Persistent Organic Pollutants ("POPs")

DDT, PCBs, dioxins and similar toxic and persistent organic pollutants ("POPs") have been spread throughout the world. They tend to accumulate in living organisms and can reach harmful levels, particularly in predators and other species at, or close to, the top of food chains.

What substances become environmental poisons?

Man has put thousands of organic compounds to use this century, often in large quantities. In the 1960s it became increasingly obvious that certain chemicals had found their way into the natural environment in large quantities. Some of them came to be known as environmental poisons – animals exposed to them often displayed symptoms of illness or injury.

Strictly speaking, all toxins entering the environment can be regarded as environmental poisons. Certain pollutants can, acting over long periods, harm living organisms even in low concentrations. This means that pollutants that are *stable* and thus *persistent* have a great ability to act as environmental poisons. Their stability means not only that their effects are long-lasting, but also that they are dispersed over large areas before being broken down.

The risk of a stable compound causing biological effects increases if it is capable of *bioaccumulation*, i.e. of being stored in living tissue. Stable organic compounds that are *fat-soluble* are usually able to bioaccumulate. Fat-soluble pollutants can accumulate in fatty tissues of living organisms in concentrations many times higher than in the surrounding environment.

Predators may accumulate certain persistent pollutants in even higher concentrations than their prey, a phenomenon known as *biomagnification*. The very highest concentrations of toxins in living organisms are usually found in mammals and birds that feed on fish or other aquatic animals. Biomagnification also occurs in the terrestrial fauna, although concentrations there are consistently lower.

Many *aromatic hydrocarbons* are both fat-soluble and persistent. If these compounds become *halogenated* (i.e. if their hydrogen atoms are replaced by chlorine, bromine or other halogens), their stability and their solubility in fat both tend to increase yet further. In some cases toxicity also increases. The majority of well-known persistent organic pollutants thus belong to the category halogenated aromatic hydrocarbons.

Three main categories of substance

Some of the "classic" environmental poisons – such as DDT, toxaphene, chlordane and hexachlorocyclohexane (HCH) – are insecticides. These have been deliberately dispersed over agricultural land. Their use has gradually been phased out in Sweden

and other industrial nations, but some of these agents continue to be used elsewhere (in the tropics, for example). Substances of this kind remain present in the Swedish environment, including substances never used in this country.

The pesticides used today in Swedish agriculture are all degradable to varying degrees. However, locally at least, these agents too may be unintentionally dispersed beyond the fields. Low but not insignificant concentrations of pesticides and pesticide residues sometimes occur in streams draining agricultural areas and also sometimes in the groundwater.

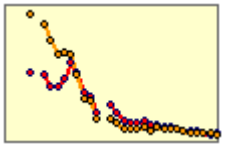
Industrial chemicals never intended for dispersal outdoors can also leak into the environment. PCBs (polychlorinated biphenyls) are the best-known example; other compounds of this kind are polychlorinated naphthalenes (PCNs), chloroparaffins and brominated flame retardants. Some stable industrial chemicals are no longer manufactured. The use of PCBs has been gradually banned completely in Sweden and many other countries. It has been found to be more difficult to replace some other chemicals with less hazardous substitutes. The use of brominated flame retardants continues almost unabated for this reason.

A third category of persistent organic pollutants occur mainly as *by-products* of various manufacturing or combustive processes. These include hexachlorobenzene (HCB), polycyclic aromatic hydrocarbons (PAHs) and dioxins. To a limited extent many of these compounds can also be formed naturally, but anthropogenic emissions have now declined substantially thanks to a number of steps that have been taken.

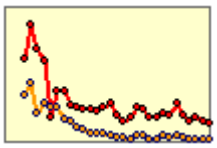
Occurrence and dispersal in the environment

Most persistent organic pollutants may be dispersed over great distances in the air. Concentrations in the environment are normally highest closest to the source, although some volatile compounds such as HCB and HCH are now fairly evenly dispersed throughout the globe. Some of them have even reached the polar regions in large quantities. However, pollutant emissions have always been far greater in southern Sweden and the surrounding area than further north. Therefore, concentrations of organic pollutants generally fall with increasing latitude in Sweden.

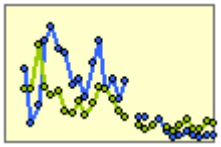
Dispersal of organic pollutants is less effective in water than in the atmosphere. Owing to their low solubility in water, persistent organic pollutants mainly occur adsorbed to particles, which subsequently settle on the bottom. In the Baltic Sea, which is almost cut off from other seas and oceans, organic pollutants have accumulated in higher concentrations than in most other marine areas. Organic pollutants can seep back into the water from contaminated sea and lake beds many years after emissions themselves have ceased. In time, however, the contaminated layer of sediment will become buried under new sediment.



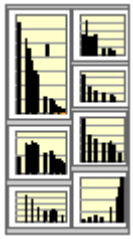
DDT and PCBs in guillemot



DDT and PCBs in pike



HCB and HCHs in pike



Pollutants in breast milk

Concentrations of several well-known organic pollutants have fallen markedly in Sweden's natural environment since the 1970s. The same is true of samples taken from the Swedish population. A similar trend has been observed in other parts of the world. However, just a decade or so ago, concentrations of PBDEs (a group of brominated flame retardants) were still increasing in the aquatic fauna, and levels of this substance in human samples continue to rise.

Effects on living organisms

It is difficult to establish the effects persistent organic pollutants have on living organisms. Reasons for this include the fact that the substances involved are so numerous and that they may affect organisms in so many different ways. Even pollutants which are chemically closely related variants within the same group of compounds may have widely differing biological effects. In addition, the effects of different substances may exacerbate or counteract each other. Moreover, the sensitivity to a given pollutant often varies dramatically from one species to another.

All animals, including man, have a certain ability to neutralise natural toxins by metabolising them into less harmful substances. Pollutants are usually also capable of triggering the natural detoxification systems of organisms. In some instances detoxification is successful, but sometimes the process may have adverse consequences. For example, it may lead to a breakdown not only of the foreign substance, but also of substances naturally present in the body and essential for bodily functions.

A substantial number of organic pollutants impair the turnover of hormones, i.e. the control of biological functions that occurs by the transfer of chemical messages between different parts of the organism. Dioxins and substances akin to them (including certain PCB variants) can cause an entire spectrum of adverse effects. Dioxins are acutely toxic to several animal species even in low doses.

Chronic damage to the central nervous system has recently come to the fore as one of the most serious effects of persistent organic pollutants. Even in minute quantities, both DDT and some variants of PCBs and PBDEs are capable of impairing the brain development of young individuals, the consequence being lifelong behavioural impairment.

Effects on Swedish fauna

Our knowledge of the effects of persistent organic pollutants on living organisms is largely based on studies of laboratory animals under controlled conditions. It is much

more difficult to identify effects of this kind in wild animals or the human population. One reason for this is that both man and animals are exposed to numerous different pollutants, mostly at low levels. Another is that, in addition to the toxins, they are exposed to many other kinds of influence, which cannot always be identified.

Nonetheless, it has been established in a number of cases that Swedish fauna has been harmed by persistent organic pollutants. DDT and other pesticides poisoned birds and other animals locally in agricultural areas in the 1950s and 1960s. These toxins then travelled up the food chains, concentrations in several species of raptor becoming so high that their breeding success declined dramatically. DDT caused eggshells to become so thin that they were often broken by the parent birds during incubation. The worst affected species were close to extinction in Sweden in the 1970s. However, as pollutant levels have fallen, birds of prey have staged a full or partial recovery.

The breeding success of Baltic seals also declined sharply in the 1960s and 1970s, resulting in a serious decline in numbers and the threat of extinction. There is much to suggest that PCBs were the main culprit. Symptoms included foetus fatalities followed by womb damage and sterility. Similar problems appear to have occurred in otter and mink, which are also fisheaters. The otter disappeared completely from large areas of southern and central Sweden. These species have recovered somewhat in recent years, although the frequency of certain kinds of damage indicating impairment of the immune system has increased in seals.

Deformity and other damage has occurred locally in fish and benthic fauna in the vicinity of pulp mills, particularly where pulp was bleached using chlorine gas. Discharges from chlorine gas bleacheries contained large quantities of chlorinated organic matter. Most of this remains unidentified, although dioxins and other highly toxic substances were among the pollutants. Chlorine gas bleaching has now been phased out in Sweden, and the state of the fauna close to pulp mills has improved. Some injurious effects remain, however.

Effects on man

In some countries it has also happened that humans have suffered obvious harm as a result of persistent organic pollutants. Most injuries have occurred following exposure to these agents as a result of accidents, unhealthy working environments or unusual diets. Symptoms have tended to persist, but few acute fatalities have occurred. Nor has there been any marked increased in the incidence of cancer among those affected.

However, there is evidence of slightly retarded physical or mental development in children exposed to organic pollutants. The effects are most marked among victims of pollution disasters in Japan and Taiwan, for example, although it is possible that they also occur among much broader categories. For example, the average birth weight of children of Swedish east coast fishermen (who ingest a considerable amount of persistent organic pollutants by eating large quantities of Baltic fish) is somewhat lower than that of children of fishermen on the west coast. It has not been proved that organic pollutants are responsible for this difference, however.

As far as can be judged, PCBs continue to account for a substantial proportion of the total toxic effect of food. For instance, dioxin-like PCB variants are found in such

high concentrations in food that their toxic effects are comparable with those of dioxins themselves. The total dose of dioxins and dioxinlike compounds ingested by the average Swede is not far from that regarded as the maximum tolerable intake. Certain categories of people, such as breast-fed babies, may be receiving in excess of this limit. However, infants only receive this dose for a limited period, and the positive effects of breast feeding are considered to far outweigh the risks posed by organic pollutants.

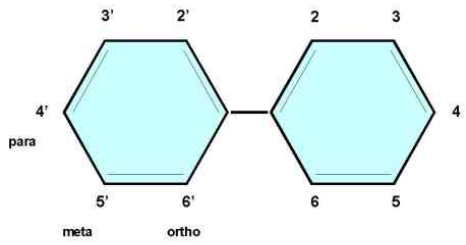
However, we have no data whatsoever on which to base meaningful risk assessments of many categories of persistent organic pollutants and set limit values for health purposes. Our health may also be affected by pollutants we do not even know about.

Limiting the risks

The authorities in Sweden and abroad have considered it best to attempt to restrict people's intake of persistent organic pollutants, notwithstanding the continuing uncertainty about the extent to which they constitute a health risk to the general public. A number of steps have been taken to reduce the production and dispersal of stable organic compounds. Pending results, limit values have been introduced for concentrations of certain organic pollutants in food.

Approximately half the total quantity of dioxins and dioxinlike compounds consumed by the Swedish population come from fish. Dietary recommendations have therefore been issued for the consumption of certain kinds of fish in Sweden. Fatty Baltic fish contain such high concentrations of organic pollutants that they should not be eaten too often. In practice, these recommendations are aimed solely at major consumers. The majority of Swedes could double their fish consumption many times over without departing from the recommendations.

Polychlorinated Biphenyls (PCBs)



Structure of Polychlorinated Biphenyl (PCB) Molecule

PCBs or polychlorinated biphenyls are a group of chemicals consisting of 209 individual compounds. PCBs were widely used as a fire preventive and insulator in the manufacture of transformers and capacitors because of their ability to withstand exceptionally high temperatures. They are complex mixtures of chemicals (100 – 130 in the average environmental sample) which were used (and subsequently released as 'technical mixtures' named in various ways which indicate how chlorinated they are : Arochlor 1042, Arochlor 1254, Arochlor 1262). Each component has its own

chemical and toxicological properties. They are difficult and expensive to unambiguously analyse.

PCBs were introduced in 1930 as a non-flammable, chemically inert fluid. There use increased for approximately 40 yrs. Unfortunately, their properties of chemical and thermal stability which gave them industrial utility made them very refractory in the environment so that they became ubiquitous in the environment. Since they are toxic and potentially carcinogenic with the ability to bioaccumulate and magnify up food chains they have caused considerable environmental problems. They were actually discovered by Jensen in 1966 as an interference during the analysis of DDT in Swedish environmental samples.

PCBs were banned in new uses by the USEPA in 1979, with a complete ban in 1984. They are classified as a probable human carcinogen by numerous national and international health-protective organizations, such as the EPA, The Agency for Toxic Substances and Disease Registry (an arm of the U.S Public Health Service) and the World Health Organization. Research also links PCB exposure to developmental problems.

PCBs **effects**

Neurological damage

10 studies or sites found PCBs were linked to several neurological problems, such as reduced intelligence, hyperactivity, attention deficits, and reduced memory, 1 study found no association between PCBs and neurological damage, 17 studies didn't look at this issue or didn't comment

Immune system damage
8 studies or sites found PCBs were linked to changes in the immune system and/or increased infections, 1 study found no association between PCBs and immune changes, 19 studies didn't look at this issue or didn't comment

Low birth weight
10 studies or sites found PCBs were linked to lowered birth weight, 1 study found no association between PCBs and birth weight, 1 study found PCBs were linked to increased birth weight, 17 studies didn't look at this issue or didn't comment

Shorter gestation period
5 studies or sites found PCBs were linked to a shorter length of pregnancy, 2 studies found no reduction associated with PCBs, 21 studies didn't look at this issue or didn't comment

Smaller heads at birth
2 studies or sites found PCBs were linked to smaller head circumference in newborns, 2 studies found no association between PCBs and head size, 24 studies didn't look at this issue or didn't comment

Impaired or slowed growth
6 studies or sites found PCBs were linked to impaired or slowed growth in babies and/or children, 22 studies didn't look at this issue or didn't comment

Dioxins and Furans

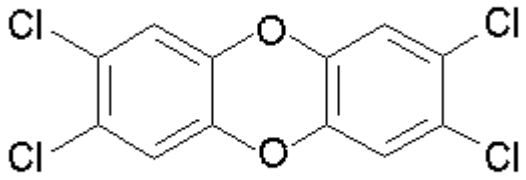
Dioxins (polychlorinated dibenzo-para-dioxins, or PCDDs) and furans (polychlorinated dibenzofurans, or PCDFs) are a group of toxic chemical compounds which are inadvertently generated and released into the environment as by-products of various combustion and chemical processes. Due to their toxicity, tendency to bioaccumulate, and persistence in the environment, dioxins and furans have been the subject of ongoing public health and environmental concern. Despite existing controls, they are distributed widely in the environment, sometimes at levels which may pose risk. For example, dioxins/furans have been the cause of numerous fish consumption advisories in the Great Lakes region, and the U.S. Environmental Protection Agency (EPA) has recently estimated that the risks for the general population based on dioxin exposure could be as high as the range of a 1 in 100 to 1 in 1,000 increased chance of experiencing cancer related to dioxin exposure (USEPA, 2000b). In response, various local, state, regional, and national efforts are focusing on achieving further reductions in dioxin contamination. One of these efforts is the Great Lakes Binational Toxics Strategy (Binational Toxics Strategy or GLBTS), which encompasses various activities and strategies being considered under the guidance of a multi-stakeholder GLBTS dioxin/furan workgroup.

Chemical Description And Health Effects Of Dioxins/Furans

Dioxins and furans are halogenated aromatic hydrocarbons which can have from one to eight chlorine substituents. There are 75 individual chlorinated dioxins and 135 individual chlorinated furans. Each individual dioxin and furan is referred to as a congener. Both the number of chlorine atoms and their positions determine the physical and chemical properties, and therefore, the fate and toxicity of a given congener. In addition to dioxin and furan congeners, coplanar polychlorinated biphenyls (PCBs), a subset of PCBs, also exhibit dioxin-like toxicity due to their structural and conformational similarities to dioxin compounds. Dioxins, furans, and dioxin-like PCBs are commonly found as complex mixtures when detected in environmental media, biological tissues, or as releases from specific sources. Generally, dioxins and related compounds are colorless crystals or solids that have a low water solubility, high fat solubility (i.e., are lipophilic), and low volatility. They bind strongly to soils and sediments and are extremely stable under most environmental conditions, making them persistent once released in the environment. Because they are lipophilic, they also tend to bioaccumulate.

Only dioxin/furan congeners with chlorines attached at a minimum in the 2,3,7, and 8 positions, as those shown in Figure exhibit the high toxicity associated with dioxin. One compound, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), is the best studied of this class of compounds and serves as the reference compound for assigning toxicity equivalence factors for related congeners. For risk assessment purposes, estimates of the toxicity of sources which contain a mixture of PCDD and

PCDF congeners are often expressed as toxicity equivalents (TEQ). TEQ is calculated by multiplying concentrations of each dioxin and furan congener present in a source with a toxicity equivalency factor (TEF). The TEF is an estimate of each congener's toxicity relative to the toxicity of 2,3,7,8-TCDD. The TEQ values for each congener are added together for the total TEQ concentration. Thus, concentrations of dioxins and furans represented as a TEQ concentration provide a quantitative estimate of toxicity as if all congeners present in the mixture are a toxic equivalent mass of 2,3,7,8-TCDD. Thirteen of the total 209 PCB congeners are also thought to have dioxin-like toxicity, and are often included in the calculation of dioxin/furan TEQs in toxicity assessments.



2,3,7,8 TCDD - Tetrachlorodibenzo dioxin