values of half-life in the environment is less that the above estimated by an order of magnitude. Hence, spatial distribution of emissions may be useful for estimating overall persistence of a pollutant in the environment.

The above results show that, according to our model estimates, PCP is a regional pollutant with transport distance from 1500 to 3000 km and average half-life time in the environment equal to about 1.5 months.

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ANNEX 5-1: REPORT FROM SUBGROUP 1

APPLICATION OF MULTIMEDIA MODELS FOR OVERALL PERSISTENCE AND LRT POTENTIAL

Objectives

As identified in the draft agenda, the objectives of working group 1 were as follows:

- Summarise the user needs of stakeholders in both OECD and non-OECD nations for multimedia models (MMM);
- Summarise currently available methods/approaches based on multimedia models for estimating overall persistence (Pov) and long-range transport potential (LRTP);
- Evaluate available methods/approaches for developing pass/fail criteria that can be used to identify substances having Pov and LRTP sufficient to warrant concern;
- Discuss ways in which estimated Pov/LRTP can be incorporated into and enhance current and future hazard/risk assessment activities.

Objective 3 elicited additional discussion, as it was felt that as originally stated, it seemed to assume that reasonable approaches existed. It was emphasised that the objective should be to summarise and evaluate such methods if indeed any existed, while drawing appropriate attention to uncertainties in model results and criteria. Therefore, the Objective 3 should be reworded as follows:

♦ Evaluate possible approaches to establishing pass/fail criteria, including uncertainties of model outcomes and criteria.

Procedure

In order to stimulate thinking and initiate discussion, group members were invited to discuss their experiences in POPs/PBTs assessment, whether or not Pov/LRTP had been included in these activities. G. Bengtson, M. Bonnell, J. de Bruijn, N. Suzuki, H.S. Larsen, and B. Wahlstrom obliged.

M. Scheringer then presented an overview of the terminology and definitions applicable to Pov and LRTP. The intent was to summarise and reinforce knowledge gained from the morning's plenary presentations, and in so doing lay the groundwork for subsequent discussions within the group.

These discussions addressed several key topics. The remainder of this report summarises workgroup discussions and conclusions; issues recognised as potentially important but deferred for lack of time; and consensus recommendations.

Discussion topics 1 and 2

What is the potential role of MMM in POPs/PBTs assessment in OECD and non-OECD nations? What methods/models are currently available to estimate Pov and LRTP?

Why use MMM to estimate persistence?

♦ Convenience derives from the fact that with MMM Pov and LRTP are calculated at the same time.

- Using MMM, it is possible to assess the properties and behaviour of a chemical more comprehensively than is the case otherwise.

- MMM automatically address partitioning, and thus are likely to represent environmental behaviour more realistically than other approaches.

- MMM can guide efforts for improving single-medium (i.e. compartment-specific) half-lives. Therefore, the "single-medium approach" and Pov as derived from MMM should not be viewed as mutually exclusive. Rather, they can be used in an integrated assessment approach.

- With MMM, fractions in different media and corresponding degradation rates are considered simultaneously. The benefit to the user is that the model calculates the medium-specific mass fractions and makes this information available as an integral part of the results. This is important because the relative contributions to overall persistence from the individual media are then evident. If, in contrast, model-calculated values of Pov alone are used in assessments, the critical compartmental insight can be lost.

- However, most participants in working group 1 agreed that the *value added* by Pov, as compared to using single-medium persistence criteria, is still not adequately established and warrants further work. In part this results from the fact that Pov estimates are model specific, because they are based not only on medium-specific half-lives but also on assumptions about the model geometry and the release pathway. In addition, it is not sufficiently clear how Pov results should be interpreted and evaluated.

Why use MMM to estimate LRTP?

- As with Pov, MMM automatically address partitioning, and thus are likely to represent environmental behaviour more realistically than do other approaches.

- Moreover, MMM are the only reasonable way to calculate LRTP. In principle one could, for example, use degradation rates in air (more specifically, for the gas phase) in combination with assumed values for wind speed, but such an approach would not address partitioning to and degradation in surface media, and the influence of aerosol particles.

- Therefore, in the case of LRTP the value added by using MMM is widely accepted.

What descriptors are used to represent Pov and LRTP derived from MMM?

- Pov: characteristic time; overall residence time; time to reach 50% disappearance (or some other value) from a steady-state level after emission to the environment ceases. The last descriptor may be more transparent to non-experts, and therefore of value in communicating the concept of overall persistence.

- LRTP: characteristic travel distance (CTD); spatial range (SR); average radius of contaminated area (two dimensions); "arctic accumulation potential" (AAP). The latter may not yet be ready for general application.

When is it important to consider long-range transport via water? What methods and measures are available?

- Long-range transport via water is especially relevant when there is significant emission to water (or runoff to water), and a substance's water solubility is relatively high. The classic example is the isomers of hexachlorocyclohexane, of which lindane is the most familiar. It should be noted that many chemicals in current use have releases to water, so the relevance of this transport medium may be underappreciated.

- As noted above, available models already address LRT in water. If LRT in water is considered in assessments, it is important to distinguish freshwater and ocean currents as transport media.

Discussion topic 3
What is the role of Pov and LRTP in screening for POPs/PBTs?

Meaning of the term "screening"

- Screening can have several meanings, all legitimate. For example, screening may be

- Selecting substances from the universe of chemicals for PBT/POPs assessment, for ranking, prioritisation, categorisation, etc;

- Studying a specific chemical substance with limited data. Often this is done using a scenario that is deliberately conservative;

- Providing guidance to decision-makers in the absence of data.

- A common feature is the intention to provide information for some subsequent activity, e.g. risk assessment, classification/labelling, or enhancement of databases. It is important to understand and communicate this intended use!

Interpretation of LRTP estimates

- LRTP can be used by itself if the aim is to prevent any pollution of a remote or protected area. However, the typical use is in hazard-based screening along with other hazard properties (such as toxicity), to "red flag" a substance for further scrutiny.

- High LRTP is an indicator of the *potential* for exposure in remote areas.

- High LRTP may be viewed as an indicator of the *potential* that a chemical may cross national/political borders. But since nations vary greatly in size and proximity of neighbours, this application of LRTP can be controversial.

- Conversely, low LRTP doesn't necessarily mean there is no concern.

- If possible, when estimated LRTP is high, model results should be compared to field data (concentrations in remote areas and spatial concentration gradients) to verify model estimates. The overall aim is "validation", although it is noted that in the strictest sense generic MMM cannot be validated.

- Use of a matrix containing LRTP values along with other relevant screening data could be helpful, since it would facilitate comparison of parameter values for the listed chemicals.

Relative merits of available approaches to estimating Pov/LRTP

Different approaches to calculating LRTP have been shown to yield similar results in chemical ranking and scoring exercises. Therefore, they can be used interchangeably for this purpose. For Pov, there is less agreement among different approaches and further work is needed (Wania and Mackay 2000).

Discussion topic 4
Do pass/fail criteria exist for Pov/LRTP? Is it reasonable to develop and apply such criteria? Are there better alternatives, such as using benchmark chemicals?

Estimates of Pov and LRTP are model specific and this makes it difficult or impossible to define absolute criteria values.
Therefore, a series of benchmark chemicals should be identified and used to provide a yardstick for assessing other chemicals.
To address the effect of different scenarios (i.e. different environmental parameters; model designs; modelling objectives) on ranking results, a series of modelling runs using different models and scenarios should be performed, and Pov/LRTP results compared.
An inter-model comparison exercise, possibly conducted by convening a workshop, may help meet this objective. This is addressed in more detail below under Recommendations.

Discussion topic 5
What is the role of Pov and LRTP in risk assessment for POPs/PBTs?

- The potential for risk is always the ultimate driver in assessment of specific substances. Pov/LRTP have value mainly as "additional assessment factors" to be considered in the assessment process.

- As in screening (Discussion topic 3, above) Pov/LRTP can indicate if the possibility for exposure in remote areas does or does not exist.

- MMM results provide guidance on media most likely to be affected, the duration of possible exposure, and pathways and locations of possible effects. Note that this is a benefit of MMM generally, and accrues even if Pov/LRTP are not explicitly considered in the assessment.

- Pov may be useful in risk *management*, as an indicator of how long recovery might take after elimination of emissions and/or implementation of a remediation strategy.

- Pov/LRTP can help advance pollution prevention goals. For example, Pov and LRTP estimates for various chemicals could be compared (along with other factors) in order to help identify safer alternatives. All other things being equal, chemicals with dispersive uses might be given priority in efforts to reduce use, and Pov/LRTP would seem especially relevant for these. These and other user needs in the arena of pollution prevention are summarised in appendix 1.

Discussion topic 6
Other issues in using Pov/LRTP in chemical screening and assessment

- Pov/LRTP are most effectively used in a multi-tiered approach that proceeds from simple to more complex models of different scale, and is consistent with the intended application of the assessment.

- Models that are highly resolved spatially and temporally ("geo-referenced" models) can be used to advantage in evaluating generic models, and vice versa.

- In principle MMM are applicable to all climatic zones. However, many needed input data are uncertain or missing altogether, and the model structure (design) itself may need adjustment to accommodate different conditions.

Open questions

Two questions were raised in the group that could not be discussed. It is recommended that they be addressed by the OECD Task Force on Exposure Assessment.

Why are P and LRT of concern?

There is general agreement that LRT in combination with persistence is of particular concern. But are Pov and LRTP relevant only in combination with bioaccumulation potential and toxicity, or do they have importance by themselves, as proxies for unknown effects? As noted above working group 1 agreed that LRTP can be used by itself when the aim is preventing any pollution of a remote or protected area. However, the issue is broader than this. It encompasses defining the appropriate role (if any) of the Precautionary Principle in POPs/PBTs assessment.

Transformation products

There is a need to develop clear and specific guidance on how transformation products should be addressed. There was agreement that in principle MMM-based methods and tools are equally applicable to parent substances and their transformation products. However, there is uncertainty regarding when Pov/LRTP should be calculated for degradation products, assuming they can be identified, and how the information should be used. A related issue concerns mineralisation vs. primary degradation. For many substances only data on mineralisation (ultimate degradation) exist. Complete degradation is often viewed favourably because it tends to reflect lower likelihood of environmental impact, but MMM demand data on compartmental transformation rates, not ultimate degradation.

Recommendations

- Biotic (especially microbial degradation) and abiotic degradation rates and physical/ chemical properties should be studied to better determine how values may change with climatic conditions. Temperature is especially important. Environmental parameter data should also be collected for different zones.

- A tiered approach to assessment of persistence–using Pov and single-medium half-lives in tandem–should be a principal focus of further work aimed at developing and refining POPs/PBTs screening methods.

- More effort should be made to weigh Pov/LRTP, or at a minimum information on partitioning as derived from MMM, in ongoing and future POPs/PBTs assessment. Some possible examples:

    - Stockholm Convention (identification of additional POPs for possible inclusion in the UNEP global POPs negotiation);
    - POPs/PBTs work in the context of EU risk assessments for marine environments;
    - The US/EU High Production Volume Chemicals (HPVC) Challenge program, which currently includes a “transport/distribution” data element, but only requires submission of MMM level I results (i.e., percentages of a substance in the different environmental compartments assuming thermodynamic equilibrium). However, working group 1 advised against including actual values of Pov and LRTP since the values are model specific. This view might change if an OECD protocol for estimation of Pov/LRTP became available.

- An inter-model study is needed to advance knowledge of how and why chemical rankings based on Pov/LRTP vary.
    - Principal goals of such a study would be to improve consistency among approaches and models, and develop guidance for both regulatory and non-regulatory applications.
    - Uncertainty and variability would be important issues in the study and should be addressed separately, possibly by using Monte-Carlo methods.
    - The study should be conducted with a standardised set of chemical substances and input data for them.
    - Explicit approval of the models/scenarios/conditions selected for inclusion in the study should be sought from national authorities. This is important because there is a general desire to ensure that all national interests are adequately addressed and all parties endorse the process.
- A core set of assessment tools should be made available to the user community free of charge. All tools and models should be downloadable from the internet. A central location such as the OECD website may be most convenient.

Solid gold nuggets

M. Bonnell summarized the workgroup's most important conclusions and recommendations in a series of bullets, as follows:

- Pov as an endpoint itself may oversimplify the determination of persistence and may not directly provide added value to chemical screening exercises. However, the distribution of the substance among the compartments (as calculated using a multimedia model) and the significance of the compartment in the calculation of Pov can be used to determine which medium-specific half-lives should be used to determine persistence for chemical screening.

- Determining absolute or cut-off criteria for Pov was considered to be difficult if not impossible because of the uncertainty of what these thresholds should be, how they may determined, what they mean or how they could be used.

- A tiered approach to using single-medium persistence values and Pov should be investigated for use in chemical screening.

- For chemical screening, the applicability and use of LRTP were more easily understood than the applicability and use of Pov.

- LRTP should not be used on its own when screening chemicals using hazard-based approaches (i.e. POP/PBT approaches), but should be combined with other hazard properties (e.g. bioaccumulation and toxicity) to "red flag" substances for further investigation.

- It was recommended that the screening of substances according to Pov and LRTP should be performed using a relative ranking approach that incorporates benchmark chemicals as a means to relate these endpoints to known persistent and mobile substances.

- It was recommended that some activity be undertaken to determine how the process for relative ranking of substances could be done (e.g. standard environmental scenarios for use in the model or models).

It was determined that Pov and LRTP provide useful information for use in risk assessment and may be important for certain risk assessment activities (e.g. Stockholm Convention, new substances, pesticides).

Research Needs

Uncertainty analysis of model input parameters and model output using different environments; Development of a standard environment or series of standard environments.

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ANNEX 5-2: ISSUE PAPER NO.1

USING ESTIMATES OF LRT AND OVERALL PERSISTENCE IN CHEMICAL SCREENING AND RISK ASSESSMENT

1. BACKGROUND

1.1 Chemical Screening and Risk Assessment

The degree to which a substance – an industrial chemical or a pesticide - persists and can be transported in the environment is often used as part of the measure of a substance's potential to cause an exposure to human and non-human biota. When exposure potential is combined with a substance's potential to elicit adverse effects in human or non-human organisms, a more complete assessment of the potential to cause harm (i.e., risk) can be determined for a substance.

There are two main mechanisms for assessing a substance's potential to cause harm: chemical screening and risk assessment. These activities can be linked (as in a tiered approach) or may occur as separate activities. Recent developments in the field of multi-media modeling for estimating overall persistence and long-range transport (LRT) potential has contributed to increased consideration of these endpoints in assessment schemes. These endpoints have potential application to the assessment of both new and existing substances. Although application of overall persistence and potential for LRT as stand alone endpoints is only now being examined, the scientific basis for estimating these endpoints and the advantages of using multi-media models with or in preference to traditional half-life approaches is well documented (e.g. Mackay et al. 1996; Scheringer 1997; Webster et al. 1998; Beyer et al. 2000; Wania and Mackay 2000; Gouin et al. 2000; Pennington 2000a; Pennington 2000b; Scheringer et al. 2001; Bennett et al. 2001).

Chemical screening exercises (e.g. POP, PBT) often involve the assessment of a list of chemicals in accordance with pass-fail criteria established for specific chemical properties (e.g. persistence, bioaccumulation, inherent toxicity). The purpose of chemical screening is to identify those chemicals in chemical inventories that have specific properties that may be of concern. Risk assessment, both ecological and human health, is aimed at characterizing the risk a substance poses to receptors based on a substance's toxicity and exposure potentials. Chemical screening can often be followed by risk assessment in a tiered assessment scheme.

1.2 Estimating Persistence and Long-Range Transport Potential

Historically, the assessment of chemical persistence has involved the comparison of half-life estimates to half-life criteria for individual media (e.g. persistence criteria in PBT/POPs programs). The lack of

environmental realism of the single medium half-life approach has led to the observation that overall persistence, here called $P_{overall}$, may be a truer measure of a substance's persistence in the environment (e.g., Webster 1998) $P_{overall}$, calculated using a steady-state mass-balance model or multi-media model, is the weighted mean of media-specific half-lives taking into account the partitioning of the substance and sometimes the transfer of a substances between media. In essence, $P_{overall}$ is an indication of the residence time of a substance in the entire environment. To date, overall persistence estimates have not found their way into many chemical screening or risk assessment frameworks. This is due mainly to the lack of framework development to support the use of a $P_{overall}$ endpoint as well as the novelty of models to calculate this endpoint. However, the lack of reliable degradation estimates that are required as input variables in a mass-balance model also restricts their use.

The ability of a substance to be transported over long distances is not often as a stand-alone property in chemical screening or risk assessment activities. LRT potential is typically combined with persistence half-life estimates in air to help establish an overall picture of a substance's potential to cause harm in the environment[15]. LRT potential can also be estimated for inputs into aquatic systems because substances can also be transported over long distances in water by river flow and ocean currents. LRT can also be calculated in coupled air-water systems (Beyer and Matthies, 2001).

Historically, establishing LRT potential for a substance has been based on field measurement of POPs in near and remote regions and relating this back to known sites of emission. However, recent model developments now enable model users to estimate the spatial range (Scheringer 1996) or characteristic travel distance (CTD, Bennett et al. 1998) of a substance in order to determine LRT potential in its own right (see Wania and Mackay 2000). Further work is needed to establish how LRT may be used in chemical screening and risk assessment exercises. LRT may be particularly important for new substances because better prediction of this endpoint may limit a new substance's benefit in chemical commerce.

1.3 Existing Approaches to Identifying POPs and PBTs

Advances in multi-media modeling have increased the ability to predict environmental persistence and LRT and have helped increase the understanding of the fate and behaviour of substances. The regulatory community and other end users now have the opportunity to develop approaches that incorporate these endpoints in assessment schemes as well as to stimulate continued development of these models and the data required to run them. Many organizations have already begun to identify POPs and PBTs using various tools, approaches or frameworks developed for their political or economic unit. Approaches have been discussed or developed for both industrial chemicals (e.g., USEPA PBT Profiler) and pesticides (e.g., Unsworth et al. 1999). The OECD is interested in obtaining feedback on the tools that are being developed by various organizations in order to provide an historical perspective on how POPs and PBTs are being isolated from chemical inventories or as new substances. The question below is designed to obtain feedback from members on this issue.

What tools or approaches does your organization use to identify POPs or PBTs?

The remainder of this paper formulates questions as to when multi-media models may be needed, why they may be needed and how they may be used in chemical screening and risk assessment. Each question is followed with a perspective on the issue being raised.

[15] However, there are exceptions to this (e.g., Canada's Persistence and Bioaccumulation Regulations 1999).

2. CHEMICAL SCREENING USING LRT AND $P_{OVERALL}$

2.1 Understanding the Role of LRT and $P_{overall}$ in Chemical Screening

Multi-media models provide a means for screening chemicals for LRT potential and persistence that is more comprehensive and, thereby, potentially more realistic and accurate than using degradation half-lives for individual media. Because multi-media models have not commonly been used in decision making for these endpoints, several issues related to using model output for LRT and $P_{overall}$ require discussion. These are presented below.

(a) What does it mean when a substance has a high LRT potential in chemical screening?

While LRT potential itself is independent of the amount of a substance emitted to the environment, the potential can be used in initial chemical screening to simply indicate the capacity or potential for a substance to be transported over long ranges. LRT potential is not related to the environmental concentration or risk in these remote locations. High LRT values could trigger the need for further more detailed chemical assessment (e.g., using risk assessment) at a higher tier including the need to estimate environmental concentrations.

(b) If a substance is not expected to have a significant presence in a medium, do half-life criteria for that medium need to be considered for determining persistence?

The equilibrium partitioning of a substance between water, sediment, soil and air will result in percentages or fractions of the substance in each medium. For chemical screening, it must be recognized that at some level of partitioning, a substance's presence in a medium can be considered low enough as to be not significant. Lack of appreciable partitioning to a particular medium may suggest that the medium need not be considered further in the screening exercise. Cut-off values (%) for "realistic presence" may be appropriate depending on specific program, agency or country needs. For example, preliminary work conducted by Woodfine and Mackay (2001) for the categorization of 12,000 organic substances on the Canadian Domestic Substances List (DSL) according to overall persistence has revealed that if less than 5% ml of a substance is found to partition to a medium, the medium specific half-life criterion need not be considered due to lack of presence in that medium.

(c) Can a similar idea be used for determining when estimates of LRT should used in chemical screening? If not, when should LRT estimates be used in chemical screening?

Modeling studies as well as experimental findings indicate that the problem of LRT emerges even with very low mobile (air-borne) fractions of a chemical (Gouin et al. 2000; Scheringer et al. 2000; Jones et al. 2001). This implies that "triggers" for LRT potential may have to be more sensitive than that for $P_{overall}$.

Knowledge of the release of a substance to the environment may also be used to assess the potential impact from the LRT or persistence of an industrial chemical or pesticide. For example, emission rate (or production volume when emission rate is reliably known) might be combined with LRT and $P_{overall}$ estimates to determine if a substance poses a concern in the environment or to humans. A low emission rate or production volume may suggest that the substance is not as great a concern as one that is released to the environment at a high rate or being produced at a high volume. Emission rate may be considered at this point, but this may no longer be viewed as chemical screening based on hazard

potential. Accordingly, emission rate may most often be considered at a next tier of investigation (e.g., risk assessment).

(d) When should estimates of $P_{overall}$ vs. estimates of single media half-lives be used to screen substances for persistence?

Although estimates of $P_{overall}$ can provide a more realistic estimate of chemical fate in the environment, lack of reliable degradation data for some media may limit their application in chemical screening. The media specific half-life approach may thus provide the only practical means to screen large sets of chemicals for persistence. However, a tiered approach could be structured that makes use of all available data. For example, at the first tier or preliminary stage, worst-case half-life estimates in individual media can be used as a conservative measure of $P_{overall}$, although this can result in a high number of false positives (Pennington 2000a). Under circumstances where reaction and partitioning data are plentiful or where absence of some of these data does not significantly affect model estimates (e.g. see Gouin et al. 2000; Pennington 2000a), a multi-media estimate of $P_{overall}$ can be used to refine the screening at a second tier. A final tier can be used to provide a more detailed assessment of $P_{overall}$ by taking into account mode of entry or other factors when they become known.

2.2 Understanding Approaches to Using LRT and $P_{overall}$ in Chemical Screening

There are two basic approaches to applying estimates of LRT and $P_{overall}$ for the screening of substances for these endpoints. The first approach, which can be referred to as the relative or ranking approach, classifies chemicals into groups according to criteria set out for a group, such as a representative chemical or chemical class. An example of a chemical ranking approach is that described by Beyer et al. (2000). Actions can then be taken based on the priority of the group or classification of the chemical. The second approach, often referred to as the absolute approach, determines if a substance passes or fails when an estimate of LRT or $P_{overall}$ is compared to a specific criterion for that property. This approach is common among international POP/PBT initiatives. A discussion of both approaches is given by Bennett et al. (2001).

The following questions are designed to address when it may be most appropriate to use relative and/or absolute approaches in chemical screening activities and how this may be done.

(a) When would a relative vs. absolute approach be more appropriate to screening chemicals for LRT potential and $P_{overall}$? When can a combination of approaches be used?

It seems appropriate to use a relative approach, for example, to classify the LRT potential and $P_{overall}$ of a compound when not much is known about it. For example, for new substances, estimates of LRT and $P_{overall}$ can be compared to model estimates for benchmark chemicals (e.g. known POPs) to determine the transport and persistence potentials for the new substance (i.e. as greater or less than that of the benchmark). Relative approaches may also be applicable in cases where the desired outcome of the screening of large sets of chemicals is the establishment of priority classes of substances for further assessment or action.

Absolute approaches may be best suited to circumstances where a simple “pass or fail” decision is required for examining large sets of chemicals for specific properties (e.g. PBT). 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 a high priority for further investigation or in some cases may trigger immediate actions.

It is possible that a combination of both absolute and relative methods could be used to screen chemicals based on LRT or $P_{overall}$. One approach to this could involve using an absolute method first to "pass" or "fail" large numbers of substances in an inventory based on relevant media-specific half-lives or an established CTD cut-off. Since this approach is conservative and may result in false positives, the failed substances could then be further ranked into priority groups relative to the LRT and/or $P_{overall}$ estimates for chemical benchmarks. Degradation data might then be generated for the substances in the priority groups so that a more accurate estimate of LRT and $P_{overall}$ can be generated using multi-media models. This approach focuses time and effort on generating reliable estimates of LRT and $P_{overall}$ for priority substances first.

(b) If a relative approach is to be used to screen substances for LRT and $P_{overall}$, how might this be done?

Relative values could be calibrated by using benchmark chemicals with known persistence and LRT values which would give more confidence in the selection process. Such an approach has been proposed by Beyer et al. (2000) for classifying chemicals according to CTD. Alternatively, chemicals might be classified or ranked based on criteria that are considered in addition to a relative ranking that is based on LRT potential and $P_{overall}$. For example, emission rate, as discussed in section 2.1, may be used in the selection process.

(c) Is it reasonable to establish absolute criteria for LRT and $P_{overall}$ for chemical screening?

Although it is not the intent of this workshop to establish what the absolute criteria for LRT and $P_{overall}$ should be, the basic question of whether this approach is reasonable merits discussion.

3. USING LRT AND $P_{OVERALL}$ IN RISK ASSESSMENT

The application of LRT and $P_{overall}$ in human and ecological risk assessment will differ from application in chemical screening exercises. This is because the endpoints for risk assessment require that the potential for exposure and effects be assessed according to how a receptor may come into contact with a substance. Multi-media models can play a role in the exposure assessment of new and existing substances by helping to identify the pathways of exposure and media of concern in a risk assessment based on the fate of a substance. Knowledge of the mode of entry and emission rate is critical to determining the fate of a substance since the medium of release will govern fate and transport processes in the environment and the amount will lead to an environmental concentration.

Most likely LRT and $P_{overall}$ will benefit an exposure assessment at the screening level. However, because these endpoints have not traditionally been used in screening level risk assessment, questions on how these endpoints can be used in risk assessment are presented below. Discussion of these questions should make clear what additional steps or considerations need to be included in risk assessment to accommodate these endpoints.

(a) How can estimates of LRT be used in ecological risk assessment?

A substance need not have a high $P_{overall}$ to be transported over long distances (Scheringer 1997; Beyer et al. 2000). In risk assessment, the definition of "long-range" may not be as important as determining where a substance is largely deposited during transport (e.g. according to ETDs, "stickiness"). This can help define the geographical scale of the risk assessment. Estimates of LRT potential could also be combined with octanol-air partition coefficient (K_{oa}) or octanol-water partition coefficient (K_{ow}) data to determine if these substances are likely to be detected in the terrestrial or aquatic food chains of

sensitive species in areas of deposition (e.g. sensitive environments). These substances may require a higher tier of risk assessment where more detailed site-specific exposure and effects information can be collected or generated.

(b) How can estimates of $P_{overall}$ be used to help assess potential for risk?

For example, if a tiered risk assessment approach is used, a substance with a high $P_{overall}$ calculated at the screening level may require more detailed investigation at a higher tier of risk assessment since preliminary assessment based on acute exposure data and assumptions may not be valid. More detailed models that incorporate regional or geographical zone considerations (e.g. the Arctic) can then be used at this tier to more closely examine the effects of specific environments (e.g. Wania et al. 1999; Scheringer 2000). Persistence estimates from a multi-media model may also help identify those media in which the substance has a "realistic presence" and is expected to have a long residence time. This can help to focus the pathways analysis in the exposure assessment and determine if chronic effects data are needed.

(c) How can estimates of LRT and $P_{overall}$ be used to assess potential for human exposure?

LRT and $P_{overall}$ endpoints in human health risk assessment may be used similarly to that in ERA. LRT potential may indicate a capacity for humans to come into contact with LRT substances in areas of deposition rather than or in addition to occupational exposure. Persistence estimates from multi-media models may help to identify in which media a substance will predominantly reside over long-periods of time. The potential for humans to come into contact with these media according to the use pattern or occurrence in the environment can thus be identified and more closely examined.

4. OTHER ISSUES FOR USING LRT AND $P_{OVERALL}$

The following are issues for using multi-media models for estimating LRT and $P_{overall}$ common to chemical screening and risk assessment.

(a) What scale of assessment should these models be able to address?

Depending on the need, different scales of investigation may be warranted. The scale of investigation may range from local or more site-specific assessment (e.g. industrial discharges of new substances) to global levels of assessment (e.g. for POPs/PBTs). Regional modeling may be required to address fate in distinct geographical or ecological areas and national assessment may be required to address assessment within a political boundary.

(b) How should estimates of LRT and $P_{overall}$ from more than one model be considered?

Beyer et al. (2000) and Wania and Mackay (2000) observed that absolute values of LRT and $P_{overall}$ differed, in some cases, substantially between models while relative ranking did not vary as much. Different values can lead to different outcomes for LRT and $P_{overall}$. This may be important when the estimates of LRT and $P_{overall}$ are being compared to absolute criteria.

(c) What is the relative importance of using a generic model vs. a model that can be adapted or modified for specific circumstances?

The use of a generic model with default parameters (e.g. TaPL3 model) can provide assessment consistency between end users. However, a generic model may not be easily adapted to specific

countries or regions and therefore may not be applicable in these circumstances. The use or development of models for estimating LRT and $P_{overall}$ that can be adapted to specific situations (e.g. Wania et al. 1999; Scheringer et al. 2000), may be required to address regional concerns or perhaps to address greater complexity at a higher tier of assessment.

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ANNEX 6-1: REPORT FROM SUBGROUP 2

MODEL DESIGN

Regulators must make decisions based on available data and/or models. Actions will be based on legislative and political mandates and timeframes, using best options rather than the ideal. Regulatory needs for multimedia modelling (MMM) vary between different countries and programs within countries. From a regulatory perspective, MMM activities should consider the following needs of regulators:

- What chemicals should we be concerned about?
- Where will a chemical go after emission to the environment?
- How will it get there and through which media?
- Over what timeframe will it move?
- How long will it last?
- How much will accumulate in the environment?
- What insights can be provided for management strategies?
- How confident are we in these predictions?

In outlining possible regulatory uses for multimedia modelling, the importance of the availability, relevance, and validity of input data for these models cannot be emphasised enough. These data include the single compartment half-lives, intermedia partition coefficients, mode of entry, etc., and their associated uncertainty and variability.

There are two general types of regulatory assessment activities where MMM may be useful:

1. Screening Exercises of Large Numbers of Chemicals:
These activities relate to programs on new and existing chemicals, potentially covering many thousands of substances. Measured information on physical and chemical properties are generally absent at this stage. The purpose of screening is to: i) identify chemicals for more detailed investigation, and/or ii) identify additional data requirements.

- Overall persistence: Regulators will likely continue to use single media compartment criteria, but overall persistence estimates (Webster et al. 1998) may be a useful addition. Multimedia models also provide information on compartmental distribution and highlight the relevance of mode of entry. Use of overall persistence is currently country and program dependent.

- Long-range transport: Envision a particular need for MMM to inform long-range transport estimates, as an adjunct to monitoring data.

- Benchmarks/standards: Benchmarking to known chemicals will be valuable in a regulatory context to inform results on "distance" and "persistence". Benchmark chemicals should be validated to include, e.g. range and bounding estimates.

2. Detailed Examination of Prioritized/Short-listed Chemicals:
Whether determined from screening exercises or listed for other reasons (e.g. detected during monitoring), MMM can be used to further inform decision-making at the domestic, regional or multinational level (e.g. Stockholm Convention). At this stage, there is generally more data than for large-scale screening exercises, although data gaps often remain. These models are generally resource intensive and could be considered for the following uses:

- Detailed assessments for high priority chemicals;

- Information on time to steady state and recovery rates;

- Assist in source attribution, identification of vulnerable regions and abatement strategies

- Confirmation of screening level results and benchmark chemicals, thereby increasing confidence in multimedia model results;

- Validation and refinement of multimedia model and parameters based on comparisons to monitoring and emissions data

Recommendations:
- Models should be based on available data.

- Results should be expeditious.

- Need for transparent functioning of models and ability to replicate model results.

- Confidence in robustness of models results.

- Ability to provide reasonable worst case scenarios and bound confidence intervals on best estimates.

- Consistency of results/comparison between models .

- Need to consider breakdown substances (degree of breakdown dependent on mandate).

- Clarity of output and context of the results in terms of the models.

- Models should be freely available to all interested parties (including NGOs).

Limitations with respect to chemical classes that can be simulated

The following specific classes of chemicals were distinguished:

- Non-polar, non-ionizing organics
- Polar non-ionising substances
- Ionising substances
- Insoluble in waters
- Non-volatile
- Polymer
- Metals
- Mixtures
- Biological substances of anthropogenic origin

Break down products would fit within one or more of the above categories.

The basic existing models calculate partitioning, overall persistence and long-range transport (LRT) potential. To generate these outputs the models need input data including partition coefficients and single media half-life data. Current models build on basic theory associated with partitioning with an initial focus on non-polar/non-ionising substances. This approach has been expanded to other groups of chemicals. However, there are not as much chemical specific data for partition coefficients and/or degradation rates. Thus extensive chemical specific measurements are required to use the model. Additionally, the models require some modifications to deal with specific chemical properties such as ionisation and resulting changes in speciation as a function of pH.

Table 1 shows various categories of substances for which estimates are given on the possible distribution among environmental compartments, the most relevant distribution coefficients, and an indication of if the model needs adjustments for this specific category of substance (Model Tuning).

Table 1:
Different classes of chemicals with information on likely partitioning into several environmental media, distribution coefficients needed for MMM, and the need to adjust the model (Model Tuning).
A given substance can fall into more than one chemical class (e.g. a chemical can be polar and involatile at the same time).

	Distribution			**Distribution Coefficients ***				
Category	**Water**	**Air**	**Soil/ Sediment**	**A→W**	**A→S/Veg**	**W→S**	**W→B**	**Model Tuning**
Non-polar neutral organics	0-100%	0-100%	0-100%	+	+	+	+	No
Non-ionizing polar organics	0-100%	0-100%	0-100%	+	+	+	+	Yes
Ionizing chemicals	0-100%	~0	0-100%	~0	~0	+	+	Yes
Insoluble in water	~0	0-100%	0-100%	Infinity	+	~0	~0	Yes
Non-volatile organics	0-100%	~0	0-100%	~0	~0	+	+	Yes
Polymers	0-100%	~0	0-100%	~0	~0	+	~0	Yes
Metals (inorganic)	0-100%	0-100%	0-100%	+	+	+	+	Yes
-Organometals	0-100%	0-100%	0-100%	+	+	+	+	Yes
Mixtures	0-100%	0-100%	0-100%	+/?	+/?	+/?	+/?	Yes
-Reactive mixtures	0-100%	0-100%	0-100%	+/?	+/?	+/?	+/?	Yes
Biologicals	0-100%	0-100%	0-100%	~0	+/?	+/?	+/?	Yes

* Data available or required on:
A→ W: Air-to-water distribution coefficient
A→ S/Veg.: Air-to-soil (or sediment or vegetation) distribution coefficient
W→ S: Water-to-soil (or sediment) distribution coefficient
W→ B: Water-to-biota distribution coefficient

Because the models initially focused on non-polar neutral organics, methods should be developed to standardize the tuning of these models for use with all the other classes of chemicals. Some attempts have been made to adapt these models to other classes of chemicals (Mackay 2001). The modifications to the models should be done using a consistent approach, so that the chemicals can be compared in a consistent way.

Additional work is needed to develop half-life data and partition/distribution coefficients for most classes of chemical. Metals are inherently persistent even though they undergo reactions converting one metal compound into other compounds of the same metal. A small subset of non-polar neutral organics has been widely studied. Some categories of substances, such as non-polar neutral organics, non-ionising polar organics, and ionising organics have well-established methodologies for determining input data. Research efforts should focus on the development of methods that can be used to generate estimated input data for other categories of substances including biological substances of anthropogenic origin, mixtures and polymers.

One comprehensive model for all classes of chemicals seems to be an admirable goal, but it is not likely achievable with the current state of knowledge. Such a comprehensive model could also become extremely complex and difficult to handle due to the flexibility imposed by the various applications.

Therefore the concept of "fitness for purpose" is appropriate, allowing a selection of models or modules (with different compartments, processes, temporal and spatial scales) to be used for a selected purpose.

Guidance on how to select a model for a specific application is also an important user-need. A website providing guidance on model applicability and fitness for purpose could be one way to meet this need. In addition information on reliability, data availability and model adaptations should be provided within this guidance.

Recommendations

- Model applications should be expanded to other categories of chemicals, taking into account modifications to the models.
- The further data needs should be addressed, including chemical specific input data, e.g., for partition/distribution coefficients and/or degradation rates
- Guidance should be developed for users on model applicability and fitness for purpose. In addition information on accuracy, data availability and model adaptations should be provided within this guidance.

Environmental compartments

The conclusions with respect to the consideration of different compartments are summarised in Table 2.

Table 2:
Consideration of compartments in multimedia models targeting persistence and LRT potential at different degrees of detail. A question mark indicates that no consensus was reached on whether open ocean sediments should be included or not.

	Screening level	**Detailed models**
Air	One compartment	Vertical and horizontal segmentation
Soil	One compartment	Vertical and horizontal segmentation, groundwater
Water	Fresh water, ocean, suspended matter in both	Fresh water, estuarine, coastal, open ocean (vertical and horizontal segmentation), suspended matter
Sediment	Fresh water, ocean	Fresh water, estuarine, coastal, open ocean
Vegetation	Research needed	Include if possible
Others		Research needed

Screening Level Models

For the screening level MMM there is consensus on the need for compartments for air, soil, surface water, and sediment.

Air Compartment: Within the air compartment, there is both a gas phase and an aerosol phase and the chemical is in equilibrium between these phases. A single homogeneous air compartment is assumed.

Soil Compartment: A single homogeneous soil compartment is assumed.

Water and Sediment Compartments: There should be two surface water compartments, one representing fresh water and one representing ocean waters. Again, suspended matter should be included and assumed in equilibrium with the water phase. Deposition of particles in water has a significant impact on long-range transport for lipophilic compounds. Both the fresh water and ocean water have underlying sediment compartments.

Vegetation Compartment: Although it is clear that vegetation is an important compartment, there was no clear agreement as to whether or not it should be included at this time due to insufficient data. It has been shown that it can be advantageous to include a vegetation compartment. For example, mass balance simulations for PCBs with the MSC-E POP model showed that a considerable part of a chemical could accumulate in vegetation (Pekar et al. 1999). There can be elevated particle deposition rates when vegetation is present. There also is evidence of transport from vegetation to soil as well as degradation on or within the foliage. Further, vegetation is important because there is transport from air to soil through leaf litter deposition. Vegetation also acts as a vector for human and wildlife exposure, moderating the microclimate at the surface, which can affect the release of contaminants back to the atmosphere, and storage of chemicals in timber. Chemical reactions occurring on leaf surfaces are not well understood.

More Detailed Models

In the case of more complex models, additional compartments and sub-division of the compartments may need to be included. A compartment should be included if there is a significant amount of mass in that compartment or if a significant amount of mass passes through or is degraded in that compartment. A similar criterion should be applied to subdividing. If there are different concentrations or different processes occurring in the two portions of the compartment, then the compartment should be subdivided. The definition of 'significant' depends on what endpoint you are looking at. For example, a compartment may lead to human exposure but does not influence the mass balance, in this case it can be modelled externally from the MMM because it does not effect the mass balance. Another criterion for including a compartment is the additional understanding of fate and transport that can be gained, weighed against the uncertainties that are added by including that compartment.

Air Compartment: In the air compartment, resolution in both vertical and horizontal dimensions may be applicable. The wind velocity is much higher in the upper troposphere than the lower troposphere. The rates of transfer between layers and their heights vary seasonally and spatially. Transport to the upper atmosphere leads to rapid transport.

Soil Compartment**:** There may be the need for vertical and horizontal disaggregation. Consideration should be given to leaching to groundwater. People are potentially exposed to chemicals in ground water when it is used as tap water.

Water and Sediment Compartments**:** The water compartment should be disaggregated into freshwater, estuaries, near-coastal ocean, and open ocean compartments. The first three compartments definitely need to have an associated sediment compartment. The depth of the sediment compartment should be that which is accessible to biota and transport to the water column through diffusive or advective processes. There was no clear agreement on whether an associated sediment compartment is needed for the open ocean compartment. Resolution in both horizontal and vertical dimensions is adequate for the study of substances, which are long-lived in ocean water.

Vegetation Compartment**:** A vegetation compartment should be included as part of more detailed models. There is a need for additional research on this issue, such as partitioning rates and degradation

rates associated with different vegetation types. We recognise that ultimately multiple compartments might be needed to represent vegetation. Possible segmentation may include trees, both coniferous and deciduous forests, foliage (e.g. grasses, crops), or a surface microlayer to account for photodegradation.

Comparison between screening level models and more detailed models

As we develop more complex and detailed models, we need to ensure we are not getting divergent information on the persistence and potential for long range transport between the screening and complex models. A comparison between screening and complex models may help to identify processes that need to be further assessed in order to better understand chemical behaviour in the environment. This may in turn lead to changes in the screening level model.

Overall persistence

Overall persistence is based primarily on reactive losses. There are some permanent losses that may be considered. In some instances burial loss in sediment can be permanent. If there is a decision to consider burial loss, the screening level model may use a given average rate. If the burial loss is significant relative to other loss rates, the chemical will de-facto be persistent, because the rate of burial in deep sediment is slow. The same holds for the case where there are persistent losses to the stratosphere, the process of which is also slow. The average burial rate takes into consideration the fact that there are different sediment burial rates between compartments, i.e., no permanent losses from rivers, while there may be measurable loss rates in lakes and oceans. The different rates should be explicitly considered in the more complex model.

Degradation products should be included and proposals have been made of how to include degradation products into the persistence assessment (Fenner et al. 2000). In the EU regulatory context, persistence is defined as ending with mineralisation. At its second meeting the UNEP-POP Criteria Expert Group (CEG) defined a substance as the parent compound and all its transformation products with POPs characteristics (UNEP 1999).

Models to be used for calculating overall persistence

There will always be improvements to models as research progresses. Tools are available for assessing persistence at least at the screening level. Ranking of chemicals is considered to be quite robust at present. Current confidence in the models allows for application of these models to determine long-term characteristics in relatively homogeneous regions. Limits, again, are subject to data availability. If partition coefficients and half-lives are available, level II simulations can be completed which give a general idea of the compartmental distribution.

For screening level assessments we recommend level III models. Level III calculations require intermedia mass exchange rates, which can often be derived from partitioning data. For Level III models, mode of entry information is also needed, and should be used when it is available. However, if no information is available total emission into the medium with the longest half-life will provide a conservative estimate of overall persistence.

Level IV models are recommended for more detailed evaluations. These models simulate accumulation, the time needed to achieve steady state in individual compartments and the total environment, as well as the clearance dynamics. One possible measure of overall persistence can be derived from the dynamics

of the clearance of the substance from all media (total environment) upon cessation of emission (all net sources to the total environment). Level IV models can also accommodate time dependent emission scenarios when these are available.

For chemicals with sufficiently slow intermedia mass exchange rates, the difference between persistence results obtained from level III and level IV models may be significant. The results of steady-state and dynamic models of different degrees of complexity should be compared for this and other reasons.

Temperature is certainly an important parameter for many environmental processes, such as degradation processes and atmospheric deposition. Temperature and emission patterns can be correlated. However, for many substances data are not available to perform temperature dependent calculations. In conclusion, although temperature is important, it may not be possible to include it consistently at the screening level. Temperature dependent calculations are not recommended at the screening level as long as information is incomplete. However, it is recommended to include temperature dependent calculations in more detailed models for chemicals where sufficient data are available.

Long-range transport potential

Ranking of chemicals might be done with generic models, while studying the actual fate of a chemical requires geo-referenced models.

With respect to the screening of chemicals for their long-range transport potential in air, four approaches have been suggested so far, i.e. spatial range (Scheringer, 1996), half-distance in air (van Pul et al., 1998), CTD (Bennett et al., 1998), transport distance (TD; Rodan et al., 1999) [note: chronological order]. These approaches deliver similar rankings; therefore, any of them can be used for the screening level and any of these simple approaches can be used to evaluate the LRT of the substance. Different multimedia models can be used for deriving the above measures as long as the model accounts for the interaction among the various environmental media. This type of model should be used to evaluate both air and water transport and the simultaneous transport in both media. There is a need to better develop these models especially to cover the situation when both air and water are moving simultaneously. Examples of models that incorporate these approaches are Chemrange (Scheringer et al. 2001), ELPOS (Beyer and Matthies 2001a/b), or TaPL3 (Beyer et al. 2000, Webster et al. 1998). All three models assess transport in air and water. The model GloboPOP developed by Wania and Mackay (2000) estimates the zonally averaged global distribution of POPs, while accounting for the characteristics of different climatic zones. It therefore operates at a higher level of complexity. Another model accounting for differences in climatic zones and operating at a higher level of complexity is Scheringer et al. (2000).

Geo-referenced models can provide comparable measures to the screening level models, which would be useful for comparing the results to those of screening models. In addition, one can gain further information on the ability of the substance to undergo long-range transport by looking at the simulated distribution in the various media (e.g. shape and location of plume) (e.g. Lammel et al., 2001; Shatalov et al., unpublished results). Also any increase in spatial and temporal resolution will allow for better accounting for temperature and other geophysical parameters. The time and location of emission can also be better accounted for in such models. The application of these more complex models is considered to be most valuable at higher levels of assessment when priority substances have been identified.

Relevance of long-range transport in water

The atmosphere is the most mobile compartment. Thus it is of primary interest for LRT. However, under particular conditions (e.g. the chemical is less volatile and/or significantly water soluble) the transport with ocean currents and river water can also be important for LRT. In some cases it might even constitute the only transport path. The separate consideration of the transport mechanisms (and individual measures for LRT in air and water) allows for such insights.

LRT in seawater can be particularly important for assessment of contamination of the high latitudes (AMAP 1997). It was also shown that the inclusion of sea currents influences significantly the storage of PCB-153 in the ocean and might change concentrations in air and soil in coastal regions on the order of 10-20% (Strukhov et al., 2000). It is unclear how many substances undergo significant oceanic transport.

Biota can also provide a means for LRT, namely marine mammals but also potentially other migratory animals. This has not been covered by multimedia models so far and is certainly difficult to include in screening models. Albeit only very small absolute amounts are related to this LRT path, concern is justified because this mass is stored within living organisms and is an integral part of the food chains ('biopresent').

Model reliability, sensitivity, uncertainty and robustness with respect to overall persistence and long-range transport

Model sensitivity relates to the relative effect of different parameters/input values on the output value. Sensitivity analysis does not provide any information about the precision of the input, but it helps in understanding how important a certain parameter is in influencing the output, and whether it has to be determined with high accuracy. For this analysis both chemical-specific and environmental/media specific variables need to be varied. Sensitivity analysis is performed to find out which input variables exert the greatest influence (i.e., introduce the greatest uncertainty to the output), so that future efforts can be directed to reduce the uncertainty of these parameters.

Uncertainty relates to the possible error or variance of the output value. Uncertainty of the prediction can result from three sources:

a) Input uncertainty
To derive one 'output number' (e.g. Pov and LRT), perhaps 50 input variables need to be defined (in a generic level III model), including both chemical parameters and average values of environmental parameters. One can determine which input parameters exert the greatest influence on the output (prediction). This analysis can be performed in a number of ways, most frequently by varying input parameters through a range of values (e.g. Monte Carlo simulations to determine the contribution to variance or similar measures). This enables the quantification of the statistical distribution of output values as well as identification of the key, most influential, variables.

b) Scenario uncertainty
Scenario uncertainty may arise because it is unclear which scenario is most appropriate for a given chemical. Examples include uncertainties of the chemicals' mode of entry, or the timing of the chemicals' emission pulse.

c) Model uncertainty
There is uncertainty introduced by the model structure – the model is only an estimate of reality. There may be a non-representation or mis-representation of environmental processes. For example, one might want to quantify the difference in long-range transport that results from using an average ocean velocity vs. using specific ocean currents. Model uncertainties can be addressed by carefully structured comparisons of various types of models that have been used or can be used for a different process. When presenting results, the model developer should include a qualitative analysis of the model uncertainty in the model documentation.

Once we have an understanding of the uncertainties, we need to determine if these uncertainties are acceptable from a regulatory perspective. The uncertainty in degradation rates can often be 1-2 orders of magnitude; they are also highly spatially and temporally variable, which may need to be captured in models. This leads to uncertainty in persistence and LRT predictions of at least an order of magnitude, and often more.

The level of uncertainty that is acceptable for regulation will vary depending on the regulatory endpoint. For example, more uncertainty may be acceptable for ranking the chemicals, rather than determining the numeric value of the persistence or long-range transport. It is important to ensure that lower tier (i.e. ranking) models can adequately 'discriminate' between substances. We note that when ranking chemicals, a wide range of chemicals, including benchmark chemicals, should be included in the ranking. It is thought that model uncertainties are generally less important in the ranking/screening evaluative models than in higher tier models (i.e. ranking of different chemicals given a fixed mode of entry is quite robust).

Further uncertainties may be introduced in more detailed or spatially resolved models, due to the increased need for input parameters and characterisation of more environmental processes. At the same time, complex models provide an additional means for validation, for example, comparisons of patterns in space and time, rather than a comparison of mean values. It is therefore important to understand what improvements are achieved by adding more complexity to models and how they compare to uncertainties in the data.

In many cases, uncertainty of the chemical properties, especially uncertainty and variability in degradation rates, may be greater than the uncertainty from all the other sources. Thus, reductions in uncertainty can be achieved by a greater focus on obtaining reliable degradation data. For chemicals with well-defined input parameters, we note that overall uncertainty may be underestimated if model uncertainties are not taken into account.

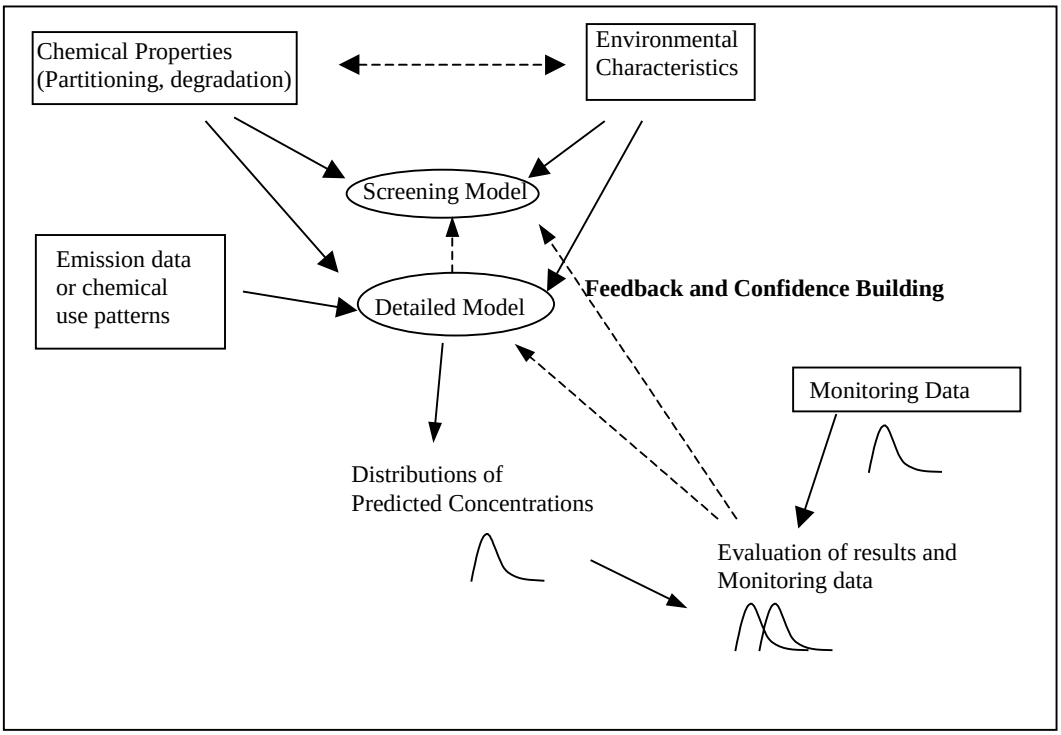
Recommendations

In screening level models and detailed modelling efforts, model sensitivity and uncertainty of the results should be reported and made clear to the user (e.g. the regulatory agency). The uncertainty will vary between compounds due to different levels of certainty in the input parameters. Identification of the main sources of uncertainty is key to identifying where/when higher quality data is required.

Model validation: can model predictions of persistence and LRT be validated /verified?

A validation of screening level models in its strict sense is impossible. However, an important approach is to evaluate higher tier models against environmental monitoring data, learn from that experience and feed that information back to the screening level models (Figure 1). Comparisons between calculated concentration distributions and monitored (measured) distributions can be made to improve/support a model. Improvements can then be transferred to the generic model, to increase confidence and reliability.
Hence, environmental monitoring data is critical for multimedia model validation and there is a real need to combine modelling and monitoring approaches.

Figure 1:
Data needed for running models at different levels of detail and feedback of knowledge gained from comparison with monitoring data.
Direct evaluation is possible with detailed models but not with screening models.



Ideally, monitoring data for 'validation' purposes should take the form of data for air and other environmental compartments obtained in the same places, at the same time and over a multi-year period. Unfortunately, 'multi-media, synchronous datasets' are very limited worldwide and restricted to very few compounds. Further needs with respect to the comparison of model results and monitoring data are:

- Data for the compartments with high contaminant burdens (i.e. soils, sediments) are particularly important, both from source and remote areas.
- Reliable emission estimates for the compounds of concern.
- Reliable information on mode of entry.
- Trends in levels in different media over time.

- Monitoring concentrations of PBT in biota could be a very good indicator of the level of exposure to living organisms in the environment. It is also a way to check the partitioning of chemicals to biota, which could be important if the substance is liable to bioaccumulate.

The evaluation of a model with monitoring data will typically involve:

When a generic model is used, it must be adapted to represent the real environment (i.e. input parameters are selected to reflect the environmental characteristics, degradation rates, input rates, etc.).
Uncertainties in the input parameters need to be taken into account (in particular degradation rates). So, statistical distributions of parameters (or another means to trace the impact of this uncertainty) should be used, to derive realistic distributions of concentrations in the various compartments.
Estimates of the chemical emissions and releases into the environment are very important and often have an unknown uncertainty attached to them.
Concentrations in the various compartments are then calculated. Temporal and spatial variability can be addressed by dynamic (Level IV) and spatially resolved models, respectively.
The model outputs (i.e. concentrations, multi-media distributions, spatial and temporal trends) are then compared to the environmental monitoring data, appropriately averaged in time and space, preferably for several different compounds with a range of physico-chemical properties.

Useful information can be obtained, if the relative proportions of different compounds in different media are available, and by comparing well known chemicals.

Recommendations:

1) Determine the core set of models that could be used in the screening evaluations.
2) Provide guidance on how to incorporate uncertainty of the input parameters in the model and how to interpret the results
3) Define procedures to backtrace problems and for identifying and making improvements to models.
4) Set criteria for the validation of models. The criteria and the process depend on the tier at which the model results are used and on the user needs.
5) The group indicates the need for an intercomparison of models of different degrees of complexity[16].

[16] The MSC-E indicated that it is willing to coordinate such a study of model comparisons.

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ANNEX 6-2: ISSUE PAPER NO. 2

MULTIMEDIA MODELS

In the Introductory Background paper a number of features and properties of multimedia models (MMMs) are discussed, especially their use to evaluate persistence (P) and potential for long-range transport (LRT). In this paper a number of issues related to model design and selection are introduced and discussed in the expectation that they will be the basis for discussion at the Workshop.

First there must be a clear enunciation if the objective is to evaluate chemicals either for hazard or risk. Hazard can be deduced from intensive chemical properties. Risk evaluation however, also requires quantity and mode of entry information.

What chemicals can be included?

A large body of information exists on non-polar, hydrophobic substances such as the PCBs. Numerous studies have demonstrated that these substances can be well described by existing multimedia models.

The situation is less satisfactory for polar substances partly because they tend to be less bioaccumulative and less persistent. A body of knowledge does exist on chemical classes such as phenols, carboxylic acids and surfactants. MMMs have been successfully applied to these classes of substances with appropriate modifications. The problem is usually that simple rules such as the assertion that organic carbon-water partitioning can be quantified by octanol-water partitioning may fail. Chemical-specific partition coefficients are often needed.

In some cases the substance does not partition into a specific medium, for example surfactants, dyes and metal ions do not evaporate. This is not a problem because a medium can be readily ignored.
If a chemical is an acid or base, the acid dissociation constant pK_A can be used to calculate the non-ionized form for which the partition coefficients such as K_{OW} (octanol-water) and K_{AW} (air-water) can be applied. The ionic form is assumed to be completely dissolved in the water phase.

More problematic are situations where the chemical speciates into different ionic or complexed forms. Again these models can be applied, but care is necessary and additional relevant data will be needed.

It is believed that MMMs can, in principle, be applied to all chemical substances including organics, inorganics, metals and organometals. It must be recognized, however, that models applied to exotic substances are subject to greater error than those developed and tested on more conventional contaminants. Obviously for metals, persistence based on reaction is infinite, but this does not prevent models being used. Organics such as trifluoroacetic acid are probably also essentially infinitely persistent.

The alternative of using different models and assessment processes for different classes of chemical substance is likely to lead only to controversy and chaos. This issue deserves discussion. Specifically, do we need different models for different chemical classes? If different models are needed, can we ensure a degree of consistency between them? How do we obtain the relevant data for each class?

What media should be included?

As discussed in the introductory paper, an absolute minimum segmentation is regarded as the three-compartment system, air, water and soil plus sediment. Because of the importance of sediments most models separate them from soils and employ a four-compartment system. Other options include the following:

- Separating soil horizontally into industrial, agricultural and natural areas as done in EUSES (EC, 1996), or vertically into a number of layers as done in CalTOX (McKone, 1993).
- Adding vegetation as a compartment because of its key position at the base of food chains. It is also a factor in controlling LRT.
- Separating the atmosphere into different vertical layers.
- Segmenting sediments into layers of different accessibility.
- Some discussion of these issues is warranted with a view to recommending an appropriate number of media.

What loss processes should be included?

When calculating persistence from the mass balance results of a MMM there has been some debate about which processes should be treated as true losses.

Obviously degrading reactions should be included as a true loss process in which the substance is irreversibly transformed to another substance. On the other hand, if the reaction is reversible (e.g. ionization or complex formation) then some argue that these are not true losses since the loss is temporary. A compelling case can be made that it is the total quantity of chemical in all reversible forms that should be addressed, thus it is only loss of total quantity that is relevant.

Advection processes are not usually included as true losses when calculating persistence because they only relocate the chemical; they do not remove it permanently. It is possible that the chemical may return. A case can be made, however, for treating processes that irreversibly remove the chemical from the biosphere such as sediment burial and deposition to deep or abyssal oceanic sediments as effectively permanent or true losses. Exposure is most likely from surficial freshwater sediments. Loss to the stratosphere can also be considered as a true loss.

Intermedia transport processes are not considered as true loss processes because they merely transport the chemical within the system. For this reason, sediment deposition or leaching to groundwater should not be considered as true losses from the system because they merely redistribute the chemical within the system.
An option exists in that the model can be run with advection losses included or excluded. If advection is excluded the overall persistence is simply the mass in the system divided by the total rate of non-advective losses. If advection is included, a similar persistence can be calculated as the mass in the

system divided by the rate of the non-advective losses. For Level II models these times are equal, but in Level III they are slightly different. In the interests of simplicity and conservatism it seems preferable to exclude advective losses from the model.

Which LRT model?

As discussed in the Introductory paper, there are three approaches for estimating LRT namely the connected multimedia models resulting in an interquartile distance advocated by Scheringer and colleagues (Scheringer, 1996, 1997), the Lagrangian approach developed by van Pul (van Pul et al, 1998), Bennett (Bennett et al., 1998), Beyer (Beyer et al, 2000) and others and the expandable box suggested by Hertwich (Hertwich, 1999). Are these different approaches essentially identical (Scheringer et al, 2001)? Which should be used, or can more than one be used? Should different models be used at various tiers of the assessment process or in different contexts (e.g. screening many substances vs. detailed assessment of one substance)?

When should the multimedia model be used with a generic environment versus a specific environment in the evaluation of overall persistence and LRT? What should the characteristics of an environment be? Should they be representative of temperate climates where most of the chemicals are used, or a more extreme environment? Should there be an adjustment of temperature from the usual 25˚C employed in the laboratory? Should there be more than one evaluative environment?

LRT in air and/or water?

Usually, the long-range transport in air is taken as a measure of the potential to reach remote regions because it is the fastest environmental transport process. Ocean currents can, however, also transport significant amounts of persistent water-soluble substances to remote regions. Beyer and Matthies (2001a) calculated the Characteristic Travel Distance (CTD) in water with the same approach as for air assuming water as a mobile compartment. Moreover, both transport processes have been combined for the long-range transport of semi volatile compounds in a coupled air-water system (Beyer and Matthies 2001b). The coupled CTD can be significantly longer than the isolated CTDs.

Tiered Assessment Options for P and LRT

Note that it may be appropriate to use different approaches for calculating P and LRT at different tiers, but for convenience they are grouped below into a series of suggested options.

Option 1.

The simplest option for evaluating persistence, and one that broadly reflects current regulatory practice, is to obtain estimates of the half-lives of the substance in all media and compare them solely against media-specific criteria. Intermedia exchange is ignored. This approach is already used by regulatory agencies in their chemical evaluation processes. The problem with this approach that has been discussed in detail by Webster (1998) is that a chemical can be penalized even if it does not partition significantly, or at all, into a specific medium in which it is judged to have a relatively long half-life.

For evaluating LRT, a CTD could be calculated simply as the half-life in the medium multiplied by an assumed velocity divided by 0.693. For example, a two-day (48 hour) half-life in air with a velocity of 15 km/h would give a CTD of 1039 km, i.e. 48 x 15/0.693. The half distance is 48 x 15 or 720 km.

In neither case is a MMM needed.

Option 2.

The second option for evaluating persistence, which could be considered for a second tier evaluation, is to use a Level II model with assumed relative volumes of air, water and soil. Sediment could be included if desired but since its volume is probably small compared to soil, it is unlikely to prove important unless it is known that half-life in sediment is much longer than in soil.

The required data are the equilibrium partition coefficients between the compartments and the half-lives in each compartment. If a half-life is not known it can be assumed to be infinite (no reaction). This is essentially the approach suggested by Gouin (2000), P is calculated as mass in the system divided by the total rate of loss by reaction. This overall persistence proves to be a weighted mean half-life (divided by 0.693) where the weighting is on the basis of mass fraction in each medium.

A LRT distance or CTD could be calculated as the product of a velocity in a medium, the overall persistence and the fraction in that medium.

Option 3.

The third option for evaluating persistence is to use a model consisting of air, soil and water plus sediment, assuming that water and sediment compartments reach equilibrium. There will then be three mass balance equations and three options for mode of entry. The required input data are the four partition coefficients, the four half-lives and intermedia transport rate coefficients for air-water exchange, air-soil exchange and soil-water transfer (run off). No water-sediment transport information is needed because instantaneous equilibration is assumed. Burial in sediment could be included as a loss process if desired, possibly as a pseudo reaction with a half-life of say 10 years. No advective losses from air or water would be included, nor would leaching to groundwater.

Three persistence values would be calculated for each mode of entry i.e. to air, water and soil separately, or a specific mixed mode of entry could be selected (e.g. 50% to air, 20% to soil and 30% to water). The mixed mode of entry result will be the discharge-weighted mean of the three separate persistence values.
For evaluation of LRT a CTD could be calculated for air and water by assuming a velocity and using the appropriate P and fraction in the medium as discussed earlier.

Option 4.

The next option for evaluating persistence is to use a full four-compartment Level III model (air, water, soil and sediment) using the same information as above but also including sediment-water exchange expressions. The sediment and water will not then be at equilibrium. Since it is unlikely that chemical will be discharged to sediment, this mode of entry may be ignored.

For evaluating LRT, a CTD can be calculated as before. This model is essentially the TaPL3 model described by Beyer et al. (2000) or the ELPOS model based on a modified EUSES/SimpleBox model (Beyer and Matthies, 2001a).

Other Options.

Further options could include addition of other compartments such as vegetation, but it is likely that this will only be useful when there is a demonstrated need to include such a compartment and more degradation data are available (Bennett et al, 1998, Beyer and Matthies, 2001a).

Dynamic versions could also be considered but again it is unlikely that they will be needed for routine assessments.

General issues worthy of discussion

There should be a clear statement of intent regarding the use of model output. Is it to rank chemicals? Will numeric criteria be applied for persistence (e.g. 100 days)? How will uncertainty in the model output and in the criteria be included in the application? How does the choice of criteria, and approaches for handling uncertainty relate to the consequences of exceeding criteria?

Should experimental input data be used in preference to estimated data or vice versa? Are different data sources consistent?

How should difficult or exotic substances be treated?

If different models are used in different jurisdictions or for different substances, how can model consistency be established?

How can different geographical and climatic conditions be addressed?

Although this is really a regulatory and not a modelling issue, the issue will inevitably arise of selecting cut-off values.

Numeric persistence and LRT potential criteria are used to identify and select substances with POP properties (UNEP, 2001). Up to now, mainly cut-off values for individual media-specific half-lives have been suggested. Annex D of the Stockholm Convention states criteria of >60 days for water and >180 days for soil and sediment. An atmospheric half-life of 2 days has been suggested as a surrogate for the LRT potential; but no spatial scale was suggested. A first attempt to classify chemicals according to their LRT potential was based by Beyer et al. (2000) and Matthies et al. (1999) on the CTD in air. They proposed three classes: Class 1 (long CTD) have an in air CTD greater than 2000 km. These are mostly well known POPs, e.g. HCB and the HCHs. Class 2 (intermediate CTD) contains chemicals with values between 700 and 2000 km. A typical example is DDT, which is frequently found in the Arctic but is not necessarily transported over long distances. Substances in class 3 (short CTD) with values below 700 km have a minimal LRTP and are rarely detected in remote regions. Although the CTD is a fictional distance it might be an appropriate yardstick to classify chemicals according to their LRT potential

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ANNEX 7-1: REPORT FROM SUBGROUP 3

DATA NEEDS

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Appendix 1 – Key data set to run a generic model

Appendix 2 – Selected Data Sources

1. Introduction

At an early stage during the discussion, it was agreed that the discussion would focus on generic multimedia models (MMMs) (i.e. a model consisting of four well-mixed compartments – air, water, soil, sediment – with a fixed temperature). Specifically, the objectives of the subgroup were to identify the data needs, availability, sources and quality indicators of data for screening models for overall persistence (P_{ov}) and long-range transport potential (LRTP), in particular:

- chemical substance characteristics
- environmental characteristics
- mode of entry

2. How to use generic models in the regulatory process

Generic models can be used as a screening tool for the ranking or grouping of substances as persistent and/or having long-range transport potential. In a first screening, existing physical chemical property data and applicable QSAR data can be used.

At the international level, data used in the screening step as well as the result of this screening should be made available through organisations like OECD, in order to have them used in regional assessment programmes. If classes of persistence are defined on the basis of these screening tools, it should be made clear what kind of consequences could follow in terms of regulatory and/or management process.

As a result of this screening, based on a simple model, the regulatory bodies could,

ask industry for better quality (experimental) data to re-run the assessment model or to refine the answer and define compartments of possible concern using a higher tier model that may also include risk assessment and
consider monitoring data to better assess the potential risk in relationship with other properties like bioaccumulation potential and toxicity.

3. Data Needs, Sources, Quality and Uncertainty

3.1 Environmental Phase Distribution

To describe the environmental fate of a chemical, multimedia fate models require quantitative expressions of equilibrium distribution between the various environmental phases. Specifically the generic screening model requires expressions for the following phase pairs: Air-Water; Air-Atmospheric particulates (aerosols); Air-Soil; and Water-Solids (suspended solids, sediments and soil).

It was recognised that generic models might evolve to also require expressions for further compartments and their partition coefficients: Air-Vegetation; and Air-Snow.

Non-Polar, Non-Ionizing Organic Substances

Presently existing generic multimedia models for P_{ov} and LRTP assessment such as TAPL3 (Beyer et al. 2000), ELPOS (Beyer and Matthies, 2001) and ChemRange (Scheringer, 1996; Scheringer et al.,

2002) rely 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:

1. Sorption to solids in air, water, soil, and sediments is dominated by partitioning or absorption into the organic fractions of these solids.
2. 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:

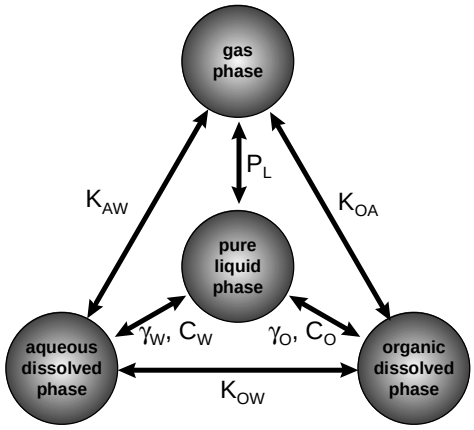
$$\log K_{Aerosol/Air} = a \cdot \log P_L + b \quad \text{(Eq. 1)}$$

$$\log K_{Organic\ matter/X} = a \cdot \log K_{Octanol/X} + b \quad \text{(Eq. 2)}$$

where 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).

3. The empirical parameters a and b for a particular organic phase are relatively invariant for non-polar organic chemicals.

Figure. 1 Phase distribution equilibria involving pure phases 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, P_L (supercooled) liquid vapor pressure, C_W and C_O saturation solubility in water and octanol, γ_W and γ_O activity coefficient in water and octanol).



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 1 (taken from Wania, in press). They

can also 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. (in press) 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.

One advantage of the LFER approach is that:

- 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 C_W and, and

- numerous and established quantitative structure property relationships (QSPRs) exist that allow the estimation of K_{OW}, P_L, C_W from molecular structure.

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. It may not be necessary to determine such extreme values, because:

1. The model result may be insensitive to the actual value of that 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 C_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. Except that there are not “established internationally accepted technical guidelines” for K_{AW}.

Polar, Non-Ionizing Organic Substances

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 the linear free energy relationships (Equation 1) 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 compound.) 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}.

A research need has thus been identified to develop methods for estimating environmental phase distribution that are applicable to all non-ionizing chemicals, i.e. are not restricted to a particular class of related compounds.

Ionizing Compounds

Compounds that ionize in the aqueous phase can be treated as the 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.

Other Compound Classes

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.

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 the most appropriate tool and the attempt to do so may be misguided. For example, there is not much point in estimating a characteristic atmospheric travel distance for a polymer or a biological macromolecule.

3.2 Degradation

Data Considerations

Reactivity information (degradation rate) for the various environmental compartments is required to run the model. These rates can be either measured in the various media or estimated. Experimental rate data are preferred for assigning degradation half-lives and these data need to be as relevant as possible to the natural environment. However, data are unlikely to be available for the majority of chemicals. For some compartments, other test methods are available that can be used to provide estimates of half-lives for modeling. In the absence of any data, relevant QSAR estimates can be used as model input. However, use of estimated data will increase the uncertainty of the results. To reduce uncertainty, additional environmentally relevant data may need to be generated. References to guidance documents for data generation, generation of surrogate data, and QSAR estimation sources for parameters described below are given in Appendix 1.

Degradation vs. dissipation

It is important to differentiate between degradation and dissipation. Degradation measures the reduction of a compound from parent to degradation products. Dissipation can include various degradation processes as well as transport of the compound from one compartment to another.

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. For screening level MMM standard temperature is assumed.

Transformation Products

When degradation rates are determined it should be noted that degradation as measured in hydrolysis or biodegradability tests does not necessarily represent complete mineralisation. Instead, other persistent and toxic transformation products might be formed. Ways of accounting for them in persistence calculations have been suggested by Fenner et al. (2000). In order to integrate transformation products into MMM and into the calculation of P_{ov} and LRTP, the same input data as for the parent compound is needed for each transformation product as well as an estimate of the amount of them being formed.

3.2.1 Air

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 region for direct photolysis. Also ozone and nitrate radicals react photochemically, however these reaction rates are usually much smaller than those with hydroxyl radicals. Experimental values exist for about 600 organic substances measured in the gas phase (literature review of Klöpffer and Daniel 1991). Many organic chemicals have low vapour pressures ($<10^{-3}$ Pa) so that they ad- or absorb on aerosols in the atmosphere. For such semi-volatile chemicals, the OH rate constant is difficult to measure and very few experimental data exist so far. It is common to calculate these rate constants with the software programme AOPWIN (Atmospheric Oxidation Program, Meylan and Howard, 1999). It is also common to use this air degradation rate constant in multimedia models, however only the gas phase fraction is being considered. This fraction is calculated by the Junge (1977) equation or more recently by the approach of Finizio et al. (1997) and Harner and Bidleman (1998) using the K_{AO}-model. 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.

$$kdeg_{air} = k_{OH} * [OH] * 24 * 3600 \qquad \text{(Eq. 3)}$$

Explanation of symbols:

$kdeg_{air}$ pseudo first order rate constant for degradation in air [d^{-1}]
k_{OH} degradation rate constant with OH-radicals [$cm^3.molec^{-1}.s^{-1}$]
[OH] concentration of OH-radicals in atmosphere [$molec.cm^{-3}$]
conversion seconds into days 24 * 3600.

The conservative OH radical concentration is $5*10^5$ $molec.s^{-1}$ (EU TGD 2001)

3.2.2 Water

The degradation pathway in water is composed of hydrolysis, direct and indirect photolysis and biodegradation. The overall degradation rate constant is calculated as the sum of these three rate constants (but note that measurements on one process may also include the contribution of other processes):

$$k\deg_{water} = khydro_{water} + kphoto_{water} + kbio_{water} \qquad \text{(Eq. 4)}$$

Explanation of symbols

$k\deg_{water}$	rate constant for degradation in water	[d^{-1}]
$khydro_{water}$	rate constant for hydrolysis	[d^{-1}]
$kphoto_{water}$	rate constant for direct photolysis in water	[d^{-1}]
$kbio_{water}$	rate constant for biodegradation in water	[d^{-1}]

Hydrolysis and photolysis other than biodegradation are often not dominant for organic chemicals and do not contribute substantially to the overall degradation constant $k\deg_{water}$.

Hydrolysis

Values for the half-life of a hydrolysable substance can be converted to degradation rate constant. The results of a ready biodegradability study will show whether or not the hydrolysis products are themselves biodegradable. Only, if the rate of hydrolysis is significant relative to the 28-d duration of the ready test. The rate of hydrolysis will always increase with temperature.

Phototransformation (Direct Photolysis in Water)

The direct photolysis is measured in water and only plays a role for substances that absorb light at wavelengths greater than 290 nm because of the overlap with the sun absorption spectrum. The photolysis degradation rate depends upon the light intensity of the respective geographical region and the season (OECD 1997, 2000).

Biodegradability in Water

A number of internationally accepted standard tests are available for measuring biodegradability in water. The OECD biodegradability tests provide qualitative results. Multimedia models require half-lives. Therefore, EU countries and the US EPA translated these qualitative results into rate constants and half-lives.

Table 1.
First order rate constants and half-lives for biodegradation in surface water based on results of screening tests on biodegradability (EU TGD 2001)

Study result	Rate constant $kbio_{water}$ [d^{-1}]	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	To be determined

The EPA uses slightly different values.

Study result	Rate constant $kbio_{water}$ [d^{-1}]	Half-life [d]
Ready biodegradable	0.14	5
Intermediate results in Ready test	0.069 - 0.023	10 – 30
Inherent biodegradable	0.0069	100
Not biodegradable	0	To be determined

3.2.3 Soil

The degradation pathway in soil is composed 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 (but note that measurements on one process may also include the contribution of other processes):

$$kdeg_{soil} = khydro_{soil} + kphoto_{soil} + kbio_{soil} \qquad \text{(Eq. 5)}$$

Explanation of symbols

$kdeg_{soil}$	rate constant for degradation in soil [d^{-1}]
$khydro_{soil}$	rate constant for hydrolysis [d^{-1}]
$kphoto_{soil}$	rate constant for photodegradation in the soil top-layer [d^{-1}]
$kbio_{soil}$	rate constant for biodegradation on soil [d^{-1}]

Hydrolysis and photolysis other than biodegradation are often not dominant for organic chemicals and do not contribute substantially to the overall degradation rate constant $kdeg_{soil}$.

Biodegradability in Soil

There are test methods available to determine biodegradability in soil. Data on soil biodegradation do not exist for many organic chemicals other than pesticides. Where no soil data are available, results from biodegradability test 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 solid/water partitioning has been developed (EU TDG 2001). In the PBT profiler program, the US EPA uses a fixed ratio of 1:2 for water to soil degradation rate, taking the water rate from either the Ready or Inherent test results.

Photodegradation

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 the sun's absorption spectrum.

3.2.4 Sediment

Data on biodegradation in sediments do not exist for many chemicals and therefore the half-life for the model must be estimated. In the EU, the half-life in sediment is estimated to be 10 times that in soil. In the PBT profiler program, US EPA uses a ratio of 1:9 for water to sediment degradation rate, taking the water rate from either the Ready or Inherent test results.

3.2.5 Vegetation

Vegetation was found to be an important factor affecting the atmospheric transport and persistence of organic pollutants, e.g. 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:

i. Partitioning from the gas phase to leaves and subsequent litter fall (scavenging) and
ii. enhanced degradation in and on plants/leaves.

It is assumed that metabolism in plant tissue is less relevant to non-ionic, airborne substances. 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.

3.3 Environmental Characteristics

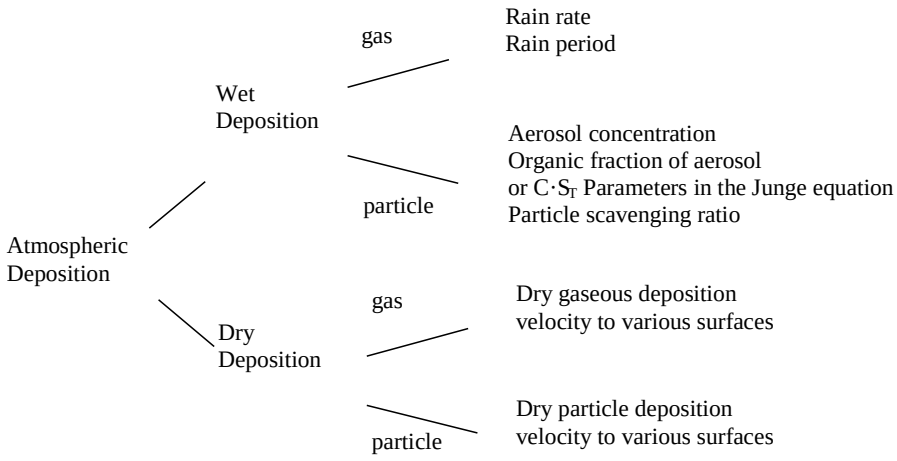
Generic models for estimating P_{ov} and LRTP generally supply default values for environmental characteristics. Beyer (2001) investigated which parameters had the most influence on the calculated P_{ov} and LRTP estimates in ELPOS for a number of representative chemicals. LRTP was highly sensitive to wind speed, but the choice of input value has no implication for the relative ranking of substances as the calculated CTD (characteristic travel distance) is linearly related to wind speed.

Another important environmental parameter is the height of the atmospheric compartment, as it determines the relative importance of either volume-based processes (i.e. degradation) or surface area-based processes (i.e. air-surface exchange processes). It thus has the potential to affect the relative ranking of chemicals with respect to P_{ov} and LRTP. The "correct" atmospheric height is probably dependent on chemical properties, more persistent chemicals requiring a higher value than chemicals that quickly degrade in the atmosphere. A similar reasoning applies to the choice of soil depth. Both

LRTP and P_{ov} estimates are sensitive to the environmental parameters that determine the extent of atmospheric deposition (see Figure 2 for an overview of these processes).

Figure 2.

Overview of environmental parameters influencing atmospheric deposition pathways.



Specifically, the capacity of the aerosol for organic chemicals (as defined by the aerosol concentration, the organic fraction of the aerosol or the $c \cdot S_T$ parameters in the Junge equation), the particle scavenging ratio, and gaseous and particle deposition velocities have been shown through sensitivity analysis to be important to the calculation, depending on the characteristics of the chemical. Current models use default values for these parameters. The default values used in the models should be reviewed and considered in light of this analysis. As the generic assessment models are assuming steady state, a constant rain rate is typically the only option, although it has been shown that the episodicity of precipitation can have a significant effect on chemical fate (Hertwich, 2001).

3.4 Data quality and uncertainty

Quality criteria

Reactivity and environmental partitioning data can be obtained from a variety of sources as discussed earlier. It is recommended that, if both experimental and estimated data are available, that the experimental data be used over the estimated values. The data compiled must then be reviewed for reliability, which can be done by assessing if internationally accepted test methods were 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
- Whether benchmark chemicals were used for comparison
- 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.

Overall, the variance found in partition coefficients is generally lower than the variance in degradation rates due to the fact that degradation rates are subject to both uncertainty and variability at the same time. In this context, it was noted that for estimating P_{ov} the quality of the degradation data is less important for media into which a chemical does not significantly partition e.g. <1%, 5% (except for assessing LRTP in air).

Regarding the quality of QSAR methods to estimate substance-specific input data such as the EPISuite (Meylan and Howard, 1999), information is generally supplied about the scope and quality of the training and the validation set. The reliability of the predictions 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 specific substance classes. Therefore the developers of QSARs are encouraged to supply substance class-specific information on the predictive capability of a given QSAR method.

Uncertainty in the output

The uncertainty inherent in the substance-specific input data gets propagated through the model resulting in uncertainty in the output (Schwartz et al. 2000, Berding et al. 2000, Berding et al. 2001). Uncertainties in calculated P_{ov} values are usually around a factor of 10 to 100 for the 90% confidence interval (Fenner, 2001), while uncertainties in LRTP are around a factor of 5 to 50 for the 90% confidence interval (Beyer and Matthies, 2001; Bennett et al., 2001). The analysis of contribution to variance for the two indicators shows that uncertainty in persistence values is dominated by over 90% by uncertainty in the degradation rates. This is due to the fact that persistence is most sensitive to degradation rates, which at the same time are the most uncertain model input parameters. Findings by Hertwich et al. (1999, 2000) and Schwartz (2000) confirm the high contribution to variance of degradation rates to any kind of exposure calculation in closed models. For LRTP, which is calculated in open model system, the variance is influenced not only be the half-lives but also by partition properties such as the vapor pressure and the water solubility, the model geometry (height of air compartment), and the landscape parameters influencing the deposition processes (e.g. rain rate).

Consequences for the use of persistence and LRT as screening criteria

The uncertainties inherent in calculated persistence and LRTP values are large compared to the differences between point estimates for different substances, e.g. factors of approx. 2 between persistence of different POPs. This means that the probability distributions between neighboring, rank-ordered chemicals are largely overlapping. Thus it might not be sensible to put too much effort in a

detailed ranking of substances nor does the comparison with deterministic cut-off values seem appropriate given the large uncertainties. There are two ways to resolve this situation. One possibility is to determine probabilistic criteria for cut-off values and rank substances based on their probability distributions. This might not be feasible in a first tier screening assessment because it encompasses conducting a full, probabilistic uncertainty analysis. The second possibility is to define P_{ov} and LRTP classes rather than ranking single chemicals, or, equivalently, to calculate relative P_{ov} and LRTP values by comparing them to the results for a benchmark chemical. This might be a more truthful representation of the quality of input and output data. Suggestions along this line of thought have been made by Gouin et al. (2001) in a report prepared for ECETOC. They distinguish 10 persistence classes, which are given different priorities with regard to ensuing, more detailed analysis of the belonging chemicals.

3.5 Mode of Entry

The mode of entry indicates 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.

- OECD Pollutant Release and Transfer Registry (PRTR) inventories provide probably the most extensive release and transfer data for chemicals to air, water and land. From that 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 UN ECE LRTAP Convention (United Nations Economic Commission of Europe: Long-range Transport of Air Pollutants) are to provide annual inventories. In addition some countries estimate releases from traffic and other sources.

- Another possibility to obtain estimates for the mode of entry are Emission Scenario Documents (ESDs). They are used, on an industry-specific basis, to estimate environmental releases to air, water and land.

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

- Information on how a chemical is used may also be “guessed” about releases to air/water/land.

- In some cases it may be possible to estimate the mode of entry for a chemical based on information for an analog chemical that has similar physical chemical properties and uses.

It is important to consider the whole life cycle of the substance, as significant emissions may occur at different stages of the life cycle. 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 PRTR Compendium Document (http://www.oecd.org/ehs)

- OECD Use and Release Database (http://www.oecd.org/ehs)

- Individual Country PRTR Guidance Documents on Estimating Releases
- Individual Country Emission Scenario Documents
- Individual Country Media Specific Programmes.
- Preliminary review of emission data sources for release estimation and development of emission scenario documents (CEFIC LRI, 2001)

3.6 Data Sources

In many countries regulations on pesticides and new industrial chemicals require industry to provide most of the key data as set out in the Appendix 1 to run generic MMM. However, the situation is different for the bulk of existing industrial chemicals for which experimental data need to be searched in the scientific literature, in handbooks, company catalogs, material safety data sheets, and databanks. In the future, the Internet will prove to be an important data source. Selected data sources are listed in Appendix 2.

4. Conclusions

- Presently existing models for overall persistence (P_{ov}) and long-range transport potential (LRTP) assessment such as TAPL3, ELPOS and ChemRange rely 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 substances, other means to derive at partitioning coefficients between environmental media are needed.
- Although in principle environmental input data to the models (such as rain rate and temperature) are not chemical specific, some of the environmental parameters (namely the depth of the atmosphere and soil compartments) may need to reflect the ability of various chemicals to penetrate into an environmental medium. Sensitivity analyses have identified the environmental parameters controlling gas/particle partitioning and atmospheric deposition to be of importance, and the default values in the models should be reviewed in light of these analyses.
- Persistence is most sensitive to degradation rates, which at the same time are the most uncertain model input parameters. However, it is noted that the quality of degradation data is less important for media into which a chemical does not significantly partition.
- Generally, there is more detailed (measured) data available for pesticides than for other chemical classes e.g. industrial chemicals.
- Currently there is no concerted, international effort for using MMMs for screening chemicals with regard to P_{ov} and LRTP. However, such a concerted effort is desirable since it would allow sharing the burden of data collection and screening of chemicals, and helping to avoid duplication.

- There is considerable uncertainty with the absolute values of chemicals as P_{ov} and/or LRTP.

- OECD PRTR data are available for a number of chemicals to estimate the mode of entry as well as the emission rates.

5. Recommendations

- A data hierarchy scheme should be employed when choosing input data for MMMs. Priority is given to

1. measured data derived using OECD test guidelines, if a guideline exists for the endpoint in question. For example, for biodegradation, there have been only ready biodegradation tests, which as indicated above do not provide the needed half-lives. This is about to change with the finalization of some guidelines for determining biodegradation rates (e.g. OECD 309). Particularly, for biodegradation it could be appropriate to use other preferred methods.
2. measured data derived from other "acceptable" methods
3. QSAR data
4. default value/expert judgment.

- Geometric means should be used when deriving average values for model input data in particular degradation rates.

- For screening chemicals it may be preferred to define bins or classes of chemicals with regard to P_{ov} and LRTP. If this is the case, it should be made clear what kind of consequences such a classification could have in terms of regulatory processes and/or management. Another option for screening is to use relative ranking by comparing P_{ov} and LRTP of a specific chemical to those of a benchmark chemical.

- OECD should encourage the incorporation of MMM-based screening on P_{ov} and LRTP in international programs (e.g. SIDS / HPV Challenge / ICCA / CEPA, EU White Paper and new chemicals and pesticide programmes) based on agreed guidelines.

- OECD Test Guidelines should be made available on the Internet for free.

6. Research Needs

- Develop a test method for assessing the OH radical degradation pathway for chemicals that are associated with aerosols or particles.

- Examining novel means of deriving degradation rates in the environment by exploiting existing historical monitoring data.

- Better characterisation of the relationship between laboratory data and the real world – i.e. improving predictive capabilities.

- Developing empirical relationships that can be used to characterise the multimedia partitioning of class “A” and “B” chemicals (A = nonpolar, non-ionizing; B = polar, non-ionizing).

- Better description of deposition rates to surfaces e.g. soil, water, and vegetation.

- Knowledge of temperature dependence for key substance properties such as physical chemical properties, partition coefficients and degradation rates.

- Data needs associated with vegetation (e.g. partitioning, degradation in and on plants/leafs) if this compartment is to be included in generic MMMs.

- Establishing error bars for QSARs that are chemical class specific.

Appendix 1:
Key Data Set to Run a Generic Model

This Appendix provides the selected references for QSAR methods of Meylan and Howard (1999). It should be mentioned that other methods are available as well (see Appendix 2).

Substance Identity

- Common name
- CAS Number
- Molecular weight
- SMILES Code

Substance Data

Property	**Dimension**	**OECD Test Guideline**	**QSAR Method** (Meylan and Howard, 1999)
Properties of pure substance			
Melting point	C	OECD 101	MPBPVP
Vapour pressure	Pa	OECD 104 (OECD 2001)	MPBPVP
Water solubility	mg/L	OECD 105	WsKow
Dissociation constant, pKa	---	OECD 112	PKalc
Partition coefficient			
Octanol/water partition coefficient	---	OECD 107 OECD 117 OECD 122 (Draft)	KowWIN
Optional partition coefficient			
Air/water partition coefficient	---	Mackay et al. 2000	HenryWIN
Air/octanol partition coefficient	---	Harner and Bidleman (1998); Harner and Mackay (1995)	
Adsorption coefficient	L/kg	OECD 106 OECD 121	PCKOC

Property	**Dimension**	**OECD Test Guideline**	**QSAR Method** (Meylan and Howard, 1999)
Degradation rate constant			
Photooxidation	Rate constant ($d^{-1)}$	OECD Draft (OECD 2000)	AOPWIN
Water Direct photolysis	Rate constant (d^{-1})	OECD Draft (OECD 2000)	There is no programme
Water Hydrolysis	Rate constant (d^{-1})	OECD 111	HydroWIN
Water Biodegradation	Rate constant (d^{-1})	OECD 301 (ready) OECD 302 (inherent)	BIOWIN Tunkel et al. 2000
Soil Biodegradation	Rate constant (d^{-1})	OECD 304A OECD 307 (Draft)	---
Photodegadation on soil	Rate constant (d^{-1})	US EPA No 835.2410 OECD Draft Test Guideline (OECD 2002)	
Sediment	Rate constant (d^{-1})	OECD 308 (Draft)	---
Vegetation foliar dissipation	Rate constant (d^{-1})	US EPA No. 875.2100	
Mode of entry			
Mode of entry	Percent emission into air, water, soil	---	---

Appendix 2:
Selected Data Sources

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The Merck Index - An Encyclopedia of Chemicals, Drugs and Biologicals, Merck&Co., Inc.

The Pesticide Manual, British Crop Protection Council and Royal Society of Chemistry, Cambridge.

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Kloepffer W and Daniel B (1991): *Reaction Rate Constants on abiotic degradation processes of organic chemicals in the atmosphere - Literature review*, Umweltbundesamt (Ed.) Berlin, UBA-Texte 51/91.

UNEP (IRPTC) and OECD. *Screening Information Data Sets (SIDS) for high Production Volume Chemicals*, United Nations, New York and Geneva.

Company Catalogues

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
CHEMFATE, Syracuse Research Corporation, http://www.syrres.com
DATALOG, Syracuse Research Corporation, http://www.syrres.com
BIOGEG, Syracuse Research Corporation: http://www.syrres.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), http://esc.styrres.com/efdb.htm
Hazardous Substances Data Bank (HSDB), http://toxnet.nlm.nih.gov
Environmental Chemicals Data and Information Network Databank (ECDIN), http://ecdin.etomep.net
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, 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
National Institute of Technology and Evaluation, Japan: Chemical Management Center: http://www.safe.nite.go.jp (English site under construction).

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ANNEX 7-2: ISSUE PAPER NO.3 -

DATA NEEDS FOR MULTIMEDIA MODELS FOR ESTIMATING OVERALL PERSISTENCE AND LRT POTENTIAL

The objective of the Data Needs subgroup is to identify, discuss and prioritize various data requirements of multimedia models. Multimedia models (MMMs) are important tools for assessing risk based on an evaluation of a chemical's persistence (P) in the environment and potential for long-range transport (LRT). Confidence in model results and ultimate success of the assessment and regulatory process however, relies heavily on the quality of the input data.

Annexes 5-2 and 6-2 are partner issue papers to this one. Annex 5-2 considers the role of MMMs in the regulatory framework and the various approaches that may be employed. Annex 6-2 considers model structure and design and several options for evaluating P and LRT are presented.

Our current level of understanding of MMMs and associated data needs is the culmination of previous studies and workshops. A good example is the recent SETAC-sponsored Pellston workshop held in 1998 ("Pellston workshop on criteria for persistence and long-range transport of organic chemicals in the environment"). Findings from this workshop are summarized in a SETAC publication entitled "Evaluation of persistence and long-range transport of organic chemicals in the environment" edited by Klečka et al. (2000). Another useful reference is the handbook by Boethling and Mackay entitled "Property Estimation Methods for Chemicals" which addresses in detail many of the data needs outlined in this paper.

Participants of the Data Needs subgroup are encouraged also to refer to the issue paper by Mackay et al. Because of the strong influence of MMMs on the assessment process, data needs often arise as a result of how the models are designed and applied.

In this paper, data requirements that are key to the modelling process are identified and briefly outlined.

These include:

1. Removal rates in air.
2. Degradation rates in soil, water and sediment.
3. Physical Chemical Properties and Intermedia partitioning
4. Additional considerations
    - ♦ emission rates
    - ♦ mode of entry
    - ♦ monitoring data for model validation
    - ♦ environmental characteristics

The paper ends with several concluding remarks and a series of thought-provoking questions. Ultimately, this paper is intended to aid workshop participants and serve as a framework for discussions. During the workshop data needs will be prioritized, available data and preferred methods of estimation considered, and conclusions made on preferred approaches. The results of the workshop will also identify topics that require further and immediate research.

Overview of Data Needs

As discussed earlier the data requirement for a specific assessment will depend on how the model is used. For instance, a second tier evaluation of a chemical may require a Level II model. This may consist of air, water and soil compartments that are well-mixed and able to exchange chemical. Here the key data needs are the degradation rates in each compartment and the equilibrium inter-media partition coefficients. For more detailed, higher-level assessments a level III model may be more appropriate. In this case mode of entry (details regarding the proportion of the chemical emitted to each compartment) becomes crucial since this will directly effect LRT and P. In some instances even more complex models (e.g. level IV) with additional model compartments (e.g. sediment, vegetation) may be required.

Data needs associated with assessments and MMMs can be divided into several categories. Parameters that are inherent to a chemical include degradation rate constants and physical chemical properties (that also govern partitioning behaviour). These can be determined experimentally and may vary with temperature, sometimes by several orders of magnitude over the range of environmental temperatures. Other data, such as emission rates and mode of entry, involve knowledge of the production volumes and usage of a chemical. The last category includes miscellaneous parameters that are measured, sometimes during routine monitoring programs (e.g. concentrations in specific media) and various environmental characteristics. These parameters may vary spatially and temporally and must sometimes be averaged to be included in MMMs.

1. Removal rates from air

Atmospheric Chemistry

- *reaction with OH radicals , NO_3 radicals or O_3.*
- *photolysis reactions*

Atmospheric Deposition

- *dry deposition*
- *wet deposition*
- *dry particle deposition.*

1.1 Degradation

Removal of chemical from the atmosphere occurs by either reaction or deposition. Removal reactions include reactions with hydroxyl (OH) and nitrate (NO_3) radicals and ozone (O_3). There is also the possibility for direct photolysis of persistent organic chemicals (POPs).
The OH radical pathway is thought to be key for most POPs and rate constants (k_{OH}, cm^3 $mole^{-1}$ s^{-1}) have been measured for several classes including: PCBs, PCDD/Fs, α- and γ-HCH and HCB in the gaseous state (Atkinson, 2000). The PHYSPROP database (http://www.epa.gov/opptintr/exposure/docs/episuite.htm) lists OH radical rate constants for several compound classes.

Measured rate constants are thought to have an accuracy of ±30%. Despite the importance of the OH pathway few data are available for other classes of organic chemicals, including POPs listed under the UNEP "dirty dozen". The scarcity of data can be attributed to the complexity of the experimental determinations of k_{OH}, especially for compounds having vapour pressures below 10^{-5} Pa, which includes many POPs. Consequently, k_{OH} is often estimated for modelling purposes.

Several estimation methods for k_{OH} are available. One of the more popular approaches, proposed by Atkinson, uses structure-activity relationships and includes four possible reaction pathways and rate constants that are additive (Atkinson, 2000). In other words, the rate constant for the molecule is then the sum of the rate constants for each group. When tested against experimental data, the results of this method are generally within a factor of two for most POPs. The method becomes limited however for other classes of chemicals that are not included in the database used to build the estimation method. In these instances uncertainties in k_{OH} of about a factor of 5 or greater can be expected. Thus there is a general need to expand the experimental data base for the estimation methods to other classes of chemicals and to develop improved experimental methods for measuring k_{OH} (and k_{O3}, K_{NO3}) directly.

Another complication in determining OH-mediated removal rates is the uncertainty associated OH radical concentrations in the atmosphere. The OH radical concentration is not constant and depends on presence of sunlight and precursor chemicals in the atmosphere. Consequently it may vary temporally and spatially by several orders of magnitude (Prinn et al., 1995). This variability has a large impact on the atmospheric half-life of a chemical (Webster et al., 1998).

During photolysis a molecule undergoes a transformation reaction as a result of energy absorbed from sunlight. The rate of photolysis of a chemical depends on several factors: 1.) light intensity 2.) absorption cross-section. This is a measure of how much of the light intensity is absorbed by the chemical, and 3.) photolysis quantum yield. This is the fraction of the excited species that results in a transformation reaction. Because of the difficulty in measuring these factors, the relative importance of the photolysis pathway for removing chemicals is still not fully known.

Photolysis reactions occur mainly in the gas-phase. However, it is also thought that chemicals absorbed on the first few monolayers of a particle or other surface are also subject to reaction but few studies have investigated this process.

1.2. Deposition

Chemical may also be removed from the atmosphere through various deposition processes - dry deposition (gas-exchange with soil, water and other surfaces), dry particle deposition (removal through association with settling atmospheric particulate matter), and wet deposition. Wet deposition includes removal through dissolution in precipitation (usually rain) and via particle scavenging by rain droplets.

Rates of dry deposition will depend a chemical's volatility. This can be described by its vapour pressure (p^o) or octanol-air partition coefficient (K_{OA}) which are both strongly temperature-dependent physical-chemical properties. Partitioning to water is controlled by the Henry's Law constant (H). Mass transfer rates in the real environment are also important for describing transfer of chemical accurately.

Deposition via dissolution in rain can be described using the Henry's Law constant (H) and its dependence on temperature. It is important to understand the relationship between scavenging rates and the volume of precipitation, since most chemical will be stripped out of the atmosphere in the initial period of a precipitation event. Certain organic chemicals may be enriched in fog, and this may be an important consideration in parts of the world.

Chemical partitioning is considered further in section 3.

1.3 Particle-gas partitioning

Particle-associated deposition involves knowledge of the fraction of chemical associated with the particle and knowledge of its composition, size distribution and settling rate. Particle-gas partitioning can be described using p^o_L-based (p^o_L is the sub-cooled liquid vapour pressure of a chemical, Pa) and K_{OA}-based models.

It is a common practice of MMMs to employ an "average" aerosol having an "average" deposition velocity. In reality the type and size-distribution of aerosols is important. For example small aerosols have much lower deposition rates and are therefore able to be transported greater distances than large aerosols. It is also important to know properties such as surface area or organic matter fraction that control the aerosol's capacity for chemical.

The ability to accurately predict particle-gas partitioning for semi-volatile organic compounds (SOCs) is also important because it determines the extent of removal by atmospheric removal reactions (OH-, NO_3-, O_3-mediated and photolysis) which occur primarily in the gas-phase.

2. Degradation rates in soil, water and sediment.

Biotic

- *microbial degradation*
- *phytodegradation*

Abiotic

- *hydrolysis (neutral, acidi, basic)*
- *photolysis (direct and indirect)*
- *oxidation / reduction reactions*

Chemicals are degraded in soil, water and sediment through biotic and abiotic processes. The dominant biotic process is microbial degradation. Phytodegradation which refers to degradation in plants is also a consideration however very few studies on POPs have investigated this pathway. Abiotic removal processes include hydrolysis (neutral, acidic, and basic), photolysis, and oxidation/reduction reactions.

2.1 Microbial Degradation

Microbial degradation is usually described according to a second order rate expression of the form,

$$(dS/dt)_b = -k_b [B] [S]$$

Where [B] is the biomass concentration and [S] is the concentration of the substrate (chemical). Since [B] changes slowly this expression becomes pseudo-first order. An important consideration in applying the rate coefficient in fate models is that it is specific to the chemical and the biomass type and concentration. Biomass concentration and activity will depend on several parameters including, temperature, water content, nutrient levels and pH. This complicates the modelling process since the selection of an average or representative value is not straightforward and perhaps not even appropriate.

2.2 Hydrolysis

Hydrolysis reactions are important for dissolved species in surface water, ground water and sediment. Little information exists regarding hydrolysis in soil. Hydrolysis removal reactions occur under neutral, acidic and basic conditions according to the following equations:

$$(dS/dt)_{nh} = -k_{H20}\,[S] \quad \text{(neutral)}$$
$$(dS/dt)_{ah} = -k_{H+}\,[H^+][S] \quad \text{(acidic)}$$
$$(dS/dt)_{bh} = -k_{OH-}\,[OH^-][S] \quad \text{(basic)}$$

Concentrations of [H+] and [OH-] are determined from pH. The presence of dissolved ions such as sulfide and chloride may also be important and enhance hydrolysis rates.

2.3 Photolysis

As discussed previously, direct photolysis in water may occur through absorption of solar radiation. Although photolysis may occur in moist surface soils very little information is available. Some organic chemicals have been shown to be enriched in surface water films and thus be more susceptible to surface photolysis reactions.

Reaction rates for direct photolysis are first order. Photolysis may also occur indirectly by a second order reaction involving a photosensitizer compound or oxidant present in solution. Photosensitizers transfer energy to the target chemical.

2.4 Oxidation/Reduction Reactions

Oxidation / reduction reactions are emerging an important area of study and may be key to removing organic chemicals. Reduction reactions, which are usually important in sediments occur in the dissolved phase and are described by second order kinetics.

$$(dS/dt)_{red} = -k_{red}\,[S][R],$$

[S] is the chemical and [R] is the reducing agent. However, [R] is difficult to quantify and often it is replaced by the organic carbon content [OC] which is easily quantified and found to be proportional to [R].

Oxidation reactions may be important for POPs in near-surface waters. The process involves the absorption of UV light by precursors that produce OH radicals. These radicals are then available to oxidize dissolved organic chemicals.

2.5 Sources of Data

Field measurements of biotic and abiotic degradation in water, soil, and sediment are the most accurate and preferred for modelling purposes because they take into account heterogeneity of the system and other intrinsic factors controlling removal rates. However, one complicating factor is that these data are sometimes difficult to interpret because it is difficult to differentiate biodegradation from other types of losses. There is a need for a consistent approach for extrapolating this short-term experimental data to the real environment.

When field data is not available laboratory type tests (e.g. batch tests and screening tests) may be useful for approximating degradation rates or determining whether or not degradation is important process for a specific chemical. Estimation methods based on QSARs may be employed when accuracy is less critical.
Mackay et al. (1991-1997) and Howard et al. (1991) report reaction half-lives for chemicals in soil and sediment. Two recent reports by Aronson and Howard (1997) and Aronson et al. (1998) review laboratory and field measurements of biodegradation rates for organic chemicals.

3. Environmental Partitioning

Partition Coefficients

- *air-water partition coefficient, K_{AW}*
- *octanol-air partition coefficient, K_{OA}*
- *octanol-water partition coefficient, K_{OW}*

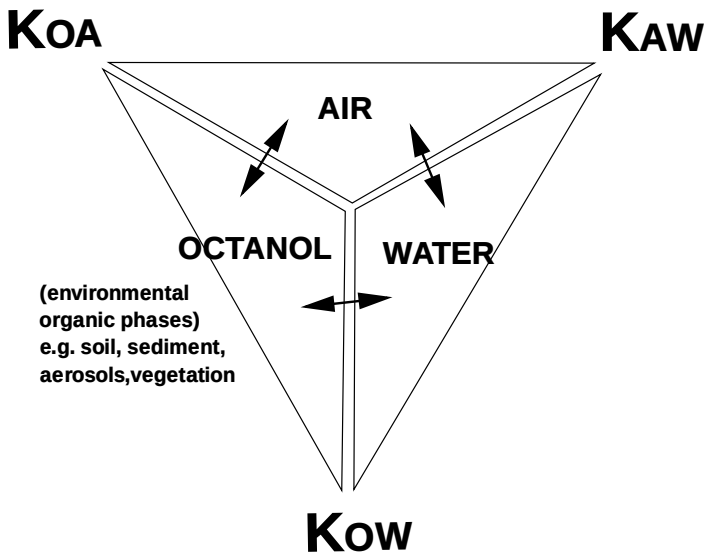
Descriptions of Phase Partitioning

- *aerosol-air*
- *soil-air*
- *vegetation-air*
- *air-water*
- *sediment water*

Partitioning data are key to MMMs for predicting the concentration of chemical in each medium and for properly applying degradation and removal rates that are phase specific.

Figure 1 illustrates a simple model of chemical partitioning between three main compartments: air, water, and octanol-equivalent material. Octanol represents environmental organic phases that have a high capacity for POPs and other hydrophobic chemicals. These types of phases include soil, vegetation, aerosols, and sediment. The complexity of the chemical assessment will determine the complexity of the model. For instance a screening level assessment may require a level I or II approach that considers equilibrium partitioning of chemical between air, water and soil. Higher level assessments may include additional compartments (e.g. fresh water plus ocean water, vegetation etc) and transport /advection of chemical between compartments (non-equilibrium, e.g. level III model).

Figure 1.
Illustrative diagram showing relationship between key media and partition coefficientfor modelling chemicals in the environment.



Partitioning between these media is governed by three partition coefficients. K_{AW} describes equilibrium partitioning between air and water (K_{AW} is the dimensionless expression of the Henry's Law Constant, i.e. $K_{AW} = H/RT$); K_{OA}, between octanol and air; K_{OW}, between octanol and water.

When a measured partition coefficient is not available a calculated value may be used. The handbook by Boethling and Mackay (2000) considers this topic in detail. A variety of methods for measuring and estimating physical chemical properties and partition coefficients is presented. Quantitative structure property relationships (QSPRs) are increasingly applied to estimate physical chemical property data and partition coefficients.

3.1 Temperature-Dependence

Chemicals may show drastically contrasting partitioning behaviour in different climate regions or at different times of the year as a result of changes in temperature. From a modelling and assessment standpoint it is important to understand the temperature-dependence of the key partition coefficients. The global distillation effect (grasshopper effect) is driven by this temperature-dependent partitioning.

Of the three partition coefficients in Fig. 1, the strongest temperature-dependence is observed for K_{OA} where every 10 ^{o}C decrease in temperature results in an approximately three-fold increase in K_{OA}. Consequently, organic chemicals will more strongly partition to environmental organic phases at colder temperatures. Measured values of K_{OA} as a function of temperature are now available for several classes of organic chemicals.

Temperature-dependent data for K_{OW} and K_{AW} (H, which also exhibits a strong temperature dependence) are limited. Values at 25 ^{o}C are reported in handbooks (Mackay et al., 1991-1997) and databases for numerous classes of organic chemicals. A difficulty from the modellers perspective is choosing a value from a range of literature values for a single substance that may span several orders of magnitude. In such instances expert judgement is required.

3.2 Intermedia Partitioning

When the relevant partitioning data are known, the next step is to relate these to how a chemical partitions in the real environment. Laboratory investigations and field studies are instrumental in deriving these empirical relationships (e.g. K_{OA} and the fraction of organic matter may be used to describe partitioning to soil). For a simple level I or II model the key partitioning interactions include:

1. soil-air
2. water-air

Higher level assessments may also consider:

1. aerosol-air
2. vegetation-air
3. sediment-water
4. snow / ice - air

Treatment of these interactions is beyond the scope of this paper. These processes are considered in detail in the handbook by Boethling and Mackay (2000).

4. Additional Considerations

- mode of entry
- identifying relevant input data
- monitoring data
- treatment of anomalous chemicals

4.1 Mode of Entry

An important consideration for MMMs is the manner in which a chemical is introduced into the environment. A chemical emitted into air will have a "head start" with respect to atmospheric transport. The same applies to one that is emitted to water and undergoes advective transport in rivers or ocean currents. Chemicals that are released directly onto soils and sediments will be less mobile since most organic chemicals are hydrophobic and bind strongly to organic phases. However, persistence will increase since the chemical is shielded from photolysis removal reactions.

Thus the compartment into which a contaminant is introduced into the environment will determine its P and LRT. Webster et al. (1998) use a level III model to demonstrate the importance of mode of entry and partitioning in the overall evaluation of persistence of a chemical. In reality each compartment will receive some fraction of the total chemical discharged into the environment. Information on production and usage can be used to determine this distribution for a particular chemical so that it can be modelled accordingly. The US Toxics Release Inventory (TRI) and other chemical substance inventories that exist in other nations are sources of this information. However, for many chemicals there is no data available.

If an assessment is conducted for past-use chemicals such as the PCBs, PCNs (polychlorinated naphthalenes) or organochlorine pesticides (e.g. toxaphene, dieldrin, DDT) thought must be given to the historical usage. For these chemicals re-emission from soils is an important consideration. For most organic chemicals that are hydrophobic, the soil is a reservoir that will buffer atmospheric concentrations when direct emissions cease. Modelling the re-emission and transport of these chemicals requires good spatial information on soil residues. This is especially important for organochlorine pesticides that are concentrated in agricultural regions.

4.2 Monitoring Data

Better integration of monitoring data and models / modellers would be beneficial. For instance adjusting temporal and spatial resolution of sampling programs may improve model validation exercises. Efforts can also be made to monitor during certain meteorological events – e.g. during rainfall, windy days, very hot days. It may be that 90% of the LRT of chemical occurs 10% of the time and that transport events (e.g. "single hops") are very important.

4.3 Environmental Characteristics

Environmental characteristics are model input parameters that help to define the assessment scenario. They can be divided into two categories: 1) meteorological parameters and 2) characteristics of the physical environment. Meteorological parameters include things such as temperature, windspeed, precipitation volume, light intensity, OH radical concentrations. Physical parameters on the other hand, describe the composition of the multimedia environment and include parameters such as soil composition, aerosol composition and concentration, vegetation cover etc. The selection of these factors will impact model output and perhaps the conclusion of the assessment process. Because they vary spatially and temporally, it is necessary to choose representative values of environmental characteristics when defining the MMM. This is not a straightforward process.

Concluding Remarks and Questions

The intention of this paper is to identify and discuss data needs that are most critical for running MMMs for assessing P and LRT of chemicals. Several points are listed below summarizing some key concerns:

Selecting "average" values?

It is often the case in the assessment process that an average value must be selected from a range of literature values that span orders of magnitude. This is especially a concern if the parameter under consideration has a strong influence on the outcome of the assessment. If a mean value is determined, should the geometric mean or arithmetic mean value be used? How should outliers be treated? Should expert judgement be considered even though this may introduce bias to the process? Should guidelines be developed for dealing with these types of scenarios in order to improve consistency in the assessment process.

In the case of degradation rates or half-lives it is important to use the geometric mean since different results will be obtained for the arithmetic mean depending on whether it is based on half-lives or degradation rates. Similarly, when fitting distributions to degradation data, only log-distributions should be used.

Environmental characteristics vary spatially and temporally and often require the selection of a representative or average value. The scale of the model (i.e. regional versus global) will also play a role in how this determination is made. Should a generic set of environmental characteristics be used to define different model environments?

How to deal with uncertainty in input data?

An impending issue is recognizing and quantifying data uncertainty. In some cases fate processes and chemical and physical parameters have been measured or characterized with a high degree of certainty and application in models is straightforward. In other cases however, the treatment is more difficult due to conflicting, or sparse data, or issues related to the complexities and heterogeneity of the real environment. Ultimately, modellers must decide how to resolve this uncertainty. Options include: 1) using expert judgement to select a "most reliable" measured value, 2) employing an estimation method when measured data is not available, recognizing the inherent uncertainty in the approximation, 3) including this uncertainty in the model by using confidence factors or log-normal distribution of selected input values. [Webster et al. (1998); Bennett et al. (2001)], e.g. Monte-carlo analysis, and 4) reducing the required input data to a smaller and more relevant set.

Is it appropriate to identify and exclude data as irrelevant?

Because of the large data requirement of MMMs it is useful to identify data that are irrelevant or non-essential to the assessment. Gouin et al. (2000) presents a graphical technique to identify phases into which a chemical will predominantly partition. Half-lives in these media are then weighted more heavily in the calculation of overall persistence. In some cases degradation rates in media into which a chemical will not partition can be deemed unnecessary, thus alleviating the data requirements of the model by assuming that the chemical does not degrade in these media. However, caution is warranted when using this approach.

How to deal with anomalous chemicals?

The treatment of "anomalous" or unusual chemicals is becoming increasingly important. Chemicals in this category include very polar chemicals and surface-active chemicals such as surfactants that may ionize and partition very strongly to water. Conventional partition coefficients (e.g. K_{OW}) and intermedia partitioning relationships may not be useful for understanding the environmental fate of these chemicals.

Research needs?

Because of the large number of chemicals required to undergo screening and assessment efforts it is not feasible to expect that all data requirements will be fulfilled. It may be useful to prioritize data needs that are most critical and work to obtain "good" values for these parameters.

The most important data needs are often identified by means of conducting a probalistic uncertainty analysis and comparing the contributions to variance of different input parameters. The resulting properties will depend on whether a closed or open system is investigated. For closed systems the importance of substance-specific input data is normally predominant (Hertwich et al., 1999), with degradation rates generally being very important (Hertwich et al., 1999; Fenner, 2001). For open systems the landscape and meteorological parameters become more important (Schwartz, 2000). Because P is normally calculated in closed systems and LRT in open systems, different priority lists regarding the most critical data needs are expected to be obtained for those two indicators.

For some classes of compounds partitioning between specific media may be highlighted as a key factor of LRT and P (Wania and MacLachlan, 2001). For these chemicals, it would be wise to investigate the process in detail and derive descriptive, empirical relationships that are reasonably accurate.

In conclusion, the results of the Data Needs working group will assist modellers by identifying key areas of uncertainty and options or preferred approaches for dealing with this problem. Participants in the regulatory process will also benefit by having a better feel for the relationship between model design, complexity and data needs. Lastly (and perhaps most importantly), data gatherers will be able to assess the current state of knowledge and identify research topics that merit further attention.

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