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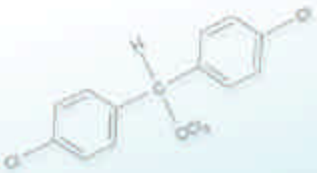
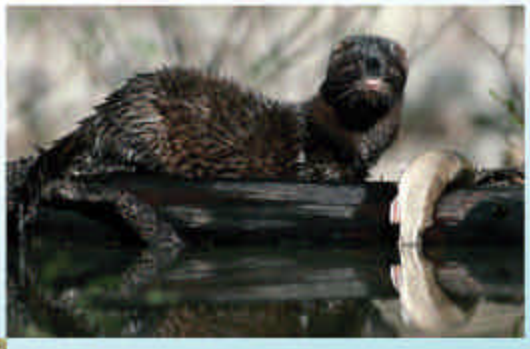
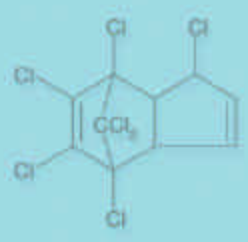
The Foundation for Global Action on Persistent Organic Pollutants: A United States Perspective







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Office of Research and Development
Washington, DC 20460

EPA/600/P-01/003F
NCEA-I-1200
March 2002

www.epa.gov

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Acknowledgment: The authors wish to thank the many internal EPA peer reviewers, the external peer review panel (Drs. Peter deFur, Derek Muir, Bernard Weiss), and the members of the public who submitted comments for their valuable insights, suggestions, and additions.

Executive Summary

Persistent organic pollutants (POPs) are a small group of organic chemicals exhibiting the combined properties of persistence, bioaccumulation, toxicity, and long-range environmental transport. This small group of pollutants encapsulates the genesis and development of pollution awareness in the United States. These are the pollutants that Rachel Carson described in *Silent Spring*, that contaminated Agent Orange during the Vietnam War, and that contributed to Love Canal, Times Beach, and the pollution of the Great Lakes. Legislative, regulatory, legal, and voluntary actions in the United States have eliminated domestic production of many POPs as pesticides and industrial chemicals, and have greatly reduced their emissions as byproducts. Yet, although uses and levels in the lower 48 United States have stabilized or declined, elevated levels are now being found in what had been thought pristine, uncontaminated environments, notably in the Arctic and remote oceans. Air and water movement are transporting POPs across international borders to these remote locations, where they can be elevated to potentially toxic levels through biomagnification in the food chain. Most poignantly, the first exposure of offspring may be through a loading dose of toxicant to the fetus or in milk, during the most sensitive period of development.

Bald eagle, chick, and egg. POPs impacts have been particularly severe on the reproductive success of birds of prey.

Photo: D. Best

On May 23, 2001, the United States joined 90 other nations in signing the Stockholm Convention on Persistent Organic Pollutants. Under the Convention, countries commit to reduce and/or eliminate the production, use, and release of the 12 POPs of greatest concern to the global community and to establish a mechanism by which additional chemicals may be added to the treaty in the future. This report is directed toward educating decisionmakers, academia, and the public on the science underpinning this global action, focusing on the 12 priority substances or substance groups, commonly known as the "dirty dozen."

The 12 Priority POPs of Global Concern

aldrin
dieldrin
endrin
DDT
chlordane
heptachlor
mirex
toxaphene
hexachlorobenzene (HCB)
polychlorinated biphenyls (PCBs)
polychlorinated dibenzo-*p*-dioxins
polychlorinated dibenzofurans

The report provides an overview of the human and ecological risks posed by POPs to U.S. ecosystems and citizenry. Recognizing the immense technical literature on these POPs, the report focuses on the most salient topics, while pointing to additional literature sources for readers requiring further information. The chapters are based on the following general themes:

- *Chemical profiles*: A narrative introduction is provided for each of the 12 POPs. This is accompanied by tables summarizing important chemical properties and the regulatory history covering production and use in the United States. The narrative highlights selected toxicological issues not directly discussed elsewhere in this report. For instance, the agricultural problems caused by prolonged, indiscriminate toxicity from the cyclodiene POPs insecticides are noted (e.g., dieldrin), along with the availability over time of improved chemical, physical, and integrated alternatives for pest management. For DDT, particular attention is drawn to the need to balance malaria vector control in some developing countries with epidemiological evidence of increased preterm human births associated with DDT exposure, and its demonstrated adverse ecological impacts. Notable in this context, the Stockholm Convention provides for continued DDT use for disease vector control in countries registering such a need, where safe and cost-effective alternatives are not available. This use is subject to World Health Organization recommendations and guidelines, which allow indoor application only.

Alaska native hunter and boat; a way of life for many communities.
Photo: U.S. Department of the Interior

- *Human and ecological effects in the United States:* Historical and contemporary data are summarized demonstrating why POPs gained notoriety in the United States and internationally. Two regions are highlighted: the Great Lakes and marine ecosystems. In the Great Lakes, the contribution of POPs, especially DDT, to eggshell thinning and population declines in raptors (e.g., bald eagles, osprey, falcons) is well known. PCBs and polychlorinated dioxins and furans have combined to affect Great Lakes fish populations (blue-sac disease), fish-eating birds (GLEMED syndrome), and mammalian reproductive success, especially in mink. For humans, POPs intakes continue through the consumption of Great Lakes sport fish. Epidemiological evidence in these populations has associated PCB levels in mothers with adverse neurodevelopmental outcomes in their children.

POPs effects have also been demonstrated in marine ecosystem bird and marine mammal populations, both in coastal areas and in remote oceans. In the early 1970s, brown pelican populations on U.S. coasts were brought to the edge of extinction following DDT-induced eggshell thinning, principally mediated

through its long-lived metabolite DDE. Contemporary elevated levels of PCBs and dioxins accumulated in albatross on Midway Atoll in the remote North Pacific Ocean may be interfering with their reproductive success.

Birds on remote Midway atoll in the north Pacific are exposed to POPs.

Photo: NASA

These findings from the Great Lakes and marine ecosystems demonstrate that it is possible to sufficiently contaminate environments with POPs residues to cause adverse effects on a regional and global scale, along with the prolonged and continuing nature of these impacts. The experience is also one of hope, in that controls on the production, use, and release of POPs can, and have, resulted in reduced environmental concentrations and wildlife recovery. The bald eagle saga offers an inspiring metaphor. Once nearly extinct in the lower 48 United States, bald eagle populations have recovered dramatically with the cessation of DDT use in the United States, yet the reproductive impacts linger.

- *Long-range transport of POPs:* POPs move to regions such as the Great Lakes, marine ecosystems, and the Arctic through long-range environmental transport in air, water, and migratory species. This transboundary movement occurs principally through the atmospheric pathway, either on suspended particles or through a process of global distillation and cold condensation. Global distillation results from the semivolatile nature of some POPs, where they can be present in more than one phase in the atmosphere, either as gases or attached to airborne particles. Because of the normal decrease of temperature with increasing latitude, compounds in the vapor phase will tend to condense on surfaces as they are transported northward by winds associated with passing weather systems. This cold condensation results in a net transport of POPs from lower latitudes to high latitudes (polar regions) in a series of jumps. The different affinities of POPs for soil particles, water, and/or lipid molecules, and their rate of volatilization, determine the pathway and time course each chemical is likely to take in its journey through the environment.

- *POPs in Alaska:* Risks to Arctic environments and indigenous human populations were central to negotiating the Stockholm Convention on POPs. For the United States, many of the physical, climatic, and social aspects that make Alaska unique — particularly for the indigenous population — also make this region peculiarly prone to risks from global POPs. Alaska is downwind and geographically close to continuing sources of POPs production and use in Asia, where populations and economic growth are expanding rapidly. The Alaskan climate facilitates the deposition of POPs, delays their degradation through environmental processes, and places unusual stresses on ecosystems. Fat becomes the currency of life in the harsh Arctic environment for both wildlife and humans, serving as the ideal medium for transferring and magnifying the concentrations of lipophilic POPs between species and up the food chain.

Previously pristine in remote areas, all of Alaska's environmental media and species now contain measurable levels of POPs. However, POPs levels in Alaska are generally low compared with the lower 48 United States. Accompanying these comparatively low levels are isolated examples of elevations that serve as a cautionary warning in the absence of interna-

tional action. DDT and PCB levels in transient Alaskan killer whales are as high as those found in highly contaminated east coast dolphins. On Kiska Island in the Aleutians, DDT levels in bald eagle eggs approach effect levels seen in the Great Lakes. And, serum concentrations of DDT and chlordane in a limited sample of Alaska Natives underscore their proximity to areas of continuing production and use internationally. It is important to emphasize, however, that there are no known POPs levels at this time in Alaska that should cause anyone to stop consuming locally obtained, traditional foods or to stop breastfeeding their children. Current information indicates that the risks associated with a subsistence diet in Alaska are low, whereas the benefits of this diet and breastfeeding children are well documented. Further investigation and assessment are needed for specific species and foods in traditional diets, and to broaden the database across Alaskan communities.

- What might the future hold in the absence of POPs controls? The passage of time is central to evaluating the merits of the Stockholm Convention. Emission scenario models forecast large increases in the scale of worldwide economic activity over the next half-century, with overall economic activity predicted to increase about fourfold in the "business as usual" scenario. The human population is predicted to increase to around 9 billion persons. The large majority of increases will occur in developing countries. Although different model inputs lead to different results, all projections share a common future of much higher total economic activity, and hence of potential uses and emissions of POPs in the absence of active control policies and alternatives.

The United States is not alone in having experienced POPs problems, with many countries suffering local and transboundary pollution effects. In response, the United States has signed international agreements on persistent toxic substances under the Great Lakes Binational Toxics Strategy (US, Canada); the North American Agreement on Environmental Cooperation (US, Canada, Mexico); and the UNECE Long-Range Transboundary Air Pollution POPs Protocol (US, Canada, Western and Eastern Europe, Newly Independent States, Russia). The consensus for global action on POPs under the Stockholm Convention is commensurate with the extent of the pollution and the need to include all countries in the solution. To this end, the Convention contains the following central elements:

- Measures to eliminate or restrict the production, use, and trade of intentionally produced POPs
- Development of action plans to address the release of byproduct POPs, along with the obligation to use best available techniques to reduce byproduct emissions from newly constructed facilities in specified major industrial source categories
- Measures to reduce or eliminate POPs releases from stockpiles and wastes
- Technical and financial assistance to developing countries, and countries with economies in transition, to implement their obligations under the Convention
- Science-based criteria and procedures for the addition of new POPs chemicals

The Stockholm Convention will enter into force following ratification by 50 nations. The Convention is aimed at protecting human health and the environment from POPs chemicals on a global scale. Through implementation of the Convention, nations have the opportunity to make POPs a relic of the 20th century, and a warning from history for the 21st century.

Chapter 1 Genesis of the Global Persistent Organic Pollutant Treaty

Each day the resilience of the Earth offers humanity a new beginning by mitigating the pollution and wastes of yesterday. Through wind and water, pollutants are dispersed and diluted; through chemical and biological degradation, toxic substances are eliminated; and through the fidelity of DNA replication, life begins anew. But for a small group of persistent organic pollutants (POPs), natural processes and ecosystem services have proven inadequate to rectify, and in some cases have contributed to, environmental contamination. The resistance of POPs to degradation and their environmental persistence serve as a foundation for prolonged and disseminated adverse effects. Air and water move POPs far from their sites of release to the environment, including to previously pristine locations such as the Arctic. The low levels of POPs reaching remote locations can then be elevated to potentially toxic levels through biomagnification in the food chain. And, most poignantly, the first exposure of offspring may be through a loading dose of toxicant to the fetus or in milk, during the most sensitive period of development.

PCB concentrations are elevated in Aleutian Island sea otter populations.
Photo: U.S. Fish and Wildlife Service

It is to this group of substances—the persistent organic pollutants—that this technical report is addressed.

The report summarizes the science underpinning contemporary action on POPs, focusing on the 12 substances or substance groups prioritized for global action in the recently signed Stockholm Convention on Persistent Organic Pollutants, developed under the auspices of the United Nations Environment Programme (UNEP). These 12 substances, the "dirty dozen," are:

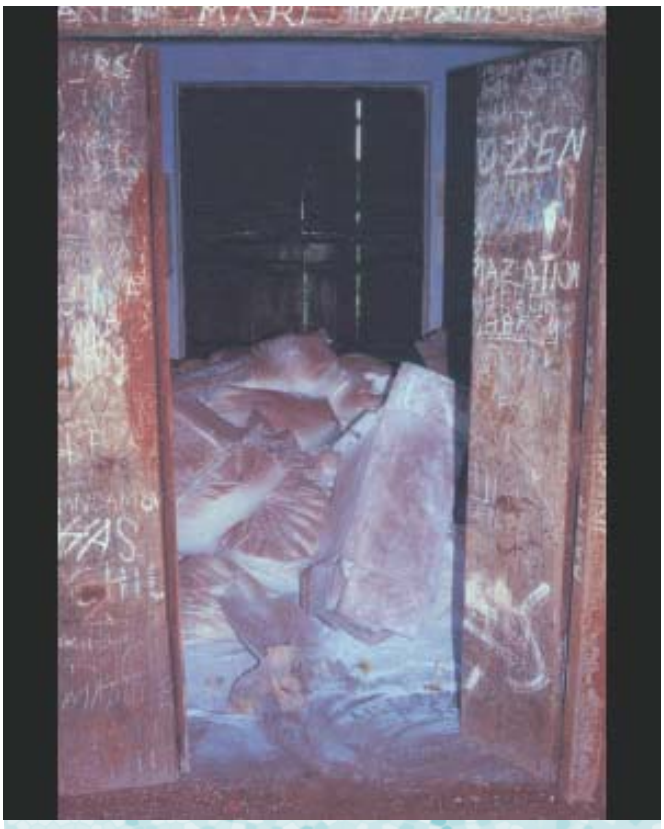
- Pesticides: dieldrin, aldrin, endrin, chlordane, heptachlor, DDT, toxaphene, mirex
- Industrial chemicals: polychlorinated biphenyls (PCBs; also a byproduct), hexachlorobenzene (HCB; also a pesticide and byproduct)
- Byproducts: polychlorinated dibenzofurans, polychlorinated dibenzo-*p*-dioxins (dioxin)

The report is directed toward educating decision-makers, academia, and the public on the foundation and relevance to the United States of the Stockholm Convention on POPs. The report consolidates and summarizes the large volumes of data developed on these substances over decades of scientific concern and regulatory experience, as published in multiple source documents from individual peer-reviewed literature, through single-chemical profiles, to multivolume risk assessments. Its objective is to provide an overview of the human and ecological risks posed by POPs to U.S. ecosystems and citizenry. Emphasis is placed on making the document easily readable, while maintaining its technical accuracy and balance. To this end, citations are provided to more comprehensive and detailed literature for those seeking a more complete elaboration of technical issues.

Why Focus on POPs?

Public concern and scientific and regulatory efforts regarding this small group of pollutants encapsulate the genesis and development of environmental pollution awareness in the United States. These are the pollutants that Rachel Carson wrote about in *Silent Spring* (Carson, 1962), that contaminated Agent Orange during the Vietnam War, and that contributed to Love Canal, NY, Times Beach, MO, and numerous other pollution episodes. All 12 substances prioritized under the Stockholm Convention are now deregistered, banned, or out of production in the United States, or their emissions have undergone major reductions. Yet their effects are still felt through a legacy of past pollution, continuing emissions, and movement across international borders.

For the nine organochlorine pesticides (including hexachlorobenzene as a fungicide), the extent of adverse human health and/or ecological effects



Poor storage of donated DDT in Zanzibar.

Photo: R. Hedlund, USAID

Dieldrin-containing drums in Niger.

Photo: Janice Jensen

led to the withdrawal of all registered uses in the United States during the 1970s–1990s, either by the U.S. Environmental Protection Agency (EPA) or voluntarily by the registrant. Production of the last of these, heptachlor, has ceased and its registration was voluntarily cancelled in 2000. Because U.S. pesticide laws are based on registrations for specific uses, problem chemicals are dealt with through withdrawal of these registrations, rather than bans on production. The net effect of these actions is that there is currently no production of any of the POPs in the United States for sale domestically or internationally, except for laboratory-scale research consistent with the requirements of the Stockholm Convention.

For polychlorinated biphenyls (PCBs), the magnitude of environmental problems was central to the passage of the Toxic Substances Control Act (TSCA). PCB production was banned under this legislation in 1979, although production ceased prior to this date. Existing PCBs in electrical equipment must be prevented from entering the environment and destroyed at the end of the equipment's service life. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, better known as "dioxins," have been controlled through a variety of means, principally emission controls on incinerator sources, process changes to remove elemental chlorine from pulp and paper production, and the

deregistration of contaminated herbicides such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T; a constituent of Agent Orange).

The breadth of POPs pollution that led to these U.S. regulatory actions is still evident in contemporary environmental concentrations. POPs pollution has touched every region of the United States, as illustrated by the geographic distribution of DDE (a long-lived toxic metabolite of

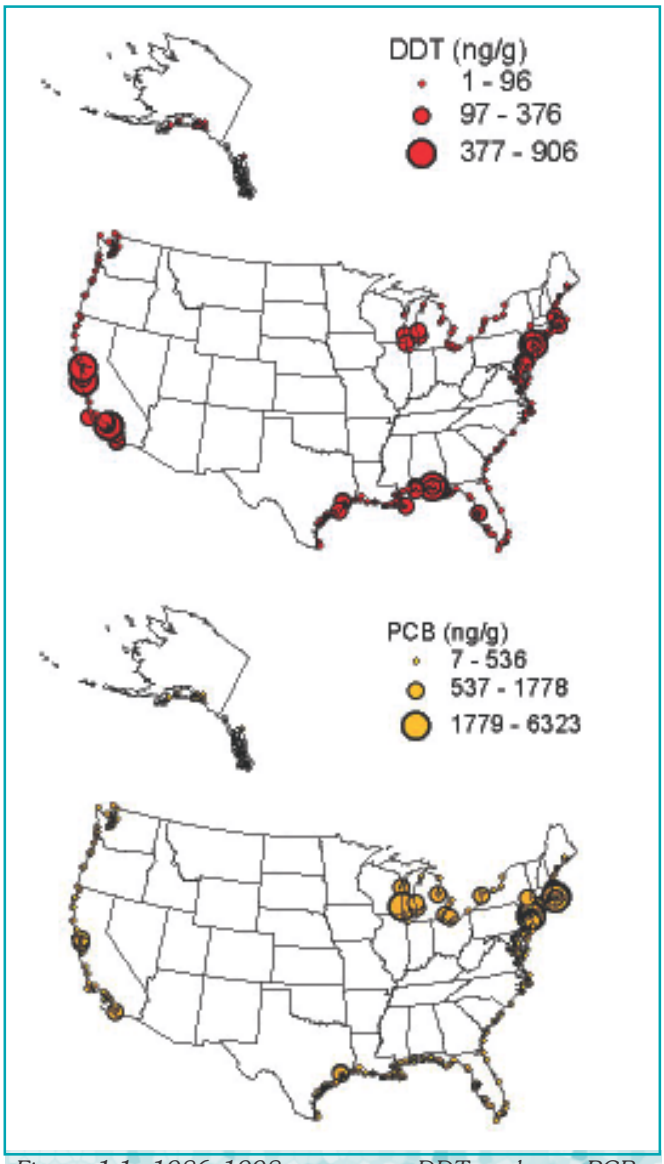


Figure 1-1. 1986–1998 mean sum-DDT and sum-PCB concentrations in coastal mussels (dry weight) collected by the National Oceanic and Atmospheric Administration (NOAA) through its ongoing Status and Trends Mussel Watch Program. http://ccma.nos.noaa.gov. Data courtesy of Tom O'Connor, NOAA. See also trends discussion in Chapter 6.

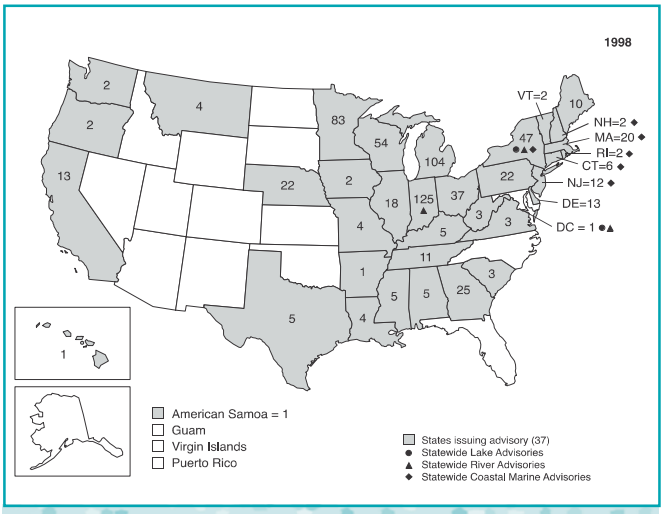


Figure 1-2. 1998 fish consumption advisories reported for polychlorinated biphenyls (PCBs) to the U.S. EPA by states, territories, and Native American tribes. See Chapter 4 for further details on fish advisories. U.S. EPA 1999.

DDT) and PCB concentration elevations in coastal mussels (Figure 1-1), PCB fish advisories (Figure 1-2), and contemporary measurements of atmospheric dioxin levels in nonurban locations across the United States (Figure 1-3). Impacts on the Great Lakes (Chapters 3, 4) and marine ecosystems (Chapter 6) are highlighted in this report as examples of POPs pollution exposures and effects, along with a summary of the existing science on POPs concentrations and risks in Alaska (Chapter 5). Many more sites of POPs contamination are scattered across the United States, but these cannot be detailed here because of space constraints. One such example is Lake Apopka in Florida, where high levels of several POPs (principally DDE) and other pollutants (Figure 1-4) have been postulated as causing reproductive impairment and male genital abnormalities in alligators following embryonic exposure, although the specific causal agent(s) remains uncertain (Guillette et al., 1999).

The extent to which POPs remain problematic is also manifest through continuing regulatory and policy initiatives, both domestically and in international fora in North America. Domestically, the EPA is engaged in a variety of initiatives on persistent, bioaccumulative, toxic (PBT) chemi-

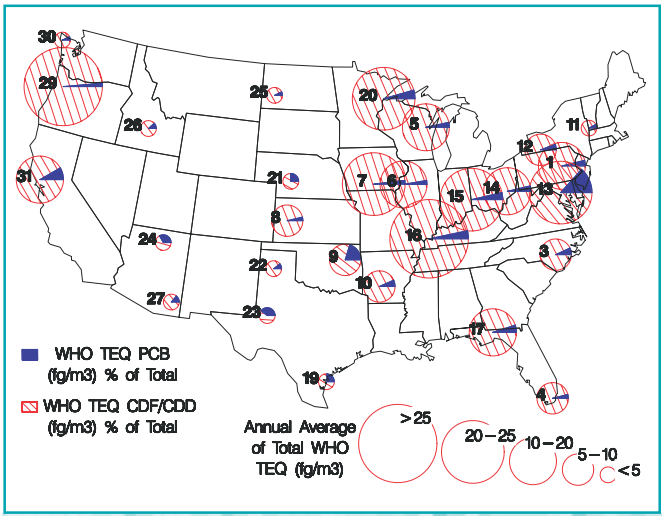


Figure 1-3. Average atmospheric concentrations of dioxin TEQ (from PCDDs, PCDFs, coplanar PCBs) in femtograms (10^{-15} grams) per cubic meter for the year 2000, collected by the National Dioxin Air Monitoring Network (NDAMN). Site locations listed after references. Source: David Cleverly, U.S. EPA

Sites: 1 - Penn Nursery, PA; 2 - Penn Nursery, PA, QA duplicate; 3 - Clinton Crops, NC; 4 - Everglades National Park, FL; 5 - Lake Dubay, WI; 6 - Monmouth, IL; 7 - McNay, IA; 8 - Lake Scott, KS; 9 - State Park West of Tulsa, OK; 10 - Arkadelphia, AR; 11 - Bennington, VT; 12 - Jasper, NY; 13 - Beltsville, MD; 14 - Caldwell, OH; 15 - Oxford, OH; 16 - Dixon Springs, IL; 17 - Quincy, FL; 18 - Stennis Space Center, MS - insufficient data in Yr. 2000; 19 - Padre Island, TX; 20 - Fond du Lac Indian Reservation, MN; 21 - North Platt Agricultural Experiment Station, NE; 22 - Goodwell Research Station, OK; 23 - Big Bend National Park, TX; 24 - Grand Canyon National Park, AZ; 25 - Theodore Roosevelt National Monument, ND; 26 - Craters of the Moon National Park, ID; 27 - Chiricahua National Park, AZ; 28 - Proposed Dairy Reseach Facility, CA; 29 - Hyslop Farm, OR; 30 - Lake Ozette, WA; 31 - Fort Cronkite, San Francisco, CA; 32 - Craig, AK, recently operational; 33 - Trapper Creek, AK, recently operational.

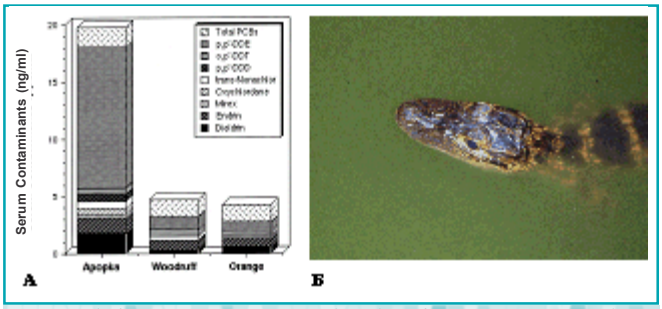


Figure 1-4. A. Mean serum levels of POPs in juvenile male and female alligators from three different lakes in the same drainage in Florida (Guillette et al., 1999). B. A yearling alligator swimming in the eutrophic water of Lake Apopka.

Photo: Howard K. Suzuki

cals. PBTs encompass a somewhat broader domain than POPs, including metals, whereas POPs are limited to organic substances (i.e., containing carbon). Domestic activities include the EPA's PBT program to coordinate action regarding these pollutants (*www.epa.gov/pbt*), the Toxics Release Inventory (TRI) PBT reporting requirements under the Emergency Planning and Community Right-To-Know Act (EPCRA) (*www.epa.gov/tri/pbtrule.htm*), and the prioritization accorded PBT parameters when evaluating new chemical notifications under the Toxic Substances Control Act (TSCA) and when registering pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).

Internationally, the Great Lakes Binational Strategy with Canada prioritizes primary and secondary lists of substances slated for "virtual elimination" (*www.epa.gov/glnpo/p2/bns.html*). Central to these lists are the 12 priority POPs listed in the Stockholm Convention. With Mexico, under the environmental side agreement of the North American Free Trade Agreement (NAFTA), the United States and Canada have focused their Safe Management of Chemicals (SMOC) efforts on PBTs (*www.cec.org*). Action plans have been developed for DDT, PCBs, and chlordane, as well as mercury, and are under development for dioxins, furans, and hexachlorobenzene.

Contributing to the difficulties in eliminating some POPs are their advantages in the industrial and building sectors. PCBs made excellent dielectric fluids in electrical capacitors and transformers because they are highly resistant to degradation and fire. These same properties contribute to their persistence in the environment and biological organisms. A single application of chlordane, an organochlorine termiticide, provides household termite protection for years. Unfortunately, not all the chlordane stays where it is applied, and it may continue to bioaccumulate far from basement soil and injure or kill creatures for which it was not intended. DDT's ability to repel and injure or kill malaria-carrying mosquitoes can provide several months of household protection, yet ultimately DDT is mobilized and spread outside of the immediate area of application. The benefits of DDT for malaria control, principally due to its persistence, low cost, and past success, remain a major consideration when balancing public health needs with environmental concerns.

The Four POPs Parameters: Persistence, Bioaccumulation, Toxicity, Long-Range Environmental Transport

A suite of four characteristic parameters distinguish POPs from the multitude of other organic chemicals:

Persistence

Persistence is the propensity of a substance to remain in the environment by resisting chemical and biological degradation, particularly the effects of microbial processes. Persistence is best represented as the degradation of a POP to a non-POP chemical, rather than as declining environmental concentrations that combine degradation with loss due to dispersion. Persistence is often measured as a half-life, the time (hours, days, months, or even years) necessary for half the chemical to be degraded. Reliance on half-life measures assumes first-order kinetics, where the amount degraded in a fixed period of time is a constant proportion of the amount present initially, i.e., $C_t = C_0\, e^{-rt}$, where C_0 and C_t are concentrations at times zero and t, and r is the rate constant for degradation (Figure 1-5). The first-order kinetics assumption may not always apply where early degradation is more rapid, delayed degradation is enhanced through bacterial acclimation and selection, or chiral (mirror image) molecules may be preferentially degraded. The degradation product may also exhibit POPs characteristics. Half-life values in the different air, soil, water, and sediment media have been included in most POPs screening criteria (see Chapter 9, Table 9-1). These half-life values are considered pragmatically useful for screening chemicals, but are recognized as oversimplifying the persistence of chemicals in the environment (Klecka et al., 2000). Persistence screening values for the Stockholm Convention are based on 2 months in water or 6 months in soil or sediment, with a 2-days screening criterion for air transport.

Environmental degradation in the atmosphere occurs principally from reaction of the POP with hydroxyl radicals (OH). The levels of hydroxyl radicals in the air vary considerably with geographic location and time of day and year. For instance, hydroxyl levels are essentially zero in the Arctic atmosphere during winter and generally decline with increasing latitude. Other atmospheric POPs degradation processes include photolysis (light-induced degradation) and reaction

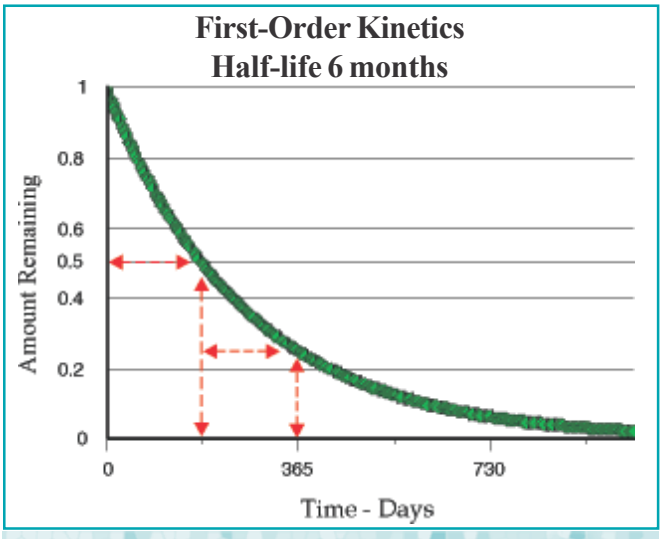


Figure 1-5. First-order decay kinetics diagram.

with ozone and nitrogen oxides. In soil, water, and sediment, microbial degradation is the predominant mechanism. The rate of degradation depends on the types of bacteria present, their concentration, induction relevant to the chemical undergoing degradation, and ambient environmental conditions such as temperature, moisture, and substrate availability. Other processes include photolysis, hydrolysis, and chemical reaction. Details of technical considerations in deriving and using persistence data are contained in the report of a Society of Environmental Toxicology and Chemistry (SETAC) Pellston workshop, focusing on POPs persistence and long-range transport issues (Klecka *et al.*, 2000).

Bioaccumulation

Bioaccumulation is the phenomenon whereby a chemical reaches a greater concentration in the tissues of an organism than in the surrounding environment (water, sediment, soil, air), principally through respiratory and dietary uptake routes. For example, if the environment in which a fish lives contains 1 µg free chemical/kg of water, and the fish's body contains 5,000 µg chemical/kg body weight, this would equate to a whole-body bioaccumulation factor (BAF) of 5,000 (i.e., the Stockholm Convention screening criterion value). The magnitude of bioaccumulation is driven by the hydrophobicity, or water insolubility, of the chemical, principally operating through the ability of a species to eliminate the chemical from its body by excretion and/or metabolism. The terms bioaccumulation, bioconcentration, and biomagnification are variants of this same concept. Bioaccumulation factors measure the preferential accumulation of a chemical in a living organism through all routes of uptake with respect to concentrations in the organism's exposure environment (water, sediment, soil). The term "bioconcentration factor" (BCF) is used when the bioaccumulation factor is based exclusively on uptake from water in laboratory studies, using species (most commonly fish) maintained in a known concentration of pollutant but fed an uncontaminated diet. Biomagnification relates to the most highly accumulative substances (many of the POPs), where the concentration of the chemical in an organism exceeds that predicted for equilibrium of the organism with its diet, the concentration having been "magnified" in species higher up the food chain (Figure 1-6).

BCF/BAF values can be reported either in relation to the whole-body weight of the test species or in a more standardized manner related to the lipid (or fat) content of the animal, usually a fish. These two measures can be quantitatively linked through the fat content of the animal because the POPs are concentrated in the fatty portions of tissues. This relationship is often simplified by assuming a standard fish fat content to facilitate comparison between chemicals in different study protocols and species, known as lipid normalization (e.g., 3.1% lipid in the case of the Great Lakes Water Quality Assessment for trophic level 3 fish).

A common surrogate for calculating BCF/BAF values is the octanol-water partition coefficient (Kow). This ratio reflects the preferential accumulation of a substance in an organic medium (n-octanol) compared with water. To illustrate, in a cup containing half n-octanol and half water, this is the amount of a chemical placed in the cup that would dissolve in the n-octanol divided by the amount dissolving in the water. The Kow is now most often calculated using chemical models. It should be noted that mathematical

Figure 1-6. Simple biomagnification diagram.

formulae linking the Kow with BCF/BAF values do not apply where there is active metabolism of the substance, or for large molecules, and are generally not applicable to organometals. Additional detail on bioaccumulation in aquatic environments is available in the U.S. EPA Great Lakes Water Quality Criteria documents (U.S. EPA, 1995).

Toxicity

A principal tenet of toxicology is that the dose makes the poison (Paracelsus, 1493–1541), a concept elaborated upon more recently as knowledge has increased on the complexity and timing of dose-response relationships. The toxicity of a substance can be reported in a variety of ways, such as acute (short-term) or chronic (long-term) effects, lethal or effective dose levels (LD_{50} or ED_{50}, the dose that will kill or affect 50% of test animals), or tissue levels associated with an adverse effect. Whereas certain toxic effects and levels may be easily detected and quantified in laboratory settings, their measurement in the natural environment is considerably more difficult. In field situations, the animal's environment is impossible to control.

This situation is similar to the difficulties experienced with human epidemiological studies. Multiple substances may combine to form a "toxic soup" from which individual chemical contributions can be difficult to disentangle. A corollary of multiple simultaneous exposures is that the cumulative toxicity risk is likely to be greater than when individual chemicals are evaluated in isolation. Furthermore, the low-level effects of interest in field situations may be subtle and difficult to measure, yet vital to species survival. For example, subtle POPs-induced neurological impairment may not cause overt effects in a caged, fed, and protected animal, but may be of dire consequence in the complex and dangerous natural environment. Difficulties also occur when attempting to transpose laboratory toxicity data, generally measured as daily dose, to field situations where the metric is tissue concentration of a toxic substance and daily doses cannot be measured.

For a further detailed discussion of wildlife toxicology and the effect levels pertinent to POPs impacts on wildlife, see Beyer et al. (1996). Toxicity data on POPs pertinent to humans can be obtained from online databases maintained by the National Library of Medicine (*www.nlm.dhhs.gov*; Hazardous Substances Data Bank), the EPA's Integrated Risk Information System (IRIS) database (*www.epa.gov/iris*), and the Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles (*www.atsdr.cdc.gov*).

Long-Range Environmental Transport

There would be little need for a global treaty if POPs remained close to their sites of release. However, on a dynamic planet the forces of air and water, along with the migratory behavior of certain species, move these pollutants to remote locations (see Chapter 7 for details). A major impetus for the global POPs negotiation was the finding of POPs contamination in the Arctic, thousands of miles from their presumed sites of release to the environment. Figure 1-7 shows the intermittent transport of massive dust clouds from Asia and North Africa toward North America. Within a few days these clouds can cross the Atlantic and Pacific Oceans, transporting pollutants and microorganisms along with the dust. Images such as this provide visual confirmation of atmospheric pathways between continents.

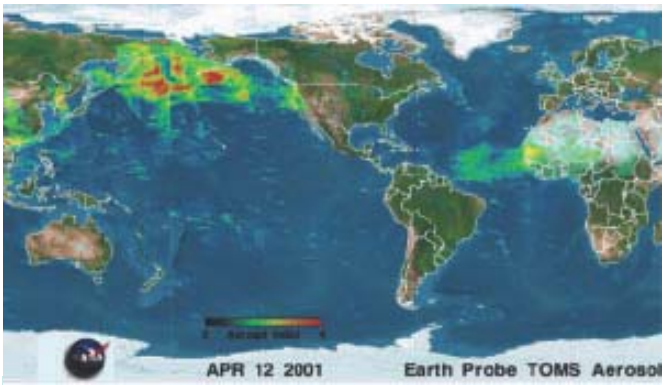


Figure 1-7. False color image of the aerosol abundance in the atmosphere obtained by NASA's Earth Probe TOMS satellite. The aerosol index is a measure of the absorption of solar ultraviolet radiation by airborne particles.

Source: National Aeronautics and Space Administration

Beyond physical transport on dust and sediment particles, empirical data and the physical properties of a number of POPs indicate that these substances may be preferentially accumulating in cold polar climates through global distillation. Certain POPs that exhibit a particular range of physical properties—often characterized as semivolatile—may evaporate in tropical and temperate climates and condense in cold regions. In a more absolute sense, and independent of whether transport occurs via volatilization or physical transport on particles or in water, once a substance reaches the frozen polar regions, normal physical degradation time scales and half-lives lose their relevance.

It is the combination of persistence, bioaccumulation, toxicity, and long-range environmental transport that makes POPs problematic. All 12 prioritized POPs or their breakdown products rank high to extreme on measurements of these parameters. Low values on any of the parameters will substantially reduce transboundary concern, although local problems may remain. The parameters also serve as the basis for screening levels in virtually all international POPs agreements, including the Stockholm Convention. In screening for potential POPs using these parameters, the limitations of such an approach are recognized through an emphasis on flexibility and expert judgment in determining the level of risk produced by a substance and what action is warranted.

POPs History—Cut Short

The story of POPs begins with the growth of the organic chemical industry in the early 20th century, and with foresight will end as we enter the 21st century. DDT was first synthesized in 1874, but its insecticidal properties remained unknown until reported in 1939 by the Swiss chemist Paul Hermann Müller. A skin rash called chloracne was reported by Karl Herxheimer (Herxheimer, 1899) to be afflicting German workers in the chlorinated organic chemical industry in 1899, although the causal agent, dioxin, remained elusive for many decades (Figures 1-8, 1-9). PCBs were first produced commercially in 1929, peaked in 1970, and were banned from production in the United States by 1979. Dieldrin and aldrin were first synthesized as pesticides in the United States in the late 1940s. They were named for Drs. Otto Diels and Kurt Alder, who developed the Diels-Alder process for diene (2 double bonds between carbon atoms) synthesis in 1928. With World War II and reconstruction came a broad public awareness of the potential marvels of chemicals such as DDT for disease vector control, exemplified by international efforts seeking to eradicate diseases such as malaria. At the same time, newly developed organochlorine pesticides and herbicides were rapidly filling the needs of the growing agrochemical industry.

But as the use of halogenated, particularly chlorinated, organic chemicals rose in agricultural and industrial sectors, so did warnings about potential adverse consequences to human health and the environment. In 1962, a sentinel event occurred with the publication of Rachel Carson's *Silent Spring*. Through this book and the surrounding media attention, the public first became aware of a downside to the proliferation of chemicals, with warnings of spring devoid of songbirds. Chemicals intended for insect control were being found to accumulate in the food chain, causing eggshell thinning, chick mortality, and other

Figure 1-8. Agent Orange barrels during the Vietnam War, contaminated with dioxin.

Source: USAF

Figure 1-9. Aerial spraying Agent Orange defoliant, Vietnam.

Source: USAF

unforeseen damage. Adding halogen atoms (fluorine, chlorine, bromine, iodine) had been used to make organic molecules more resistant to degradation. The persistence of these organochlorine structures, and the propensity of some to bioaccumulate, were central to the problems being experienced. Increased persistence meant that mistakes made with POPs lingered, such as the prolonged ecological damage caused by chemical spills. Because persistent organochlorine pesticides were nonselective in their toxicity to insects, they caused prolonged killing of both pest insects and beneficial creatures that preyed on these pests. Prolonged, indiscriminate lethality also precipitated secondary pest outbreaks, where insect species not generally considered a problem rose in prominence through disruption of ecological processes.

Beyond these agricultural and ecological concerns lay the human dimension of pesticide and PCB residues in the food supply. Data from tests in rodent species showed that many of these substances were possible or probable human carcinogens. Passage of the Delaney Clause in the 1958 Food Additives Amendment to the Food, Drug, and Cosmetic Act (FDCA) mandated that no carcinogens be added to the food supply—a zero-risk policy. Legal and regulatory decisions to operationalize this requirement stimulated efforts to quantify cancer risk estimates and led to the concept of a *de minimus* concentration, a level below which risks were considered too small to warrant legal attention. The organochlorine POPs, both industrial and chemical, were central to many of these debates. Compounding this pressure for risk quantification was increasing public concern about contaminated industrial sites and toxic chemical pollution. In response, a combination of legislative, regulatory, legal, and voluntary actions ultimately facilitated the development and use of newer pesticides and industrial alternatives in the United States, replacing the problematic organochlorines.

But while uses and levels in the environment, food, and tissue were stabilizing or declining in the lower 48 United States, reports began appearing in the scientific literature of increasing levels in what had been thought pristine, uncontaminated environments. In particular, increasing haze and contamination in the Arctic became a priority concern of northern countries. In 1991, Environment Ministers from the Arctic rim countries (Canada, Denmark/Greenland, Finland, Iceland, Norway, Sweden, Russia, United States; Figure 1-10) established the Arctic Monitoring and Assessment Programme (AMAP; *www.amap.no*) to measure the levels and assess the effects of man-made pollutants in the Arctic environment. Priority attention was directed toward POPs, together with heavy metals and radioactivity. The AMAP efforts, consolidating and supported by domestic programs in Arctic countries (e.g., Canadian Northern Contaminants Program, Jensen et al., 1997), helped focus attention on the long-range transboundary movement of POPs. Long-range environmental transport concerns were reinforced with the finding of elevated POPs levels in wildlife on remote mid-Pacific islands (Jones et al., 1996).

Transboundary pollution issues, and the opportunity to address them, also gained greater prominence with the easing of Cold War tensions. In 1979, member countries of the United Nations Economic Commission for Europe (UNECE) had signed the Convention on Long-Range Transboundary Air Pollution (LRTAP), initially directed at controlling transboundary sulfur and acid rain pollution. Beyond its name, the

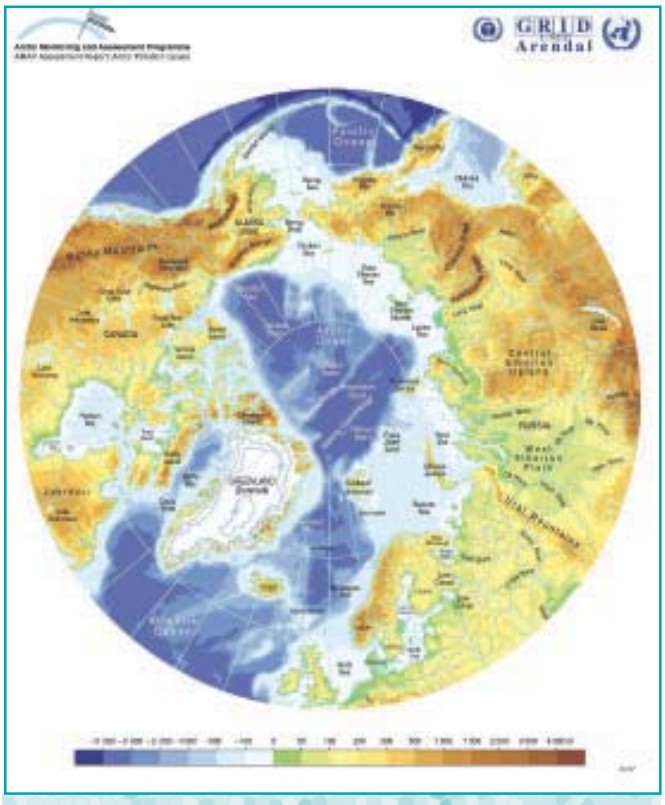


Figure 1-10. Arctic topography and bathymetry.

Source: AMAP.

UNECE region includes Canada, the United States, Western Europe, Eastern Europe and Newly Independent States, and Russia, circling the upper Northern Hemisphere. With a growing understanding of the transboundary nature of POPs pollution, the UNECE-LRTAP agreement offered an ideal vehicle to advance POPs control efforts. In 1992, background work commenced on parallel UNECE-LRTAP protocols to address POPs and heavy metals. Criteria for the priority scoring and selection of POPs were developed, along with a process for reviewing individual chemicals for potential action by the LRTAP parties (AEA, 1995, 1996). Negotiations on a formal POPs protocol began in 1994 and were completed in 1998 (*www.unece.org/enc/lrtap*), following which the protocol was signed by the United States.

UNEP Global POPs Negotiations

The written record of the global POPs negotiation traces to Agenda 21 of the Rio Declaration on Environment and Development in June 1992 (United Nations, 1993). The foundation and priority for POPs action were enunciated in Objective 17, Protection of the Oceans, and Objective 19, Environmentally Sound Management of Toxic Chemicals. Under Protection of the Marine Environment, section 17:18 stated:

> Many of the polluting substances originating from land-based sources are of particular concern to the marine environment since they exhibit at the same time toxicity, persistence and bioaccumulation in the food chain. There is currently no global scheme to address marine pollution from land-based sources.

Similar concerns were echoed in section 19:44, Establishment of Risk Reduction Programmes, where Agenda 21 called for

> the phasing out or banning of chemicals that pose unreasonable or otherwise unmanageable risks to human health and the environment and of those that are toxic, persistent and bioaccumulative and whose use cannot be adequately controlled.

In May 1995, these concerns about POPs served as the basis for Decision 18/32 of the United Nations Environment Programme Governing Council (UNEP-GC), which commenced a technical review process to document POPs risks and response strategies. The initial list of POPs consisted of the 12 under discussion at that time by the UNECE-LRTAP Parties. The following principal events trace the chronology and developing consensus for international action on POPs:

November 1995: Washington Declaration on Protection of the Marine Environment from Land-Based Activities (*http://www.unep.org/unep/gpa/pol2b12.htm*).

December 1995: Inter-Organization Programme for the Sound Management of Chemicals (IOMC) Persistent Organic Pollutants Assessment Report (Ritter *et al.*, 1995).

March 1996: Intergovernmental Forum on Chemical Safety (IFCS), second meeting of the Inter-Sessional Group (ISG-2), Canberra, Australia (ISG/96.5a).

June 1996: Intergovernmental Forum on Chemical Safety (IFCS) Experts Meeting on POPs: Persistent Organic Pollutants: Considerations for Global Action. Manila, Philippines (IFCS/EXP.POPs./Report.1, 20 June 1996).

February 1997: UNEP Governing Council, Decision 19/13C. International action to protect human health and the environment through measures that will reduce and/or eliminate emissions and discharges of persistent organic pollutants, including the development of an international legally binding instrument (*http://irptc.unep.ch/pops/*).

Decision 19/13C of the UNEP Governing Council in February 1997 constituted the formal agreement to create an intergovernmental negotiating committee (INC) to develop the text for a binding global POPs convention. Negotiations were to commence in 1998 and conclude by 2000. Decision 19/13C provided a detailed mandate to guide the negotiations, centered around the UNEP-GC decision that

> immediate international action should be initiated to protect human health and the environment through measures which will reduce and/or eliminate … the emissions and discharges of the twelve persistent organic pollutants specified in Governing Council decision 18/32 and, where appropriate, eliminate production and subsequently the remaining use of those persistent organic pollutants that are intentionally produced.

Negotiations began in Montreal, Canada, in June 1998, following a series of awareness-building workshops in developing countries to inform governments on scientific issues concerning POPs. Subsequent negotiating sessions were held in Nairobi (January 1999), Geneva (September 1999), and Bonn (March 2000), culminating in the agreement reached in Johannesburg (December 2000) (Figure 1-11). Technical considerations on criteria for the addition of substances were covered during two criteria expert group (CEG) meetings in Bangkok (October 1998) and Vienna (June 1999). Signing of the treaty by the United States and 90 other nations was held in Stockholm, Sweden, in May 2001, hence the designation Stockholm Convention (Table 1-1).

The treaty is currently open for signature and ratification by countries. Ratification by individual countries confirms their signature and makes them a party to the treaty, following review and consent through the domestic political, legal, and legislative process. The Convention will enter into force after it has been ratified by 50 nations. Entry into force applies only to parties that have ratified the Convention.

Science Clarifications—Separating Facts from Assumptions

Before detailing POPs case studies in the United States and links to long-range environmental transport, it is worthwhile clarifying some assumptions and misconceptions that often occur when evaluating POPs. In particular, an under-

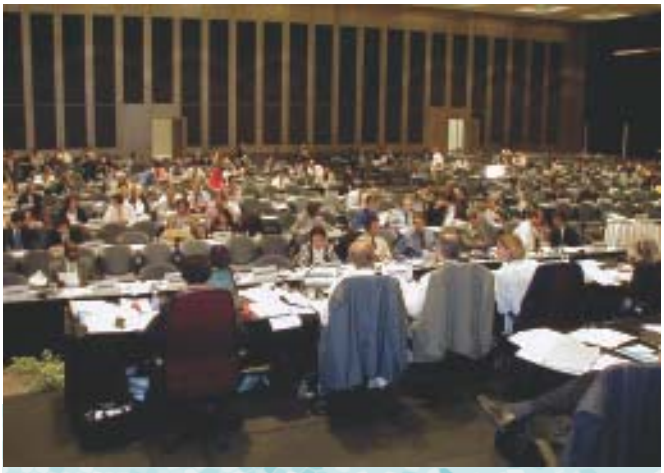


Figure 1-11. Concluding the POPs negotiations, Johannesburg, South Africa, December 2000.

Source: International Institute for Sustainable Development.

Table 1-1. Elements of the Stockholm Convention

Objective: (Article 1)	"... to protect human health and the environment from persistent organic pollutants."
Article 2	Definitions
Article 3	Measures to reduce or eliminate releases from intentional production and use
Article 4	Register of specific exemptions
Article 5	Measures to reduce or eliminate releases from unintentional production
Article 6	Measures to reduce or eliminate releases from stockpiles and wastes
Article 7	Implementation plans
Article 8	Listing of chemicals in Annexes A, B, and C
Article 9	Information exchange
Article 10	Public information, awareness, and education
Article 11	Research, development, and monitoring
Article 12	Technical assistance
Article 13	Financial resources and mechanisms
Articles 14–30	Interim financial arrangements; reporting; effectiveness evaluation; noncompliance; settlement of disputes; conference of the parties; secretariat; amendments to the Convention; adoption and amendment of annexes; right to vote; signature; ratification, acceptance, approval or accession; entry into force; reservations; withdrawal; depository; authentic texts
Annex A	Chemicals listed for elimination
Annex B	Chemicals listed for production and use restrictions
Annex C	Unintentionally produced POPs, source categories, and control measures
Annex D	Information requirements and screening criteria
Annex E	Information requirements for the risk profile
Annex F	Information on socio-economic considerations

standing of POPs problems requires a movement beyond standard considerations of timing, causes, and effects of pollution. The evaluation must also consider the peculiar impacts of extremes of persistence, bioaccumulation, toxicity, and long-range environmental transport.

- *POPs pesticides are still being produced:* From the United States' perspective, the listed POPs pesticides (all organochlorines) are generally considered "dinosaur" chemicals from a bygone era whose production has ceased. They have been superseded by more carefully tailored, selective, and less persistent and bioaccumulative alternatives. These alternatives, although in some cases potentially more acutely toxic to applicators (e.g., some organophosphates), are usually less prone to inducing pest resistance, lead to fewer secondary pest infestations, and result in less food contamination. But, as the UNEP POPs negotiations demonstrated, on a world scale POPs are not gone, with many still being produced and used, especially in developing countries. A number of factors, principally economic, contribute to this continuing use. Organochlorine pesticides are often cheap, easy to produce, and off-patent. Their persistence contributes to their perceived economic benefit, because one application of chlordane termiticide or DDT insecticide can last much longer than modern alternatives. Finally,

some organochlorine pesticides are also perceived to exhibit lower acute mammalian toxicity, and are applied in developing countries with less emphasis on training and expensive protective equipment for applicators.

- *All POPs are not the same:* Although the 12 priority substances exhibit similar high to extreme measures for persistence, bioaccumulation, toxicity, and long-range transport, there is large variability in other physical properties. Values for volatility, solubility, and Henry's Law constant (water-air partition coefficient, important for air transport modeling) vary by up to 5 orders of magnitude between substances (100,000-fold). A consequence is that not all POPs are expected to exhibit the same propensity for global distillation (Wania and Mackay, 1996).

- *POPs concentrations are higher near their sites of release:* The focus on a global POPs convention and transboundary pollution should not obscure the reality that the highest POPs concentrations are generally found close to the sites of release. Problems in the United States are generally homegrown. This proximity does not negate the importance of international action, but emphasizes the need for care in determining appropriate actions. For example, POPs levels in marine mammals in the lower 48 United States are often much higher than those found in Alaska. However, marine mammals constitute a dietary staple in the subsistence lifestyle of many Alaska Natives. Their health and cultural well-being are threatened by substances from beyond U.S. borders that they neither used nor derived benefit from and yet now contaminate their environment.

- *Low concentrations in remote locations do not preclude a substance being a POP:* Concentrations in remote locations reflect a combination of POPs parameters, emission levels, and accumulation time. For a substance such as endrin, an isomer of dieldrin, the relatively low concentrations found at long range are principally a result of the lower historic use levels in temperate climates. Endrin has POPs parameters similar to dieldrin, so any increased use of endrin as a substitute for dieldrin would be expected to lead to similar long-range risks.

- *Contemporaneous appraisals of pollution cause and effect are insufficient:* Often when we think of environmental pollution we equate contemporary emissions with contemporary concentrations and effects on those exposed. These assumptions do not hold for POPs and must be modified by a more detailed examination of the science underlying POPs properties.

  – *Cumulative dose measures are preferable.* The long environmental and biological half-lives of POPs result in a cumulative dose, where current tissue concentrations are a modified sum of past exposures. For persistent chemicals, tissue-concentration metrics that integrate dose, rather than daily dose measures, should be used to assess toxic risk (unless daily dose is interpreted consistent with half-life considerations).

  – *Concentrations will build up for decades.* As a result of cumulative exposure, it is incorrect to assume that if a pesticide has been used for several years at a consistent level, then the concentrations now in the environment represent the peak or worst-case scenario. Persistence values for many of the POPs may be of such duration that, at a steady use rate, environmental concentrations could continue increasing for more than a century. Thus, actions to assess impacts and reduce use must be guided by predicted concentrations at the end of the accumulation cycle.

  – *Momentum.* Solving POPs pollution problems takes time. These substances persist and recycle in the environment, potentially moving long distances. For those environments and peoples at the receiving end of this migration—e.g., sinks such as the

Arctic—cessation of release at the source may not end POPs accumulation, which will take considerably longer.

– *The world of the future will be different.* We must look beyond the world of the present and to the future when evaluating potential long-term benefits of the Stockholm Convention. As illustrated in Chapter 8, the world of the future will have higher population levels (Figure 1-12), increased industrial activity, and chemical development and production concentrated in what are now developing countries. A central consideration should be the future POPs emissions potential and impact on the United States from these countries, if unconstrained by an implemented Stockholm Convention.

* *A toxic legacy of POPs at birth.* Growing embryos and newborns of all species undergo extremely complex developmental changes to reach their peak performance potential (Figure 1-13), necessary to survive in a competitive and often dangerous world. This period of development is protected by biological defenses developed over eons of evolution, from maternal detoxification and placental barriers to the rich nutrients and proteins in mother's milk. POPs thwart these barriers through their resistance to metabolism, passage across biological membranes facilitated by their relatively low molecular weight, and high lipid solubility leading to concentration in body fats. The high energy demands of growth and development are also best satisfied through high-fat-content milk, the ideal POPs dosing mechanism. Indeed, through lactation and nursing her young, a female mammal can purge herself of POPs by transfering the lipophilic (i.e., fat-soluble) substances to her offspring. Toxic effects during sensitive periods of development have not been adequately studied.

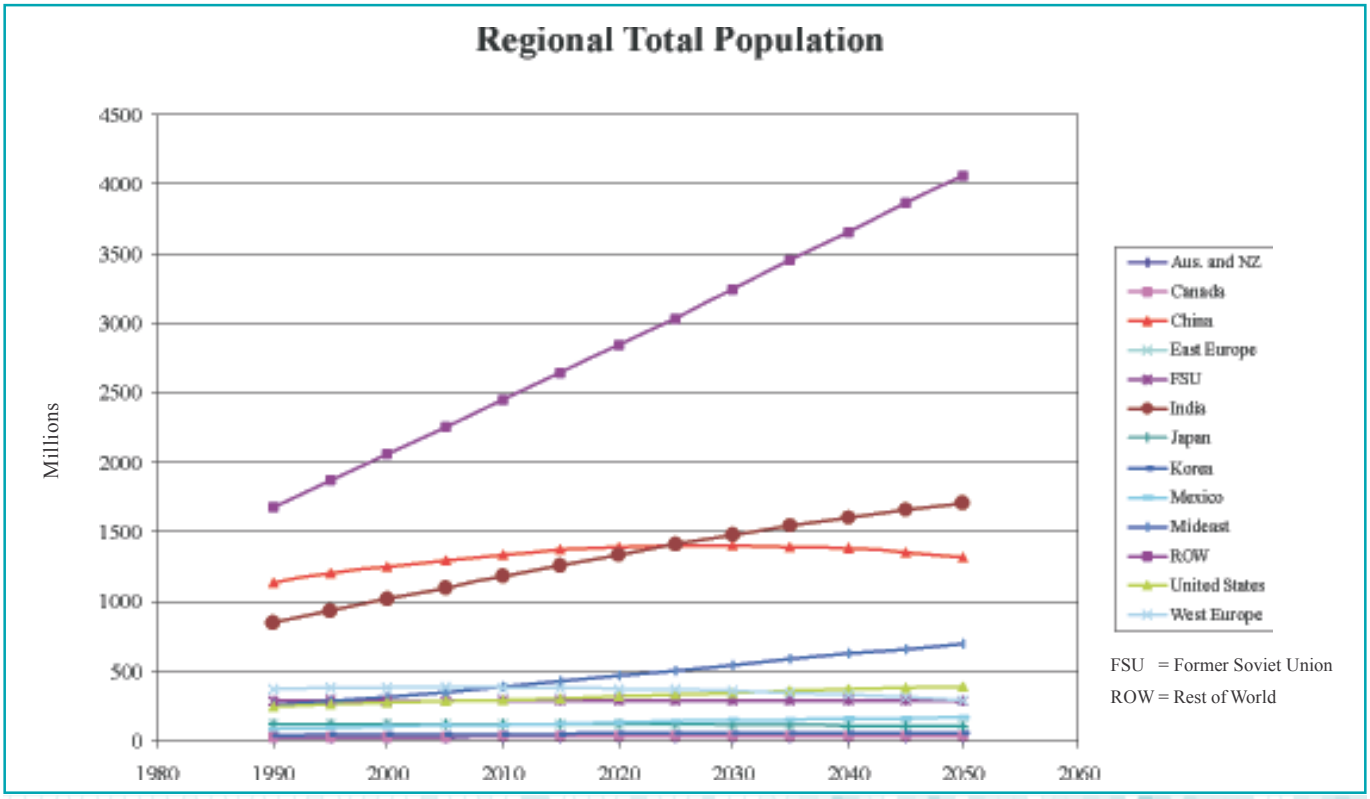


Figure 1-12. World population growth projections.

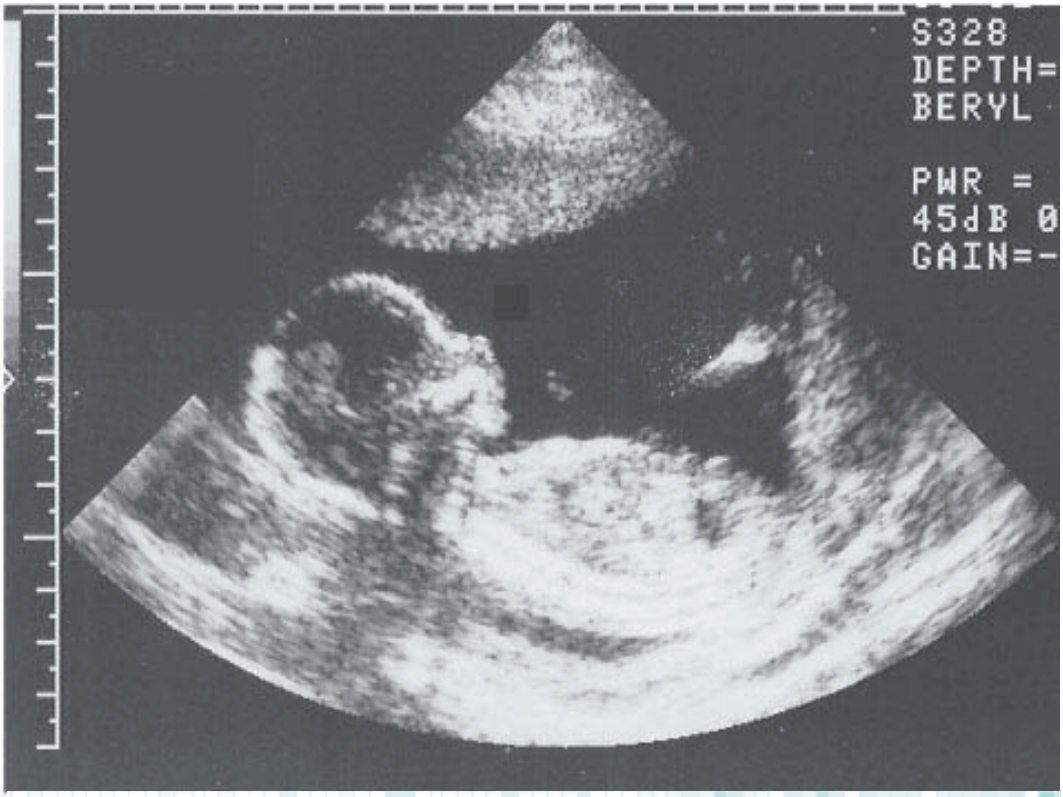


Figure 1-13. Normal four-month human fetus, in utero ultrasound image.
Photo: B. Rodan

All too often, scientists and regulatory agencies must account for risks to the newborn by relying on data derived from adult animals or limited reproductive and physical development studies in rodents.

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Chapter 2 Profiles of the POPs

The scientific literature on persistent organic pollutants (POPs) is voluminous, complex, and intriguing. These are some of the most researched chemicals in existence, yet that research has served to stimulate even more investigation, down to their effects on the intricacies of DNA replication control and cellular differentiation. With this as the backdrop, this chapter seeks to demystify what these chemicals are, why they were developed, what they do, what was discovered about their toxic effects, and why they are the focus of global action.

Twelve substances or substance groups are initially included under the Stockholm Convention on Persistent Organic Pollutants (Table 2-1). These POPs all exhibit the properties of prolonged environmental persistence, bioaccumulation, toxicity, and the potential for long-range environmental transport (see Chapter 9). They can be divided into three general categories of pesticides, industrial chemicals, and unintentional byproducts. Several of the POPs occur under more than one category, such as hexachlorobenzene, which has been used as a fungicide and an industrial feedstock and product, and is also emitted as an unintentional byproduct from incineration and the manufacture of other pesticides. Several of the substances represent groups of chemicals with similar structures and properties, namely the congener families of polychlorinated dioxins and furans, polychlorinated biphenyls (PCBs), and the mixed chlorinated camphenes (toxaphene).

This chapter provides a narrative introduction to each of the POPs. To avoid repetition, narratives are combined for similar chemical groups, such as the cyclodiene pesticides and polychlorinated dioxins and furans. More detailed information can be found from a variety of federal databases and texts, examples of which are included in an appendix at the end of this chapter. Each chemical description includes a table of technical and numerical data on the POP. These tabular data categories, an explanation of their relevance to understanding the chemical's potential environmental impact, and the information sources (unless otherwise specified in the table) are as follows:

- Chemical information and structure (Klecka et al., 2000; a subset of chemical structure drawings is used with permission of SETAC). Representative examples are provided for substance groups where physical, chemical, and biological properties vary between members of the substance group.
- Environmental persistence estimates, recognizing the wide variability of these parameters in different physical environments (i.e., light, temperature, moisture, bacteria, etc.) (Klecka et al., 2000).
- Chemical properties important for evaluating the potential for long-range environmental transport, such as the vapor pressure and the air-water partition coefficient or Henry's Law constant, which measures the pressure in air over the concentration in water at a constant temperature (Ritter et al., 1995). A high air-water partition coefficient indicates that movement of the chemical is facilitated to the vapor phase, increasing the likelihood that it can undergo long-range transport in the atmosphere.
- Bioaccumulation, through both the octanol-water partition coefficient (equilibrium concentration in an n-octanol solution over the concentration in contiguous water; Klecka et al., 2000) and measured estimates from fish species (summarized in Rodan et al., 1999; whole body lipid-adjusted to 5%).

Table 2-1. The 12 POPs under the Stockholm Convention and their current U.S. status

POP	2001 Status for Production and/or Emissions under TSCA,[a] FIFRA,[b] CAA,[c] and CWA[d,e]
Aldrin	❊ No registrations, most uses canceled in 1969, all uses by 1987 ❊ No production, import, or export ❊ All tolerances on food crops revoked in 1986 ❊ Priority toxic pollutant under the CWA
Chlordane	❊ No registrations, most uses canceled in 1978, all uses by 1988 ❊ No production (stopped in 1997), import, or export ❊ All tolerances on food revoked in 1986 ❊ Regulated as a hazardous air pollutant (CAA) ❊ Priority toxic pollutant under the CWA
Dichlorodiphenyl-trichloroethane (DDT)	❊ No registrations, most uses canceled in 1972, all uses by 1989 ❊ No production, import, or export ❊ All tolerances on food and feed crops revoked in 1986 ❊ The metabolite DDE regulated as a hazardous air pollutant (CAA) ❊ DDT, *p,p'*-DDE, and *p,p'*-DDD priority toxic pollutants under the CWA
Dieldrin	❊ No registrations, most uses canceled in 1969, all uses by 1987 ❊ No production, import, or export ❊ All tolerances on food crops revoked in 1986 ❊ Priority toxic pollutant under the CWA
Endrin	❊ No registrations, most uses canceled in 1979, all uses by 1991 ❊ No production, import, or export ❊ Priority toxic pollutant under the CWA
Heptachlor	❊ Most uses canceled by 1978, registrant voluntarily canceled use to control fire ants in underground cable boxes in early 2000 ❊ No production (stopped in 1997), import, or export ❊ All tolerances on food crops revoked in 1989 ❊ Regulated as a hazardous air pollutant (CAA) ❊ Heptachlor and heptachlor epoxide priority toxic pollutants under the CWA
Hexachlorobenzene (HCB)	❊ No registrations as a pesticide, all uses canceled by 1985 ❊ No production, import, or export as a pesticide ❊ Production and use as a closed-system intermediate consistent with the Stockholm Convention ❊ Regulated as a hazardous air pollutant (CAA) ❊ Priority toxic pollutant under the CWA
Mirex	❊ No registrations, all uses canceled by 1977 ❊ No production, import, or export ❊ Recommended nonpriority toxic water pollutant (U.S. EPA, 1999)[f]
Polychlorinated biphenyls (PCBs)	❊ No manufacture and new use prohibited in 1978 (TSCA) ❊ Regulated as a hazardous air pollutant (CAA) ❊ Priority toxic pollutant under the CWA
Polychlorinated dibenzo-*p*-dioxins (dioxins)	❊ As a contaminant in production, regulated under TSCA and FIFRA ❊ Hazardous air pollutant and emission standards regulated under the CAA ❊ 2,3,7,8-TCDD a priority toxic pollutant under the CWA
Polychlorinated dibenzofurans (furans)	❊ As a contaminant in production, regulated under TSCA and FIFRA ❊ Hazardous air pollutant and emission standards regulated under the CAA
Toxaphene	❊ No registrations, most uses canceled in 1982, all uses by 1990 ❊ No production, import, or export ❊ All tolerances on food crops revoked in 1993 ❊ Regulated as a hazardous air pollutant (CAA) ❊ Priority toxic pollutant under the CWA

[a] Toxic Substances Control Act
[b] Federal Insecticide, Fungicide, and Rodenticide Act
[c] Clean Air Act
[d] Clean Water Act
[e] Effluent limits and standards for all POPs are authorized under the CWA.
[f] National Recommended Water Quality Criteria-Correction. US-EPA 822-Z-99-001. Office of Water.

- Acute toxicity in rats, estimated as the acute dose that would kill half the experimental rats (lethal dose 50%; LD_{50}), noting that within species there is a spectrum of individual resistance to toxic effects, and that between-species LD_{50} values can vary to a large degree (Meister, 2000).
- Chronic toxicity reference dose (RfD) in the United States, which is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. The RfD is based on experimental or epidemiologically determined doses at which there is no statistically or biologically significant indication of toxic effects. RfDs include uncertainty factors to account for animal-to-human interspecies differences, variability between humans, and database deficiencies (*www.epa.gov/IRIS*).
- History of production and use in the United States, providing a brief summary of historical manufacturing data, years during which these activities occurred, and when they were curtailed and ultimately ceased (UNEP, 2000).
- International production and use, summarizing data collected by the United Nations Environment Programme (UNEP) during the POPs negotiation and from national requests for chemical-specific use exemptions under the Stockholm Convention (UNEP, 2000).

1. Intentionally Produced POPs: Pesticides

The nine pesticide POPs were introduced into commercial use after World War II and dramatically changed modern pest control. These compounds were effective against a wide range of pests, often for extended periods of time. Ironically, the chemical property of long environmental persistence that enhanced the pesticides' efficacies also increased their environmental destructiveness. Repeated applications of the pesticide POPs (Figure 2-1) led to widespread contamination, impacts on nontarget species, and residues in foods.

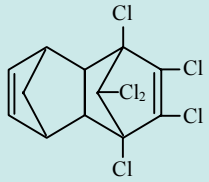
Figure 2-1. Aerial spraying of pesticides on crops.
Photo: U.S. EPA

Cyclodiene Insecticides

Aldrin, dieldrin, endrin, chlordane, heptachlor, and mirex are all cyclodiene organochlorine insecticides. They are highly persistent compounds, exhibiting especially high resistance to degradation in soil. Aldrin, dieldrin, and particularly endrin exhibit high acute mammalian toxicity (oral LD_{50}s between 7 and 90 mg/kg); chlordane, heptachlor, and mirex are moderately acutely toxic (oral LD_{50}s between 100 and 400 mg/kg) (Meister, 2000). Due to the persistence of these insecticides, surface application on food crops proved problematic because residues remained on produce after harvest. The cyclodienes were, however, widely used as soil insecticides in the United States, particularly against termites and soil-dwelling insects that attack the roots of crop plants. Although the agricultural uses of the cyclodienes were cancelled by the EPA during the 1970s, they continued to be used under restricted conditions as termiticides well into the 1980s (Ware, 1989).

Aldrin, dieldrin, and endrin are extremely similar chemically, the latter two being stereoisomers of each other (Tables 2-2, 2-3, and 2-4). Aldrin is rapidly transformed into dieldrin both in air and in soil (Glotfelty, 1978; Gannon and Bigger, 1958). Endrin was used initially as a general insecticide, particularly on nonfood crops such as cotton and tobacco. It also served as an avicide (bird-killing agent) and rodenticide, exploiting its high toxicity

Table 2-2. Aldrin



Chemical information	CAS number: 309-00-2 Molecular formula: $C_{12}H_8Cl_6$ Molecular weight: 364.92
Persistence	Half-lives: < 0.4 days (air) ~1.1–3.4 years (water) ~1.1–3.4 years (soil)
Properties related to environmental transport	Henry's law constant: 4.96 x 10^{-4} atm-m^3/mol at 25°C Vapor pressure: 2.31 x 10^{-5} mm Hg at 20°C Solubility in water: 17-180 µg/L at 25°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{6.5}$ BAF/BCF ~ 6100
Acute toxicity	Oral LD_{50} = 38-67 mg/kg Dermal LD_{50} = 98 mg/kg
Chronic toxicity	Reference dose (RfD) = 3 x 10^{-5} mg/kg/day (UF = 1000)
US production history	Years produced[a]: 1948-1974 Peak usage in 1966[b]: 8,600 tonnes (19 million lbs) No present production, import, or export in USA
US use history	– Insecticide on cotton, citrus, and corn crops – Termiticide All uses canceled by 1987
Current (2001) international production and reported use	– No known current producers – Reported use as an ectoparasiticide in one country

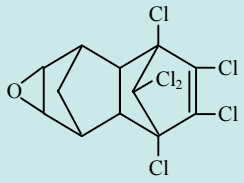
[a]Sittig, 1985.
[b]ATSDR, 1993a.

to vertebrates. Aldrin and dieldrin, which were inexpensive to manufacture, were produced in large quantities in the United States during the 1960s and used most frequently as insecticides to control soil pests affecting corn and citrus crops, as well as termites in buildings and other structures.

The long persistence of dieldrin (whether from initial dieldrin formulations or from aldrin formulations) and its acute toxicity to nontarget wildlife led to environmental concerns, particularly after numerous mass bird deaths were associated with the use of dieldrin as a seed treatment (Beyer et al., 1996). However, long before regulatory actions to restrict or cancel these insecticides were instigated, technical problems had emerged because of their broad-spectrum toxicity and long persistence. The production and uses of aldrin, dieldrin, and endrin declined significantly by the mid-1970s in the United States, due in large part to the development of resistance in target pests (Ware, 1989) and problems with secondary pest upsets caused by the elimination of natural predators (DeBach and Rosen, 1991). The development of other pesticides (organophosphates, carbamates, synthetic pyrethroids and, more recently, insect growth regulators) that were considered more effective and less environmentally destructive also reduced demand for the cyclodiene insecticides (ATSDR, 1993a).

Aldrin was also produced and widely used overseas, particularly for the control of cotton pests and termites, until human health and environmental concerns led to bans in many countries (Pearce, 1997). Dieldrin was initially used for indoor house spraying to control mosquitoes that carry malaria, but it is no longer used or recommended by the World Health Organization (WHO) because of its high mammalian toxicity and resistance problems among many target mosquitoes (Rozendaal, 1997; Shidrawi, 1990). Dieldrin was also donated to African countries until the late 1980s to control plagues of migratory locusts, creating numerous

Table 2-3. Dieldrin



Chemical information	CAS number: 60-57-1 Molecular formula: $C_{12}H_8Cl_6O$ Molecular weight: 380.92
Persistence	Half-lives: ~1.3–4.2 days (air) ~1.1–3.4 years (water) ~1.1–3.4 years (soil)
Properties related to environmental transport	Henry's law constant: 5.8 x 10^{-5} atm-m^3/mol at 25°C Vapor pressure: 1.78 x 10^{-7} mm Hg at 20°C Solubility in water: 140 µg/L at 20°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{5.2}$ BAF/BCF ~ 920,000
Acute toxicity	Oral LD_{50} = 37-87 mg/kg Dermal LD_{50} = 60-90 mg/kg
Chronic toxicity	Reference dose (RfD) = 5 x 10^{-5} mg/kg/day (UF = 100)
US production history	Years produced[a]: 1948 – 1974 Peak US usage in 1966[b]: 455 tonnes (1 million lbs) No present production, import, or export in USA
US use history	– Insecticide control on cotton, citrus, and corn crops – Termiticide All uses canceled by 1987
Current international production and use	– No known current producers – Insecticide used until 1980s for control of plague locusts. No current uses except for agricultural operations in one country (for 2 years to exhaust existing stocks)

[a] Sittig, 1985.
[b] ATSDR, 1993a.

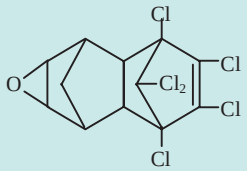
stockpiles of obsolete chemicals that remain an environmental hazard in many countries (FAO, 1998) (Figure 2-2). Newer pesticides, including phenylpyrazole compounds, are now available for locust control, although the economic costs and environmental damage associated with these large-scale pesticide applications suggest that information-based integrated pest management approaches using less total pesticide are more appropriate locust control strategies (Showler and Potter, 1991).

Figure 2-2. Obsolete drums of dieldrin, previously used for locust control, Morocco.

Photo: Janice Jensen

Chlordane, heptachlor, and mirex were used extensively in the United States in the 1950s and 1960s for the control of soil insects in agricultural crops, and for termites and other structural pests in buildings (Figure 2-3). Chlordane and heptachlor have very similar chemical structures (Tables 2-5 and 2-6). Chlordane was manufactured and used as a complex mixture of related compounds (cis- and trans-chlordane, heptachlor, nonachlor, plus many lesser compounds), often referred to as technical chlordane (Sovocool et al., 1977). It was often applied

Table 2-4. Endrin



Chemical information	CAS number: 72-20-8 Molecular formula: $C_{12}H_8Cl_6O$ Molecular weight: 380.92
Persistence	Half-lives[a]: ~2.2 days (air) ~1.0–4.1 years (water) ~4–14 years (soil)
Properties related to environmental transport	Henry's law constant[b]: 6.36 x 10^{-6} atm-m^3/mol at 25°C Vapor pressure: 7 x 10^{-7} mm Hg at 25°C Solubility in water: 220-260 µg/L at 25°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{5.2}$ BAF/BCF ~ 7,000
Acute toxicity	Oral LD_{50} = 7-15 mg/kg Dermal LD_{50} = 15 mg/kg (female)
Chronic toxicity	Reference dose (RfD) = 3 x 10^{-4} mg/kg/day (UF = 100)
US production history	Years produced[c]: 1951-1986 Peak US usage in 1962[d]: Estimated 2270–4545 tonnes (5 to 10 million lbs) No present production, import, or export in USA
US use history	– Insecticide on cotton crops – Rodenticide in orchards – All uses canceled by 1991
Current international production and use	– No known current producers – No current use reported

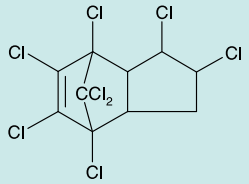
[a]Air: HSDB, 2002; Burton and Pollard, 1974. Water: Sharom et al., 1980; Callahan et al., 1979. Soil: Menzie, 1972; HSDB, 1997.
[b]HSDB, 2002.
[c]ATSDR, 1996a.
[d]IARC, 1974.

directly to soil to create a chemical barrier against subterranean termites, frequently remaining effective for 25 years or more in temperate areas (Grace et al., 1993). Heptachlor was applied both directly to soil and seeds for agricultural uses and to wood for termite protection (ATSDR, 1993b). Heptachlor is converted in the environment to heptachlor epoxide, prolonging its persistence and toxicity. The last registered use for heptachlor in the United States, now cancelled, was as an insecticide in small containers placed in cable boxes in the southeast to prevent nest building by fire ants in electrical equipment. Registered chlordane uses in the United States were cancelled by 1988 in response to evidence of human exposure through accumulation of chlordane in fat, and human cancer risks based on animal bioassay results. Both chlordane and heptachlor are still used in several African, Asian, and Eastern European countries for termite control (UNEP, 2000). Mirex, structurally similar to the now deregistered cyclodiene insecticide chlordecone (Kepone), was produced in smaller quantities and used for ant control, often in the form of a bait (Table 2-7). Mirex was also used in the United States as a fire retardant additive (U.S. EPA, 1998).

Figure 2-3. Subterranean worker termites, a target of chlordane and some other POPs pesticides.

Photo: Clemson University Cooperative Extension Service - USDA joint project

Table 2-5. Chlordane



Chemical information	CAS number: 57-74-9 Molecular formula: $C_{10}H_6Cl_8$ Molecular weight: 409.78
Persistence	Half-lives: ~1.3–4.2 days (air) ~1.1–3.4 years (water) ~1.1–3.4 years (soil)
Properties related to environmental transport	Henry's law constant: 4.8 x 10^{-5} atm-m^3/mol at 25°C Vapor pressure: 1 x 10^{-6} mm Hg at 20°C Solubility in water: 56 µg/L at 25°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ 10^6 BAF/BCF ~ 250,000
Acute toxicity[a]	Oral LD_{50} = 283 mg/kg Dermal LD_{50} = 580 mg/kg (rabbit)
Chronic toxicity	Reference dose (RfD) = 5 x 10^{-4} mg/kg/day (UF = 300)
US production history	Years produced[b]: 1946 – 1997 Average annual US usage prior to 1983[b]: >1600 tonnes (3.6 million lbs) No present production, import, or export in USA
US use history	– Insecticide in agriculture and home gardens – Termiticide – All uses canceled by 1988
Current (2001) international production and use	– China, Singapore[c] – Chlordane is still used in a number of countries in Africa and Asia, primarily as a termiticide

[a]Ware, 1989.
[b]EPA, 1998.
[c]The basic producers are Sino Agro-Chemical Industry Ltd. (China) and Agsin Pte. Ltd. (Singapore) (Meister, 2000).

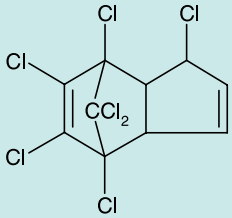
A number of alternative chemical control strategies can now be used effectively to replace the cyclodienes, although most do not exhibit the same persistence in soil. These include long-acting organophosphate pesticides and several synthetic pyrethroids (Mauldin et al., 1987; Su et al., 1993; Kard, 1996). Nonchemical alternatives, such as physical barriers and heat treatment, can provide effective and less toxic termite control in buildings (Grace and Yates, 1999; Pearce, 1997; Woodrow and Grace, 1998).

Dichlorodiphenyl trichloroethane (DDT)

DDT was the first organochlorine insecticide developed, and is probably the most famous and controversial pesticide ever made. Worldwide, an estimated 2 million tons have been produced and applied since 1940, primarily in agriculture (Table 2-8) (Ware, 1989; ATSDR, 2000). Unlike many of the other synthetic organic pesticides developed later, DDT exhibited relatively low mammalian toxicity, was initially highly effective at controlling a variety of insect pests, and, perhaps most importantly, was very inexpensive to produce. This unique combination of properties led to DDT's widespread use in public health, beginning with the control of louse-borne typhus during World War II. DDT was a central tool in the malaria eradication programs of the 1950s and 1960s (Figure 2-4). Although the malaria eradication goal proved elusive in much of the tropical world, DDT nonetheless contributed to improved health and saved countless lives in many malarious countries (Oaks et al., 1991).

In the United States, malaria had been largely eradicated prior to the introduction of DDT, although DDT was widely used for nuisance mosquito control. The primary use of DDT was as a broad-spectrum insecticide on agricultural crops, principally cotton (~90% of total use), but also on potatoes, corn, tobacco, and apples, and against

Table 2-6. Heptachlor



Chemical information	CAS number: 76-44-8 Molecular formula: $C_{10}H_5Cl_7$ Molecular weight: 373.32
Persistence	Half-lives: ~1.3–4.2 days (air) ~0.03–0.11 years (water) ~0.11–0.34 years (soil)
Properties related to environmental transport	Henry's law constant: 2.3 x 10^{-3} atm-m^3/mol Vapor pressure: 3 x 10^{-4} mm Hg at 20°C Solubility in water: 180 µg/L at 25°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{5.27}$ BAF/BCF ~ 8,500
Acute toxicity	Oral LD_{50} = 147-220 mg/kg Dermal LD_{50} > 2000 mg/kg (rat); 119-320 mg/kg (rabbit)
Chronic toxicity	Reference dose (RfD) = 5 x 10^{-4} mg/kg/day (UF = 300)
US production history	Years produced[a]: 1953-1997 No present production, import, or export in USA
US use history	– Termiticide – Insecticide for control of fire ants in underground cable boxes – Most uses canceled by 1978, all uses canceled 2000
Current (2001) international production and use	– No known current producers, although an exemption has been requested for use as a pesticide and pesticide solvent – Insecticide for control of termites and other soil insects by several countries – Solvent in pesticides by two countries

[a]ATSDR, 1993b; EPA Office of Pesticide Programs.

forest pests (Ware, 1989; U.S. EPA, 1998; ATSDR, 2000). DDT use in the United States peaked in 1961, but began to decline thereafter because of several technical complications. One problem was mounting resistance, as continual exposure to the heavily used and persistent chemical selected for resistant insects. DDT resistance was observed in apple pests as early as 1954 (Cutright, 1954). By 1984, DDT resistance was documented in 233 species of insects and mites worldwide, including many important agricultural pests (Georghiou, 1986). DDT's broad spectrum of activity against virtually all insects, pests and beneficials alike, and its long environmental persistence also led to serious secondary pest problems. Secondary pests are normally suppressed by natural predators, but their populations spiral upward out of control when the predators are killed by DDT. For example, an important pest of California citrus, the cottony cushion scale, was controlled by the Vedalia beetle until growers in 1946 applied DDT to control a different pest (Figure 2-5). The DDT applications killed off the predator but not the white-colored scale, whose populations

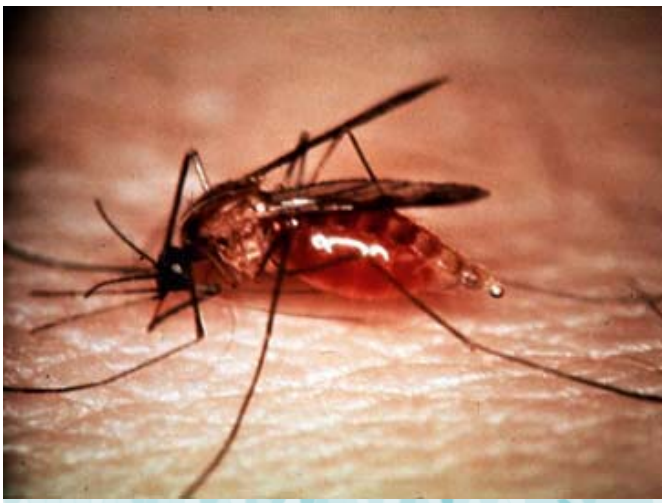
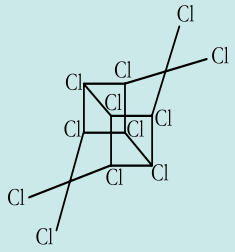


Figure 2-4. Anopheles mosquito, vector of malaria and target of DDT.
Photo: WHO/TDR/Gwadz

Table 2-7. Mirex



Chemical information	CAS number: 2385-85-5 Molecular formula: $C_{10}Cl_{12}$ Molecular weight: 545.5
Persistence	Half-lives: ~4.2–12.5 days (air) ~0.34–1.14 years (water) > 3.4 years (soil)
Properties related to environmental transport	Henry's law constant[a]: 8.3 x 10^{-3} atm-m^3/mol at 20°C Vapor pressure: 3 x 10^{-7} mm Hg at 25°C Solubility in water[a]: 5.45 x 10^{-5} µg/L at 25°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{6.9}$ BAF/BCF ~ 2,400,000
Acute toxicity	Oral LD_{50} = 306 mg/kg Dermal LD_{50} = 800 mg/kg (rabbit)
Chronic toxicity	Reference dose (RfD) = 2 x 10^{-4} mg/kg/day (UF = 300)
Past production in USA	Years produced[b]: 1954-1976 Total US production ~1500 tonnes (3.3 million lbs). Peak US usage between 1963 and 1968[c]. No present production, import, or export in USA
History of use(s) in USA	– Insecticide for fire ant control – Industrial fire retardant additive All pesticide uses canceled by 1977
Current (2001) international production and use	No known current producers. China has requested a production exemption for termiticide manufacture An exemption has been requested by two countries for use in termite control

[a]AMAP, 1998.
[b]EPA, 1998.
[c]EPA, 1998. Total is for Hooker Chemical Company only. Two other US companies also manufactured mirex during this time.

exploded, covering trees so densely the orchards looked snow-covered. The Vedalia beetle had to be reintroduced at a cost of up to $1 per beetle to regain control of the scale (DeBach and Rosen, 1991).

Figure 2-5. Vedalia beetles, a nontarget species killed by DDT, eating cottony cushion scale.
Photo: J.K. Clark, University of California IPM project

At the same time that DDT use peaked in the 1950s and 1960s, there was mounting evidence of the environmental impacts from DDT and its long-lived metabolites, DDE and DDD (Ratcliffe, 1967; Wurster et al., 1965; Riseborough, 1972). These DDT, DDE, and DDD concentrations are often added together and reported as sum-DDT, s-DDT, or Σ-DDT values. Their impacts were particularly severe on bird populations through eggshell thinning and chick mortality in raptors (e.g., bald eagles, falcons) and oceanic birds (e.g., pelicans) (Beyer et al., 1996) (Figure 2-6). Although DDT was considered to exhibit relatively low acute mammalian toxicity, concerns were being expressed about potential chronic reproductive impacts on humans (O'Leary et al.,

Table 2-8. DDT

Chemcial information	CAS number: 50-29-3 Molecular formula: $C_{14}H_9Cl_5$ Molecular weight: 354.49
Persistence	Half-lives: ~4.2–12.5 days (air) ~0.34–1.14 years (water) ~1.1–3.4 years (soil)
Properties related to environmental transport	Henry's law constant: 1.29 x 10^{-5} atm-m^3/mol at 23°C Vapor pressure[a]: 1.6 x 10^{-7} mm Hg at 20°C Solubility in water: 1.2-5.5 µg/L at 25°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{6.19}$ BAF/BCF ~ 1,800,000
Acute toxicity in mammals[b]	Oral LD_{50} = 87 mg/kg Dermal LD_{50} = 1,931 mg/kg (rabbit)
Chronic toxicity	Reference dose (RfD) = 5 x 10^{-4} mg/kg/day (UF = 100)
US production history	Years produced[b,c]: 1940 – (none by 1993) Peak US production in 1962[c]: 82,000 tonnes (180 million lbs) (Metcalf, 1995) No present production, import, or export in USA. Contaminant of the pesticide dicofol.
US use history	– Broad spectrum insecticide on many crops – Most uses canceled by 1972. All uses canceled by 1989
Current (2001) international production and use	Production: China, India Insecticide used in at least 25 countries for control of insect vectors of human disease, particularly malaria. Used in the production of dicofol.

[a]HSDB, 2002.
[b]Ware, 1989.
[c]EPA, 1998.

1970; Saxena et al., 1981; Wassermann et al., 1982). Subsequent information has shown p,p'-DDE, a DDT metabolite, to bind to the androgen receptor, antagonizing androgen action (Kelce et al., 1995, 1997; Gray et al., 1999; Maness et al., 1998; NAS, 1999). A recently published human epidemiological study has demonstrated an association between DDT concentrations and increased preterm human births, a major contributor to infant mortality. Longnecker et al. (2001) analyzed frozen maternal serum samples that had been collected between 1959 and 1965 and stored as part of the U.S. Collaborative Perinatal Project (CPP). During this time of peak DDT use in the United States, the median DDE concentration of 25 mcg/L was several-fold higher than current U.S. levels. Taking into consideration data on potential confounding variables collected during this study (age, birth order, socioeconomic status, etc.), the association of increasing serum DDE concentrations with preterm birth was highly statistically significant (Figure 2-7, trend $p<0.0001$). Dose-response data were consistent with serum DDE levels above 10 mcg/L affecting the risk of preterm birth. These human epidemiological findings warrant consideration when balancing the risks of DDT against its benefits for malaria vector control and the costs of alternatives.

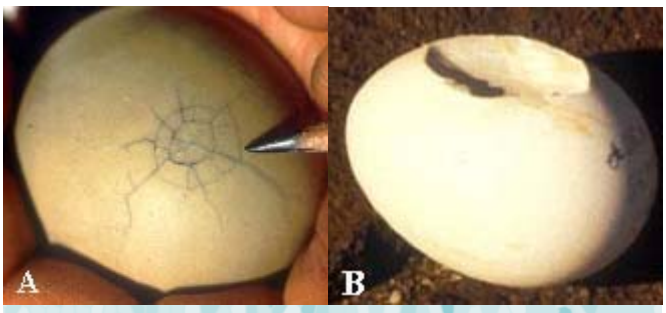
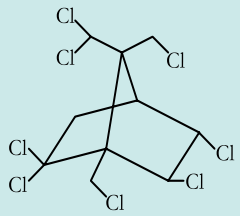


Figure 2-6. Bird eggshell effects after population DDE exposure. A. Cracked shell. B. Dented shell.
Photo: US FWS

All uses of DDT in the United States were cancelled by EPA in 1972, primarily because of

Table 2-9. Toxaphene[a]



Chemical information	CAS number: 8001-35-2 Molecular formula: $C_{10}H_{10}Cl_8$ Molecular weight: 413.82
Persistence	Half-lives: ~4.2–12.5 days (air) >3.4 years (water) >3.4 years (soil)
Properties related to environmental transport[a]	Henry's law constant: 6.3 x 10^{-2} atm-m^3/mol Vapor pressure[b]: 5 x 10^{-6} – 0.4 mm Hg at 20°C Solubility in water: 550 µg/L at 20°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient)[c] ~ $10^{4.8}$–$10^{6.6}$ BAF/BCF ~ 1,100,000
Acute toxicity in mammals[d]	Oral LD_{50} = 40 mg/kg Dermal LD_{50} = 600 mg/kg (rabbit)
Chronic toxicity	Reference dose (RfD) = under development
US production history	Years produced[e]: 1946-1990s Peak US production in 1972[b]: 21,000 tonnes (46 million lbs) No present production, import, or export in USA
US use history	– Insecticide to control cotton pests and plague grasshoppers and for mange control on cattle – Most uses canceled by 1982 – All uses canceled by 1990
Current (2001) international production and use	No known producers No known registered uses

[a]Toxaphene is a complex mixture of various chlorinated bornanes and camphenes. There are discrepancies noted in the literature regarding physical properties; see ATSDR 1996b for details.
[b]ATSDR, 1996b.
[c]Fisk et al., 1999.
[d]Ware, 1989.
[e]EPA, 1998.

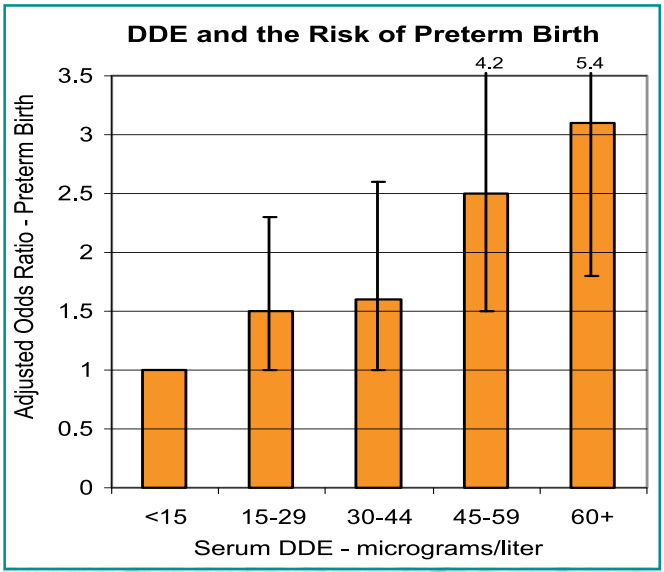
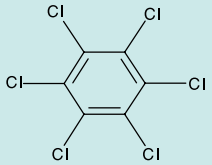


Figure 2-7. Graph of the association between maternal serum DDE levels and preterm birth risk. Adjusted odds ratios and 95% confidence intervals (from Longnecker et al., 2001).

positive cancer results in rodent bioassays. DDT production in the United States for export occurred until at least 1985 (ATSDR, 2000). DDT use for disease (mostly malaria) vector control continues in an estimated 25 or more developing countries, primarily because of its low cost and persistence (WHO, 1999). Many other insecticides are available for indoor house spraying (Chavasse and Yap, 1997), but DDT's lower cost remains an advantage, at least in some countries (Walker, 2000). Other approaches to disease control such as case detection and treatment, or pyrethroid-treated bednets, may prove more cost-effective and sustainable in the long term (Goodman et al., 1999). For the future, the Stockholm Convention strives for a balance among the public health benefits of DDT for malaria control, the availability and cost of alternatives, and the impacts of DDT on ecosystems

Table 2-10. Hexachlorobenzene (HCB)



Chemical information	CAS number: 118-74-1 Molecular formula: C_6Cl_6 Molecular weight: 284.78
Persistence	Half-lives: ~ 417–1250 days (air) >3.4 years (water) >3.4 years (soil)
Properties related to environmental transport	Henry's law constant: 7.1 x 10^{-3} atm-m^3/mol at 20°C Vapor pressure: 1.089 x 10^{-5} mm Hg at 20°C Solubility in water: 40 µg/L at 20°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{5.5}$ BAF/BCF ~ 110,000
Acute toxicity in mammals[a]	Oral LD_{50} = 3,500 mg/kg
Chronic toxicity	Reference dose (RfD) = 8 x 10^{-4} mg/kg/day (UF = 100)
US production history	Years produced as a fungicide[a]: 1945–late 1970s HCB is produced as a byproduct or contaminant of certain chemicals. Estimated annual US production as a byproduct or impurity range from 68–689 tonnes (0.15–1.52 million lbs), the majority of which is destroyed onsite
US use and source history	– Fungicide for seed and wheat – Currently imported for use as an intermediate; import anticipated to cease in future to comply with the closed-system, site-limited exemption
Current (2001) international production and use	– No current production for fungicide applications. – No current reported uses as a fungicide. – Several countries have requested exemptions as an intermediate, a closed-system, site-limited intermediate, or contaminant in pesticides.

[a]ATSDR, 1996c.

and, potentially, human health. While working toward a goal of reducing and ultimately eliminating the use of DDT, parties may use DDT only for disease vector control in accordance with World Health Organization recommendations (UNEP, 2000).

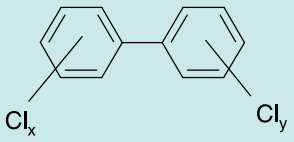
Toxaphene

Toxaphene is a mixture of at least 670 chlorinated terpenes, produced through chlorinating camphene (Table 2-9; image shown is a chlorinated bornane structure). Its primary use was on cotton, where it was generally applied with another insecticide, first DDT and subsequently organophosphate insecticides such as methyl parathion. U.S. production of toxaphene peaked in 1972, when it was the most heavily manufactured pesticide in the country, largely as a replacement for DDT. Toxaphene was also used as a piscicide to eradicate fish species considered undesirable for sport fishing in Canada and the northern United States (U.S. EPA, 1998). Fish restocking efforts were sometimes difficult because of the longevity of active toxaphene residues, highlighting the problem of environmental persistence. Most registered uses in the United States were withdrawn in 1982, on the basis of studies showing tumors in toxaphene-exposed laboratory animals, evidence of acute toxicity to aquatic organisms, and impacts on nontarget animals including endangered species.

Worldwide, toxaphene was one of the most widely used agricultural insecticides during the 1960s and 1970s, primarily for control of cotton pests. Between 1950 and 1993, when all production ceased in the United States, an estimated 2.6 billion pounds had been manufactured worldwide (ATSDR, 1996b). Stockpiles of toxaphene continue to threaten the environment in some areas. For example, in Nicaragua, 230 metric tonnes of toxaphene were recently reported stockpiled in a zone at high risk for earthquakes near Lake Managua, a unique ecosystem

Table 2-11. Polychlorinated Biphenyls (PCBs)

Example: *Aroclor 1254 mixture*



Chemical information	CAS number[a]: 11097-69-1 Molecular formula: $C_{12}Cl_{(x+y)}$ Molecular weight: 328[a] (188.7–498.7, PCB range)
Persistence	Half-lives: ~4.2 days (air) [PCB congener group] ~5.7 years (water) [PCB congener group] ~1.14 years (soil) [PCB congener group]
Properties related to environmental transport[a]	Henry's law constant: 2.0 x 10^{-3} atm-m^3/mol at 25°C Vapor pressure: 7.71 x 10^{-5} mm Hg at 25°C Solubility in water: 57 µg/L at 24°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{6.5}$ BAF/BCF ~ 3,000,000
Acute toxicity in mammals	Oral LD_{50} = 1,010 mg/kg
Chronic toxicity	Reference dose (RfD) = 2 x 10^{-5} mg/kg/day (UF = 300), under review ATSDR[a] chronic MRL = 0.02 mcg/kg/day (UF = 300)
US production history	Years PCBs produced: 1929–1977; banned under TSCA Section 6(e) effective 1979 Peak PCB production 1970, ~3900 tonnes (8.5 million pounds) annually for all PCBs No present production, import, or export in USA
Current (2001) US source and use history	Use allowed if in certain existing equipment; environmentally sound destruction/disposal after service life of equipment
Current (2001) international production and use	Manufacture discontinued[b] No recorded new uses; widespread residual use in existing equipment and products

[a]ATSDR, 1997.
[b]AMAP, 2000.

and home to many rare species of wildlife (EARTH, 2000).

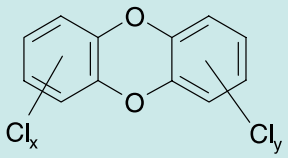
Hexachlorobenzene

Hexachlorobenzene (HCB) is included under all three general categories of POPs: as a pesticide, an industrial chemical, and an unintended byproduct (Table 2-10). HCB was introduced as a pesticide in the United States in 1945 for antifungal seed and soil treatment. All U.S. pesticide uses were canceled in 1985 (Ware, 1989; ATSDR, 1996c). The human toxicity of HCB was sadly demonstrated in Turkey during the late 1950s, when an estimated 3,000 to 4,000 people ingested bread inadvertently made from HCB-treated grain at approximately 2 kg HCB per 1,000 kg wheat. The HCB led to porphyria cutanea tarda in adults, a metabolic defect of blocked hemoglobin synthesis that causes light-sensitive skin lesions, colored urine, and, in some cases, death. All children born to porphyric mothers during this epidemic died, with an estimated 1,000 to 2,000 children dying from related skin lesions, exacerbated by the HCB transfer in breast milk (Peters et al., 1982, 1987).

Industrial uses of HCB have varied, including pyrotechnic coloring in military ordnance, synthetic rubber production, and as a chemical intermediate in dye manufacture and organic chemical synthesis (Bailey, 2001). There are no current uses of HCB as an end product in the United States, although it is imported for use as a production intermediate. An exemption is available under the Stockholm Convention for the use of HCB as a closed-system, site-limited intermediate. HCB is still produced as an unintended byproduct during the manufacture of chlorinated solvents and as an impurity of certain pesticides

Table 2-12. Polychlorinated Dibenzo-*p*-Dioxins

Example: *2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)*



Chemical information for TCDD	CAS number[a]: 1746-01-6 Molecular formula: $C_{12}H_4Cl_4O_2$ Molecular weight: 322.0
Persistence	Half-lives: 4.2–12.5 days (air) [range for PCDDs] ~0.11–0.34 years (water) [range for PCDDs] ~0.34–1.1 years (soil) [range for PCDDs]
Properties related to environmental transport[a]	Henry's law constant: $1.6 \times 10^{-5} - 1.0 \times 10^{-4}$ atm m^3/mol at 25°C Vapor pressure: $1.5 \times 10^{-9} - 3.4 \times 10^{-5}$ mm Hg at 25°C Solubility in water: 0.019 µg/L at 25°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{6.9}$ BAF/BCF ~ 130,000
Acute toxicity in mammals[a]	Hamster oral LD_{50} = 5051 mcg/kg Rat oral LD_{50} = 22 – 165 mcg/kg Mink oral LD_{50} = 4.2 mcg/kg Guinea pig oral LD_{50} = 0.6 mcg/kg
Chronic toxicity	Under EPA review: *www.epa.gov/ncea/dioxin.htm* ATSDR[a] chronic MRL = 0.000001 mg/kg/day (UF = 100)
Major sources (US and international)	Municipal and medical waste incineration Open and barrel burning of waste Elemental chlorine bleach pulp and paper manufacture Certain thermal processes in the metallurgical industry Selected chemical manufacturing processes, e.g., 2,4,5-trichlorophenol production (now ceased)

[a]ATSDR, 1998.

(picloram, PCNB, chlorothalonil, DCPA, and PCP) (ATSDR, 1996c). It is also created and emitted during incineration practices. Due to its chemical structure, HCB is extremely stable, globally distributed, and considered among the most persistent of all POPs.

2. Intentionally Produced POPs: Industrial Chemicals

Polychlorinated Biphenyls (PCBs)

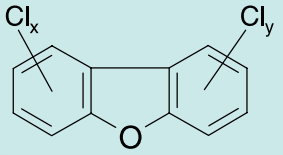
PCBs are a mixture of synthetic organic chemicals with the same basic chemical structure and similar physical properties, ranging from oily liquids to waxy solids (Table 2-11). Because of their nonflammability, chemical stability, high boiling point, and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications, including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics, and rubber products; and in pigments, dyes, and carbonless copy paper. First manufactured in 1929, more than 1.5 billion pounds of PCBs were manufactured in the United States (plus elsewhere in the world) before domestic production ceased in 1977.

PCBs are principally addressed under the Stockholm Convention as intentionally produced industrial chemicals. PCBs are also closely linked to the polychlorinated dioxin and furan byproduct POPs for the following reasons:

- Coplanar PCBs have a similar chemical structure and spatial configuration to the polychlorinated dioxins and furans, and much of the toxicity of all three congener groups is linked through a common mode of action (mediated through binding to the aryl hydrocarbon [Ah] receptor in the cell) and the concept of dioxin toxicity equivalence (see under byproduct POPs).

Table 2-13. Polychlorinated Dibenzofurans

Example: *2,3,7,8-Tetrachlorodibenzofuran (TCDF)*



Chemical information for TCDF	CAS number[a]: 51207-31-9 Molecular formula: $C_{12}H_4Cl_4O$ Molecular weight[a]: 306.0
Persistence	Half-lives: 4.2–12.5 days (air) [range for PCDFs] ~0.11–0.34 years (water) [range for PCDFs] ~1.1–3.4 years (soil) – for all furans [range for PCDFs]
Properties related to environmental transport[b]	Henry's law constant[a]: 1.48 x 10^{-5} atm-m^3/mol Vapor pressure[a]: 9.21 x 10^{-7} mm Hg at 25°C Solubility in water[b]: 0.692 µg/L at 26°C
Bioaccumulation	K_{ow} (octanol-water partition coefficient) ~ $10^{6.1}$ BAF/BCF ~ 61,000
Acute toxicity in mammals	See for dioxins, based on TEQ values
Chronic toxicity	Under review: *www.epa.gov/ncea/dioxin.htm*
Major sources (US and international)	See for dioxins

[a]ATSDR, 1994.
[b]HSDB, 2002.

- Burning and high-temperature treatment of PCB mixtures can lead to the creation of polychlorinated dibenzofurans (PCDFs), further exacerbating the potential toxicity from PCBs. This occurred during the Yusho and Yu-Cheng poisoning incidents in Japan and Taiwan, respectively, where the cooking of rice oil contaminated with PCBs resulted in the production of PCDFs. The combined presence of PCBs and PCDFs in the cooked food caused chloracne and other toxic effects in the adults, and fetal mortality and developmental defects in their offspring (Rogan *et al.*, 1988; Hsu *et al.*, 1994).

- Like polychlorinated dioxins and furans, PCBs can be produced in small amounts during incineration processes and are therefore included in the unintentional byproduct category under the Stockholm Convention.

Beyond the rice oil contamination poisonings, PCB toxicity has been demonstrated in wildlife and humans following environmental exposures. As detailed in the chapters to follow, PCBs have been associated with reproductive effects in wildlife populations in the Great Lakes (Chapter 3) and far out in the North Pacific Ocean (Chapter 6). For humans, increased PCB concentrations in children from environmental exposures are associated with neurodevelopmental impacts (Fein *et al.*, 1984; Jacobson and Jacobson, 1996), findings supported by followup studies in the Great Lakes region (Lonky *et al.*, 1996; Stewart *et al.*, 2000) and in Dutch children (Patandin *et al.*, 1999) (Chapter 4).

Concern over the toxicity and persistence of PCBs in the environment led Congress in 1976 to enact Section 6(e) of the Toxic Substances Control Act (TSCA). This includes prohibitions on the manufacture, processing, and distribution in commerce of PCBs. Under the Stockholm Convention there is a global ban on the manufacture of PCBs (UNEP 2000). Because of the magnitude of past use of PCBs and the continuing economic importance of previously manufactured PCB-containing equipment, countries must make determined efforts to identify, label, and remove PCB-containing equipment from use by 2025. During this interval, the Stockholm Convention mandates a series of measures to reduce exposures and risk from further releases of PCBs to the environment, accompanied by prohibitions on reuse and export and import, except for the purpose of environmentally sound waste disposal.

3. Byproduct POPs

Polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF)

The term "dioxin" refers to a group of chemical compounds that share certain similar chemical structures and toxicological characteristics. Thirty toxic dioxin-like compounds exist and are members of three closely related families: PCDDs, PCDFs, and coplanar PCBs. The term dioxin is also used for the most well-studied and toxic of the dioxins, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (Table 2-12). PCDDs and PCDFs (Table 2-13) are not created intentionally, but can be produced inadvertently in nature and by a number of human activities. Combustion (Figure 2-8), elemental chlorine bleaching of pulp and paper (Figure 2-9), certain types of chemical manufacturing and processing, and other industrial processes all can create small quantities of dioxins. PCBs are no longer manufactured in the United States, but formerly were widely used in electrical equipment as coolants and lubricants. PCBs can also be formed in a similar manner to dioxins as byproducts of combustion processes (see previously).

Dioxins have been central to a number of environmental controversies in recent decades. Dioxin (2,3,7,8-TCDD in particular) was a contaminant of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) sprayed in Agent Orange defoliant during the Vietnam War (Figure 2-10). Ensuing sprayer (Operation Ranch Hand personnel), soldier, and civilian exposures have resulted in ongoing inquiries, research, and veterans' health benefits compensation (IOM, 1994). In 1976, an explosion at a trichlorophenol herbicide production plant in Seveso, Italy, led to widespread environmental contamination, local livestock and wildlife mortality, very high human exposures and clinical illness (e.g., chloracne, a severe and prolonged acneform condition) (Figure 2-11), and evacuation of the surrounding region (Bertazzi et al., 1998). Residential dioxin exposure and evacuation also occurred at Times Beach, Missouri, following the spraying of dioxin contaminated waste oil for dust control in the early 1970s (Webb et al., 1984). In occupational studies, cancer mortality increases have been reported in several groups of workers exposed to dioxin during herbicide production (Steenland et al., 2001; Ott and Zober, 1996; Becher et al., 1998). The US EPA is currently assessing the impacts of dioxin on the general public in its draft document "Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin (TCDD) and Related Compounds" (*www.epa.gov/ncea/dioxin.htm*).

Figure 2-8. Stack emissions, New Orleans, Louisiana, 1973.
Photo: U.S. EPA

Dioxins have the potential to produce an array of adverse effects in wildlife and humans. Dioxins can alter the growth and development of cells in ways that can lead to many kinds of impacts. These include adverse effects upon reproduction and development, suppression of the immune system, chloracne, and cancer. Although data on risks to children are limited, fetuses, infants, and children may be more sensitive to dioxin exposure because they are exposed during critical windows of development and during rapid growth.

Dioxins are believed to exert these toxic effects in similar ways; that is, they share a common mode of toxicity. As a result, scientists use an approach that adds together the toxicity of individual dioxins in order to evaluate complex environmental mixtures to which people are exposed. Because dioxins differ in their toxic potential, the contribution of each component in

Figure 2-9. Pulp mill effluent, a source of polychlorinated dioxins and furans, Columbia River, 1970s.
Photo: U.S. EPA

Figure 2-10. Aircraft spraying Agent Orange, contaminated with dioxin, in Vietnam.
Photo: USAF

the mixture must be accounted for in estimating the overall toxicity. To do so, international teams of scientists have developed toxicity equivalence factors (TEFs) that compare the toxicity of different dioxins to the most toxic congener, 2,3,7,8-TCDD. Given these factors, the toxicity of a mixture can be expressed in terms of its toxicity equivalents (TEQ), which is the amount of 2,3,7,8-TCDD exposure it would take to equal the combined toxic effect of all the dioxins found in that mixture.

Most dioxin enters ecological food webs by being deposited from the atmosphere, either directly following air emissions or indirectly by processes that return dioxins already present in the environment to the atmosphere. Once they reach the environment, dioxins are highly persistent and

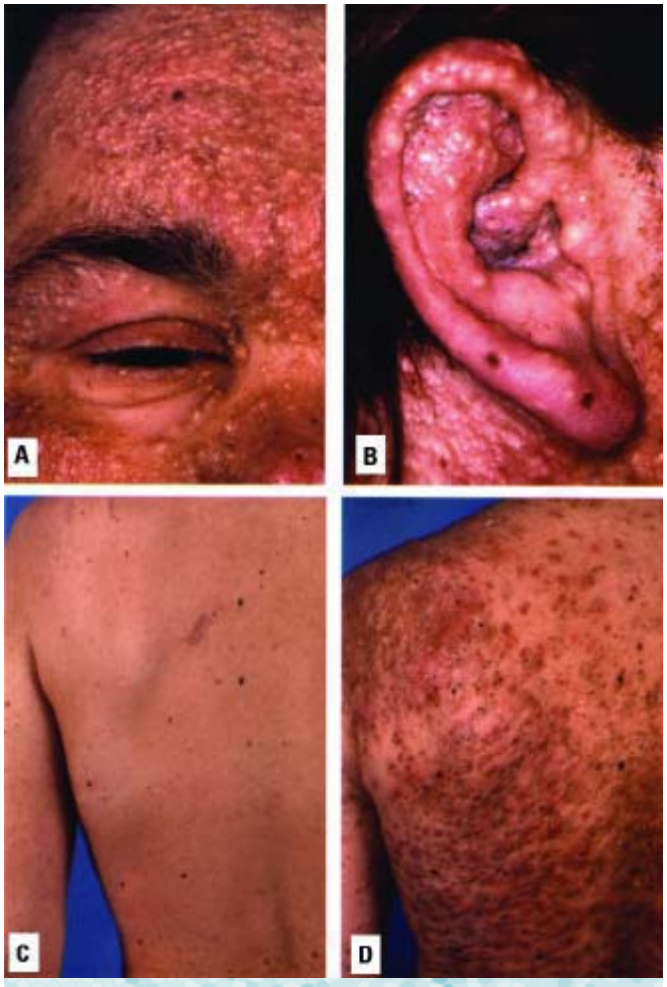


Figure 2-11. Chloracne caused by high exposure to dioxin.
Photo: A. Geusau (Geusau et al., 2001/EHP)

can accumulate in the tissues of animals. Most dioxin exposure occurs through the diet, with more than 95% of dioxin intake for a typical person coming through dietary intake of animal fats. Fortunately, dioxin levels in the environment have declined significantly since the 1970s, following EPA regulatory controls and industry actions. EPA's best estimates of emissions from sources that can be reasonably quantified indicate that dioxin emissions in the United States decreased by about 75% between 1987 and 1995, primarily through reductions in air emissions from municipal and medical waste incinerators. Substantial further declines continue to be documented.

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Appendix. Selected Federal Sites for POPs Toxicity Information

- U.S. Department of Health and Human Services, National Library of Medicine (NLM; *www.nlm.nih.gov*)
  - Medline/PubMed, covering medical literature;
  - Toxnet, toxicology data network;
  - HSDB, Hazardous Substances Data Bank, focusing on the toxicology of potentially hazardous chemicals, with information on human exposure, industrial hygiene, emergency handling procedures, environmental fate, regulatory requirements, and related data
- U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR; *www.atsdr.cdc.gov*)
  - ToxFAQs, summaries of hazardous substance information;
  - Toxicological Profiles of hazardous substances (*www.atsdr.cdc.gov/toxpro2.html*)
- U.S. Environmental Protection Agency (U.S. EPA; www.epa.gov)
  - IRIS, Integrated Risk Information System (IRIS), a database of human health effects that may result from exposure to various substances found in the environment (*www.epa.gov/iris*)
  - PBT, Persistent Bioaccumulative Toxic, home page, containing summaries of PBT chemicals, EPA action plans, and regulatory initiatives (*www.epa.gov/pbt*)
  - ECOTOX database system, providing chemical-specific toxicity values for aquatic life, terrestrial plants, and terrestrial wildlife (*www.epa.gov/med/databases/databases.html#aquire*)
- U.S. Department of the Interior, U.S. Geological Survey, Patuxent Wildlife Research Center (*www.pwrc.nbs.gov/research/ecr/*)
  - Contaminant Exposure and Effects Terrestrial Vertebrates Database
  - Contaminant Hazards Review On-Line

For further information on toxicology data sources, see Toxicology, Volume 157, Issues 1-2, Pages 1–164, 12 January 2001. For federal sources, see specifically Brinkhuis, 2001. Hard copies of many federal documents are available from performing agencies, the Government Printing Office, and/or the National Technical Information Service (NTIS Tel: 703-605-6000).

Chapter 3 Persistent Organic Pollutant Residues and their Effects on Fish and Wildlife of the Great Lakes

Introduction

For nearly two centuries the Great Lakes of North America have been the receiving waters for industrial and municipal wastes. Their story is illustrative of persistent organic pollutant (POPs) impacts in many lakes, streams, and rivers across the United States. The contamination of the Great Lakes with persistent and bioaccumulative compounds, including those designated as POPs under the Stockholm Convention, has been studied in detail and demonstrated to cause population-level effects on wildlife. The large size of the lakes had led to the commonly held, yet mistaken, belief that it was impossible to contaminate them sufficiently to cause adverse effects. As human populations and industrialization of the Great Lakes basin increased, and the complexity and magnitude of the industries grew, it became apparent that it was indeed possible to contaminate the lakes to the extent that adverse effects would be observed. The release of persistent and bioaccumulative compounds eventually resulted in thresholds for adverse effects being exceeded in a number of wildlife populations.

Literally thousands of contaminants can now be found in the tissues of fish and wildlife of the Great Lakes (Figure 3-1). Concentrations of all of the compounds designated for control under the Stockholm Convention have been found at elevated levels in Great Lakes wildlife, and all could have contributed to some of the observed adverse effects in some species. However, several of the POPs were responsible for most of the observed effects. These include the insecticides dieldrin and DDT, the industrial polychlorinated biphenyls (PCBs), and the byproducts of incineration and chemical production, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Although these POPs may have had adverse impacts on a number of species, their effects have been best documented for a few sentinel species such as lake trout (*Salvelinus namaycush*) (Giesy and Snyder, 1998), bald eagles *(Haliaeetus leucocephalus*) (Bowerman et al., 1995, 1998), colonial fish-eating water birds such as the cormorant (*Phalacrocorax auritus*) and Caspian tern (*Sterna caspia*) (Giesy et al., 1994a,b), and the mink (*Mustela vison*) (Giesy et al., 1994c; Tillitt et al., 1996).

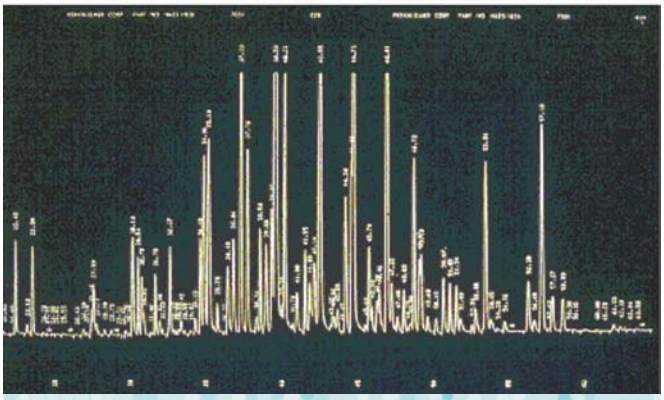

Figure 3-1. Chromatogram showing organochlorine compounds in extract of Great Lakes fish.
Photo: J.P. Giesy

The experiences in the Great Lakes have resulted in a greater understanding of the potential hazards of releasing persistent, bioaccumulative, toxic compounds into the environment. Many of the substances are no longer manufactured or their use is heavily restricted. Concentrations of the most problematic compounds such as DDT and PCBs have declined, but the current rates of decline are very slow, such that it will be a long time before the concentrations in both fish and birds of the Great Lakes environment reach "background" concentrations (Figures 3-2 to 3-4) (Giesy and

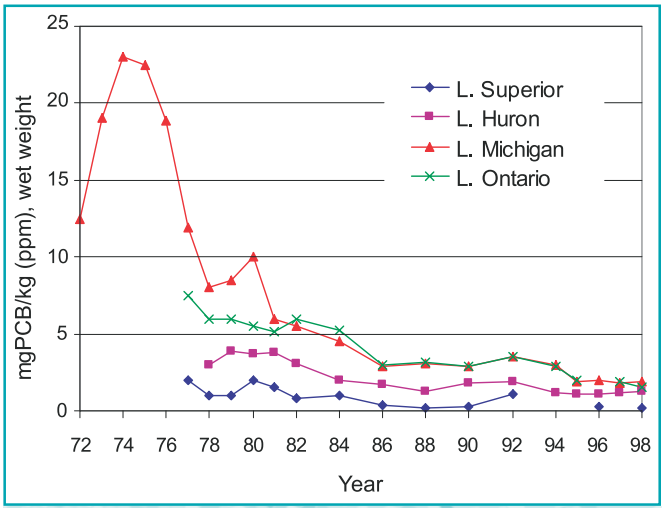

Figure 3-2. Concentrations of PCBs in lake trout from the four uppermost Great Lakes between 1972-1993. Redrawn from MDNR (2001).

Snyder, 1998). The trends for PCBs and DDTs are similar to those for the other Stockholm Convention POPs in both fish and birds. These trends demonstrate several things. First, fish and wildlife became contaminated with POPs residues soon after they were introduced, reaching maximum concentrations in the early 1970s. Second, when use of these compounds was restricted in North America, concentrations began decreasing immediately, and within approximately 20 years had decreased to concentrations

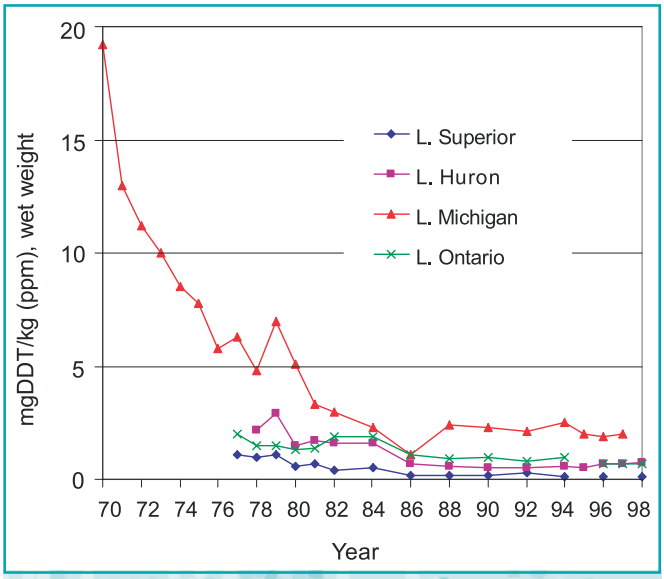

Figure 3-3. Concentrations of total DDTs in lake trout in the four uppermost Great Lakes. Redrawn from MDNR (2001).

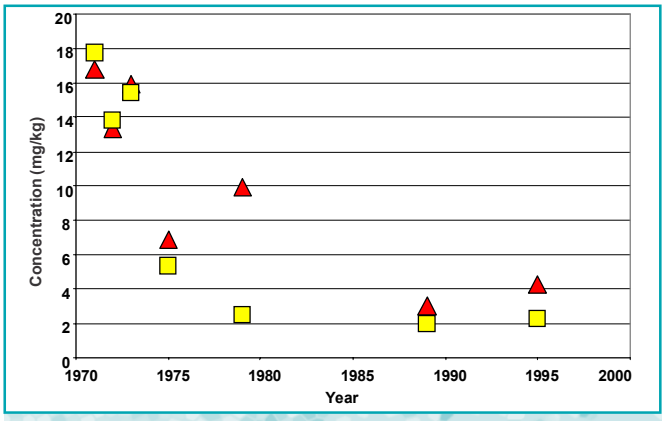

Figure 3-4. Mean wet weight concentrations of PCBs and DDE in double-crested cormorant eggs collected from the Great Lakes (yellow squares = DDE; red triangles = PCBs). Data from Environment Canada, www.ec.gc.ca/ind/English/Toxic/default.cfm

at or near the threshold for effects. Even though the manufacture of these compounds ceased over 25 years ago, they remain at significant concentrations in wildlife. This lingering effect occurs because concentrations of POPs, once introduced into the environment, take a long time to decrease to nondetectable concentrations. Third, current concentrations in biota are no longer decreasing at the same rate that they once were. This slower rate is caused, in part, by continued input to the lakes from reservoir sources and from long-range atmospheric transport (Giesy and Snyder, 1998; Simcik *et al.*, 1999).

In this report, we provide examples of the concentrations of selected POPs in wildlife and the adverse effects that have been caused by exposure to these compounds in the Great Lakes. To do this, we perform a simple risk screening by comparing concentrations of the POPs in tissues or the diets of wildlife with the threshold concentration for adverse effects. This comparison is done by calculating hazard quotients (HQs) (Table 3-1). The HQ is the ratio of the measured concentration divided by the threshold concentration for effects, using either tissue or dietary concentrations. For instance, the concentration of PCBs in fish in the diet of a fish-eating bird can be compared with the dietary No Observable Adverse Effect Level (or concentration) (NOAEL).

Table 3-1. Calculation of Hazard Quotients (HQs)

$$HQ = \frac{\text{Concentration in Fish}}{\text{NOAEL}}$$

HQs were calculated for:

Total PCBs

TCDD-TEQ (calculated)

Calculation of the HQ assumes animals eat only the fish species of interest. This is a conservative or "worst-case" estimate.

The NOAEL is the highest dose or concentration at which no adverse effects have been observed. Effects would be increasingly expected as doses or concentrations rise above the NOAEL value. A HQ value of 10 indicates that the dietary concentration of PCBs is 10-fold greater than the threshold for causing an adverse effect in the piscivorous birds. Said another way, the concentration of PCBs in that species of fish would need to decrease by a factor of 10 before it would not be expected to cause any adverse effects to the birds that ate it. A HQ below 1 indicates that, to the best of our current knowledge, adverse effects would be unlikely to occur.

Fish

Fish from all of the Great Lakes contain measurable concentrations of POPs and many other contaminants (Giesy and Snyder, 1998). In general, fish from Lakes Ontario and Michigan tend to have the greatest concentrations of POPs. Fish from Lake Ontario contain the highest concentrations of the insecticides mirex, DDT, and dieldrin. The lowest concentrations of most persistent, synthetic, chlorinated hydrocarbons are observed in fish from Lake Superior. The relatively high concentrations of toxaphene found in fish from Lake Superior have been the subject of several investigations (Swackhamer et al., 1998; Shanks et al., 1999; Glassmeyer et al., 2000). Concentrations of POPs in fish tissues have decreased by a factor of approximately 25 since maximum concentrations were reached in the lower Great Lakes in the mid-1970s. Although there are differences among species and locations, in general the trends for POPs are either decreasing or stable.

There is considerable difference of opinion in the literature about the extent to which effects on Great Lakes fish should be attributed to and among chemical contaminants. The types of effects that have been reported in Great Lakes fish include changes in behavior, reduced reproductive success, thyroid enlargement and decreased thyroid hormone content, premature sexual maturation in males, loss of secondary sexual characteristics, lessened plasma gonadotropin and gonadal hormone content, lessened egg fertility, and greater than expected embryo mortality and deformities (Leatherland, 1993). There is strong evidence that the endocrine systems of salmonid fish such as lake trout and chinook salmon are impaired, but at this time it is not clear if these observed imbalances are the result of exposure to POPs.

Populations of several fish species have changed drastically from historical population levels. Many factors have been implicated in these declines, such as fishing, habitat loss, changes in genetic strains, and effects of the sea lamprey, in addition to a likely role for POPs and other pollutants. Historically, the reproductive success of salmonid fish in the Great Lakes was much poorer than that of the same species raised on the Pacific coast of the United States (Giesy et al., 1986; Willford et al. 1991). These adverse effects were often attributed to toxic substances, but it was difficult to demonstrate a cause-effect linkage. Specifically, several fish species have exhibited reproductive deficits that could be caused by exposure to POPs, although isolating the causal agent(s) has proven problematic because the mixtures of chemicals to which the fish are exposed vary over time and location.

Of the many contaminants measured in fish and their eggs, DDTs, PCBs, polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) are most often implicated in adverse effects (Giesy and Snyder, 1998).

The highest concentrations of POPs observed in fish eggs were for PCBs (11 mg/kg) and DDT (7 mg/kg). Based on these levels, it was initially hypothesized that DDT and PCBs were most likely responsible for the observed egg mortality and reproductive toxicity. However, although both DDT and PCBs could cause lethality of lake trout eggs and fry in laboratory studies, the concentrations required to cause 30%–50% mortality were as much as 25 times greater than the concentrations observed in the eggs at that time. Thus, although concentrations of DDT observed historically in Great Lakes salmonids were in the range of the thresholds for adverse effects, as determined in laboratory studies, it is unlikely that these concentrations were the major cause of adverse effects seen in the eggs of feral fish from the Great Lakes. Current evidence indicates that PCDD, PCDF, and some of the non- and mono-*ortho*-substituted PCBs are principally responsible for blue-sac syndrome (Figure 3-5) and impaired reproductive performance of salmonid species in the lower Great Lakes, especially for lake trout (Walker and Peterson 1991, 1994a,b; Zabel et al., 1995; Giesy and Snyder, 1998).

Lake Trout

Lake trout in Lake Michigan have not been naturally reproducing successfully for some time. The lake trout populations in both Lakes Michigan and Huron are maintained by stocking programs because natural reproduction of the populations is not sufficient to sustain populations (Willford et al., 1981). Nevertheless, there has been evidence of natural reproduction in Lake Huron (Weber and Clark, 1984). Populations of lake trout have continued to reproduce naturally in Lake Superior, and reproductive success is improving (Curtis, 1990). A number of studies have indicated that the lake trout population recoveries in Lakes Huron and Michigan are related to reduced toxic organic residues in the eggs (see Giesy and Snyder, 1998, for a comprehensive review).

Between 1978 and 1981, annual rearing mortalities in lake trout fry as great as 97% were described for hatchery-reared fish (Mac et al., 1985). Mortality in these studies could not be attributed to disease or nutrition, and was characterized by erratic swimming behaviors and loss of equilibrium prior to death (swim-up syndrome). Poor survival was significantly correlated with the source of eggs and sperm, more so than the quality of the water in which the eggs were reared (Mac et al., 1985). In addition, a number of the adult lake trout produced fry that developed "blue sac" syndrome. This syndrome presents itself as an edematous (swollen with excessive fluid) condition that results in fluid filling the yolk sac, leading to a bluish color (Figure 3-5).

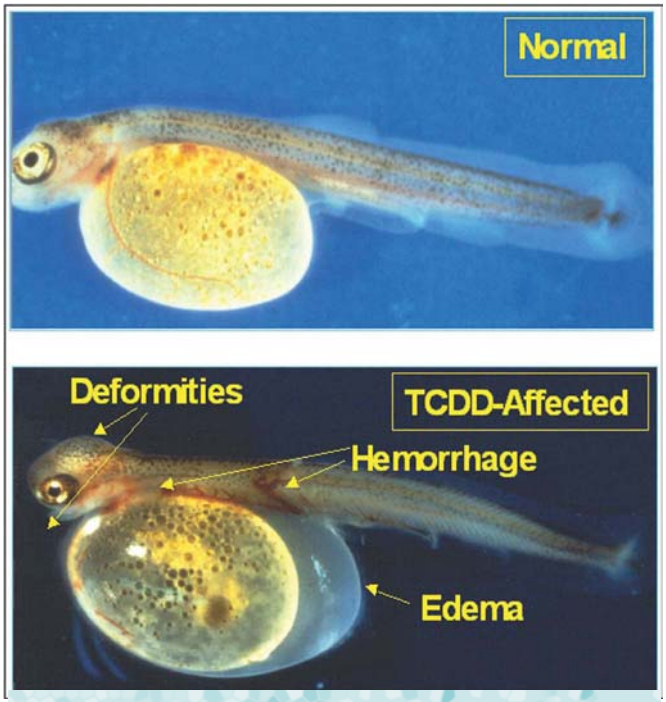

Figure 3-5. Effects of dioxin-like chlorinated hydrocarbons on developing lake trout fry (Spitsbergen et al., 1991).
Photo: J. Spitsbergen (labels added). With permission of Elsevier Science.

Studies during the early 1980s by scientists at the U.S. Fish and Wildlife Service (FWS) research laboratory in Ann Arbor, Michigan, indicated that the most likely cause of poor reproductive success was toxic chemicals (Mac et al., 1985; Willford et al., 1981; Giesy and Snyder, 1998). Their analyses identified 167 chlorinated hydrocarbons in fish, although many more have been identified since. FWS researchers considered it unlikely that a correlation could be established

between specific chemicals and effects because of the large number of compounds observed in fish. They believed contaminants must be involved for the following reasons:

1. Mortality was restricted to lake trout from southern Lake Michigan, which was also the area where the lake trout contained the greatest concentrations of PCBs and DDT. The mortality rate of fry from Lake Superior was small and that lake had the lowest concentrations of PCBs and DDT.

2. Mortality occurred during the swim-up stage of development, during which time fry were most sensitive to the toxic effects of chemicals.

3. The syndrome reached a maximum effect in both lake trout and chinook salmon populations at the same time.

Thus, it was thought that DDT and PCBs were most likely responsible for the observed toxicity. However, no blue-sac disease, the syndrome observed in the fry hatched from eggs of feral females, was observed in laboratory studies of the effects of DDT or PCBs. This finding suggested that the complex mixture of contaminants in fish, and the cause of blue-sac disease, had not been completely identified or quantified.

Further studies on lake trout in the lower Great Lakes demonstrated the link between blue-sac disease/impaired reproductive performance and the levels of PCDD, PCDF, and some of the non- and mono-*ortho*-substituted PCBs measured as dioxin toxicity equivalents (TEQs) (Walker et al., 1991; Walker and Peterson, 1991, 1994a,b; Cook et al., 1997; US EPA 2001). The threshold for toxic effects of TEQ on lake trout sac fry is approximately 30-40 ng/kg and the lethal dose for 50% mortality (LD_{50}) is approximately 47–70 ng/kg wet weight body burden (Figure 3-6) (Walker et al. 1991; Walker and Peterson, 1994a,b). Toxicity is manifest from 1 week prior to hatching through the sac-fry stage of development (Spitsbergen et al., 1991). Lake trout are among the most sensitive species to dioxin toxicity. Thus, they can be used as sentinels for other species. Current concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin TEQs remain near the threshold for mortality in lake trout fry (Walker and Peterson, 1994a). By 1988, concentrations of TEQs had decreased to 8 and 29 ppt in Lakes Michigan and Ontario, respectively. These concentrations are less than the threshold of approximately 40 ppt, but only slightly in the case of Lake Ontario (see Giesy and Snyder, 1998, for further details).

No measurements of historical concentrations of TEQs in fish tissue are available. However, the use of sediment TEQ concentrations from a dated sediment core to infer historical concentrations in lake trout indicate that, historically, the threshold concentration would have been exceeded (Cook and Burkhard, 1998). Furthermore, until recently lake trout hatched from females collected from the Great Lakes suffered a relatively high incidence of blue-sac disease. Although it has been reported that this incidence can be caused by bacterial infections (Symula et al., 1990), the edematous condition seen is characteristic of exposure of lake trout to 2,3,7,8-TCDD or structurally similar compounds (Walker and Peterson, 1994a; Cook et al., 1997). Because the dose-response relationship for the dioxin-like compounds in lake trout is so steep, it is likely that the concentrations of dioxin TEQ in the eggs were well above the toxicity threshold for blue-sac syndrome (Guiney et

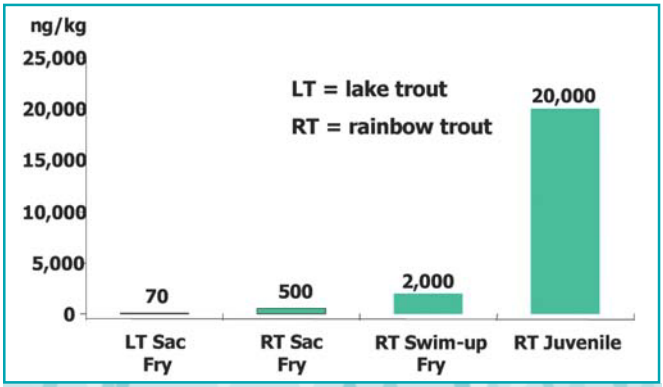

Figure 3-6. LD_{50} concentrations for effects of TEQs on lake trout (redrawn with permission from Walker and Peterson, 1994a).

al., 1996) in the recent past. Problematic levels are still reported, where extracts of whole adult lake trout from Lake Michigan continue to lead to lethality when injected into rainbow trout eggs in graded doses (Wright and Tillitt, 1996). The extract, which contained PCDD, PCDF, and PCB congeners, caused yolk-sac edema, cardiofacial deformities, and hemorrhage. All of these symptoms have been observed in Great Lakes fish and can be caused by exposure of fish eggs to TCDD.

In summary, it is not possible to determine the actual degree to which POPs have affected lake trout populations in the Great Lakes (Zint et al., 1995). It is likely that dioxin TEQs, primarily from dioxin-like PCB congeners, have caused reproductive impairment of lake trout in the lower lakes, but not Lake Superior. Declines in lake trout populations began in Lakes Ontario, Huron, and Michigan before concentrations of POPs were high enough to drastically reduce reproduction. This observation, along with the fact that "catch per unit effort" generally declines after populations have declined, indicates that initially non-contaminant effects were most likely the cause of the population declines of lake trout. Also, because populations began to decline before sea lamprey numbers were sufficiently high to cause severe population reductions, the most likely cause of the decline in lake trout populations in the lower lakes was overexploitation by the commercial fishery. POPs may have played a significant role in delaying reestablishment of lake trout in the lower lakes, but the effects should begin to abate now that concentrations of these compounds have declined to near the threshold for mortality of eggs and fry.

Birds

During the 1960s and 1970s, when the pesticide DDT was being used in the North American environment, populations of several sensitive bird species declined as individuals became unable to successfully incubate eggs because of abnormally thin shells (Cooke, 1973). The eggshell-thinning effect of DDT and its potent, stable, metabolite *p,p'*-DDE in sensitive species is well known, even to the lay public. Indeed, the contributions of DDT to population declines in bird species such as brown pelicans (*Pelecanus occidentalis*), peregrine falcons (*Falco peregrinis*), and bald eagles are probably the most famous incidents in wildlife ecotoxicology. Although many populations worldwide were adversely affected, some of the more notable species that suffered catastrophic declines in the Great Lakes basin included the osprey (*Pandion halieatus*), bald eagle, and many colonial fish-eating birds such as herring gulls (Figure 3-7), common and Caspian terns, and double-crested cormorants (Figure 3-8). In fact, some of these species were almost completely extirpated from the Great Lakes basin. These effects, including declines in popu-

Figure 3-7. Herring gull colony in Lake Michigan.
Photo: John P. Giesy

Figure 3-8. Double-crested cormorant colony, Lake Huron.
Photo: John P. Giesy

lations, have been best documented for colonial, fish-eating water birds (Gilbertson et al. 1991; Peakall and Fox, 1987). Although effects were not restricted to the Great Lakes basin, a number of species in the Great Lakes experienced significant population declines (Bowerman et al., 1995, 1998). Many of these species, such as the double-crested cormorant, have experienced dramatic population increases since DDT was deregistered in the United States and environmental concentrations have declined (Ludwig, 1984; Weseloh and Ewins, 1994).

Bald Eagles

There is no question that bald eagle (Figures 3-9, 3-10) populations declined greatly from historical levels, but the specific reasons for these declines

Figure 3-9. Bald eagle egg in eagle nest with habitat in background.
Photo: D. Best/U.S. FWS

Figure 3-10. Bald eagle in flight.
Photo: U.S. FWS

are less clear (Bowerman et al., 1995). The numbers of bald eagles in North America declined greatly after World War II (Grier, 1982; Postupalski, 1985). This decline was particularly acute in the Great Lakes region (Colborn, 1991). Habitat changes and killing of adults certainly played a role in the population dynamics of bald eagles in the continental United States and Great Lakes basin. However, the greatest effect on bald eagle populations was from DDT residues, specifically the degradation product *p,p'*-DDE, which is known to cause eggshell thinning in eagles (Peakall et al., 1973; Feyk and Giesy, 1998). The effect of DDT residues on bald eagle reproductive success, like many other raptors, is inversely proportional to the dose of *p,p'*-DDE (Figure 3-11). It is clear that this compound exceeded concentrations sufficient to cause population-level declines in bald eagles of the Great Lakes basin (Wiemeyer et al., 1984, 1993; Bowerman et al., 1995). Beyond this, it is impossible to separate the potential effects of other organochlorine compounds, such as dieldrin, PCBs, and dioxins, all of which accumulated in eagles to concentrations that may have contributed to population-level declines (Wiemeyer et al., 1984, 1993; Giesy et al., 1995; Bowerman et al., 1998).

In 1976, just after the use of DDT was cancelled in North America, there were approximately 30 breeding pairs of eagles along the shores of the Great Lakes and 80 and 100 pairs in the interior regions of Michigan and Minnesota, respectively

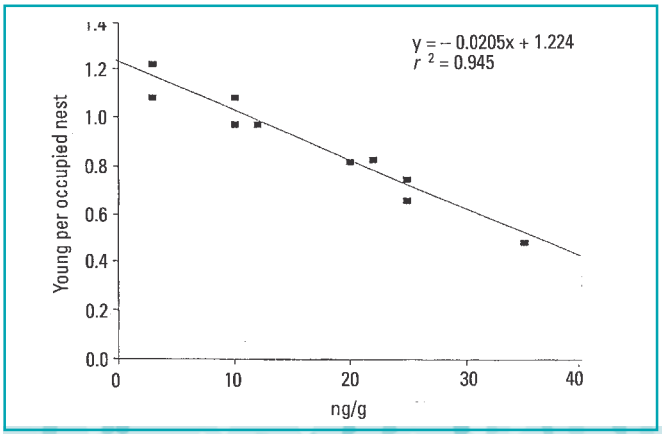

Figure 3-11. Productivity of bald eagles as a function of the geometric mean p,p'-DDE concentration (ng/g wet weight) in the plasma of nestling bald eagles between 1977–93 (Bowerman et al., 1995).

(Figure 3-12). On ceasing the use of DDT in North America, concentrations of *p,p'*-DDE in the environment, particularly in the diets of fish-eating birds, began to decline. Subsequently, once the concentrations had declined below the threshold for population-level effects, populations of eagles began to increase (Grier, 1982; Postupalsky, 1985). The number of breeding pairs has increased steadily since 1976 (Postupalsky, 1985).

Currently, bald eagles nesting along the shoreline of the Great Lakes do not reproduce as well as those nesting on inland bodies of water (Bowerman et al., 1995). Two common

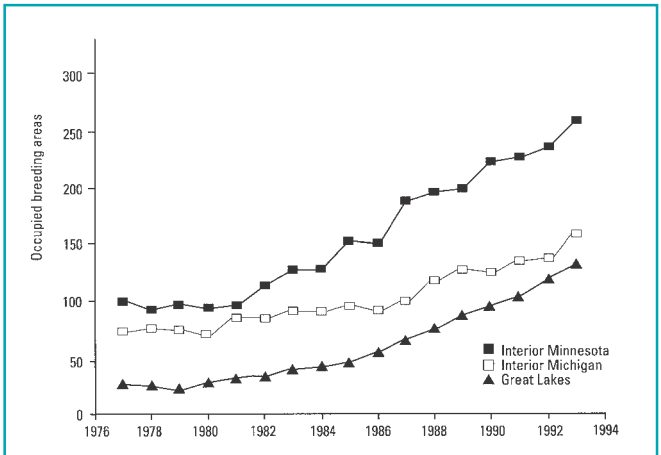

Figure 3-12. Numbers of breeding pairs of bald eagles along the Great Lakes shorelines and in the interiors of Michigan and Minnesota for the period 1977 to 1993 (Bowerman et al., 1995).

measures of the reproductive success of bald eagles are the number of young fledged per occupied nest, referred to as productivity (compared over the total number of nests in a specified region or area), and the reproductive success of each nest (given as the number of young produced in a specific nest, e.g., 0, 1, 2 chicks). Maintenance of a stable bald eagle population requires a productivity of approximately 0.7 chicks/occupied nest/year. A healthy population, capable of exporting excess productivity to colonize other areas, is characterized by a productivity of greater than 1.0. Productivities less than 0.7 are insufficient to replace the loss of adults (Bowerman et al., 1995). The average productivity for bald eagles nesting along the shorelines of the Great Lakes is 0.7, which is just sufficient to maintain a stable population, but not to expand. Any expansion of bald eagle populations along the shoreline of the Great Lakes is due to immigration from other more productive areas. The productivities for the Michigan shoreline on Lakes Michigan and Huron are 0.53 and 0.25, respectively, which are insufficient to maintain stable populations, let alone support any expansion (Figure 3-13). Bald eagles along rivers with anadromous (fish that return to inland streams to breed) populations of

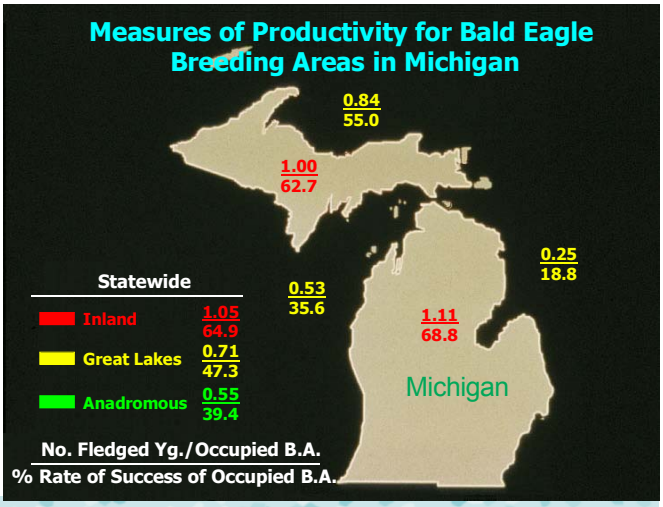

Figure 3-13. Reproductive success of bald eagles in Michigan. B.A. = Breeding area, the area bald eagles frequent when they are paired, breeding, and raising chicks, which may include several nests, only one of which is used per year (data from Bowerman et al., 1998).

salmon from the Great Lakes have a very low productivity of 0.55. The reduced productivities along the shores of the Great Lakes and anadromous salmon streams may be due to a number of factors, including exposure to residual concentrations of *p,p'*-DDE, but may also be caused by exposure to PCBs, PCDDs, and PCDFs or other compounds (Giesy et al., 1994, Bowerman et al., 1995). In addition, there may be microclimatological effects in some areas and impacts of low food availability (Dykstra et al., 1998). Although it is impossible to know the exact contribution of each of the POPs to eagle reproductive impairment, it is likely that current concentrations of POPs such as PCBs (Figure 3-14) in the Great Lakes are sufficient to cause population-level effects on some subpopulations of bald eagles (Bowerman et al., 1995).

Colonial Fish-Eating Birds

Current concentrations of PCDD, PCDF, and PCBs in both Great Lakes piscivorous birds and their prey are less than they were in the 1960s and 1970s. Some bird populations, such as double-crested cormorants and herring gulls, have made dramatic recoveries since that time. Populations of other species, such as common and Forster's terns, continue to decline. The concentrations of TEQ in several species appear to be greater than the threshold for discernible, population-level effects at several locations around the Great Lakes (see Giesy et al., 1994b, for a comprehensive review). For instance, subpopulations of double-crested cormorants and Caspian terns in Saginaw Bay and Green Bay continue to display embryo lethality (Figures 3-15 and 3-16) and abnormally high rates of developmental deformities (Figures 3-17 and 3-18). In general, all of the populations of fish-eating birds from the Great Lakes are displaying symptoms of exposure to chlorinated chemicals at the biochemical level.

PCDDs, PCDFs, and certain structurally similar PCBs have been demonstrated to cause a syndrome referred to as Great Lakes Embryo Mortality Edema and Deformities Syndrome (GLEMEDS) (Table 3-2). This syndrome, which

Figure 3-15. Cormorant eggs. One died while hatching.
Photo: John P. Giesy

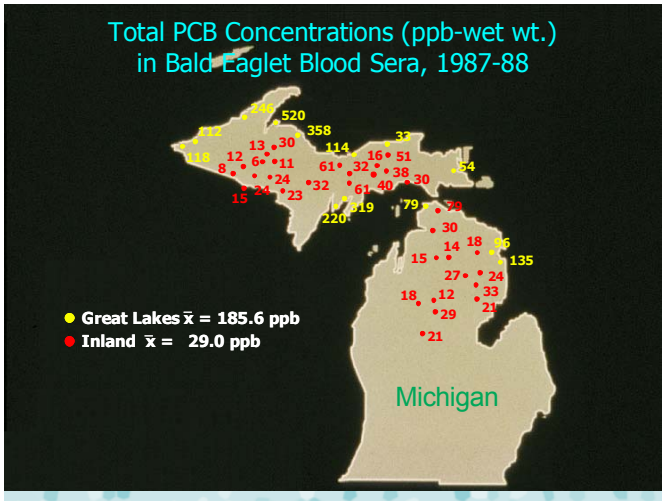

Figure 3-14. Concentrations of PCBs in blood plasma of bald eagles in Michigan (data from Bowerman et al., 1991).

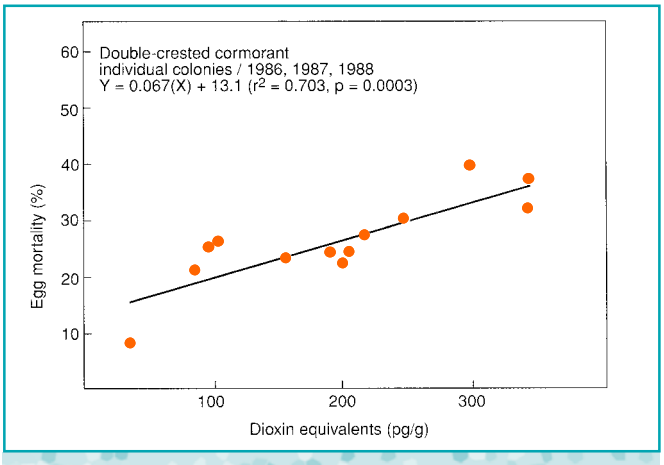

Figure 3-16. Correlation between embryo lethality (egg death) as a function of total dioxin toxicity equivalents in double-crested cormorant eggs from the Great Lakes (Giesy et al., 1994a; Tillitt et al., 1992).

Figure 3-17. Cormorant with cross-bill malformation.
Photo: John P. Giesy

is similar to chick edema disease, results in embryo lethality and developmental deformities in fish-eating birds. Although the degree of expression of GLEMEDS has decreased as concentrations of PCDDs, PCDFs, and PCBs have declined, certain species in some locations are still affected. These exposures are still causing lethality and deformities in embryos of all of the populations examined by research groups from the United States and Canada, including those from Michigan State University (extensively reviewed in Giesy et al., 1994a,b). The observed effects are greater than those observed in less contaminated populations not breeding on the Great Lakes, although these effects are translated into biologically significant population-level

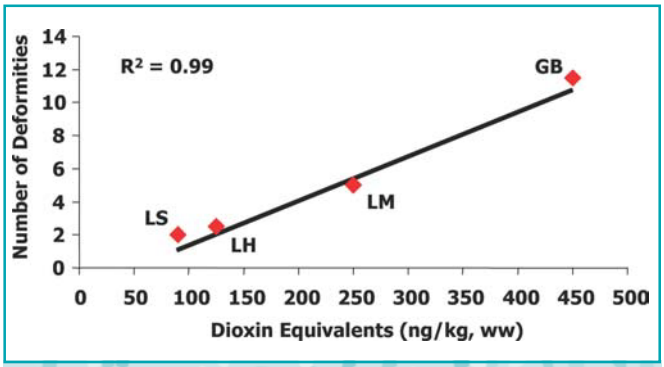

Figure 3-18. Rates of deformities per thousand double-crested cormorant embryos for the Great Lakes (Giesy et al., 1994a). LS–Lake Superior, LM–Lake Michigan, LH–Lake Huron, GB–Green Bay

Table 3-2. Clinical signs of GLEMEDS

- Embryo lethality
- Liver mixed function oxidase (MFO) induction
- Unabsorbed yolk sacs
- Vitamin A depletion
- Porphyria
- Teratogenesis

Source: Gilbertson et al. (1991).

effects only in the more contaminated areas, such as Saginaw and Green Bays.

As with fish, the results of laboratory and field studies indicate that the lethality and deformities (Table 3-3) of embryos of fish-eating birds from the Great Lakes are caused by the toxic effects of multiple compounds expressed through the Ah receptor. The use of TEQ as the measurement unit also explains the observed effects better than single measurements of individual compounds (Geisy et al., 1994a). When the current concentrations of PCBs and PCB-derived TEQs in the diets of fish-eating birds of the Great Lakes were compared with NOAEL values for these species, based on both laboratory and field studies with these species as well as surrogates, the hazard quotients and exceedence values were greater than 1.0 for all of the species in all of the lakes (Giesy et al., 1994b; 1995). The magnitude of the hazard quotient values varies among species and lakes. Bald eagles are the most exposed and the most sensitive, whereas cormorants are relatively tolerant of the effects of PCB-derived TEQs.

Mammals

In addition to colonial, fish-eating water birds, several other wildlife populations have been

Table 3-3. Deformities caused by exposure to TEQs

- Gastroschisis
- Crossed bills
- Clubfoot
- Dwarfed appendages
- Edema/ascites
- Hemorrhaging
- Abnormal feathering
- Abnormal eyes
- Hydrocephaly
- Anencephaly

Source: Giesy et al. (1994a).

reported to be affected by contaminants in Great Lakes fish. Populations of mustelids, including mink (*Mustela vison*) (Figure 3-19) and river otter (*Lutra canadensis*), have declined in regions along the Great Lakes or along rivers that are not blocked by dams, to which fish from the Great Lakes have access (Giesy et al., 1994c). It is difficult to conduct a risk assessment for mink because accurate information on their diets is limited. A number of researchers have reported that feeding fish from the Great Lakes has resulted in adverse effects on ranch mink, and several analyses have been conducted to examine the effects of contaminant compounds (Giesy et al., 1994c; Kannan et al., 2000). In studies feeding Great Lakes fish, mink are simultaneously exposed to a number of synthetic, halogenated compounds, including POPs insecticides. Because the concentrations of many of these compounds are intercorrelated, it is difficult to separate their effects and determine which are most likely to have caused adverse effects in populations of wild or ranch mink. As little as 1% Great Lakes fish in the diet of mink is sufficient to cause adverse effects on survival and growth of the kits (Restum et al., 1998; Giesy et al., 1994c); 40% Great Lakes fish in the diet causes mortality of adult female mink (Heaton et al., 1995a,b). When adult female mink were fed 10% Great Lakes fish, the number of surviving kits was significantly reduced (Figure 3-20). Historically, when the concentrations of insecticides such as DDTs in the tissue of

Figure 3-19. Mink in the wild eating fish.
Photo: J. McDonald/Corbis.com

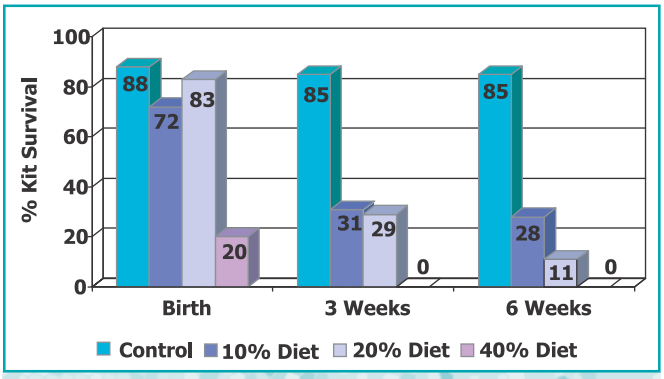

Figure 3-20. Survival of mink kits as a function of varying proportions of Great Lakes fish in the maternal diet (Tillit et al., 1996; Heaton et al., 1995a).

fish from the Great Lakes were higher, it was concluded that that they were unlikely to be the cause of the effects observed when fish from the Great Lakes were fed to ranch mink. The most likely causes of the observed effects are again the PCDDs, PCDFs, and PCBs. Although it is difficult to determine the exact cause of the observed effects, it is clear that residues present in fish from the Great Lakes can cause significant effects on the survival and reproduction of mink.

Of all the pollutants to which mink have been exposed, PCBs seem to have had the greatest impact. Mink are one of the most sensitive species to the effects of PCBs. In an attempt to determine if current concentrations of PCBs represent a risk to mink, hazard quotients were calculated assuming that mink ate only Great Lakes fish in their diet (Heaton et al., 1995a,b). Hazard quotients for PCBs in fishes from the Great Lakes ranged from a minimum of 6.4 to a maximum of 83. Percent allowable consumption values for feeding Great Lakes fish to mink were all less than 100%, and ranged from as little as 1.2% to as much as 19%, depending on the fish species and its source. Thus, there is no combination of Great Lakes fish that would result in a nonhazardous diet to mink. The average allowable fish content in the mink diet for all of the Great Lakes fish was 7.5% (Giesy et al., 1994c).

The onset time and duration of exposure of mink to salmon is also problematic, such that mink

could be eating large quantities of salmon for several months during sensitive reproductive periods. The late fall and early winter is a critical period for exposure to toxicants, when mink are mating and the females are pregnant. During this period, several species of anadromous salmonid fish migrate into Michigan rivers to spawn. The coho and chinook salmon die soon after spawning and are deposited on the shores of the river. With the onset of cold weather, the carcasses of the salmon can persist along the shore for a prolonged period of time. In this way, these fish could be a substantial source of contaminants to mink. For instance, using average concentrations of TEQs in fish from the Great Lakes, HQ values were all greater than 1.0, indicating some degree of risk to mink (Table 3-4). Most of the TEQs were contributed by PCBs.

From a time perspective, consuming chinook salmon for as little as 2 weeks could deliver the annual dose to mink that would be expected to affect reproduction (Giesy et al., 1994c).

Table 3-4. Hazard quotients for consumption of TEQ-containing Great Lakes fishes by mink

Common carp	47
Chinook salmon	11
Alewife	5.8
Northern pike	30

Calculated from information contained in Heaton et al. (1995a,b) and Tillitt et al. (1996), and unpublished data on concentrations of residues in fish tissue, J.P. Giesy.

Conclusions

- All of the compounds listed in the Stockholm Convention on POPs have been identified in fish and wildlife of the North American Great Lakes, even though some of these compounds, such as toxaphene, were never used in significant quantities in the region. This finding indicates that the source of some POPs in the Great Lakes ecosystem is long-range atmospheric transport.
- Concentrations of POPs in Great Lakes fish have decreased significantly, approximately 25-fold, since the use of these compounds ceased within the Great Lakes basin.
- Concentrations of the key POPs, such as *p,p'*-DDE and PCBs, in Great Lakes wildlife are currently either not declining or declining only slowly. POPs declines in Great Lakes waters have also slowed, reflecting a complex interrelationship among loss to sediments, temperature-dependent fluxes to and from the atmosphere, and continuing inputs from urban and other sources, local and remote (Miller et al., 2001; Swackhamer et al., 1999; Simcik et al., 1999). Further input reductions of POPs and the continued recovery of wildlife populations depends, in part, on controlling long-range atmospheric transport of POPs from other parts of the world (US EPA, 2000).
- Historically, several POPs accumulated to sufficient concentrations to cause adverse effects on fish and wildlife in the Great Lakes.
- The degradation product of the organochlorine insecticide DDT, *p,p'*-DDE, which causes eggshell thinning in raptors such as peregrine falcons, ospreys, and bald eagles, resulted in decreases in populations of these species to the point where they were almost completely extirpated from the Great Lakes basin.
- PCDDs, PCDFs, and certain structurally similar PCBs caused a syndrome referred to as GLEMEDS in colonial fish-eating water birds of the Great Lakes. This syndrome, which is similar to chick edema disease, results in embryo lethality and developmental deformities in birds. The degree of expression of GLEMEDS has decreased as concentrations of PCDDs, PCDFs, and PCBs have declined, but certain species in some locations are still affected.
- Concentrations of POPs residues, primarily PCDD, PCDF, and PCBs, in fish are still sufficient to cause mortality in adult mink and

severely reduce reproduction at as little as 1% Great Lakes fish in the diet.

- Historically, concentrations of dioxin-TEQs, primarily from PCBs, were sufficient to cause blue-sac syndrome in sensitive fish species such as lake trout, and probably contributed to their population declines and restricted recovery. Currently, concentrations have decreased to a point where the incidence of blue-sac syndrome is rare.

- At present, bald eagles nesting along the shorelines of the Great Lakes and along anadromous, accessible rivers have diminished reproductive capacity compared with those living at inland sites.

- Even though concentrations of many of the POPs have decreased in Great Lakes wildlife subsequent to restriction of their use in the Great Lakes basin, some species of wildlife in some locations continue to be affected.

- Failure to control sources of POPs outside the Great Lakes basin will limit the ability of the Great Lakes wildlife to recover.

- The Great Lakes experience demonstrates that it is possible to sufficiently contaminate environments with residues to cause adverse effects. The experience in the Great Lakes is also one of hope, because controls on the production and release of POPs can result in reduced environmental concentrations and wildlife recovery.

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Chapter 4 Persistent Organic Pollutants in the Great Lakes: Human Health Considerations

Introduction

Animals often act as sentinels for human health (NRC, 1991). This is especially true for humans who, through cultural tradition or free choice, live closer to nature and have lives intimately linked to the subsistence food sources in their local region. In turn, these susceptible populations can act as sentinels to the mainstream U.S. population, for whom the complexity of modern society and diverse dietary sources diffuse connections and make causal linkages to health outcomes difficult to isolate. Thus, the early findings of persistent organic pollutant (POPs) exposures and adverse effects on wildlife reproduction, development, and survival in the Great Lakes and other water bodies stimulated research to determine if similar effects were occurring in human populations. In particular, efforts centered on the families of sport fishers and Native Americans known to consume large amounts of Great Lakes fish. This chapter summarizes this research, providing information on human exposures, epidemiological results, and regulatory considerations for human populations in the Great Lakes region. Although the discussion is centered on the Great Lakes, its message relates to all communities in the United States exposed to POPs pollution.

The chapter is based on epidemiological information: the study of disease in human populations. Epidemiological research is a difficult endeavor, reflecting the complexity of the species under investigation. This complexity affects the multiple exposures and endpoints experienced by humans and the variations, patterns, and linkages in exposures, as well as the statistical methods necessary to tease these apart. Laboratory confirmation of low-level toxicological results in humans is not usually an option because of ethical considerations. As a result, when interpreting data consideration must be given to the inherent difficulties in analyzing potential effects from low-level exposures. For instance, an adverse human health impact may be difficult to demonstrate because the number of people affected is small relative to the statistical power of the study to isolate this effect. For POPs, the control group in a study may also be exposed, albeit to a lesser degree, leading to a situation where both exposed and control groups may be exhibiting adverse effects and there appears to be no difference between the two. Misclassification of exposure, a common difficulty, also tends to diffuse results and weaken findings of effects.

From another perspective, there may be no adverse effects from a POPs exposure and yet statisti-

Paper company waste disposal basin in 1970: A source of pollutants to the Great Lakes.
Photo: Minnesota Sea Grant, March 1970

cally significant differences are found between control and exposed groups. This can be the result of such simple factors as performing multiple tests, some of which will eventually appear "abnormal" by chance alone because of the common $p < 0.05$ (1 in 20) statistical significance value. More difficult to isolate are the effects of confounding and bias, where the control and exposed groups become unbalanced through study design limitations. For instance, lifestyle differences between sport fishers in the Great Lakes and the general population need to be considered before assigning health outcomes solely to dietary differences in POPs intake. For a more detailed analysis of these epidemiological data and considerations, see De Rosa et al. (1999) and Johnson et al. (1998).

Historical Background on POPs Exposure Studies in the Great Lakes

The first human exposure study of POPs in the Great Lakes was the 1974 study of polychlorinated biphenyl (PCB) intake from sport fish consumption (Michigan Sports Fishermen Cohort; Humphrey, 1976). Sport fish eaters were found to consume on average 14.5 kg (32 pounds) of fish per year, some eating as much as 119 kg (262 pounds) per year. During the 1970s, this average was approximately five times the national per capita fish consumption rate commonly used in risk estimates. Individuals who regularly ate 11 kg (24 lbs) per year or more of Great Lakes fish had higher ($p < 0.001$) serum levels of PCBs than individuals who seldom or never ate such fish. The study was repeated in 1982, again indicating that individuals in the upper range of fish consumption had serum PCB levels approximately four times greater than unexposed individuals. These studies identified a positive correlation between human intake of toxic pollutants and the consumption of Great Lakes fish (Humphrey, 1976, 1988a,b, 1989).

Recreational fishers and the Great Lakes.
Photo: ATSDR

A similar assessment of body burden levels of PCBs and DDE was undertaken in the Wisconsin Sports Fish-Consumers Cohort Study (Fiore et al., 1989; Sonzogni et al., 1991). Using new technology for analyzing toxic chemicals in human blood, the investigators were the first to determine PCB-specific congeners in Great Lakes sport anglers. They determined that the congeners most frequently identified in human sera were also the most abundant congeners in the tissues of a variety of Wisconsin fish (Maack and Sonzogni, 1988). Body burden levels of PCB congeners and DDE were significantly correlated with the number of sport fish meals consumed.

Both of these early studies demonstrated that human populations can be exposed to POPs through consumption of fish. Multimedia analyses support this finding, showing that most human exposure to chlorinated organic compounds (80-90%) comes from the food pathway (Figure 4-1). A lesser amount (5-10%) comes from air, and very small amounts (less than 1%) come from water (Birmingham et al., 1989; Newhook, 1988). Recent data indicate that fish consumption appears to be a major pathway for exposure to POPs chemicals, especially for compounds such as PCBs and dioxins (Fitzgerald et al., 1996; Schaum et al., 1999).

Identification of Critical Great Lakes Pollutants

Cooperation between Canada and the United States on the Great Lakes is managed through the International Joint Commission (IJC), established under the 1909 Boundary Waters Treaty. Among the IJC's mandates is the responsibility for protecting the lakes and river systems along the border for the benefit of citizens and future generations. In 1985, the IJC identified 11 of the most persistent and widespread toxic substances as critical Great

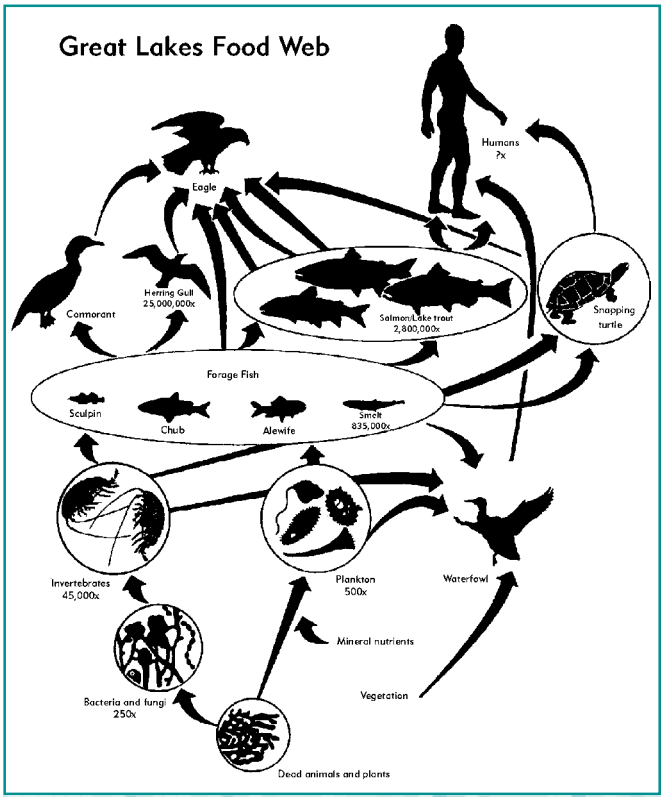

Figure 4-1. The Great Lakes food web. Heavy metals and many synthetic chemicals are absorbed by organisms and biaccumulate, with concentrations reaching toxic levels if exposure is great enough. The concentration is magnified at each step of the food web (Hicks et al., 1996).

Lakes pollutants: PCBs, DDT, dieldrin, toxaphene, mirex, methylmercury, benzo[a]pyrene (a member of a class of substances known as polycyclic aromatic hydrocarbons [PAHs]), hexachlorobenzene (HCB), polychlorinated dibenzo-*p*-dioxins and dibenzofurans, and alkylated lead (IJC, 1983). Eight of these pollutants are on the initial list for the Stockholm Convention, with the remaining four global POPs incorporated under subsequent Great Lakes binational agreements (*http://www.epa.gov/glnpo/bns*).

Forty-two geographic locations in the U.S. and Canadian Great Lakes basin have been identified by the IJC as "Areas of Concern" because of high concentrations of these toxic pollutants (National Health and Welfare Canada, 1991) (Figure 4-2). Of these 42 locations, 31 are located within the boundaries of the United States (Hicks, 1996). Beyond the substances and locations prioritized by the IJC, many more commercial and industrial compounds (~30,000) are produced or used in the Great Lakes basin, about 1,000 of which have been identified in the Great Lakes environment.

ATSDR Great Lakes Human Health Effects Research Program

In 1990, the U.S. Congress amended the Great Lakes Critical Programs Act to investigate human health concerns and pollutants in the Great Lakes. In response, the Agency for Toxic Substances and Disease Registry's (ATSDR) Great Lakes Human Health Effects Research Program (GLHHERP) was initiated in 1992. This program is designed to characterize exposure to toxic chemicals from consumption of Great Lakes fish and to investigate the potential for short- and long-term adverse health effects. The research program focuses on the initial 11 critical Great Lakes pollutants identified by the IJC, as well as other chemicals of con-

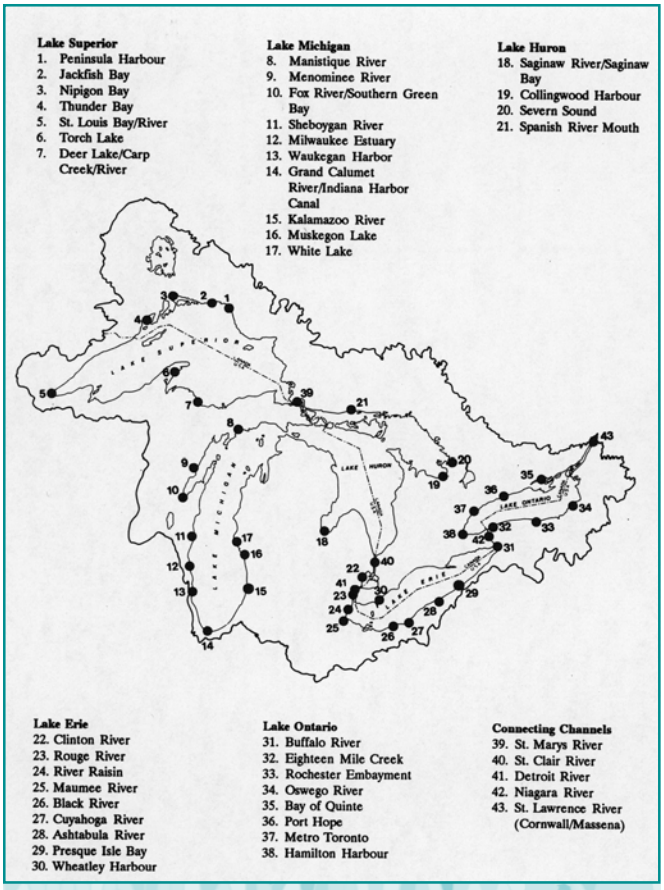

Figure 4-2. IJC areas of concern in the Great Lakes Basin (Great Lakes Fishery Commission, 1993). (#19 Collingwood Harbor has been delisted as an area of concern.)

cern in the Great Lakes basin. The program has identified several sensitive human health endpoints for study, including behavioral, reproductive, developmental, neurologic, endocrinologic, and immunologic measures. ATSDR's Great Lakes research further identified several human populations that may be at particular risk because of higher exposures to Great Lakes pollutants via fish consumption (Table 4-1). Predisposition to toxic injury in these populations can be due to behavior (e.g., degree of contaminated fish consumption), nutritional status, physiology (e.g., developing fetuses), or other factors. These communities of concern include subsistence fish anglers, Native Americans, pregnant women, fetuses, nursing infants of mothers who consume contaminated Great Lakes sport fish, young children, the elderly, the urban poor, and those with compromised immune function.

Contemporary data continue to support the association between the consumption of contaminated Great Lakes fish and elevated body burdens of POPs, summarized by the following findings (Table 4-2):

- Communities of concern in the Great Lakes basin are still exposed to POPs, including PCBs, polychlorinated dibenzo-*p*-dioxins and furans, and chlorinated pesticides (e.g., DDT) (Hanrahan et al., 1999; Stewart et al., 1999; Schantz et al., 1999; Johnson et al., 1998; Anderson et al., 1998; Dellinger et al., 1996; Fitzgerald et al., 1996; Lonky et al., 1996; Schantz et al., 1996; and Humphrey et al., 2000).

Table 4-1. Human populations at increased risk

- Native Americans
- Sport anglers
- Elderly
- Pregnant women
- Fetuses
- Nursing infants
- Women and men of reproductive age
- Immunologically compromised persons

- Levels of some contaminants in Great Lakes sport fish are above the advisory limits set by the state and federal governments (Dellinger et al., 1996).
- Sport fish eaters consume on average two to three times more fish than the estimate of 6.5 g/day for the general U.S. population (Courval et al., 1996, 1999; Fitzgerald et al., 1996, 1999; Schantz et al.,1996, 1999; Anderson et al., 1998; Hanrahan et al., 1999; He et al., 2001). In one survey in Michigan, Great Lakes sport fish consumers reported eating on average 42 g/day (Michigan Department of Environmental Quality, 1996). The reported weight of fish consumed declined from the early 1970s to 1990s (He et al., 2001).
- Consumption of Great Lakes fish appears to be the major pathway of exposure for some POPs (Fitzgerald et al., 1996, 1999; Stewart et al., 1999). Men eat more fish than do women, both genders eating Great Lakes fish during most of their reproductive years (Courval et al., 1996; Fitzgerald et al., 1996, 1999; Lonky et al., 1996; Waller et al., 1996; Hanrahan et al., 1999).
- Body burden levels for some of the POPs are two to eight times higher than those of the general U.S. population (Anderson et al., 1998; Hanrahan et al., 1999; Schantz et al., 1996, 1999; He et al., 2001). A significant trend of increasing body burden is associated with increased fish consumption (Fitzgerald et al., 1996, 1999; Falk et al., 1999; Hanrahan et al., 1999).
- Although background levels of PCBs appear to have declined in Great Lakes residents by the early 1990s, serum PCB levels among consumers of sport-caught Great Lakes fish did not significantly decrease (He et al., 2001).

Epidemiological Data

Epidemiological studies of Great Lakes populations have centered principally on reproductive effects and neurobehavioral/cognitive impacts on children.

Table 4-2. Exposure studies in human populations

Population	Findings	Reference
Lake Michigan fisheaters cohort	PCB levels in breast milk and maternal serum correlate with consumption of contaminated fish.	Humphrey, 1983
Native Americans (Mohawk) in New York State	Mean serum PCB level in men of 5.4 parts ppb (max. 31.7 ppb), versus 2 ppb in the general population (Jensen, 1989). Serum PCB levels were positively related to the number of fish meals consumed per year and increasing age.	Fitzgerald et al., 1996
Elderly cohort of Lake Michigan sport anglers	PCBs and DDE levels were significantly higher in high fisheaters. High fisheaters presented disproportionately higher body burden levels of PCBs and DDE than low fisheaters in each age group, i.e., 50-59, 60-69.	Schantz et al., 1996
Pregnant women who consumed Lake Ontario fish	Women in the high fish consumption group ate an average of 2.3 salmon or trout meals per month for an average of 16 years.	Lonky et al., 1996
Pregnant African-American women who consumed Lake Michigan fish	Women were exposed to POPs via fish consumption during most of their reproductive years. Seventy-five percent were less than 26 years of age and consumed lake fish for more than 15 years.	Waller et al., 1996
Reproductive-age (18-34) Lake Michigan sport anglers	Approximately 50% ate 1-12 sport-caught meals in the past year, and 20% consumed 13-24 meals. Fish consumption was greater in males than females, with some males consuming 49 or more fish meals per year.	Courval et al., 1996
Charter boat captains, their spouses, and Great Lakes anglers	Serum levels of dioxins, furans, and coplanar PCBs vary by gender. Fish species consumed predicted coplanar PCBs and furan body burden levels, but not dioxin.	Falk et al., 1999

On the basis of these and similar studies, the National Research Council (1999) concluded that:

> In humans, results of cognitive and neurobehavioral studies of mother-infant cohorts accidentally exposed to high concentrations of PCBs and PCDFs and of mother-infant cohorts eating contaminated fish and other food products containing mixtures of PCBs, dioxin, and pesticides (such as DDE, dieldrin, and lindane) provide evidence that prenatal exposure to these HAAs [hormonally active agents] can affect the developing nervous system.

Many of the studies on which this conclusion is based originated from Great Lakes epidemiological research and are summarized below.

Reproductive Effects

In a cross-sectional mail survey of reproductive-age Michigan licensed anglers and their partners, Courval et al. (1999) reported a modest association

in men between sport-caught fish consumption and the risk of conception failure after trying for at least 12 months. The authors examined the association between exposure and effects by calculating odds ratios, the odds of illness among the exposed group divided by the odds of illness in an unexposed group. On the basis of answers to questionnaires, 15% of couples had reported conception failure. Among men, the unadjusted odds ratios (ORs) for conception failure were 1.2, 1.3, and 2.0 across the three increasing levels of sport-caught fish consumption compared to no consumption (trend test p = 0.06). Adjusting for a number of variables that may affect study results, i.e., age, region of Michigan, smoking, and alcohol consumption, the ORs were 1.4, 1.8, and 2.8, respectively. For women, the unadjusted ORs for conception were 0.9, 1.0, and 1.4 with increasing fish consumption (trend test p = 0.35). When the same covariates and partner's sport-caught fish consumption were included in the model for conception failure in women, the ORs became 0.8, 0.8, and 1.0, respectively, indicating no increased risk from female exposure.

A series of studies on reproductive health has been performed on a cohort of New York State anglers and their spouses. In this cohort, questionnaires provided data on each person's species-specific fish consumption pattern, medical and reproductive histories, sociodemographic characteristics, and other lifestyle behaviors. Individual fish consumption at the time of enrollment in this study was characterized by self-reported duration and frequency, and used to calculate a PCB exposure index. Health outcomes were assessed through a combination of questionnaires and birth certificates. Multiple regression statistical analyses were carried out to control for identified variables. Findings from this cohort include the following:

- Mendola et al. (1995) reported no significant relationship between estimated low-to-moderate PCB intake from Great Lakes fish (up to 7 mg/lifetime) and the risk of clinically recognized spontaneous fetal death.
- Mendola et al. (1997) identified significant menstrual cycle length reductions with consumption of more than one fish meal per month (1.11 days). Women who consumed contaminated fish for 7 or more years also had shorter cycles (–0.63 days). The results were consistent with measures of frequency of consumption and the index of lifetime PCB exposure having a stronger relationship with menstrual cycle length than the number of years of fish consumption.
- Buck et al. (1997) reported no adverse association between the duration of consumption of contaminated fish from Lake Ontario and time-to-pregnancy.
- Buck et al. (2000) reported that maternal, but not paternal, consumption of fish from Lake Ontario may reduce fecundability (ability to conceive) among couples attempting pregnancy.

Neurodevelopmental Effects

Of the epidemiological studies of POPs exposures, none is more central than the Lake Michigan Maternal/Infant Cohort Study (Fein et al. 1984; Jacobson et al. 1985, 1990a,b). This study reported both developmental disorders and cognitive deficits in the offspring of mothers who were exposed to PCBs via fish consumption for at least 6 years before and during pregnancy. Developmental effects included a statistically significant decrease in gestational age (by 4.9 days), birth weight (by 160 to 190 g), and head circumference (by 0.6 cm). Decreased weight and neurological effects were still evident compared with the control population at 5 and 7 months post-term (Jacobson and Jacobson, 1988; Jacobson et al., 1985). Neurobehavioral deficits observed in babies included greater inclination to startle; poorer motor reflex and neuromuscular function; depressed responsiveness, as evidenced by a greater number of hypoactive reflexes; impaired visual recognition; and poor short-term memory at 7 months of age. At 4 years following birth, these deficits were still evident in weight gain, depressed responsiveness, and reduced performance on the visual recognition-memory test, one of the best validated tests for the assessment of human cognitive function (Jacobson et al., 1990a,b).

Although these data provide substantial evidence of in utero effects from PCBs, some significant questions were raised regarding causality because of recognized limitations in the studies. These included loss of study participants over time, a nonrandom sampling technique for the selection of the study population, limited statistical power because of the size of the control group, and analysis only of total PCBs. Also, the standards used (Aroclor 1016 and 1260) as references to quantify total PCBs accounted for only a small portion of the PCB congeners detected (Swain, 1991). Therefore, the analytical methods used to measure PCB levels may not have been appropriate. Moreover, many potential confounding variables have been identified, including exposure to other chemical contaminants and the mothers' health status at the time of the study. Nevertheless, a subsequent retrospective analysis by Swain (1991) found that the relationship between PCB exposure and transplacental passage was strongly affirmed, and the relationship between PCB exposure and developmental effects and cognitive deficits was affirmed with reasonable certainty.

Neurobehavioral testing of a child.
Photo: ATSDR

In a followup examination of 212 children from the Lake Michigan Maternal/Infant Cohort Study, the neurodevelopmental deficits assessed in infancy and early childhood were found to persist at age 11 (Jacobson and Jacobson, 1996). The study results indicated that the most highly exposed children, those with prenatal exposures equivalent to at least 1.25 µg/g in maternal milk, 4.7 ng/mL in cord blood, or 9.7 ng/mL in maternal serum

- Were three times as likely to have low average IQ scores ($p < 0.001$)
- Were twice as likely to be at least 2 years behind in reading comprehension
- Had poorer short- and long-term memory
- Had difficulty paying attention.

The authors concluded that these intellectual impairments were attributable to in utero exposure to PCBs, and that concentrations of PCBs in maternal serum and milk at delivery were slightly higher than in the general U.S. population.

The initial findings of the Lake Michigan Maternal/Infant Cohort Study have now been replicated in independent cohort analyses. Similar results were seen in the Oswego Newborn and Infant study, a prospective longitudinal cohort study examining behavioral effects in newborns, infants, and children exposed pre- and postnatally to environmental toxicants. Lonky et al. (1996) found that maternal exposure to Lake Ontario fish contaminants (e.g., PCBs) was associated with neurobehavioral deficits when assessed shortly after birth. A total of 559 newborns of women who had high exposure, low exposure, or no exposure to Lake Ontario fish were examined using the Neonatal Behavioral Assessment Scale (NBAS) 12-24 hours after birth and again at 25-48 hours after birth. Newborns of high-fish-consuming mothers exhibited the following deficits:

- A greater number of abnormal reflexes ($p < 0.001$)
- Less mature autonomic responses ($p < 0.001$)
- Less attention to visual and auditory stimuli in comparison to newborns of low- or no-fish-consuming mothers ($p < 0.01$)

These results indicate that newborns of mothers who consumed 2.3 salmon or trout meals per month scored more poorly on the NBAS than newborns from the low-exposure or control groups. These results represented the first replication and extension of the neonatal results of the Lake Michigan Maternal/Infant Cohort study by Jacobson et al. (1984).

Further analysis of the Oswego data on newborns revealed significant relationships between cord blood concentrations of the most highly chlorinated PCBs and performance impairment on the NBAS habituation and autonomic tests. No significant relationship was found between PCBs of lesser chlorination, DDE, hexachlorobenzene, mirex, lead, or mercury on any NBAS performance test (Stewart et al., 2000). The relationship between prenatal exposure to PCBs and performance on the Fagan Test of Infant Intelligence (FTII) was also assessed in the Oswego infants at 6 months and again at 12 months of age. The results indicated a significant relationship between exposure to PCBs and poor performance on the FTII. No significant relationship was found between exposure to DDE or methylmercury on any tests of the FTII (Darvill et al., 2000).

Studies of the impact of POPs, particularly PCBs, on human neurobehavioral development are not limited to the Great Lakes region of the United States and have been performed in other regions of the United States and abroad. In the early 1980s, the North Carolina Breast Milk and Formula Project was conducted with more than 800 mother-infant pairs who were exposed to background levels of PCBs (Rogan and Gladen, 1985; Rogan et al., 1986; Rogan and Gladen, 1991). When the North Carolina children were tested after birth, children of mothers with higher PCB concentrations in their breast milk exhibited the same behavioral deficits that were characteristic of the children studied in the Lake Michigan Maternal/Infant Cohort and the newborns of the Oswego Newborn and Infant Study. However, at 3 years of age the behavioral deficits were no longer detectable in the children from the North Carolina study. In an occupational study of women exposed to PCBs during the manufacture of capacitors in New York State, decreased gestational age and depression of weight at birth were associated with PCB exposure (Taylor et al., 1989).

Internationally, a series of studies in Europe are investigating the effects of exposure to PCBs and polychlorinated dioxins and furans on neurological development in the developing fetus and newborn (Huisman et al., 1995). These studies have linked high maternal levels of PCBs, PCDDs, and PCDFs with reduced neonatal neurological performance. The data also indicate that high in utero exposure to PCBs (measured in maternal serum) is associated with lower psychomotor scores at 3 months of age (Koopman-Esseboom et al., 1996) and with poorer cognitive functioning in preschool children at 42 months of age (Patandin et al., 1999). In another European mother-infant cohort, PCBs in maternal milk were associated with decreased performance on the Bayley II mental development index at 7 months, but not with other tests of neurotoxicity (e.g., FTII) or when using serum PCB concentration measures (Winneke et al., 1998).

Neurobehavioral changes have also been demonstrated in monkey and rat offspring following low perinatal doses of dioxin (Schantz and Bowman, 1989; Markowski et al., 2001) and PCBs (Rice, 1999; Schantz et al., 1989; Levin et al., 1988).

Other Cognitive and Systemic Health Effects

Beyond the developmental neurobehavioral findings reported above, additional studies have been conducted on Great Lakes fish consumers across different age groups and different health endpoints. These include the following:

- The effects of POPs on the immune system have been investigated in breast-fed infants whose mothers consumed contaminated Great Lakes fish. Maternal serum PCB levels during pregnancy were positively associated with the number and type of infectious illnesses occurring in infants during the first 4 months of life (Smith, 1984; Humphrey, 1988b). The inci-

dence of infections has also been found to correlate with the highest rate of fish consumption (at least three times per month for 3 years) and with cumulative lifetime fish consumption (Swain, 1991).

* In an older population of sport anglers, 50-90 years of age, fine motor function skills were assessed to determine the effects of exposure to PCBs and DDE. This population consisted of two groups: (a) high fisheaters who had consumed 24 pounds or more of Great Lakes sport-caught fish annually for more than 15 years, and (b) low (or non-fisheaters) who consumed less than 6 pounds annually. The study demonstrated that serum levels of PCBs and DDE were highly correlated, and both were significantly higher in high fisheaters than in low fisheaters. The mean serum PCB concentrations for low versus high fisheaters were 6 ppb and 16 ppb, and the maximum values were 26 ppb and 75 ppb, respectively. The mean serum DDE concentrations for low versus high fisheaters were 7.3 and 15.9 ppb, with maximum values of 33 and 145 ppb, respectively. In the cross-sectional data analysis, the authors concluded that PCB and DDE exposure from consumption of Great Lakes fish did not impair fine motor function (Schantz et al., 1996). The study also included a longitudinal component, where changes in individual scores for motor function over time were postulated to be a more sensitive indicator of exposure-related effects (Schantz et al., 1999). Recently published results of this longitudinal component reported that exposure to PCBs, but not DDE, was associated with lower scores on several measures of memory and learning in this older population of fish-eaters, but not on executive visual-spatial or motor function endpoints (Schantz et al., 2001).

Commercial fishing on the Great Lakes, Duluth, Minnesota.

Photo: Minnesota Sea Grant

Fish and Wildlife Advisories

States, U.S. territories, and Native American tribes issue food consumption advisories in order to protect residents from the health risks associated with contaminated noncommercially caught fish and wildlife. These advisories, primarily for fish consumption, inform the public on which species to avoid or limit eating because of elevated levels of pollutants. The advisories apply primarily to noncommercial fish and shellfish obtained through sport, recreation, and subsistence activities. Each advisory is different: it may recommend no or limited consumption; be targeted to everyone or limited to women and/or children; or may apply to certain species or sizes of fish. The fish advisories are submitted annually to EPA and compiled into a national listing (*www.epa.gov/ost/fish*).

Fish consumption advisories in the United States exist for a total of 38 chemical contaminants, but most advisories involve 5 primary pollutants: mercury, PCBs, dioxin, DDT, and chlordane. Four of these five pollutants are under the Stockholm Convention. The fifth, mercury, is generally emitted to the environment as a nonorganic metal, and is currently slated for a global risk assessment review by the United Nations Environment Programme. The number of advisories in the United States reported in 2000 (2,838) represents a 7% increase from the number reported in 1999 (2,651) and a 124% increase from the number issued since 1993

(1,266) (U.S. EPA, 2001). The national survey indicates that 100% of the Great Lakes and their connecting waters, and 71% of the coastal waterways, were under advisory in 2000 (Table 4-3). The total number of advisories increased for mercury, PCBs, dioxins, and DDT, although often the increased number of advisories is considered to represent better monitoring of fish contamination rather than increased pollution (U.S. EPA, 2001). Advisories for PCBs (see Figure 4-3) increased 3% from 1999 to 2000, from 703 to 726, and increased 128% from 1993 to 2000 (319 to 726). To date, 75% of the 726 PCB advisories in effect have been issued by 9 states, 8 of which are Great Lakes states (U.S. EPA, 2001).

The issuance of fish advisories is not a solution to POPs pollution, but rather a protective measure until pollutant reductions to safe levels can be achieved. Indeed, sociobehavioral and demographic data from the Great Lakes region reveal substantial nonadherence to fish advisories for a variety of reasons, further emphasizing the need for POPs pollution prevention at the source rather than relying on dietary pathway advisories.

- A recent survey of adult residents of the eight Great Lakes states estimated that 4.7 million people consumed Great Lakes sport fish in a given year, 43.9% of whom were women (Tilden et al., 1997).
- Knowledge of, and adherence to, health advisories for Great Lakes sport-caught fish vary across different genders and populations, e.g., men compared with women, whites compared with Native Americans (Fitzgerald et al., 1996, 1999; Waller et al., 1996; Tilden et al., 1997).
- 50% of survey respondents who had eaten Great Lakes sport fish were aware of the health advisory for fish; awareness differed significantly by race, sex, educational level, fish consumption, and state of residence (Tilden et al., 1997).
- 80% of minorities who had eaten Great Lakes sport fish were unaware of the fish advisory, and awareness was particularly low among women (Tilden et al., 1997).
- 97% of Native American men were aware of local advisories against consuming Great Lakes sport fish. However, 80% of the men ate those fish (Fitzgerald et al., 1999).
- Fish is an essential component in the diets of many minority populations and Native Americans. These populations consume fish that

Table 4-3. Fish advisories issued for the Great Lakes

Great Lakes	PCBs	Dioxins	Mercury	Chlordane
Lake Superior	●	●	●	●
Lake Michigan	●	●	●	●
Lake Huron	●	●		●
Lake Erie	●	●		
Lake Ontario	●	●		

Source: U.S. EPA (2001).

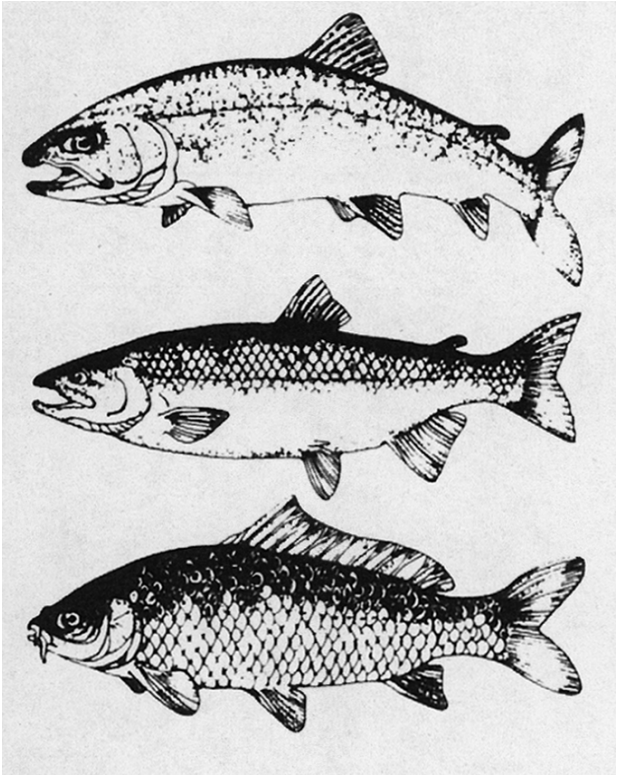

Figure 4-3. Fish most affected by PCB advisories: lake trout, coho salmon, and carp.

Credit: The ABC's of PCBs, University of Wisconsin Sea Grant Institute

tend to have higher levels of contaminants (Fitzgerald et al., 1996; Waller et al., 1996).

In response to these sociobehavioral and health effects findings, advisories now target their message and actions to vulnerable subpopulations, such as pregnant women, nursing mothers, and children. There are now 5 categories of consumption advisory: (1) no consumption for the general population, (2) no consumption for sensitive subpopulations, (3) restricted consumption advisory for the general population, (4) restricted consumption advisory for sensitive subpopulations, and (5) a commercial fishing ban. The value of strategically targeted fish advisories has been demonstrated through health education outreach efforts in two populations of Native Americans. In these vulnerable communities, body burden levels had been elevated two- to eightfold for some POPs. These levels were reduced through working with community "gatekeepers" and organizing health fairs and public meetings to provide information on cooking practices to reduce exposures. The targeted intervention strategies helped to reduce body burden levels to U.S. population averages within a 6-year period, without sacrificing fish as a nutritionally important dietary component (Hicks et al., 2000).

The continuing need for fish advisories over the entire Great Lakes region emphasizes that POPs remain a major concern. However, the reductions seen for POPs in many places are encouraging. In particular, PCB concentrations in fish from the Great Lakes region have declined over the years (ATSDR, 2000). In 1985, coho salmon from Lake Michigan contained 0.99 ± 0.6 ppm of PCBs, whereas by 1992 the level was 0.78 ± 0.29 μg/g (Eggold et al., 1996). Between 1976 and 1994, mean levels of PCBs declined in Lake Ontario rainbow trout from 3.9 to 0.97 ppm wet weight (Scheider et al., 1998). Similar trends in PCB levels were found for other fish species (ATSDR, 2000). These initial reductions in POPs levels following pollution control by industry and through government regulation have now, in a number of instances, slowed or plateaued, unmasking the importance of long-range atmospheric transport as a continuing source to the Great Lakes (Figure 4-4; see Chapter 7, Appendix A). As stated by the IJC (1996):

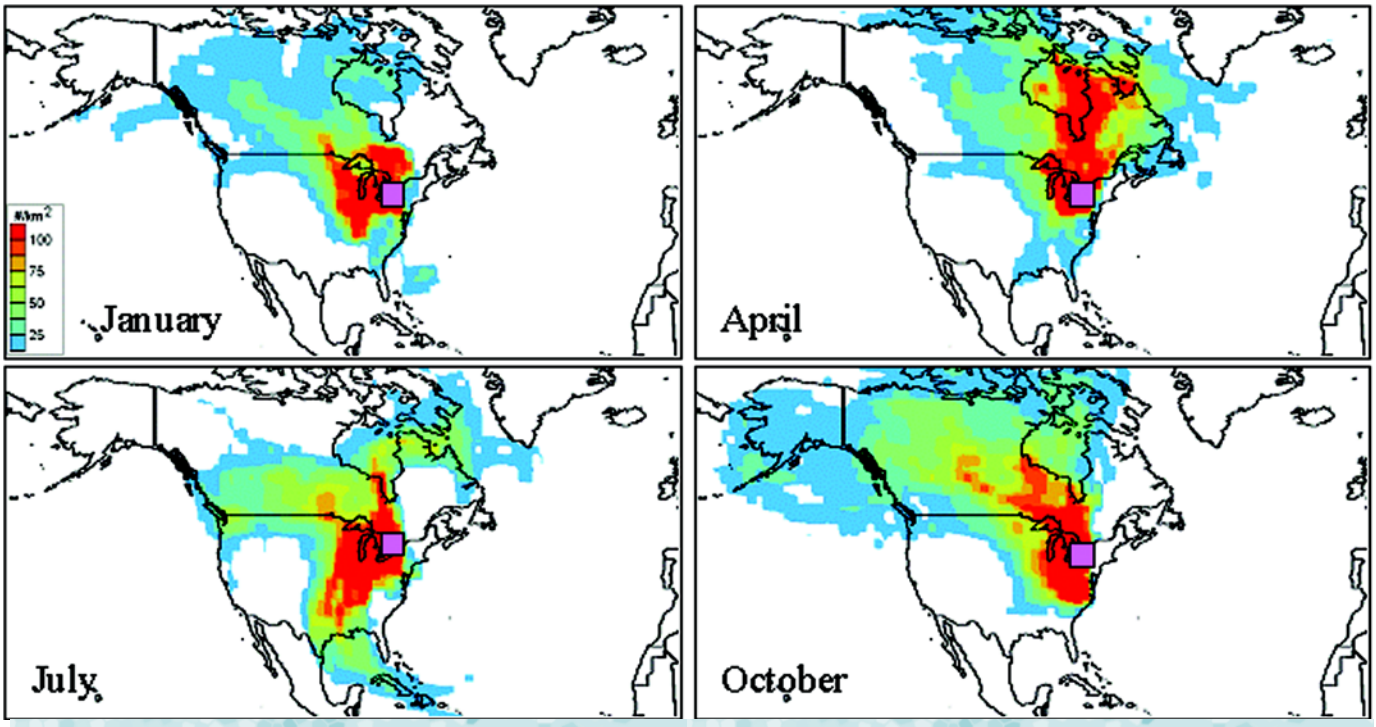

Figure 4-4. 10-day back trajectories from Rochester, NY, for the year 1999. Color shading refers to the likelihood that trajectories passed over a given area before arriving at the receptor site.
Source: Husar and Schichtel (2001).

A successful day's fishing.
Photo: ATSDR

> We are increasingly recognizing that a variety of pollutants emitted to and transported by the air have become the major pathway of pollution to the Great Lakes. These pollutants may come from direct sources, … distant sources in North America and beyond…

Additional detail on the deposition and contribution of atmospheric transport loadings to the Great Lakes can be found in Deposition of Air Pollutants to the Great Waters, Third Report to Congress (U.S. EPA, 2000).

Conclusion

Adverse effects from POPs have been demonstrated on Great Lakes wildlife and in laboratory studies at environmentally relevant levels. Similar effects are reported in epidemiological studies of human populations with high consumption of Great Lakes fish. Many of these vulnerable populations are still being exposed to higher levels of POPs than the general U.S. population. These findings have national as well as international public health implications because of the known toxicity of these chemicals and their persistence and ubiquity in the environment (Hicks et al., 2000). The good news is that levels of POPs pollutants in the Great Lakes environment have declined dramatically, particularly in the 1970s and 1980s. This is a success story of primary prevention, in this case pollution prevention through a partnership among federal, state, and local regulatory and health agencies, with industry and communities to reduce emissions to the environment. More recent trends in environmental levels are less clear, indicating a possible plateau and unmasking the importance of inputs from outside the Great Lakes basin via atmospheric transport. Further progress in reducing exposure levels will require increased attention to pollution prevention, particularly toward addressing long-range atmospheric sources. Great Lakes sport fish still contain POPs levels that are potentially harmful to human health, even though two decades of environmental regulation have significantly reduced chemical residues in waters, sediments, fish, and shellfish (U.S. EPA, 2001). Considering the societal, cultural, and health benefits (Albert et al., 1998) from fishing and fish consumption, pollution prevention efforts must be maintained consistent with the goal of virtual elimination of POPs from the Great Lakes.

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Chapter 5 Alaska—At Risk

To find a diet free from DDT and related chemicals, it seems one must go to a remote and primitive land, still lacking in the amenities of civilization. Such a land appears to exist, at least marginally, on the far Arctic shores of Alaska—although even there one may see the approaching shadow. (Rachel Carson, 1962)

Risks posed by persistent organic pollutants (POPs) to Arctic ecosystems and human populations were central to the genesis of the Stockholm Convention, and remain a primary concern when evaluating potential POPs impacts. For the United States, "Arctic ecosystems" means Alaska. Once, not too long ago and within the living memory of Native Alaskans, the Arctic was a pristine wilderness where POPs were never used and could not be detected in wildlife or humans. But the face of Alaska is changing, with increasing urbanization, industrialization, extractive resource activity, and commercial and social contacts with the global community. Accompanying these changes are concerns that the physical, climatic, and social aspects that make Alaska unique—particularly for the indigenous population—also make this region peculiarly prone to risks from global pollutants. Although exposures to POPs are being noted at this time, their impact will be more evident in the future unless pollution issues are addressed now.

As the data to follow demonstrate, Alaska's wildlife and human residents are experiencing POPs contamination from local, regional, and international sources. The levels in most environmental media typically remain substantially below those found in highly polluted areas of the lower 48 United States, but in high-trophic-level feeding species—including killer whales and humans—some POPs levels have been recorded that are comparable to those found in the general United States population and similar marine mammal species. POPs contamination of the Great Lakes started as a predominantly regional and local phenomenon, and the initial management successes from domestic and binational strategies with Canada reflected this scale. For Alaska, however, the intervention options mandate a much more global approach. From a polar perspective, "close" to Alaska and its surrounding waters means the huge and growing industrial and population centers in Asia, less regulated neighbors just a few miles distant in Russia, and sources across the Arctic Ocean in Europe that are all closer than Washington, DC (Figure 5-1; polar projections in Figures 5-2 and 5-4).

Figure 5-1. Map of Alaska. Major roads in red.
With permission of the National Geographic Society

This review of POPs in Alaska links assessment of human health with the state of the environment and ecosystems. For Alaska Natives, there is a deep connection among the air, the water, the animals, and humans. When people perceive that they are one with the environment, and the environment is contaminated, then they also are contaminated. This integrated world view differs from traditional "Western" practice, which has, in the past, tended to separate humanity from its supporting ecosystems. The many similarities in

POPs toxicities between humans and other mammalian species suggest that it would be unwise to hold to the belief that humanity is somehow impervious to and distinct from impacts on the supporting ecosystems.

Why Is Alaska at Special Risk?

For a variety of reasons, the Arctic ends up as an ultimate receptor and "sink" for POPs. The persistence and potential effects of these deposited POPs may also be more pronounced in polar climates. Factors in evaluating POPs risks to Alaska include:

- *Location:* The large expanse of the State of Alaska, accentuated by its island chains (Aleutians, Pribilofs), means that its neighbors are not limited to the great ocean expanses or to Canada and Mexico/Caribbean, as is the situation for the other United States. In addition to Canada, Alaska's neighbors are Russia, Japan, China, Korea, and other upwind Asian countries. Russia is the nearest trans-Pacific neighbor, only a short kayak excursion away, and human and wildlife populations regularly traverse these artificial national boundaries.

- *Physical climate:* Needless to say, winter is cold in Alaska, but spring and summer are times of relative warmth (Figure 5-2) and rapid biological activity. The cycle of prolonged winter darkness and cold, followed by warmth and 24-hour light, places peculiar stresses on ecosystems. Through the winter, mammals rely on fat stores, thereby releasing lipid-soluble POPs within their bodies as the fat is metabolized. In the spring melt, POPs that have accumulated in the ice are released to the food chain during the limited time of peak productive and reproductive activity. And, throughout all of this, the predominantly cold temperatures and permafrost reduce or eliminate the microbial activity necessary to degrade POPs.

- *Ecological sensitivity:* Cold temperatures and long periods of darkness are associated in the Arctic with slow growth, low productivity, and low diversity in terrestrial ecosystems. Anthropogenic damage to such ecosystems can require a long period for recovery.

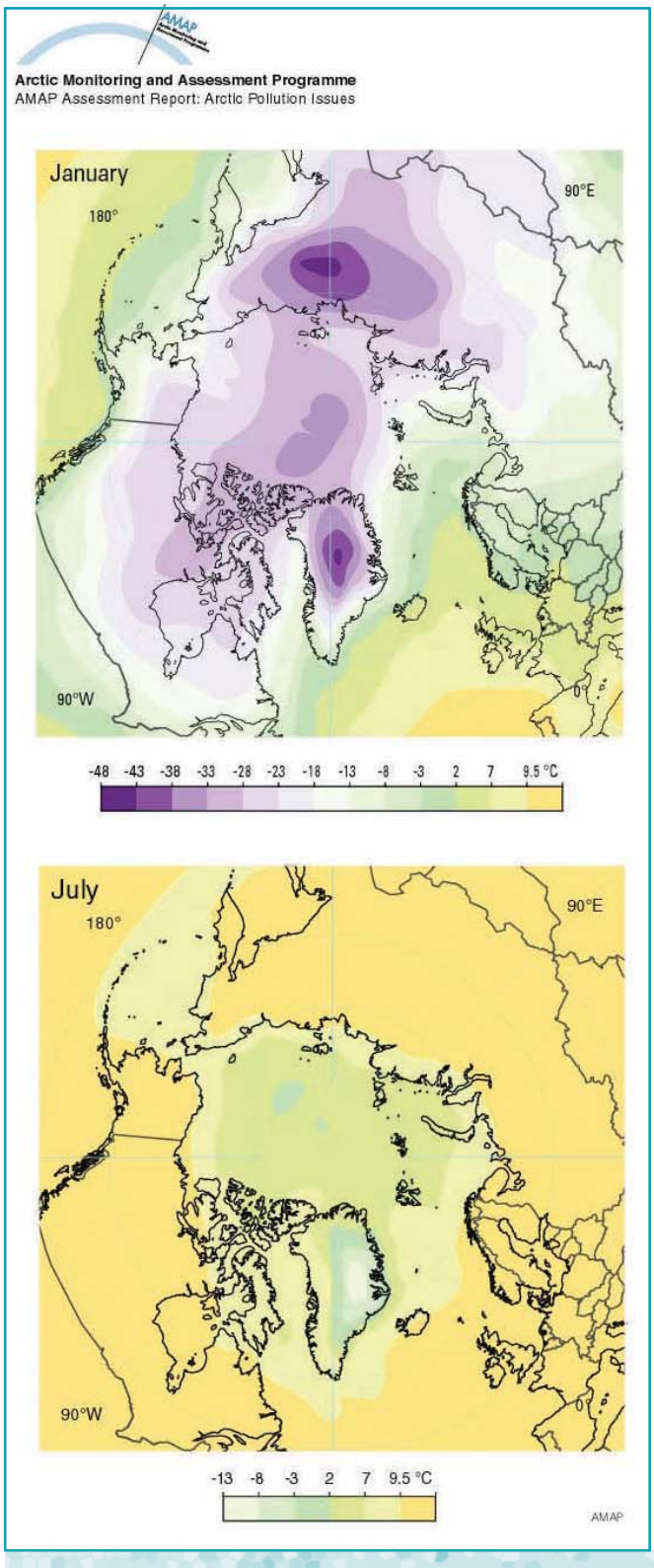


Figure 5-2. Arctic temperature profiles: January and July. AMAP.

- *Fat as the currency of life:* Survival for all species in polar climates rests on securing and maintaining energy levels. Some animals have a

round body design with thick layers of insulating fat (e.g., fish, seals, walrus, and whales). Another strategy is to secure a regular supply of high-energy food, as used by sea otters and weasels. Fat is high-energy food. Polar bears eat seals by killing them and then stripping off and consuming the skin and fat. Likewise, brown and black bears catch salmon and strip off the skin and fat, which are consumed. Fat becomes the currency for survival in the Arctic. Each predator targets the consumption of fat to maximize energy transfer. In this process, lipophilic contaminants are passed efficiently up the food chain and, at each trophic level, are biomagnified, accentuated by both their persistence and volume of consumption. This economy includes humans near the top of the web, as is evident in the fat rich diet of Alaska Natives.

- *Human populations:* A large proportion of Alaskans are indigenous peoples—16% by the 2000 Census. In the more isolated regions of the state, Alaska Natives make up a majority of many community populations (Figure 5-3). The indigenous population has a greater proportion of children than the overall Alaskan population. Obtaining wild food is central to the cultural, religious, and economic identity and survival of these peoples. Through traditional fishing, hunting, gathering, and food processing, known as subsistence, the culture and society of native indigenous populations are maintained. Because of concerns about contamination in subsistence foods, people turn to the purchase of imported foods. This is an economically untenable position in remote Alaskan villages, as well as unfortunate because foods purchased at stores also contain POPs (Schecter et al., 1997; Schecter and Li, 1997). Subsistence hunting and fishing by humans at the top of the food chain also relies on high fat intake, including the consumption of other predators, which can compound the biomagnification of POPs. Thus, the reliance of Alaska's people on wild and traditionally obtained local foods contributes to Alaskans' concerns regarding international sources of pollution (Hild, 1995).

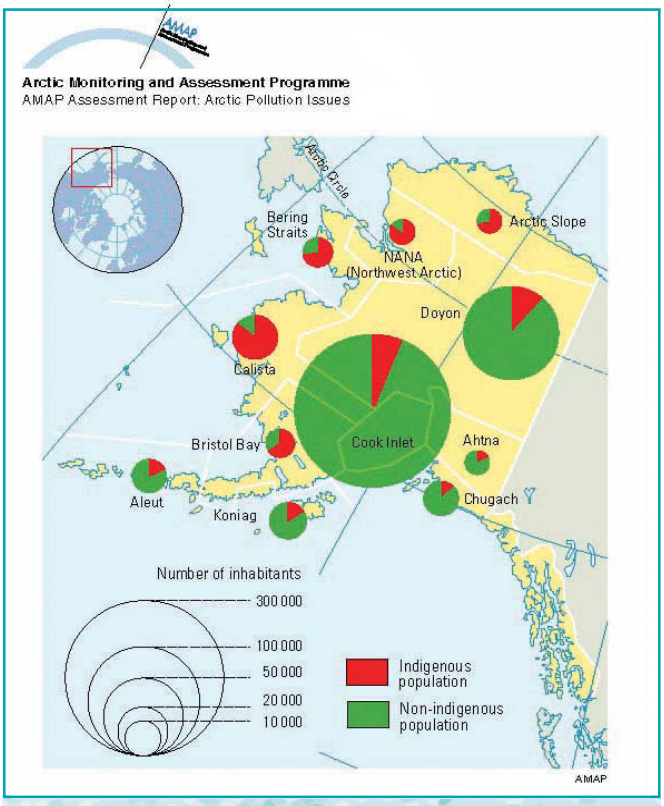


Figure 5-3. Total and indigenous populations of Alaska. AMAP.

- *Previous absence of contamination:* Compounding Alaska's susceptibility is the recognition that its remote areas were previously uncontaminated, with little to no local use of POPs pesticides and industrial pollutants except around urban settlements and military bases (Durham et al., 1961; Hayes et al., 1958). Any contamination comes in stark contrast to the expected purity, even if Alaskan levels remain below those in the lower 48 States. There is significant economic value in safeguarding this food supply, and likely more so in the future. This is particularly significant for a region such as Alaska where primary production (e.g., seafood) exports to the rest of the United States and the world are central to economic prosperity. Approximately 2 million tonnes of seafood are harvested annually from the Bering Sea alone, and over 80% of the world's wild salmon are supplied by Alaskan fishermen.

POPs Transport to Alaska

POPs are transported through the environment to Alaska through the movement of air, water, and migratory species (e.g., fish, birds). These processes are anticipated under the Stockholm Convention and elaborated upon in Chapter 7 of this report. Many physical aspects of the circumpolar region now appear to contribute to a natural transboundary movement of POPs to Alaska. Review of these pathways in the context of a global treaty must not, however, be interpreted as overlooking the contribution of other regional or local sources. Although Alaska has not had industrial POPs manufacturers, there are incidents of past usage that include military sites (e.g., PCBs) and mosquito control efforts (e.g., DDT). Some local waste burning may contribute byproducts (e.g., polychlorinated dioxins and furans). These are under further domestic and local investigation, and source reduction strategies are taking place.

Atmospheric Transport

Atmospheric air patterns move pollution from around the Northern Hemisphere into the Arctic (Figure 5-4; see also AMAP Arctic atmospheric circulation maps with additional detail and seasonal effects at www.amap.no). Winds blow in the midlatitudes from west to east, bringing Asian air into southern and central Alaska. During Russian and Chinese nuclear testing in the 1960s and 70s, Alaskans were concerned because they were a short distance downwind. At the same time, in the high latitudes of northern Alaska, winds blow from the east to the west, bringing pollution from northern and western Europe.

As detailed in Chapter 7, air movement can lead to POPs transport and deposition in two basic ways: global distillation of semivolatile chemicals, and mass transport and deposition of POPs attached to dust and soot.

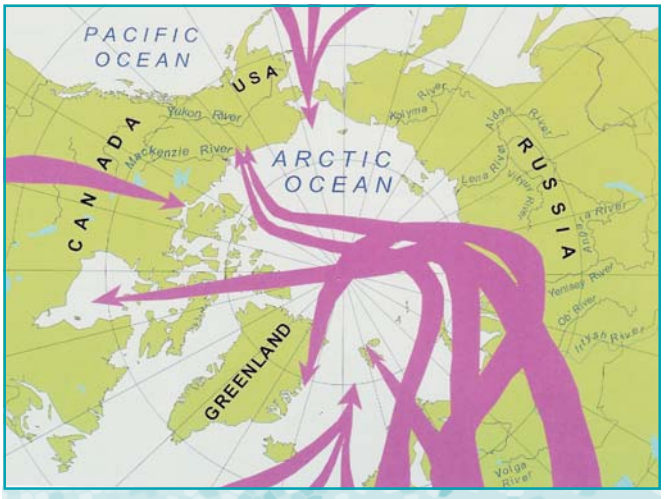


Figure 5-4. Atmospheric transport pathways to the Arctic (Crane and Galasso, 1999, map 3).

For global distillation, a number of the POPs are considered "semivolatile," evaporating in warmer climates, moving north (or south) and then precipitating out in colder climates. This cycle can repeat itself, moving materials poleward in a process known as the "grasshopper" effect (or global fractionation and cold condensation) (AMAP, 1998; Mackay and Wania, 1995; Wania and Mackay, 1993). In addition, all POPs can move to the Arctic through episodic events that move dust particles long distances. As demonstrated through back-trajectory mapping and satellite imagery (Chapter 7), Alaska is downwind of many Asian and European sources.

The atmospheric peculiarities of the Arctic, and the impact of global pollution, are most evident through the phenomenon of Arctic haze. Arctic haze is predominantly attributed to the movement of sulfur oxides, hydrocarbon gases, and particles north from their industrial sources. In the 1970s, Matthew Bean, an Alaska Native Yupik elder from Bethel, recognized that the plants were not as green, the sky not as blue, and the horizon not as clear as when he was a boy. He soon found himself talking with academic researchers who corroborated his observations with their air quality measurements. Arctic haze did exist (Rahn and Lowenthal, 1984; Shaw et al., 1993). Further research determined that this haze not only contained pollution from the far north, but contaminants from all over the northern half of the globe. The haze from these materials becomes increasingly dense during the cold, dark winter. In the spring, the higher angle of the sun warms the air, deepening the mixing layer and depositing pollutants on the earth's surface. The return of the sun also initiates a number of biological activities and unique photochemical phenomena (Lindberg et al., in press) leading

to the "Arctic sunrise" effect. The deposition, availability, and metabolic uptake of global contaminants into Alaska's plants, animals, and people generally coincides with the commencement of spring biological activity.

Hydrologic Transport

The very low water solubility of most POPs—counterbalancing their high lipid solubility—leads to water transport predominantly attached to fine particles. However, some organic pollutants, such as the hexachlorocyclohexanes (e.g., lindane) are more soluble in water and can be transported through a combination of prolonged persistence in cold waters and large volumes of oceanic water movement. Hydrologic pathways are also interconnected with atmospheric transport through the semivolatile nature of POPs, where contaminants can exchange between environmental media.

For Alaska, a combination of riverine and oceanic transport can bring POPs from long distances. The major rivers draining the agricultural and industrial areas of Russia flow into the Arctic Ocean. A number of Russian rivers are known to have readily detectable levels of various pesticides, including DDT, that do not appear to be decreasing over time (Zhulidov et al., 1998). These rivers release POPs to the Arctic Ocean, after which contaminants can be transported by the prevailing currents generally westward from the contaminated Ob and Yenisey Rivers, and eastward from the less contaminated Lena River.

Oceanic currents in the Pacific also provide a transport pathway for contaminants (Figure 5-5). After contaminants have traveled down rivers and into the ocean from agricultural fields and industrial areas of Southeast and Central Asia, the western Pacific currents can carry these contaminants to other parts of the world. The currents move along Japan, Korea, and Russia, and finally flow through the Bering Sea and into the Arctic Ocean (AMAP, 1998). Surface water studies of PCBs have identified this movement and the accumulation of materials within the Bering Sea (Yao et al., 2001). Work from Japan on the "Squid Watch Program" is tracking the movements of POPs in the North Pacific driven by the prevailing west wind and the Kuroshio warm current (Hashimoto et al., 1998).

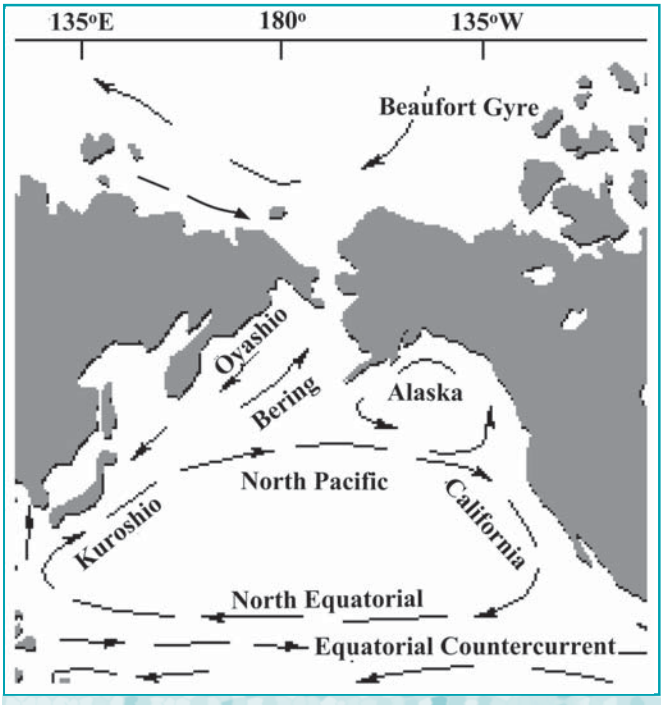


Figure 5-5. Ocean currents impacting Alaska.
Source: Adapted with permission from Apel, 1987; NOAA.

Migratory Species

Transport of contaminants from other regions of the globe to the food supply of Alaska Natives and other Americans can also occur through the movement and harvesting of migratory species. The springtime return of waterfowl is the first fresh meat many Alaska Natives have after a long winter of eating dried meat and stored foods. In addition to adult birds, eggs are also collected and consumed. Some of these birds have wintered in Asia and Central America. In those regions, feeding areas (such as fallow fields) may have been sprayed with organochlorine insecticides. The bodies of birds can carry pollutants that may be banned in the American communities that consume them (Figure 5-6).

Migratory fish do not travel as far as migratory birds, but the mechanism for accumulation of contaminants is similar. Recently, it was shown that the very low concentrations of HCB, s-DDT, and a number of PCB congeners detected in sockeye (red) salmon returning to interior Alaskan lakes can

Figure 5-6. Migration routes of land, lake, and wetland birds (Crane and Galasso, 1999, Map #9).

contribute more POPs to the lake ecosystem than the amount contributed by atmospheric deposition (Ewald et al., 1998). No studies to date have assessed the sources of chemicals that might be found in low levels in fish species such as salmon, capelin, and pollock that range in the Bering Sea between the United States and Russia. These commercial fish species end up on tables throughout the world, and all have come from an international ocean that receives water from the Western Pacific and Asia (Crane and Galasso, 1999) (Figure 5-7).

Further up the food chain, migratory marine mammals cover large areas, consuming a variety of food sources. These sources in turn lead to different levels of POPs biomagnification. Most seals, sea lions, toothed whales, and polar bears are near the top of the food chain and move among international waters (Crane and Galasso, 1999). Animal species feeding lower on the food chain generally have corresponding lower levels of POPs overall, as well as different specific chemicals. Walrus and bearded seals feed on benthic populations and therefore have a different POPs profile than predators that feed on fish or other marine mammals. Ringed seals eat crustaceans and fish. Likewise, filter-feeding whales, such as bowhead whales, feed low on the food chain, eating krill, and have a very different POPs profile and lower levels overall than the upper trophic level feeders.

POPs Levels in Alaska

Insights into levels and potential risks from POPs in Alaska are best gained through comparing exposure data to either effect levels in species of concern or to levels found in the lower 48 States.

Figure 5-7. Migration routes of salmon (Crane and Galasso, 1999, Map #13).

Although zero levels would be the preferred value for all of the POPs, it must be recognized that with the global distribution of these pollutants, their persistence, and modern laboratory equipment, scientists will invariably be able to detect some level of pollutant, especially in species higher on the food chain. This complexity is compounded by the multiple environmental media and species in which measurements are taken, and the multiple POPs and their metabolites under consideration. Care must also be taken in comparisons between different studies because units of measurement, analytic protocols, and methods of reports may vary.

For this report, we compare levels found in Alaska to those in the lower 48 States and, where possible, to the effect levels found in these or similar species from other areas of the United States. Reflecting the integrated nature of the Alaskan situation, the species discussion commences with wildlife, proceeds through wildlife that are used as food, and concludes with human consumers. For those seeking additional details on species levels across the Arctic, excellent references are available in AMAP (1998), Canadian Northern Contaminants Program (Jensen et al., 1997), Landers and Cristie (1995), and Ritter et al. (1995).

Wildlife Levels

Bald Eagle

Bald eagle.
Photo: U.S. Fish and Wildlife Service

The decline of bald eagle populations to the verge of extinction in the lower 48 States is emblematic of the effect of POPs, DDT/DDE in particular. Although residual DDE contamination continues to affect reproductive rates in some areas, the recovery of bald eagle populations in the lower 48 States following the cessation of DDT use and protection as an endangered species has been a remarkable

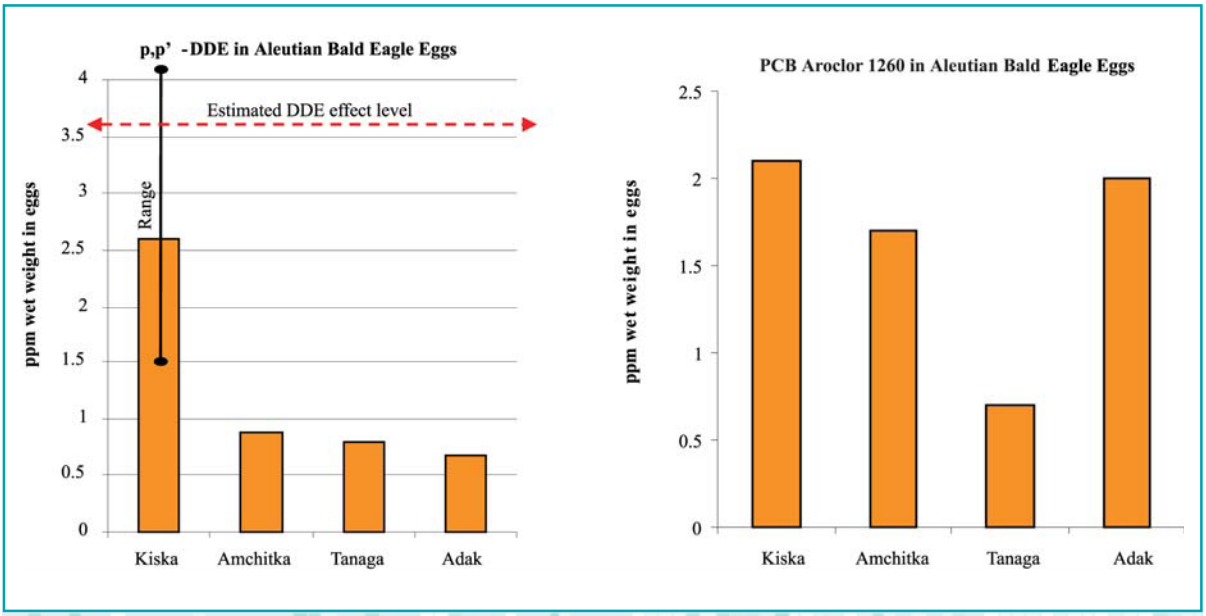


Figure 5-8a,b. Bald eagle levels of DDT and PCBs in the Aleutians (Anthony et al., 1999), geometric mean values.

success. In Alaska, bald eagle populations have remained robust, with DDT/DDE levels generally well below the potential effect level of ~3.6 µg/g DDE (Anthony et al., 1999; Wiemeyer et al., 1993). Eagles nesting along the Tanana River in the interior of Alaska in 1990-91 had DDE levels below concentrations known to result in sublethal or lethal effects, and most organochlorine concentrations were an order of magnitude lower than concentrations in bald eagle eggs from elsewhere in the United States (Richie and Ambrose, 1996). However, even in the presence of this apparent success there are warning signs. Eagles in the western Aleutian Islands have been found to have ratios of DDT/DDE that indicate new DDT sources, and DDE levels in some eggs on one island (Kiska) may be depressing reproductive success (Anthony et al., 1999; Estes et al., 1997) (Figure 5-8). Although the sources are not yet known, the prey species, especially migratory birds from Asia where DDT is still used, need to be assessed further. It also should be noted that although DDE is suspected as the causative agent in the above-mentioned studies, DDE concentrations in eagle eggs were positively correlated with other organochlorines, including oxychlordane, beta-HCH, dieldrin, and hexachlorobenzene.

Peregrine Falcon

Peregrine falcon.
Photo: U.S. Fish and Wildlife Service

Historic declines in peregrine falcon populations at several locations, including Alaska, have been correlated with DDE concentrations in their eggs causing eggshell thinning and hatching failure (Ambrose et al., 1988a,b; 2000). Threshold concentrations of ~15-20 ppm p,p´-DDE have been associated with a 20% eggshell thinning in peregrine falcons (Peakall et al., 1990). Populations are expected to decrease if eggshells are at least 17% thinner than pre-DDT measurements (Kiff, 1988). Peregrine falcons in interior and northern Alaska declined during the 1960s, stabilized in the mid-1970s, began to increase in the late 1970s, and have since stabilized or continued to increase. Eggs from two subspecies of peregrine falcons were collected from interior and northern Alaska between 1979 and 1995 and analyzed for orga-

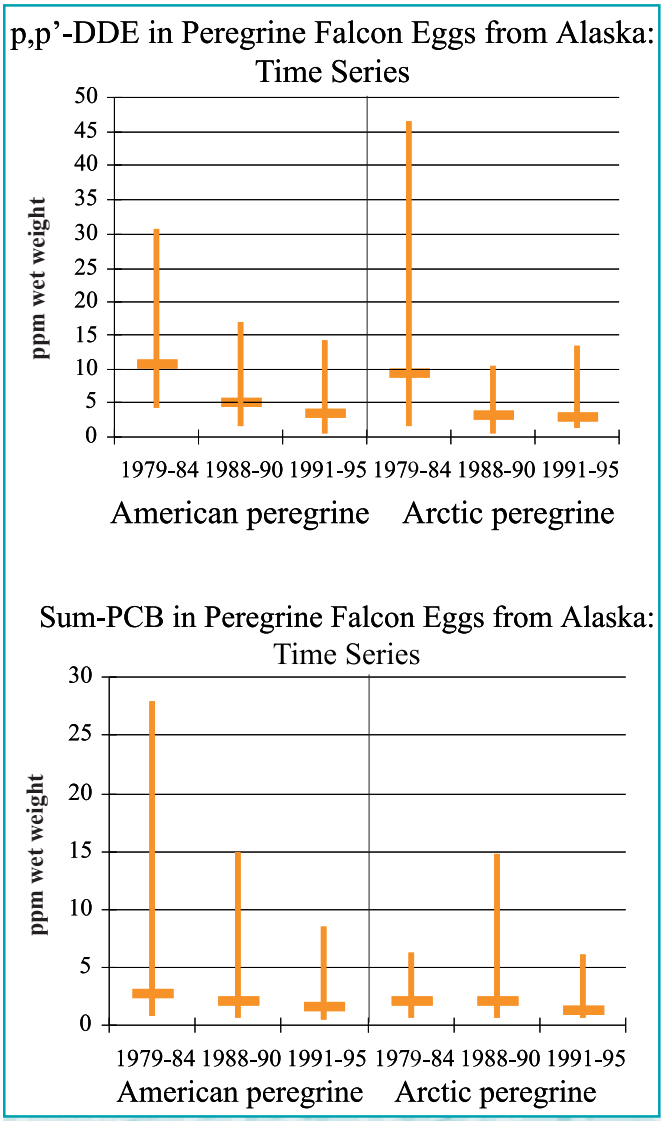


Figure 5-9a,b. Time trends for DDE and PCBs in Alaskan peregrine falcon eggs (Ambrose et al., 2000). Geometric mean and range. (n = 19–32)

nochlorine compounds and metals (Ambrose et al., 2000) (Figure 5-9). This study represents one of the few relatively long-term data sets from Alaskan biota and can offer some insight into POPs residue trends with time. In general, organochlorines declined over time, although the trend was not as strong for PCBs, which declined more slowly. These results agree with trends observed in other peregrine falcon populations, which show that PCB concentrations have not decreased as clearly as other organochlorine compounds (Peakall et al., 1990; Newton et al., 1989; Johnstone et al., 1996). Although organochlorine levels have decreased over time, evidence for cumulative and single-contaminant reproductive effects was found in remote locations (Ambrose et al., 2000). Contaminant monitoring remains a necessary management tool for this species, which is recovering from near extinction caused largely by environmental contaminants, and continues to remain vulnerable to persistent and bioaccumulative compounds.

Killer Whale

Killer whales spy-hopping.
Photo: Craig Matkin

Certain populations of killer whales (*Orcinus orca*) have been extensively studied over the past 30 years, including populations in Puget Sound, Washington, the inside waters of British Columbia, Southeastern Alaska, and Kenai Fjords/Prince William Sound, Alaska. The POPs concentrations found in some populations of Alaskan killer whales are similar to those recently reported in pinnipeds and cetaceans that occur in more contaminated waters (Ylitalo et al., 2001). Levels of total PCBs in blubber ranged up to 500 ppm, and total DDTs ranged up to 860 ppm, while median levels and some group levels were significantly lower (Figure 5-10). Concentrations of POPs in transient killer whale populations (marine mammal-eating) were much higher than those found in resident animals (fish-eating), apparently because of differences in diets (amounts and types of fat consumed) and feeding locations (localized or broad-ranging) (Ylitalo et al., 2001). Both resident and transient whale groups described in the report reside in Alaskan waters, although the transient pods may move hundreds of miles up and down the coast beyond Alaska and through international waters.

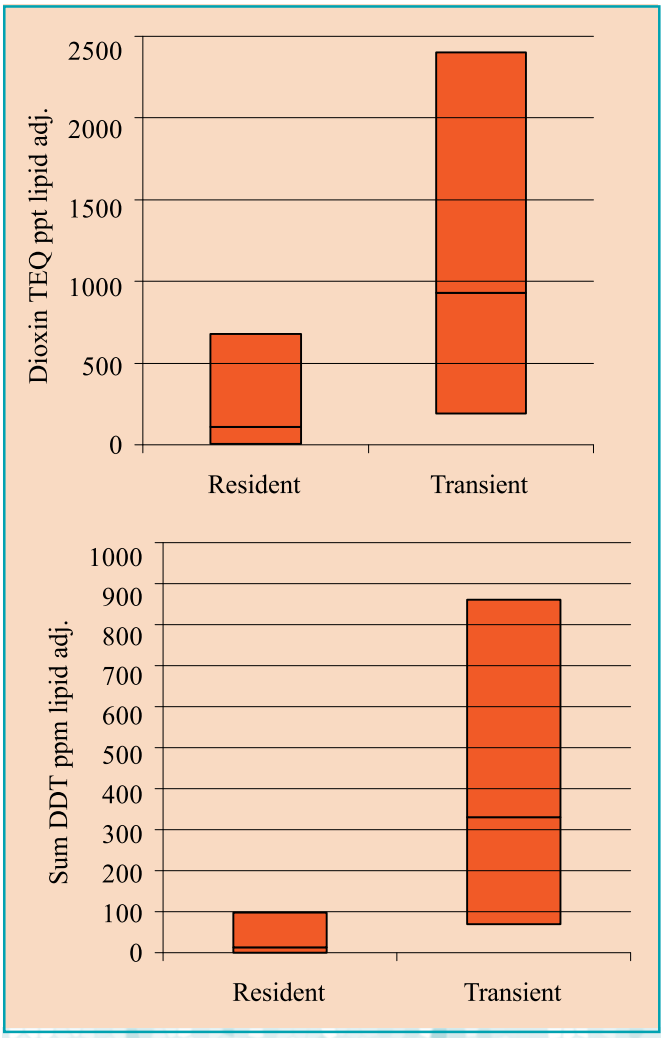


Figure 5-10. Dioxin TEQ and sum-DDT in Alaskan resident v. transient killer whales (Ylitalo et al., 2001). Mean denoted by horizontal line, range as vertical bar.

Life-history parameters such as sex, age, and reproductive status also influence the concentrations of POPs in Alaskan killer whales. Reproductive female whales contain much lower levels of POPs than sexually immature whales or mature male animals in the same age class. This is likely due to transfer of POPs from the female to her offspring during gestation and lactation. Birth order also influences the concentrations of POPs. Adult male, resident, first-born whales contain much higher POPs concentrations than are measured in subsequent offspring to resident animals in the same age group (Ylitalo et al., 2001). There is also some evidence of decreased survival of the firstborn transients that have the highest POPs levels (Matkin et al., 1998, 1999).

Reports of POPs levels in killer whales have been associated with decreases in reproductive success (Matkin et al., 1998, 1999). The causal factors for low reproduction and population decline of certain transient groups of killer whales from Prince William Sound/Kenai Fjords are not known. The low reproduction and population decline may be a natural cycle, related to human factors (e.g., oil spill), exposure to natural toxins (e.g., biotoxins), decline in the primary prey species (harbor seal), or a combination of environmental and anthropogenic factors. Exposure to toxic POPs may also be a contributing factor (Ylitalo et al., 2001).

Sea Otter

Sea otters.
Photo: Craig Matkin

Sea otters have declined precipitously throughout the Aleutian Islands over the past decade (Estes et al., 1998). Although investigations to date suggest predation may be the primary cause of the decline, contributing factors such as contaminants have not been completely ruled out. Sea otters at several

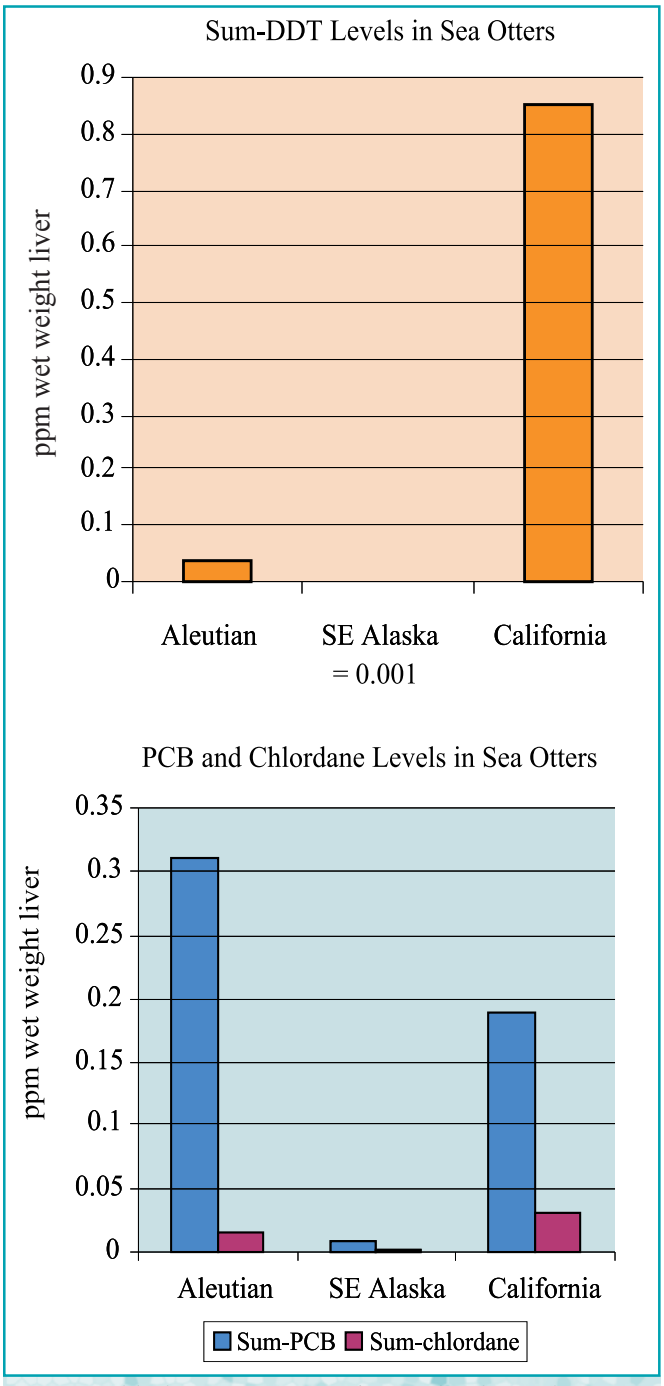


Figure 5-11a,b. Comparison of POPs levels in Aleutian (n=7), Southeastern Alaskan (n=7), and California (n=9) sea otters (Bacon et al., 1999). Mean values.

isolated sites in the Aleutians (Adak, Shemya) have been recorded with elevated levels of certain POPs, particularly PCBs (Giger and Trust, 1997). PCB levels in sea otters from the Western Aleutian Islands (Adak and Amchitka Islands) were somewhat higher than levels found in California sea otters, and were significantly elevated relative to PCB concentrations in sea otters from southeast Alaska (Bacon et al., 1999) (Figure 5-11). The relative contribution to PCB levels in Aleutian sea otters from long-range sources compared to local contamination from old defense sites cannot be ascertained using currently available data (Bacon et al., 1999; Estes et al., 1997). Sum-DDT levels in Aleutian otters, although much higher than the very low values found in Southeast Alaska, remain substantially lower than in California otters. These sum-DDT concentrations were not in the range that causes reproductive impairment in captive mink, a commonly used comparison and related species. However, there is little information that can help evaluate whether there may be interactive effects among POPs and other stressors affecting Aleutian sea otters.

Species Consumed by Humans

Beluga

Beluga whales (*Delphinapterus lucas*) are a preferred food for many Alaska Natives. The muktuk (the skin and outer layer of fat) is considered a choice item for consumption. This outer layer of fat contains the highest levels of POPs in the animal (Wade et al., 1997). The blubber of beluga whales from Alaska contains POPs in concentration ranges similar to those found in beluga whales from the Canadian Arctic (Muir and Norstrom, 2000) but much lower than levels in whales from the highly contaminated St. Lawrence River in eastern Canada (Krahn et al., 1999) (Figure 5-12). Within Alaska, the low levels in the Cook Inlet stock are noteworthy, as these animals reside in

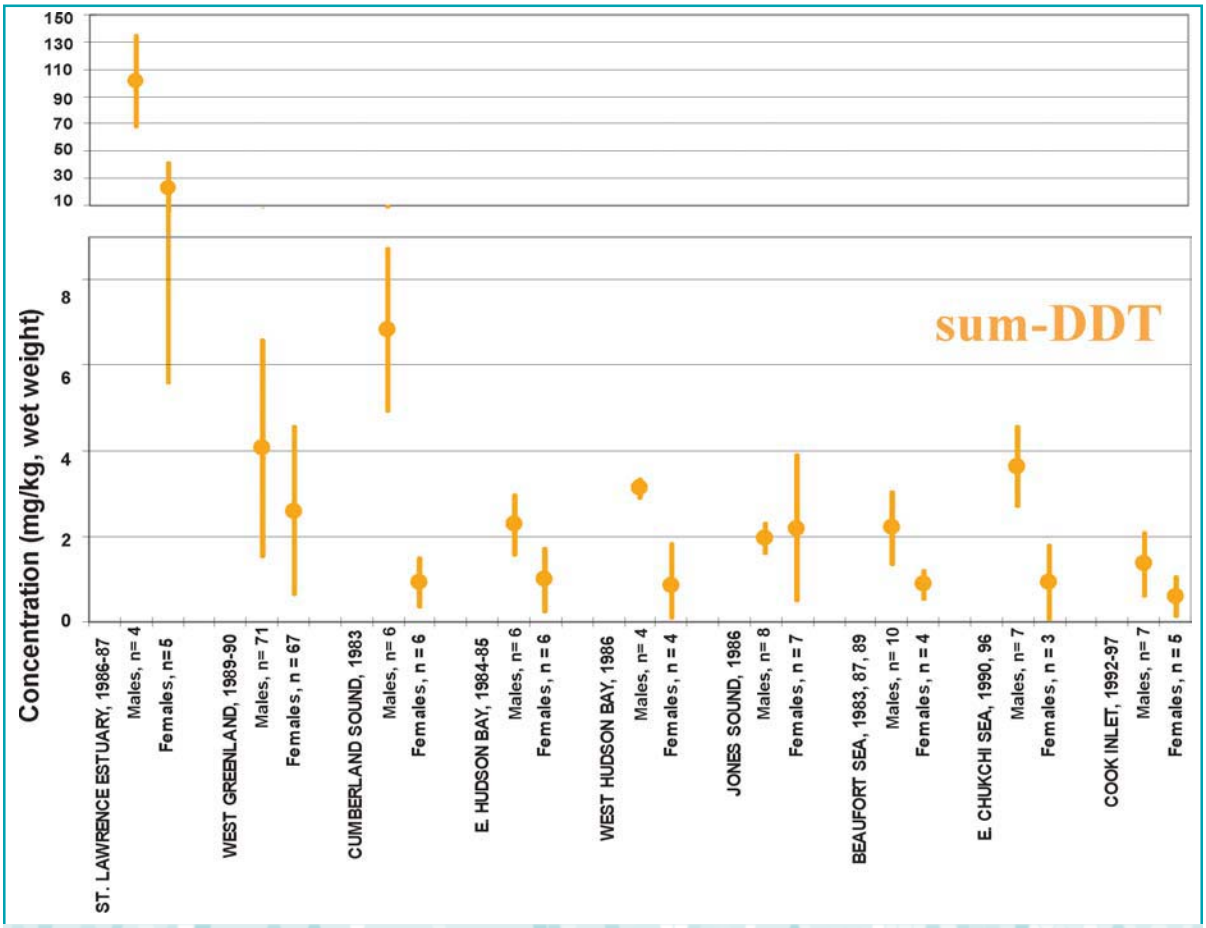


Figure 5-12. Sum-DDT levels in beluga blubber. Mean (•) +/– one standard deviation (vertical bar) (Becker et al., 2001).

Beluga whales.
Photo: NOAA

Bowhead whales.
Photo: NOAA

one of the most "urban" areas of Alaska, where anthropogenic contamination could be expected to result from the relatively higher density of human residents and commercial activities (Krahn et al., 1999).

Gender is an important factor to consider when interpreting differences in POPs concentrations among beluga whale stocks (Krahn et al., 1999). For example, the adult males of each stock had higher mean concentrations of all contaminant groups than did the adult females of the same stock. This is considered to be an effect of POPs transfer from the mother to the calf during gestation and lactation. This theory is supported by the finding that upon reaching sexual maturity, the levels of toxaphene, PCBs, DDTs, and chlordane steadily go down in females as they produce calves and lactate (Wade et al., 1997).

Bowhead Whale

The bowhead whale stock (*Balaena mysticetus*) migrates through the Bering, Beaufort, and Chukchi Seas and is listed as an endangered species. Alaska Natives are the only U.S. citizens permitted to harvest the bowhead whale for food. Studies have shown relatively low levels of PCBs in bowhead whale (Figure 5-13) blubber, but these levels tend to increase with age (McFall et al., 1986; O'Hara et al., 1999). Previous reports support the view that these large filter-feeding whales, consuming at a lower level on the food chain, have lower concentrations of POPs in their blubber. Toothed whales, eating higher on the food chain, may have one or two orders of magnitude more POPs than the filter-feeding whales (O'Hara and Rice, 1996; O'Shea and Brownell, 1994; Borell, 1993).

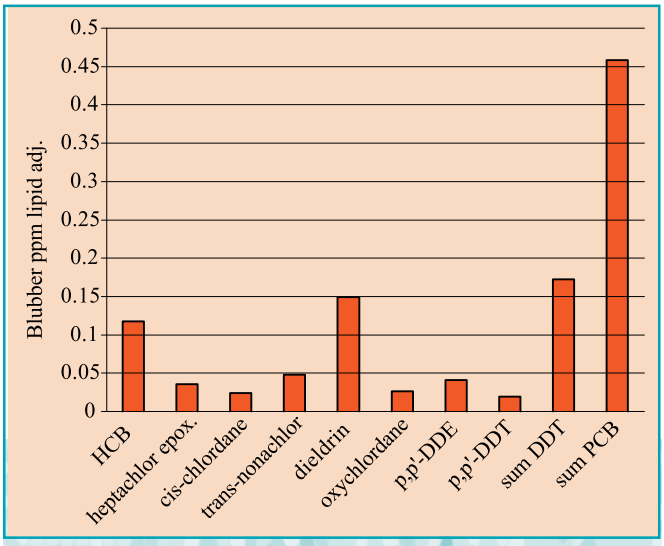


Figure 5-13. POPs levels in bowhead whale blubber (O'Hara et al., 1999). Mean values. n=26.

Seals

The various seal species in Alaska constitute a substantial portion of the marine mammal diet of numerous predator species, including humans. Blubber samples from four Alaskan seal species (bearded seal, *Erignathus barbatus*; harbor seal, *Phoca vitulina*; northern fur seal, *Callorhinus ursinus*; ringed seal, *P. hispida*) have been col-

Northern fur seals.
Photos: Suzanne Marcy

lected and analyzed for POPs contaminants (i.e., total PCBs, total DDTs, total chlordanes, HCB, and dieldrin) (Krahn et al., 1997). Harbor seals, frequently consumed by Alaska Natives, were found to have low but measurable levels of several of these POPs (Figure 5-14). The concentrations of POPs in harbor seals from Prince William Sound were generally much lower (e.g., total PCBs up to 100-fold and total DDTs up to 30-fold lower) than those recently reported for harbor seals from the northwestern U.S. mainland, including animals involved in mass mortality events (Krahn et al., 1997) (see Chapter 6, Marine Ecosystems). For Alaska, however, in contrast to other parts of the United States, the potential for POPs biomagnification continues through the consumption of harbor seals by humans, an additional one or more trophic levels higher.

Notable among the multiple studies of seal species is the finding that POPs concentrations in male subadult northern fur seals sampled in 1990 at St. Paul Island in the Bering Sea were higher than

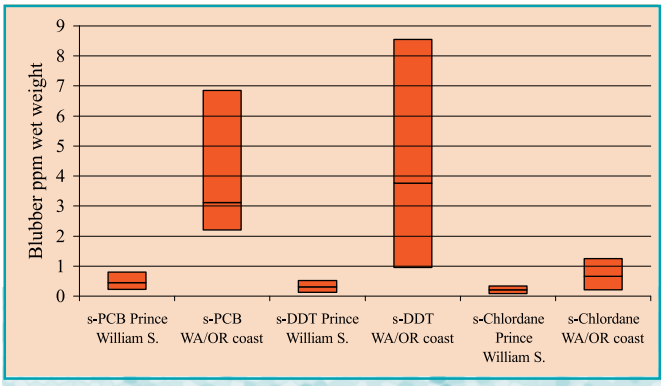


Figure 5-14. POPs levels in Alaskan v. West Coast U.S. harbor seals (Papa and Becker, 1998). The "s" prefix indicates summation of related chemical substances.

concentrations in the ringed and bearded seals from the Bering Sea or in the harbor seals from Prince William Sound. Fur seals feed mainly on oceanic species such as squid and pollock. Female and juvenile fur seals migrate long distances into the open ocean of the northern Pacific far south of Alaska and even to the shores of Japan, as well as California. The higher POPs concentrations in fur seals are consistent with exposures occurring during these long oceanic migrations. Harbor seals feed on different species of fish that tend to be very coastal, like perch. Harbor seals do not migrate, but stay close to their coastal feeding and haul-out areas.

Steller Sea Lion

Steller sea lions.
Photo: NOAA

Studies show that PCBs are the predominant POPs in sea lion blubber, followed by levels of DDT/DDE. Levels of chlordane compounds were an order of magnitude lower. Higher concentrations of PCBs and DDTs were found in Steller sea lions from Alaska compared to those from the Bering Sea, indicating that the populations have different sources of exposure (Lee et al., 1996). Like beluga whales, as Steller sea lion females become sexually mature they show a dramatic decline in POPs levels. It has been calculated that they may lose 80% of their PCBs and 79% of DDT/DDE through lactation while nursing the first pup (Lee et al., 1996). Two studies of PCBs in Steller sea lion blubber found an average of 23 ppm (Varanasi et al., 1993) and 12 ppm in males (Lee et al., 1996).

These PCB levels in Steller sea lions generated concern among local subsistence populations, who requested an evaluation of potential human health impacts (Middaugh et al., 2000a,b; see following).

Salmon

Alaskan fisher and sockeye salmon.
Source: NOAA

Salmon species are key to Alaska's commercial fisheries and to the well-being of many subsistence communities. For the Alaskan fishing industry, salmon is a billion-dollar business. For subsistence communities who catch and consume their own, fish by weight make up about 59% of the total subsistence harvest for Alaska Natives, with salmon being the most important species (AMAP, 1998). In western Alaska, the fish harvest can approach 220 kg (485 lb) per person per year and make up more than 73% of all locally harvested food (Wolfe, 1996). The U.S. Fish and Wildlife Service and Alaska state government are currently assessing contaminant levels and evaluating fish health in salmon from selected Alaskan rivers.

The migratory and reproductive patterns of sockeye salmon (*Oncorhynchus nerka*) are known to provide a means of transport for very low levels of chemicals such as PCBs and DDT to waters used by other species of Alaskan freshwater fish, such as grayling (*Thymallus arcticus*) (Ewald et al., 1998). Migrating salmon carry these low but measurable levels of POPs to spawning areas where, after spawning, they die and decay. The POPs then become bioavailable to other local species. The levels of POPs delivered by salmon to Alaskan interior lakes and rivers have been estimated to be slightly above the levels deposited through atmospheric means, although these levels are far below those found in fish from the Great Lakes region (Figure 5-15).

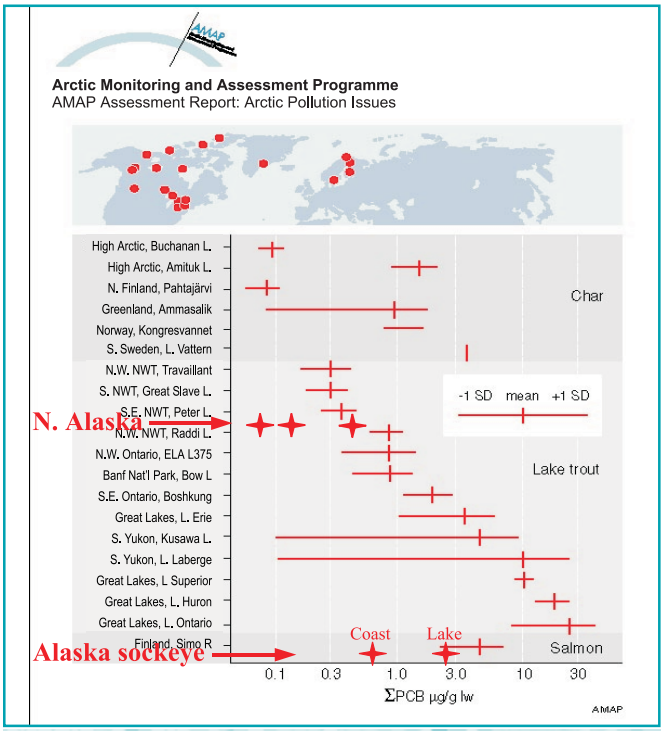


Figure 5-15. PCB levels in salmonid fish: preliminary Alaskan results overlaid AMAP summary figure (Ewald et al., 1998; Allen-Gil et al., 1997). Mean concentrations in lake trout from Elusive, Feniak, and Schrader Lakes in northern Alaska (Allen-Gil et al., 1977). Mean concentrations in sockeye salmon from the same run in Alaska, taken at the coast and upstream lake, where PCB concentrations have increased as lipids have been metabolized during the migration (Ewald et al., 1998).

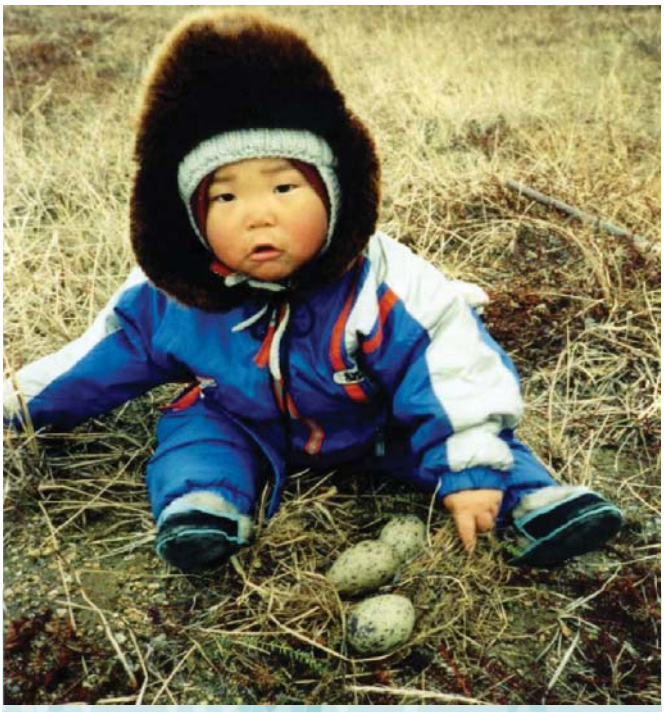
Polar Bear

Polar bear.
Photo: U.S. Fish and Wildlife Service

Polar bears are at the top of the Arctic marine food web. Norstrom et al. (1998) investigated chlorinated hydrocarbon compounds in polar bears from much of the circumpolar Arctic. They found strong relationships among contaminant concentrations and sex. Individual dietary preferences, regional differences in species availability, and food-chain structure also contributed to variability within the data. For example, baleen whale and walrus carcasses may be seasonally important food sources for polar bears in the Bering Sea and Chukchi Sea region, supplementing their primary diet of ringed and bearded seals. Walrus (except when eating seals) and baleen whales feed at lower trophic levels than other Arctic marine mammal species. Conversely, polar bears feeding on beluga carcasses in eastern Canada exhibit higher POPs levels. Thus, prey selection can affect the pattern of chlorinated hydrocarbon uptake in these different polar bear populations. Total chlordanes (sum of 11 chlordane-related compounds) were the most uniformly distributed POPs in this study, reflecting a similar pattern found in air and seawater sampling (Norstrom et al., 1998).

Although sample sizes were small, concentrations of total PCBs, total chlordanes, DDE, and dieldrin in polar bears from the Bering, Chukchi, and western Beaufort Seas tended to be among the lowest in the study area. The atmospheric circulation of this area is dominated by eastward airflow from Asia and the North Pacific Ocean. Sources of POPs in the Bering, Chukchi, and western Beaufort Seas are, therefore, more likely to have originated in eastern Asia. PCBs were generally used less often in Asia, except Japan, than in North America and Europe (Norstrom et al., 1998). The U.S. Fish and Wildlife Service, Office of Marine Mammal Management, continues to work with Alaska Native hunters to collect samples for analysis of environmental contaminants.

Native Peoples of Alaska



Alaska Native child with eggs—a subsistence food.
Family photo: Jesse Paul Nagaruk

Food is central to culture. Alaska Natives, although sharing different cultural heritages, are linked to their environment through the foods that they gather locally and consume. The social structures that define behavior in the sharing of subsistence harvests and through feasts are the traditions of Alaska Natives—the cultural values of the people. Children and youth are taught about their environment and about their relationship to the community through hunting, fishing, gathering, and sharing. The survival knowledge of the group is passed

down from generation to generation, ensuring the transmission of language and values. The work of obtaining one's own food is rigorous and promotes self-reliance and self-esteem. For all of these factors, continued confidence in the quality of locally obtained foods is essential (Egeland et al., 1998).

Alaska Natives eat 6.5 times more fish than other Americans (Nobmann et al., 1992). Under the Marine Mammal Protection Act, Alaska Natives are the only people in the United States allowed to hunt marine mammals, which they then eat. By doing so, Alaska Natives consume predator species (seals, sea lions, bears, and toothed whales) at the very top of the food chain. Many Alaskans have wide seasonal variation in their dependence on locally available foods. Their diet shifts in response to short intense summers and the migration of wild birds, fish, and mammals. Alaska Natives eat more fat, albeit different types, than most U.S. citizens. Marine mammal fats and fish oils differ significantly from pork and beef fats in their ability to provide health benefits (Jensen and Nobmann, 1994; Nobmann et al., 1992; Scott and Heller, 1968). Estimates of the amount and type of subsistence foods consumed by Alaska Natives are summarized in Figure 5-16, documenting levels of dependence and species preferences by area.

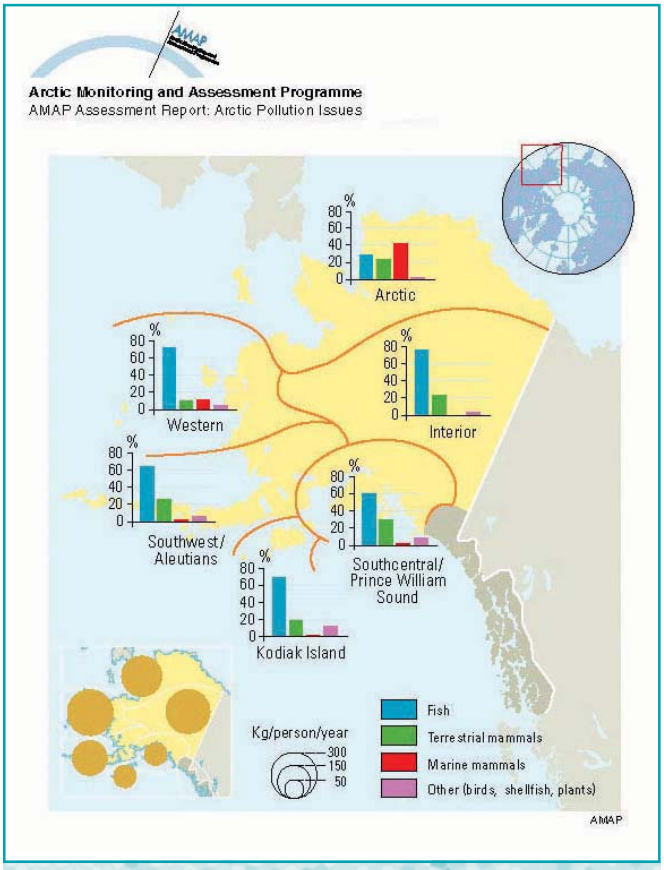


Figure 5-16. Total and composition of subsistence production in Alaska. AMAP.

In regions where employment opportunities are scarce or seasonal, locally obtained foods remain an economic necessity. Shifting food consumption in remote Alaskan communities is not beneficial for several reasons. Food that is purchased is expensive and rarely fresh owing to the long distances it must be shipped and the number of times it must be handled as it goes into smaller and smaller stores. Many people in these remote communities have very limited food budgets because of the scarcity of jobs and high costs of heating and other costs associated with life in a remote and challenging environment (Egeland et al., 1998).

Store-bought foods in remote Alaskan communities need to have a long shelf life. Therefore, the foods have been frozen, canned, or chemically preserved. Many of these foods do not have the nutritional value of fresh foods from the local area. Store-bought foods are much higher in processed sugars, saturated fats, sodium, and simple carbohydrates, contributors to such conditions as obesity, diabetes, heart disease, and dental caries. These conditions are growing at alarming rates in Alaska (APHA, 1984; Ebbesson et al., 1996; Lanier et al., 2000; Nobmann et al., 1992; Nobmann et al., 1998; Nutting, 1993; Schraer et al., 1996). Health surveys have also indicated that, in some communities, the individuals who are most concerned about environmental pollution are the same people who most frequently consume less traditional foods and are shifting to buying food from the store (Dewailly et al., 1996; Egeland et al., 1998; Hild, 1998).

Adding to concerns about contaminants in local foods, Alaska Natives have reported changes in the subsistence species they hunt. These changes include seals with diseases they have not seen before, no hair, yellow fat, fat and meat that does not taste as it should, and seals with abnormal

growths and abnormal sex organs. Similar concerns have been raised about other subsistence species. These observations, collected now by the Alaska Native Science Commission, may contribute to an understanding of what is occurring in the changing Arctic (www.nativeknowledge.org). In the absence of key information to answer specific questions, and in response to media reports about contamination of the Arctic, the conclusion being reached by many Alaska Natives is that the animals may not be healthy, and the health of their children may be at risk.

POPs Levels in Alaska Natives

Most of the POPs under the Stockholm Convention were never used in or near Alaska. For the other POPs (e.g., PCBs, DDT, polychlorinated dioxins/furans), local use in Alaska and emissions to the environment are much less than has occurred in the lower 48 states. Yet there is considerable concern among residents—particularly Alaska Natives—that they may have become contaminated through consuming traditional foods. The most expeditious way to assess the extent to which Alaskans have been exposed to these persistent toxic substances is to measure levels in human tissue (Hild, 1995). Unfortunately, there is no statistically based survey of POPs levels in Alaskans. Indeed, there is no national statistically based survey of POPs levels in the U.S. population, although serum has been collected under the NHANES IV study and is being analyzed at the Centers for Disease Control and Prevention (CDC).

POPs levels have been measured in small studies of selected Alaska Natives, lower-48 background comparison groups, and Great Lakes fishers, providing valuable indicative and comparative information on POPs levels (Figures 5-17 and 5-18). These data can help inform hypotheses and conclusions regarding sources of human exposure to POPs and the resulting concentrations and trends. For example, as with marine mammal exposures, high trophic level feeding is generally more problematic than lower on the food chain. Thus, it can be hypothesized that Alaska Native diets based on plants and plant-eating animals are of less concern

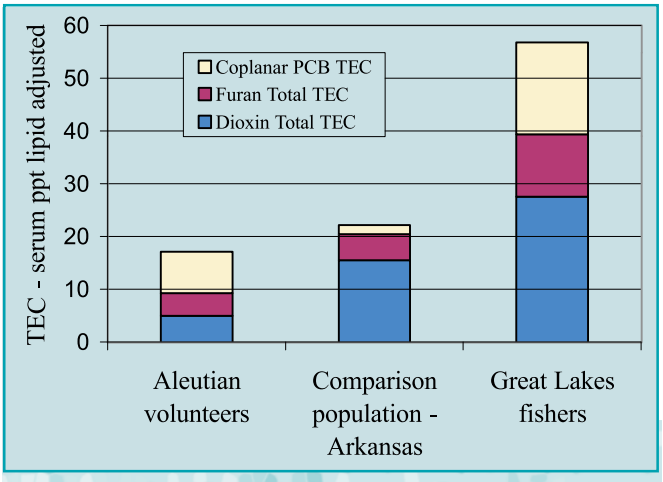


Figure 5-17. Serum dioxin toxicity equivalence concentrations (TEC) in Aleutian volunteers (n=48) compared with Arkansas (n=70) and Great Lakes fisher (n=31) comparison groups (Middaugh et al., 2000a).

than those relying on the consumption of marine mammal predator species. The importance of location and proximity to emission sources and transport pathways can also be evaluated, as the western Aleutians represent a quite different locale from the Beaufort Sea off northeastern Alaska. Likewise, the subject's age may be a major determinant of many POPs levels. As has been evident in lower-48 studies, POPs levels tend to increase with age because of the fundamental persistent and bioaccumulative nature of the contaminants, espe-

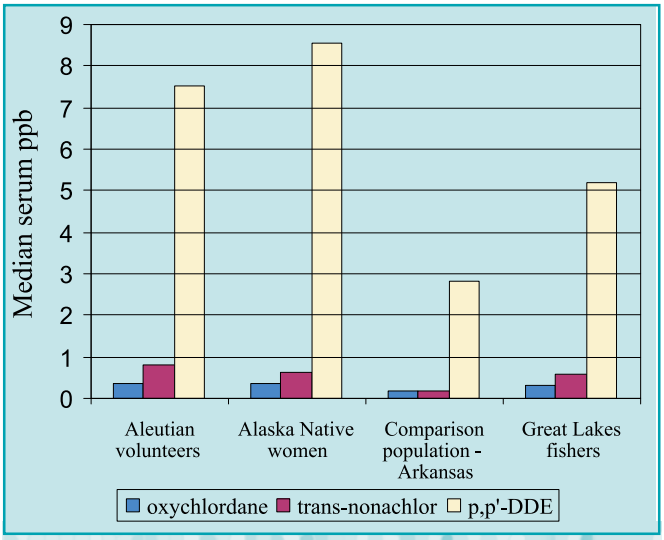


Figure 5-18. POPs levels in Alaskan v. comparison U.S. populations (Middaugh et al., 2000b, 2001; pers. comm. C. Rubin 2002 for median levels in Alaska Native women). n=166 (Aleuts); 131 (Alaska Native); 180 (Arkansas); 30 (Great Lakes). Results not lipid adjusted.

cially in males where there is no excretion through lactation. Age is also an important consideration in evaluating Alaska Native levels, as dietary practices and the proportion of traditional foods in many diets have changed over recent years.

In response to citizen concerns, the State of Alaska, Department of Health and Social Services, conducted a targeted study of POPs in five Aleutian communities (Middaugh et al., 2000a,b, 2001). These communities had become concerned because some Alaskan Steller sea lion blubber had been reported to contain relatively high levels of PCBs (23 ppm, Varanasi et al., 1993; 12 ppm in males, Lee et al., 1996) potentially impacting their use of sea lions as a source of meat and oil. As graphed in Figure 5-17, total PCB, dioxin, and furan toxicity equivalence concentrations (TEC) levels in the Aleutian volunteers (Middaugh et al., 2001) were similar to those in the background U.S. population (Arkansas) and considerably below fisher exposures on the Great Lakes (Anderson et al., 1998). Middaugh et al. (2000a) also analyzed the age relationship to concentration levels (Figure 5-19), demonstrating increased POPs levels with age. Similar age-related findings are evident in other studies from lower-48 populations and cannot necessarily be ascribed to dietary pattern changes. Because the Aleutian sample sizes were very low and from volunteer populations in isolated, select communities, few conclusions can be drawn, and a broader surveillance is needed to answer key questions and address community concerns.

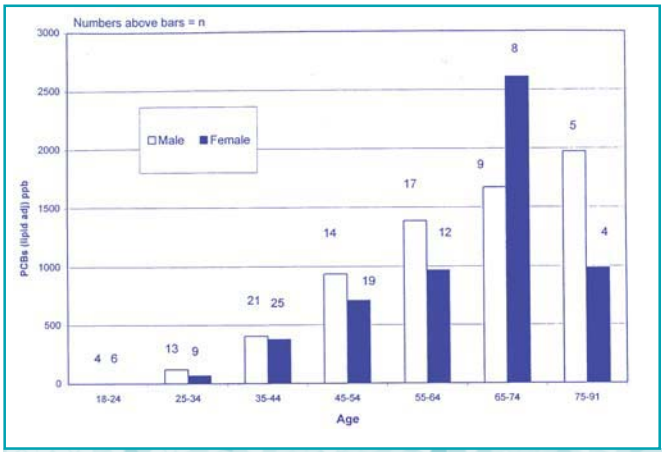


Figure 5-19. Distribution of serum PCB concentrations in Aleutian volunteers as a function of participant's age (Middaugh et al., 2000a).

A small group of Aleut women of childbearing age—not pregnant at the time—was identified in the Middaugh et al. (2001) study. If their levels were to be compared with the maternal plasma study data of the Arctic Monitoring and Assessment Programme (AMAP, 1998), the Aleut women would have the highest levels of p,p'-DDE (geometric mean 0.503 ppm lipid) so far found in the circumpolar region. They were second highest among the other Arctic nations for trans-nonachlor (g. mean 0.0498 ppm lipid) and oxychlordane (g. mean 0.0285 ppm lipid) (Middaugh et al., 2001). Note, again, that the Aleutian studies are only preliminary and cannot be considered statistically representative of this population. The relative elevations of DDT and chlordane derivatives are, however, consistent with the location of the Aleutians near continuing use regions for these POPs in Asia.

From the other side of Alaska, Arctic Slope mothers have POPs levels (DDT, DDE, mirex, trans-nonachlor, oxychlordane, and PCBs) that are lower than those in the Aleutian/Pribilof Islands women of childbearing age (Simonetti et al., 2001). These levels are comparable with levels in the lower 48 states for background populations (Anderson et al., 1998).

At this time, POPs movement and deposition trends to the north are unknown. An ongoing national surveillance program has not been in place to clearly indicate whether the 12 POPs under the Stockholm Convention are increasing, stable, or decreasing. There is an indication that in other Arctic nations some forms of PCBs are declining, whereas no trends are apparent for the more chlorinated forms (Hung et al., 2001).

Ongoing POPs Research in Alaska

Human health and ecological research on POPs levels and effects in Alaska is increasing, linking the domestic and transpolar efforts of the Arctic Monitoring and Assessment Program (AMAP), Arctic Council, U.S. federal agencies, Alaska state gov-

ernment, and tribal groups. These research efforts cover a spectrum from expanding work on environmental levels through measurements of body burdens and effects along the food chain to wildlife and humans. Emphasis is placed on community involvement in the planning, decision making, and communication of this work. Among these research efforts, measurements are underway of POPs levels transported in the air to Alaska and of levels in water and sediments of the Yukon River. Studies have been conducted on POPs levels in a wide range of species including chinook and chum salmon, Stellers eiders, black-capped chickadees, red-throated loons, and wood frogs. This research is accompanied by expansion of data collection on marine mammals and other high-trophic predators, notably bald eagles and polar bears. With Alaska Natives, traditional food practices are being documented and analyzed to assess not only the contaminant loads but also the nutritional benefits of the diet. POPs levels in mothers and the umbilical cord blood of their offspring are being measured to assess the body burden of contaminants. These data serve as an essential link in studies of potential effects (e.g., developmental, immunological) on the children. Research data have also been published as part of ongoing studies assessing the link between POPs levels and breast cancer (Rubin et al., 1997) and on the effect of HCB and DDE in human cell cultures (Simonetti et al., 2001).

These research efforts in Alaska parallel the POPs reduction and elimination activities under the Stockholm Convention. While the current Alaskan data outlined in this chapter serve to inform U.S. consideration of the Stockholm Convention, the ongoing work will further help to:

- Monitor increases or declines in POPs levels in Alaska
- Detect any wildlife or human hotspots of POPs contamination
- Identify potential domestic and international sources of ongoing POPs contamination
- Guide communities on the risks and benefits of traditional practices
- Increase the general scientific knowledge of the effects of these toxic substances and the levels at which these effects occur.

Conclusion

POPs can now be measured in all environmental media and species in Alaska. POPs levels in Alaska are generally low, however, when compared to the lower 48 United States. Accompanying these comparatively low levels are isolated examples of elevations that portend a cautionary warning in the absence of international action. DDT/DDE and PCB levels in transient Alaskan killer whales are as high as those found in highly contaminated east coast dolphins, reaching to the hundreds of parts per million in lipid. On Kiska Island in the Aleutians, DDE concentrations in bald eagle eggs approach effect levels seen in the Great Lakes. And Aleuts have some of the highest average DDE and chlordane levels measured in Arctic human populations, highlighting their proximity to continuing emission sources in Asia. Indeed, Alaska's location—geopolitically and climatically—suggests that POPs pollution could be exacerbated in future years in the absence of international controls.

The hunting and dietary practices essential to survival in the Arctic make indigenous humans and wildlife especially vulnerable to POPs. Where animal fat is the currency of life, this intensifies the unique combination of POPs properties to migrate north, associate with fat, persist, bioaccumulate, and biomagnify. For Alaska Natives, current POPs levels vary with location and diet. In the human populations measured (Aleutian, Pribilof, North Slope), POPs levels are similar to those experienced by the background U.S. population, and generally below those of fisher communities around the Great Lakes. It is, therefore, important to emphasize that there are no known POPs levels at this time in Alaska that should cause anyone to stop consuming locally obtained, traditional foods or to stop breastfeeding their children. Current information indicates that the risks associated with a subsistence diet in Alaska are low, whereas in contrast the benefits of this diet and breastfeeding children are well documented (Ebbesson et al.,

1996; Jensen and Nobmann, 1994; Nobmann et al., 1992; Scott and Heller, 1968; Bulkow et al., 2002). Further investigation and assessment are needed for specific species and foods in traditional diets, and to broaden the database across Alaskan communities. The international AMAP (1998) report came to the same conclusion for the entire Arctic, and Alaskan levels of most of the POPs are generally lower than for other polar nations. The international community has also moved to further reduce POPs contamination through negotiation of the Stockholm Convention on POPs, implementation of which should help minimize future increases in levels of the listed POPs.

We are as one with our ancestors and children.

We are as one with the land and animals. [Alaska Native anthropologist Rosita Worl]

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Chapter 6 Accumulation and Effects of Persistent Organic Pollutants in Marine Ecosystems and Wildlife

Introduction

The accumulation and effects of persistent organic pollutants (POPs) in marine ecosystems testify to the magnitude and global scale of these pollutants. On the coasts of the continental United States, POPs concentrations in some marine mammals reach very high levels, such as in the bottlenose dolphins familiar off the Atlantic coast. In remote regions in the middle of the North Pacific Ocean, thousands of miles from industrial centers, albatross have been found to have high PCB and dioxin levels that may be interfering with their reproductive success. And POPs are now measured, albeit at much lower levels, in remote reaches of the Southern Hemisphere and Antarctic. Although these oceanic ecosystems often fall under no national jurisdiction, they are valuable economic and esthetic resources for all. The species that inhabit these areas recognize no national boundaries, nor do the contaminants to which they are exposed. As with the Great Lakes, past assumptions of the limitless potential of these vast water bodies to absorb chemicals are thwarted by the persistent and bioaccumulative nature of these contaminants, focusing and maintaining their presence in biological food chains amidst the vast oceanic distances.

The very high levels of POPs found in some marine mammals, e.g., dolphins, killer whales, and beluga whales, inevitably lead to questions about their links to mass strandings and mortality events. The popular scientific literature contains many stories, articles, and opinions suggesting that the concentrations of POPs accumulated by various marine mammal species are sufficient to be causing adverse effects. However, these exposure data are not backed by the rigorous toxicological information necessary to allow a sound estimate of the actual impacts of these contaminants. Resolution of these questions, necessary because POPs levels are indeed troubling, is difficult because modern society treats these highly intelligent and social creatures with great deference, formalized through the Marine Mammal Protection Act. As with humans, it is very difficult to obtain permission to experimentally dose marine mammals with contaminants. As with human epidemiology, it is difficult to isolate causal agents in the presence of viral and bacterial infective illness, natural toxins (e.g., red tides), food shortages, predation, and the soup of chemical contaminants and exposures.

This chapter examines POPs in the marine environment: their transport and the resulting levels, trends, and distributions. Examples are provided of adverse effects on the species most at risk from POPs—those at the top of the food chain accumulating the greatest concentrations of contaminants. Field observations of ocean birds, inshore and offshore, are summarized, demonstrating adverse reproductive effects both historically and recently. Research data are then provided summarizing the evidence for adverse effects on marine mammals.

Transport of POPs and the Role of Oceans as Sinks

POPs have spread over the entire surface of the Earth, as evidenced by their occurrence in the air, water, and wildlife of the open oceans. The characteristics of POPs that favor their long-range transport are semivolatility, persistence in the atmosphere, and high chemical and biological stability (see Chapters 7, 9). POPs are transported by runoff and rivers. They are deposited and accumulate in marine sediments, particularly in estuaries and other near-shore areas. The POPs present in these sediments represent an ongoing source of contaminants that can be recirculated into the food chain and accumulated by top predators. Atmospheric transport is also of considerable importance

to near-shore marine environments where, despite the influence of terrestrial runoff, short-range transport of contaminated particles may represent a significant contribution to the total input.

Available information demonstrates that the oceans, including deep ocean waters, also function as a major and ultimate sink for POPs (Ballschmiter, 1992; Preston, 1992; Loganathan and Kannan, 1991; 1994; Tanabe et al., 1994; Wania and Mackay, 1999; Macdonald et al., 2000; Froescheis et al., 2000). In the late 1970s, the U.S. Environmental Studies Board (1979) estimated that about 50% to 80% of the total PCB residues in the U.S. environment were present in North Atlantic waters. It has also been estimated that over 60% of the world's environmental PCB load is present in open-ocean waters (Tanabe, 1988).

Status and Trends of POPs in North American Marine Ecosystems

Analysis of time trends in environmental concentrations is necessary for understanding and managing the causes and effects of POPs contamination in marine ecosystems. On the simplest level, time trend studies indicate the persistence of a substance by simply watching its rate of decrease with time. On a more complex level, historical trend studies can be used to predict future toxic impacts or indicate times when such impacts are no longer significant.

Time-trend monitoring programs for POPs exist in several countries. The International Mussel Watch Program and the National Status and Trends Program of the United States National Oceanic and Atmospheric Administration (NOAA) are examples (O'Connor, 1996). Temporal trend studies of POPs in biota (fish and oysters) from inshore/coastal aquatic ecosystems have shown clear declines in tissue concentrations following bans on the use of POPs. Although the concentrations of POPs in marine biota are generally declining, the rates of decline are slow (Loganathan and Kannan, 1991, 1994). This slowness results from the long residence time of POPs in the marine environment and cycling from sediments and other sources of contamination.

To assess the current status and long-term trends of POPs in U.S. coastal marine environments, NOAA's Status and Trend Mussel Watch Program has been monitoring the coastal waters since 1986 (*http://ccma.nos.noaa.gov/NSandT/New_NSandT.html*). Concentrations of POPs have generally declined in mussels from 154 sites along the U.S. coast, although some local trends remain uncertain (O'Connor, 1996, 1998) (Figures 6-1, 6-2). For fish, the National Benthic Surveillance Project, a component of NOAA's Status and Trends Program, has monitored levels from the West Coast of the United States since 1984 and found no consistent trend in POPs concentrations (Brown et al., 1998). These studies have also documented that fish, mussels, and sediment collected near urbanized coastal areas continue to contain relatively high concentrations of POPs (Daskalakis and O'Connor, 1995; O'Connor, 1996; Brown et al., 1998).

Although the concentrations of POPs in sediment and oysters from coastal areas have declined following use restrictions, concentrations in marine mammals have declined only slightly over the past few decades. Very few studies have examined temporal trends of POPs using marine mammal tissues. No significant differences in concentrations of PCBs and DDT were observed in striped dolphins col-

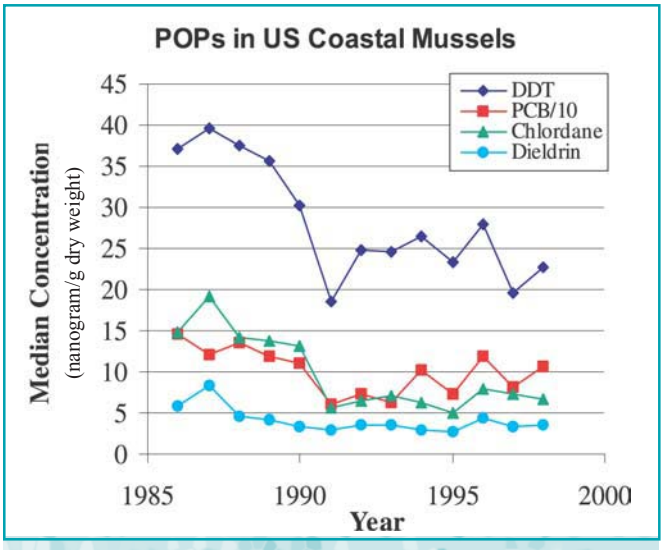

Figure 6-1. Decreasing national median concentrations of contaminants in mussels. Sum values; PCB value divided by 10.

Source: NOAA

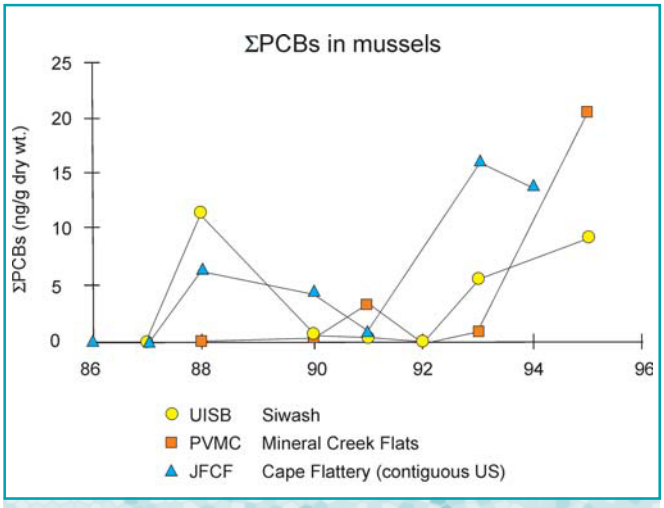

Figure 6-2. Time trends of PCBs in Alaskan mussels.
Source: NOAA, http://ccma.nos.noaa.gov/NSandT/AKtPCB.html

lected from the western North Pacific Ocean between 1978–79 and 1986 (Loganathan et al., 1990) (Figure 6-3). Similarly, fur seals collected from the northern North Pacific Ocean showed no decline in concentrations of PCBs during the 1980s (Tanabe et al., 1994). Six- to ten-year trends in the concentrations of POPs in the Canadian Arctic have been examined in female ringed seals and male narwhal and beluga whales. Concentrations of DDTs, PCBs, chlordanes, and toxaphene showed no significant decline in these marine mammals (Muir et al., 1999). In fact, concentrations of PCBs have increased in minke whales from the Antarctic since 1984, and the other POPs have remained at a steady state (Aono et al., 1997).

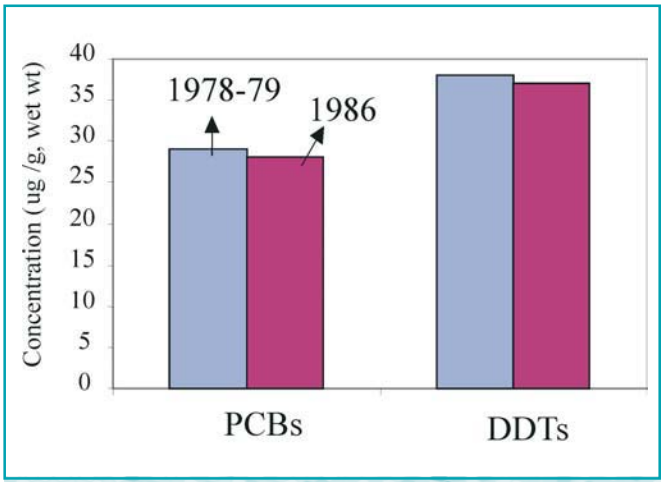

Figure 6-3. POPs concentrations in North Pacific dolphins (Loganathan et al., 1990).

Similarly, concentrations of PCBs and chlordanes in minke whales collected from the North Pacific Ocean in 1994 were higher than those collected in 1987 (Aono et al., 1997). The current absence of a reduction in the residue levels of POPs in marine mammals is consistent with an ongoing redistribution of POPs up the food chain into long-lived animals, and emphasizes the long-term potential toxic impacts of POPs.

Routes of Exposure of Marine Mammals and Seabirds to POPs

POPs reach marine environments by atmospheric deposition or in terrestrial runoff from rivers. Because of their relatively low water solubilities, POPs tend to be strongly bound to particulate matter in sediments in aquatic ecosystems. Invertebrate animals living in sediments, such as worms and shellfish, eat the POPs bound to food particles and also receive some uptake of POPs directly from water. Fish and other predators consume these invertebrates and accumulate a variety of organic contaminants. POPs biomagnify at each subsequent step up the food chain (i.e., reach higher concentrations in the predator than in its food). In marine ecosystems, many of these top predators are birds or marine mammals. A study from the western North Pacific Ocean has shown the concentrations of PCBs and DDTs in striped dolphins to be 10 million times greater than in surface waters (Tanabe et al., 1984) (Table 6-1). Although the concentrations in water or prey items were low, marine mammals have large pools of fatty tissues, long lifespan and reduced capacity to metabolize POPs. As a result, they accumulate high concentrations of POPs in their tissues (Tanabe et al., 1994).

Table 6-1. PCBs and DDTs biomagnify in the North Pacific Ocean from surface waters through plankton to marine mammals (Tanabe et al., 1984)

Concentration (pg/g)	PCBs	DDTs
Surface water	0.28	0.14
Zooplankton	1800	1700
Myctophids	48000	43000
Squid	68000	22000
Striped dolphin	3700000	5200000

Concentrations in squid in the North Pacific provide further evidence of the link between environmental pollution and subsequent contamination high on the food chain in marine mammals and birds. Hashimoto et al. (1998) measured polychlorinated dioxin and furan levels in predatory squid in a transect of the North Pacific from Japan to near the coasts of Canada and the United States, with additional samples from New Zealand waters (Figure 6-4). Squid taken from waters near industrial centers, such as Japan, showed considerably higher levels of dioxins and furans. The lowest levels were found in the far South Pacific. The levels of dioxins and furans in these abundant and relatively short-lived (1–2 years) predator/prey animals in the remote North Pacific Ocean provide a clear marker of the level, extent, and contemporary nature of POPs contamination. This contamination of the North Pacific offers potential insights when considering the sources of elevated POPs levels in albatross on Midway Atoll (see below).

Further POPs transfers can still occur once contaminants have reached adult predators at the top of food chains. POPs are passed on to the next generation by transfer into the eggs of birds, and they are passed either directly or via milk into the progeny of marine mammals. Such transfers of relatively high concentrations of POPs to the developing young raise serious questions about the potential effects of these compounds on wildlife populations.

Adverse Effects on Wildlife

The global distribution of POPs has been well documented (Tanabe et al., 1983; Iwata et al., 1993; Zell and Ballschmiter, 1980). The adverse effects of POPs on test animals have also been demonstrated in many studies in laboratories and in the field. It is the challenge of ecotoxicology to identify and/or predict the possibility of adverse effects in wildlife populations based on the known chemical distributions and known toxic effects. In many

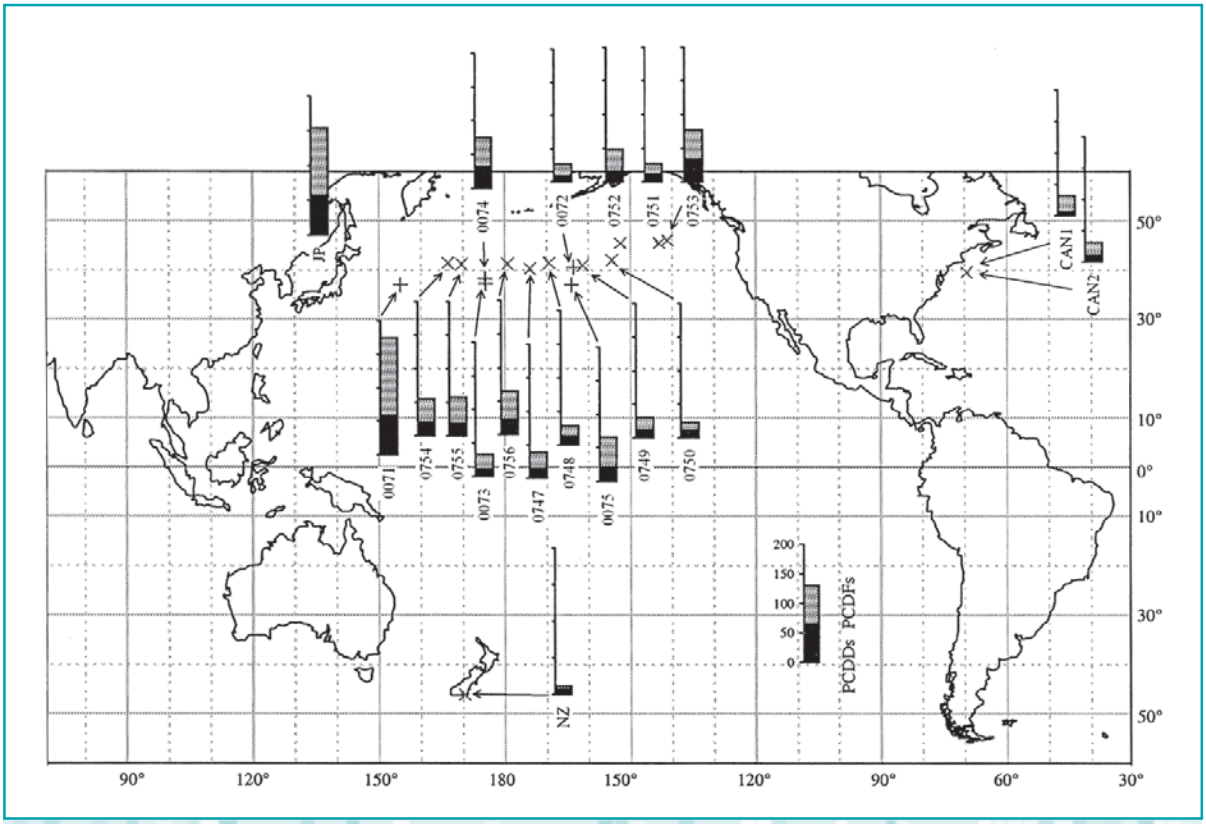

Figure 6-4. Polychlorinated dioxin and furan levels in North Pacific squid (pg/g squid liver) (Hashimoto et al., 1998).

cases where discrete chemical applications occur and adverse effects are clearly evident, such as acute lethality (e.g., fish kills), it is easy to link the chemical exposure to the adverse effect. However, in the case of POPs, many of the adverse effects are chronic and subtle, and evaluating their relevance to population level effects is difficult. Wildlife are also more commonly exposed to relatively low environmental concentrations of POPs, and these exposures accumulate over long time periods—whole lifetimes for most animals. Finally, although most POPs are generally metabolized slowly, if at all, there are differences in uptake and elimination that lead to differences in the patterns of compounds accumulated in different species. These dissimilarities can result in different contaminant exposures to different animals living in the same environment. In the following sections of this report, we provide information on the exposures and effects of POPs on different classes of marine species.

Inshore Birds

The effects of POPs on a number of bird species have been demonstrated in laboratory and field studies (Beyer et al., 1996; Blus, 1996; Wiemeyer, 1996). At high concentrations, many POPs can be acutely toxic. This toxicity is particularly pronounced in pesticides, such as dieldrin, which are neurotoxins. However, of more concern at current, relatively low environmental concentrations are the chronic effects of a number of POPs on the reproductive success of birds. PCBs and dioxins have been shown to adversely affect the reproductive success of fish-eating water birds in the Great Lakes (see Chapter 3). A more historically significant effect was the near extinction of some bird species resulting from the adverse effects of DDT residues.

Pelicans (*Pelicanus occidentalis*) in the Gulf of Mexico were particularly affected by DDT and its residues (Figure 6-5). These compounds accumulated in the adult birds and caused the production of abnormally thin eggshells (Figure 6-6). During incubation in the nest, these thin shells were easily broken by the relatively clumsy adults. The result was severe depopulation in this and other species around the Gulf of Mexico and in other parts of the

Figure 6-5. DDT use led to severe impacts on brown pelicans in the Gulf of Mexico.
Photo: NOAA

United States. On the Pacific coast, daily discharges into the Los Angeles sewer system contained hundreds of pounds of DDT in the 1960s. This DDT was eventually discharged to the Pacific Ocean. Coastal waters became contaminated, and brown pelicans nesting on Anacapa Island more than 60 miles away suffered near-complete nesting failure. The colony was littered with broken eggs, with eggshells averaging 31% (for intact eggs) to

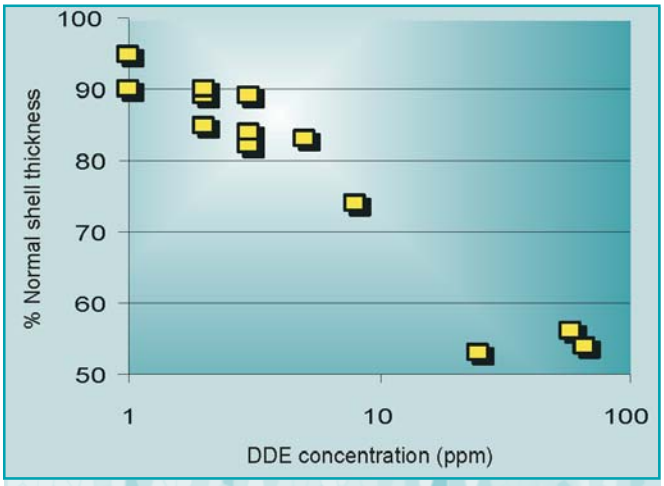

Figure 6-6. Effect of DDE on eggshell thickness in pelicans from North America (data from Blus, 1996).

50% (broken eggs) thinner than normal. In 1969, 1,125 pairs of pelicans were able to fledge only 4 young birds, and in 1970, 727 pairs produced 5 chicks (Anderson et al., 1975).

By the end of 1970, the DDT discharge had been stopped, leading to a remarkable recovery in reproductive success (Anderson et al., 1975). By 1974, DDT residues in anchovies, the primary food of the pelicans, had declined by 97%—from 4.3 ppm to 0.15 ppm. Contamination of pelican eggs by DDT residues had declined 89%. Eggshell thickness also improved to 16% (intact eggs) and 34% (broken eggs) thinner than normal, indicating that by 1974 the abnormal shell thinning caused by DDT and DDE had been reduced by nearly half. Eggshell thinning up to about 10% can be tolerated without affecting reproduction at the population or colony level. The improvement in reproductive success was spectacular. In 1974, 1,286 pairs of pelicans fledged 1,185 young birds. In terms of the number of young birds raised per nest, the figure rose from a low of 0.004 in 1969 to 0.922 in 1974—an improvement in reproductive success of more than 200-fold. These figures confirm the severity of DDT's effect on the reproduction of carnivorous birds, and exemplify the remarkable improvement possible when the release of DDT into the local environment is stopped.

Although the principal chemical of concern to aquatic birds has been DDT, other organochlorines are usually measured at the same time. In North America, much of the data collected have been compiled by the U.S. Geological Survey and are available electronically (*http://www.pwrc.usgs.gov/bioeco/*). The distribution of POPs in marine ecosystems is such that bird samples analyzed contain most, if not all, of the "dirty dozen" POPs (Table 6-2). In most cases, the absence of a particular POP in one of these species is because it has not been looked for, not because the POP is not present.

The degree of concern regarding POPs contaminants in birds has led to the use of DDE, PCBs, and dioxin concentrations in double-crested cormorant eggs as a "National Environmental Indicator" in Canada. Although many of these initial monitoring programs focused on the Great Lakes, their use as indicators has been extended to coastal and maritime regions. Concentrations of POPs have declined in maritime regions since their peaks in the 1970s and 1980s, but the rate of decline has slowed in recent years (Figure 6-7). As concentrations in the environment have decreased, so have the adverse effects attributable to these compounds. The decreases in adverse effects are demonstrated by the recovery of many inshore bird populations since their historic lows.

Much of the contaminant decline in inshore-living bird species can be attributed to the large decrease in inputs to near-shore environments resulting from the banning, deregistration, and emission reductions for all of the POPs in North America. However, now that these chemicals are no longer intentionally produced and released in the United States, we cannot expect to see a continuation of the dramatic decreases of the past. Future declines in near-shore environments will be slower and will result from the global redistribution of the contaminants currently present. Whether ultimately sequestered to the deep ocean and sediments, or transferred to open waters and accumulated in animals, this process can be expected to continue for a long time

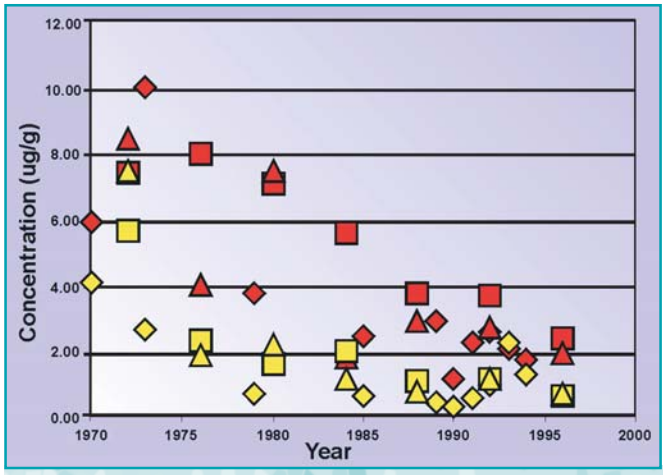

Figure 6-7. PCB (red) and DDE (yellow) concentrations in Canadian coastal birds (double-crested cormorant eggs) have declined since their peaks in the 1960s and 1970s. Monitoring sites in the Straits of Georgia (diamonds) [British Columbia], Bay of Fundy (triangles), and St. Lawrence estuary (squares). Data from Environment Canada: www.ec.gc.ca/ind/English/Toxic/default.cfm.

Table 6-2. POPs detected in North American coastal birds

POPs	Pelican	Cormorant	Gull	Eagle	Albatross
Aldrin[a]					●
Chlordane	●	●		●	●
DDT[b]	●	●	●	●	●
Dieldrin	●	●	●	●	●
Dioxins		●	●	●	●
Endrin	●	●		●	
Heptachlor	●	●	●	●	●
HCB		●		●	●
Mirex	●		●	●	●
PCBs	●	●	●	●	●
Toxaphene	●			●	●

Note: Data from USGS *(http://www.pwrc.usgs.gov/bioeco/)*; Great Lakes data NOT included.
[a]In birds, aldrin is rapidly converted to dieldrin.
[b]"DDT" includes DDT and residues (e.g., DDE).

(Loganathan and Kannan, 1994). Furthermore, although production and use of POPs such as DDT has ceased in North America, it continues in other regions through limited exemptions available under the Stockholm Convention and in nonsignatory countries.

Offshore Birds

Recent studies of offshore-living birds have highlighted the presence of relatively high concentrations of POPs in remote ocean environments (Jones et al., 1996; Auman et al., 1997). Several studies have focused on albatross colonies on Midway Atoll in the North Pacific Ocean (Figure 6-8). The atoll, a former U.S. air base, is located 2,800 miles west of San Francisco and 2,200 miles east of Japan (see Figure 6-9). It is situated close to the northwestern end of the Hawaiian archipelago. These studies demonstrate that, despite living in remote parts of the North Pacific Ocean, albatross accumulate concentrations of POPs similar to those observed in the North American Great Lakes (Figure 6-10). POPs concentrations in one albatross species were sufficient to suggest a significant risk to the reproductive success of the population.

Figure 6-8. Birds on remote Midway atoll in the north Pacific are exposed to POPs.
Photo: NASA

Populations of albatross species in the North Pacific are presently on the increase following the cessation of hunting, which in the early 1900s almost drove the birds to extinction (McDermond and Morgan, 1993). Nonbreeding Laysan albatross (*Diomedea immutabilis*) mainly frequent the western Pacific and Asian coasts, while black-footed albatross (*D. nigripes*) are more common along the northeastern Pacific and North American coasts. Thus, albatross are useful indicators of different sources of marine pollution in the North Pacific Ocean. Studies on similar species in the South Pacific also provide useful information on the global distribution of POPs in these species (Jones, 1999). Relatively high concentrations of chlorinated aromatic compounds, including PCBs and their hydroxylated and methyl

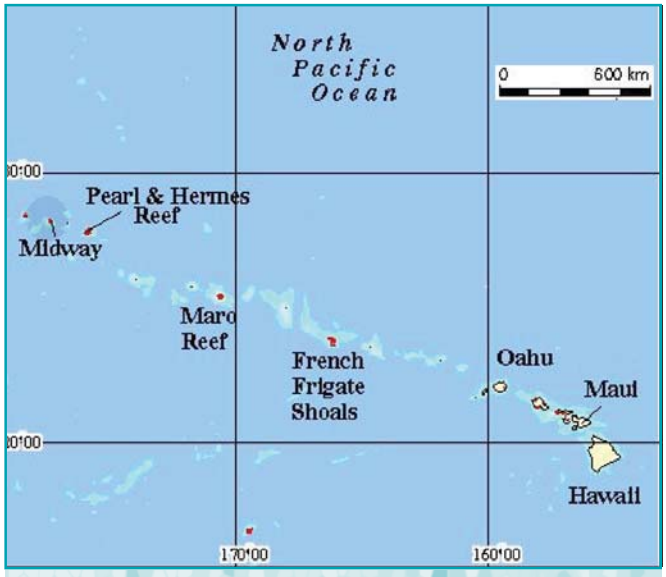

Figure 6-9. Midway Atoll is located in the very center of the North Pacific Ocean at the end of the Hawaiian chain.

Source: UNEP World Conservation Monitoring Centre

sulfone metabolites (Klasson-Wehler et al., 1998), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and non-ortho-substituted PCBs were found in fat samples from the North Pacific populations (Jones et al., 1996). Lower concentrations were measured in the South Pacific species (Jones, 1999). Ortho-substituted PCBs and DDT-related compounds were also reported in plasma samples from these populations, as were a range of other POPs (Auman et al., 1997). The concentrations in the black-footed albatross are reported as sufficient to cause subtle adverse effects on reproduction (Auman et al., 1997; Jones et al., 1996). Although historical data are scarce, they indicate that the egg-crushing rates and hatching rates for black-footed albatross between 1962 and 1964 were comparable to those of Laysan albatross from 1993 to 1994. However, the recent rate of cracked eggs in black-footed albatross, which accumulate greater concentrations of POPs, is greater than 5%, twice the rate observed in the less contaminated Laysan albatross. A statistically significant difference was also found in the hatching rate for the black-footed albatross compared with the Laysan albatross (Auman et al., 1997).

Figure 6-10. Levels of POPs may be sufficient to decrease reproduction in albatross from remote Pacific islands.

Photo: John Giesy

The concentrations of some POPs measured in North Pacific albatross do not differ greatly from concentrations measured in fish-eating birds in the North American Great Lakes. For example, pooled egg samples of black-footed albatross contained 3.8 ppm of total PCBs and 1.8 ppm of DDE, whereas similar samples from Laysan albatross contained 1.0 ppm PCBs and 0.3 ppm DDE (Auman et al., 1997). These concentrations can be compared with concentrations of 9.4 ppm and 6.1 ppm of total PCBs found in 1988 in the eggs of Great Lakes Caspian terns and doubled-crested cormorants, respectively (Yamashita et al., 1993). The finding of elevated POPs concentrations in such a remote location underscores the global transport of these chemicals and the limitations of the global environment to assimilate or "dilute" them to safer concentrations (Jones et al., 1996).

Marine Mammals

No situation indicates more the global nature of the POPs problem than the concentrations detected in marine mammals from around the world. Even though many marine mammals are not directly exposed to POPs sources, particularly in the oceans of the Southern Hemisphere, every marine mammal tissue analyzed contains at least some of the "dirty dozen" POPs (Colborn and Smolen, 1996).

The life history parameters of many marine mammals result in their accumulating high concentrations of POPs. Marine mammals inhabit aquatic

environments that are the ultimate sinks for many of these compounds. They have a unique lifestyle that requires thick layers of blubber to provide thermal insulation and energy reserves for fasting periods in their life cycles. These fatty tissues act as a reservoir for the accumulation of POPs, and also act as a continual source "resupplying" the rest of the body with these contaminants when fats are metabolized. The long lifespan and generally predatory feeding habits of marine mammals lead to high levels of POPs in blubber. In addition, marine mammals appear to be limited in the biochemical processes required to metabolize and eliminate these chemicals (Tanabe et al., 1988). Finally, because of the high lipid content of marine mammal milk, POPs are passed via lactation to the developing young.

Of the compounds studied in marine mammals, PCBs appear to accumulate to the greatest concentrations in the widest range of species (Table 6-3) (Tanabe et al., 1983; 1994). Very high POPs levels have been measured on the U.S. East Coast in bottlenosed dolphins, reaching 620 and 200 ppm lipid weight for PCB and DDE, respectively, in mature males (Geraci, 1989). To put these concentrations in perspective, U.S. hazardous waste regulations for PCB liquids commence at 50 ppm.

It has been contended that, since 1968, 16 species of aquatic mammals have experienced population instability, major stranding episodes, reproductive impairment, endocrine and immune system disturbances, or serious infectious diseases (Colborn and Smolen, 1996). The authors also suggest that organochlorine contaminants, particularly PCBs and DDTs, have caused reproductive and immunological disorders in aquatic mammals (Colborn and Smolen, 1996). The presence of high concentrations of PCBs in tissues has also been associated with

- High prevalence of diseases and reduced reproductive capability of the Baltic grey seal (*Halichoerus grypus*) and ringed seal (*Phoca hispida*) (Olsson et al., 1994)
- Reproductive failure in the Wadden Sea harbor seal (*Phoca vitulina*) (Reijnders, 1986) and St. Lawrence estuary beluga whales (*Delphinapterus leucas*) (Martineau et al., 1987)
- Viral infection and mass mortalities of the U.S. bottlenose dolphin (*Tursiops truncatus*) (Kuehl et al., 1991; Lipscomb et al., 1994), Baikal seal (*Phoca sibirica*) (Grachev et al., 1989), and Mediterranean striped dolphin (*Stenella coeruleoalba*) (Aguilar and Raga, 1993; Kannan et al., 1993)

However, unequivocal evidence of a "cause-effect" linkage between disease development and mass mortalities in marine mammals is lacking, because of confounding factors that limit the ability to extrapolate results from field studies.

Compelling evidence that marine mammals can experience toxic effects comes from data on the feeding of wild-collected fish from different regions to confined seals (Reijnders, 1986, 1994; Ross et al., 1995, 1996, 1997). In the Reijnders study, two matched groups of captive harbor seals were maintained in the same location. One group was fed Baltic Sea herring, the other North Atlantic herring. The group fed Baltic Sea fish suffered near-complete reproductive failure, while the group fed less contaminated Atlantic fish reproduced normally. Similar impacts were evident on immune function. However, although the effects of consuming contaminated fish were clear, the specific causal agent(s) was not. As with field studies, several confounding factors prevent a conclusive connection between specific substances and effects in these studies. These factors include limited sample sizes, the presence of chemicals other than POPs in the food fish, the presence of chemical contaminants in the "control" diet, as well as general concerns about the nutritional quality and similarity of the "control" and "exposed" diets. Additional toxic effects attributed to PCBs and DDT in seals resident in the Baltic Sea include uterine stenosis and occlusions in ringed seals, skull-bone lesions (osteoporosis) in Baltic gray seals and harbor seals, adrenocortical hyperplasia in Baltic ringed and gray seals, lowered levels of vitamin A and thyroid hormones in harbor seals, and lowered immunocompetence in harbor seals (Reijnders, 1994; Hutchinson and Simmonds, 1994).

Table 6-3. Global PCB distribution in marine mammal populations

Species	Location	PCBs, µg g^{-1} wet weight, blubber	Reference
Bottlenose dolphin	East USA	81.4	Kuehl et al., 1991
White-sided dolphin	East USA	50.1	Kuehl et al., 1991
Common dolphin	East USA	36.5	Kuehl et al., 1991
Pilot whale	East USA	17	Varanasi et al., 1993
Minke whales	West USA	3.3	Varanasi et al., 1993
Harbour porpoise	United Kingdom	55.5	Morris et al., 1989
Pilot whale	United Kingdom	36.9	Law, 1994
White-sided dolphin	Japan	37.6	Tanabe et al., 1983
Dall's porpoise	North Pacific	8.6	Tanabe et al., 1983
Baird's beaked whales	Japan	3	Subramanian et al., 1988
Bottlenose dolphin	South Africa	13.8	Cockroft et al., 1989
Dusky dolphin	South of New Zealand	1.4	Tanabe et al., 1983
Common dolphin	New Zealand	0.75 –>1.0	Jones et al., 1999
Pilot whale	New Zealand	0.31	Schroder, 1998

Much of the controversy over marine mammal levels of POPs centers on the widely publicized mortality episodes among bottlenose dolphins along the Atlantic Coast of North America. Numerous causal agents, or combinations of agents, have been proposed, but none proven. Apart from chemical contaminants, exposure to natural marine toxins has been hypothesized as a possible cause for the bottlenose dolphin mortality episodes (Anderson and White, 1989). However, later studies have indicated that this evidence is circumstantial (Lahvis et al., 1995). Morbillivirus infection appears to have been at least a contributing factor in the dolphin mortality (Belfroid et al., 1996). Lahvis et al. (1995) hypothesized that synthetic chemicals, specifically AhR-active POPs, render marine mammals more susceptible to opportunistic bacterial, viral, and parasitic infection. Debilitating viruses such as morbillivirus may result in further immunosuppression, starvation, and death (Lahvis et al., 1995). Conclusions about causality are further complicated by the fact that marine mammals are exposed simultaneously to a number of synthetic halogenated hydrocarbons, many of which are not quantified or identified. Despite the high accumulation and possible adverse effects of PCBs in marine mammals, tissue concentrations of PCBs that would affect the immune system in marine mammals have not been established. Similarly, factors such as population density, migratory movement, habitat disturbance, and climatological factors have been proposed as playing roles in mass mortalities of marine mammals.

Probably the most convincing case for observable adverse effects of chemical contaminants on marine mammals is in beluga whales (*Delphinapterus leucas*) resident in the Gulf of St. Lawrence on the U.S.-Canada border (*http://www.medvet.umontreal.ca/services/beluga/beluga_homepage.html*). Whales from this population have been shown to have a high incidence of cancers not common in other animals (Figure 6-11), as well as a variety of other lesions (DeGuise et al., 1994). It is known that these animals accumulate large concentrations of POPs, and it has been suggested that such accumulation may be a contributing factor to the observed effects. However, these animals also accumulate, or are exposed to, high concentrations of other environmental pollutants, including polycyclic aromatic hydrocarbons (PAHs). Because Ah-receptor active POPs are tumor promoters, POPs may be a significant contributing factor to the observed cancer occurrence in these animals. However, because of the limited amount of quantitative toxicological information

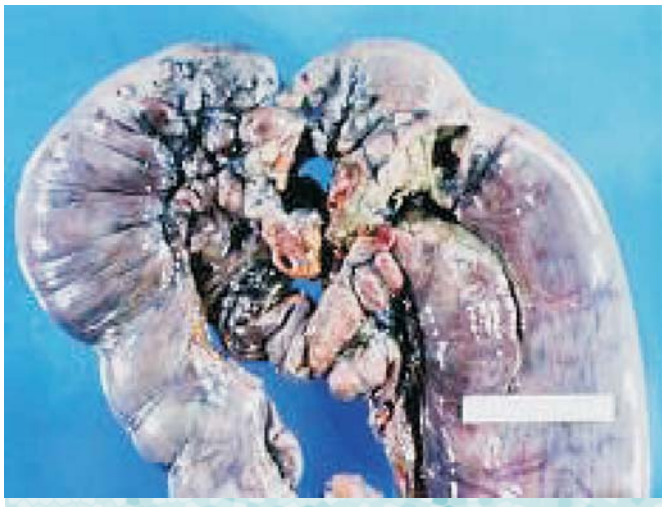

Figure 6-11. Intestinal cancer in a beluga whale.
Source: Daniel Martineau, University of Montreal

available about marine mammals (as discussed above), the relative contribution of POPs to these effects may never be known.

The above-mentioned field studies indicate an association between POPs and adverse health effects in marine mammals, although the association is not conclusive to specific chemicals. Other studies have focused on the in vivo and in vitro effects of POPs on marine mammal immune function (De Guise et al., 1998). These studies have shown some effects, but it is difficult to relate the effects observed to a functional deficit in the immune systems of free-living marine mammals. It has been suggested that immune suppression as the result of POPs exposure may be a contributing factor to marine mammal mass die-offs, such as occurred in the Mediterranean in 1992 (Aguilar and Raga, 1993).

Toxicological data for the effects of PCBs and dioxins on marine mammals were recently compiled, analyzed, and used to derive toxicity reference values (TRVs) (Table 6-4) (Kannan et al., 2000). The TRVs express the best available estimate of the concentrations of chemicals that will result in adverse effects. Adverse effects can be increasingly anticipated if the concentration of the chemical in an animal's tissue rises above the TRV. The TRVs were derived on the basis of the concentration of chemicals in the food that marine mammals were consuming, or on the concentrations of these chemicals in the blubber (fat) of the animals. They were based on studies examining physiological effects such as vitamin A depletion, suppression of natural killer cell activity, and the proliferative response of lymphocytes to mitogens. Details regarding derivation of the TRVs are discussed in Kannan et al. (2000). Because PCBs, dioxins, and furans are considered to act through the same mechanism of action, the authors used a weighted sum of all the exposures to these chemicals, called "toxicity equivalence" or TEQ.

Table 6-4. Toxicity reference values for marine mammals (lipid weight basis)

	Total PCBs
Food based	10-150 ng/g
Tissue based (blubber)	17,000 ng/g

Source: Kannan et al., 2000.

Using these TRVs, it is possible to conduct a risk screening for the possibility of adverse effects from these chemicals in marine mammals. For example, the blubber concentrations of PCBs in pilot whales and bottlenose dolphins from the United States exceed the TRV values (Table 6-5). This suggests that these animals may be subject to adverse effects from these chemicals. In contrast to the North American samples, PCB concentrations in marine mammals in the Southern Hemisphere are far lower.

Other Marine Mammals: Pinnipeds, Manatees, and Otters

A wide range of POPs have been measured in the tissues of seals, sea lions, and walruses (collectively called pinnipeds) (Figure 6-12). These include chlordanes, heptachlor epoxide, HCB, dieldrin, toxaphene, PCBs, PCDDs, and PCDFs (Hutchinson and Simmonds, 1994; Ames and Van Vleet, 1996). POPs concentrations vary widely depending on species, location, and feeding patterns. Concentrations in species feeding at low trophic levels in remote locations, such as walrus in the Bering Straits (Figure 6-12), remain in the sub-ppm range (Seagars and Garlich-Miller, 2001).

Table 6-5. Risk screening of PCBs in marine mammals

Species	Blubber PCB TRV (ng g^{-1})	Blubber PCB (ng g^{-1})	PCB Exceedance (Ratio PCB/TRV)
Bottlenose (USA)	13,600	81,400	6.0
Pilot whale (USA)	13,600	17,000	1.25
Dall's porpoise (Pacific)	13,600	8,600	0.63
Pilot whale (NZ)	13,600	310	0.023
Baleen whales (NZ)	13,600	12.9	0.0001
NZ fur seal (NZ)	13 600	1,069	0.08

Note: TRVs are given on a wet weight basis.

Source: Kannan et al., 2000.

Closer to sources, the relatively high concentrations of PCBs (85 to 700 ppm) found in harbor seal blubber, such as in the Wadden Sea, have been implicated in their mass mortalities and reproductive impairment (Reijnders, 1986). Similarly, elevated exposure of California sea lions to DDT in the 1970s has been linked to reproductive problems (Figure 6-13) (DeLong et al., 1973). California sea lions collected in the early 1970s from coastal California contained a mean DDT concentration of 980 ppm lipid weight in the blubber (DeLong et al., 1973). A recent study has reported DDT concentrations of up to 2,900 ppm lipid weight in the blubber of California sea lions from the California coast (Kajiwara et al., 2001). DDT concentrations as high as 169 ppm lipid weight were also found in the livers of sea otters from coastal California (Nakata et al., 1998). The occurrence of several tens of ppm of PCBs and DDTs has been reported in harbor seals collected in 1990–1992 (approximately 20 years after the ban on the use of DDT) from the northeastern United States (Lake et al., 1995). And the Florida manatee, *Trichechus manatus*, an endangered species, has been reported to contain several ppm levels of PCBs and DDT in blubber (Ames and Van Vleet, 1996).

Summary and Conclusions

Adverse effects from POPs on marine mammals and birds demonstrate the potential for these substances to affect species in regions far from the sources of the POPs emissions. At the peak of DDT use in the United States, many marine bird species suffered eggshell thinning from DDT, most particularly the brown pelican which became threat-

Figure 6-12. Pinniped marine mammals, like these walrus, accumulate POPs to varying degrees depending on species, location, and feeding patterns.
Photo: NOAA

Figure 6-13. DDT is believed to have caused reproductive problems in California sea lions in the 1970-80s.
Photo: NOAA

ened with extinction. Impacts on birds continue in some locations, including elevated exposures in remote reaches of the Pacific Ocean. For marine mammals, controlled studies of high environmental pollutant exposures in their food have demonstrated reproductive impairment and immune changes. But although many marine species are exposed to POPs, there are few studies that "prove" a causal link between specific POPs at more general environmental levels and adverse effects in populations or individuals. Nevertheless, risk evaluations indicate cause for concern. Concentrations of POPs in some species and locations are currently at levels close to those with the potential to cause adverse effects. Therefore, it can no longer be assumed that the world's oceans can dilute these chemicals to "safe" concentrations.

As with the Great Lakes, however, there have been remarkable recoveries in wildlife populations with the cessation or reduction of POPs release. POPs levels in U.S. coastal regions are declining in sediments and invertebrates. Less evident are reductions in POPs levels in fish and mammal species, testifying to the peculiar hazard posed by these persistent, bioaccumulative, toxic substances and their ability to remain in the food chain and pass from generation to generation. Decreases in marine POPs levels following production and use controls indicate that regulatory actions can be successful. However, because of the problems of global transportation and deposition of these contaminants, the desired decreases in global POPs will not be achieved without global cooperation.

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Chapter 7 Long-Range Environmental Transport of Persistent Organic Pollutants

Introduction

Persistent organic pollutants (POPs) are now nearly ubiquitous in their distribution over the Earth. They can be found in remote locations distant from industrial and agricultural regions, as well as close to their point of introduction into the environment. Their propensity for long-range environmental transport, and the extent of their distribution, are evident from the levels reported for the Great Lakes, Alaskan Arctic, and marine ecosystems. This chapter provides information on how POPs are transported such long distances by winds, river and ocean currents, and migratory animals. The focus is on transport of POPs into the United States, recognizing that POPs also leave the United States and have impacts on other countries through similar processes. Particular attention is directed to transport in the atmosphere, because this is the principal medium through which POPs are distributed globally, either as vapor or on particles. Examples are provided of the transport of pollutants between continents, accompanied by an overview of the atmospheric chemistry of POPs relating to entrainment, degradation, and deposition. Methods for tracking the transport of POPs through the atmosphere are discussed, with examples provided of the pathways they may take. This discussion is followed by a summary of information on hydrologic movement and transport of POPs via migratory species.

The behavior of POPs in the environment is complex because they are multimedia chemicals, existing and exchanging among different compartments of the environment such as the atmosphere, natural waterbodies, soil, and sediments, where they degrade at different rates over time. POPs are also referred to as semivolatile, meaning they can be present in more than one phase in the atmosphere, either as gases or attached to airborne particles. The fate and preferential transport of a POP are strongly determined by its specific physical chemistry properties, even its particular isomer (i.e., same molecular formula but different spatial structure). The different affinities of POPs for soil particles, water, and/or lipid molecules, and their rate of volatilization will determine the pathway each species or isomer is likely to take in its journey through the environment. These properties also influence how far and fast a POP can move from where it was released into the environment.

Comprehensive monitoring studies support the conclusion that POPs concentrations are generally highest in areas where they were once released, or are still being released. Concentrations generally decrease with increasing distance from such source areas. Thus, concentrations are most strongly dependent on past and present release rates in the immediate vicinity under investigation, and are also strongly influenced by regional releases (Kalantzi et al., 2001). In addition, however, the finding of surprisingly high concentrations of POPs in polar areas, particularly the Arctic (Bidleman et al., 1989; Barrie et al., 1992; Iwata et al., 1993), has led to an emphasis on the natural processes that are responsible for this wide-ranging transport through the global environment. These processes include:

- Volatilization of POPs from terrestrial and/or aquatic surfaces into the atmosphere
- Adsorption of POPs vapor onto particles already entrained in the atmosphere
- Entrainment from a surface of particles with an adsorbed POPs layer into the atmosphere
- Transport of air masses throughout a hemisphere by means of persistent, large-scale circulation patterns or by means of episodic rapid transport processes

- Photochemistry and interaction of POPs with free radicals, which can modify and degrade their chemical form while they are undergoing atmospheric transport
- Deposition by means of wet (e.g., snow, rain, mist) or dry (e.g., turbulent transport and particle settling) atmospheric processes onto terrestrial and aquatic surfaces of POPs that are either in vapor form or adsorbed onto particles
- Transport of POPs in aquatic systems by means of flowing water (primary surface flows such as rivers and ocean currents)
- Transport of POPs in terrestrial and aquatic ecosystems in the lipids of migrating mammals, fish, and birds
- Deposition of POPs into aquatic sediments
- Eventual physical accumulation in receptor locations, uptake, and bioaccumulation that increases concentrations in ecosystems and humans

Atmospheric Transport of Pollutants to the United States

When describing winds in the atmosphere and their ability to transport trace substances over long distances (e.g., the equator to the pole or around the globe) a convenient first approximation is to focus on their long-term average behavior. This focus is useful because winds fluctuate in strength and direction in passing cyclonic and anticyclonic weather systems, resulting in net displacements that are relatively small compared with the global scale. Average, or prevailing, winds blow much more in east-west directions than in north-south directions. In midlatitudes, the prevailing winds are westerly (i.e., from the west), whereas easterly winds prevail at very high latitudes and in the subtropics (e.g., southern Florida), the latter especially in spring and summer. In principle, pollutants released at the surface can travel eastward completely around the globe at midlatitudes in about 10 days if they are lifted by convective activity (strong upward air motions that produce clouds) to the altitude of the jet stream. The average wind speeds at this level are much stronger than they are near the surface and can exceed 100 mph in the core of the jet stream (e.g., Stull, 2000), and the wind speeds and directions are more constant than they are near the surface. In contrast to this rapid west-east transport in the jet stream, it takes several months for pollutants to spread from equator to pole. It can take even longer, about a year to a year and a half, for pollutants to cross the equator and be evenly distributed over the globe (Warneck, 1988). Mixing caused by small-scale turbulence normally causes pollutants to disperse so they no longer form a coherent plume that can be tracked over long distances. However, on occasion, plumes of airborne substances remain coherent and can be tracked for long distances.

Much of the evidence for long-range transport of airborne gaseous and particulate substances to the

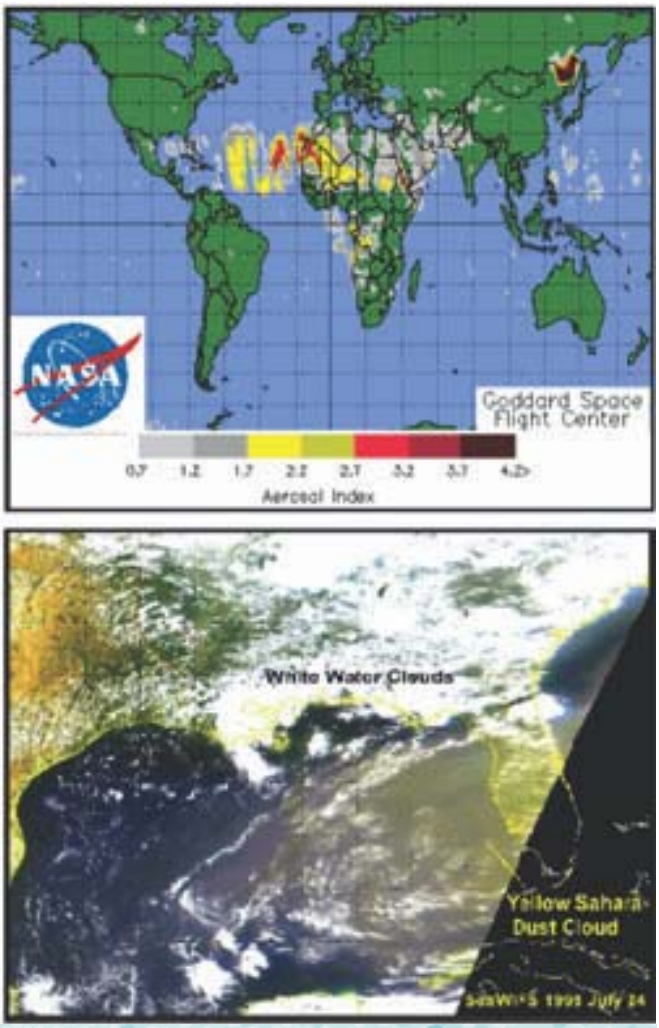

Figure 7-1. Atmospheric transport of Saharan dust to the United States.

Source: National Aeronautics and Space Administration, 2001.

United States focuses on dust or smoke because these are visible in satellite images or when deposited. Examples include transport of dust from the Sahel and Sahara Desert in northern Africa, dust from the Taklamakan and Gobi Deserts in Asia, and emissions from uncontrolled wildfires in Central America and southern Mexico. Windblown dust from individual dust storms in the Sahara Desert has been observed in satellite images as plumes crossing the Atlantic Ocean and reaching the southeast coast of the United States. These storms can last for several days at a time. A false color satellite image obtained by NASA's Earth Probe TOMS satellite showing successive pulses of Saharan dust propagating eastward across the Atlantic Ocean and reaching Miami is presented in the top portion of Figure 7-1. The bottom portion of Figure 7-1 shows a true color image of the dust cloud over Florida obtained by NASA's Sea Star satellite on the same day. Analysis of data obtained by the IMPROVE (Interagency Monitoring of Protected Visual Environments) network indicates that incursions of Saharan dust into the continental United States have occurred, on average, about three times per year. These events have persisted for about 10 days, principally during the summer. As might be expected, the frequency of Saharan dust events is highest in the southeastern United States. About half are observed only within the State of Florida, and these are associated with dense hazes in Miami (see Figure 7-2) such that African dust is the dominant aerosol constituent in southern Florida during the summer (Prospero, 1999a). Puerto Rico and the Virgin Islands are even more strongly affected, as might be expected. Figure 7-3 shows a false color satellite image of the passage of a cloud of dust across the Pacific Ocean to North America. This dust cloud was raised by a storm in the Gobi and Taklamakan Deserts in April 2001. The highest concentrations of Asian dust can be seen over the Aleutian Islands. Also shown in Figure 7-3 is a dust cloud from northern Africa traveling eastward over the Atlantic Ocean.

Biomass burning for agricultural purposes occurs normally during the spring of each year in Central America and southern Mexico. During the spring of 1998, fires burned uncontrollably because of abnormally hot and dry conditions associated with

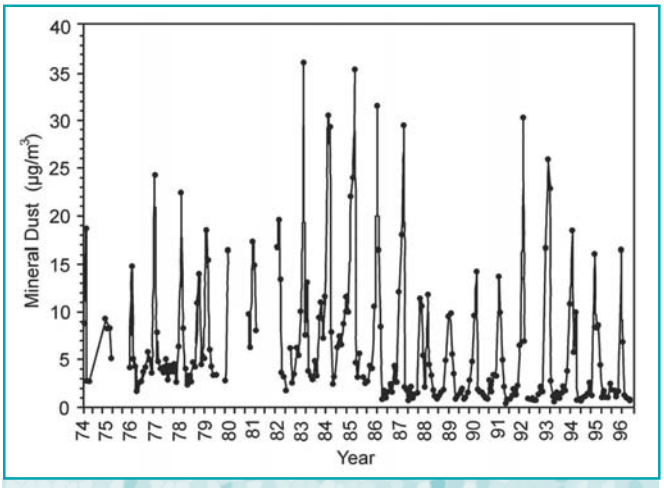

Figure 7-2. Saharan dust episode chronology impacting Miami, FL.
Source: Prospero, 1999a.

the intense El Niño conditions in 1997–1998. Figure 7-4 shows the extent of the spread of the particles emitted by the fires. Concentrations of particles throughout the central and southeastern United States were elevated substantially, such that National Ambient Air Quality Standards for particulate matter were exceeded briefly in St. Louis, MO, and in a number of other cities in the central United States. The reader should bear in mind that the atmospheric processes that transport dust or smoke, as given in the examples above, are also transporting pollutants, including POPs, either as vapor or attached to particles. Indeed, microorganisms including various fungi and bacteria have been found attached to North African dust particles

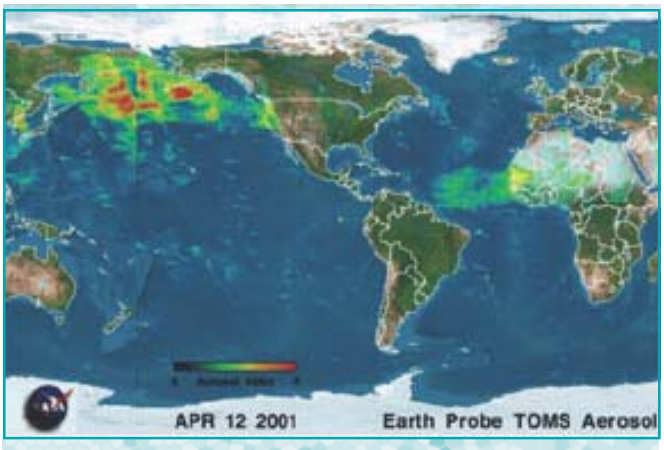

Figure 7-3. Asian dust storm episode crossing the Pacific Ocean. NASA.

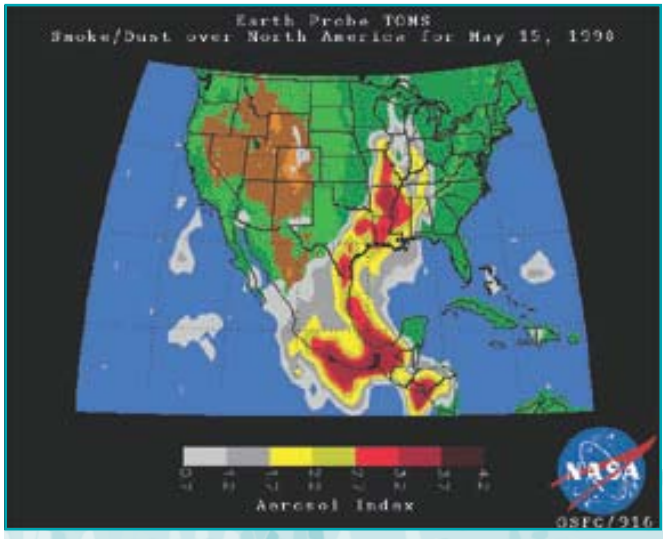

Figure 7-4. Smoke from Central American fires. NASA.

in Caribbean air samples (Griffin et al., 2001). Pollutants, including trace metals that may have been emitted in North Africa or Europe, have been found along with North African dust particles in Miami, FL (Prospero, 1999b).

Rapid transport of pollutants from south to north can also occur, bringing pollutants from mid-latitudes to the Arctic in a few days. Many of these pollutants are relatively short-lived with respect to degradation in the atmosphere, and are unlikely to reach the Arctic by the average winds described above. These transport events occur during winter and are caused by transient weather events that result in strong winds directed toward the north in a narrow current lying typically between a strong high-pressure region to the east and a low-pressure system to the west. These weather situations occur mainly in the former Soviet Union, although they can also occur in North America. These events result in the formation of Arctic haze, which regularly affects air quality in Alaska (Shaw and Khalil, 1989).

Although these episodes are infrequent, the amount of POPs deposited can be substantial, given the otherwise pristine nature of some of the receptor locations. For example, Welch et al. (1991) documented a long-range transport event that deposited thousands of tonnes of Asian dust onto a region of the central Canadian Arctic over a brief (<3-day) period. Analysis of the resulting brown snow revealed elevated levels of the following POPs: PCBs (6.9 ng/g particles), DDT (4.2 ng/g), toxaphene (3.0 ng/g), HCB (0.7 ng/g), chlordane (0.6 ng/g), heptachlor, and dieldrin, along with other organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and hexachlorocyclohexanes (e.g., lindane). The authors estimated that this single episode may have contributed up to 10% of the annual loading of DDT to lakes in this region, and up to 1%–3% for the other measured POPs (depending on loading scenario assumptions).

Atmospheric Chemistry of POPs

Many POPs, including pesticides and PCBs, are classified as semivolatile, meaning that they can exist either as gases or attached to particles. The relative amounts in the gaseous and particle-associated forms depend on air temperature. Less volatile POPs tend to partition into surface reservoirs such as soil, vegetation, rivers, and oceans, where they associate with organic matter. Warmer temperatures favor their evaporation and residence in the atmosphere as gases; colder temperatures favor their deposition to the Earth's surface and their incorporation into airborne particles. Generally, warmer temperatures are found close to the Earth's surface with decreasing latitude (tropics), whereas colder temperatures are found with increasing latitude (polar) or altitude. Characteristic temperatures at which half of a particular compound ($T_{½}$) would be present as a gas can be calculated to indicate the tendency of a POP to remain as a gas or to attach to a particle (Wania et al., 1998). The more volatile POPs, such as hexachlorobenzene (HCB), reach this temperature at –36°C; dieldrin at –11°C; DDE –2°C; DDD +7°C; DDT +13°C; and PCBs with at least 6 Cl atoms at about +10°C. As the number of Cl atoms increases in PCBs, polychlorinated dibenzo-*p*-dioxins (PCDDs) and furans (PCDFs), this characteristic temperature also increases, such that molecules with more than 5 Cl atoms tend to be partitioned mainly onto particles (Brubaker and Hites, 1998). Compounds such as mirex and toxaphene (higher molecular weight fraction of the mixture) are expected to be found mainly attached to particles, because they have very

high values of $T_{1/2}$. Observations show that compounds with the lowest $T_{1/2}$ tend to have the highest potential for global scale transport and to remain in the gas phase even at high latitudes, whereas compounds with the highest values of $T_{1/2}$ tend to remain concentrated close to their sources.

Although the meteorological processes transporting gases and particles are the same, particles and gases are subject to different removal processes that affect the time they remain airborne. Soluble gases can be removed from the lower atmosphere by being incorporated into cloud droplets that then fall out as rain, or by being washed out by falling raindrops. This limits their lifetime in the atmosphere typically to several days, and also limits the distances they can travel from their sources. However, gas-phase POPs are not very soluble and so their removal by precipitation is not effective. For example, the removal time for chlordane, dieldrin, and PCBs can be up to several years by this mechanism (Atlas and Giam, 1981).

POPs present as atmospheric gases can be destroyed by atmospheric photochemical reactions involving hydroxyl (OH) radicals in the atmosphere. Reactions involving other species or photodegradation by solar ultraviolet radiation are considered to be minor loss processes, although data are sparse. Calculated atmospheric half lives, $t_{1/2}$ (defined as the time it takes to reduce their concentrations by one-half due to reaction with OH radicals), for several compounds are shown in Table 7-1, along with their concentrations in both the gas and particle phases observed on the shores of the Great Lakes. As can be seen, $t_{1/2}$ in the atmosphere ranges from a couple of days for DDT to a couple of years for HCB. Notably, the presence of hydroxyl radicals is integrally linked to the presence and level of sunlight. The absence of sunlight in polar regions for many months of the year effectively eliminates the generation of hydroxyl radicals, thereby greatly increasing the persistence of atmospheric pollutants that would otherwise be degraded through this mechanism during daylight.

If POPs become attached to particles, their lifetimes in the atmosphere are determined by particle removal mechanisms, in addition to reactions involving hydroxyl radicals or other free radical species in the particles and photodegradation by solar ultraviolet radiation. However, the effectiveness of these processes in particles has not been studied as well as for the gas phase. The lifetime of particles in the lower atmosphere is about 1 week with respect to removal by precipitation. However, particles above cloud layers can remain airborne much longer and hence can be transported over much longer distances. Particles also can be deposited on the Earth's surface when they are transported downward by turbulent air motions (dry deposition). Atmospheric lifetimes with respect to dry deposition depend on particle size, meteorological variables near the surface, and microphysical conditions at the air-surface interface. Lifetimes in the atmosphere for fine particles (i.e., smaller than a few micrometers in diameter) with respect to dry deposition are about a couple of weeks (U.S. EPA, 1996).

Deposition on to the surface does not, however, mean that a POP has been permanently removed from the atmosphere. Through a variety of mechanisms, such as microbial activity and photochemical reactions occurring near the surface of the soil or a waterbody, POPs that were attached to particles

Table 7-1. Atmospheric concentrations of selected POPs at IADN[a] sites and their estimated globally averaged atmospheric half-lives ($t_{1/2}$)

Compound	Concentration Range (pg/m^3)[b]		$t_{1/2}$[c]
	Gas	Particle	
Hexachlorobenzene	80-130	0.1-0.2	728 d
Dieldrin	14-34	1.5-3.2	6.2 d
PCB44	3.4-14	0.09-0.2	16 d
DDT	3.9-91	0.3-3.6	2.3 d

[a] Integrated Atmospheric Deposition Network. IADN consists of five sites situated on each of the Great Lakes.
[b] 1 pg = 1 trillionth (10^{-12}) of a gram.
[c] Defined here as the time needed in days to reduce the concentration of the compound by one-half, using a globally averaged OH concentration of 1.0×10^6 OH/cm^3 (e.g., Krol et al., 1998) and a mass weighted mean atmospheric temperature of 273°K (0°C).

Source: Hoff et al. (1996) for concentration data.

may be released and evaporate into the atmosphere. Only through processes such as reaction with OH radicals in the atmosphere, or biologically mediated reactions in either soil or natural waterbodies, is a POP finally gone from the environment. These processes are all strongly temperature dependent and proceed faster at higher temperatures, so that POPs tend to persist longer at higher latitudes. Lifetimes of most POPs due to degradation in the marine or terrestrial environment are estimated to be several years, with degradation occurring more rapidly in tropical than in polar regions. A degradation product of the original POP may also be a POP, or may be toxic in the environment. For example, dieldrin is formed during the degradation of aldrin.

Global Distillation of POPs

An intriguing consequence of the combined semivolatile and persistent nature of POPs is their potential to volatilize in warm regions, be deposited in colder ones, and repeat this process until a location is reached where it is too cold for the POP to again revolatilize. This process is similar to industrial distillation processes, such as separating petroleum products from crude oil. On a planetary scale, global distillation has been hypothesized to result in a net transport of POPs from lower latitudes to high latitudes (polar regions) in a series of jumps (Wania and Mackay, 1996) (Figure 7-5). Because of the normal decrease of temperature with increasing latitude, compounds will tend to condense on surfaces as they are transported northward by winds associated with passing weather systems. Various thermodynamic constants can be used to estimate the "stickiness" of POPs to a surface. One of the most useful is the octanol-air partition coefficient (K_{OA}), which is measurable in the laboratory and relates to the tendency of a POP to adhere to organic matter in the soil or natural waterbodies. Values of K_{OA} range over many orders of magnitude, and the higher its value the greater the tendency for a POP to associate with organic matter.

The environmental levels of POPs predicted in remote locations following global distillation depend heavily on the physicochemical properties of the particular POP and the meteorological factors generating poleward transport. The balance between POPs concentrations in temperate regions versus their preferential accumulation toward the poles is influenced by the following factors:

- *Source proximity:* The strength and proximity of emission sources act as the primary forces generating pollutant levels. All things being equal, pollutant concentrations should be greater at the source and taper off with distance, with this tapering effect proportional for all pollutants. But a variety of factors can differentially influence the transport potential of POPs and their isomers, leading to differential accumulation.
- *Physicochemical properties of different POPs:* As already noted, differences among POPs regarding their propensity to exist in the vapor phase (e.g., K_{OA}, Henry's law constant, vapor pressure) have an impact on each POP's susceptibility to global distillation and the rate at which such movement can occur. Differences occur even within families of POPs, such as among the 209 PCB congeners. Lower chlorinated PCBs, with two or three chlorines, are more volatile and amenable to global transport. They tend, however, to be less persistent than the higher chlorinated PCB congeners, somewhat countering their propensity to preferentially move toward the poles.

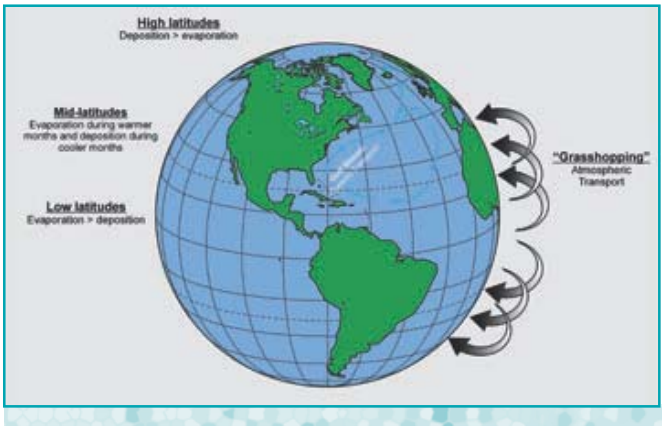

Figure 7-5. Grasshopper effect moving POPs poleward.
Source: Adapted from Wania and Mackay, 1996.

- *Temperature dependence of physicochemical properties:* Decreased temperatures and reduced microbial activity toward the poles increase POPs persistence, thereby inherently increasing the potential for physical accumulation (see Chapter 9). Decreased temperatures also alter environmental media partitioning properties, such as the water-air partition coefficient (Henry's law constant), increasing the proportion of a chemical in water compared with the amount in the adjacent air column. Hexachlorocyclohexane (HCH; listed as a POP under the UNECE-LRTAP POPs Protocol) isomers change from an aquatic persistence of only a few days in the tropics to many months or years in Arctic waters. The Henry's law constant also changes for the HCHs, increasing the proportion in water compared with air as the environment cools. Both of these changes contribute to the higher absolute levels of HCH in Arctic waters compared with those that had been found close to the presumed sources in Asia (Iwata et al., 1993).

Temperature-dependent gradients have been demonstrated on a global or regional scale for several of the more volatile POPs, although direct evidence for transfer of POPs from the tropics to the Arctic remains to be demonstrated (Klecka et al., 2000). Calamari et al. (1991) reported that HCB concentrations in vegetation increased with latitude by almost a factor of 10 between the tropics and polar regions, whereas concentrations of the less volatile DDT were found to be higher in tropical compared with polar areas by almost a factor of 100. Simonich and Hites (1995) reported similar results on the global distribution of 22 organochlorine compounds in tree bark samples. Here, the distribution of relatively volatile organochlorines, such as HCB, was dependent on latitude, whereas less volatile and persistent organochlorines (e.g., endosulfan) remained close to the region of release. Iwata et al. (1993) measured geographic gradients for HCH in sea water on a global scale, finding higher concentrations toward the poles even though emission sources were in temperate and tropical regions, predominantly Asia. Sea water and air concentrations of DDT were substantially higher near the sources measured in Asia.

Increased altitude and the related decrease in temperature also are associated with increasing levels of POPs, as demonstrated over a 770 to 3,100 m altitude gradient in the western Canadian Rocky Mountains (Blais et al., 1998). Increasing snowfall at higher altitudes led to a 10-fold increase in deposition with height of less volatile compounds, such as DDT. For the more volatile organochlorines (e.g., lower chlorinated PCBs, HCH, and heptachlor epoxide) this increase with altitude was up to 100-fold, demonstrating enhancement through cold-condensation effects. The concentration gradient with altitude is particularly informative because it was performed in a single geographic location, making the study less likely to be confounded by proximity to sources, which can occur when there are several geographically dispersed measurement sites.

Global-scale distillation effects were observed originally for the heavy isotopes (deuterium, oxygen-18) compared with the light isotopes (hydrogen and oxygen-16) of water vapor (Dansgaard, 1953). Light isotopes are more volatile than their heavier counterparts. The ratio of light to heavy isotopes increases with latitude, because of selective condensation of the heavier isotopes in accord with the Rayleigh distillation formula. For POPs, current field data relate to a small subset of the most volatile persistent organic substances, consistent with theoretical predictions (Wania and Mackay, 1996), i.e., hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), hexachlorocyclohexanes (HCH), and, to a lesser extent, chlordane.

The basis of empirical support for global distillation comes from the differential increase in accumulation of more volatile PCB congeners (lower chlorinated) and HCH isomers ($\alpha > \gamma$) in higher latitudes. Many of the factors noted above as influencing POPs levels in remote locations can be seen affecting, and are consistent with, these measured congener and isomer ratios. Total PCB levels were found to decline with increasing latitude (consistent with increasing distance from the source), but the levels of di- and trichlorobiphenyl stayed relatively constant with latitude (they are more volatile), thereby increasing as a proportion of the total PCB mix (Muir et al., 1996; Ockenden et al., 1998a).

Notable, too, is the delayed onset of PCB deposition to sediments in high Arctic lakes compared with midlatitude and subArctic lakes, providing further evidence of ongoing global distillation (Muir et al., 1996). Similar latitude-related ratio changes favoring more volatile compounds in northern, colder sites were reported for α-HCH versus γ-HCH (lindane), the former having a higher Henry's law constant and vapor pressure (Ockenden et al., 1998b).

Calculating and Modeling Atmospheric Transport of POPs

The distribution and movement of POPs in the atmosphere can be calculated by computer modeling. The outputs from these models may be used for making predictions of future trends, for evaluating the effects of control strategies, and for improving understanding of the processes controlling the distribution of POPs. A complete model of the distribution, ultimate fate, and trends for POPs in the environment would include modules calculating the changes of emissions with time; transport by the atmosphere and oceans; deposition to the surface and volatilization from the surface; transfers to rain and snow; and degradation in the atmosphere, oceans, terrestrial waters, and soils. Although information and models are available for each of these modules for some POPs, a complete and validated global model has not been published, principally because of the complexity of the calculations and the uncertainties in input parameters. More pragmatically, because of their persistence, POPs concentrations can be directly measured in the animal species of interest, reducing the need for modeling to determine dose and risk. To date, POPs models have focused on either (1) bulk transfers among different media (i.e., multimedia models) or (2) simulations of atmospheric movement. The multimedia models currently include simplified treatments of transport, whereas the atmospheric models include highly simplified treatments of the transfers among the different reservoirs. These two modeling fields are now merging. Multimedia models are addressed in Chapter 9 of this report (see also Klecka et al., 2000). The remainder of this section focuses on air transport modeling.

There are two basic approaches for calculating the transport of pollutants in the atmosphere. The first approach is to calculate trajectories, which are the three-dimensional paths followed by the center of mass of an imaginary air parcel, either forward from a source or backward from a receptor location. These are known as Lagrangian models. The second approach is based on numerical grid models, which include a number of physical processes such as the mixing of air parcels, chemical transformations, emissions, and deposition to the surface. These calculations are performed on individual boxes in a three-dimensional grid matrix, thereby tracking the dispersion of a pollutant across this grid (Eulerian models). Both approaches rely on the use of meteorological data obtained from ground-based measurements, weather balloons, and satellites. In some cases, global climatological model simulations are used rather than real observations.

Both approaches have advantages and limitations. The first, or trajectory, approach has the advantage of simplicity, although it minimizes the physical processes mentioned above. For example, after a short time, typically a few days, the air parcels lose their identity because of mixing. On the other

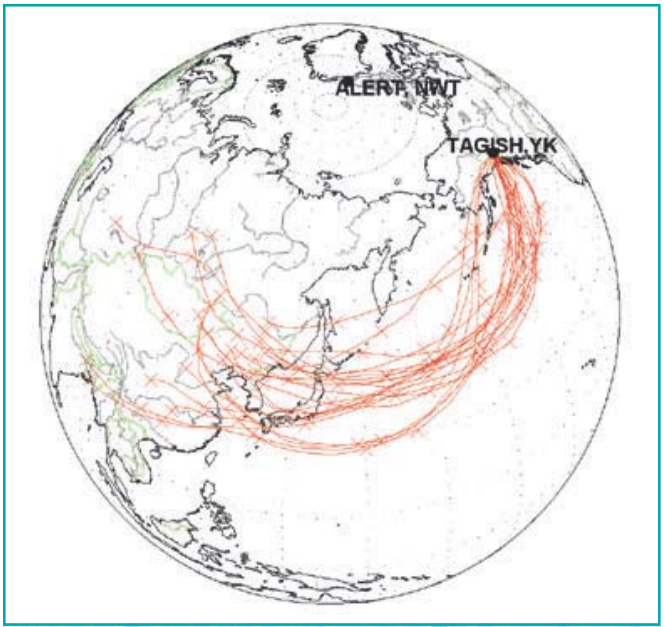

Figure 7-6. Air movement back trajectories from Tagish, Yukon, to Asia.

Source: Bailey et al., 2000.

hand, although the second, or dispersion modeling, approach includes these important processes, they are subject to considerable uncertainties. NOAA's Air Resources Laboratory maintains a Web site (*http://www.arl.noaa.gov/ready.html*) for researchers on which it is possible to calculate trajectories extending either backward or forward for anywhere in either the Northern or Southern Hemispheres.

Back trajectory models are particularly useful to ascertain the source of pollutants. For instance, high levels of a number of POPs, such as α-HCH, γ-HCH, DDT, and chlordane, were found in atmospheric samples at a monitoring site in Tagish, Yukon, Canada (Bailey et al., 2000). As shown by the trajectories in Figure 7-6, the pollutants were associated with long-range transport from Asia, occurring generally within the previous 5 days. Coupling emissions data with the trajectory methods can further inform inferences that POPs observed at monitoring sites came from particular source regions.

The results of the calculation of a large number of backward trajectories can be assembled to trace "transport pathways" leading to a particular monitoring site. Several thousand trajectories from Alaska were calculated backward for 10 days during the entire year of 1999. Results for 4 months of the year (January, April, July, and October) are shown in Figure 7-7 to give an idea of the seasonal variation in the transport pathways through the atmosphere (Husar and Schichtel, 2001). The different-colored shading in Figure 7-7 reflects the probability that trajectories passed over a given area before arriving at the Alaska Peninsula National Wildlife Refuge in the Aleutian Islands. The boundaries of each shaded region represent lines of constant probability. The areas shaded in red have the highest probability of being traversed by trajectories, whereas those shaded in light blue have a lower probability. Similar calculations for a number of receptor sites throughout the United States are shown in Appendix A. By comparing the locations of the dust and smoke plumes shown in Figures 7-1, 7-3, and 7-4 to the transport pathways shown in the figures in Appendix A, it can be seen that the plumes visible in the satellite images occur within defined transport pathways. Even though smoke or dust may not be visible in satellite images, the transport of other airborne compounds, including POPs, still occurs within these pathways.

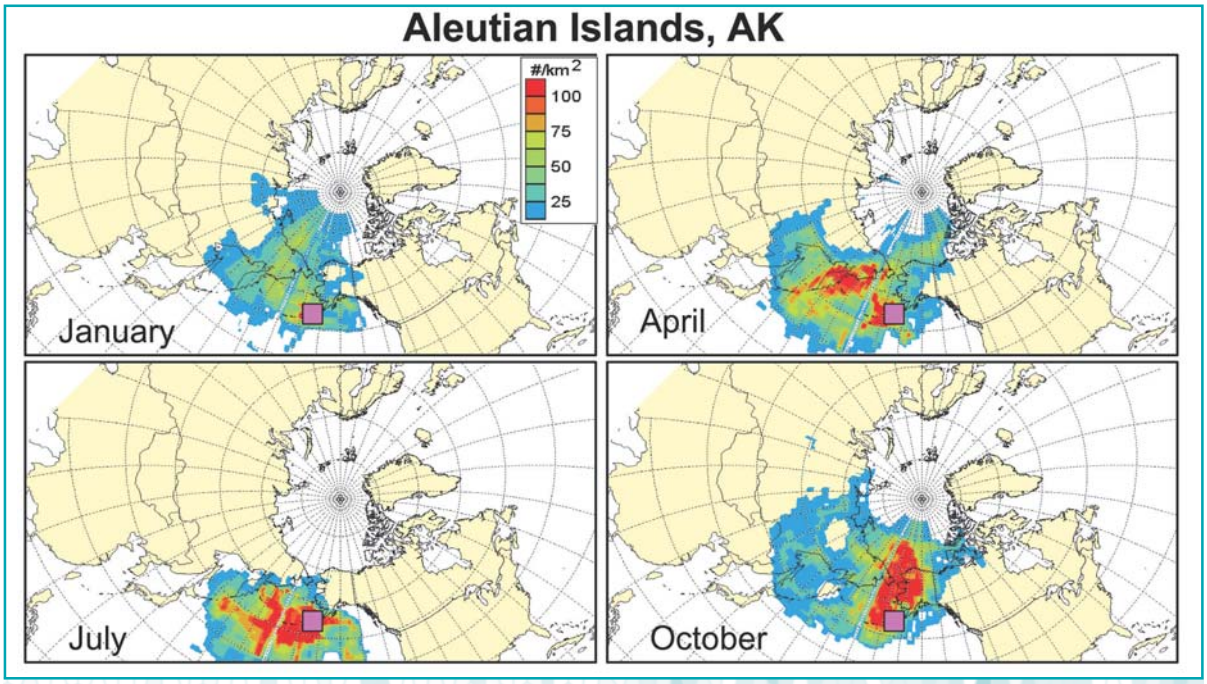

Figure 7-7. Aleutian 10-day back trajectories for the year 1999. Color shading refers to the likelihood that trajectories passed over a given area before arriving at the receptor site.

Source: Husar and Schichtel, 2001.

During the springtime, after the winter snows have melted and before a vegetation cover has appeared, extensive clouds of yellow dust can be raised from the Gobi and Taklamakan Deserts (Duce, 1995). Strong cold fronts originating in Siberia are associated with strong upward air motions in front of them as they travel southward. The vertical motions carry whatever pollutants are found near the surface upward to the altitude of the jet stream, where they can be rapidly transported eastward to North America (Figure 7-3). Siberian cold fronts can travel all the way to southern China, so a broad range of pollutants from different regions can be transported to North America during a single frontal passage. Sinking air over northwestern North America allows suspended material in the air to be brought to the surface. It is only during the spring that the effects of these events are visible in satellite images. The frontal passages occur at other times, and may transport pollutants to North America without raising dust clouds.

Figure 7-8 shows the results of a three-dimensional, chemistry-transport model simulation of the transport of dust from the Gobi Desert to North America during the dust storm of April 1998 (Hanna et al., 2000). The "dust" plume shown in Figure 7-8 was produced by both horizontal and vertical motions. In general, long-range transport of pollutants involves movement vertically as well as horizontally. Events such as those shown in Figure 7-8 result in rapid transport, on the order of a few days, over transcontinental distances. This simulation included emissions from different points within Asia and the effects of atmospheric mixing during the transport of the emissions. Emissions from different regions of Asia follow their own pathways to North America, where they affect different areas. Figure 7-8 also shows that transport does not terminate abruptly at the coast of North America; rather, there can be deposition on mountains near the coast and even further inland. The frequency of these events and their importance as a transport mechanism to North America remain to be determined. The next step will be to include in the model the chemical losses and multimedia transfers described above so that the transmission of POPs and other chemicals during intercontinental transport can be determined.

The results of a three-dimensional, chemistry-transport model simulation of the global distribution of hexachlorobenzene (HCB), a long-lived POP, are shown in Figure 7-9 (Olaguer and Pinto, 2001). The distribution of HCB was calculated using data for the emissions of HCB and loss by OH radicals calculated with the model. The areas of high concentration in Figure 7-9 basically result from a combination of high emissions and meteorological conditions that favor trapping emissions close to the surface. The model was able to simulate successfully a number of observed features of the global distribution of HCB, including its ratio between the Northern and Southern Hemispheres, lending credence to this approach. Simulations such as these will permit quantitative testing, by comparison with observations, of many of the concepts presented in this chapter.

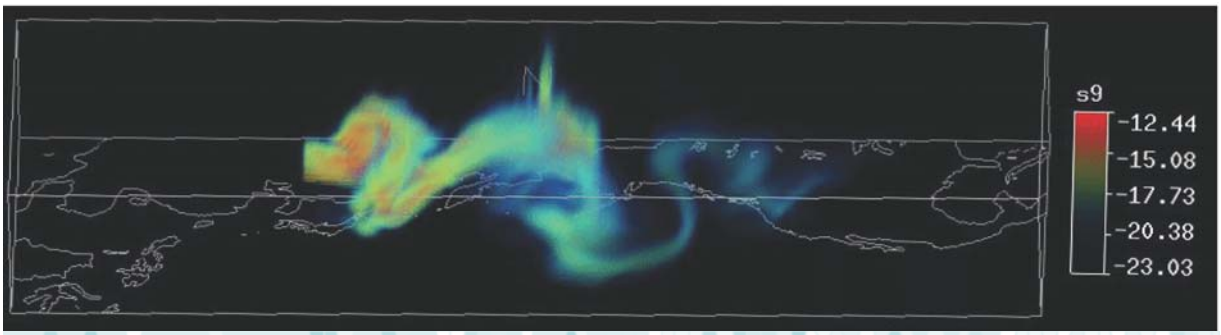

Figure 7-8. Forward trajectory simulation of dust from the Gobi Desert to North America, April 1998.
Source: Hanna et al., 2000.

POPs Transport in Water

Long-range transport can also occur through hydrologic pathways, with POPs entrained on sediment, in microscopic species, or in solution (for the more water-soluble compounds). POPs released or deposited onto terrestrial areas are transported down rivers to oceans, and then potentially to remote locations through oceanic currents. POPs deposited and accumulated on ice in the Arctic can also be transported into the North Atlantic by ice floes. The contribution of hydrologic transport to global POPs pollution has not been quantified, although it is generally considered to be substantially less than occurs through atmospheric transport of these semivolatile, hydrophobic substances.

Oceanic currents can be wind generated at the ocean surface or result from water temperature and density (thermohaline) differences. Wind generated currents are generally limited to the first 1,000 meters of depth, whereas thermohaline currents can extend down to the deep sea. Oceanic current speeds are highly dependent on location. Movement in the Gulf Stream or Kuroshio currents can be rapid (7–11 km/hr, 4–6 knots) over thousands of kilometers, whereas within localized gyres (circling currents) or deep oceanic regions little to no net water transport may be occurring. The major surface currents in the North Atlantic Ocean form a large gyre, or closed clockwise circulation, in which the Gulf Stream current flows northward along the east coast of North America to Cape Hatteras, NC, then travels to the northeast, then southward along the coast of Europe, and finally westward across the tropical Atlantic Ocean in the North Equatorial Current to close the circulation (Figure 7-10).

A similar circulation pattern is found in the North Pacific Ocean, in which the Kuroshio current flows northward along the coast of Asia to the southeast coast of Japan through the East China Sea. Its width is about 100 km, its speed 6–7 km/hr (3–4 knots), and it transports 30–60 million tons of water per second (Pickard, 1975). Pacific currents can transport POPs from Asia to continental Alaska and its island chains. The transit time around the

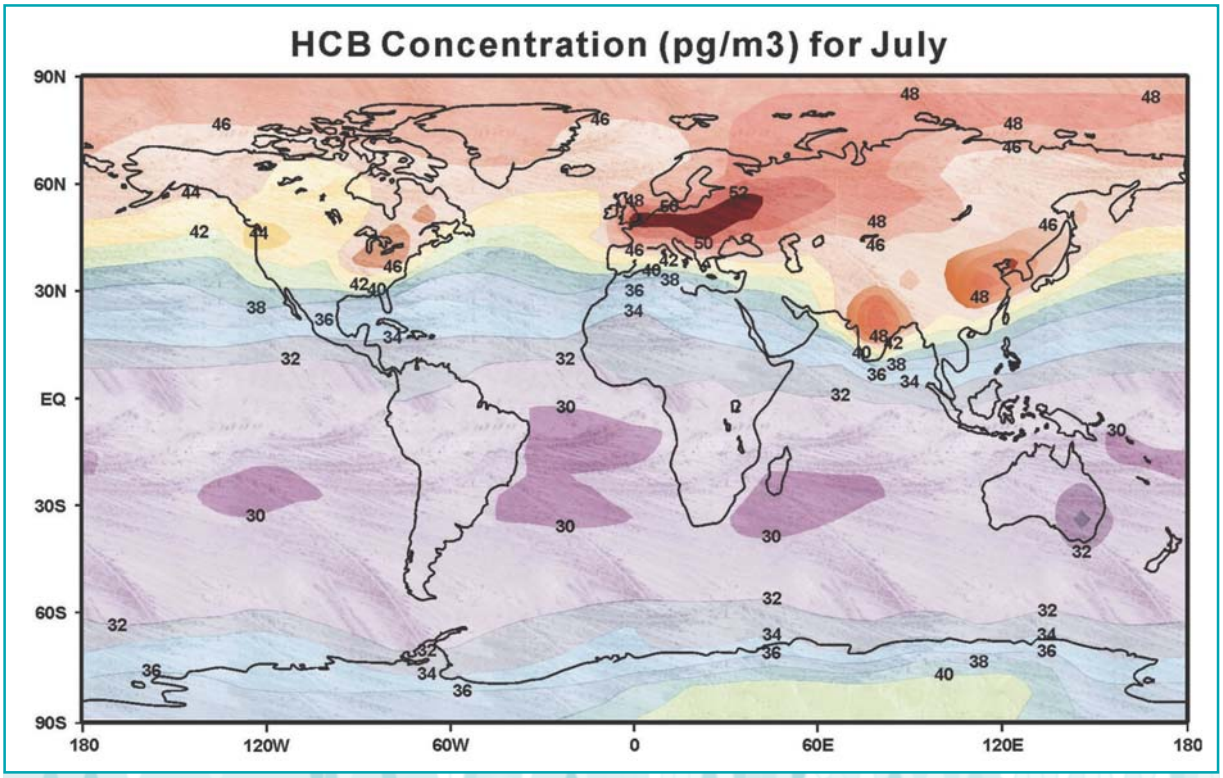

Figure 7-9. Calculated global distribution of hexachlorobenzene at the earth's surface.

Source: Olaguer and Pinto, 2001.

Bering Sea was estimated in the order of 1 year, as measured by satellite tracking of drift markers (Royer and Emery, 1984). Measurements of the latitudinal distribution of POPs in seawater are sparse. Concentrations of at least one organochlorine, α-HCH, in seawater were found to increase with latitude by roughly a factor of 20 on a transect from the Java Sea to the Beaufort Sea (Wania and MacKay, 1996; and references therein). This increase is probably the result of atmospheric deposition. Although computer models of the ocean's circulation exist and have been coupled with atmospheric models to study problems related to climate change, they have not yet been applied to problems of POPs transport.

The ocean can also act as an ultimate sink for POPs, either through the deposition of dead biological organisms or via deep-current circulation. POPs can be concentrated up the marine food chain, starting with phytoplankton. Some POPs are transported to deeper layers of the ocean by settling phytoplankton, or "marine snow." Evidence for this pathway is provided by elevated concentrations of POPs in marine fish, with higher concentrations found in deeper living varieties (Froescheis et al., 2000; Looser et al., 2000). Sinking water, such as part of the Gulf Stream near Iceland, also carries with it pollutants such as POPs. POPs transported to the deep sea by either of these pathways will probably remain there and be degraded, because it takes several hundred years for water in the deep sea to return to the surface again in a region of upwelling.

POPs Transport by Migratory Animals

POPs transport through migratory species is also considered a potential source of contaminant movement under the Stockholm Convention. Evaluation of this mechanism differs from the previous assessments of atmospheric and hydrologic transport, because POPs transported through migratory species are often focused on a localized region (lakes, nesting sites) or injected directly into the food supply. Through this means, the POPs concentration in lipid is maintained, dilution is prevented or minimized, and the POPs are potentially targeted at a

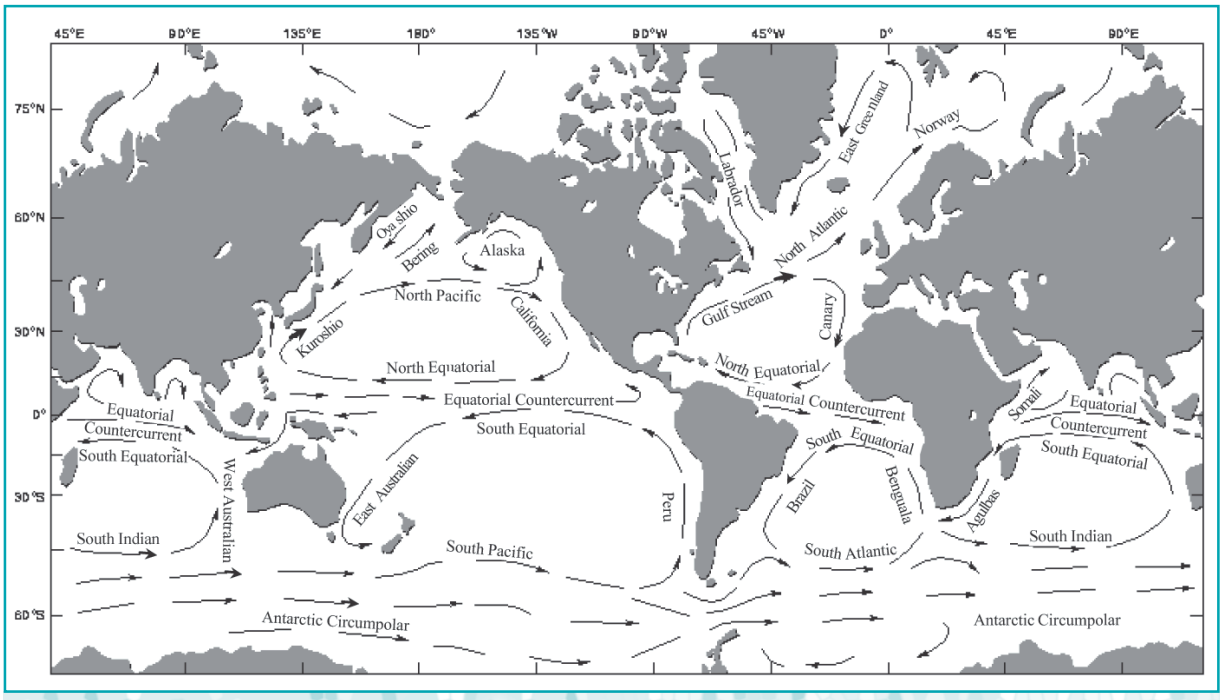

Figure 7-10. Oceanic surface currents.
Source: Adapted with permission from Apel, 1987.

receptor animal species. This can be viewed as more of a stiletto approach, compared with the blunderbuss of atmospheric transport.

The bulk amount of POPs transported long distances by migratory birds, fish, and/or marine mammals is highly uncertain, and estimates are not available (van de Meent et al., 2001). However, it has been calculated that the POPs loading from spawning and dying salmon swimming to localized lakes in Alaska is greater than air deposition levels (Ewald et al., 1998). POPs may also be transported by migratory birds to remote rookeries, and from there be transferred to resident species. Most importantly for high trophic predators and human risks, the oceanic movement of some fish and marine mammals can transfer the POPs loads obtained throughout this migratory journey directly to the end predator.

Monitoring and Modeling POPs Trends

Atmospheric monitoring and modeling provide reassurance that efforts on POPs can be, and are, effective in regions such as the Great Lakes. On the basis of data collected by the Integrated Atmospheric Deposition Network (IADN; *www.epa.gov/glnpo/iadn/*), trends in concentrations of a number of key POPs can be calculated and extrapolated to give approximate dates when atmospheric concentrations will be beneath minimum detection limits of the measurement techniques used (i.e., "virtual elimination"; Cortes et al., 1998). Results of these extrapolations are shown in Figure 7-11. Atmospheric levels of DDT and DDD are predicted to be the first below detection limits, disappearing at all sites by about 2010. HCB will remain in the atmosphere the longest of all the compounds considered, mainly because of its continued production as a byproduct. Overall, though, these data suggest that most of the compounds will disappear from the atmosphere of the Great Lakes by the middle of this century.

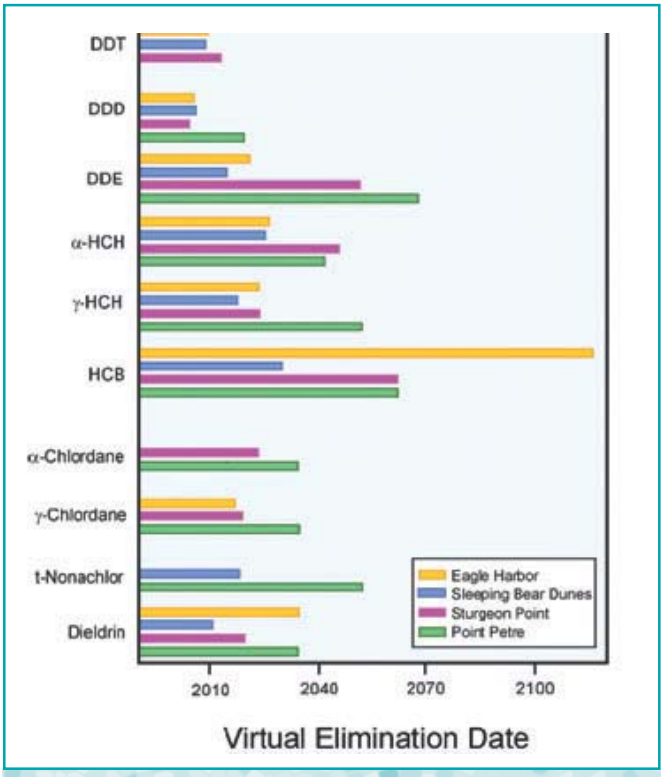

Figure 7-11. IADN virtual elimination dates for atmospheric concentrations in the Great Lakes region. Virtual elimination date estimates assume no significant new sources.
Source: Cortes et al., 1998.

Acknowledgments

The help of Dave Leonhard and Dianne Caudill in producing the figures is gratefully acknowledged. Dr. Rudolf Husar kindly supplied the calculations of transport pathways used here. Helpful comments by colleagues including Drs. Eduardo Olaguer, Elliott Atlas, and Leonard Barrie are also gratefully acknowledged.

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Chapter 8 Contemplating POPs and the Future

Treaties are guided by past experiences, negotiated in the present, and look to a better future. For the Stockholm Convention, a fundamental consideration is what the future might hold in decades to come in the absence of action. As with the accumulation of POPs in the environment, the passage of time necessitates thinking beyond the present day. What will be future sources and levels of POPs emissions, and could the Stockholm Convention affect these emissions? This chapter informs these considerations by summarizing the results of existing demographic and economic futures forecasts. The models demonstrate that future POPs source regions will likely be different from current ones, and that very large regional growth rates in human populations and economic and industrial activity could drive POPs emissions in the absence of controls.

The futures modeling scenarios to be presented were developed and reviewed as part of the Intergovernmental Panel on Climate Change (IPCC) research program. Rather than estimate specific POPs emissions, the models focus on the growth in current economic activities in which POPs are used or emitted under current production and use patterns. The intent is to indicate the general pattern of economic growth and important sectoral components of these activities. Results are presented for the Special Report on Emission Scenarios (SRES) B2 scenario, one of the four basic classes of scenarios developed for the recent IPCC report (IPCC, 2000). The SRES B2 scenario was selected because it falls roughly in the center of future projections of population and economic activity, yet is relatively optimistic about the future of presently developing countries and does not contain major new policy initiatives. Most of the data presented come from the MiniCAM (Edmonds, 1985, 1996) version of the B2 scenario developed and submitted to the Special Report by the Global Change Group (GCG) at Battelle Pacific Northwestern National Laboratories (PNNL) (IPCC, 2000; pp. 566-570), or, in some noted instances, from recent revisions based on model improvements. Results from the Second Generation Model (SGM), the GCG's larger and more detailed emissions model (Edmonds et al., 1995), were used for some of the detailed sectoral results. The SGM model run used for these results largely reproduces the aggregate population and economic activity patterns of the PNNL MiniCAM B2 model, acting as an internal validity check of the results expected in a "B2 future world."

The SRES B2 projection is commonly considered the "business as usual" scenario. Such a scenario assumes a continuation of past trends in population, technologies, and industrial output, with no major shifts in government policy. This forecast is the basis for all U.S. Administration energy and climate change analyses. For the forecasts included in this chapter, U.S. population and gross domestic product (GDP) trajectories have been modified from the SRES (IPCC, 2000) report to track the most recent Annual Energy Outlook forecast (U.S. DOE, 2000). Results are modeled to the year 2050. It is important to recognize that population, GDP, and the nature and structure of economic activity can be quite different from the values given here. Using B2 as a representative case should not be interpreted to mean that this is the most likely situation. It is used because it provides a good qualitative sense of how activities leading to POPs emissions might grow in the absence of additional control strategies.

The results of the B2 model runs are presented under two basic categories: general growth and sector-specific results. The general growth categories are factors such as population, economic,

and industrial growth that act as potential pollution drivers. These general growth drivers are not necessarily linearly associated with environmental pollution, as economic growth and prosperity have also led to enhanced pollution awareness and the means to combat it. The sector-specific forecasts have been selected for their potential relevance to one or more of the listed POPs in developing countries. For instance, if the use of chlordane and other POPs termiticides is continued, the emission levels would likely relate to such factors as housing starts. Byproduct POPs emissions have come from municipal and hospital waste incineration, open burning of wastes, chlorine bleaching of pulp and paper, and iron and steel sintering, among others. In the absence of control technologies as economies develop, future byproduct emissions from these sources could reasonably be expected to increase, with the sectoral projections acting as a proxy for these emission increases.

General Worldwide Growth Projections

Population Growth

Human population growth is central to all pollution scenarios. All of the POPs were either developed and produced to satisfy contemporary human needs, or are the byproducts of human activities. Figures 8-1 and 8-2 provide forecasts of human population growth rates and projected levels by region. The population forecast used here closely mirrors the most recent United Nations median forecast (Population Division; United Nations, 2000) that the total world population will reach 9.3 billion by 2050. As evident in Figure 8-1, the projected global population growth rate is decelerating, although it remains uncertain how long this trend will continue. The global average rate conceals large variations across regions, with the Rest of the World (ROW) region continuing to grow rapidly, whereas the population is declining in all Organization for Economic Cooperation and Development (OECD) countries, except the United States.

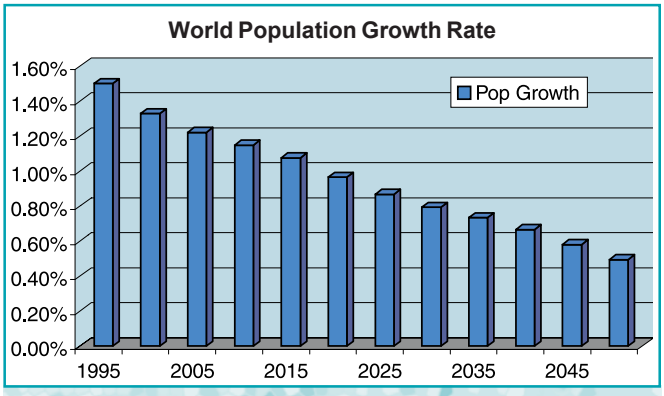

Figure 8-1. Projected declining annual rates of world population growth.

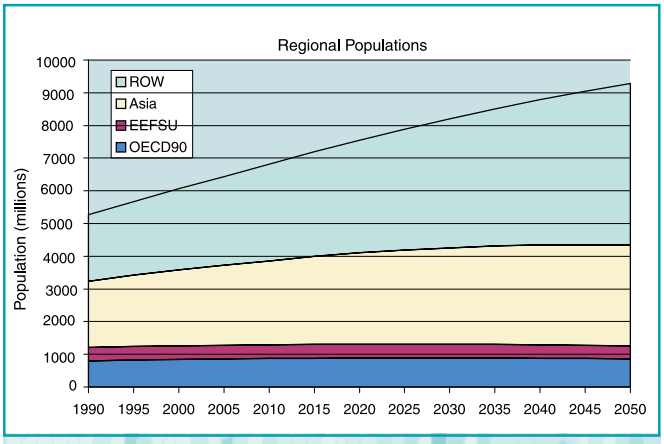

Figure 8-2. Projected world population levels, by region. ROW, rest of world; EEFSU, Eastern Europe Former Soviet Union; OECD, Organization for Economic Cooperation and Development.

The projection of total world population (Figure 8-2) demonstrates that population increases will likely be concentrated in three areas, the largest being the rest of the world category, comprised principally of Latin America and Africa in this graph. China and India are the other two large contributors, with the Chinese population estimated to have peaked by 2030 and in a slow decline by 2050. The Indian population, in contrast, continues to grow, although not as rapidly as Africa and Latin America. The current group of developed countries will constitute only about 10% of the world population by 2050. The global population will be much older on average than it is today, with the average age increasing from 26 to 36 years (United Nations, 2000).

Economic Activity

In contrast to the ~50% growth in population, global economic activity is projected to increase fourfold, from US$22 trillion in 1990 to $88 trillion in 2050 (in 1990 U.S. dollar equivalents). Average per capita income will more than double. The overall pattern of economic activity shows a large shift from its current focus in North America and Europe to Asia, Africa, and Latin America (Figure 8-3). Half the growth in economic output will occur in these areas, with their share of economic activity projected to rise from 16% to 41% over the half-century. The growth in ROW GDP is especially large, reflecting a combination of rapid population growth and increase in per capita income from just over $1,000 per capita to about $4,500 per capita. Because these areas currently have quite low per capita income levels, it is anticipated that much of this growth will go to the provision of essential physical commodities, such as infrastructure and appliances. In contrast, the economic growth in the currently developed economies will likely be focused in areas such as services, which are less intensive users of such inputs as energy and chemicals. The likelihood exists, therefore, that much of the growth in potential POPs-producing activities could occur in developing countries.

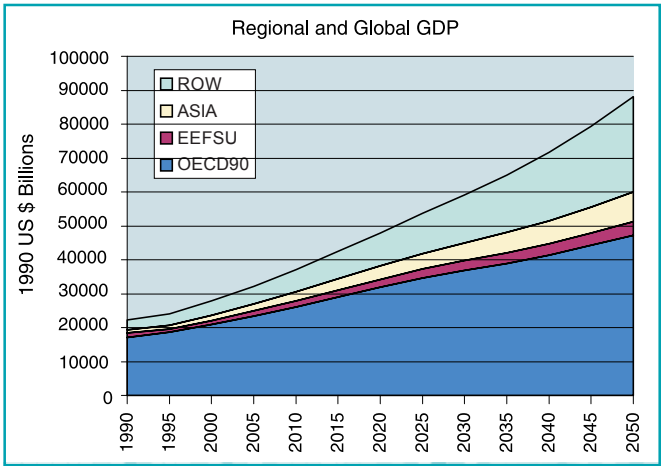

Figure 8-3. Projected growth in worldwide gross domestic product (GDP). ROW, rest of world; EEFSU, Eastern Europe Former Soviet Union; OECD, Organization for Economic Cooperation and Development.

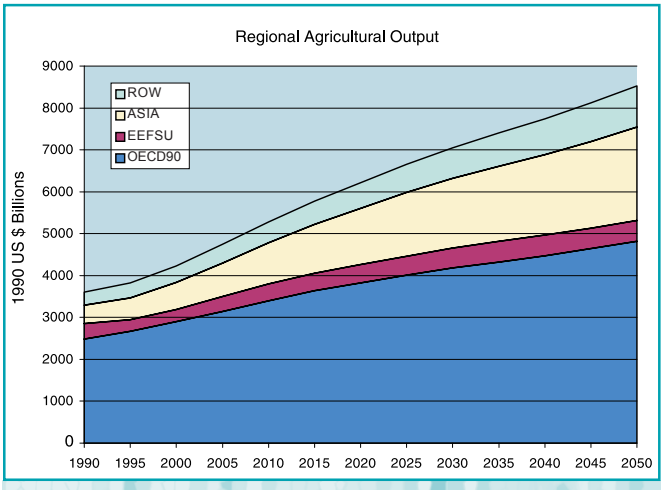

Figure 8-4. Projected increases in worldwide agricultural output. ROW, rest of world; EEFSU, Eastern Europe Former Soviet Union; OECD, Organization for Economic Cooperation and Development.

Agricultural Output

The pattern of agricultural production shows a similar, although less pronounced, shift from developed to developing countries (Figure 8-4). The models predict a nearly 2½-fold increase in agricultural output worldwide, with the OECD share falling from about two-thirds to just over one-half. Data from similar scenarios in the SRES database (CIESIN, 2001) suggest that this growth in output will occur with only minimal growth in land area allocated to agricultural production, implying a significant increase in intensity of production and a corresponding increase in agricultural chemical use.

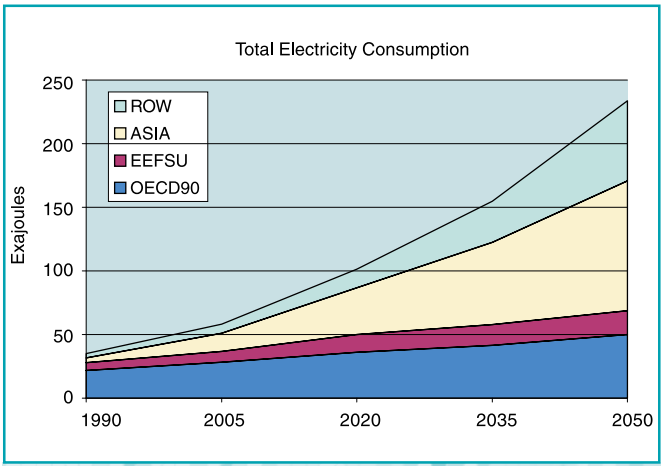

Figure 8-5. Projected growth in worldwide electricity consumption. ROW, rest of world; EEFSU, Eastern Europe Former Soviet Union; OECD, Organization for Economic Cooperation and Development.

Energy Consumption

Total energy consumption and associated gaseous and particulate emissions serve as an additional proxy for economic development. Total electricity consumption is predicted to grow by more than a factor of six, rising from 35 Ej (exa-, 10^{18} joules) in 1990 to 233 Ej in 2050 (Figure 8-5). The proportion of electricity consumed outside OECD countries also rises rapidly, from 38% in 1990 to 79% in 2050. Although the fraction of electricity generated by fossil fuel inputs declines slightly during the 1990-2050 period (60% to 52%), the strong growth in electricity demand is predicted to increase global CO_2 emissions from 5.6 billion tonnes to 12.1 billion tonnes (Figure 8-6), with the developing-country proportion rising from 59% to 77%.

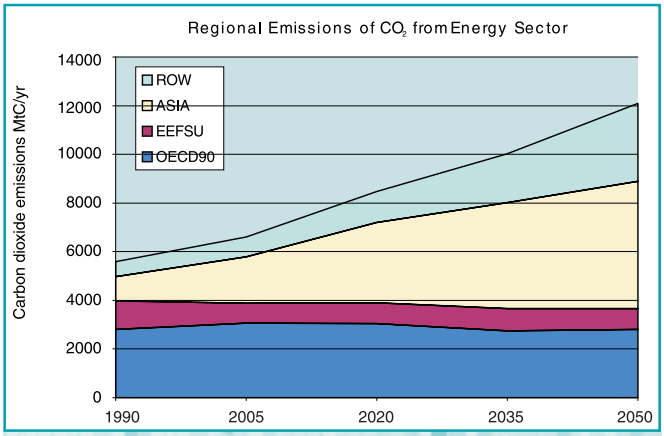

Figure 8-6. Projected worldwide emissions of carbon dioxide from the energy sector. ROW, rest of world; EEFSU, Eastern Europe Former Soviet Union; OECD, Organization for Economic Cooperation and Development.

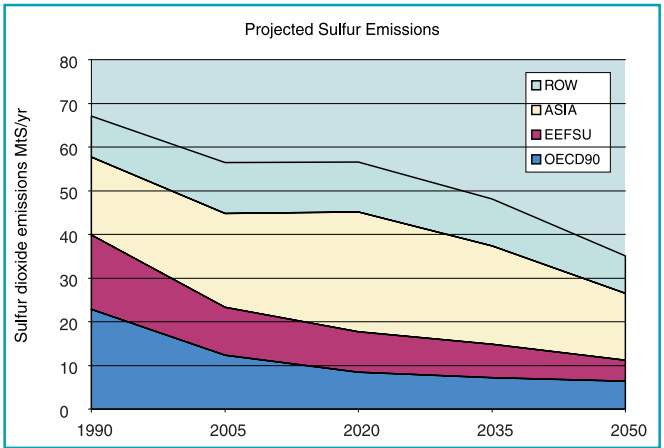

Figure 8-7. Projected worldwide declines in sulfur emissions as a result of improved technologies. ROW, rest of world; EEFSU, Eastern Europe Former Soviet Union; OECD, Organization for Economic Cooperation and Development.

Sulfur emissions provide an important counterexample to the general upward trend in emissions and economic activity. Despite the rapid growth in electricity use and coal-fired plants, sulfur emissions are expected to decline sharply over the next half-century (Figure 8-7). This decline results from the development and application of control technologies, a situation somewhat analogous to the potential for POPs byproduct controls under the Stockholm Convention.

Sector-Specific Growth Projections

The preceding demographic and economic factors act as general—but nonspecific—drivers of pollution and POPs levels. In some instances, specific sector models are available that more closely link economic activity with one or more POPs. Two such examples are summarized below: housing starts and termiticide use; and municipal waste generation and selected industrial production categories and potential byproduct emissions. Although the links between these sectoral projections and potential POPs releases are indicated, no attempt is made to perform further modeling beyond the existing projections.

Housing Starts and Termite Control

Of the POPs pesticides, chlordane (along with heptachlor and mirex) continues to be used for household termite control in both wood and brick construction in a number of developing countries. Chlordane is relatively cheap and provides long-lasting termite control in the soil beneath and around houses, but ultimately may be released into the environment and transported far from its site of application. Alternative non-POPs pesticides, physical barriers, and construction techniques are available for termite control, but the sheer persistence and toxicity of chlordane is still considered by some to be a substantial asset in the struggle against termites, especially in the

tropics. With cessation of production in the United States, China commenced chlordane manufacture and has requested an exemption for production and use as a termiticide in buildings and dams. Several other countries have requested use exemptions for chlordane as a termiticide (UNEP, 2001).

Sector-specific projections indicate that growth in households worldwide will be substantial, because of the overall growth in population and as that population ages and becomes more urban. The estimates provided here reflect only the aging and population growth components, but not the impacts of urbanization. They are based on age-specific head of household rates from MacKellar et al. (1995) (Figure 8-8). Total annual new household formation is projected to reach nearly 35 million by 2015 and then slowly decline to below 25 million annually by 2050. Almost all of this new household formation and related construction will occur in the developing world.

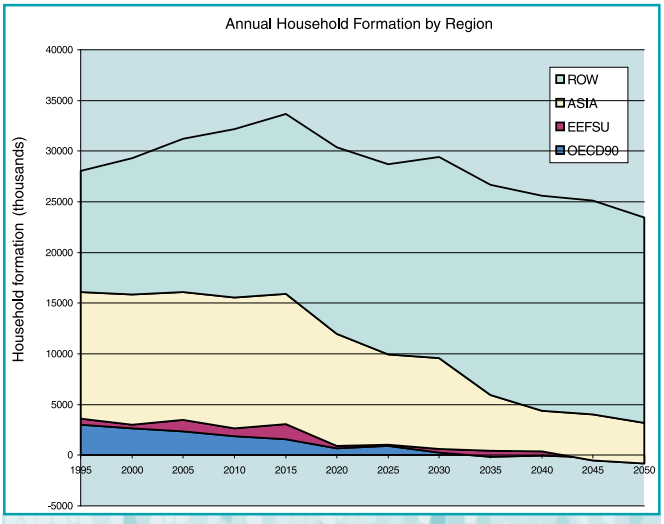

Figure 8-8. Projected worldwide new household formation. ROW, rest of world; EEFSU, Eastern Europe Former Soviet Union; OECD, Organization for Economic Cooperation and Development.

Municipal Waste Generation and POPs Byproducts

Polychlorinated dioxins and furans are principally formed and released from the poor or uncontrolled combustion of municipal and hospital wastes, particularly open burning, resulting from a combination of poor burn parameters, organic matter, chlorine, and metal catalysts. Although data quality issues exist for projections of solid waste generation, enough is known to indicate that the solid waste stream will grow rapidly over the next half-century. A recent World Bank report suggests two drivers for this growth: an increase in urban populations and an increase in the income of urban dwellers. Urban dwellers generate several times more waste than do rural dwellers (World Bank, 1999) (Table 8-1). Wealthy urban dwellers generate about 2.5 times more waste per capita than do poor urban dwellers. Over just 25 years, Asia is predicted to move from about 30% to more than 50% urban dwellers. Forecasts suggest that the rest of the developing world will follow a similar pattern. The World Bank study estimates an overall growth in municipal solid waste of 2.4-fold by 2025, to a total of two-thirds of a billion tons annually in Asia alone. The waste stream is forecast to become more combustible and organic in composition, making incineration an increasingly attractive option, while landfills become more scarce.

Table 8-1. Recent and projected municipal solid waste (MSW) generation per capita in Asia

	1990			2025		
Region	GNP/ Capita	% Urban	MSW/ Capita	GNP/ Capita	% Urban	MSW/ Capita
Low-income Asia	490	27.8	0.64 kg	1,050	48.8	0.77 kg
Middle-income Asia	1,410	37.6	0.73 kg	3,390	61.1	1.17 kg
High-income Asia	30,990	79.5	1.64 kg	41,140	88.2	2.17 kg

Industrial Processes and POPs Byproducts

Other sources of polychlorinated dioxin and furan byproducts listed in the Stockholm Convention include elemental chlorine bleaching of pulp and paper, iron ore sintering, and secondary metals production, such as poorly performed recycling through incineration of copper and other metal-containing items. Projected production increases under these sectors are shown for a subsection of regions where data are available. The extent to which production increases translate to POPs emission increases is highly dependent on the development and use of pollution prevention and control practices.

The model results for wood production, relevant to the extent they can be considered a proxy for pulp and paper manufacture, demonstrate an approximate fourfold increase over 50 years, reasonably uniform across all regions (Figure 8-9).

Total steel production, a proxy for iron ore sintering, is projected to increase threefold by 2050 in the same five regions (Figure 8-10). China is projected to be the largest steel producer by the end of this period, with Japan and the United States remaining significant producers. Nonferrous metals are a much smaller part of production, and model results are available for only four regions. Absent data for China, the production picture for the four other regions remains dominated by the United States and Japan, with somewhat slower growth than for steel (graph not shown).

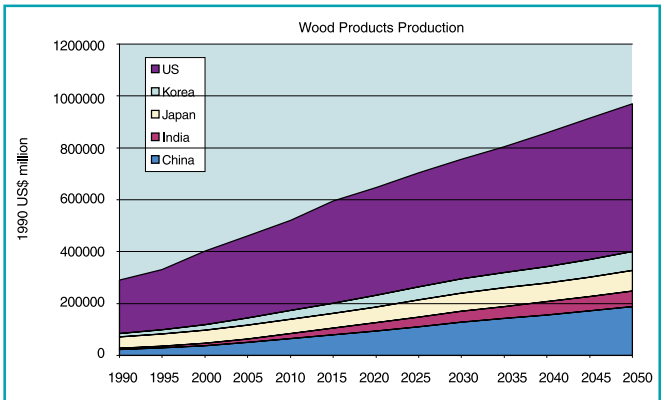

Figure 8-9. Projected wood products production from selected countries.

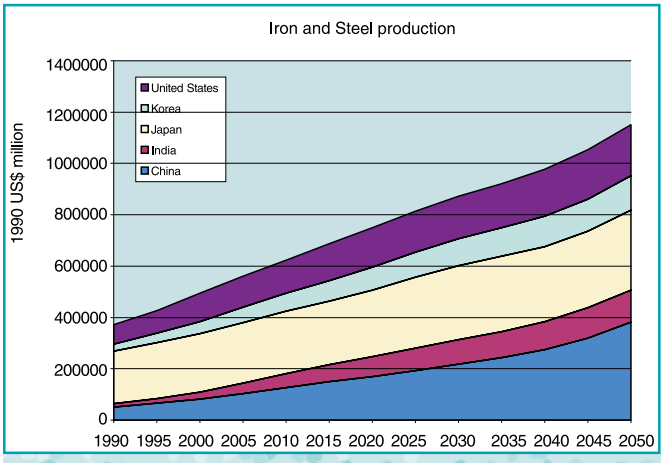

Figure 8-10. Projected iron and steel production from selected countries.

It bears noting that other POPs also have continuing connections to demographic and economic drivers in the absence of additional controls. DDT use continues for malaria vector control in the tropics, where projected increases in human populations are accompanied by a possible expansion of the range of the vector. Country-specific exemptions exist under the Stockholm Convention for limited continued use of the pesticides mirex, heptachlor, aldrin, and dieldrin, principally for termite, ant, and locust control. Hexachlorobenzene production continues as an industrial intermediate and byproduct of chemical manufacture and incineration, and PCBs remain worldwide awaiting equipment retirement and destruction or environmentally sound disposal. Agricultural use of a number of POPs also continues in some countries contrary to national laws, and the potential exists for future POPs development for agricultural or industrial purposes in the absence of an implemented Stockholm Convention.

Summary

There will be large increases in the scale of worldwide economic activity over the next half-century, with overall economic activity predicted to increase about fourfold. Individual economic and end-use activities that either use or emit POPs can increase by more or less than this overall growth rate, depending on the specifics of the activity and its

growth. Except for activities directly linked to population increases, such as new households or populations in mosquito-prone areas, none of the sectors is expected to grow by less than a factor of two, some growing by as much as sixfold. The Special Report on Emission Scenarios (IPCC, 2000) considers many scenarios other than those presented here, some with much higher levels of per capita incomes and lower populations, others with lower levels of economic well-being and higher populations. Yet all of these projections share a future of much higher total economic activity, and hence of potential uses and emissions of POPs in the absence of active control policies.

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Chapter 9 The Addition of Chemicals—A Living Agreement

Reflecting the dynamic societal, scientific, and industrial time in which we live, the Stockholm Convention anticipates change through the ability to list additional persistent organic pollutants (POPs) as new science becomes available. The United Nations Environment Programme (UNEP) mandate for the POPs negotiation had limited initial consideration to the twelve substances or substance groups. By doing so, negotiators were able to focus on developing generic procedures for addressing POPs, based on the "dirty dozen," rather than digressing into potentially controversial discussions over additional chemicals that might be added. The mandate emphasized, however, "the need to develop science-based criteria and a procedure for identifying additional persistent organic pollutants as candidates for future international action." This task was undertaken by technical experts at criteria expert group (CEG) meetings in Bangkok (1998) and Vienna (1999), and during subsequent negotiations. The resulting process and criteria for the addition of chemicals are codified in Article 8 and Annexes D, E, and F of the Stockholm Convention, respectively (*www.unep.ch*). This chapter summarizes the technical foundation and science-policy basis considered in developing these criteria and procedures, accompanied by contemporary advances in science from the published literature.

Noteworthy in technical discussions on the addition of chemicals was the speed with which consensus was reached among scientists at the CEG meetings. Numerous factors contributed to this consensus, among them: criteria precedents, e.g., UNECE-LRTAP; the "scientific method" based on the provision of data to support opinions; and external academic, industry, and nongovernmental organization (NGO) involvement. Of paramount importance, though, was the inexorable weight of evidence gathered and widespread action already taken against POPs. Only rarely now do U.S. industry and pesticide manufacturers seek to commercialize a substance with POPs characteristics, particularly if there is the possibility of a dispersive use. This reticence to develop POP/PBT (persistent, bioaccumulative, toxic) chemicals predates the domestic PBT guidelines and actions, and can be seen as responsive to technical, economic, and environmental concerns about the impacts of POPs.

Over the decades, the academic community has also provided scientific input from research on the ecological and human health problems stemming from POPs. Input from research scientists to deliberations in the United States and Canada on the UNEP POPs negotiation was consolidated through the 1998 SETAC Pellston Workshop on the "Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment." The report of this workshop (Klecka et al., 2000) provides an excellent technical summary on persistence and long-range transport.

The weight of evidence against POPs is also supported by the number of previous domestic, bilateral, and international technical reviews and policy interventions to identify and address this group of chemicals. The screening criteria used in many of the domestic actions and international POPs/PBT agreements are listed in Table 9-1. The differences in screening criteria values should be interpreted in light of the geopolitical scope of each initiative. The broader the geographic range, the higher the screening criteria values because the more problematic a substance must be to cause transboundary effects at this distance. Integral to interpreting the international POPs screening values is the recognition that they complement domestic initiatives. Most POPs contamination occurs close to the site of

Table 9-1. National and international screening criteria for POPs

	Long-Range Transport[a]			&[d] Persistence			&[d] Bioaccumulation		&[d] Toxicity
	Remote Measurements	Vapor Pressure Pascals	Air Half-life (days)	Water Half-life (months)	Soil Half-life (months)	Sediment Half-life (months)	BAF/BCF	Log Kow	
Stockholm Convention 2001[b]	✔		& 2	2	or 6	or 6	5000	5	Adverse effects; risk profile
UNECE-LRTAP 1998[b]	✔	or <1000[c]	& 2	2	or 6	or 6	5000	or 5	Risk profile
NAAEC-CEC 1997	✔	or <1000[c]	& 2[c]	6	or 6	or 12	5000	or 5	Mutual concern
Canada TSMP 1995	✔		or 2[c]	6	or 6	or 12	5000	or 5	CEPA defined
US EPA 1998 TSCA new chemicals PBT policy - ban pending testing				6			5000		Develop toxicity data
US EPA 1998 TSCA new chemicals PBT policy - release controls				2			1000		Develop toxicity data
IJC 1993 immediate action				2			or 5000		or Chr. Aq. Tox. <0.1 µg/L
IJC 1993 initial screen				0.23			or 1000		or Chr. Aq. Tox. <1 µg/L
CMA PTB policy 1996			5	6	or 12		5000	or calculated, prof. judgment	Exp. judgment. Risk assessment

[a] The "&" terminology should be applied before the "or" term, such that a chemical must have an air half-life greater than 2 days plus the vapor pressure requirement, or this combination could be substituted by remote measurements.
[b] The Stockholm Convention and UNECE-LRTAP POPs Protocol state that alternative criteria may be considered if there is evidence that the substance is otherwise sufficiently persistent or bioaccumulative to make it of concern within the scope of the Convention.
[c] The air half-life is sufficient for meeting the persistence requirement. Vapor pressure maxima were incorporated to exclude highly volatile substances.

release. But because of the propensity of these chemicals to persist, bioaccumulate, and be transported long distances, POPs contamination is dispersed widely and cannot be mitigated solely through domestic activity. Exacerbating the transboundary nature of POPs contamination are ecosystem peculiarities, particularly in the polar regions where cold temperatures and the high lipid content of animals make these areas especially vulnerable to adverse effects.

The Addition Process

All the POPs agreements in Table 9-1 anticipate the addition of substances through a process of screening followed by a more detailed technical assessment. Under the Stockholm Convention, the scientific and technical work necessitated by these activities will be performed by a Persistent Organic Pollutants Review Committee (POPRC). The following general procedures will be followed:

1. *Screening* (process Articles 8-1 to 8-5; criteria Annex D): Screening acts as a mechanism to exclude chemical proposals that have insufficient data or do not fulfill the screening criteria, thereby facilitating efficient use of technical experts.

2. *Risk profile* (process Article 8-6; Annex E): A detailed technical report is prepared expanding on the screening criteria data and additional information requirements and assessing if: "the chemical is likely as a result of its long-range environmental transport to lead to significant adverse human health or ecological effects such that global action is warranted."

3. *Risk management/socioeconomic considerations* (process Article 8-7; Annex F): Subsequent to an affirmative finding from the risk profile, management options are evaluated for the proposed substance, taking into consideration technical and socio-economic considerations.

4. *Recommendation to, and decision by, the Conference of the Parties* (COP; process Article 8-9): Based on the risk profile and management options, a technical recommendation is made to the COP whether a chemical should be considered for listing in Annexes A, B, and/or C and what control measures should be invoked. Ultimate decisionmaking rests with the COP. Set-aside and review procedures are detailed in Articles 8-5 and 8-8.

5. *Ratification of amendments* (Article 22-4): Each Party to the Stockholm Convention may opt to review its concurrence with the addition of each new chemical to the Annexes. For the United States, entry into force for additional chemicals is likely to require an affirmative statement agreeing to be bound by this addition, although domestic implementation details have not been finalized.

Scientific Foundation for Adding Chemicals

The basic process for adding POPs chemicals is consistent across a range of international agreements (UNECE-LRTAP, 1998; NAAEC, 1998) and with the conclusions of scientific bodies charged with developing such procedures (CEG, 1998; Klecka et al., 2000). The process and criteria recognize the complexity of real world environments, and the necessary balance between codifying indicative guidance criteria versus flexibility and the need for expert judgment. Earth's environments vary from steamy, microbe-rich jungles to frozen waters and anerobic sediments, all of which may play a part in the environmental fate of a POP. Reversing this scenario, the many and varied physico-chemical properties of the individual POPs influence how they pass through, accumulate, and sequester in and over the Earth. This section summarizes the technical considerations in evaluating a substance for inclusion as a POP. Additional details on screening criteria development can be obtained from Rodan et al. (1999); on persistence, transport, and modeling from Klecka et al. (2000); and on bioaccumulation from the Great Lakes Water Quality Criteria support documents (U.S. EPA, 1995).

Screening Criteria

Annex D of the Stockholm Convention provides a hierarchical structure for the initial screening of POPs candidates. This screening requires satisfying all four criteria categories of (1) persistence, (2) bioaccumulation, (3) long-range environmental transport, and (4) adverse effects (toxicity). Flexibility and expert judgment are stipulated, however, wherein a low value for one criterion should be weighed against values for other criteria and environmental fate and monitoring considerations.

Persistence

Persistence is the ability of a substance to remain in the environment. It is measured as either a half-life (time for half the amount of substance to degrade) or a residence time (average time for a molecule to remain in that environment = half-life ÷ 0.693). These measurement units assume first-order decay kinetics, which is considered a reasonable assumption at the screening stage (Klecka et al., 2000). As detailed in Table 9-1, persistence screening values for the Stockholm Convention and UN-ECE-LRTAP POPs Protocol are set at a half-life of 2 months in water or 6 months in soil or sediment, or evidence that the chemical is otherwise sufficiently persistent to justify its consideration. The numerical values are tacitly based on temperate climates, where much of the research has taken place. Persistence times can increase dramatically in dark (buried), cold (polar), sterile, or dry (desert) environments. It is recognized that such data should not be misused to inappropriately torque a chemical into meeting the screening guidance values. Application of the screening

criteria also anticipates consideration of the environmental medium into which the POP is released, preferentially distributed (air, water, soil, and/or sediment), and passes through in its transboundary movement (i.e., before it can reach cold environments such as the Arctic; Klecka et al., 2000).

Persistence in water, soil, or sediment is necessary for the chemical to be available for uptake by organisms, as a means of physical accumulation, and as a reservoir for, or receptor of, long-range environmental transport. The mechanism by which persistence leads to the buildup of chemicals in the environment is demonstrated in Figure 9-1. For this theoretical scenario, Figure 9-1a plots the accumulation over time of two hypothetical chemicals with half-lives of 1 and 12 months, in either soil, water or sediment. Two modes of release to the environment are shown for each chemical. The first models a single release of one hypothetical unit of chemical at the start of each year, and the second assumes a continuous release totaling one unit per year. The release of chemicals at the start of each year, such as would occur with once-annual pesticide application, leads to an immediate increase of 1 unit, followed by decline over the remainder of the year. Annual repetition leads to the saw-tooth appearance. Continuous release over the entire year, such as from an ongoing byproduct emission, results in a roughly linear increase in the environmental concentration until steady state is reached. At steady state for both release scenarios (after ~5+ half-lives), the amount emitted to the environment equals the amount degraded, the latter being a function of the total accumulation in the environment.

Taken a step further, Figure 9-1b graphs the relationship between chemical half-life and the concentration at steady state. In other words, based on steady state having been reached for all chemicals, the graph displays the resulting steady-state level for each and every chemical half-life. This figure demonstrates that there is no theoretical cut-off value for persistence that separates a problematic chemical from a nonproblematic one. Indeed, the accumulated concentration (C) in the environment at steady state is linearly proportional to the half-life ($T_{1/2}$), following the equation $C = RT_{1/2} / \ln 2$, where R is the application rate (Rodan et al., 1999). The longer the half-life, the greater the amount of physical accumulation that occurs. As can be demonstrated by extending Figure 9-1b, a chemical with a half-life of 10 years will build up

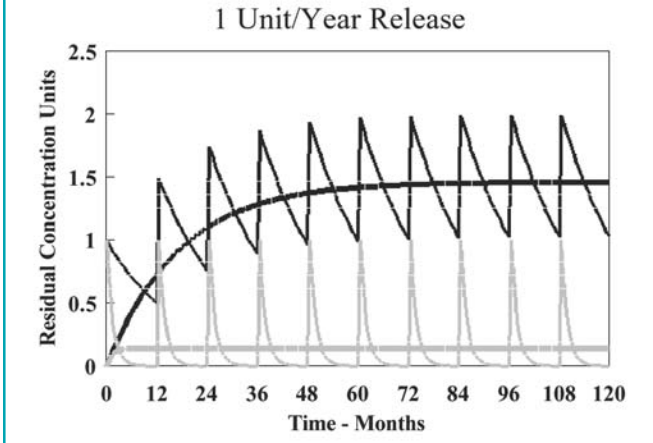

Figure 9-1a. Accumulation curves. Upper graph half-life 12 months, lower graph half-life 1 month. Repeated annual application of one unit leads to the saw-tooth appearance. Continuous application of one unit over the year leads to the smooth curve.
Source: Rodan et al., 1999.

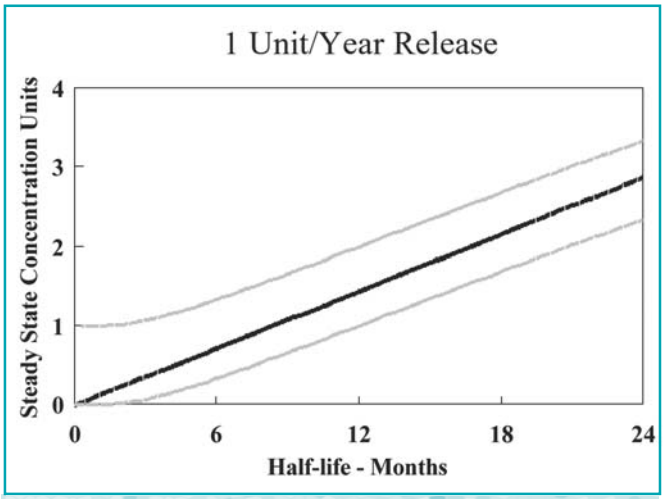

Figure 9-1b. Accumulation curves. Central line represents continuous release totaling one unit per year. Upper and lower lines bound the oscillation from a single release of one unit repeated annually.
Source: Rodan et al., 1999.

in the environment over a half century of use to a concentration 14 times the concentration that would have resulted from a single, annual application. This represents physical accumulation in the environment and is distinct from bioaccumulation (to be discussed shortly). Any physical accumulation in the environment increases the potential for exposure to, and bioaccumulation in, living creatures.

Another approach to setting screening criteria for POPs is to examine measured laboratory and field data for substances already widely acknowledged to be of concern, e.g., the "dirty dozen," compared with data on other substances that are not considered POPs (Figure 9-2). These data can then be compared with proposed criteria guidance values, marked here in gray at a persistence of 6 months and a bioaccumulation factor of 5,000. All 12 priority POPs (marked in red) or their POPs transformation products (aldrin converts to dieldrin, heptachlor to heptachlor epoxide) exceed degradation and bioaccumulation screening criteria adopted under the Stockholm Convention, usually by large margins. The extent to which these POPs exceed the screening criteria is obscured by the truncation of soil half-lives (necessary for ease of presentation) and the logarithmic scaling of the bioaccumulation axis. Similar findings are evident from graphs of overall environmental persistence generated by multimedia fate models (Rodan et al., 1999).

Bioaccumulation

Bioaccumulation is the buildup of a chemical in organisms compared with their surrounding physical environment. For POPs, bioaccumu-

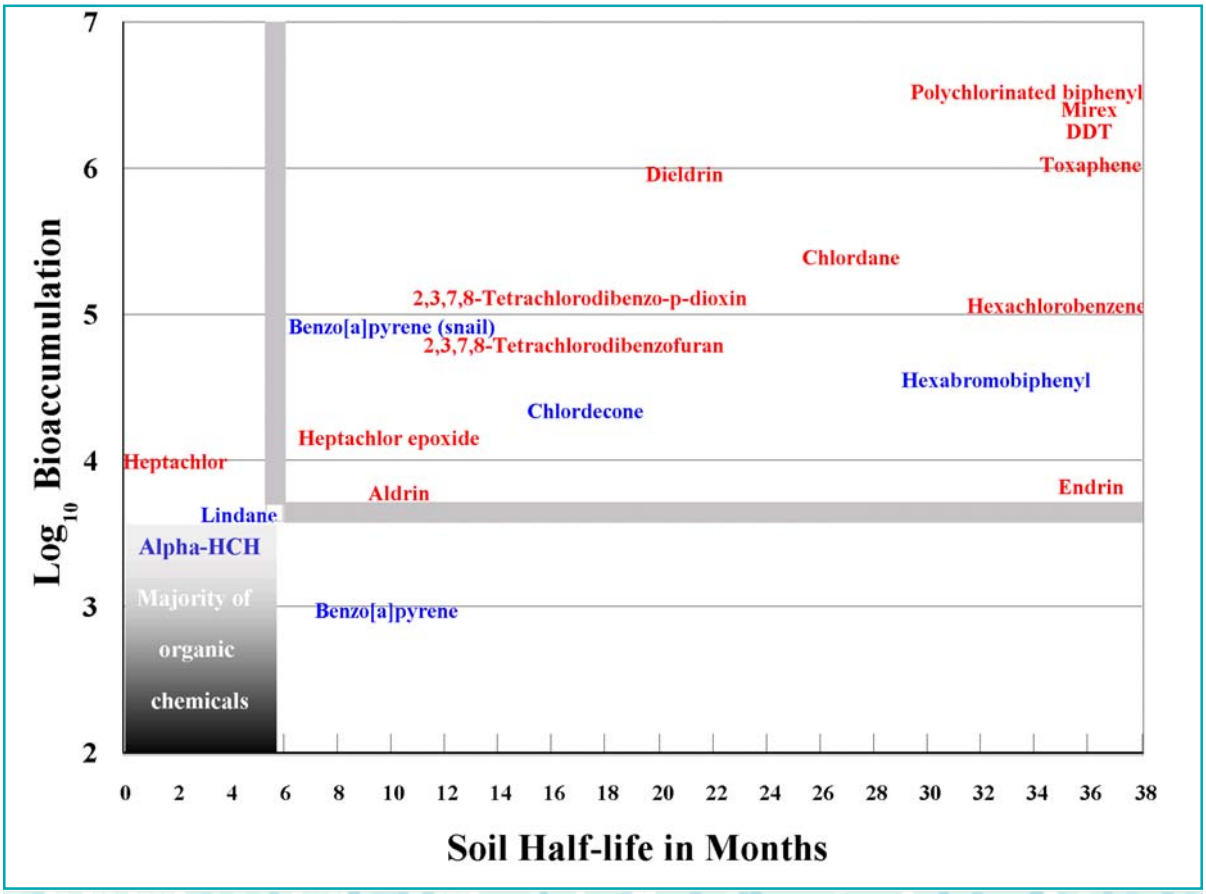

Figure 9-2. Bioaccumulation v. half-life in soil. Gray shaded bars represent POPs screening criteria. The bioaccumulation factor is normalized to 5% lipid; the persistence times are truncated at three years. UNEP POPs are listed in red; additional LRTAP POPs in blue.

Source: Rodan et al., 1999.

lation generally relates to water insolubility and the propensity of these substances to accumulate in lipid media—animal fat. An indirect measure of this propensity to accumulate is the octanol-water partition coefficient (Kow), which measures the ratio of the equilibrium concentration in an organic medium (n-octanol) compared with an adjoining water medium. The Stockholm Convention screening criterion for bioaccumulation is centered on a bioaccumulation/bioconcentration value of greater than 5,000 in fish (Table 9-1), supplemented by additional evidence of bioaccumulation potential sufficient to justify its consideration.

Figure 9-3 graphs the logarithm (base 10) of the bioaccumulation values in fish for a number of organic chemicals (the 12 POPs in red) compared with their corresponding $\log_{10}$ octanol-water partition coefficients (log Kow; data reported in Rodan et al., 1999). A log scale is necessary for this graph because of the extreme Kow and bioaccumulation values for the POPs. A base 10 logarithm value of 5 equals 10^5, or 100,000; 10^6 = 1,000,000; and $10^{3.7}$ = 5,000 (which is the BAF/BCF screening value in the Stockholm Convention). If Figure 9-3 had been graphed on a linear scale with the BCF value of 1 set at 1 millimeter height, then the page

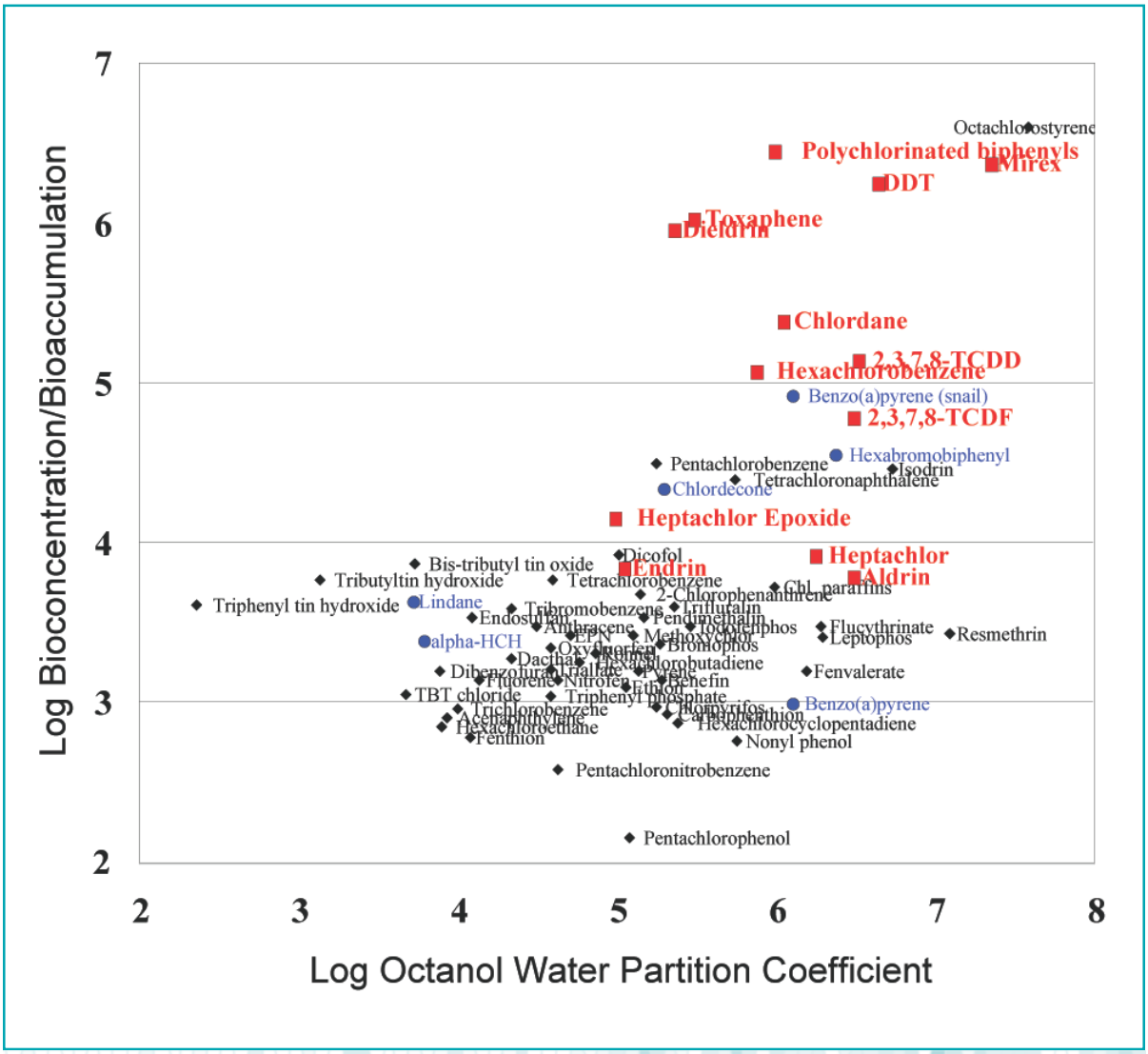

Figure 9-3. Bioaccumulation in fish v. $\log_{10}$ octanol-water partition coefficient (Kow). Bioaccumulation factor is normalized to 5% lipid. UNEP POPs are graphed in red (square marker), additional LRTAP POPs in blue (circle marker).

Source: Rodan et al., 1999.

would need to be more than 3 kilometers (2 miles) long to fit the PCB bioaccumulation value of >3,000,000.

In addition to confirming the extreme BAF/BCF values for the POPs, Figure 9-3 also demonstrates a number of technical issues pertinent to bioaccumulation and which factor into the appraisal of screening values:

- There is an approximately linear relationship between the octanol-water partition coefficient and bioaccumulation for the majority of the organic chemicals (see Isnard and Lambert, 1988), albeit not for the organometals. This relationship provides a mathematical link between the screening values of logKow >5 and BCF/BAF >5,000.
- The slope of this graph increases after logKow values of ~5, demonstrating biomagnification in the food chain.
- The metabolism of some organic chemicals in more phylogenetically developed species can limit bioaccumulation, in this case demonstrated by differences in benzo[a]pyrene bioaccumulation between snails and fish.
- The majority of organic chemicals (bottom left of graph) do not possess the extremes of bioaccumulation exhibited by POPs.

Recall that the combination of data on two of the four POPs screening values in Figure 9-2 (bioaccumulation and soil persistence) commences a process of separating chemicals that may pose transboundary or global problems from the majority of organic chemicals. The inclusion of data on the remaining two screening factors of toxicity and long-range environmental transport further informs this separation.

Long-Range Environmental Transport

Fundamental to the need for a global POPs convention is the transboundary nature of the problem, on a scale greater than can be resolved through bilateral or even regional agreements. With this understanding, the long-range environmental transport criterion can be informed by either (1) measured or monitored levels distant from sources of release to the environment or (2) modeling of a substance's environmental fate properties, compared with known POPs substances.

Measured levels of potential concern in remote locations distant from sources of release can unambiguously satisfy the long-range transport criterion. Indeed, the long-range transport properties of many of the "dirty dozen" were originally highlighted by their being found at significant levels in remote locations, such as the Arctic and mid-Pacific. It would be inappropriate, however, to await elevated levels in remote locations before anticipatory action is taken: thus, the additional criterion options of monitoring levels in transport media and modeling based on chemical properties.

For transport monitoring and modeling, it has been demonstrated that the substance's persistence in the transport medium (air or water) strongly governs the distance traveled (Rodan et al., 1999; Klecka et al., 2000). This analysis of persistence in a transport medium differs from the theoretical soil persistence analysis presented above, because it incorporates a finite time limitation, namely the time necessary for a substance to move from source to site of deposition. The key question is how long a substance needs to remain airborne or waterborne to constitute a problem warranting international action. This time period is directly related to the geographic scale of interest. For a global negotiation, that scale can be considered the transoceanic or transcontinental distance. Assuming a scale of ca. 4,000 kilometers (2,500 miles), it can be shown that approximately 7 to 10 days would be required for atmospheric transport from source to site of deposition. This assumption is based on average air movement rates across the United States of 7 m/sec (Draxler et al., 1991) and computer modeling of air movement on a global scale (Mason and Bohlin, 1995). As demonstrated in Figure 9-4, for a chemical with a 2-day degradation half-life in air, the amount remaining after this approximate 8-day period is

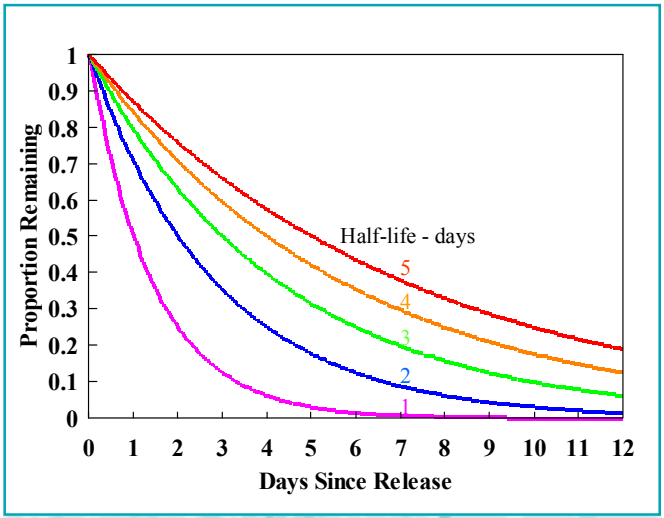

Figure 9-4. Proportion of a POPs release remaining for various atmospheric half-lives.

1/16 (2^{-4}) of the original release. Lower atmospheric half-lives lead to considerably smaller residual amounts after 8 days, due to the shape of the mathematical relationship between the proportion of chemical remaining at time t (m_t/m_0) and the half-life ($\tau_{1/2}$) [$m_t/m_0 = exp(-\ln(2)t/\tau_{1/2})$]. This is consistent with the use of a 2-day half-life screening guidance for degradation in air.

A similar analysis can be performed for water transport, although it will be more complex because water movement rates are considerably slower and much more variable. Figure 9-5 provides oceanic surface current estimates in the Pacific and Atlantic Oceans based on drifter analysis (*www.aoml.noaa.gov/phod/dac/dacdata.html*). The scale for the arrows of 25 cm/sec is equivalent to 0.9 km/hr or 0.56 mph. As discussed in Chapter 7, rapid oceanic currents are evident for the Gulf Stream (U.S. East Coast) and Kuroshio current (east Asia). Average oceanic surface water speeds are estimated at around 10 cm/sec (0.36 km/hr) (Klecka et al., 2000). Certain oceanic currents can rapidly move large masses of water long distances. For instance, the Gulf Stream off the U.S. East Coast has a speed of around 1 knot (1.7 km/hr) off Cape Hatteras, up to 6 knots (10 km/hr) maximum, and transports as much as 100 million cubic meters of water. Rivers generally move at 1–3 km/hr in nonflood situations.

To account for this variability in oceanic current speeds, Figure 9-6 presents a modified version of the theoretical analysis presented for air in Figure 9-4. Figure 9-6 again sets the necessary transport distance at 4,000 kilometers (2,500 miles), but this time plots oceanic current speed on the *x*-axis versus the percentage remaining at 4,000 kilometers on the *y*-axis. Different half-lives in water are represented by the different lines (color-coded) on the graph. Examples of representative oceanic current speeds are marked on the table (from Klecka et al., 2000; Leonard et al., 1997; Brown, 1991; Ross, 1978, 1982). Point X provides an example of how to use Figure 9-6, representing a substance with a

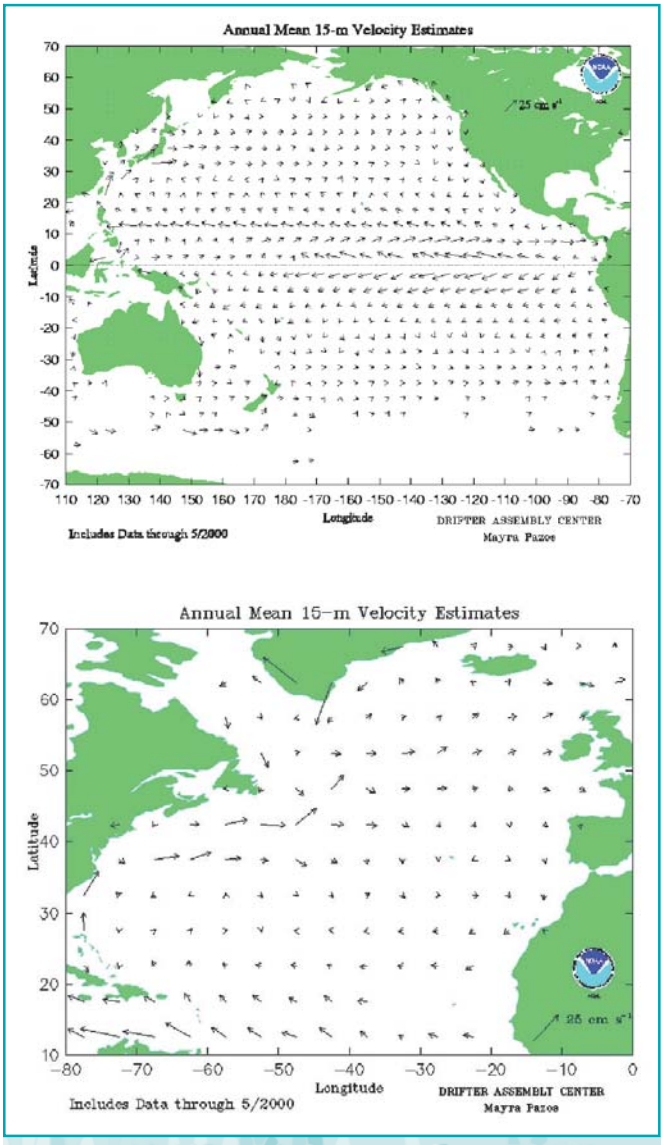

Figure 9-5. Oceanic surface current speeds (NOAA).

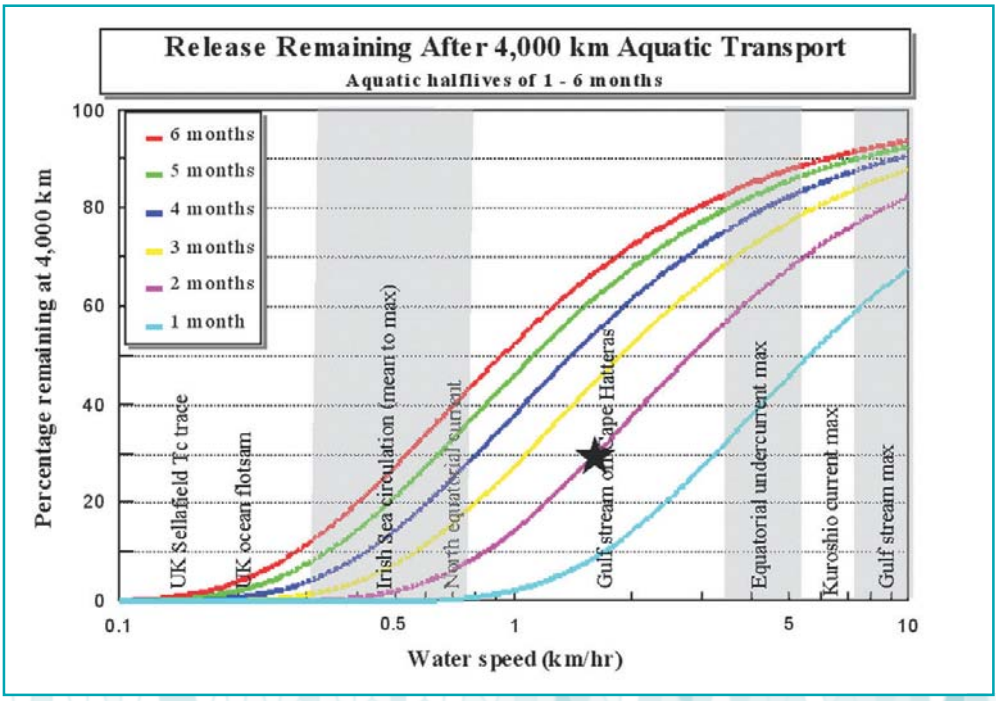

Figure 9-6. Water transport model.

half-life in water of 2 months, caught in the Gulf Stream. After 2,500 miles transport at ~1 knot, 30% of the original release would remain. Further informing the evaluation of a pertinent half-life criterion in water is the approximate 1/40 ratio for wind speed to oceanic surface current (UK Ministry of Defense, 1973). These analyses are consistent with the Stockholm Convention half-life criterion in water of 2 months (under Annex D, 1(a)), but are clearly highly dependent on which waterbody and current are under consideration.

Beyond these first-order transport comparisons, a number of multimedia environmental fate and transport models have undergone recent development (Klecka et al., 2000). It is anticipated that these or similar models may be used to satisfy the Stockholm Convention long-range environmental transport modeling requirements. Multimedia models are necessary because POPs distribute to, and move between, air, soil, water, and sediment media. To adequately understand the fate and transport of POPs in the environment, it is necessary to know how they will disperse among these media, all of which exhibit different degradation rates and abilities to act as storage reservoirs or transport media.

An example of such a multimedia model related to the 12 priority POPs is provided by Scheringer et al. (2000), and replicated here in Figure 9-7. In this graph, the *x*-axis represents total persistence in the environment; the *y*-axis shows spatial range normalized to the Earth's circumference. Total persistence is the weighted average of residence times in all the media, a method of merging persistence values in different media into a single figure. The spatial range is the distance a chemical could theoretically travel in the model before reaching a predetermined cut-off level. From this graph, it is evident that distance traveled is not linearly related to total environmental persistence. This lack of linearity is due to differences in the strengths of binding to immobile particles in soil or sediment. This is combined with the fundamental link between transport distance and the half-life in the transport medium, which sets a maximum possible distance function irrespective of degradation rates in soil or sediment. A similar modeling analysis by Rodan et al. (1999) confirmed the potential for the 12 priority POPs to travel long distances. It is important to note that these models only compare the relative distance traveled by chemicals. This is because the termination decision used for model concentration and

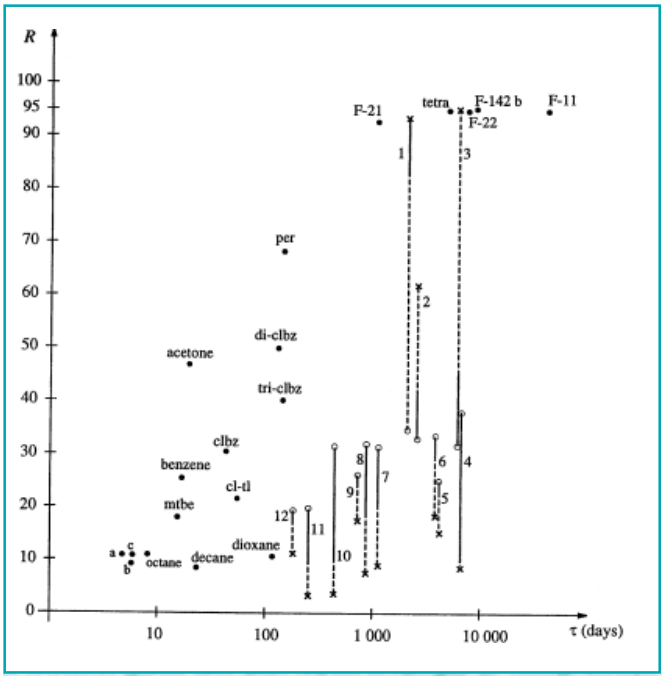

Figure 9-7. Spatial range R *(normalized to the earth's circumference) and persistence* τ *of various chemicals based on results of the global model proposed by Scheringer (1996). 1: hexachlorobenzene, 2: hexachlorobiphenyl, 3: mirex, 4: endrin, 5: DDT, 6: toxaphene, 7: chlordane, 8: dieldrin, 9: TCDD, 10: aldrin, 11: heptachlor, 12: lindane. See Scheringer et al. (2000) for a more detailed interpretation of this plot.*
Source: With permission, Wiley-VCH, ACS.

distance is arbitrary yet consistent; i.e., when is the environmental concentration low enough to conclude that the chemical is gone and the distance calculation should cease?

Adverse Effects/Toxicity

Toxicity is perhaps the most difficult criterion to quantify in the screening process because it inherently encompasses considerations of dose, the complexity of which is best dealt with at the risk profile stage. Merely finding a chemical at extremely small levels with modern laboratory equipment cannot be considered a *prima facie* case for toxic risks. This caution must be balanced against the technical limitations of toxicology and ecotoxicology to detect and quantitate subtle adverse effects and the need to not await the demonstration of overt toxicity in remote locations before action is taken—a precautionary approach. Guidance on how to resolve this dilemma, and achieve a balance between providing information at the screening stage versus the more detailed risk profile, is best found by analyzing the text of the Stockholm Convention (Annex D.1.(e) & D.2):

> D. 1. … (e) Adverse effects:
>
> (i) Evidence of adverse effects to human health or to the environment that justifies consideration of the chemical within the scope of this Convention; or
>
> (ii) Toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.
>
> 2. The proposing Party shall provide a statement of the reasons for concern including, where possible, a comparison of toxicity or ecotoxicity data with detected or predicted levels of a chemical resulting or anticipated from its long-range environmental transport….

Here, negotiators anticipated a hierarchy of toxicity evidence, with priority to be given at the screening stage to actual "evidence of adverse effects," justifying consideration in this global Convention. The adverse effects screening criterion can also be fulfilled with "data that indicate the potential for damage," again emphasizing the need for data—not speculation—but not at the expense of awaiting irreversible harm. The criterion category is then followed by a statement of concern (Annex D.2) at the screening stage, in which the proponent Party is to include, where possible, a comparison of data with detected or predicted levels. These efforts to provide quantitative information on adverse effects—measured or predicted—are to be further elaborated upon and evaluated by the POPRC in the risk profile stage (below).

A wide variety of human health and ecotoxicity data are anticipated under this criterion. For human health, numerous national and international expert scientific bodies assess data to determine if a hazard exists to humans. Many of these bodies develop standards considered protective of health. The EPA reference dose, for example, is an estimate of a daily exposure to

the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime (*www.epa.gov/iris*). The U.S. Agency for Toxic Substances and Disease Registry (ATSDR) develops Minimal Risk Levels (MRLs) for many environmental contaminants (*www.atsdr.cdc.gov*). Internationally, the WHO and International Agency for Research on Cancer (IARC) are central to developing health standards. Reliance on all of these standards should, however, be tempered by an understanding of how they are derived, the use of uncertainty factors and public health protective assumptions that reduce numerical values below the actual research data findings, and details and differences in the specific wording of the standards (e.g., tolerable versus minimal risk versus safe). Ultimately, an expert appraisal, including analysis of the primary published literature, should be undertaken to fully inform deliberations.

For ecotoxicity, a similar process of problem formulation is undertaken to identify stressors and the animals and plants at risk. Quantitative data for chemical stressors can come in the form of dose estimates related to toxic endpoints or as tissue levels associated with adverse effects. Ideally, laboratory studies of toxic doses will include the tissue levels associated with these effects, but this is not always the case. The complexity of ecotoxicity data is accentuated by species differences, interaction with the species' ambient environment, multiple simultaneous stressors, and difficulties in determining low levels of toxicity, especially in field situations (Beyer et al., 1996). Expert judgment is again essential in exercising appropriate caution in determining the potential for adverse effects.

The Risk Profile

The risk profile is central to the ultimate determination of whether a substance is a POP warranting action under the Stockholm Convention. The emphasis on a detailed scientific review and expert judgment is paramount in recommendations by scientific bodies (Klecka et al., 2000; CEG, 1998). The complexity of the detailed risk profile can appear, however, somewhat contrary to a more straightforward application of numerical screening criteria, with its expeditious, yet possibly inaccurate, clarity. With this in mind, it merits emphasis that passing the screening phase of the addition of chemicals process does not necessarily imply that a chemical will be listed as a POP. This determination can only be made after a critical review and analysis of all the pertinent data. As stated in Annex E of the Stockholm Convention:

> The purpose of the review is to evaluate whether the chemical is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and/or environmental effects, such that global action is warranted.

The information requirements for the risk profile include elaboration and review of the Annex D (screening criteria) information, supplemented by Annex E information on sources, hazards, environmental fate and models, measured levels, and national and international assessments and status. The profile will be prepared by the POPRC, with data input from Parties and observers (e.g., industry, nongovernmental, and intergovernmental organizations). It is recognized that more detailed initial submission packages by proponent Parties covering these points will expedite the process.

Risk Management Options

After a determination is made by the POPRC that a substance is likely to be a chemical warranting global action, information is then obtained on Annex F management options and socioeconomic considerations. A clear separation is considered important between the risk profile and management stages so that potential implementation considerations do not affect the scientific evaluation of whether a substance warrants consideration under the Stockholm Convention. After such a determination is made, however, Annex F explicitly requires consideration of technical and socioeconomic factors in determining the best course(s) of action in dealing with a chemical. To facilitate such decisions by the

COP, the report on management options by the POPRC will review the efficacy and efficiency of possible control measures, alternative products and processes, impacts on society of implementing possible control measures, waste and disposal implications, and additional factors influencing the ability of Parties to implement obligations.

The Decision

The ultimate decision to list a chemical in the annexes and on appropriate control strategies rests with the Conference of the Parties. This decision must give due consideration to, but is not bound by, the recommendations of the POPRC in the risk profile and management report. In doing so, the Stockholm Covention seeks to maximize the input of scientific information from multiple sources (intergovernmental, government, industry, nongovernment organizations) into a transparent decision making process. Consistent with standards maintained during the negotiation of the Stockholm Convention, decisions by the COP are to be reached by consensus. Absent such consensus, a 3/4 majority vote is necessary to add a chemical. Changes to the information requirements and criteria in Annexes D (screening), E (risk profile), and F (risk management/socioeconomics) can be made only by consensus, to maintain a consistent standard for evaluating proposals to add chemicals.

The Future

During the May 2001 signing ceremony for the POPs Convention in Stockholm, Sweden, agreement was reached to commence work on defining the structure and process for the POPRC. Proposal dossiers for the addition of chemicals may be pursued on a national basis in anticipation of entry into force of the Convention and commencement of POPRC review functions, but chemicals cannot be added in the interim. The particular approach used by the POPRC and COP to review and consider the first chemicals for addition following entry into force will yield valuable information on how the process will be implemented in the future.

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Appendix A Transport Pathways

Figures showing transport pathways traversed by air masses en route to 11 sites within the United States are provided in this Appendix. The figures and the calculations on which these figures are based were produced by the Center for Air Pollution Impact and Trends Analysis (CAPITA) at Washington University in St. Louis, MO, and can be found at *http://capita.wustl.edu*.

The figures are based on the calculation of several thousand trajectories calculated backwards for 10 days at 2-hour intervals from each of the receptor sites for the year 1999. The different color shading in the figures refers to the probability that trajectories passed over a given area before arriving at the receptor site. The boundaries of each shaded region represent lines of constant probability. The areas shaded in red have the highest probability of being traversed by trajectories, whereas those shaded in light blue have lower probability. To obtain a truly representative picture of the average transport pathways, in the same way that climatological statistics are obtained, these calculations would need to be repeated for several years. Further details regarding the calculations can be found in Husar and Schichtel (2001).

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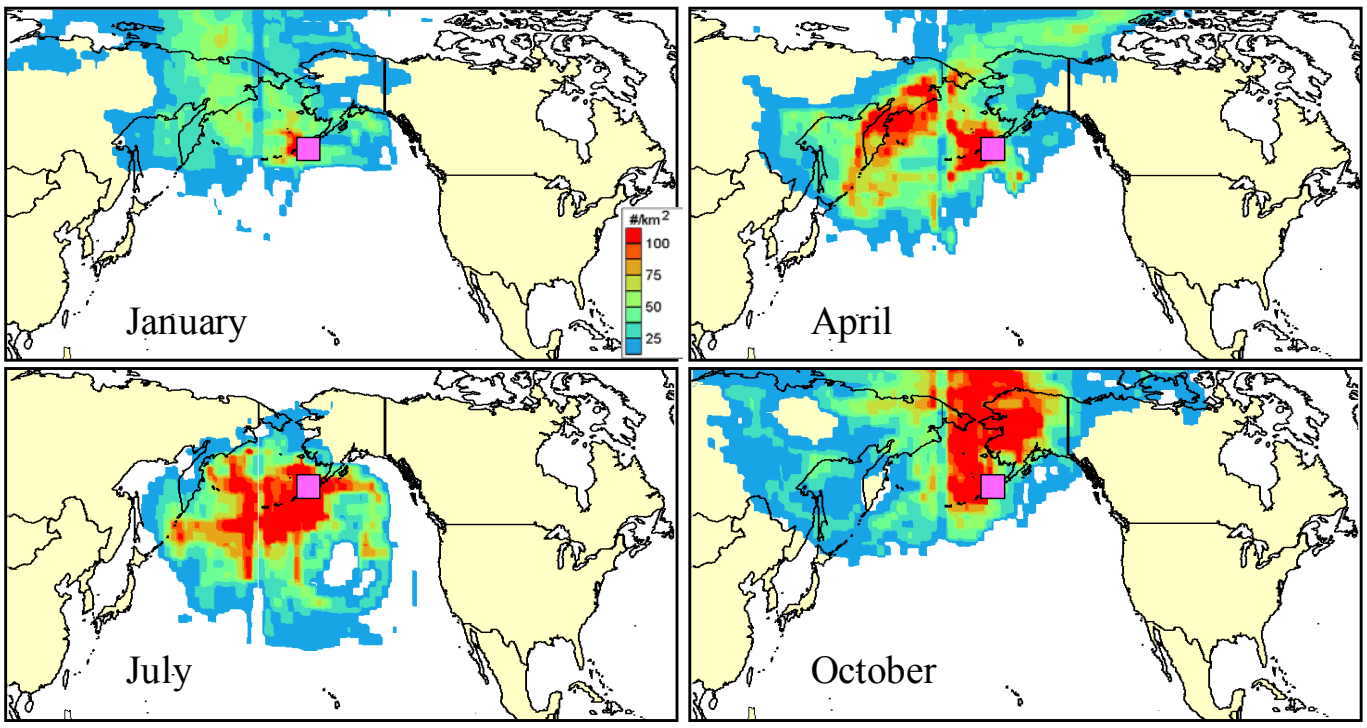

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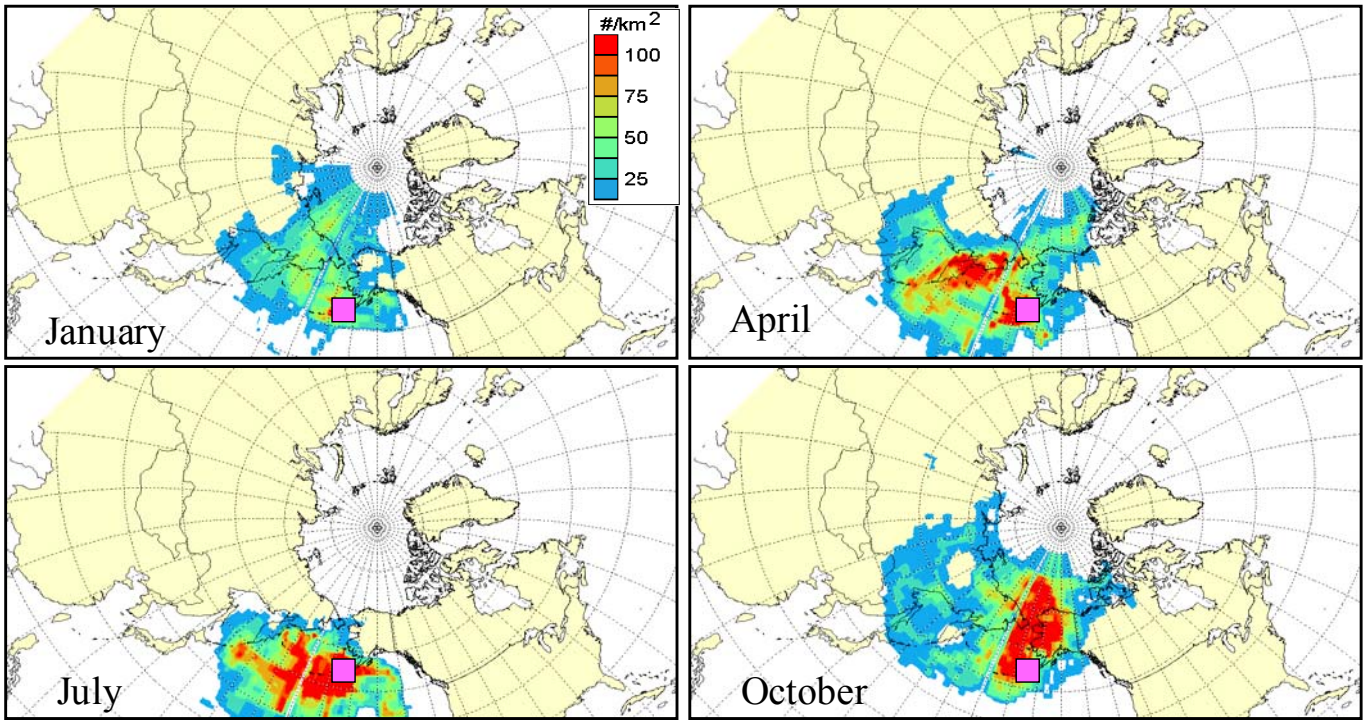

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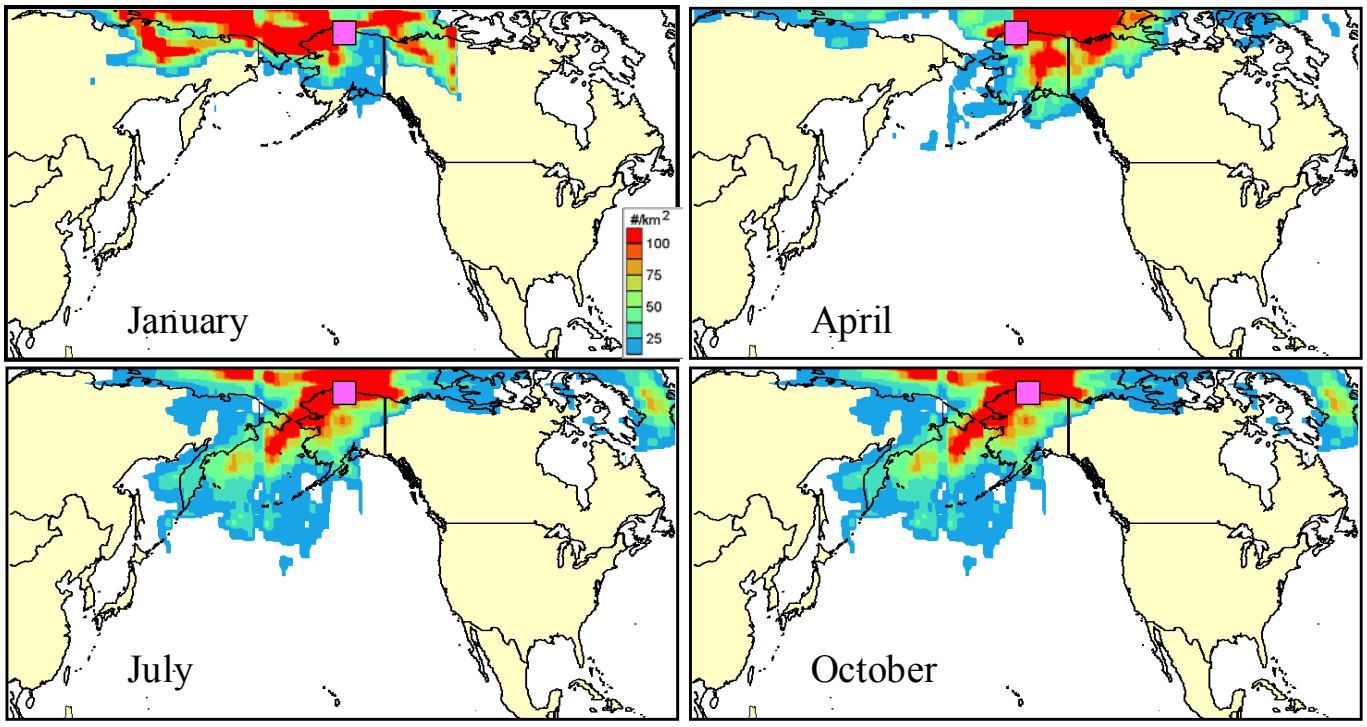

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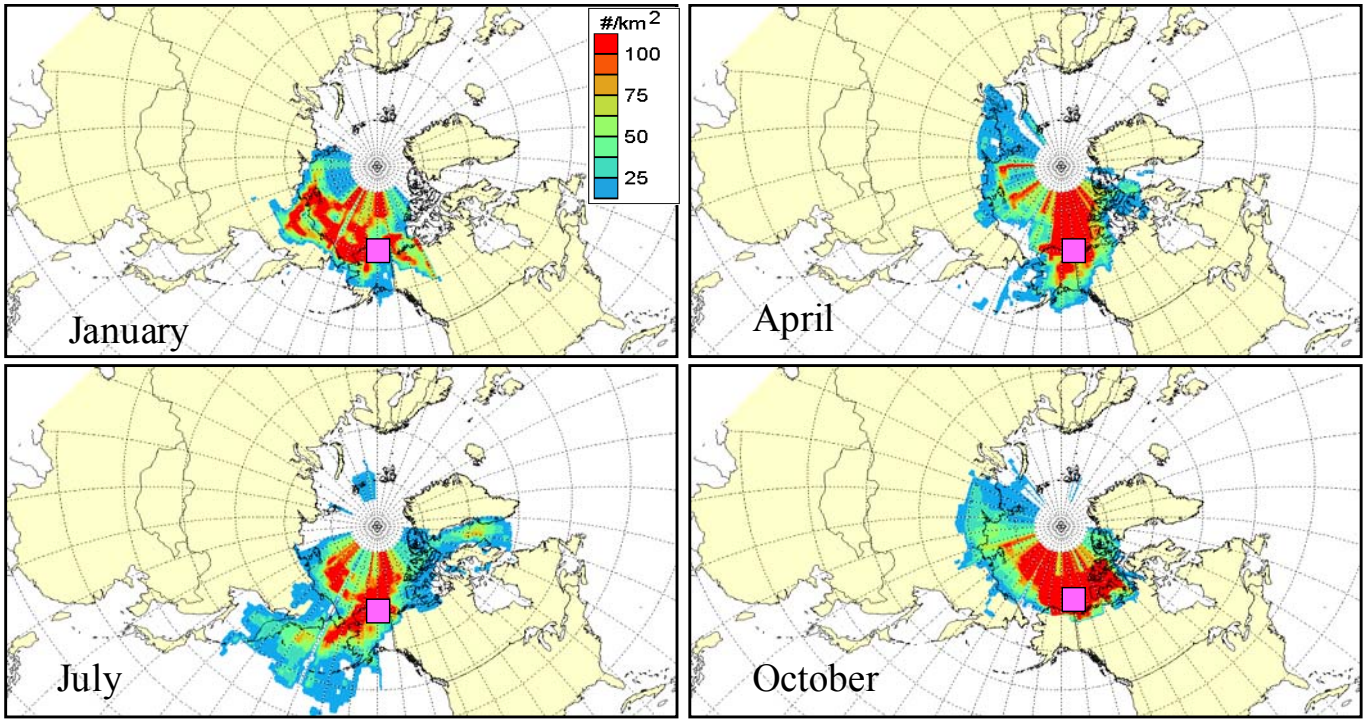
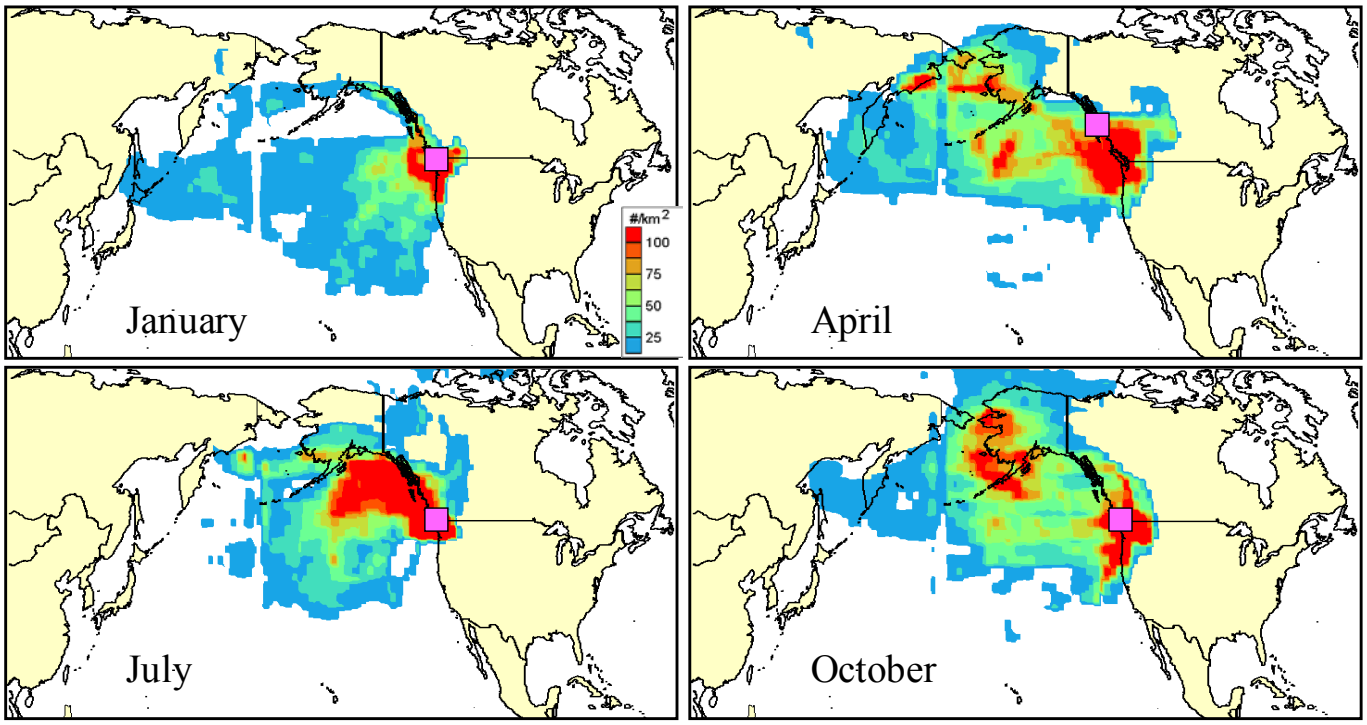
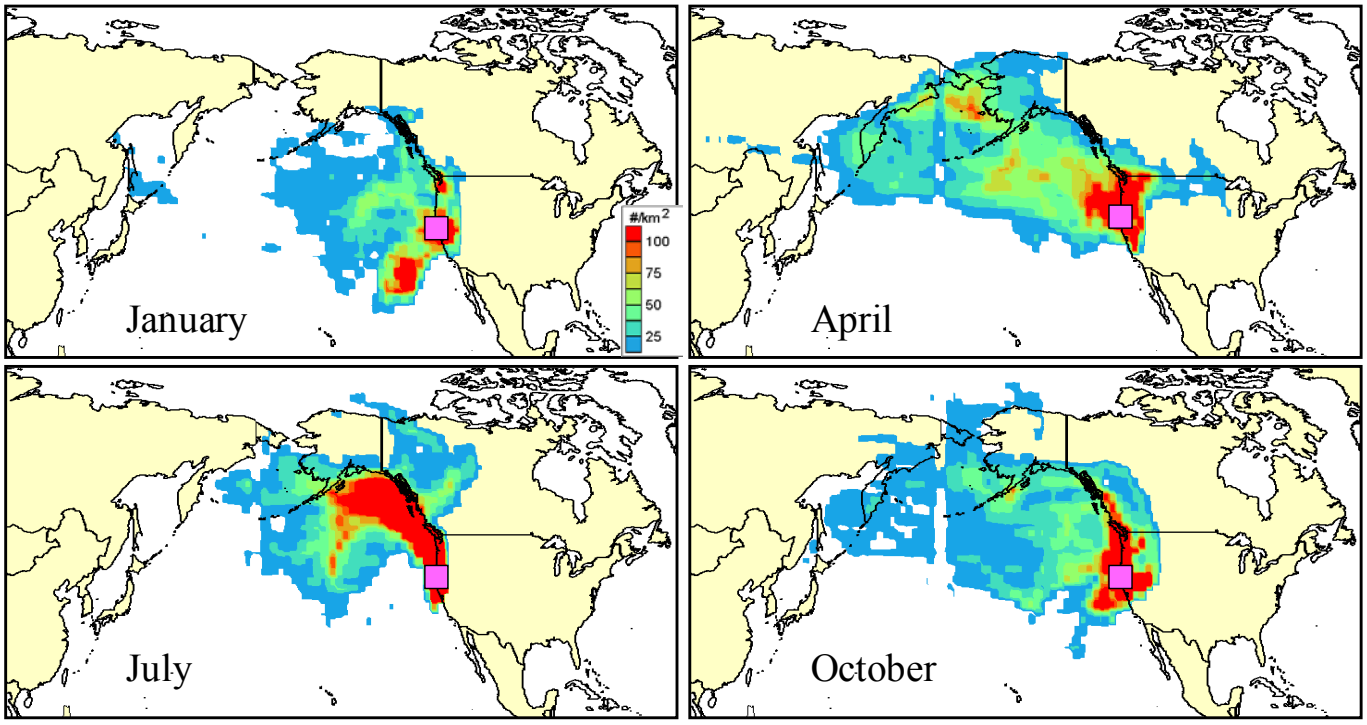


5. Seattle, WA



6. San Francisco, CA



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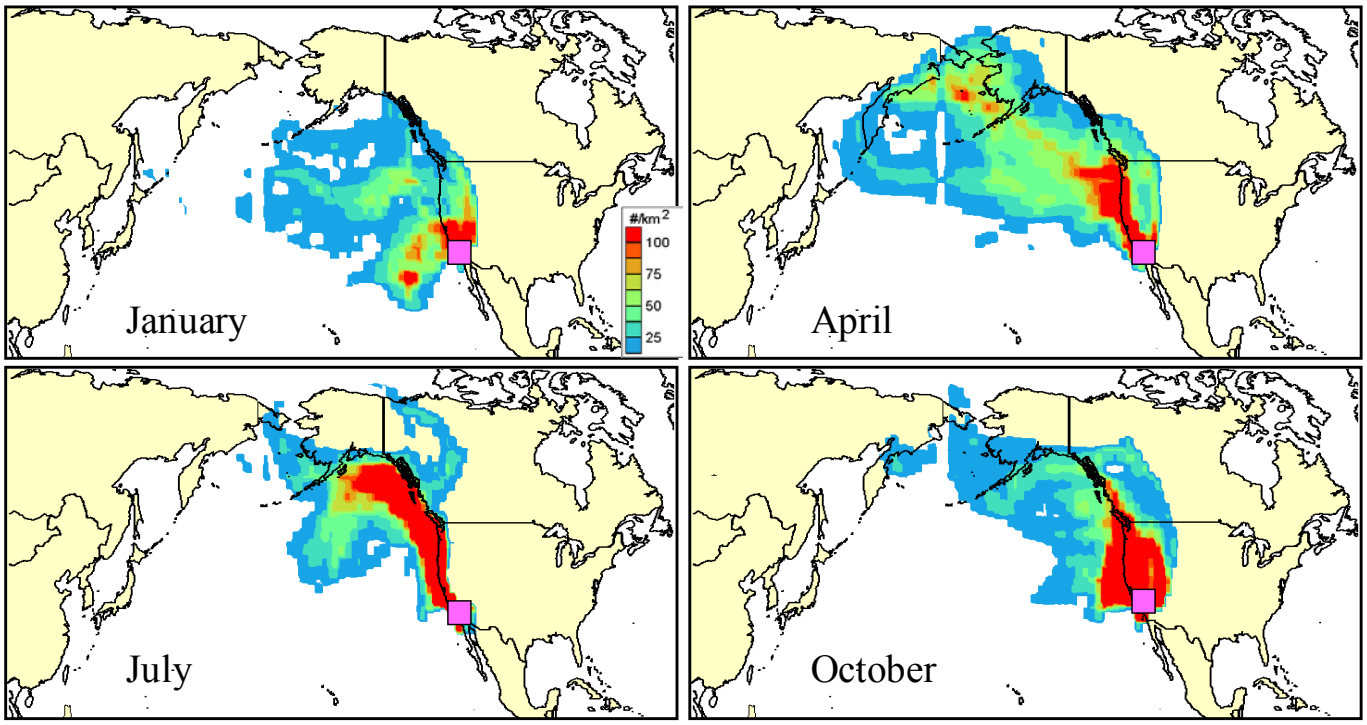
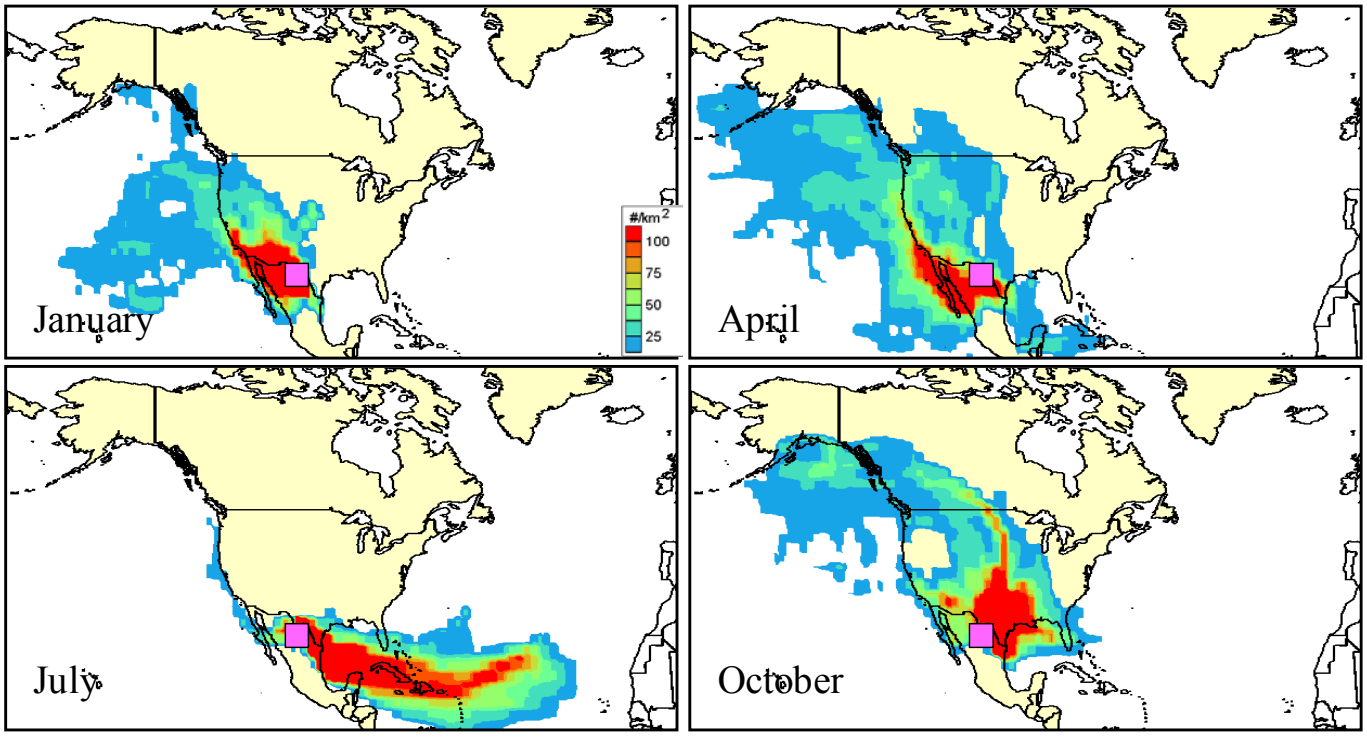


10. Big Bend, TX



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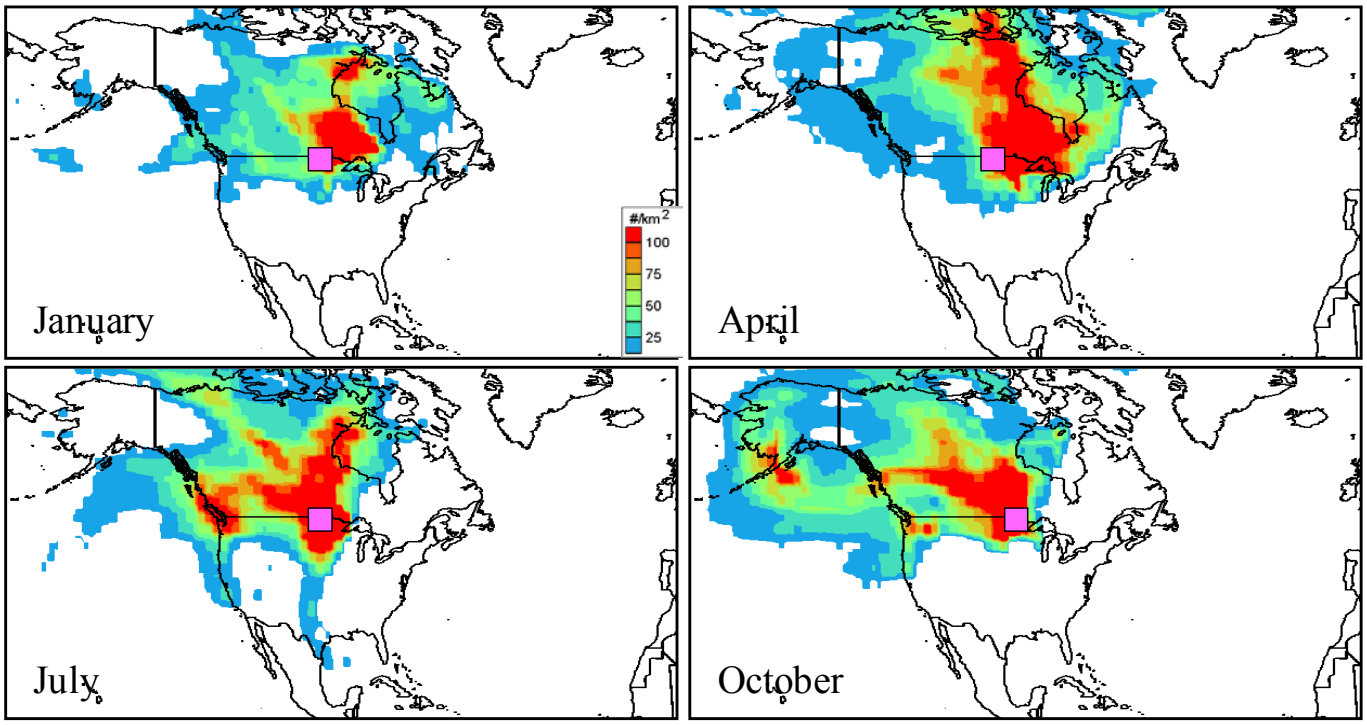
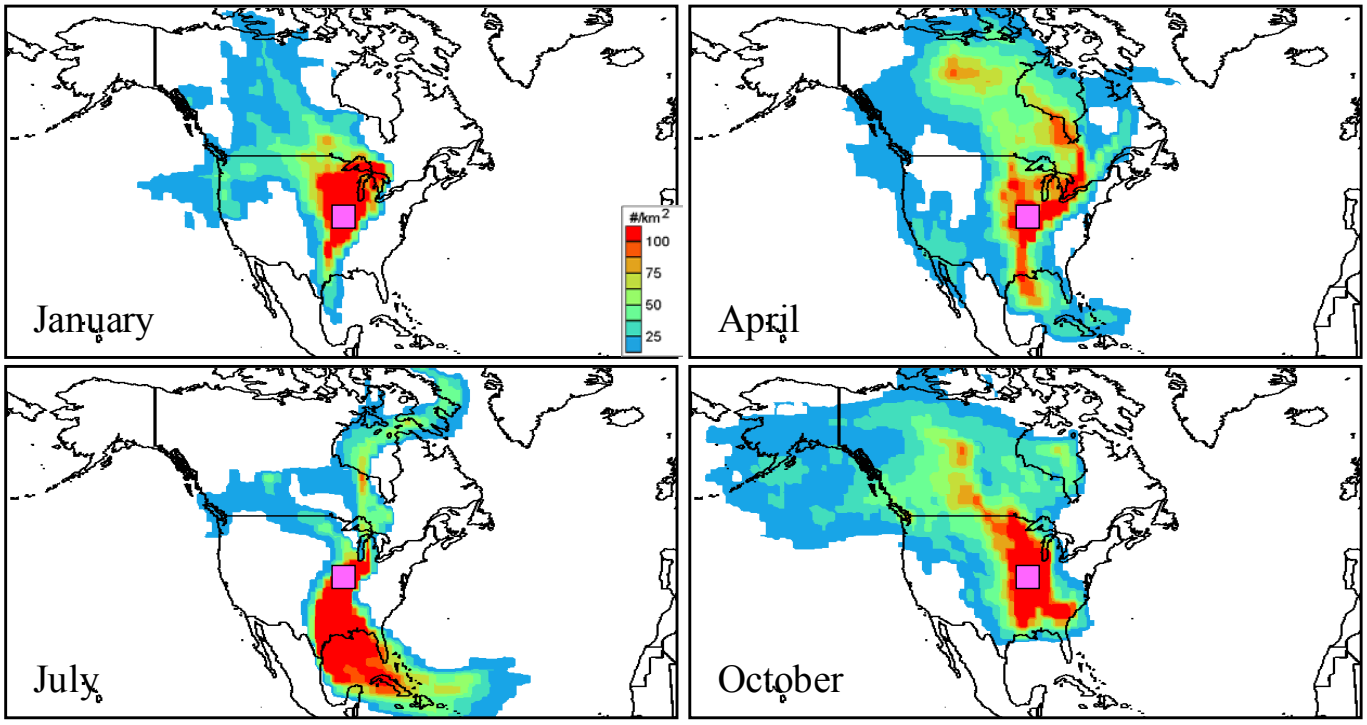
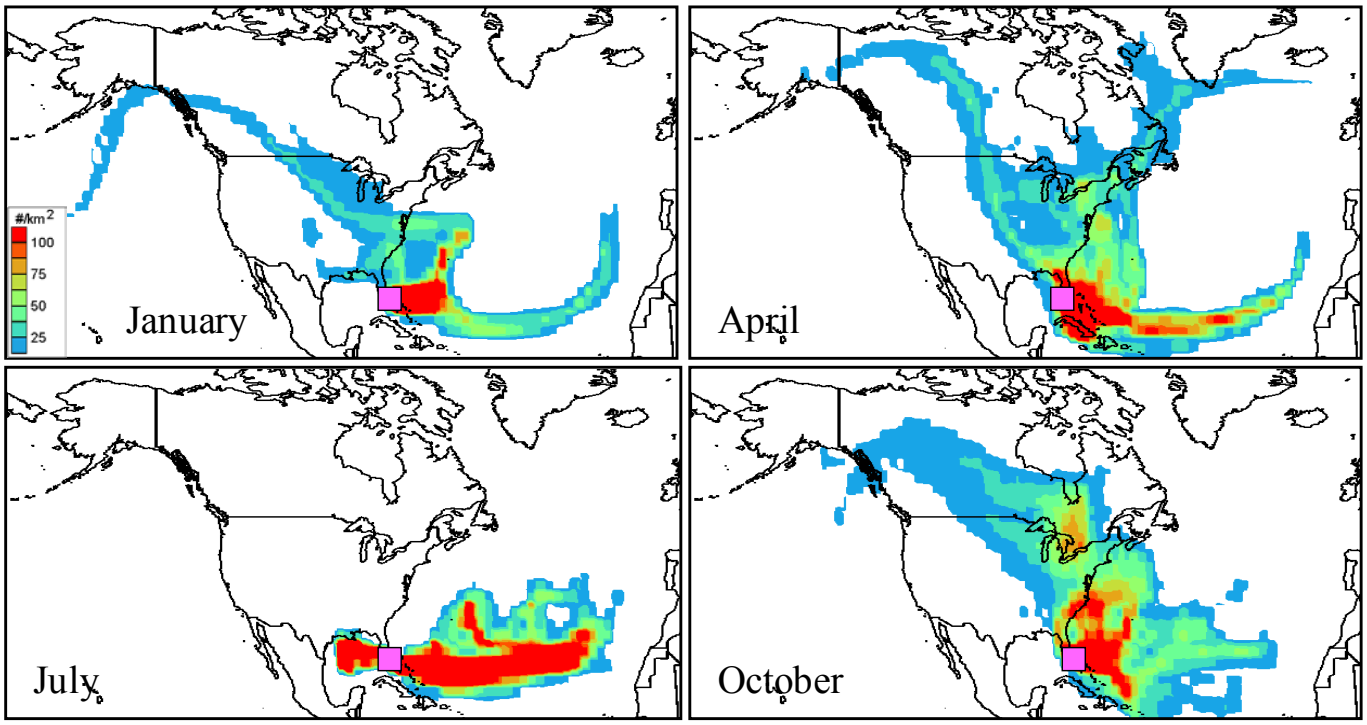


12. St. Louis, MO



13. Everglades, FL



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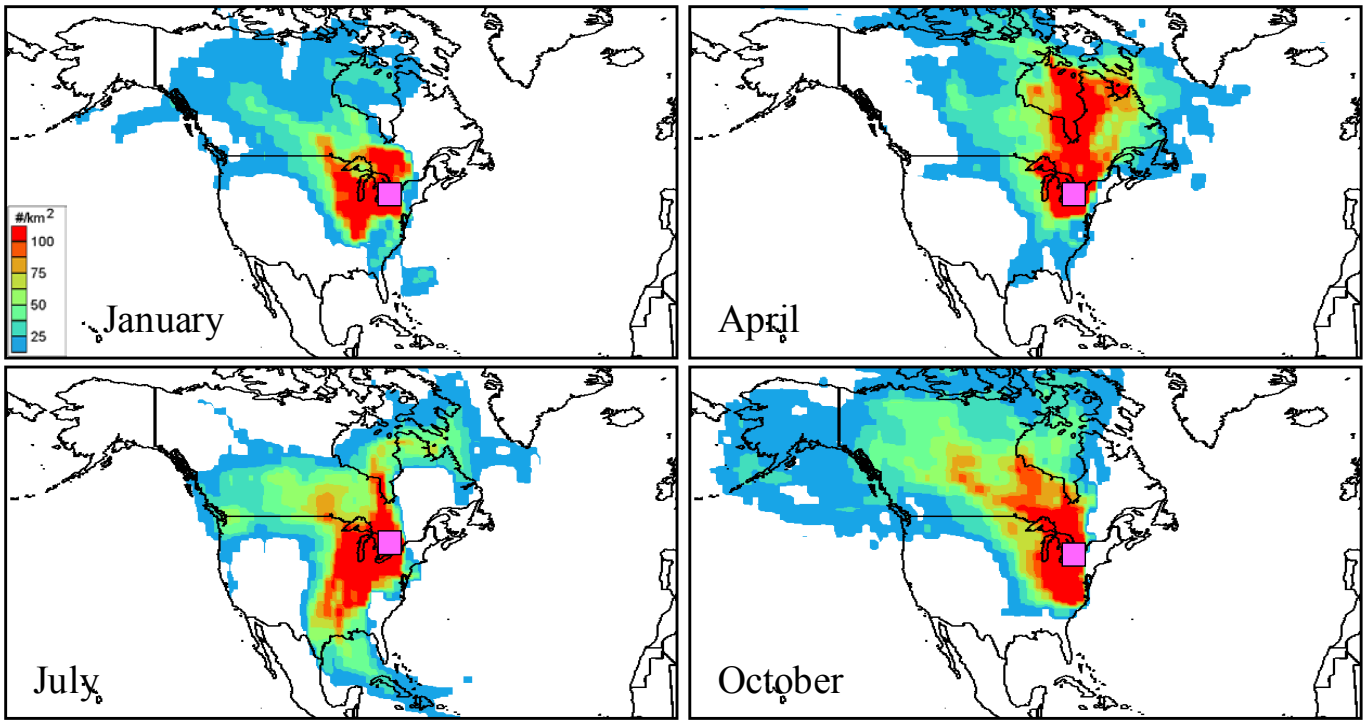
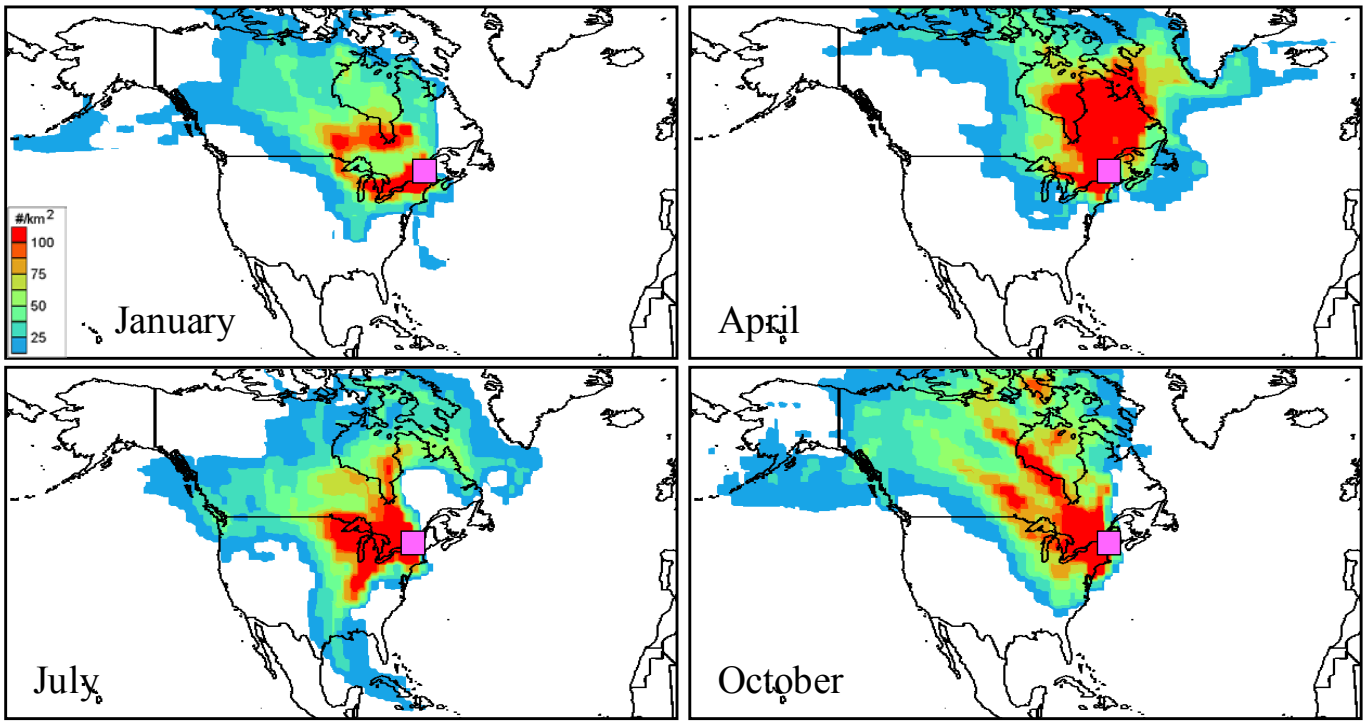


15. Burlington, VT



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