

# EVALUATION OF PERSISTENCE AND LONG- RANGE TRANSPORT OF ORGANIC CHEMICALS IN THE ENVIRONMENT

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# Monitoring as an Indicator of Persistence and Long-Range Transport

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**E**nvironmental monitoring is a means of assessing environmental quality. In general, environmental monitoring programs are necessary to develop comprehensive descriptions of environmental quality at spatial and temporal scales and to provide a sound basis for effective measures, strategies, and policies to address environmental problems. The most important objectives of routine environmental monitoring programs are to measure actual concentrations and identification of trends, to evaluate emissions and flows, to test compliance with standards and quality objectives, and to provide early warning and detection of pollution.

Monitoring is the origin of issues pertaining to persistence and long-range transport of chemicals (Goldberg 1979). In the mid- to late 1960s, measurements of dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs) in Arctic seals and Antarctic penguins provided the evidence for long-range transportability of these chemicals from the site of their application or usage. While monitoring spatial trends would provide information on the transportability of a chemical, temporal trend studies indicate environmental persistence. Earlier chapters in this book discuss the role of models in predicting persistence and long-range transport. While models are predictive in evaluating these parameters, monitoring studies provide the real evidence of persistence and potential for long-range transport. In this chapter, the role of monitoring data in evaluating persistence and long-range transport is discussed. Various approaches to monitoring and appropriate interpretation of monitoring data are suggested. Illustrations of the use of monitoring data to discern clearance rates and environmental behavior are presented. Persistent organic pollutants (POPs) such as PCBs and organochlorine pesticides such as DDT,

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hexachlorocyclohexane (HCHs), or chlordanes have been used as examples, where necessary, to describe how monitoring data has been useful in identifying compounds that are persistent and transportable to remote areas from the point of application.

One of the key requirements in monitoring programs is reliable and reproducible data. It is necessary that uniform analytical methodology of the utmost reproducibility and accuracy be used by monitoring laboratories to ensure that analytical results can be correlated and compared on a spatial and temporal scale. Several earlier publications have addressed issues pertaining to data quality, and, more recently, the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) has provided guidance on "data quality" issues such as sampling and storage, analytical quality assurance, and quality control (QA/QC) (ECETOC 1999). A brief discussion of QA/QC follows later in this chapter.

Chemicals, once they are released into the environment, seek out the environmental media (air, water, soil, or biota) in which they are most soluble. For instance, trichloroethylene and benzene are most soluble in air (volatile); thus, they readily partition to air. DDT and PCBs are most soluble in organic matter (e.g., lipid) and therefore tend to bioconcentrate in biota. The dynamics of environmental partitioning of chemicals has been described by multimedia environmental transport models, which help us to understand environmental behavior of chemicals. Despite having relatively low vapor pressures (vapor pressure  $10^{-2}$  to  $10^{-5}$  Pa at 20 °C), PCBs and DDT can reach remote areas through atmospheric transport, which is considered a primary mode of global distribution for organic chemicals. Transport of these compounds to the poles is thought to involve cyclic processes of wet and dry deposition and sublimation and evaporation combined with net atmospheric flux of heat from equatorial regions (Ottar 1981). Monitoring studies have provided evidence that this pole-ward transport can be rapid, based on episodic atmospheric events (Pacyna and Oehme 1988). There is also a close correspondence in time between worldwide production and deposition in areas remote from application (Rapaport and Eisenreich 1988) and parent forms of some compounds. Long-range transport is indirectly involved in inputs into the Arctic Ocean via ocean currents and riverine outflows. Because of their long residence time in the environment, semi-volatile, persistent chemicals tend to partition between various environmental media such as air, water, soil, sediment, and biota depending on the physicochemical properties and climatic features of a geographic region, reaching unexpected destinations in unexpectedly high concentrations. Because of these properties, monitoring a single medium will not provide adequate information about their persistence and transportability. Thus, the need for, and approaches to, multimedia monitoring are discussed in this chapter.

Multimedia monitoring not only helps us to understand partitioning behavior of persistent and semi-volatile pollutants, but also it is essential for the validation of environmental models, since monitoring data is an integral parameter of modeling.

In this chapter, the importance of the complementary relationship between monitoring and environmental modeling, which improves the predictive ability of models of chemical persistence and transportability, is highlighted.

As mentioned earlier, spatial monitoring is one of the means to explain transportability of a chemical. In this chapter, spatial monitoring studies with atrazine, a relatively less-persistent but frequently used herbicide in the U.S., provides an example to describe various factors that influence transportability. Because persistence and inter-media partitioning can vary depending on several environmental parameters (e.g., temperature), trend monitoring studies in the Baltic Sea and tropical Asian countries, which represent temperate and tropical climates, respectively, are discussed to elucidate the importance of emission sources and climatic factors in determining persistence. In addition, the need for proper samples and sampling plans to describe temporal trends using archived samples, ice, and sediment cores is discussed. For certain chemicals, parent compounds may degrade rapidly, while their degradation products metabolites, or derivatives can persist in the environment for a longer period of time. Because models are less likely to predict the persistence and transportability of breakdown products, the importance of monitoring studies to identify persistent degradation of breakdown products is discussed. Despite the progress and widespread application of monitoring studies, there exist several data gaps, which arise from improper and sometimes inadequate use of data. For instance, despite 30 y of monitoring of PCBs and DDT, data generated from different parts of the globe cannot be compared because of the lack of comparability in monitoring programs conducted by different research institutes and because of the lack of data from certain locations. In this chapter, recommendations are made to build global monitoring networks for more effective management of monitoring programs for persistent pollutants in the environment.

## Monitoring and Persistence

### Definitions

In general terms, monitoring is used to assess the quality of the environment and to provide information for the development of policies and measures to address environmental problems at a local, regional, or global scale. Most often, environmental monitoring is defined as a long-term and standardized measurement, observation, evaluation, and reporting of the environment in order to define status, trends, and mass flows (loads). A few closely related terms often used in conjunction with monitoring are "surveys" and "surveillance." A survey is a sampling program of finite duration, and for a specific purpose, such as an intensive field study or an exploratory campaign to infer semi-empirical relationships and establish tentative theories. Surveillance is a more continuous, specific measurement or observation, with the goal of environmental quality reporting (e.g., compliance with standards

and quality objectives) and/or operational activity reporting (e.g., early warning and detection of pollution).

Environmental monitoring is used to define status and trends of environmental pollutants. This means that environmental monitoring studies provide information on the occurrence and movement of pollutants in the environment. However, mere occurrence cannot be considered as a sign of persistence. Persistence is not synonymous with ubiquity (Webster et al. 1998). A chemical may be found routinely over a large area without being persistent. This occurs for a chemical that is continually emitted from a number of sources but is steadily degraded. Several definitions have been suggested for persistence. Environment Canada defines persistence as the length of time a substance resides in the environment. Similarly, persistence has been defined as the tendency of a chemical to persist (survive) in the environment without transformation into another chemical form. In some cases, persistence is defined in medium-specific terms, i.e., the tendency of a chemical to survive without transformation in a specific environmental medium (e.g., soil) and without transfer to another medium (e.g., air). Other definitions have been suggested in previous chapters of this book. A common measure of a substance's persistence is its half-life, i.e., time required for the concentration of a substance to diminish to half of its original value in a particular medium of interest. Many of these definitions narrated above are not specific. For example, Environment Canada's definition does not clearly distinguish between the time a chemical spends in the environment and the time it spends in an individual medium in the environment. Nor does it specify that the reduction in concentration is attributable to irreversible degradation reactions and not merely to a reversible change in speciation or to a loss by transport to another medium. A comparison of high-end thresholds for persistence as suggested by certain regulatory agencies is shown in Table 6-1.

### **Monitoring data: Representativeness and quality**

As mentioned above, monitoring is a key to studying environmental persistence and behavior of a chemical in the environment. However, most monitoring studies lack adequate data quality control and coherency with other monitoring programs. The keys to a cost-effective monitoring program are well-defined objectives, adequate planning, and clear sampling strategy. The objectives must always be defined first so that suitable sampling and analytical methods may be selected. These, in turn, determine the size and duration of the monitoring study and therefore the resources needed. Unfortunately, in many cases the goals of monitoring programs are unclear and the operating conditions are characterized by uncertainty. This generally leads to a lot of data with limited information and content. It is therefore important to take into account some practical considerations when designing a monitoring program. Some of these design considerations relate to the quality and representativeness of the data. Other considerations are more practical and concern the specifics of study design and implementation.

Table 6-1 Comparison of high-end threshold for persistence

Agency	Half-life (d)
United Nations Economic Commission for Europe (1997)	> 2 (air); > 60 (water); >180 (soil and sediment)
Canadian Toxic Substances Management Policy (1995)	> 2 (air); > 182 (water); > 182 (soil); > 365 (sediment)
Canadian Environmental Protection Act	$\geq 2$ (air); $\geq 182$ (water); $\geq 182$ (soil); $\geq 365$ (sediment)
North American Agreement for Environmental Cooperation – Commission for Environmental Cooperation	2 (air); 180 (water); 180 (soil); 365 (sediment)

The design criteria of a monitoring program should be selected so that the results will clearly represent a well-defined environmental concentration. There are two distinct types of representativeness. One relates to the confidence in the result, i.e., the number of samples and how far apart and how frequently they are taken. The sampling frequency and pattern must be sufficient to adequately represent the "true" concentration at the site selected. The other issue relates to how representative the site is at which the sampling is done of the setting and scenario intended within the framework of the objectives of the program.

The environment is both heterogeneous and dynamic; thus, the concentration of any particular chemical will vary in space and time as a result of variations in its rates of emission, transport, and degradation. Some examples of environmental properties that affect the variability in space and time in different compartments are

- wind speed and direction, turbulence, and precipitation (air);
- current flow rate, turbulence, stratification, depth, and dilution volume (water);
- percolation rate (porosity, rainfall, surface features), organic matter, and moisture (soil); and
- species, feeding habit, age, size, fat content, metabolism, sex, diseases, and season (biota).

Similar environmental factors affect degradation rate in addition to the interaction with other chemicals.

The most useful dataset from a monitoring program is one that captures all of these sources of spatial and temporal variability. The data may then, with proper statistical analysis, be used to estimate probability distributions in space and time. Such probability distributions may be used to choose locations for subsequent sampling

programs and, in risk assessment, to estimate the likelihood of reaching a particular concentration at specific locations and times. Knowing the intended use of the data, together with the necessary statistical treatment of the data, is important for planning a representative monitoring program.

Data quality is the key consideration regarding the degree of confidence (validity) in the result of a monitoring study. These quality issues relate to the technical aspects of both sampling and analysis. The quality of the data generated from any monitoring program is defined by 2 key factors: the integrity of the sample and the limitations of the analytical methodology. The 3 major quality features of any analytical methodology are selectivity, sensitivity, and reproducibility. The selectivity of the analysis ought to be such that all of the target analyte, and only the target analyte, is measured and that other related chemicals or contaminants do not interfere with the response. Consequently, no false-positive values will be reported. Confirmation of target analytes with more than one of the several analytical techniques involving mass spectrometry—including nuclear magnetic resonance, infrared, and ultraviolet mass spectral analysis—will improve the reliability of results generated from monitoring studies. The second important feature for a good analytical methodology is that the method ought to be sufficiently sensitive to measure the chemical concentrations expected. The method must have sufficient reproducibility so as to limit the number of replicate samples and to provide information on the actual concentrations among the samples. Numerous published analytical procedures and guidelines are available for environmental analysis of particular chemicals, and these should be utilized whenever feasible.

Data generated by monitoring programs are increasingly being used to evaluate the environmental behavior and impact of chemicals. It is essential, therefore, that the data be used correctly for the purposes originally intended. Many of the problems associated with bias and systematic errors during sampling and analysis may be assessed by a variety of internal quality control measures. The study plan should include the QA/QC procedures to be used. The QA/QC procedures are designed to establish intra-laboratory controls and checks of sample collection and preparation, instrument operation, and data analysis. The QA/QC procedures should be subjected to “Good Analytical Practices” in analogy to “Good Laboratory Practices,” and laboratories should undergo to a series of inter-calibration exercises and chemical analysis cross-validations in order to avoid false positives.

There are a number of practical considerations to be dealt with when designing a monitoring program that are generic regardless of the compartment being monitored (Figure 6-1). Some of these design considerations relate to the quality and representativeness of the data. In order to be successful, a monitoring study must be well-planned. The goals and objectives of the study need to be well-defined, as these will determine the site selection, extent of sampling, and types of samples.

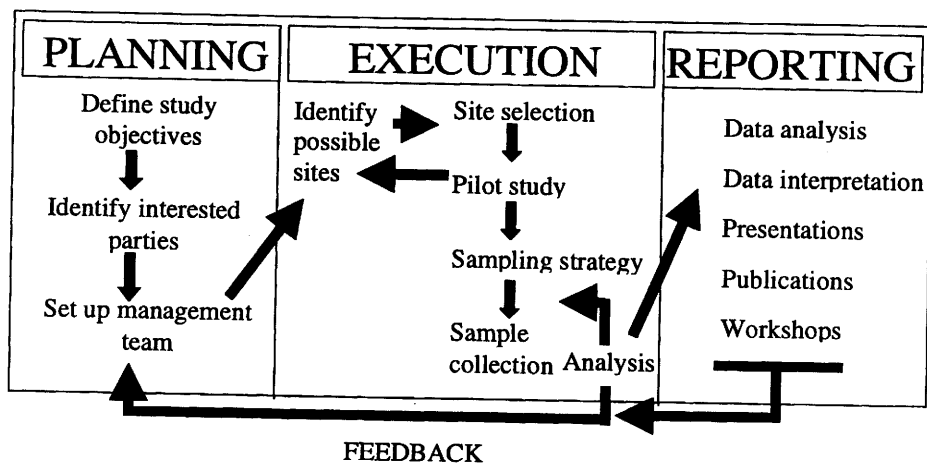


Figure 6-1 Stages in planning and execution of a monitoring program

### Use of monitoring data

While the ultimate use of monitoring data is for certain aspects of environmental risk assessment and/or model validation, information gained from monitoring data on persistence and transportability are important in priority-setting of chemicals. It has often been forgotten or overlooked that the ultimate goal of monitoring is to provide information, not data. In the past, many monitoring programs have been characterized by the “data rich, information poor” syndrome.

Based on a number of international inter-calibration studies, it is known that the analytical results of organic contaminants at trace levels (parts per quadrillion to parts per billion) can vary widely among laboratories. The best database tends to originate from a few key research groups worldwide that have developed the sophisticated and validated methodologies needed. These groups are largely based in the industrialized countries in North America, Europe, and Japan, which provides a bias in the spatial coverage for monitoring trace organic pollutants. However, it is important to obtain and compile information on the spatial and temporal distribution of chemicals both regionally and globally because this information provides evidence of their potential for long-range transport and persistence.

It is important to appreciate that semi-volatile contaminants such as PCBs in environmental matrices (notably, air and water) are subject to short-term variability, which can undermine attempts to look at longer-term time trends. Air concentrations of PCBs, for example, respond to ambient temperature, air mass direction and history, and recent depositional events. Consequently, they may vary over time scales of hours, days, and seasons, in addition to underlying year-to-year variations. Concentrations in biota may vary between species, with age and sex, and with “condition” and stage of the life cycle (i.e., starvation/feeding, through lactation, during after illness/disease) of the organism. All of these factors combine together



to provide "noise" or variability to databases, which need to be accounted for or factored out before underlying spatial and temporal trends can be observed and interpreted with confidence.

Many of the day-to-day-use chemicals may be detected in remote areas when extremely sensitive analytical methods (with detection limits less than femtogram or attogram) are used. For example, detection of individual polychlorinated dibenzo-*p*-dioxin or dibenzofuran (PCDD/F) congeners in the atmosphere at sub-fg m<sup>-3</sup> concentrations was achieved with the advent of high resolution gas chromatography coupled with mass spectrometry (HRGC-MS) techniques in the 1980s. Monitoring detects the presence of chemicals, but presence needs to be considered within the context of analytical sensitivity and emission flux, not necessarily within that of hazard or risk, because hazard is an integration of both exposure and adverse effects. In addition, presence does not distinguish between sources (natural or anthropogenic) and local or distant emission.

Several techniques have been used to monitor trends of contaminants in the environment. Archived tissues, snow, ice, and sediment and peat cores have been used routinely to understand temporal trends, while mosses, lichens, or other plant materials (leaves, bark or needles) have been used in spatial trend studies (Jones 1991; Jones et al. 1992; Tremolada et al. 1993; Simcik et al. 1996; Gevao et al. 1997; Ockenden et al. 1998). Monitoring studies using sediment core stratification have the advantage of providing information on the chronologies of accumulation rates of anthropogenic pollutants. This information is important in order to evaluate the rate of emission from probable sources, to relate specific rates of pollutant accumulation and rates of ecosystem response, and to project future patterns and rates of pollutant deposition.

### **Global inventories and emissions**

Information on historical and future trends in use and emissions of chemicals on a global scale is essential for interpreting monitoring data and, eventually, for evaluating chemicals' persistence and transportability. For instance, if the emission rate of a volatile compound is low, it may not be found in remote areas. This is because atmospheric removal rates can exceed emission rates when the latter are small. However, quantitative emission estimates are very uncertain for several pollutants. Even for DDT and HCH, estimates of global production varied by an order of magnitude (Voldner and Li 1995). There are also often data gaps and uncertainties over emissions. For example, several countries do not have toxic substances release inventories. Some contaminants such as PCDD/Fs originate from natural as well as anthropogenic sources (Alcock et al. 1998). Estimation of release inventories is also confounded by the lack of reliable quantification from multiple emission sources (e.g., combustion sources for PCDD/Fs and PAHs).

It is worth noting that despite 30 y of long-term monitoring data, which exist for some POPs like PCBs, reliable interpretation of chemical trends can be complex. Ambient concentrations and declines presumably reflect underlying changes in primary and secondary emissions and dilution processes, such as long-range atmospheric transport from source to sinks. Moreover, removal processes, such as burial in soils/peats/sediments, and degradation processes, such as atmospheric reactions with hydroxyl radicals and biodegradation, sometimes play an important role. Because of the lack of information on usage/emission, the significance of dilution, removal, and degradation processes is unclear or semi-quantitative. Laboratory studies have reported rates of degradation by hydroxyl radical reaction or biodegradation for certain trace organic pollutants (Sinkkonen and Paasivirta 2000a, 2000b).

Global or regional emissions or inventories of chemicals are needed not only to prioritize them in monitoring programs but also for use in modeling (Harrad et al. 1994; Wild and Jones 1995; Duarte-Davidson et al. 1997). While monitoring environmental concentrations in various environmental media of an ecosystem would assist in estimating chemical inventories, this would be a daunting if not impossible task given the number of chemicals in commerce. The following section therefore discusses how monitoring studies are useful in estimating mass balances of PCBs, PAHs, HCH, atrazine, and toxaphene in different ecosystems.

## Monitoring Spatial Trends

### Issues and complexities

While persistence can be expressed in terms of half-life, for which there exist some guideline values (Table 6-1), an accepted methodology for estimating long-range transport is not available. There is a need to delineate “short-range transport” arising from local contaminant sources including riverine inputs and “long-range transport” arising from distant sources primarily through atmospheric inputs. While global monitoring studies of DDT and HCHs tend to support the view that these compounds are transported to the Arctic from tropical regions (e.g., Iwata et al. 1993), there is no direct evidence to confirm this hypothesis. It can be argued that the origin of these compounds may be primarily temperate North America or Europe, where these compounds were used in large quantities in the past, or local cycles of deposition and re-emission in the Arctic (Oehme 1991). Volatilization from contaminated soils or dump sites in North America or Europe can still contribute to major sources of DDT or HCHs in the Arctic (Bright et al. 1995a). Soil, especially agricultural soil, is likely the largest reservoir of organochlorine pesticides and a major source of emissions. For example, toxaphene was heavily used in the southern U.S. on cotton and soybeans before being de-registered in 1982. Toxaphene concentrations measured in South Carolina air during the mid-1990s were 10 times higher

than levels in the Great Lakes region and showed no relationship to air transport direction, suggesting volatilization from regional soils (Bidleman et al. 1998). Moreover, DDT residues in the air over a California farm, where DDT had been applied 23 years ago, were 2 to 3 orders of magnitude higher than those in the Great Lakes region (Bidleman and Falconer 1999). Well-designed spatial monitoring studies can be used to distinguish short-range and long-range transport. For instance, aerial transport from distant sources is expected to exhibit only minimal geographic variation, since atmospheric inputs occur over a large geographic scale. Based on a spatial monitoring study, it was noted that the Canadian Arctic is influenced both by local and distant contaminant sources (Bright et al. 1995b). Short-range transport of relatively polar pesticides, including currently used organophosphorus and carbamates, has been reported recently (Majewski et al. 1998).

Recently, a simple generic procedure has been developed to determine the potential for long-range transboundary atmospheric transport of substances by means of the residence time of the substance in the air (van Pul et al. 1998). The atmospheric residence time is defined as the time period in which the mass of the pollutant in the atmospheric boundary layer is reduced by 50% (atmospheric half-life). An atmospheric residence time of, for instance, 24 h means that at an average wind speed of 5 m/s, half of the substance is transported at least to a distance of more than 400 km. The atmospheric residence time is determined by the total removal rate, resulting from all removal processes from the atmospheric boundary layer such as wet and dry deposition and photochemical degradation. Atmospheric residence time is recommended as an index to consider the spatial extent of long-range transport of substances. While atmospheric residence time provides a base to determine the potential for long-range transport, there are several assumptions and uncertainties involved in its estimations (van Pul et al. 1998). Atmospheric monitoring can be used to measure the half-life of a substance in air under field conditions, which can then be used to estimate the potential for transport. However, further studies are needed on this issue.

Monitoring programs have been established in several countries, which collectively give information on the spatial distribution of persistent organochlorine compounds such as DDT, HCHs, and PCBs in the global atmosphere. Much of this relates to temperate, industrialized regions of the globe and has a bias towards PCBs, PAHs, PCDD/Fs, DDT, and HCHs. These studies demonstrate that urban areas are key sources of PCBs, PAHs, and PCDD/Fs to the atmosphere, reflecting in some cases (e.g., PCBs) emission from past or present usage and in others emission from anthropogenic combustion sources (e.g., PAHs, PCDD/Fs). Agricultural areas of past or present use are the key global source areas for a suite of organochlorine pesticides. Volatilization of toxaphene and DDT from treated soils in the southern U.S. had been unequivocally demonstrated to supply the atmosphere with these compounds and to cause atmospheric transport to regions far removed from the

areas of use (Blais et al. 1998); obviously however, it is not the only source of these compounds to remote areas. Maps and datasets have been assembled of the past/continuing use of  $\gamma$ -HCH (Lindane) and DDT (Wania and Makay 1996), that clearly demonstrate the dominance of tropics as the key global source regions of these pesticides. A major atmospheric monitoring program in the Canadian and Russian Arctic is now providing important information on the supply and concentrations of PCBs, PAHs, DDT, and HCHs to these remote regions.

Global monitoring studies have been conducted by various authors using leaves, bark, pine needles, lichens, mosses, air, or water collected from various locations within a certain period of time (Gaggi and Bacci 1985; Calamari et al. 1991; Iwata et al. 1993; Morosini et al. 1993; Simonich and Hites 1997). Calamari et al. (1991) assembled "global distribution maps" for hexachlorobenzene (HCB), HCH, and DDT by analyzing plant samples collected from a range of locations all over the world. They hypothesized that these organochlorine compounds are supplied to the plants primarily by atmospheric concentrations and deposition and that the plant concentration would directly reflect the atmospheric concentration. Their studies clearly demonstrated that the global atmospheric distribution of HCB, HCH, and DDT differed substantially. HCB, for example, was found at the highest concentrations in plants collected in the polar regions, far from the source regions. In contrast, DDT was highest in tropical plants. This spatial monitoring study illustrates some important features of transport and persistence. A compound's behavior in the environment is clearly controlled by its physicochemical properties. HCB is sufficiently volatile and persistent to move efficiently through the atmosphere. It has a relatively low octanol-air partition coefficient ( $K_{OA}$ ) and therefore readily partitions from soils or water bodies to air. In contrast, DDT is still found largely in the tropical source regions. It partitions more strongly to soils and atmospheric particles than does HCB. It consequently enters the atmospheric gas phase less readily and has a shorter atmospheric residence time (van Pul et al. 1998). Its movement to remote regions can still occur but occurs less efficiently and less quickly.

Analysis of pine needles has demonstrated another important principle of the global atmospheric distribution of POPs, namely, that source regions and elevated concentrations will be influenced by economic features of different countries. In brief, industrialized countries tend to use and emit a different mixture of POPs than those of nearby less-developed countries; different countries could have different fingerprints of emission that are influenced by the gross national product (Calamari et al. 1995; Simonich and Hites 1997).

As noted above, much of the data on the spatial distribution of POPs has been compiled from the work of different groups, with different analytical methods, conducted in different places at different times. These differences can undermine the detailed interpretation of the datasets or models (Wania and Mackay 1996) and our confidence that the apparent spatial differences are real. Ockenden et al. (1998) therefore set out to make long-term and simultaneous measurements of the atmo-

spheric distribution of PCBs on a latitudinal transect of remote/rural European locations from  $\sim 47^{\circ}\text{N}$  to  $79^{\circ}\text{N}$ . Mean annual atmospheric temperatures varied between  $-0.1$  and  $9.6^{\circ}\text{C}$  at their sampling sites. A passive air-sampling technique with semipermeable membrane devices (SPMDs) was used, which was calibrated against the conventional high-volume air-sampling technique. It was found that PCBs demonstrated global fractionation in the atmosphere, but the effect was subtle and would have been difficult to detect unequivocally by a more disparate sampling or data-compilation strategy. The relatively light tetra-chlorinated PCB homolog was evenly distributed on the latitudinal transect. In contrast, the penta-, hexa-, and hepta-homologues were factors of 3, 5, and 7 lower, respectively, in the colder north than the warmer south. Despite the range of chemical properties between the tetra- to hepta-homologues (e.g.,  $K_{\text{OA}}$  8.0 to 11.6) and the range of environmental conditions, these concentration differences are subtle and are believed to indicate that PCBs are approaching dynamic air-surface equilibrium partitioning conditions (Ockenden et al. 1998).

Iwata et al. (1993) collected air and surface seawater in various seas and oceans during 1989 and 1990 and analyzed for the presence of PCBs, DDT, and HCHs. Among these, HCHs had the highest concentration in air and water, as result of its greater solubility in water than that of DDT or PCBs. The spatial distribution of HCHs revealed the presence of higher concentrations in the northern hemisphere, particularly in cold temperate regions and in tropical countries. While greater concentrations in tropical regions could be explained by recent usage, higher concentrations in cold water bodies was explained by the "cold condensation hypothesis." However, unequivocal evidence of transport of HCH or DDT from tropical countries to the Arctic could not be found. Further, this study estimated mass transfers of HCHs, DDT, and PCBs between air and water. It was found that ocean waters near the tropics and the Arctic could serve as sinks for HCHs and DDT because of the transfer of these compounds from air to water. The magnitude of difference in the flux estimates between tropical and temperate climates is an indication of the environmental behavior of semi-volatile organic compounds.

The results of decreasing south to north gradients of DDT and HCHs obtained from the various spatial monitoring studies mentioned above have been interpreted as an indication of long-range transport from southern sources to the Arctic. However, this does not offer direct evidence of transport from tropical countries to the Arctic. In summary, the studies on spatial trends of selected semi-volatile organic pollutants demonstrate the complexity of their behavior and the difficulties in interpreting spatial monitoring data. The global environment/atmosphere and the other environmental compartments partly reflect past and present usage and local emissions and partly reflect physicochemical properties of the compounds and the ambient climatic conditions. Future distributions will be influenced by these

factors, too, but also by their environmental persistence, recycling potential, and susceptibility to the efficiency of global transport. There is a need for harmony in spatial monitoring studies that can be attained by establishing global networks by selecting key stations in the globe representing different climatic regions.

### **Spatial trend monitoring of atrazine and alachlor: Lessons learned**

In order to make an assessment of environmental persistence and transport based on spatial trend monitoring, studies with atrazine and alachlor are used as a model for discussion. Atrazine is one of the most used herbicides in the U.S. at approximately 30 million kg per year. It is applied to corn and other row crops in a preemergent setting in early May across most of a 10-state region, i.e., "The Corn Belt." Similarly, alachlor is a herbicide used in corn cultivation. The fate and transport of the applied atrazine and alachlor have been important environmental issues because of their long history of use, the large quantities that are applied, and suggestions of possible environmental damage.

For these reasons, a detailed monitoring study was carried out to examine the fate and transport of atrazine and alachlor to the atmosphere (Thurman et al. 1991, 1992, 1994; Goolsby et al. 1997; Lerch et al. 1997), which represents a major effort to examine the transport to the atmosphere of a polar herbicide at a regional scale. Furthermore, long-range transport of atrazine from the Corn Belt to Lake Superior was examined in these studies. Atrazine and alachlor are polar and soluble. They do not bioaccumulate because they are relatively degradable, and they have not been found in significant quantities far from their source. They currently are not considered to be of concern as a persistent chemical. However, the detailed study outlined below is instructive for several reasons. First, it shows the detailed nature of sampling that may be carried out to properly examine atmospheric transport. No such detailed studies are available for other classes of compounds. Second, an immunoassay (enzyme-linked immunosorbent assay [ELISA]) was used to analyze 5000 samples for atrazine in order to carry out a large survey over a 25-state area with a reasonable cost. Third, this case study shows that there can be long-range transport even for a compound that is relatively less-persistent when it is applied in large amounts. It also shows that a compound with a low Henry's Law constant may still have considerable transport to the atmosphere (~ 1% of the applied atrazine), resulting in a regional scale distribution. The atmospheric residence time of atrazine (1 d) is shorter than compounds such as ethyl parathion (5 d) or Lindane (242 d) (van Pul et al. 1998). Considering the shorter atmospheric residence time, atrazine may not be considered to have the potential for long-range transport. However, the results of the following spatial trend monitoring studies suggest that atrazine can be transported to as far as 500 km from the point of application.

### ***Spatial and temporal distribution of atrazine and alachlor deposition***

Figure 6-2 shows the regional use pattern of atrazine and alachlor in the Midwestern U.S., and the deposition pattern of atrazine and alachlor in 1990 and 1991 is shown in Figure 6-3. The results show that the deposition of atrazine is clearly similar to its use pattern. Regarding the temporal distribution, the large fluctuation in concentration occurred throughout the 18-month sampling period (Figure 6-4). The majority of the deposition occurred during the application period and approximately 2 months after application (May through the end of July). This time period represents approximately 1 to 2 half-lives of atrazine in soil. Atrazine has a 45 to 60 d half-life in soils of the Midwestern U.S. This phenomenon is due to the rapid washout from rainfall, which is usually intense during these months. The result is that atrazine is no longer available in the shallow soil for volatilization and transport.

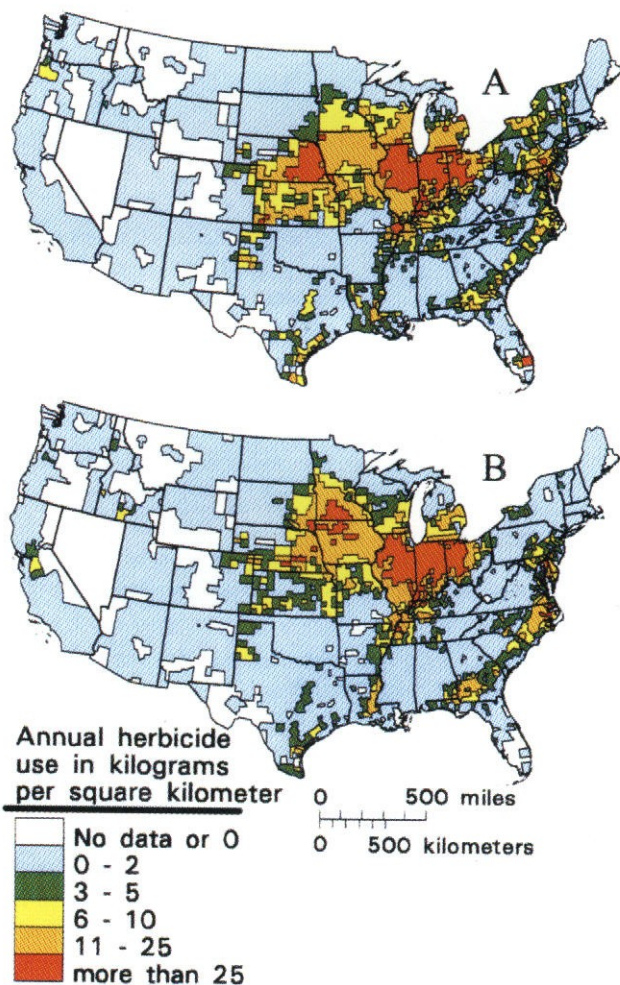
### ***Long-range transport of atrazine***

The long-range transport of atrazine occurred during a short window of time, from mid-May until the end of July. During this time, atrazine was found to be transported at least 500 km to the north of the Corn Belt with deposition into the lakes of Isle Royale National Park, which is located in Lake Superior. The highest concentrations were found in early June with washout concentrations of approximately 0.1 to 1  $\mu\text{g/L}$  (Thurman et al. 1991). Washout occurs with low-volume rainfalls in the National Park, i.e., 1 cm or less. This result, however, was considered remarkable given the fact that the distance to the nearest large cornfields was 300 to 500 km to the south. Low-altitude atmospheric transport, perhaps in thunderstorms, which are common during May through July, could have been responsible for this rapid transport. The result of this long-range transport is that concentrations of atrazine may reach 10 to 15 ng/L (ppt) in remote lakes of Isle Royale National Park (Thurman et al. 1991). Although these concentrations may not be toxic to local flora or fauna, this study clearly demonstrated the potential for long-range transport.

### ***Degradation of atrazine***

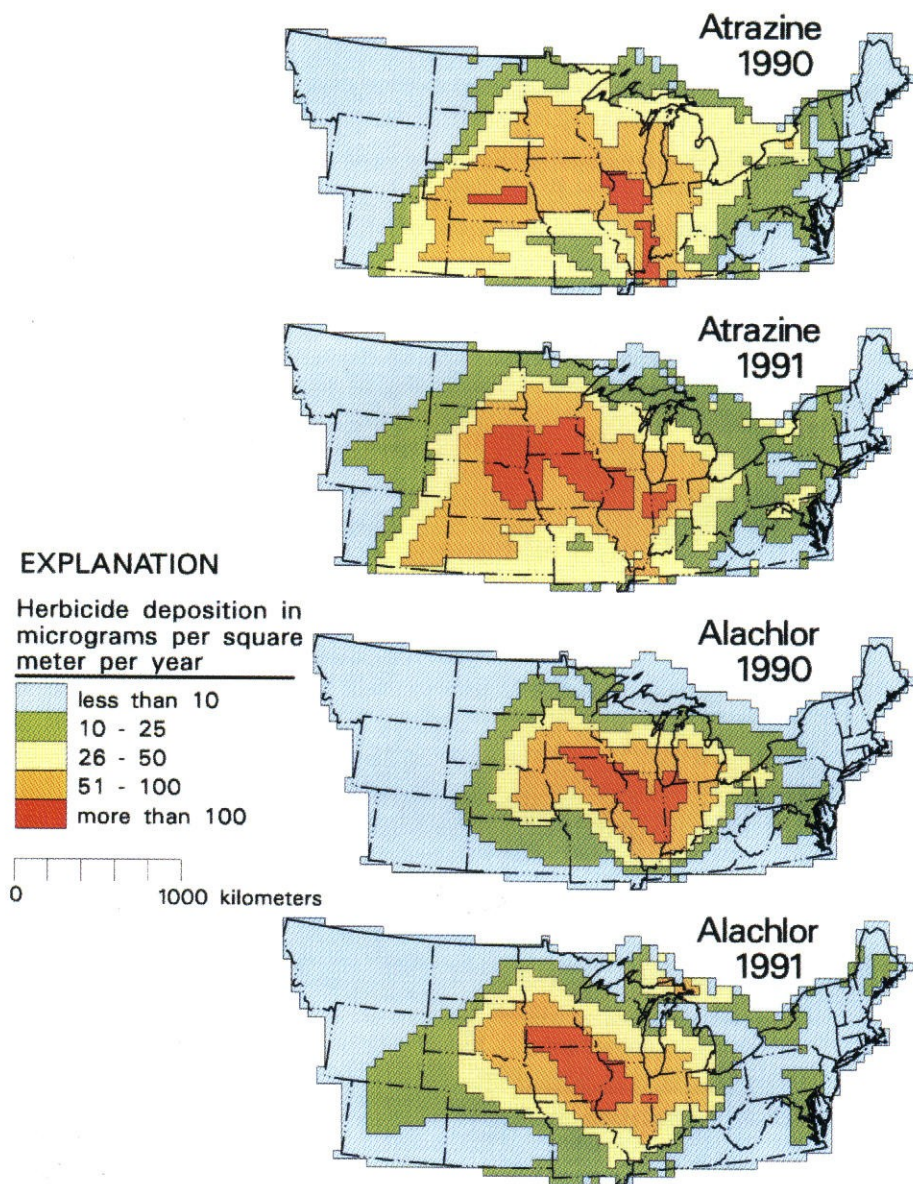
The degradation of atrazine does occur during atmospheric transport, as indicated by the occurrence of metabolites in rainfall samples. It has been shown in laboratory studies that atrazine degrades by both ozone and UV light through the alkyl side chain. An atrazine amide is formed, followed by the dealkylation of the triazine to deethylatrazine (DEA). The compound may be further degraded with ring cleavage. The amount of DEA in rainfall was measured by GC/MS in samples across the 26-state study area, as well as in the long-range transport study in Isle Royale National Park. It was found that DEA occurred in 60% of the samples that contained atrazine, typically at a concentration of about 50% of the parent compound (Lerch et al. 1997, 1999). This ratio of 0.5 for metabolite to parent was remarkably consistent throughout the study areas and is representative of the atmospheric degradation that is occurring in the troposphere. The conclusion reached from this work is that approximately 40% of the atrazine detected had not degraded and probably repre-

sented short-range transport or windblown atrazine from nearby fields into the collector. The other 40% of the atrazine was undergoing longer-range transport and was being degraded significantly in the atmosphere. The estimated half-life for atrazine in the atmosphere may be as short as a few days (van Pul et al. 1998), whereas half-lives in water varied from several days (Thurman et al. 1994; Solomon et al. 1996). However, it is still possible to move atrazine 300 to 500 km, despite its short half-life and low Henry's Law constant ( $2.5 \times 10^{-4}$  Pa-m<sup>3</sup>/mol).

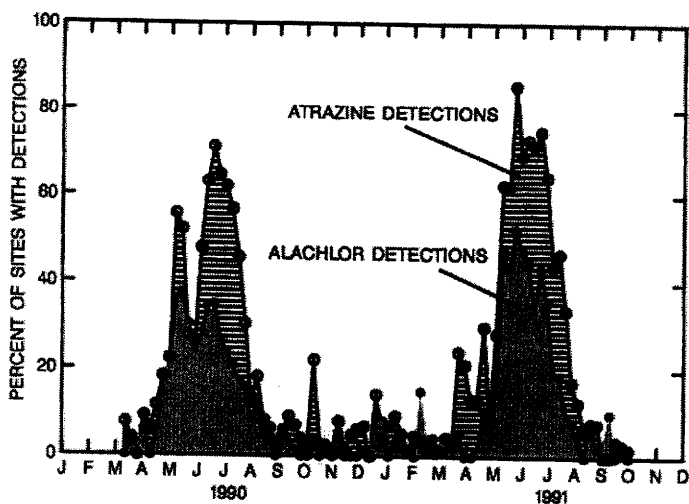


**Figure 6-2** Regional use pattern of (a) atrazine and (b) alachlor in the Midwestern U.S. Reprinted with permission from Goolsby et al. (1997) ©1997 American Chemical Society





**Figure 6-3** Atrazine and alachlor deposition in the Midwestern U.S. in 1990 and 1991  
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**Figure 6-4** Seasonal fluctuations in atrazine and alachlor in precipitation  
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## Monitoring of Temporal Trends

Temporal trend monitoring studies are valuable because they allow one to evaluate persistence of a substance by the simple concept that an increasing or constant environmental level over a period of time is an indication of persistence. Temporal trend monitoring programs are in existence in several countries, and they monitor heavy metals and organochlorine contaminants such as PCBs, DDT, and HCHs in various environmental media. The international mussel watch program and the National Status and Trends Program of the National Oceanic and Atmospheric Administration are examples of a few (O'Connor 1996). Most temporal trend monitoring studies have primarily used archived biological tissues as matrices to monitor the trends of persistent pollutants. However, in biological samples a number of factors may influence the concentration of contaminants. Before discussing how temporal trend studies are used to evaluate environmental persistence and emissions of a substance, the importance of biological variation in evaluating temporal trend data is discussed.

### Short-term variability, random variations, and pooled samples

It is essential that field time-trend monitoring data are available to help elucidate the factors that control the persistence of a substance in the environment and the response of the environment to a change in inputs of chemicals and to test models. These objectives all require that quality datasets be accrued over long time periods and that long-term trends can be distinguished from short-term variations.

Concentrations in various matrices will vary over time. Air concentrations may vary hourly, diurnally, seasonally, or yearly and can be controlled by temperature, local

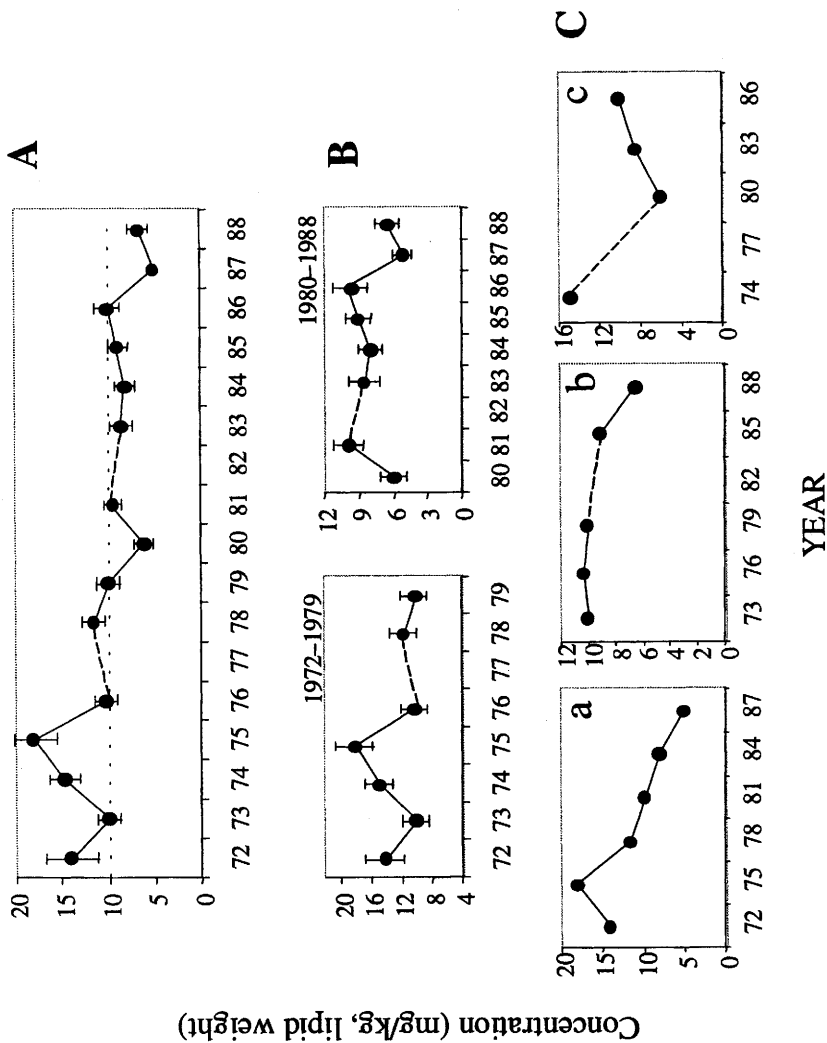
sources, wind direction, precipitation events, ice/snow cover, etc. Concentrations in a biological matrix, such as seal blubber, can vary with age, season, diet, condition, sex, reproductive history, season, habitat, territory, etc. For example, PCB concentrations in the blubber of individual Baltic grey seals varied between 5 and 5000 mg g<sup>-1</sup> (Bignert et al. 1994). Only when a clear understanding and quantitative assessment of these factors has been achieved can underlying long-term changes in concentration be interpreted.

Random variations between data points can be reduced by careful sampling and analysis. Often for economic reasons samples that have been collected individually are bulked, homogenized, and analyzed. While economically necessary, this approach can lose a lot of valuable information and resolution in monitoring studies (Bignert et al. 1992, 1994).

As highlighted above, information is needed to assess the extent of random and sample variation from underlying trends. Regardless of matrices used (air, water, sediment, soil, biota), comparison of residue levels of persistent contaminant from one year with residue concentrations from another year cannot disclose temporal variations, unless there is reasonable knowledge of the random between-year variation (Bignert et al. 1992, 1994, 1997). Figure 6-5a shows a long-term time trend of PCBs in herring collected from 1972 to 1988. The annual data points are based on individual analyses of 20 specimens/y and are the geometric means of specimens. The fish species selected were sedentary and were of the same age group. When the data was analyzed for the period from 1972 to 1988, a decline in PCB concentrations could be discerned. Using the same dataset, when the study period was separated into 2 groups of 7- to 8-y periods each, no significant change in concentration over time could be seen (Figure 6-5b). In Figure 6-5c, the same time period is covered, but a design based on sampling and analysis every third year is shown. It is apparent that very different conclusions would be drawn depending on the approach used. These issues have recently been discussed for other studies covering other compounds and time periods in relation to the problem of scattered data (Bignert et al. 1995; Olsson 1995).

### **Use of temporal trend data**

Temporal trend studies are useful for determining whether legislative actions taken to reduce the degree of environmental pollution really have had the intended effect. They also help to develop cause-effect relationships between contaminants and affected populations. Monitoring studies can be used to trace sources of certain contaminants. Ratios of parent compounds to metabolites and proportions of components in technical mixtures have been used to infer sources. Atmospheric measurements taken in the mid-1990s at Integrated Atmospheric Deposition Network stations on the Great Lakes show a DDT/DDE ratio of less than 1, suggest-



**Figure 6-5** (A) Temporal trends of PCB concentrations in herring from the Baltic Sea collected between 1972 and 1988 (B) Trends in PCB concentrations in herring when the data were separated for 1972-1979 and 1980-1988 (C) Trends in PCB concentrations in herring when data were taken at 3-y intervals starting 1972, 1973, and 1974.

ing that a substantial portion of recent DDT comes from recycled old residues (Cortes et al. 1998). However, it should be noted that the physicochemical properties of parent compounds and metabolites change considerably, making such interpretations often confounding. Recently, enantiomer (optical isomers) ratios of certain organochlorine pesticides have been suggested to be of use in tracing sources of emissions (Ulrich and Hites 1998; Bidleman and Falconer 1999).

### **Monitoring studies as indicators of clearance rates**

Long-term trend monitoring studies can provide information about the clearance rate of a substance in the ecosystem following ban on its usage. For instance, long-term monitoring on the shores of the Great Lakes revealed that airborne pesticides such as HCHs, DDT compounds, and chlordanes were declining slowly, with "virtual elimination" dates (when concentrations fall below detectability) ranging from 2010 to 2060 (Cortes et al. 1998). Concentrations of many organochlorine pesticides in air and surface water are now nearly in steady state with respect to gas exchange (Hillery et al. 1998). Evidently, certain processes are acting to stabilize atmospheric concentrations. These processes can vary from region to region depending upon several factors, including the climate. Methods that investigate emissions from soil and water, as well as discriminate between "new" and "old" sources of contamination, can contribute to our understanding of these issues. In the following sections, we describe how temporal trend monitoring studies in the Baltic Sea and Asian countries, representing temperate and tropical regions, respectively, provide some insights into clearance rates of certain organochlorine pesticides.

#### ***The Baltic Sea in temperate Europe***

In the late 1960s, it became clear that the Baltic Sea was a severely polluted marine enclosure. Since then, temporal trend monitoring has begun in some freshwater locations in southern and remote sub-Arctic regions in Sweden, as well as in the marine Baltic itself. At the end of the 1970s, the annual sampling program was enlarged to cover locations at the Swedish west coast and some terrestrial locations. Some of these data have recently been published (Bignert et al. 1997; Bignert, Olsson, Persson et al. 1998).

The Swedish Environmental Monitoring Program uses a range of biota samples, including mammals, fish, and bird eggs. The program is based on annual sampling, specimen banking, and analysis of individual samples selected so that the site-specific matrix will be comparable between years. The sampling locations have been selected to serve as reference sites to study aerially derived contamination, while avoiding local sources. Archiving of the samples, frozen since the time of collection, has allowed cross-checking when analytical methods have changed or when new substances have attracted interest, allowing retrospective analysis. Further information on the matrices used, sampling times and composition, methods of chemical

analysis and statistical treatment are given in Bignert et al. (1997) and Bignert, Olsson, Persson et al. (1998). Based on log-linear regression analysis of annual geometric means, the annual decrease in concentrations expressed as a percentage has been calculated. It is thus possible to compare the decreasing rate in various matrices and at various locations for  $\Sigma$ DDT, PCB, HCHs, and HCB in 15 different time series.

Concentration variations differ between different species and sampling sites, with the highest concentrations in the south and the lowest in the north. The concentrations found in the north are similar to those found in corresponding matrices in subarctic and Arctic regions at the North American continent. However, importantly, decreasing rates are similar, irrespective of matrix or sampling sites. For example, the mean rate of decrease for  $\Sigma$ DDT was about 10%, for  $\alpha$ -HCH about 20%, for PCB around 7%, and for HCB around 8%. The decreasing rate for PCB in the Baltic region is remarkably similar to that found recently by Hillery et al. (1998) for PCBs in air from the Great Lakes. For pesticides, the variations in rates between species and sites were very small, but for the industrial contaminants PCB and HCB, the variations between matrices and locations varied slightly more. However, neither for the pesticides nor for the industrial contaminants were there any consistent variations between southerly or northerly sites. For  $\alpha$ -HCH, for example, rates of decrease were more or less identical in guillemot eggs from the southern Baltic, Arctic char from a remote sub-Arctic lake, and reindeer in the vicinity of the lake. Interestingly, the rates were also similar to those reported in Arctic air for the corresponding time period in the Arctic (Jantunen and Bidleman 1996). In the case of walleye pollack collected from the Bering Sea in 1992, there were 2-, 4-, and 7-fold decreases in the concentrations of PCBs, DDTs, and HCHs, respectively, compared to those of the concentrations reported for walleye pollack collected in 1982 (Kannan et al. 1995).

In another study, the decreasing rates of the pesticides  $\Sigma$ DDT and  $\alpha$ -HCH were compared over 10 y after various measures to phase out or decrease use of the compounds (Bignert et al. 1997; Bignert, Olsson, Asplund et al. 1998). Various matrices (7 time series) both from the southern and the sub-Arctic parts of Sweden were used when the percentage annual decrease in concentrations over 1971–1980 for  $\Sigma$ DDT and 1987–1996 for  $\alpha$ -HCH were compared. Only minor variations and no significant differences were found when various matrices from terrestrial, freshwater, and marine environments from the north and south were compared. The rate of decrease for  $\Sigma$ DDT was 18% to 19% and 18% to 24% for  $\alpha$ -HCH. The differences are remarkably small between the two substances, and there was no indication of a difference between south and north.

In a further study, the time trends were compared in eutrophic and oligotrophic lakes. The rates of decrease were quite similar between the lakes (Bignert, Olsson, Persson et al. 1998) and also between the lakes and the marine environment (Bignert, Greyerz et al. 1998). Despite the differences in sedimentation and degrada-

tion rates, similar rates of decrease in the concentrations of organic pollutants is an interesting observation.

In summary, the trend series in terrestrial, freshwater, and marine biota samples from the Swedish monitoring program indicates remarkable similarities in the decreasing pattern for the various matrices and sampling sites. The calculated annual decreases are similar to air measurements on extensive datasets of air samples from the Great Lakes (PCB) and from the Arctic ( $\alpha$ -HCH), suggestive of regional and possibly global dispersal/mixing and clearance.

### ***Tropics and the southern hemisphere***

The occurrence of high concentrations of POPs such as HCHs, DDTs, chlordanes, and PCBs in the Arctic ecosystem, despite the ban on many of these compounds in most of the industrialized nations of the Northern hemisphere, has prompted the need to identify possible emission sources (Bidleman et al. 1989, 1992; Barrie et al. 1992; Iwata et al. 1993). Investigations conducted by numerous researchers during the last two decades suggest that mid- and low-latitude countries, particularly those in the tropical region, are possible sources of contamination in the Arctic in recent years (Oehme 1991; Tanabe 1991; Barrie et al. 1992). Although this concept is supported by the current high consumption of organochlorine pesticides in tropical developing countries, which enhances food production and eradicates vector-borne diseases (Kannan et al. 1992; Mowbray 1988), there is no direct evidence of transport of POPs from tropical Asian countries to the Arctic. The cumulative production of DDTs and HCHs in India until 1995 was 500,000 t and 1 million t, respectively (Kannan et al. 1995), contributing to a significant proportion of the global usage (Voldner and Li 1995). Concentrations of POPs in environmental matrices in certain Southeast Asian countries, such as Japan, have been slowly declining (Loganathan et al. 1989, 1993). Despite the lack of well-designed time trend monitoring studies in tropical Asian countries, a compilation of information generated by various researchers has indicated that levels have been slowly declining or have been at a steady state depending on the location and matrices. Data from the food-monitoring surveys in India have shown that the concentrations of DDTs have been declining in recent years (Kannan et al. 1997). This is attributed to the ban on the use of DDT in agriculture. However, concentrations in biota did not appear to have declined until recently (Tanabe et al. 1998; Senthilkumar et al. 1999). Concentrations of DDTs, HCHs, PCBs, and chlordanes in dolphins collected from the River Ganges in India showed an increase in concentrations from 1988–1992 to 1994–1996 (Figure 6-6). Iwata et al. (1993) reported that the atmospheric concentrations of HCHs and DDTs in the Arabian Sea were comparable between 1976–1977 and 1989 whereas the concentrations in the eastern Indian Ocean and Southern Ocean have declined since the early 1980s. These results indicate the India has been a major emission source of HCHs and DDTs in southern Asia. Concentrations of PCBs have increased in minke whales from the Antarctic during 1984–1993, while DDT declined slowly (Aono et al. 1997). In contrast, minke whale from the northern

hemisphere showed declining concentrations of DDTs, HCHs, and HCB from 1987 to 1994, while demonstrating an increase in PCB concentrations (Aono et al. 1997). These results indicate that PCBs are still being discharged from northern and southern hemisphere countries.

Although the clearance rates of organochlorine pesticides are influenced by climatic and geographic features (Loganathan and Kannan 1991, 1994), field studies conducted in tropical regions suggest that the environmental residence times of POPs are shorter in the tropics than in temperate regions (Sleicher and Hopcraft 1984, Tanabe et al. 1991).

Comparable data between continents and regions of the southern hemisphere are lacking or very limited (Loganathan and Kannan 1994, Connell et al. 1999). A systematic comparison of data for DDTs and HCHs on the northern and southern hemisphere indicated that the northern hemisphere is generally more contaminated than is the southern hemisphere. In the southern hemisphere, concentrations and patterns of POP contamination appear to depend on usage rates and/or methods of disposal. It was also noted that the process of equilibration between the two hemispheres is relatively slow (Connell et al. 1999). The critical factor for further knowledge on the distribution and control of POPs in the southern hemisphere is to obtain comparable measurements between countries and regions using selected environmental substrates from different land uses (e.g., urban, rural, and remote) (Connell et al. 1999).

### **Monitoring metabolites and degradation products**

Chemicals may be broken down in the environment or biota by various degradation pathways, including hydroxylation, dechlorination, carboxylation, hydrolysis, and in some cases, sulphonation. The parent substance may yield similarly (or more) persistent byproducts (e.g., DDT  $\rightarrow$  dichlorodiphenyldichloroethylene [DDE]) or more-polar, less-persistent byproducts (e.g., phenanthrene  $\rightarrow$  hydroxylated byproducts). It can be informative to monitor the ratio of parent:degradation product to gain clues about transport processes and the age of the chemical. For example, DDT (a parent compound) degrades to DDE or dichlorodiphenylethane (DDD) via the loss of chlorine and/or hydrogen. The rate of this degradation is generally understood; thus, the ratio of parent to metabolites gives information on the chronology of input of DDT. Knowledge on metabolism and environmental degradation of POPs is scarce, and a few attempts have been made to evaluate the molecular stability in terms of internal energy (Tremolada et al. 1992, 1993). As mentioned above, certain pesticides such as HCHs are emitted both as technical mixtures containing  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -isomers and as the purified  $\gamma$ -isomer. In addition, environmental transformation of  $\gamma$ - to  $\alpha$ -isomer is reported to occur (Malaiyandi and Shah 1984), which causes complications in using the monitoring data to interpret the sources of emission.



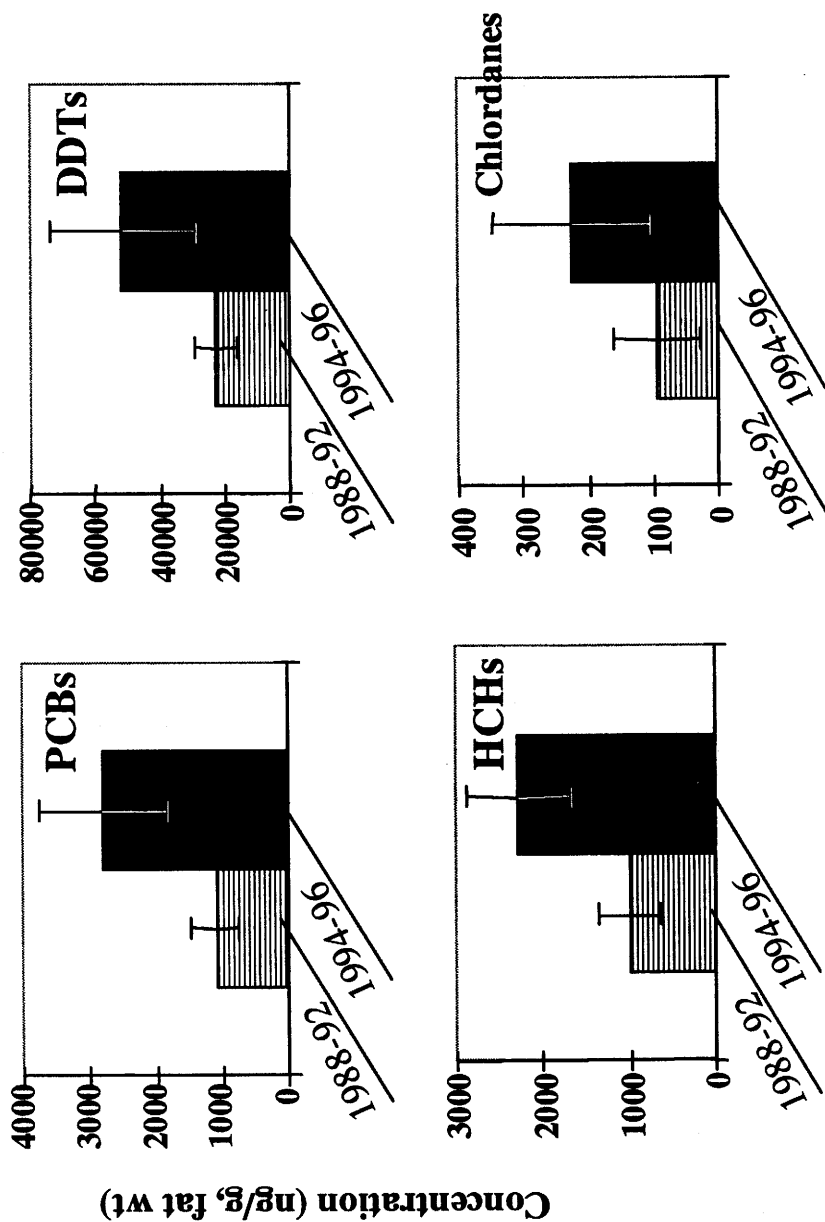


Figure 6-6 Concentrations of PCBs, DDTs, HCHs, and chlordanes (ng/g, fat wt) in the blubber of dolphins collected from the River Ganges, India, between 1988-1992 and 1994-1996 (Senthilkumar et al. 1999)

The major issue is that monitoring studies have routinely focused on tracing parent compounds rather than their metabolites. Some relatively polar, nonpersistent compounds can be degraded to produce relatively persistent metabolites in the environment. Surfactants, particularly nonionic surfactants, are a class of organic compounds that contain both a hydrophobic and a hydrophilic component. For example, nonylphenol ethoxylate (NPE) contains nonylphenol at the hydrophobic end and ethylene oxide on the other end of the molecule. The ethoxylate end degrades rapidly in the environment, leaving a more recalcitrant product, nonylphenol, which is fairly stable in the environment. While physicochemical properties of the parent compound may tend to suggest its lower persistency, the breakdown product can be persistent in the environment. Although it may not be practical to study all metabolites of a compound, some effort should be made to outline important degradation products that contribute to toxicity. Many of the simple box models that are proposed to design criteria for persistence and long-range transport do not consider degradation products. Monitoring can be a valuable means of tracing a persistent metabolite of a nonpersistent parent compound. It is important to understand the chemical degradation pathways of a substance of concern while conducting a monitoring study.

## Interpretation of Field Monitoring Data

Often field and monitoring data are presented as simple concentration data. However, monitoring studies have been used recently to interpret environmental behavior. For example, concentrations in air can be related to parallel samples of water or soil, and calculations of the instantaneous net direction of flux or closeness to equilibrium partitioning can be made. Iwata et al. (1993) and Ballschmiter (1992), for example, estimated air:water equilibrium status for a range of POPs compounds in seawater from a wide range of locations worldwide. Similar calculations have been performed for HCH in Arctic air and seawater (Jantunen and Bidleman 1995), for a range of POPs in the Great Lakes (Hornbuckle et al. 1995), and for PCBs in air and soils on a latitudinal gradient in Europe (Ockenden et al. 1998). Efficient use of monitoring data can be made if multimedia monitoring is performed (e.g., Sweetman and Jones 1999). Advantages of multimedia monitoring over single-medium monitoring are discussed below.

### Single-medium and multimedia approaches

Most of the environmental monitoring studies of POPs have focused on examining concentrations or trends in a single medium at a given time and location. However, depending on the substance's physicochemical properties and geographic features including edaphic factors and meteorological conditions, it tends to partition to one compartment or another. For example, theoretically a substance with high  $K_{OW}$  is not expected to partition into air. At the same time, if its water solubility is low, it

will tend to have a high air–water partition coefficient (which is essentially the ratio of vapor pressure to water solubility). *p,p'*-DDT has a very low vapor pressure of  $6.14 \times 10^{-5}$  Pa. Its low solubility in water ( $6 \mu\text{g/L}$ ) causes its air–water partition coefficient to be substantial ( $1.46 \times 10^{-3}$ ). Hence, *p,p'*-DDT in water will evaporate fairly rapidly (Lee and Mackay 1995). Lindane ( $\gamma$ -HCH) is more volatile (0.021 Pa), but its air–water partition coefficient is one-tenth that of *p,p'*-DDT because of its high solubility in water. Further, the physicochemical properties that control the partitioning behavior of a chemical can vary depending on the prevailing weather conditions. The vapor pressure of  $\gamma$ -HCH at 15 °C is 0.00472 Pa, whereas at 35 °C it is about 18 times higher (0.0846 Pa) (Lee and Mackay 1995). These properties result in a location- and compound-specific distribution and redistribution among environmental compartments. While environmental monitoring studies provide realistic estimates of half-lives of chemicals under field conditions, monitoring a single medium, and therefore the half-life from a single medium, may under- or overestimate the compound's overall potential for persistence. Therefore, in order to better understand persistence and environmental dynamics, it is essential to monitor the contamination levels in different environmental compartments simultaneously. The following examples illustrate the benefits of multimedia monitoring.

A study conducted in a paddy field in South India examined the half-lives of HCH isomers in air, water, soil, and paddy plants after a single topical application of technical HCH (Tanabe et al. 1991). Air, water, soil, and paddy plants were collected at 5-d intervals for over 40 d after application. About 90% of the applied HCH partitioned to air, leaving less than 10% of the residues in soil, water, and paddy plants in 2 weeks after application. The half-life in air was estimated to be 5 d, whereas the residue concentrations in water and soil decreased by about 50% in 5 and 10 d, respectively. Similarly, it was found in other studies that 50% of the HCH applied to soil in Delhi, India, was lost in 30 to 45 d (Samuel et al. 1988), while 94% was lost 60 d after its application (Kaushik 1989). The half-life of the most stable HCH isomer,  $\beta$ -HCH, was 22 d in a flooded soil in India (Panda et al. 1988). Thus, if the half-life measured in a single medium, (e.g., soil) were to be used to develop criteria for persistence, HCH would not fall under the criteria established by Environment Canada, which requires a half-life of  $\geq 182$  d in soil in order to be considered persistent (Environment Canada 1995). On the other hand, if the atmospheric half-lives are considered, i.e., 5 d in the tropical field conditions, HCH would be classified as persistent, as it exceeds the  $\geq 2$ -d criteria of Environment Canada. The half-lives of a chemical in different environmental media vary dramatically depending on the climatic features of a location. The half-life of  $\gamma$ -HCH is only 75 d in warm ocean waters, for example, whereas it is  $> 100$  y in cold ocean waters at 0 °C (Ngabe et al. 1993). These results suggest the need for multimedia measurement of concentrations and half-lives to derive overall environmental half-lives for developing persistence criteria.

## Multimedia monitoring and equilibrium partitioning

Multimedia monitoring studies of DDTs, HCHs, and chlordanes in tropical regions have shown that their atmospheric concentrations were several-fold greater than those reported in temperate regions. In contrast, despite the continuing use of these pesticides in tropical regions, their residue levels in sediment and fish tissues are relatively low and are comparable to those found in temperate regions, where these compounds were banned about 25 years ago (Iwata et al. 1994; Kannan et al. 1995). These studies suggest that the persistent chemicals used in tropical areas are rapidly dissipated during their initial transport through inland air and water, leaving lower residues in sediments and aquatic biota. Relatively short residence times of organochlorine pesticides in sediments in the tropics are illustrated by a plot of the concentration ratio of organochlorine pesticides in sediments (normalized to organic carbon) to water (S/W) at different latitudes (Figure 6-7). The plot of Log (S/W) against the latitude of sampling locations indicated smaller S/W ratios at lower latitudes. This suggested that the partitioning of organochlorine pesticides to sediments is less pronounced in the tropics than in temperature regions (Iwata et al. 1994), implying the role of meteorological conditions such as temperature in

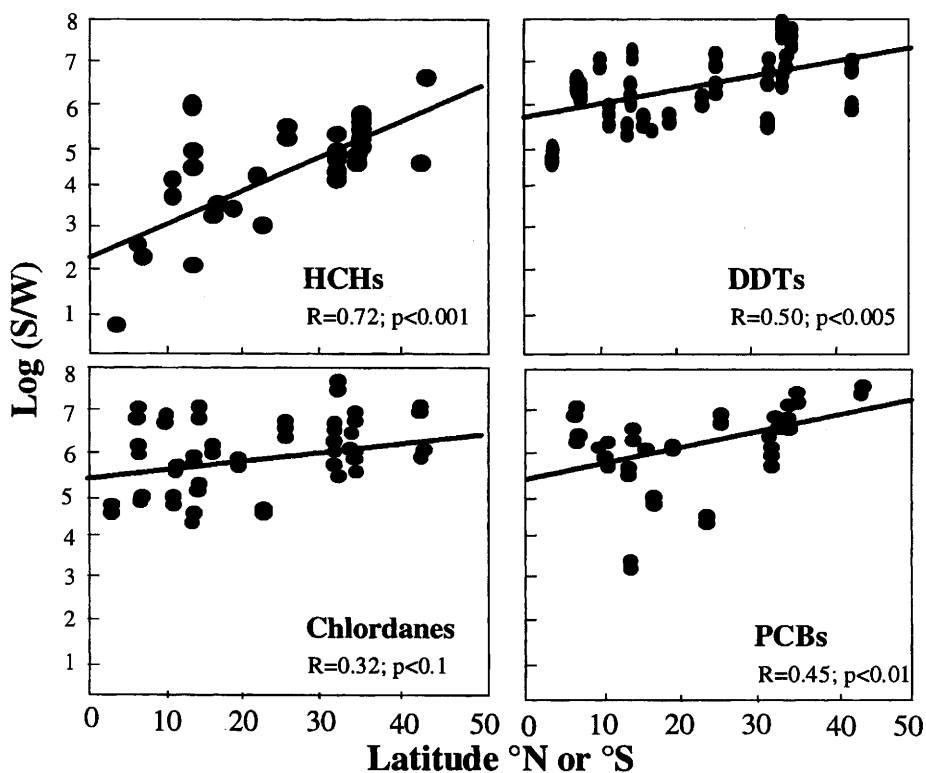


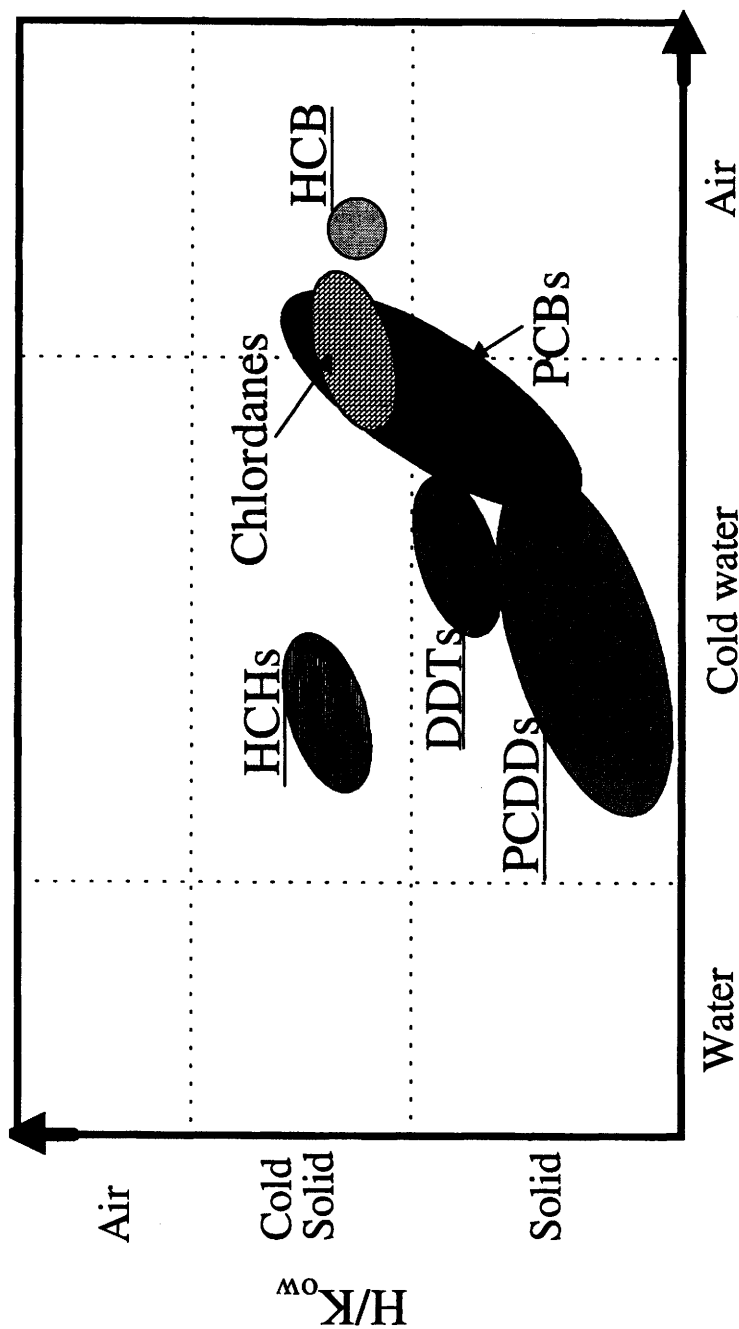
Figure 6-7 Relationship between the concentration ratios of PCBs, DDTs, HCHs, and chlordanes in sediment and water (S/W) and the latitudes of sampling locations (Iwata et al. 1994)

governing the distribution. Therefore, the half-lives of POPs derived from sediment monitoring in the tropics would underestimate their overall environmental persistence.

Multimedia monitoring studies are also useful to evaluate partition coefficients such as  $K_{OW}$ ,  $K_{OC}$ ,  $K_{AW}$ , and  $K_{OA}$ , which are used to examine the factors that influence distribution, dynamics, and fate of organic pollutants in the environment. Monitoring studies designed to elucidate the global distribution of POPs have shown that semi-volatile contaminants like HCB and HCHs have concentrated in Arctic waters, while DDTs and PCBs were higher in low- to mid-latitude regions (Calamari et al. 1991; Iwata et al. 1993). It has been shown that the semi-volatile contaminants released in the tropical low latitude regions would be redistributed to higher latitudes according to contaminant specific transportability (Wania and Mackay 1993; Iwata et al. 1993). Since  $K_{AW}$  or the related Henry's Law constant ( $H$ ) is a measure of equilibrium partitioning of a compound between gas and water phases, this parameter has been used to express the movement of a compound between atmosphere and hydrosphere by comparing the theoretical or equilibrium value of  $K_{AW}$  with the calculated ratio of concentrations, using the field measurements of concentrations in air and water (Ballschmitter 1992; Iwata 1994; Mackay et al. 1996). In addition, the transportability of a compound between gas and solid phases is expressed by the ratio of  $K_{AW}$  to  $K_{OW}$ , i.e.,  $K_{AO}$  which is usually reported as the reciprocal  $K_{OA}$ . Compounds with greater  $K_{AW}/K_{OW}$  values tend to transfer more to the gas phase than to the solid phase.

The importance of  $H$  and  $H/K_{OW}$  as two valuable parameters in describing global redistribution of chemicals has been discussed in relation to data measured in the field (Figure 6-8). Based on this concept, compounds with higher  $H$  or  $K_{AW}$  values and  $K_{AW}/K_{OW}$  ratios that could be expressed as the reciprocal of  $K_{OA}$ , for example, chlorofluorocarbons, do not tend to partition to water or to solids. Such compounds tend to be present only in the atmosphere. Compounds such as HCHs tend to partition toward cold water and cold solids, whereas HCB prefers air and cold solids. Compounds with low  $H$  and  $H/K_{OW}$  are relatively less mobile from the sources because of their greater water solubility and/or strong binding to the solid phase. DDT and PCDDs have been reported to have greater binding affinity to solids. Thus,  $K_{AW}$  (or  $H$ ) and  $K_{OW}$  and their ratios are potentially the most important descriptors for the global distribution and partitioning of a chemical.

Multimedia monitoring is useful for tracing the sources of contamination. As an example, a multimedia monitoring study conducted in the sewer district in Buffalo, New York, involved the analysis of soils, atmospheric wet and dry deposition, sanitary flows, and combined sewer overflows to evaluate the sources of PCBs to the Buffalo River (Loganathan et al. 1997). This study showed that the locally contaminated soils were the major sources of PCBs entering into the Buffalo River as opposed to atmospherically derived inputs.



### Henry's law constant (H)

Figure 6-8 Schematic illustration of redistribution of certain organochlorine compounds based on their partitioning coefficients among air, water, and solids and the influence of temperature (Iwata 1994)

## **Monitoring Data and Environmental Modeling**

Earlier chapters have discussed how models can be used to evaluate the potential for long-range transport and persistence of a chemical. While models are useful in various aspects of understanding the behavior of a substance in the environment, monitoring studies provide real estimates and are necessary to validate the models. Mechanisms affecting the transport and fate of a chemical are extremely complex and are still partially unknown. Ultimately, simulation modeling is essential for understanding their emission, transport, and fate in different environmental media. Simulation modeling generally means the use of quantitative, computer-based, deterministic relationships that describe the inventories of a substance in the environment, its multimedia partitioning, chemical reaction and transport to potentially sensitive areas (e.g., the Arctic), and its possible accumulation and adverse effects on the environment.

All simulation models are, in essence, mass-balance calculations. The simplest models may depict the environmental media by large boxes, e.g., the atmosphere as a single box with in-flux and out-flux calculations of material entering and exiting the box. Initially, box models may provide some preliminary, useful information, even though an implicit property of a box model is the uniform concentration of chemicals in each box — a condition that is easily violated for several POPs.

More-complex simulation models allow details of the property of each medium to be specified, e.g., temperature and other physical parameters and advection parameters such as the wind flow in the atmosphere and the ocean currents. Consequently, advanced simulation models are generally more credible in their reconstruction of transport and fate of environmental chemicals. Today, advanced continental and global meteorological models are available and routinely provide a depiction of local meteorology (model outputs and forecasts are routinely available on the Internet). Similarly, ocean models provide credible simulation of ocean currents and transport flows. These advanced meteorological and ocean models have often been used, for example, in simulating global climate and expected future changes as a result of increases in greenhouse gases.

The relationship between monitoring programs and modeling should be designed while keeping the following factors in mind:

- Monitoring can be and should be, at least initially, a tentative, “exploratory” effort in which individual scientists use scientific intuition to infer semi-empirical relationships and establish tentative theories. Eventually, however, monitoring should be designed with the main goal of providing the correct input data to models and suitable datasets for calibrating and validating these models.
- Models require information on the timing and magnitude of emissions. Some monitoring and experimental efforts should therefore be devoted to the collection of these data.

- Models require correct parameterization of physical (e.g., evaporation, ground deposition, sedimentation) and chemical properties (e.g., reaction rates) in the different environmental media. Therefore, some monitoring should be designed in order to collect and measure appropriate environmental data.
- Models provide, as outputs, the concentrations and fluxes in different media. Therefore, one of the main monitoring and experimental efforts should be a well-organized collection of concentrations throughout the world and, especially, in those areas considered the most sensitive and vulnerable. Data should include both regular, continuous measurements and well-focused intensive campaigns. These data should then be used to calibrate, validate, and improve models.

### **Interactions between monitoring and modeling**

Models that predict the physicochemical behavior of chemicals and the fate of chemicals in the environment are a mathematical representation of the real world. In the simplest models, the environmental heterogeneity and temporal dynamics have been substituted by a fixed generic environment and by an assessment of a steady-state situation at local, regional, or global levels.

To provide a more accurate fate assessment, a fundamental interaction between monitoring and laboratory data is needed to parameterize and validate the models for the chemical and environment of interest. Only then can the models be used to extend laboratory and monitoring data and provide a more comprehensive and validated exposure assessment.

Laboratory and field data are frequently used to provide parameters that are necessary to run fate models and develop quantitative structure-activity relationship (QSAR) models that can predict various physicochemical parameters. QSAR models have been successfully used for nonpolar, relatively hydrophobic compounds such as hydrocarbons. However, these models have a high degree of uncertainty when used to predict the physicochemical behavior of surfactants, ionizable compounds, persistent degradation products, and polymers. Experimentally derived data are the most reliable source of the physicochemical parameters for these chemicals.

Models are typically developed for specific chemicals, classes of chemicals, or environments and embody the current understanding of the chemical and the environmental compartment of interest. To ensure accurate predictions, the model results need to be validated by comparing them to monitoring and laboratory data. Each time the model predictions are validated with monitoring and/or laboratory data, confidence in the prediction increases for the environment and class of chemicals considered. However, this does not mean that the model yields accurate or even reasonably accurate predictions for all environments or all chemical classes,



unless the validation process has included a wide range of environments and classes of chemicals.

Once models have been validated for the class of chemical and specific environment of interest and parameterized using appropriate field and laboratory data, they can be applied with a certain degree of confidence

- to extend these data to larger geographical areas,
- to provide statistical distributions of concentrations,
- to explore the effect of variations in the environmental and chemical properties (sensitivity analysis),
- to evaluate "what-if" scenarios, and
- to assess responsibility.

The specific chemical under investigation and the processes to which it will be subjected in the environment will determine the minimum parameter set or the minimum number of environmental properties for which information must be given in order for the data to be useful for risk assessment or model validation. More information will be required for some chemicals than for others. For example, if a chemical ionizes or perhaps hydrolyzes at a given pH, data on the pH of the environment will need to be specified. For other chemicals, this information may not be necessary. Alternatively, a chemical may undergo processes in the environment, such as adsorption or biodegradation, whose mechanism may depend on the environmental parameters. Thus, for many organic chemicals, the amount of organic carbon present in soil or sediment will influence adsorption. Additionally, ionic organics may adsorb to charged soil constituents, if these are present at the pH present in the soil. If biodegradation of the compound takes place, the existence of aerobic or anaerobic environmental conditions will be necessary to understand the monitoring result and to correctly position it in either an exposure assessment or a specific modeling context.

The history of chemical release or deposition at the monitoring site must be known in order to correctly position the monitoring data or to determine the appropriateness of the dataset for the modeling purpose. Information is needed concerning the total load emitted and the spatial and temporal emission pattern. This information unfortunately is often missing. This is particularly important in the case of POPs, for which the sources and quantity emitted are generally difficult to define. Background concentrations, as well as the release history of the site, would have some relevance if determination of the total environmental load were the object of the modeling. This is obviously the case for the global modeling of POPs.

The analytical accuracy of an existing dataset may not a priori determine whether it is useful for exposure assessment or model validation purposes. The type of model used, and the accuracy to which the model predictions are either possible or desired must also be considered. Because obtaining monitoring data is much more expensive than is running an existing model, it is probably most cost-effective to accept

that all existing environmental monitoring datasets that satisfy the minimum parameter constraints and that meet minimum analytical standards have some degree of use for environmental exposure assessment and model validation purposes. The degree of usefulness of the dataset should be specified in the context of the model itself. However, it must be established that the model is valid for the conditions that pertain to the dataset before the data can be used to validate the model.

In summary, existing data should be used, whenever possible, for environmental exposure assessment and model validation purposes. However, it is essential that the dataset contain sufficient information concerning the chemical and the environment, the release history of the chemical with respect to the monitoring site, and the analytical methods used to determine the concentrations. The definition of sufficiency may vary with the specific chemical and also will vary with the application, i.e., the type of environmental exposure assessment or model validation under consideration.

## **Recommendations and Data Gaps**

### **Specimen banking**

In order to evaluate temporal trends retrospectively, matrices are needed that can provide information about contaminant concentrations in the past. Until now this type of information has mostly been achieved on an ad hoc basis, by analysis of samples collected and saved for other purposes in museum collections or scientific collections. An important question often has been whether the samples have maintained their integrity (i.e., have they been contaminated or lost the analyte of interest during storage). However, some countries have been proactive in establishing Environmental Specimen Banks, with carefully collected, stored, and catalogued specimens preserved for future chemical analysis. Attempts are being made to harmonize the structure of the collections and the format for record-keeping in order to increase international access to the collections. Recommendations have also been made to develop procedures for sampling, preparation, and storage (Olsson and Bignert 1997; deWit et al. 1997). Specimen banks are clearly invaluable tools in enabling scientists to monitor environmental change and investigate new contaminants retrospectively.

### **Global networking**

One of the issues that has emerged from the earlier sections of this chapter is the desirability of comparing trends in different locations. Ideally this would be achieved by cross-checking data from well-studied and well-characterized ecosystems from different parts of the world. Key sampling and environmental monitoring networks should be established in various parts of the globe representing different

climatic and geographic conditions that would enable efficient use of funds available for global environmental monitoring.

### **Oceanic transport**

While it has been acknowledged that oceans are the ultimate reservoirs for several manmade chemicals used in the terrestrial environment, movement and transport of these chemicals through ocean currents is less known. Fischer et al. (1991) studied movement of HCH through the water flow in the Atlantic Ocean and suggested that ocean currents also play a role in the transport of persistent pollutants. Similarly, Wania and Mackay (1999) noted the importance of oceanic transport of  $\alpha$ -HCH to the Arctic Ocean. Although the atmosphere has been considered to be a major route of transport (Preston 1992), further studies are needed on the role of ocean currents and riverine runoff in the transport of contaminants to remote areas.

### **Migratory animals**

The possibility that migratory birds (Tanabe et al. 1998), fish, or marine mammals could transfer considerable quantities of persistent and bioaccumulative contaminants is uncertain. This pathway is important for exposure of humans and wildlife who consume tissues of migrating birds, fish, or mammals. The relative importance of this issue can be assessed by comparing the mass of chemical in the migratory population (concentrations  $\times$  biomass) with inputs via air or ocean currents. Further studies are needed on this topic.

## **Summary and Conclusions**

Monitoring studies and surveys have made essential contributions to the discovery, description, and understanding of the problem with contaminants that have potential for long-range transport and persistence. In the early 1960s, PCBs were first detected in very remote regions of the Arctic and Antarctic. Since then, systematic monitoring studies have shown many substances to be subject to long-range atmospheric transport. Monitoring data obtained in fish and other biota indicated that these compounds are also liable to bioaccumulate into the food chain. This possibility initiated ecological risk assessments for a series of compounds that are now strictly regulated, their use having been severely restricted or banned.

Well-defined, multimedia monitoring programs can demonstrate the effectiveness of the reduction or phaseout measures taken by the regulatory authorities. Monitoring data for DDT or PCBs over recent years collected in different areas of the world generally show reductions in the environmental concentrations. There are underlying reductions in emissions of these organochlorine compounds, which are disappearing at a rate related to their global half-life in the environment.

Monitoring data, if collated in the appropriate way and over a sufficient period of time, can help to define environmental accumulation and removal and clearance times of chemicals. To do so effectively, well-planned multimedia monitoring approaches should be developed, covering significant areas of the world in order to be representative of a regional and/or global pattern. Well-structured monitoring programs should take account of the need for storage/retrospective data and should be designed to test and validate models.

The degree of confidence we can have in using monitoring data for model validation depends not only on the quality and representativeness of monitoring data but also on the quality of the model considered. Simple models can be validated with a limited set of monitoring data, but if the sophistication of the model increases, the amount and the quality of the monitoring data should be adapted accordingly.

Nevertheless, despite the importance of monitoring in assessing persistence and long-range transport, there are severe gaps in the existing monitoring programs. These include the following:

- Only limited retrospective monitoring data are available in all compartments (air, water, soil, sediments, and biota). Furthermore, there are gaps in monitoring of many compounds both in time and space.
- Monitoring has been preoccupied with measuring concentrations rather than with determining data on their global use and release. Thus, there is a lack of geographic information on use and emissions.
- Metabolites have been not emphasized in many monitoring programs. Therefore, we have missed critical information on mass balance, half-life, and fate.
- There is a lack of well-organized monitoring studies in the southern hemisphere. Moreover, gaps exist between modeling and detailed evaluation by monitoring at the global scale. There is a lack of knowledge or a reluctance to accept new monitoring methods and techniques (e.g., ELISA, biosensors, SPMDS).
- Several case studies with multimedia monitoring suggest that Henry's Law constant and octanol-water partition coefficient determine the partitioning behavior of a substance in the environment. These values are important in evaluating environmental movement.
- In addition to the above mentioned parameters, total quantity of global usage and emission are also important in designating a chemical. This information is often the most difficult to obtain, hampering our ability to model.