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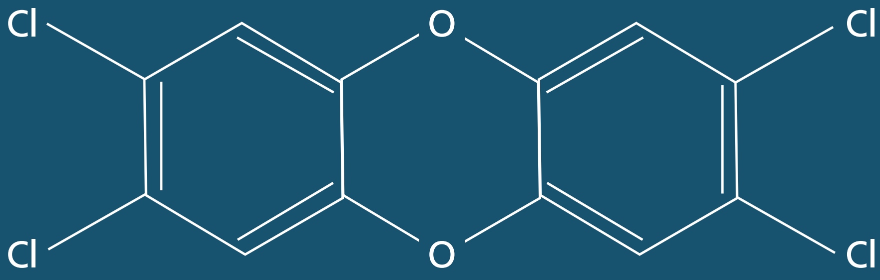

Dioxins in the Baltic Sea

Helsinki Commission
Baltic Marine Environment Protection Commission

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Introduction

This is the first in a series of short reports under the main title "Environmental Focal Point Information". This first report focuses on the intriguing subject of Dioxins, their nature and origin, the risk they pose to human well-being, the official actions that are being implemented to control them, and consideration of further actions by HELCOM.

What are dioxins and where do they come from?

"Dioxin" is a short name for chlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) compounds. There are in total 210 different members of the dioxin family called congeners. Dioxins are persistent organic pollutants (POPs), synthetic chemicals that can cause severe, long-term impacts on wildlife, whole ecosystems and human health.

The sources

Dioxins are not intentionally produced, but are formed as by-products or impurities of several different industrial processes as well as from most combustion processes, such as chemical, paper and metal industries, incineration of municipal and hazardous waste and small scale burning. Fossil energy production, traffic, and other sources both in Central Europe and in the countries around the Baltic Sea also contribute to their presence.

Dioxins enter the Baltic Sea as air fallout when transported from land-based sources and via the multitude of waterways. To a large extent in the past waterway pollution could be attributed to some chemical and forest industries, where chlorine was used in large amounts for pulp bleaching until the early 1990s. This has now stopped in Finland and Sweden but chlorine gas is still used in some Russian pulp and paper mills. Other water pollution sources include releases from coke plants and municipal waste waters.

Table 1.
According to the European Dioxin Inventory report the major industrial air emission sources in Europe account for about 62% of total dioxin air emissions.

Major industrial air emission sources (62%)	**- incinerators for municipal waste** **- iron ore sinter plants** **- incinerators for clinical waste** **- facilities of the non-ferrous metal industry**
Other industrial sources and mainly non-industrial sources (38%)	**- domestic heating facilities (particularly wood combustion)** **- accidental fires** **- traffic (mainly if petrol is used)**

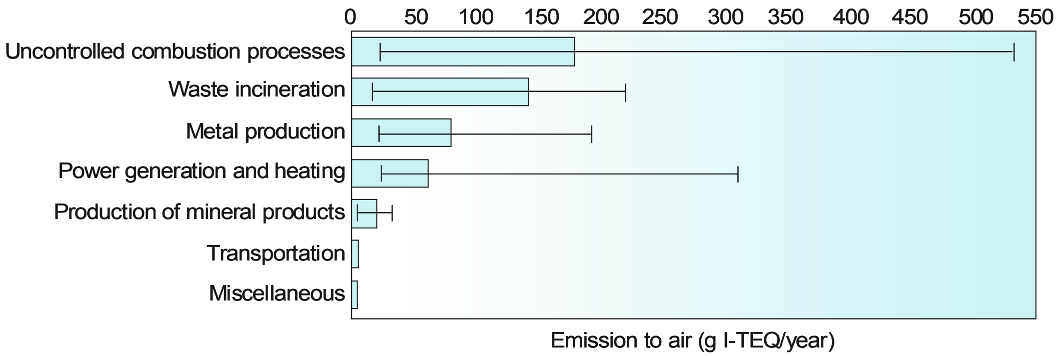
Natural events or processes such as forest or steppe fires and volcanic eruptions can also cause dioxin emissions. Apart from the current known sources and historical emissions there are also isolated incidents such as accidental emissions and building fires, which can release significant dioxin or furan emissions into the atmosphere.

Air emissions are important

Many research programmes have improved our knowledge about dioxin air emissions to the point where there are relatively accurate measurements or estimations available from some countries. However, it seems that the information concerning dioxin concentrations in waste-waters or wastes are not at the same level.

An example of the relative importance of the different sources can be seen in a recent study from Poland, which showed that the main release route for dioxins was by emission into the air. The relative distribution of sources into the atmosphere is shown in figure 1.

Figure 1.
Potential emission of dioxins to air from all sources in Poland, 2000. Medium estimated emissions (bars) and uncertainty ranges (lines) are shown (based on: DANCEE, 2002).



The potential releases of dioxins into residues may be of the same magnitude as the releases into air; furthermore, dioxins and furans also eventually end up in residues from air pollution control systems. Residues are mainly disposed of in landfills, but residues from households and sewage plants may ultimately end up in the soil and actually account for the majority of releases to the ground. Other releases to land mainly result from the deposit of ashes from fires and the burning of biomass. In the future dioxins and furans in residues may be released from existing landfills and waste dumps.

In some cases, dioxins enter into products. The major sources of dioxin in products are from the production of chlorinated pesticides and recycled paper. The dioxin content in the latter may originate from bleaching of the paper used for recycling.

What makes dioxins toxic?

Scientists consider dioxins to be one of the most toxic "man-made" chemicals ever studied.

Dioxins are persistent and fat-soluble substances found everywhere in the environment with a tendency to accumulate in higher animals - including humans. Their very slow rate of degradation means that they may be transported over long distances and result in trans-national exchanges. In addition to these factors, dioxins that were released into the environment many years ago, are still contributing to current exposure. Even very small dioxin concentrations can have negative effects on the environment and on human health, in particular on more vulnerable groups such as children and pregnant women.

The Seveso-dioxin is the most toxic

Specifically, the 17 dioxins with 2,3,7,8-chloro substitution are the most toxic and most prone to accumulating in living tissue over time; they are also most commonly found in animals and humans. The most toxic congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) or the Seveso-dioxin. It is one of the most studied chemicals, and is used as a reference for all other related chemicals. The effects of some PCB-compounds are assumed to originate from chemical properties similar to those which cause the toxicity of dioxins.

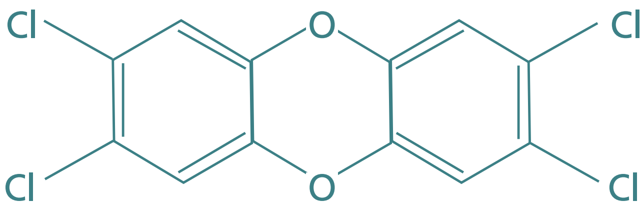


Figure 2. Chemical structure of 2,3,7,8-TCDD (TC or "tetra-chloro" means that there are four chlorine atoms in the molecule).

Effects in humans

Acute dioxin exposures in humans may result in severe skin lesions, altered liver function and lipid metabolism, general weakness associated with drastic weight loss, depression of the immune system and endocrine and nervous system abnormalities. Long-term exposure leads to increased dioxin levels in fatty tissues and may result in developmental effects in children, as well as cancer and other diseases.

Dioxins have attracted national and international attention and are the focus of many international conventions and agreements on persistent organic pollutants, which call for prohibitions on use, and the prevention or limitation of emissions.

Technical box: Toxicity

In samples dioxins are always found as a mixture of various congeners. The toxicity of the dioxins is very congener-specific, ranging from the most toxic 2,3,7,8-TCDD (tetrachloro-dibenzo-p-dioxin) to congeners more than 10,000 times less toxic. Today only congeners with chlorine atoms in the 2,3,7,8-positions are considered to have toxic properties similar to TCDD.

Dioxins in the Baltic Sea food web

Because of their emission routes dioxins are spread all over the Baltic Sea area. Since dioxins are persistent and bio-accumulative, they become more concentrated as they move up the food chain. Large quantities are stored in seabed sediments, accumulated over several decades. Smaller quantities are still reaching the Baltic Sea, although releases have decreased during the last 10-20 years.

Technical box: Comparing measurement values

Reported dioxin measurements are difficult to compare because different methods are used. The quantities reported are also presented in different ways (by dry weight, wet weight, lipid weight etc.) and cannot be immediately compared.

Furthermore, dioxins are a mixture of different compounds (congeners) with varying levels of toxicity. The most toxic is the TCDD. In order to aggregate the results for the various congeners in a sample and get a "total" dioxin content, some international systems for calculating dioxin toxicity equivalence (TEQ) have been developed. These have been based on the assumption of similar toxic action mechanisms and also on the assumption that the interactions are additive.

The systems are based on a relative ranking system which gives the congeners toxicity equivalence factors (TEF) with TCDD (the most toxic) assigned a factor of 1. The quantity of each dioxin is multiplied by its TEF to normalise the amount to TCDD equivalent amount (TEQ). The results can then be simply added to give a total TCDD equivalent amount for dioxins.

TEQ is a technical tool for risk assessment and management, and TEFs are based on convention. Therefore TEF values may change when information improves. The newest system (WHO-TEF) was recommended by a WHO Working Group.

Large reservoirs of dioxins in sediments

Little is known about the concentration of dioxins in the waters of the Baltic Sea. One investigation showed an average level of only

2.8 ng/m^3 WHO-TEQ. Because dioxins have a very low solubility in water most dioxins settle in the sediments.

Investigations of dioxins in surface sediments are available from Danish, Swedish, Finnish and German areas. The concentrations of dioxins are typically 500-1500 ng/kg dry weight; this corresponds to 10-30 ng WHO-TEQ/kg dry weight. Dioxins accumulate in sediments close to their main sources, such as old pulp and paper mills, chemical plants including vinyl chloride or biocide manufacturing, and harbours. The distribution of dioxins in surface sediments in figure 3 gives only an approximate picture of the regional distribution of dioxin concentrations, since no data are available from most parts of the Baltic Sea.

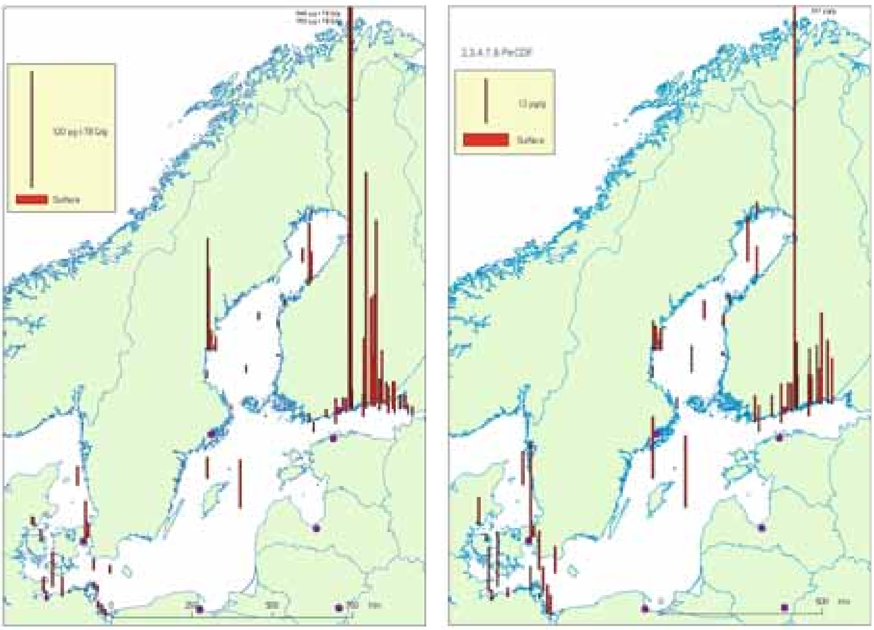


Figure 3. Spatial distribution of dioxins (PCDD/Fs) in surface sediments in the Baltic Sea (SCALE, 2004). Note that pentafurane (2,3,4,7,8-PeCDF) is the main congener found in Baltic herring and salmon.

Dioxins disintegrate very slowly. The half-lives of dioxin congeners in the Baltic have been estimated at between 20 and 275 years. Therefore, sediments serve as historical databases and analysis of dioxins in material from different depths in the sediments gives valuable information about how the pollution level in the Baltic Sea has varied over many decades. Figure 4 shows that the level of dioxins generally peaked in the 1970s after which a decrease can be observed.

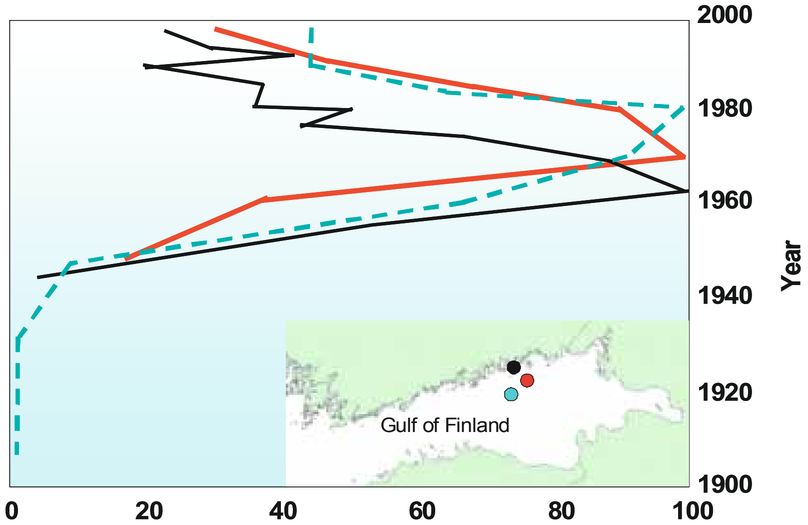


Figure 4.
The chronology of dioxin concentrations in three sediment profiles in the Gulf of Finland (based on: Isosaari et al, 2002).

Over time small amounts of dioxin are released from the sediment reservoirs and become biologically available in the food web. The rate of release however, is estimated to be slower than the rate of deposition. Dioxins are released mainly from fresh surfaces and sediments which have been disturbed. It is unclear to what extent sediment storage of dioxins is responsible for the present levels of dioxins in biota such as fish, and to what extent more recent emissions or fallout influence these levels.

Mussels link water and sediment

Mussels have an important role in the circulation of dioxins since they filter large amounts of particles in the water and also process the surface sediments. Mussels increase the deposition rate of these substances on the seabed and make them more easily available to organisms living on the sea floor. In addition to this, mussels increase the residence time of substances in the water, and accumulate and excrete them.

Fatty fish contain dioxins

The fat-soluble properties of dioxins cause them to accumulate in fatty tissues. Herring and salmon are fatty fish, and contain the highest dioxin concentrations when calculated by fresh weight. The degree of contamination varies geographically (figure 5), from year to year and according to the season (highest in the spring), the fat content, and also the size and age of the fish (figure 6).

Figure 5.
The Dioxin content in herring muscle at different fishing grounds. For Latvia the value represents the average of 2002/2003 data from the Gulf of Riga and Latvian coastal waters (based on: Karl and Ruoff (2004), the National Food Agency, Finland and the Food and Veterinary Service of Latvia.

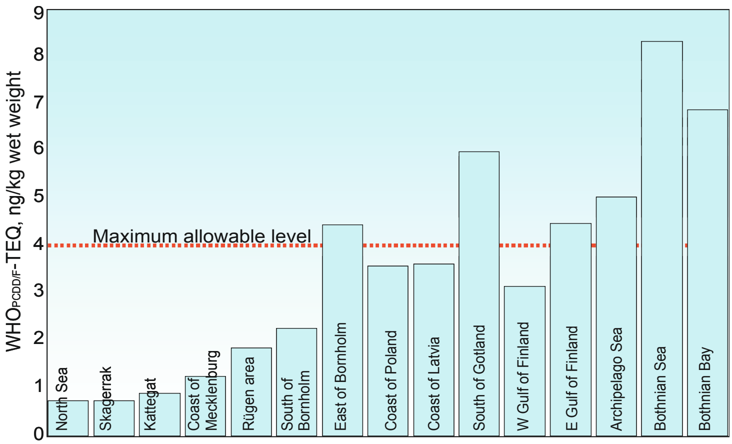
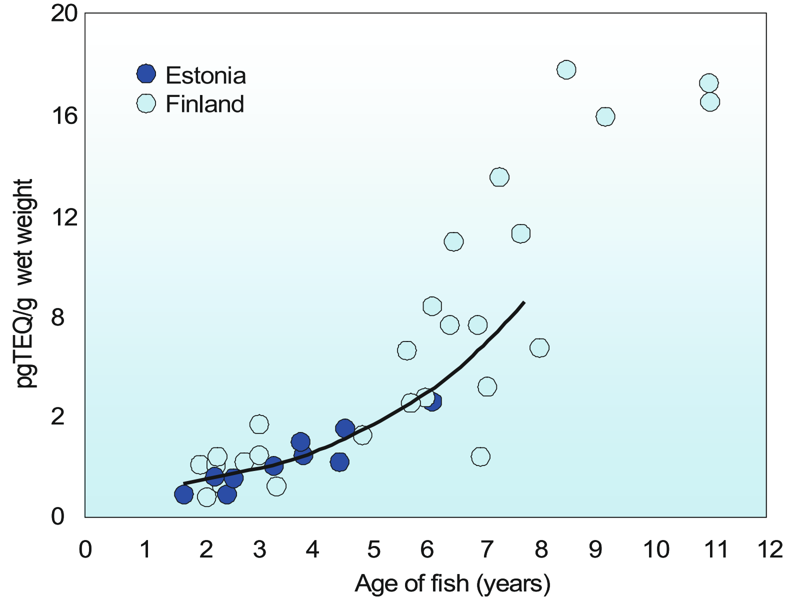


Figure 6.
Dioxin concentration (pg/g wet weight in TEQ) in Estonian and Finnish Baltic Sea herring muscle tissue (based on Roots et al, 2003).



In the south western part of the Baltic and in Danish waters the average dioxin content in herring is 2-2.5 ng WHO-TEQ/kg fresh weight. In comparison, levels are approximately double this figure in the Baltic Proper and the Gulf of Finland and four times higher in the Bothnian Sea and the southern part of the Bothnian Bay. It is particularly in these areas that chemical plants producing biocides and pulp and paper industries emitted great amounts of dioxins for many years.

Typically dioxin levels in Baltic wild salmon are currently 2-8 ng WHO-TEQ/kg fresh weight. Twenty years ago dioxin levels ten times higher than this were measured in wild salmon from the Umeå area. Figures on dioxin levels in herring do not provide enough data for reliable time-series analysis. Preliminary data from Finnish specimen bank samples at several locations indicate higher concentrations in herring during the late 1970's and early 1980's. According to Swedish investigations, no trends can be observed in the 1990's.

Fish-eating birds and mammals concentrate dioxins
Fish-eating birds and other top predators also accumulate toxic substances. Data on guillemot eggs indicate a high level of contamination (figure 7). The temporal trend in dioxin concentrations in the eggs corresponds to that found in sediments, i.e. high values in the 1970's followed by a significant decreasing trend mainly in the 1980's. The decrease of dioxins in guillemot eggs has levelled out during the recent 10 years.

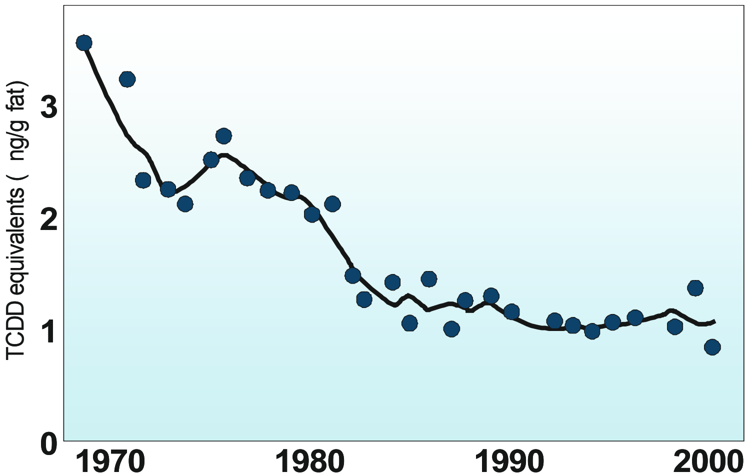


Figure 7.
Time series of dioxins in guillemot eggs (based on: Stockholms Marina Forskningscentrum, 2003).

Marine mammals living in the Baltic Sea, such as the ringed seal, grey seal, common seal and harbour porpoises, have a high intake of persistent organic pollutants including dioxins. Normally, adult females have lower dioxin residues as a result of the use of their fat deposits during lactation.

In a Finnish study the TEQ of dioxins in seals varied between 7 and 150 pg/g lipid weight; this figure is lower than in Baltic Sea birds, but approximately the same as found in seals from other parts of the Baltic Sea and the west coast of Sweden. Nevertheless, the study found no relationship between the presence of dioxins and the high mortality rate among ringed seals of the Gulf of Finland.

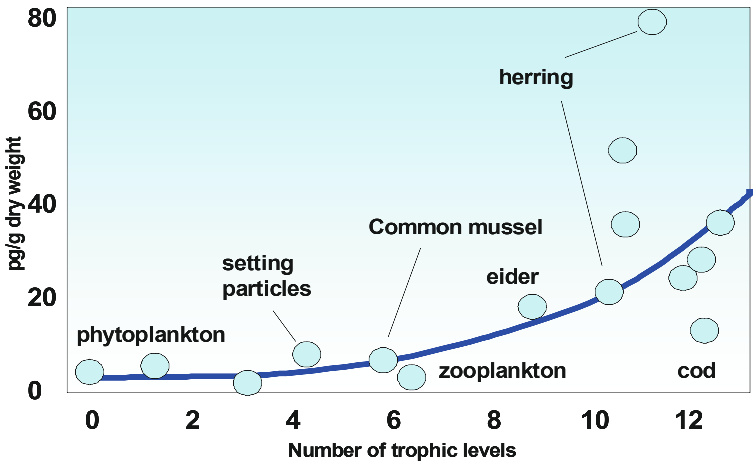


Figure 8. Dioxin concentration in various levels of the Baltic Sea food chain for the three most toxic dioxins including TCDD demonstrates bioaccumulation (based on: Bernes, 1998).

Risk to human health – threat to fish lovers?

The nutritional qualities of fish are well known. In addition to being a good source of animal protein and fatty acids, fish contain vitamins A and D, magnesium, phosphorus and mineral salts. Recent studies show that fatty fish contain certain fatty acids vital to the development of the human brain in the foetus and in infants.

In recent years however, we have seen the emergence of a number of threats to the quality of human food. The issue of dioxins in human food led to the adoption by the European Council of a Regulation establishing maximum levels of dioxin and other contaminants in both human food and animal feed. The limits apply from 1 July 2002 and will be reviewed by 31 December 2004. The overall goal is to reduce human exposure to dioxins by at least 25% by the year 2006. Other measures include the creation of the European Food Safety Authority and mandatory labelling of fish.

The problem
The main problem with dioxins is their unique chemical stability. Once ingested by living organisms dioxins are stored in the fatty tissues for a long time. Because they accumulate, their concentrations increase as they move up in the food chain. Thus top predators and humans are exposed to the highest levels of contamination.

It is not easy to determine the overall pathways of dioxins in the environment. These vary geographically depending on their sources and data are not always available for different areas and species. But some variations are known: fish from the Baltic Sea generally seem to be twice as contaminated as fish from the North Sea. Variations among species are another factor. Because dioxins accumulate in fatty tissues, fatty fish such as herring and salmon show higher levels of contamination. Farmed fish are assumed to be less exposed to dioxins than wild fish from the Baltic. Their feed can be controlled so dioxin ingestion can be minimised and the exposure time is briefer because the lifespan of farmed fish is generally shorter. However, a recent study has led to some discussion about the contamination of farmed fish and more investigations might be needed in this area.

Human intake:

About 90% of the human intake of dioxins comes from fatty food including fish. The dioxin content originates from background pollution of the natural food and the fodder the animals consume, but isolated point sources may also play a role in food contamination.

The potential dangers to human health relate to the carcinogenic risk and other harmful effects (skin lesions and dark spots on the skin), which can be produced once exposure exceeds a certain threshold. Neuro-behavioural effects and immune-system deficiencies can even be seen at markedly lower levels.

The health risk is mainly linked to accidental or occupational exposure and not to the normal consumption of fish. Considerations about the risk of contaminated fish must be balanced against the positive nutritional value of fish. In Europe fish accounts for about 12% of animal protein consumed. So while the risk does exist it depends primarily on very regular consumption of contaminated fish. This is one reason why it is important to keep those at risk well informed and to adopt measures to limit the amount of dioxins released into the environment.

Dioxins in food must be reduced

Measures to restrict human exposure to dioxins through food intake have been taken at European level. The EU has set limits for the maximum dioxin content of various types of food. For fishery products the levels depend on whether the product is fresh fish, fish oil or fish meal (table 2). In the fisheries sector one consequence is that the fish oil producing industry might need to purify its product.

Table 2. Authorised dioxin limits. To be reviewed by 31 December 2004 (EU newsletter, 2002).

Fresh fish	**4 pg/g fresh weight**
Animal feed:	
– Fish oil	**6 ng/kg**
– Fish meal	**1.25 ng/kg**
– Fish feed	**2.25 ng/kg**

Some of the Baltic fatty fish do not comply with the maximum level requirement, and would therefore be excluded from the diet, a measure which could have a negative health impact. Consequently, for a transitional period ending on 31 December 2006, Sweden and Finland have been authorised, to place on the domestic market fish from the Baltic region with higher dioxin levels. This allowance has been granted provided that a system is put in place to ensure that consumers are fully informed about the situation, and particularly about the risks associated with dioxin for identified vulnerable groups of the population.

In Denmark problems with dioxins in fish caught in the Baltic Sea have arisen in 2004. Samples of salmon showed that the EU limit was exceeded by 5-85% and the Ministry of Food, Agriculture and Fisheries decided to stop salmon fishing immediately in the Danish waters of the Baltic Sea. In addition to this, a limited sample of herring indicated an elevated dioxin content, prompting a more throughout investigation.

You are what you eat

In Sweden, fish consumption accounts for as much as 33-38 % of human dioxin exposure, and in Finland the figure is 63-83 %. The corresponding numbers in other countries in the Baltic Region with a similar traditional influence, such as Estonia, Latvia, Lithuania and Poland, are not known at present. However, since these countries do fish from the same fish stocks as Sweden and Finland, the relationship between fish consumption and human dioxin exposure can be assumed to be within the same range, if the consumption patterns are similar. In Finland, herring alone accounts for 52 % of the daily dioxin intake in humans, and in Sweden fatty fish from the Baltic Sea region contribute 19-22 %.

The influence of fish consumption on human dioxin exposure has been clearly demonstrated by some studies (figure 8). In Finnish fishermen consuming high amounts of fish, dioxin concentrations in fat were 220 ng TEQ /kg (range 51-520). An even more conspicuous finding in the study was that in fishermen consuming predominantly one fish species, the dioxins spectrum clearly resembled that of the consumed fish, e.g. herring eaters could be differentiated from pike or bream eaters. In Finland, dioxin exposure from food items other than fish is very low - in 2000 the total intake was calculated to be 0.8 pg/kg/day on an average.
If dioxin-like PCBs are also included, intake in Finland rises to 1.45 pg/kg/day.

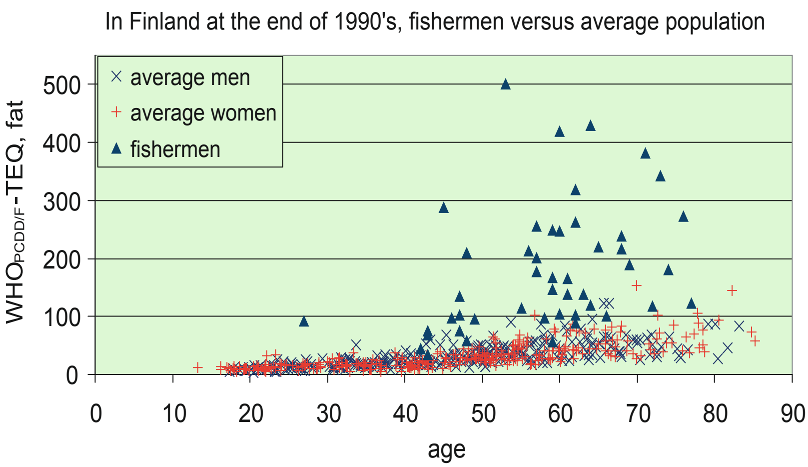


Figure 8. Dioxins concentrations in fishermen vs. average population (Kiviranta et al, 2002, figure taken from SCALE, 2004).

The total Danish human dioxin intake including dioxin-like PCBs has been calculated at 1.7 pg TEQ/kg/day (2002 data). This is the same level as the previous year and corresponds to similar results in several neighbouring countries. The value corresponds to the tolerable weekly intake (TWI) of 14 pg TEQ/kg/week, which indicates that part of the population may exceed the limit regularly. This does not mean that there is a health risk for those persons but that the full safety factor included in the TWI is not applied. Against this background there is good reason and a need for sustained efforts to reduce the dioxin content in food.

Regulations and actions

The objective of HELCOM's strategy for hazardous substances is to continuously reduce discharges, emissions and losses of hazardous substances, with a goal of their eventual cessation by the year 2020. The ultimate aim is for concentrations of naturally occurring substances in the environment to approach background values and to reduce concentrations of man-made synthetic substances to close to zero. This objective was adopted in 1998 and dioxin has been selected as one of the priority substances for immediate action.

Dioxins have already been addressed in specific HELCOM Recommendations relating to the incineration of household waste and the use of scrap material in the iron and steel industry. They are indirectly dealt with in the regulation of AOX emissions from the kraft and sulphite pulp industry. One result of these efforts is a recommendation that molecular chlorine should not be used in the bleaching of sulphite pulp after January 1997.

HELCOM has also produced a "Guidance Document" on dioxins, providing information on production and use, sources of emissions and discharges, possible pathways to the marine environment, and monitoring data. The document assesses the extent of the problem, identifies possible measures to reduce and end emissions, discharges and losses and also proposes the instruments needed to implement these measures.

Currently the main international agreements which address the threat of dioxins are the Stockholm Convention on Persistent Organic Pollutants (POPs) - requiring measures for reducing or preventing releases of dioxins to the environment - and the UNECE Protocol on POPs, which requires mandatory control measures and quantified limits.

The European Union has adopted several Directives which deal with polluting sectors and sources as well as a comprehensive legislative framework regulating chemicals and products. One key element in the EU policy is the "Communication on a Community Strategy for Dioxins, Furans and Polychlorinated Biphenyls" adopted by the European Commission in 2001. The strategy entails an integrated and systematic approach to reduce the presence of these substances in the environment and the identification of short-, medium-, and long-term actions, particularly with regard to establishing maximum limits in food and fodder. The strategy is a good basis for further research and the introduction of measures to reduce dioxin formation, emission and exposure.

New initiatives are still being developed. For example, hazardous substances are being addressed in the preparation of the European Marine Strategy and the European Environment and Health Strategy. The latter requires the formation of an EU Integrated Environment and Health Monitoring and Response System to develop an environment- and health-based "cause-effect framework". This framework will in turn support the Community policy which addresses the sources and impact pathways of health stressors.

Future work on dioxins needed

Investigations of dioxins in the environment have in the past mainly focussed on the contamination of humans, animals and their food or their impact on parts of the environment. Insufficient information has been gathered about the primary sources of dioxins and even less about the quantity and significance of different secondary sources and their contribution to the present environmental pollution. More work has to be done in this field in order to reduce input into the environment and eventually into humans.

For future regulations and implementation of measures to be effective enough to solve the problems caused by dioxins, they must be based on comprehensive knowledge of emitting sources, environmental status, exposure and risks. Consequently, the basis for future success must be the establishment of an integrated monitoring system, which combines environmental monitoring and exposure monitoring as considered by the EU. This means that simultaneous measurement of air, soil, water and fauna should be combined with environmental, indoor, occupational and consumer exposure measurements.

In the Baltic Sea where dioxin levels in fish are elevated, monitoring of selected indicator species could provide information about the general level of contamination as well as trends, ecosystem health, fish health and quantity, quality of fish on the market, the possible exposure of humans to contamination, and the resulting health risk.

Further work and the preparation of potential new measures by HELCOM should focus on the specific requirements of the Baltic Sea and also take into account the EU initiatives mentioned earlier, as well as relevant work being conducted by other international bodies. New HELCOM measures should be developed only when they can add value to existing regulations.

References and useful literature about dioxins

Bernes C. (1998): Persistent Organic Pollutants. A Swedish View of an International Problem. Monitor 16. Swedish Environmental Protection Agency

DANCEE (2002): Inventory of Dioxins and Furan Releases in Poland

EU Newsletter (2002): Fishing in Europe No. 11, March 2002

Hansen E. (2000): Substance Flow Analysis for Dioxins in Denmark. Environmental Project No. 570. Danish EPA.

Isosaari, P., Kankaanpää, H., Mattila, J., Kiviranta, H. Verta, M., Salo, S. and Vartiainen, T. (2002): Spatial distribution and temporal accumulation of polychlorinated dibenzo-P-dioxins, dibenzofurans, and biphenyls in the Gulf of Finland. Environ. Sci. Technol. 36:2560-2565.

Jensen A .A. (2003): Kortlægning af dioxinforurening samt kilder til dioxinforurening i Østersøen. Miljøprojekt Nr. 796. Miljøstyrelsen.

Karl, H. and Ruoff, U (2004): Contaminant levels of western Baltic Sea herring. - http://www.bfa-fish.de/news/news-d/tagungen/Baltic_Herring.pdf

National Food Agency, Finland (http://www.elintarvikevirasto.fi/valvonta/index.html?page=2147 (19 February 2004)

SCALE (2004): Baseline Report on "Integrated Monitoring of dioxins & PCBs in the Baltic Region" in the framework of the European Environment and Health Strategy

Roots, O., Lahne, R., Simm, M. and Schramm, K.W. (2003): Dioxins in the Baltic herring and sprat in Estonian coastal waters. Organohalogen Compounds 62:201-203. Dioxin 2003 Boston, MA, USA.

Stockholms Marina Forskningscentrum (2003): Miljötillståndet i egentliga Östersjön, rapport 2003. Swedish report on the environmental state of the Baltic Proper (including English summaries)

UNEP Global Report (2003): Regionally Based Assessments of Persistent Toxic Substances

Useful homepages:

DG Health and Consumer Protection: http://europa.eu.int/comm/food/food/chemicalsafety/contaminants/dioxins_en.htm

DG Environment on dioxins: http://europa.eu.int/comm/environment/dioxin/index.htm

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