

# Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment: Summary of a SETAC Pellston Workshop

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Summary of the SETAC Pellston Workshop on Persistence and Long-Range Transport of Organic Chemicals in the Environment, 13–19 July 1998, Fairmont Hot Springs, British Columbia, Canada

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## Preface

“Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment: Summary of a SETAC Pellston Workshop” summarizes the outcome of a workshop and consensus-building process. The workshop was conceived by a small group of people in the public and private sectors who met informally as a steering committee for more than a year to discuss the need for a scientific foundation for the criteria and process used for the evaluation of the environmental behavior of persistent organic pollutants.

The urgency and impact of the workshop are well established. For example, 1998 saw the initiation of a process by which chemicals will be controlled internationally for the first time, as nations of the world entered into treaty negotiations on persistent organic pollutants, under the auspices of the United Nations Environment Program. Furthermore, this is the global counterpart to many other national and regional initiatives. While the steering committee recognized that in addition to the environmental attributes, toxicity and bioaccumulation potential are equally important in these discussions, the workshop specifically focused on the scientific fundamentals, criteria, and processes used for the evaluation of persistence and long-range transport.

With this background the workshop brought together experts from academia, industry, government, and non-governmental organizations to reach consensus on where we are today and what we can accomplish with the current scientific understanding, as well as what should be done in the future as we address this issue. From the dialogue will come a final Proceedings, of which this is the summary.

If this Workshop helps bring together those who devote their energies to the science, regulation, and management of chemicals to work together more effectively towards a common goal of deciding how we must manage chemicals on our planet, it will have been a success. Perhaps future historians will note that as the millennium drew to a close, the worldwide scientific community took a first, exploratory, but determined step towards this challenging task. As such, the Workshop and its Proceedings are welcome evidence that the broad environmental community is striving purposefully toward this goal.

# Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment: Summary of a SETAC Pellston Workshop

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This summary outlines results of the Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment Workshop sponsored by SETAC and administered by the SETAC Foundation for Environmental Education on 13–19 July 1998. Over 50 international experts selected from academia, industry, government, and non-governmental organizations from Belgium, Canada, Germany, India, Italy, Japan, Sweden, Switzerland, The Netherlands, the United Kingdom, and the United States were in attendance. The workshop used a consensus-building process to develop recommendations based on the current state of the science as to the process and criteria for identifying organic chemicals that could constitute a concern for persistence and/or long-range transport. Ultimately, the goal of the workshop was to provide timely scientific input and guidance to national and international discussions concerned with persistent organic pollutants. A summary of the findings is presented here.

Key words: persistence; long-range transport; persistent organic pollutants (POPs); persistent, bioaccumulative, and toxic substances (PBTs); multi-media modeling

## Introduction

Persistent organic pollutants (POPs) are bioaccumulative and toxic organic compounds of natural or anthropogenic origin that resist photolytic, chemical, or biological degradation. They are characterized as highly hydrophobic, resulting in bioaccumulation in fatty tissues of living organisms. POPs may be transported in the environment at low concentrations by movement of fresh and marine waters. Recent evidence has shown that because of their semi-volatility, POPs are also transported long distances in the atmosphere, resulting in widespread distribution around the earth, including in regions where they never have been produced or used. Thus, both humans and ecosystems may be exposed, in many cases for extended periods of time.

In recent years, several national and international accords have been initiated or completed to identify, select, and require action to control the use and/or release of a variety of persistent, bioaccumulative, and toxic substances (PBTs), including both organic compounds (POPs) and those containing metals. Examples of regional or global initiatives that are directed at identifying POPs and/or PBTs and developing risk management measures to control the exposure of humans and ecosystems include the Oslo-Paris (Ospar) Convention for the Protection of the North-East Atlantic, the Canada-USA Great Lakes Water Quality Agreement and Binational Toxics Strategy, the United Nations Economic Commission for Europe (UNECE) Convention on Long Range Transboundary Air Pollution, and the United Nations Environment Program (UNEP) global convention on POPs. In addition to these intergovernmental accords, several national governments and non-governmental organizations have developed and implemented regulatory and non-regulatory initiatives to address the use and/or release of POPs and PBTs. While the list is not exhaustive, it illustrates that persistent, bioaccumulative, and toxic substances have been and will continue to be the subject of considerable attention for scientists and policy makers.

## Workshop Purpose and Goals

To foster the development of a sound scientific foundation for identifying and evaluating POPs and PBTs, an international workshop, sponsored by the Society of Environmental Toxicology and Chemistry (SETAC), was held 13–19 July 1998, to discuss scientific issues related to persistence and long-range transport of organic chemicals. The workshop had broad involvement from academia, government, industry, and other interested organizations. While it is widely recognized that substances that exhibit a combination of properties (i.e., persistence, bioaccumulation, and toxic potency) should be the focus of societal concern and regulatory management efforts, this workshop specifically restricted its attention to the need for a scientific foundation for the criteria and

processes used to evaluate persistence and long-range transport of POPs and PBTs.

The specific objectives of the workshop were to discuss the issues, reach consensus, and make recommendations based on the current state of the science concerning the evaluation of persistence and long-range transport of organic chemicals in the environment. In meeting these objectives, the workshop addressed a number of questions, including the following:

- Is it feasible to classify chemicals according to persistence and potential for long-range transport? With what level of discrimination should chemicals be classified?
- What types of data are needed for the evaluation of chemicals? What is the proper role of estimated values versus laboratory-derived data? How does one proceed when data for critical inputs are missing?
- What level of uncertainty is acceptable with respect to each parameter, and how should uncertainty be accounted for in the process of substance evaluation?
- Is it realistic to assess persistence and long-range transport potential on the basis of specific chemical properties and transformation half-lives, or is single-medium or multi-media modeling required?
- What are the proper roles of local, regional, and global monitoring data?
- Are the schemes that have been proposed for classifying chemicals scientifically valid? How could they be improved?

## Participation and Format

The workshop followed the format of previous SETAC Pellston Workshops, and it was limited to about 50 participants with broad international perspective and expertise in atmospheric and environmental chemistry, partitioning and transport, multi-media modeling, and environmental assessment (see Participants List). To address the objectives, the workshop was organized into 8 individual sessions. A general plenary was held on the first day, where invited, authoritative discussion papers were presented to stimulate dialogue. Based on expertise, each participant was assigned to a small workgroup, although interactions among the workgroups were encouraged. A major goal of each workgroup was to develop a summary of their deliberations, including discussions of the state of the science pertinent to that workgroup; a critical analysis of available approaches; and methods to integrate these approaches into a framework for assessing persistence and potential for long-range transport. Key points from the discussions are summarized below. The complete workshop proceedings document is in preparation and will be available by fall 1999.

## Quantitative Determination of Persistence in Air

The persistence of organic compounds in the atmosphere is governed by the rates at which they are removed by chemical and/or physical processes. Chemical degradation is dominated by reaction with the hydroxyl radical (OH) in most cases, but for some compounds reaction with ozone (O<sub>3</sub>) or the nitrate radical (NO<sub>3</sub>) or destruction by direct photolysis may also be significant, and therefore these processes should be assessed. Physical removal from the atmosphere can occur by wet or dry deposition of gaseous or particle-borne species.

Satisfactory methods exist for experimental determination of the rate constants for reaction with OH, O<sub>3</sub>, and NO<sub>3</sub> (with an accuracy of about  $\pm 30\%$ ), as well as experimental determination of UV-visible absorption cross-sections (at least for the more volatile compounds). For the less volatile compounds (which include many POP-type substances), new procedures are beginning to be explored and validated. Determining photolysis quantum yields is a time-consuming process for which no standard procedure exists.

Estimation of rate constants for reaction with OH using Atkinson's empirical method allows prediction, within a factor of 2, for 90% of the approximately 600 compounds used in its development. For compound classes for which no experimental data are available, the uncertainties in rate constants estimated by this method could well be a factor of 5 or greater. The accuracy of estimation methods for reactions of O<sub>3</sub> and NO<sub>3</sub> is generally lower than that with OH, and order-of-magnitude uncertainties must be expected. No reliable methods exist for quantitative prediction of absorption cross-sections or quantum yields.

Many POP-type compounds present in the atmosphere are to a large extent adsorbed on particles. There are severe limitations, however, to our understanding of the impact of adsorption on chemical degradation. In particular, reaction with OH may not cease when the substance is in the adsorbed state, as has been assumed in the literature. Furthermore, some inorganic constituents of atmospheric particulates may photocatalyze degradation of adsorbed organics.

The main factors affecting the removal of chemicals from the atmosphere by wet and dry deposition are known. They include water solubility, particle size (for species adsorbed on particulates), nature of the receiving surface (for dry deposition), and intensity and duration of precipitation (for wet deposition). Deposition processes therefore can be modeled, with varying degrees of sophistication, and their rates estimated. In addition, revolatilization must be considered.

The overall atmospheric half-life, taking into account chemical destruction and physical removal, can be calculated at the screening level by using a simple box model of the atmosphere and the earth's surface, and by assuming global, regional, or local average values of input parameters such as OH concentra-

tions, temperature, solar radiation intensity, aerosol densities, deposition velocities, etc. For more detailed evaluations, the overall atmospheric half-life can be calculated by using increasingly sophisticated models of the atmosphere coupled to other media. These models should take into account spatial and temporal variations in the input parameters, and provide a more realistic description of atmospheric transport and intermedia partitioning.

While persistence is probably easier to quantify for the atmosphere than for other environmental compartments, there are still severe limitations to both our predictive capacity for purely gas-phase processes and to our basic understanding of processes involving substances adsorbed on particles. Furthermore, few experimental data exist for POP-type compounds. Finally, it is important to note that in the winter months at mid-latitudes, the very low atmospheric OH concentrations will affect the half-lives of practically all organic compounds.

### **Quantitative Determination of Persistence in Soils, Surface Waters, and Sediments**

The persistence of organic compounds in soils, surface waters, and sediments is principally governed by the rates at which they are removed by physical, chemical, and biological processes. Biotic degradation processes include phytodegradation and microbial biodegradation. Abiotic degradation processes include hydrolysis, direct and indirect photolysis, and oxidation/reduction reactions.

A variety of experimental methods are available for measuring the biotic and abiotic degradation of organic compounds. These methods are generally organized in tiers, from screening level to more complex, and are typically implemented in a specific sequence by using standardized test procedures. Standard protocols are well-developed for some biotic process like microbial biodegradation and for some abiotic degradation processes like hydrolysis and photolysis. However, in all cases, kinetic constants or half-lives generated by standardized test protocols are relevant only to the experimental conditions used and must be normalized for physical, chemical, or biological factors to allow extrapolation to different environmental compartments. When experimental data are not available, empirical approaches or quantitative structure-activity relationships (QSARs) can be used to estimate biotic or abiotic kinetic constants. The use of QSAR predictions, however, can be supported only for materials that have similar chemical structures and are biotically or abiotically degraded by the same mechanism.

A wide variety of physical, chemical, and biological factors are known to influence biotic and abiotic degradation rates. In many cases, these factors can be identified by expert judgment and are quantified by using relatively simple mathematical expressions. For example, the factor dictating the rate of a

compound's biodegradation is the number of competent microorganisms. This number can vary by several orders of magnitude for different tests and different environmental compartments. However, in many cases, the number of competent microorganisms can be estimated by using standard assumptions. Similar approaches can be used to identify and quantify other key variables affecting biotic and abiotic degradation processes.

The quantitative determination of persistence in soil, water, and sediment environments is largely controlled by 2 factors: 1) the accurate determination of biotic and abiotic rate coefficients, and 2) the extrapolation of these rate coefficients (in the form of transformation half-lives) to relevant environmental compartments. Because a number of factors influence abiotic and biotic processes, the determination and extrapolation of transformation rate coefficients are complex. One of the goals of the workgroup was to reduce this complexity to manageable levels and to develop a technically sound approach for estimating persistence in soil, water, and sediment compartments that was broadly applicable to a wide range of organic chemicals. The recommended approach utilizes multiple data sources and databases (QSARs, experimental determination, monitoring, etc.) and encompasses both screening and detailed evaluations. The key outputs are first-order rate constants and the corresponding half-lives for both biotic and abiotic transformations in soil, water, and sediment compartments. Moreover, the first-order rate constants are calculated from the fundamental second-order rate expressions after normalizing for the known or estimated concentration of the biological or chemical reactant, that is,  $v_b = -k_b [B] [S]$  and  $v_a = -k_a [A] [S]$ , where  $k_b$  and  $k_a$  are the true second-order biotic and abiotic transformation coefficients, respectively; B is the biomass concentration for biotic reactions; A is the reactant concentration for abiotic reactions; and S is the aqueous phase substrate concentration in the environmental compartment under consideration. Thus,  $k_b$  and  $k_a$  are not "lumped" pseudo-first-order constants, i.e., expressions that contain the concentration of some reactant as a hidden term. Lumped first-order values are highly specific to individual systems and cannot be extrapolated to different systems without considerable (order-of-magnitude) uncertainty.

The expression of biological and chemical reactions by using second-order kinetics represents a further refinement of the previous pseudo-first-order approaches and was adopted to minimize the effects of environmental heterogeneity and to reduce uncertainty in the extrapolation of persistence data. By converting system-specific, pseudo-first-order rate constants to chemical-specific, second-order rate constants, the latter become, in effect, intrinsic chemical properties. This approach allows persistence data to be developed and extrapolated to a variety of different environmental compartments, as long as B or A are known or can be reasonably estimated from experimental data.

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## Partitioning, Intermedia Transfer, and Long-Range Transport

The environmental media or compartments that play a key role in controlling the fate of chemicals and hence their persistence were considered. A 3-compartment system of air, water, and soil, with soil possibly including sediment, represents the most simplistic approach for addressing chemical transport and persistence. More realistic is a system consisting of air, water, soil, and sediment compartments in which there is also treatment of subcompartments such as aerosols in air and suspended solids in water. Such a system captures the principal phases of accumulation and transport, at least for most chemicals and environmental conditions. The most difficult issue is that of including vegetation as a subcompartment of terrestrial soils. Related issues are reviewed by this workgroup, including the separate treatment of fresh and marine water, the vertical segmentation of the atmosphere, the possible inclusion of groundwater, and the effects of snow and ice.

Phase-partitioning properties of chemicals were discussed and approaches for estimating the appropriate partition coefficients and their temperature dependence were suggested. For most chemicals, there is a fairly good predictive capability, although there is a need to improve predictive correlations for some classes of polar chemicals and media, such as vegetation. Quantifying the partitioning of speciating chemicals, such as phenolic substances remains problematic.

Robust transport equations exist in most cases to describe intermedia transport processes (e.g., air and soil, air and water), but there remains doubt about specific parameter values. This is an area in which models are essential because chemical fluxes cannot be measured directly and must be inferred from measurements of related transport processes such as sedimentation rates. There is a need to document more extensively the range of transport parameters such as mass transfer coefficients or deposition velocities that are encountered in the environment in order that evaluative models use appropriate values or ranges of values.

In general, for most chemicals (especially the nonpolar substances), the key media that control persistence have been identified and the partitioning and transport processes that are essential components of any mass-balance model can be expressed by using fairly robust, reliable expressions. The magnitudes of uncertainties associated with predictions of transport and partitioning are believed to be known with acceptable accuracy. There are concerns, however, about the real possibility that predictive equations and models may be wrongly applied, especially to less frequently modeled substances. Thus, there is no substitute for insights and interpretations provided by the experienced environmental scientist or engineer.

## **Modeling Persistence in a Multi-Media Environment**

A set of working recipes is proposed for calculating the persistence and transport potentials of chemicals in the environment. "Persistence in the environment" is operationally defined as the result of model-calculated overall residence time at steady state in a multi-media environment. A simple Level III multi-media, mass-balance model is proposed for this calculation. Only irreversible losses are considered, which consist primarily of chemical transformation of parent compound, but also include transport to deep ocean layers, burial in deep sediments, and unidirectional transport to deep groundwater.

Persistence in the environment and potential for long-range transport are related in the sense that time is required for transport, i.e., the residence time in the mobile media (air or water) must be sufficiently long for a chemical to be transported over long distances. A strong correlation between persistence and transport distance among chemicals with different chemical properties has been demonstrated, but this correlation is not strong enough to predict one from the other. A separate definition of transport potential is proposed using the same multi-media modeling approach for defining persistence. While a global-scale, closed model is proposed for calculating persistence, a regional, open model is proposed for calculating transport potential. Advective transport fluxes of a chemical out of the system are controlled by wind speed and ocean currents, and they depend on the linear scale of the system. Loss by transformation, however, is proportional to the area scale of the system.

The task of assessing the persistence and transport potential of both new and existing chemicals would be a major undertaking, requiring the collection of chemical properties for use in multi-media model simulations for each chemical or the worldwide collection of data in multiple environmental media at each sample site. As an alternative, a classification system is proposed that considers sets of chemical properties that would result in the classification of a chemical as "persistent" and as "having the potential for long-range transport." One method for conducting such an analysis involves the use of a set of binary classification trees, e.g., the Classification and Regression Tree (CART) approach. This approach can be applied with multi-media models to assess the link between an output classification such as "persistence" and the range of input values that give rise to this classification.

Recommendations are as follows: 1) useful measures of persistence and transport potential can be derived from half-lives in specific media and intermedia partition coefficients by using Level III multi-media models; 2) 2-dimensional plots of persistence versus transport potential are useful for determining agreed-on concern and no-concern chemicals; 3) given appropriate protection criteria, e.g., geographic extent, overall global residence time, etc., the parameter domains that give rise to undesired persistence and transport potential

can be derived by using CART analysis; and 4) although there is no scientific rationale for selection of persistence and transport criteria, science can help in the process of developing criteria that are coherent.

## **Role of Ambient Monitoring**

Monitoring was recognized as an essential tool in the evaluation of persistence and long-range transport. Monitoring is defined as the long-term and standardized measurement, observation, evaluation, and reporting of physical, chemical, or biological parameters in order to define status, trends, and mass-flows. These studies have been essential in the discovery, description, and understanding of the environmental behavior of persistent organic pollutants. Systematic air monitoring studies have shown that a range of chemicals are subject to long-range transport, while monitoring of biological samples has demonstrated a range of compounds that are persistent and prone to bioaccumulation. In addition to identifying chemicals of concern, multi-media monitoring programs also have demonstrated the effectiveness of various emission reductions, phase-outs, and elimination measures in reducing the environmental levels of pollutants. Although time-trend data are being assembled for different ecosystems in different regions of the globe, only a few detailed case studies exist.

In the future, multi-media monitoring will be essential for assessing equilibrium conditions, mass balances, fluxes, persistence, and long-range transport. Collaborations between environmental scientists and modelers will be essential for defining values for the range of input parameters required by multi-media models. Such collaborations should be iterative and should foster both linked and parallel efforts between monitoring and modeling. In addition, more attention should be devoted to defining emission sources and environmental loadings. Ultimately, the goal of environmental monitoring should be the elucidation of the biogeochemical cycles of persistent organic compounds through mass balance calculations.

A global network should be established, consisting of a limited number of key sampling stations that would sample a variety of media in remote areas in different continents and climatic zones, both in the Northern and the Southern hemispheres. A continuous annual sampling program is essential for defining temporal trends in the concentrations of chemicals in the environment. Global specimen banks are also needed to verify previous analytical results, to intercalibrate new analytical techniques, to develop correction factors that allow the use of historical data, and to keep a record for future investigations of new substances. Pathways of degradation and metabolites should be studied also, and low-cost analytical and real-time monitoring techniques should be developed.

## **Case Studies on Persistence and Long-Range Transport of POPs**

Traditionally, persistence has been viewed as a property of chemicals with slow environmental degradation rates which allowed the distribution of a chemical in the environment. In contrast, a more specific measure of persistence is given by the response of environmental chemical concentrations to source reduction. A series of case studies were considered that illustrate and emphasize the role played by the receiving environment in determining the persistence of a chemical. The case studies are drawn from arctic, temperate, and tropical locations and include: hexachlorocyclohexane (HCH), polychlorinated biphenyls (PCBs), and toxaphene in the Arctic Ocean; PCBs and toxaphene in Lake Superior; atrazine in Lake Michigan; polycyclic aromatic hydrocarbons (PAHs) and PCBs in the Western Mediterranean Sea; PCBs in the Baltic Sea; HCH and PCBs in Lake Malawi (Africa) and the Vellar Estuary (India); and PCBs in soil (Great Britain). A common finding is that biogeochemical processes in the receiving environment are as crucial to the manifestation of persistence as are the chemical properties themselves. The lessons learned from each of these studies lead to insights of how environmental reservoirs become loaded and what controls their eventual clearance when sources are reduced or removed.

Regional or global-scale atmospheric transport is an important pathway for contaminants in most of these systems. For semi-volatile compounds like PCBs and the lighter PAHs, the atmosphere plays a crucial role during the loading and clearing phases of aquatic reservoirs. Appreciable partitioning into the air from water, plants, or soil is important for the most rapid transport in the atmosphere. PCBs are presently in the clearing phase for many temperate reservoirs but, as part of that process, other more distant regions like the Arctic Ocean continue to be loaded. As a consequence, these distant regions ultimately set global boundaries on persistence. Although partition coefficients suggest that particle fluxes (especially of organic carbon) should provide an important route of clearance for PCBs in aquatic environments, rapid mineralization of particulate organic carbon can circumvent that process and lead to recycling in lakes or to transport to deep oceans rather than permanent burial in sediments.

The budget for PAHs in the Mediterranean Sea illustrates that the pathway of the chemical into an aquatic reservoir can dominate its later behavior; for example, light PAHs mimic PCBs, and the air-water exchange is important, whereas heavier PAHs arrive as soot and behave like particles in both the air and the water. For HCH and toxaphene, strong partitioning from air into water is a master control, and the relatively low Henry's Law constant for cold water explains the global phenomenon of high concentrations in the Arctic Ocean when compared to other regions, as well as the regional phenomenon of high toxaphene concentration in Lake Superior. For toxaphene in Lake Superior,

proximity to large soil reservoirs that continue to supply the atmosphere will further delay clearance, a factor that may also be relevant for parts of the Arctic Ocean. The poor partitioning of HCH and toxaphene onto particles in aquatic reservoirs, combined with limited degradation, delays clearance.

Atrazine provides a surprising illustration of how relatively biodegradable chemicals can accumulate in environments in which their degradation rate is low. High use, coupled with a long lifetime under certain conditions, has resulted in substantial buildup in local reservoirs, such as Lake Michigan, that are affected by local runoff and regional atmospheric transport and deposition. Due to the long half-life in oligotrophic waters, atrazine concentrations may ultimately increase in the oceans.

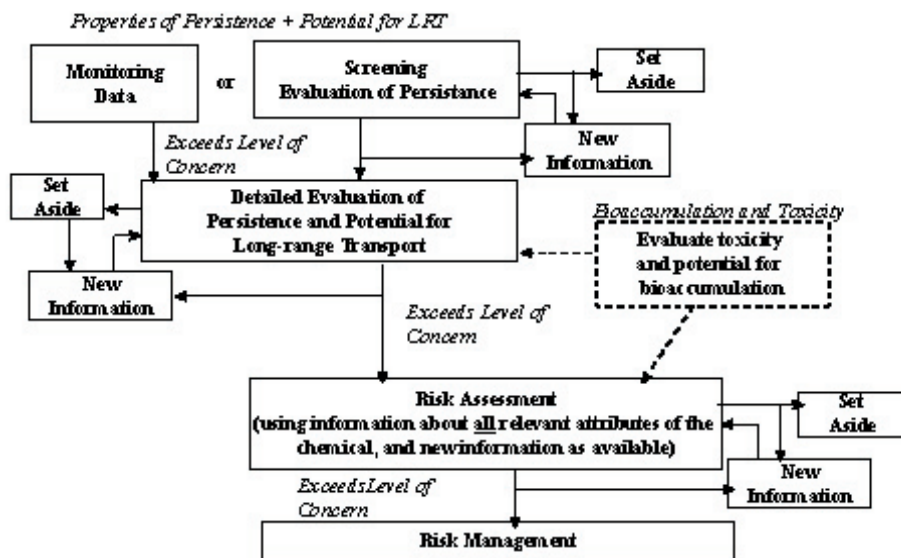
In the tropics, volatilization and degradation assume much greater importance in determining the behavior of POPs than in temperate and arctic regions. Lakes in the tropical regions of the Southern Hemisphere probably provide a sink for some chemicals (e.g., HCH) because of degradation and low prevailing concentrations in water when compared to the atmosphere. Other compounds may be rapidly recycled (e.g., PCB). The behavior of persistent chemicals in tropical reservoirs is poorly studied, and further work is clearly required.

Soils and plants provide important reservoirs that resupply the atmosphere via volatilization and delay clearance after sources have been removed. Upon revolatilization, POPs may enter aquatic or terrestrial food chains.

## Framework and Criteria for Evaluation

The development of a framework for evaluation of the environmental behavior of chemicals with respect to their persistence and long-range transport potential was addressed. It is envisioned that the evaluation process will be part of the broader framework for identifying persistent, bioaccumulative, and toxic substances. Furthermore, although the primary focus was on current regional and global regulatory initiatives, the framework for substance evaluation may prove useful also at the national level as part of a procedure for early identification of potentially problematic substances and in industry for evaluating alternative substances before marketing. The principles underlying this framework are that the process 1) is based on sound scientific principles; 2) allows for expert judgment and flexibility; and 3) incorporates the logic and spirit of the Precautionary Principle. Within this context, application of the Precautionary Principle means that if the evidence (i.e., available data and the quality and relevance of such data) for making the decision is not conclusive or is contradictory, the substance would proceed to the next tier of evaluation.

The recommended framework (Figure 1) for substance evaluation is based on a tiered approach, proceeding from screening to more detailed evaluations. In



**Figure 1** Framework for substance evaluation

the screening phase (Tier 1), the focus is on persistence alone, recognizing the fact that a substance must be sufficiently persistent in the environment to be transported long distances. The primary objective of the screening evaluation is to eliminate substances that are clearly nonpersistent. Half-lives for persistence in the various environmental compartments (air, water, soil, sediment) are compared to previously established criteria, and substances whose half-lives in the environmental media are lower than the criteria values will be judged to be nonpersistent and/or unlikely to undergo long-range transport. The accuracy of and confidence in the results of the screening evaluation can be greatly improved by including information on the likely distribution of the substance among the environmental compartments. This distribution will indicate which half-lives are most relevant for the screening evaluation of a particular substance and which are not. Further, because half-lives can vary greatly with environmental (and laboratory test) conditions, it is important to understand 1) the reference conditions assumed for the criteria; 2) the conditions under which measured half-lives for evaluated substances were determined; 3) the quality of the measurements; and 4) the distribution (range) of measured half-lives. Because of the inherent uncertainties in the measured and/or estimated half-lives, it is important to recognize that the criteria should be applied as guidelines and not as immutable quantities or “bright lines.”

Substances that are identified in Tier 1 for further evaluation are examined in more detail in Tier 2 in order to 1) confirm, refute, and/or clarify the results of the Tier 1 evaluation; 2) determine whether the substance that meets the persistence criteria has the potential for long-range transport; and 3) identify

additional factors that warrant consideration, such as the influence of climatic and other regional characteristics. By using multi-media environmental models, substances whose overall persistence and transport potentials are determined to be less than the criteria values will be judged to be nonpersistent and/or unlikely to undergo long-range transport. These models can represent local, regional, or global scales, depending on the scope of the evaluation. Monitoring data also play an important role in determining whether a substance is persistent and subject to long-range transport. When such data indicate that a substance resides in remote regions at environmentally significant concentrations, these substances should proceed directly into the detailed evaluation.

Because it is recognized that substances must exhibit a combination of properties to be of concern, additional tiers of evaluation are required to designate a substance as a POP or PBT. It is important to note that toxic potency and bioaccumulation potential are considered in Tiers 2 and 3 and were beyond the scope of this workshop. The final tiers of risk assessment and risk management allow for consideration of all relevant attributes of a chemical, including exposure concentrations, availability in the environment, and any new information that may become available. These latter elements of the framework were also beyond the scope of this workshop.

Because persistence and transport criteria must be selected before any substances can be evaluated, 4 approaches for criteria selection that may be used individually or in combination were proposed. Because the scientific understanding of the environmental behavior of chemicals is continually advancing, the criteria and processes used for evaluation should be based on up-to-date, sound science. One approach to establishing criteria is to simply rely on precedent, i.e., use criteria previously set for other similar initiatives. However, there are ways in which science can improve the process. The empirical approach uses available data for one or more chemical properties for a wide range of substances, specifically including substances already widely acknowledged as PBTs or POPs, to derive criteria for these properties. The modeling approach takes advantage of the fact that most substances of potential concern are likely to partition into more than one environmental compartment (i.e., they are “multi-media” substances). Properties such as overall persistence, calculated by using multi-media fate models, can be graphed versus chemical properties, to assist in establishing internally consistent criteria, or to identify constraints in the criteria values. Finally, a theoretical approach can be envisioned in which multi-media models and computerized data classification algorithms are used to help derive relevant criteria values. This approach takes advantage of tools such as Monte Carlo and CART analysis. However, further work is needed to understand the practical application of this approach.

Additional considerations in applying the framework were also discussed. Transparency and openness must be characteristics of both the substance evalu-

ation and criteria selection processes. Transparency is the ability of educated laypersons and policy makers to understand the process, whereas openness is the opportunity for all interested parties to comment and provide input on an ongoing basis. Other considerations relate to the availability and quality of data. The effectiveness of any process for substance evaluation will be affected by the availability, relevance, accuracy, and confidence in the required input data. Guiding principles for data evaluation are that properties should pertain to environmentally relevant conditions and that measured parameter values are always preferred over estimated values if the data are of sufficient quality and are representative of the conditions of interest. In addition, any data that are estimated must be clearly identified as such, and all parties should be permitted to bring any and all relevant data into the process. Finally, because of the inherent uncertainties in environmental properties, expert judgment is essential for both the substance evaluation process and the development of criteria, especially when deciding which data will be used, how the data are interpreted, and which approaches will be used to analyze the data. Because of the limitations in resources, expert involvement may need to be limited; therefore, it is important at each step of the process to identify where expert judgment can be used most effectively and efficiently.

## **Summary and Conclusions**

The Workshop was successful in bringing together an international group of experts, each of whom brought individual insights into aspects of the formidable task of evaluating persistence and long-range transport of organic chemicals. The current state of the science in this subject area was discussed in detail, consensus was reached, and will be captured in print in the Workshop Proceedings. It is clear from this review that as a result of research over recent decades we now know a great deal about how chemicals behave in the environment. In some specific areas, such as atmospheric oxidation and inter-media partitioning, reliable predictive capabilities exist for many, but not all substances. In other areas, such as intermedia transport and the transformation kinetics in soils, waters, and sediments, a fairly clear picture exists of the key process mechanisms and some predictive capability exists. However, there is often considerable uncertainty about the extrapolation of values for key parameters, including transformation rate constants, half-lives, and transport coefficients, that have been determined for specific chemicals under specific environmental conditions. Continuing efforts on measurement and interpretation are needed to enhance our ability to forecast chemical fate, especially for less studied chemicals. Since the actual persistence and long-range transport of a chemical depends on these transport and transformation processes, it is self-evident that society must exploit the available and emerging science when reaching deci-

sions about chemical management. To ignore the science would be unthinkable and would inevitably lead to distorted decision-making.

A major challenge exists to marshal the scientific information in a format suitable for informing the regulatory process. It is likely that most progress will be made by building, testing, and modifying a variety of mass-balance models and decision-support systems which can predict persistence and long-range transport characteristics. But the models must be supported or validated by monitoring data and by demonstrated successful application to specific case studies. A 3-pronged approach of general monitoring, documentation of case studies, and successful modeling of these studies can create a climate of confidence, suggesting that we understand the mechanisms dictating the persistence and long-range transport attributes of substances of present concern. This confidence may lead to the assumption that we can, with some measure of reliability, predict and prioritize these attributes for new and emerging chemicals.

The key features of the overall evaluation framework for identifying persistent, bioaccumulative, and toxic chemicals have been identified. The most effective framework is likely to be a tiered process in which a logical sequence of decisions is made based on sound scientific principles, guided by expert judgement. Early assessment of persistence and long-range transport is desirable, preferably prior to consideration of bioaccumulation and toxicity. Regardless of the system adopted, it must be transparent so that the public can understand how decisions are being made, and it must be open so that all interested parties can provide input.

An important message from the Workshop, but one which is perhaps not directly articulated in the report, is that there is a widespread, earnest desire among the environmental science community to contribute to improved decision making at local, national, and international levels in the expectation that this will lead to more effective management of those substances which are persistent and may be transported long distances in the environment. This desire is shared by the industrial, governmental, and academic sectors that comprise SETAC. Where gaps in knowledge and in evaluation techniques exist, there is enthusiasm to advance environmental science in these areas. What is needed is to bring together the needs and those who can satisfy those needs in a continuing collaborative effort. The Workshop has initiated this process, and the participants and sponsors hope it will continue.

It will be a challenging task to evaluate the large number of chemical substances in commerce for persistence and long-range transport. The Workshop has identified not only how existing environmental science can contribute to this process, but also it has demonstrated the compelling need to exploit this science, and it has identified where the key advances must be made to enhance this contribution.

It is the hope of the participants and sponsors that the Proceedings will provide timely input into national and international deliberations and will be valuable in shaping policies and in directing future scientific efforts.

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