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**SUBSTITUTES TO BE USED AS ALTERNATIVES TO
PRIORITY 12 PERSISTENT ORGANIC POLLUTANTS**

Background and Guidelines

In cooperation with



WHO

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PART A: Substitutes to be used as alternatives to priority 12 POPs

1. INTRODUCTION

1.1 Background

1.1.1 Stockholm Convention¹

The Stockholm Convention on Persistent Organic Pollutants (POPs) was adopted and opened for signature on 23 May 2001. The objective of the Convention is to protect human health and the environment from POPs. It is a legally binding instrument that will require its Parties to adopt policies to reduce or eliminate the release of designated POPs, by means of a series of measures.

The Stockholm Convention sets out measures covering the production, import, export, disposal, and use of POPs, as well as the obligation of the Parties to minimize their release. Governments are to promote the best available technologies and practices for replacing existing POPs, while preventing the development of new ones. They will also be required to ensure that appropriate national legislation and regulations are applied, and action plans developed for carrying out their commitments and obligations.

Most of the 12 POPs chemicals in question are subject to an immediate ban. However, exemption has been granted for the use of DDT because it is still necessary in many countries for the control of malarial mosquitoes. This exemption will permit governments to protect their citizens from the risk of contracting malaria - a major killer in many tropical regions – until they are able to replace DDT with cost-effective and environmentally friendly chemical and/or non-chemical alternatives.

In the case of PCBs, these chemicals have been and still are widely used in substantial amounts in electrical transformers and other equipment. In order to provide enough time to secure PCB-free replacements, governments may permit the use of existing equipment, suitably modified to prevent release into the environment, until 2025. However, PCBs that are no longer in use must be contained, properly stored and ultimately destroyed in compliance with international standards. A number of country-specific and time-limited exemptions have been agreed upon for other chemicals.

Governments have agreed to reduce the release of furans and dioxins, which are accidental by-products and thus more difficult to control, while continuing to minimize their use until possible ultimate elimination.

The obligations of the Parties to the Stockholm Convention² are laid down in the text as a series of controls and general provisions and the chemical substances involved are listed in the annexes to the present document. The controls and provisions for the POPs are as follows:

Parties are obliged to take measures to reduce or eliminate release of the POPs covered by the Convention, namely:

- Eliminate production and use of the POPs listed in Annex A (aldrin, chlordane,

¹ <http://www.pops.int/>

² All the Parties of Barcelona Convention have signed or signed and ratified the Stockholm Convention, with the exception of Cyprus and the Libyan Arab Jamahiriya

- dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene) with the exception of PCBs in use and certain limited exemptions;
- Restrict to limited use, the production of POPs listed in Annex B (i.e. DDT for disease vector control in accordance with WHO guidance);
 - Restrict the export of POPs listed in Annexes A and B: (i) to Parties that have a specific exemption or permissible purpose; (ii) to non-Parties whose compliance with relevant provisions of the Convention is certified; and (iii) for the purpose of environmentally sound disposal;
 - Ensure that PCBs are managed in an environmentally sound manner and that action is taken by the year 2025 to eliminate the use PCBs found above certain thresholds;
 - Ensure that countries who have registered to use DDT are restricted to vector control, in accordance with WHO guidance, and report on amounts of the chemical used;
 - Develop and implement an action plan to identify sources and reduce the release of POPs by-products listed in Annex C; develop and maintain source inventories and release estimates; promote measures, including the use of best available techniques and best environmental practices; and
 - Develop strategies for identifying stockpiles of POPs listed in Annexes A and B and products containing POPs listed in Annexes A, B and C; take measures to ensure that wastes thereof are managed and disposed of in an environmentally sound manner, in accordance with international standards and guidelines (e.g. the Basel Convention on the Control of Transboundary Movement of Hazardous Wastes and their Disposal); and, endeavour to identify POPs contaminated sites for possible remediation.

Parties to the Convention must develop an action plan within two years, involve all relevant stakeholders and endeavour to implement, review and update the plan on a periodic basis.

1.1.2 Strategic Action Programme

The Strategic Action Programme (SAP) was developed by MED POL and adopted by the Contracting Parties to the Barcelona Convention, to facilitate the implementation of the Land Based Sources Protocol (LBS Protocol). It has been designed to assist Parties in taking actions, either individually or jointly and in conformity with their respective policies, priorities and resources, which will lead to the prevention, reduction, control and/or elimination of the degradation of the marine environment.

The question of POPs (namely, nine chlorinated pesticides and PCBs and other POPs), is addressed in the Strategic Action Programme under substances that are toxic, persistent and liable to bioaccumulate. The SAP targets are:

- “By the year 2010 to phase out inputs of 9 pesticides and PCBs and reduce to fullest possible extent, inputs of unwanted contaminants;
- By the year 2005 to reduce by 50%, inputs of the priority 12 POPs;
- By the year 2005 to collect and dispose of all PCB waste in a safe and environmentally sound manner.”

These targets will be achieved by means of a set of regional and national activities based on strategies and plans for the management of POPs and devised using environmentally sound management processes.

By the year 2005, Mediterranean countries should develop an inventory of POPs.

All deadlines included in the SAP are subject to discussion to ensure that ample time

is provided for effective implementation.

Development of the proposed regional plan for the management of POPs is based on the assessment of management status and inventories of POPs in the Mediterranean region (Annex I of document "Regional inventory of quantities and uses of pesticides and PCBs") and regional considerations.

The development and implementation of the action plans is the cornerstone for the implementation of the regional plan.

Mediterranean countries should consider the integration of elements of these plans in their national environment action plan, if available.

1.2 Objectives

The present document aims to provide information and also form a guideline for the Contracting Parties to the Barcelona Convention, on the use of substitutes as alternatives to POPs within the Mediterranean Region.

For this purpose, efforts have been made throughout the document to identify both alternatives proposed by the different sources of information consulted, and considerations derived as to their feasibility or appropriateness.

1.3 Scope

Current alternative methods utilized to avoid the twelve POPs included in the Stockholm Convention are outlined in the present document. The substances in question are:

1. Aldrin
2. Chlordane
3. DDT
4. Dieldrin
5. Endrin
6. Heptachlor
7. Hexachlorobenzene
8. Mirex
9. Toxaphene
10. PCBs
11. Dioxins
12. Furans

The alternative methods covered include information on the different uses and sources (both intentional and unintentional), and consist mainly of chemical substitutes, management alternatives, and modification/substitution of processes. For unintentional emissions (dioxins and furans), Best Available Techniques (BATs) and Best Environmental Practices (BEPs) have been included. Wherever possible, the analysis is focused specifically on those issues applicable to the Mediterranean Region.

Although chemical substitutes quite often represent hazardous and/or regulated alternatives themselves, they have been included in this document together with available information on the extent of their hazardousness and regulation state. Sources of information have been referenced for further study.

1.4 Structure of the document

The present document is divided into two main parts:

The report itself provides information on emission sources and methods to avoid the use of the main groups of POPs: Pesticides, PCBs, Hexachlorobenzene and Dioxins and Furans. Also included in the report are viewpoints obtained from the different sources of information consulted, some examples of proposed alternative methods, and a description of the different alternatives.

The guidelines consist of twelve fact sheets for each of the POPs covered. Detailed information on the various uses, sources and main alternatives to each of the twelve substances is included to provide an overview of the most common alternatives, as well as related comments and considerations. Specific information sources are referenced to enable the reader to obtain further information.

1.5 The POPs issue in the Mediterranean region

Since the beginning of the MED POL Programme (one of the three main components of the Mediterranean Action Plan) several actions have been launched to monitor POPs.

This issue has become important because the characteristics of the Mediterranean differ from other regions. As stated by several experts (Ramos *et al.*, 2000) regarding the case of pesticides, these differences, not only in meteorological data (temperature, solar irradiation, or rainfall volume and annual distribution) but also in farm distribution, crop typologies (like olive groves, vineyards or citric), soil or sediment properties and surface or groundwater, require specific and realistic methodologies and recommendations.

The first data collected through MED POL (Civili, 1999) shows that the most relevant pollutants in the Mediterranean marine and coastal environment are PCBs, DDT and its metabolites (DDE, DDO), hexachlorohexane, hexachlorobenzene, heptachlor and the pesticides aldrin, dieldrin and endrin. Around 80% of the total input into the sea is by way of the atmosphere and 20% via rivers.

Today, the definition of sources for most POPs has to take into consideration the fact that most of the compounds in question have been banned in the majority of Mediterranean countries. Hence, the main sources consist of stockpiles and inventories remaining from former production and/or import, and more importantly, compounds still present in the main environmental vectors and reservoirs from previous usage and from accidental spills. The contribution from industrial production will only be important in those cases where some restricted usage of the POPs is allowed (i.e. DDT as precursor of Dicofol) and for POPs generated as inadvertent secondary products (i.e. PCDDs from combustion).

The main sources, environmental vectors and reservoirs of POPs in the Region are summarised in Table 1, which includes only the main direct sources (although there are important indirect sources resulting from transfers between different reservoirs, particularly through atmospheric deposition).

For POPs pesticides, the sources are multiple and diffuse. Although these compounds have a tendency to disappear as a result of the implementation of PIC procedure and the associated conventions, there is a worrying lack of control over existing stockpiles in the Mediterranean region.

Table 1

Main sources, environmental vectors and reservoirs of POPs in the Region. The most important sources are shown in bold (UNEP Chemicals, 2002).

Compound type	Air sources	Soil sources	Freshwater sources	Seawater sources
Pesticides	Agricultural use Spraying/Land application	Stockpiles, production waste, DDT - dicofol production	Runoff from agriculture use, DDT - dicofol production	Major rivers and coastal runoff
PCBs	Emission from equipment and stocks Sewage sludge incineration	Equipment stocks and landfills Sewage sludge	Leakage from equipment	Major rivers and coastal runoff Sewage sludge dumping
POCDs	Emission from combustion	By-products of PCBs		Major rivers and coastal runoff

2. PESTICIDES

2.1 Source characterization

Organochlorine pesticides have been used profusely in the Region. However, with some exceptions to be discussed below, production and usage has been banned in the majority of countries in the region as a result of the application of the PIC protocols³. According to Regulation EC 850/2004, Aldrin, Chlordane DDT, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex and Toxaphene are prohibited in the EU except for the production and use of DDT as intermediate for the production of Dicofol. Endrin and Mirex are not subject to the PIC procedure although many countries have banned its use (PIC, 2002). Specific exemptions have also been requested by Algeria (chlordane, DDT and heptachlor) and Morocco (DDT) in the framework of the Stockholm Convention (UNEP Chemicals, 2002).

DDT is the only organochlorine pesticide that is still in production and use in the Region. In some Mediterranean countries, both in the north and south, uses for the production of dicofol and vector control against malaria, are still in practice. For example, in 1998 Italy imported 1200 tonnes from Mexico for total conversion to dicofol. At the same time, a decline has been noted in the amounts of DDT used for agriculture in developing countries. In the European countries of the region, up until the mid-nineties DDT was produced in Italy and sold (amongst others in the region) to Italy and Spain. In France, DDT was produced until 1988. At present, DDT is being produced in Spain as a precursor of dicofol at a yearly rate of 1500 tonnes (UNEP Chemicals, 2002). WHO has developed recommendations and conclusions on the use of DDT for public health purposes and these are listed in Annex I.

Apart from the vector use of DDT, the major remaining uses of the listed POPs pesticide occur in plant protection and for the protection of building constructions. However, the use of these POPs pesticides has decreased drastically during the last decades. There is

³Rotterdam Convention: <http://www.pic.int/>

today very limited use against pests on plants and plant parts (e.g. wood in building constructions). The main sources of chlorinated pesticides in the Mediterranean Region are shown in Table 2.

Table 2

Main sources of chlorinated pesticides in the various environmental vectors and compartments. Main vectors and reservoirs are shown in bold (UNEP Chemicals, 2002)

	Air sources	Water resources	Soil sources	Sea
Chlorinated pesticides	<ul style="list-style-type: none"> • Agricultural usage • Spraying/Land application • Production 	<ul style="list-style-type: none"> • Agricultural usage • Run-off • Production 	<ul style="list-style-type: none"> • Stockpiles • Production waste • Misuse 	<ul style="list-style-type: none"> • Agricultural run-off • Major rivers and drains • Atmospheric deposition

Available information concerning the remaining stockpiles of pesticides in some of the countries of the region has been extracted from the Obsolete Pesticide Database (FAO, 2004) and is summarised in Table 3.

2.1.1 Aldrin

Aldrin is a pesticide used to control soil insects such as termites, corn rootworm, wireworms, rice, water weevil, and grasshoppers. It has been widely used to protect crops such as corn and potatoes and has been effective to protect wooden structures from termites. Aldrin is readily metabolized to dieldrin both by plants and animals (Ritter *et al.*, 1995).

Since one of the major uses of aldrin is for soil insecticide, aldrin-treated soil constitutes a considerable source of aldrin in the environment (WHO/IPCS, 2004).

2.1.2 Chlordane

Chlordane is a broad spectrum contact insecticide that has been used on agricultural crops including vegetables, small grains, maize, other oilseeds, potatoes, sugarcane, sugar beets, fruits, nuts, cotton and jute. It has also been used extensively in the control of termites (Ritter *et al.*, 1995).

Chlordane has been released into the environment primarily from its application as an insecticide (National Library of Medicine, USA, 2004).

2.1.3 DDT

DDT was widely used during the Second World War to protect the troops and civilians from the spread of malaria, typhus and other vector borne diseases. After the war, DDT was widely used on a variety of agricultural crops and also for the control of disease vectors. It is still being produced and used for vector control. The largest agricultural use of DDT has been on cotton. DDT is still used to control mosquito vectors of malaria in numerous countries (Ritter *et al.*, 1995).

Because DDT has been sprayed on people, domestic animals, buildings, agricultural crops, and forests, it is now distributed widely in the environment (WHO/IPCS, 2004).

Table 3

Some POPs pesticides stocks in countries of the Mediterranean region (FAO, 2004)

Country	Location	Common name	Commercial name	Container Type	Qty. Kgs	Year
Algeria	Ain temouchent	DDT	DDT	Kraft	5000	
Algeria	Alger	DDT	DDT	Plast	1000	
Algeria	Mustaganem	DDT	DDT	Kraft	180000	
Algeria	Sidi bel abbas	DDT	DDT	Kraft	2000	
Algeria	Tizi ousou	DDT	DDT	Kraft	800	
Algeria	Mascara	DDT	Magirol	Metal	1000	
Algeria	Mascara	DDT	Magirol	Metal	400	
Algeria	Tipaza	DDT	S.clodet	Kraft	425	
Algeria	Tizi ousou	DDT	Sectum	Kraft	275	
Algeria	Tipaza	Aldrin	Aldrex	Metal	25	
Algeria	Alger	Aldrin	Aldrex	Metal	320	
Libya	Tripoli-Bengazi-Locust	Dieldrin	Dieldrin	Carton	20	1975
Morocco	?	Heptachlor	Heptachlor	?	2626	
Morocco	?	Mixture Prophenophos+DDT	Prophenophos+DDT	?	10	
Morocco	?	Mixture Triazophos+DDT	Triazophos+DDT	?	69	
Morocco	?	Endrin	Endrin	?	122	
Morocco	?	Dieldrine	Dieldrine	?	130	
Morocco	?	Dieldrine	Dieldrine	?	750	
Morocco	?	DDT	DDT	?	2062	
Syria	Hamah	DDT	DDT	Carton	1500	

2.1.4 Dieldrin

Dieldrin has been used in agriculture for the control of soil insects and several insect vectors of disease but this latter use has been banned in a number of countries because of environmental and human health concerns (Ritter *et al.*, 1995). It is believed that Dieldrin is no longer produced. Despite this, it may still be in use in some countries where it is available from old stockpiles (Abildgaard, 2000).

The former production and use of Dieldrin as an insecticide resulted in its direct release into the environment. Dieldrin is also a degradation product of the insecticide Aldrin, and the former use of Aldrin has contributed to the occurrence of Dieldrin in the environment

(National Library of Medicine, USA, 2004).

2.1.5 Endrin

Endrin is a foliar insecticide used mainly on field crops, such as cotton and grains. It has also been used as a rodenticide to control mice and voles (Ritter *et al.*, 1995).

Endrin is not believed to be available on the market. However, use from stockpiles may still occur (Abildgaard, 2000).

Former production and use of Endrin as an insecticide, rodenticide and avicide has resulted in its widespread environmental release (National Library of Medicine, USA, 2004).

2.1.6 Heptachlor

Heptachlor is a non-systemic stomach and contact insecticide, used primarily against soil insects and termites. It has also been used against cotton insects, grasshoppers, some crop pests and to combat malaria (Ritter *et al.*, 1995).

Its production and former use in termite control, seed/seed furrow treatment, and wood treatment did result in its direct release to the environment (National Library of Medicine, USA, 2004).

2.1.7 Hexachlorobenzene

Historically, HCB had many uses in industry and agriculture. The major agricultural application for HCB used to be as a seed dressing for crops, such as wheat, barley, oats and rye to prevent growth of fungi. The use of HCB in such applications was discontinued in many countries in the 1970s owing to concerns about adverse effects on the environment and human health. HCB may continue to be used for this purpose in some countries. For example, HCB was still used in 1986 as a fungicide, seed-dressing and scabicide in sheep in Tunisia (Jemaa *et al.*, 1986). Industrial purposes and other emission sources are discussed in section 4.1.

2.1.8 Mirex

Mirex is mainly used as a flame-retardant and as a stomach insecticide, formulated into baits, for the control of ants, especially fire ants and harvester ants. The same chemical substance has also been used, under the name Dechlorane, as a fire retardant in plastics, rubbers, paints, etc. (WHO/IPCS, 2004).

Release into the environment has occurred via effluents from manufacturing plants and sites where Mirex was utilized as a fire resistant additive to polymers, and at points of application where it was used as an insecticide (National Library of Medicine, USA, 2004).

2.1.9 Toxaphene

Toxaphene is a non-systemic and contact insecticide that was used primarily on cotton, cereal grains, fruits, nuts and vegetables. It has also been used to control ticks and mites in livestock (Ritter *et al.*, 1995).

Its production and use as an insecticide has resulted in its direct release into the environment (National Library of Medicine, USA, 2004).

2.2 Effects on health and environment

2.2.1 Properties

POPs pesticides are semi-volatile, they are transported over long distances and their residues are now found as pollutants all over the world. This volatility is greater in tropical than in moderate or cold climates, and they eventually end up being trapped in the coldest parts of the planet.

The persistent nature of POPs pesticides is demonstrated by their slow rate of degradation in soil, particularly in cold climates. Their half-life sometimes extends over more than a decade. Several metabolites of POPs pesticides are stable and toxic as well.

Another property of these compounds is their solubility in fatty substances and tissues, which leads to their accumulation in body fat. Concentrations will further increase hundreds of times through food webs. At the higher consumer levels in such webs, harmful effects such as egg thinning have been observed. These are thought to reflect a broader range of more insidious disruptive impacts on vertebrate endocrine systems.

Low levels of POPs in the environment can equally cause disturbances to organisms. Studies on predatory birds, aquatic mammals (i.e. dolphins and whales) and laboratory rodents have shown effects such as immunotoxicity, carcinogenicity and reproductive disorders (Mörner *et al.*, 2002)

2.2.2 Toxicity

Although all POPs pesticides are toxic to humans, acute toxicity varies – Endrin being the most toxic, while others such as Heptachlor and HCB are less acute. Acute toxicity is a property POPs pesticides share with other pesticides. Many insecticides and nematicides of the organophosphate and carbamate groups have much higher acute toxicity than the “worst” POPs. The decisive criteria for compounds to be included on the POPs list, however, have been their persistence and bio-accumulation, and consequently, their long-term toxicity.

Chronic adverse effects of pesticides on human health, due to prolonged periods of exposure, were first recognised in the 1960s. Several of the POPs pesticides are carcinogenic in experimental animals and are, therefore, possibly carcinogenic to humans. It is also suspected that some depress the immune system (Repetto and Baliga, 1996). Toxicity values (LD50) and established or seriously suspected health effects of the current POPs pesticides collected from Mörner *et al.*, 2002, are summarized in Annex II.

More recently, the health hazard presented by prolonged low-level exposure has become a matter of concern. There is a suspected link to disruptions of the endocrine system, whereby pesticides mimic or block normal hormone activity. Such hormones include androgen, oestrogen and testosterone.

Since the introduction of persistent organic pesticides new hazards have been discovered with great regularity, adding to the accumulated weight of evidence of the risks they represent for global ecology and health (Mörner *et al.*, 2002).

Box 1 Example of effects on health and environment (IOMC, 2002)

Taking the example of DDT, there is conclusive evidence that:

- populations of birds of prey declined already in the 1960s as a result of eggshell-thinning. This was caused by DDE, a very stable metabolite of DDT.
- DDT disturbs sexual development and behaviour in birds, such as gulls.

And there are strong indications that:

- the capacity of the immune system is impaired by DDT and also by certain synthetic pyrethroids - pesticides that have been promoted as DDT alternatives.
- the nervous system can suffer permanent damage from exposure during the foetal stage or early in life.
- lactation in women can be impaired by DDT/DDE - providing a possible link to oestrogen mimicry.

2.3 Development and use of substitutes

The main source of information on alternatives to POPs pesticides is the UNEP database (UNEP/POPs, 2004), which includes reference information on the different alternative approaches to POPs pesticides: chemical substitutes, biological control, physical barriers and integrated pest management for each pesticide within specific areas of use. The other sources of information consulted, assess advantages and disadvantages from existing alternatives.

According to all information sources consulted, POPs pesticides alternatives should be classified into two main groups: substitution by other chemicals or adoption of alternative measures.

2.3.1 Chemical substitutes

As for chemical substitutes, Table 4 shows a brief summary of the possible chemical alternatives to POPs pesticides which have been proposed by the sources consulted: assessment report of the Canadian Network of Toxicology Centres for the IPCS (Ritter *et al.*, 1995), report of the Nordic Chemical Group (Abildgaard, 2000) and UNEP database (UNEP/POPs, 2004).

All the above chemicals are feasible substitutes to POPs pesticides. However, according to the same sources, most of these chemical alternatives can present risks to human health and the environment.

Table 4

Summary of chemical substitutes of POPs pesticides

Persistent Organic Pollutant	Chemical substitute
Aldrin	acephate, carbaryl, carbofuran, carbosulfan, chlorpyrifos, cypermethrin, diazinon, endosulfan, isofenphos, malathion, methomyl, permethrin, phorate, pirimiphos-methyl, pyrethrum, resmethrin
Chlordane	acephate, alphamethrin, bendiocarb, carbaryl, carbofuran, carbosulfan, chlorpyrifos, creosote, cyfluthrin, cyromazine, endosulfan, deltamethrin, diazinon, dichlorvos, fenithion, fenitrothion, fonofos, isazophos, malathion, permethrin, propoxur, phorate, pyrethrin, phoxim, trichlorphon
DDT	acephate, alphacypermethrin, bendiocarb, carbaryl, chlorpyrifos, cyfluthrin, deltamethrin, demethoate, diazinon, dichlorvos, dicofol, endosulfan, etofenprox, esphenvalerate, ehyil azinphos, fenthion, fenitrothion, fluvalinate, lambda-cyhalothrin, malathion, methamidophos, methomyl, metidathion, monocrotophos, perm ethrin, phorate, phosmet, pirimiphos-methyl, propoxur, rotenone, sulfur, thiodicarb, trichlorphon
Dieldrin	acephate, ethyl-azinphos, bendiocarb, bromophos, carbaryl, carbofuran, chlorpyrifos, cyfluthrin, deltamethrin, diazinon, dichlorvos, endosulfan, ethyl-pirimphos, fenitrothion, fenthion isazofos, malathion, methomyl, monocrotophos, permethrin propoxur, prothiophos, pyrethrin, sulprophos
Endrin	carbaryl, chlorpyrifos, endosulfan
Hexachlorobenzene	bitertanol, carboxin, fuberidazol, quazatine
Heptachlor	acephate, bendiocarb, carbaryl, carbofuran, carbosulfan, chlorpyrifos, cyfluthrin, diazinon, dichlorvos, ehyil-azinphos, ethyl-pirimphos, etoprofos, terbufos
Mirex	carbaryl, deltamethrin, diazinon, diflubenzuron, sulfuramid
Toxaphene	alachlor, chlorpyrifos, demethoate, trifluralyn, metribuzin

The *Nordic Chemical Group* report (Abildgaard, 2000) describes the effects of the three groups of chemicals, organophosphorous insecticides, carbamate insecticides and synthetic pyrethroids (more often used as alternatives to POPs pesticides), as well as the group of chlorinated hydrocarbon pesticides, as follows:

1. *Organophosphorous*: Acephate, chlorpyrifos, diazinon, phorate, fenitrothion and malathion are examples of insecticides belonging to this group. The compounds have a potential for bioaccumulation, which is considered to be of a lower magnitude than for the POPs pesticides. This group of insecticides degrades by hydrolysis and by the activity of microorganisms in soil and water, so they are not considered persistent in the environment.
Many of these insecticides are supposedly highly toxic to aquatic organisms, mammals and birds; moreover, they may be absorbed through all routes of exposure by humans.
2. *Carbamates*: Carbofuran, carbosulfan, bendiocarb, carbaryl and propoxur are examples of insecticides from this group. Carbamates act in two ways, as a contact insecticide (kills the insect by direct contact) and as a systemic insecticide to cause overall systemic poisoning in insects. The bioaccumulation potential is rather low and

they are not considered persistent in the environment.

Some carbamates are highly toxic to aquatic organisms and also to birds, earthworms, honeybees and other non-target arthropods. Toxicity to humans is based on the same mechanisms as for organophosphates (acetyl cholinesterase inhibition) and the toxicity signs are similar. However, the effects are shorter in duration than for organophosphates because carbamates generally are excreted rapidly

3. *Synthetic pyrethroids*: Alphacypermethrin, cyfluthrin, deltamethrin, etofenprox and permethrin are examples of insecticides from this group. Pyrethroid insecticides kill insects by contact and through digestion. Synthetic pyrethroids are rather rapidly degraded in soil and plants. They are strongly adsorbed on soil and sediments. Synthetic pyrethroids are highly toxic to aquatic organisms. Although toxicity is reduced under field conditions (mainly due to adsorption to sediment) the toxicity to aquatic organisms remains a problem. The synthetic pyrethroids are generally less toxic to humans than organophosphates and they require less safety precautions
4. *Chlorinated hydrocarbon*: all POPs pesticides belong to this group. Lindane, endosulfan and mehtoxychlor have similar properties. These insecticides are contact poisons used for a wide variety of insects and mites.

Both endosulfan and lindane have a potential for bioaccumulation and are persistent in the environment. Both compounds are highly toxic to aquatic organisms. Endosulfan is moderately/highly toxic to birds, and lindane also poses a risk to birds. Human effects can occur from inhalation, ingestion or skin absorption. Furthermore, it should be highlighted that lindane is prohibited in the European Union (except for some specific uses as a public health insecticide) by Regulation 850/2004; restricted by the Protocol to the 1979 Convention on long-range transboundary air pollution on POPs, and is likely to be included in the Stockholm Convention in the near future (see section 6 for further regulations).

Due to the above-mentioned effects, the *Nordic Chemical Group* report (Abildgaard, 2000) states that the use of alternative pesticides requires workers to be protected during manufacturing, formulation and application. Moreover, inappropriate dosages, spray drift, spillage and disposal may lead to exposure of the general public, non-target species, water and soil.

Before the selection of alternative pesticides, there should be an evaluation at local level of relevant dosage and application technique, as well as the need for protective clothing and equipment in order to avoid adverse environmental and health effects. Relevant activities to prevent adverse effects generally include:

- information
- public awareness raising
- training and education

Financial support will, in many cases, be necessary in order to perform the above-mentioned precautionary activities.

According to the "Beyond POPs" report from Pesticide Action Network (PAN Germany, 2001), the chemical substitutes of the POPs pesticides listed in the UNEP "POPs Database on Alternatives" are dangerous to human health and the environment and cannot be seen as sustainable alternatives. Out of the 60 evaluated chemical substitutes listed as "alternatives" to POPs pesticides in the UNEP "POPs Database on Alternatives", the same report highlights, among other conclusions, that:

- 7 have been classified for their acute toxicity as "extremely hazardous" by the World Health Organisation (alachlor, aldicarb, disulfoton, fonofos, parathion, phorate and fosfamidon);

- 17 have been classified for their acute toxicity as “very toxic” the European Union (aldicarb, azinphos-methyl, carbofuran, chlorfenvinphos, cyfluthrin, dichlorvos, dicrotophos, disulfoton, fonofos, isazophos, lambda-cyhalothrin, methamidophos, methomyl, monocrotophos, parathion, phorate and phosphamidon); and
- 2 two are known to cause cancer in animals (lindane and propoxur) and 11 are possibly carcinogenic to humans (acephate, bifenthrin, carbaryl, cypermethrin, dichlorvos, dimethoate, ethofenprox, parathion, permethrin, phosphamidon, tryfluralin) according to the U.S. EPA Office of Pesticide Programmes.

Furthermore, thirty-eight of the evaluated chemical substitutes have been classified as “Dangerous for the Environment” by the European Union and assigned with the symbol “N”.

As the chemical substitutes listed in the UNEP “POPs Database on Alternatives” will be used under conditions of poverty - under conditions where a safe use of pesticides cannot be ensured - PAN Germany does not recommend the use of any of the 60 pesticides as ‘alternatives’ for the nine POPs pesticides.

2.3.2 Alternative measures

Alternative measures are generic management tools which minimize or eliminate the need for pesticides. In principle, they can be implemented in place of any type of pesticide. Proposals extracted from the Nordic Chemical Group report (Abildgaard, 2000) are based on:

Environmental Management - a management approach to reduce the overall environmental impacts (on nature, wildlife and humans). The aim is to reduce environmental impacts of the suggested vector control measures. Reduction of environmental impacts may include the application of the substitution principle, reduction of the amounts of chemicals used (frequencies and/or concentrations) or the selection of an alternative non-chemical solution.

Three major approaches are used in Environmental Management in disease vector control:

- modification of the environment to create a long-term change of the disease vector's habitat;
- creation of temporary or repeated changes in the habitat to adversely affect the vector population; and
- reduce man-vector contact by changes in building (house) constructions, changes in human behaviour or divert vectors from man to farm animals.

Integrated Pest Management (IPM) - combines a better pesticide application regime with biological control and other ecological and biological crop protection techniques. This results in reduced use of pesticide. Integrated Pest Management (IPM) uses a mix of approaches to control pests. The approaches include cultural, mechanical, biological and chemical control by the use of synthetic pesticides.

Integrated Vector Management (IVM) - represents the use of alternative pesticides, targeted pesticide use, and non-pesticide vector control methods. The alternative solutions to control malaria and other diseases transmitted by insects are all based on an IVM approach, which includes environmental management and biological control rather than the use of insecticides.

All three approaches are characterised by leading to a decrease in pesticide use. The alternatives should, in each case, be evaluated at the local level and should be regarded as ideas for the further development of alternative measures.

Some examples of alternative measures are summarised in Table 5 and were collected from the World Wildlife Fund (WWF, 1999).

Table 5

Integrated Pest Management and Integrated Vector Management tools

Integrated Pest Management tools	Integrated Vector Management tools
<p>Cultural controls</p> <ul style="list-style-type: none"> • the use of crop rotation or crop mixtures to increase crop diversity • timed planting dates to avoid pests <p>Mechanical and physical controls</p> <ul style="list-style-type: none"> • pest barriers • insect traps <p>Biological controls</p> <ul style="list-style-type: none"> • direct introduction of natural enemies of the pest such as predators, parasites and disease pathogens • indirect encouragement of already present enemies <p>Bio-rational methods</p> <ul style="list-style-type: none"> • deployment of pheromones to trap pests or disrupt mating • release of sterilized insects to limit reproduction • manipulation of the atmosphere in closed storage areas to kill pests <p>Chemical controls</p> <ul style="list-style-type: none"> • the use of less toxic pesticides as a last alternative 	<ul style="list-style-type: none"> • bed nets and traps impregnated with synthetic pyrethroids (which are not as persistent and bio-accumulative as DDT) • application of biological insecticides • release of natural enemies of vectors • elimination and management of vector breeding sites • physical barriers such as mosquito nets and screens on doors and windows

3. PCB

3.1 Source characterization

The main use of PCBs has been for dielectric insulating materials in electrical equipment such as capacitors and transformers. However, products containing PCBs have had many other applications, as shown in Table 6.

According to the Helsinki Commission (HELCOM, 2001) the main PCB emission sources at present are:

- leakage and spillage from equipment containing PCB still in use or stored;
- fires and accidents at sites where equipment containing PCB is still in use or stored;
- inappropriate disassembling of equipment containing PCB;
- improper waste disposal;
- various thermal processes (production, waste incineration, burning of fuel, etc.);
- open applications (e.g. products in buildings); and
- "uncontrolled" applications (e.g. small capacitors in household appliances).

Table 6

Applications of PCBs (OSPAR, 2004)

Category	Application
Closed system	Transformers Capacitors
Circulatory systems	Hydraulic oils Thermal oils Lubricating oils
Open systems	Plasticiser for rubber Plasticiser for synthetic resins Carbonless copy paper Adhesives Paints, printing inks, sealants

Like Dioxins, Furans and Hexchlorobenzene, PCBs can be emitted unintentionally from various thermal processes. De-novo synthesis of PCB may occur in the presence of impurities with chlorine compounds and organic components (OSPAR, 2004). For this reason, potential sources of unintentional PCBs are the same as the ones described for Dioxins, Furans and Hexachlorobenzene (see section 4.1).

However, the European Environment Agency (EMEP/CORINAR, 2001) states that the majority of emissions of PCBs arise from leaks from electrical transformers and capacitors which contain PCBs and which are in a poor condition and/or are poorly maintained. It is likely that the oil in some transformers that were not originally deliberately filled with PCBs has become contaminated with PCBs. The source of this contamination is likely to be the lack of segregation in the past of oil and PCB-filling lines at manufacturers' works, and the subsequent use of recycled oil.

As for the Mediterranean Region, PCB-containing equipment has been widely used. The first regulation on PCBs was applied by the EEC was in 1976 when their usage was restricted to closed circuits. The second regulation was applied in 1985 when the use of PCB as a raw material or chemical intermediate was banned. Finally, in 1987, the use of PCBs was completely banned in new closed circuits and a Directive issued in September 1996 (96/59) imposed total elimination before December 2010 (UNEP Chemicals, 2001).

PCBs are part of the PIC procedure followed by most countries of the region. In spite of legislation in force, there are still large amounts of PCB in use. This is because in many countries (e.g. Algeria, Croatia, FYR of Macedonia, Morocco and Slovenia), exemptions exist for restricted uses in devices in use for long durations. Moreover, there are stockpiled amounts waiting to be eliminated (UNEP Chemicals, 2001).

3.2 Effects on the health and environment

3.2.1 Properties

The value of PCBs for industrial applications is related to their chemical inertness, resistance to heat, non-flammability, low vapour pressure and high dielectric constant. There are 209 possible PCBs, from three monochlorinated isomers to the fully chlorinated decachlorobiphenyl isomer. Generally, the water solubility and vapour pressure decrease as the degree of substitution increases, and the lipid solubility increases with increasing chlorine substitution. PCBs in the environment may be expected to associate with the organic

components of soils, sediments, and biological tissues, or with dissolved organic carbon in aquatic systems, rather than being in solution in water. PCBs volatilize from water surfaces in spite of their low vapour pressure and partly as a result of their hydrophobicity; atmospheric transport may, therefore, be a significant pathway for the distribution of PCBs in the environment (Ritter *et al.*, 1995).

3.2.2 Toxicology

PCBs have a long and documented history of adverse effects on wildlife. They have been associated with poor reproductive success and impaired immune function of captive harbour seals in the Arctic. After a major flood in the Saginaw River basin in Michigan in 1986 allowed PCB contaminants to spread through the ecosystem, the following year's hatch rate of Caspian terns in the area dropped by more than 70 percent. Hatching chicks showed developmental deformities, and none survived more than five days. Hatch ability of this Caspian tern colony did not show recovery after three more breeding seasons.

Acute effects of PCB exposure in humans were documented following ingestion of contaminated rice oil in Japan in 1968 and Taiwan in 1979. Long-term studies of the more than 2,000 people who were exposed during these events revealed increased mortality due to PCB intake. A positive association was established between PCB dosing and acute liver damage, with liver disease being the cause of death in a significant number of exposed people. Acute exposure to PCBs has also caused chloracne, a chemically induced acneform eruption (Orris *et al.*, 2000).

3.3 Development and use of substitutes

Although PCB has been substituted in many countries, it is still present in numerous existing products and closed electrical systems. Table 7 presents the alternatives used for specific purposes, according to the Nordic Chemical Group report (Abildgaard, 2000).

Table 7

PCB alternatives (Abildgaard, 2000)

Use	Alternative
Dielectric fluid in transformers	Alternative design (encapsulated transformers, etc) Mineral oils Silicone oils Tetrachlorobenzene Chlorinated diphenylethane Chloroalkylene Biphenyl
Dielectric fluid in capacitors	Mixture of methyl (phenylmethyl)benzene and methylbis (phenylmethyl) benzene Phenylxylene Alternative design for small capacitors
Heat exchange fluid	Mineral oil Silicone oil Biphenyl Diphenyl oxide
Hydraulic fluids	A vegetable based oil (turnip oil)

Dielectric fluids represent the major PCB application in the past (Swedish National Chemicals Inspectorate, 1996). The most frequently used alternatives for transformers are mineral oils, silicone oils and ester-based materials, but other alternatives may also be in use.

PCBs also serve as insulators in capacitors that store electrical charges. According to the World Wildlife Fund (WWF, 1999), mineral oils, silicone oils, and ester based materials can also be used as substitutes in this application, as can decylbenzene and phenylxylethane, two additional chemicals with low toxicity and persistence.

According to the same source (WWF, 1999), alternatives also exist for other PCB uses such as heat exchange fluids, hydraulic fluids, lubricants, and plasticizers used to make plastics and other products flexible. Mineral oils or silicone oils are alternative heat exchange fluids. Sealants and paints that use PCBs as plasticizers can be replaced by products like polyurethane and polysulfides, which do not require plasticizers. Vegetable-based compounds, such as turnip oil, can replace PCBs in hydraulic fluids.

The Swedish Environmental Protection Agency (Swedish National Chemicals Inspectorate, 1996) states that the main drawback with compounds like biphenyl and ditolylether, is a relatively high toxicity to aquatic organisms. They are, on the other hand used in closed systems and furthermore, are readily biodegradable. However, the main options for avoiding PCBs and similar products are not necessarily the more acceptable chemical substitutes, but the introduction of alternative engineering designs. Thus, resin (glass, nomex, high temperature potting compounds) encapsulated transformers equipped with air cooling can be used instead of PCB-containing (askarels) transformers.

Although technically appropriate, some chemical substitutes have proved to be inadequate because of their toxicological and ecotoxicological properties, which are similar to those of PCBs. Some examples are polychlorinated terphenyls (PCTs), alkyl-substituted chlorodiphenyls and polychlorinated naphthalenes (PCNs).

Other chemical substitutes considered hazardous by the World Wildlife Fund (WWF, 1999) are: Butylated monochlorodiphenyl ether; Chloralkylenes; Chlorinated benzenes; and Chlorinated hydrocarbons.

As for unintentional emissions (as PCBs are generated by the same processes which release Dioxins and Furans and Hexachlorobenzene), efforts to minimise such emissions are also likely to substantially reduce emissions of PCBs (mainly elimination of chlorine precursors and Best Available Techniques), which have been elaborated in 5.3.

4. HEXACHLOROBENZENE

4.1 Source characterisation

The main non-pesticide uses of HCB (see section 2.1.7 for pesticide uses) have been:

- as a wood-preserving agent;
- in the manufacture of pyrotechnics and tracer bullets;
- fluxing agent in the manufacture of aluminium;
- porosity-control agent in the manufacture of graphite anodes; and
- peptizing agent in the production of nitroso and styrene rubber for tyres.

According to the Swedish Environmental Protection Agency (Swedish National Chemicals Inspectorate, 1996) and WHO (WHO/IPCS, 2004), HCB is not likely to be manufactured for any of the above industrial purposes.

However, HCB is also generated as a waste by-product during the manufacture of chlorinated solvents, chlorinated aromatics and pesticides (WHO/IPCS, 2004):

- HCB is a waste by-product from the production of pentachloronitrobenzene (PCNB), chlorothalonil and dacthal and from the production of pentachlorophenol, atrazine, simazine, propazine and maleic hydrazide. These pesticides are also known to contain HCB as an impurity in the final product, usually at levels of less than 1% HCB when appropriate procedures are used for the synthesis and purification stages.
- In the manufacture of chlorinated solvents (mainly carbon tetrachloride, trichloroethylene and tetrachloroethylene) HCB is formed as a reaction by-product of thermal chlorination, oxychlorination, and pyrolysis operations.

The chlor-alkali industry produces chlorine (Cl_2), hydrogen and caustic soda (NaOH) by electrolysis of purified and concentrated sodium chloride (NaCl). Processes using graphite anodes are known to produce HCB as a by-product, owing to the reaction of chlorine with graphite anode materials such as carbon and oils. Depending on the purification procedures, the final products might also be contaminated with HCB (WHO/IPCS, 2004).

Heating and combustion processes involving organic matter, chlorine compounds and a catalyst, like PCBs and dioxins and furans, are also important sources of unintentional HCB in the environment (WHO/IPCS, 2004).

According to the Stockholm Convention, the following industrial source categories have the potential for comparatively high formation and unintentional release of dioxins and furans, PCBs and hexachlorobenzene into the environment:

- Waste incinerators, including co-incinerators of municipal, hazardous or medical waste or of sewage sludge;
- Cement kilns firing hazardous waste;
- Production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching; and
- The following thermal processes in the metallurgical industry:
 - Secondary copper production;
 - Sinter plants in the iron and steel industry;
 - Secondary aluminium production; and
 - Secondary zinc production.

Furthermore they may also be unintentionally formed and released from the following source categories, including:

- Open burning of waste, including burning of landfill sites;
- Thermal processes in the metallurgical industry not mentioned in Part II;
- Residential combustion sources;
- Fossil fuel-fired utility and industrial boilers;
- Firing installations for wood and other biomass fuels;
- Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil;
- Crematoria;
- Motor vehicles, particularly those burning leaded gasoline;

- Destruction of animal carcasses;
- Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction);
- Shredder plants for the treatment of end of life vehicles;
- Smouldering of copper cables; and
- Waste oil refineries.

4.2 Effects on health and environment

4.2.1 Properties

HCB is highly insoluble in water and is soluble in organic solvents. It is quite volatile and can be expected to partition into the atmosphere as a result. It is very resistant to breakdown and has a high partition coefficient (KOW=3.03-6.42), and is known to bioconcentrate in the fat of living organisms as a result (Ritter *et al.*, 1995).

4.2.2 Toxicology

Acute high dose exposure to HCB is associated with porphyria cutanea tarda due to its liver toxicity. In Turkey, people exposed to HCB-contaminated flour developed this condition and although most recovered after exposure ceased, some continued to experience porphyria through several years of follow-up. HCB is also associated with enlarged thyroid glands, scarring, and arthritis exhibited in offspring of accidentally exposed women. Children born to mothers known to have ingested HCB-tainted food during pregnancy, experienced acute illnesses and rashes. These children were additionally exposed through breast milk. Follow-up studies reported porphyria cutanea tarda, reduced growth, and arthritic symptoms in children directly exposed to contaminated bread or mothers' milk. There was also a 37 percent prevalence of enlarged thyroids. Finally, HCB has been shown to alter a white blood cell function following occupational exposure, although the clinical meaning of this finding is not clear (Orris *et al.*, 2000).

4.3 Development and use of substitutes

The UNEP Database on POPs Alternatives (UNEP/POPs, 2004) does not provide alternatives for HCB uses other than agricultural (see 2.2).

Regarding industrial uses, the Swedish National Chemicals Inspectorate report (Swedish National Chemicals Inspectorate, 1996) states that HCB has been replaced by chlorine gas in aluminium smelting. Graphite anodes have been replaced by dimensionally stabilized anodes (DSA), which do not generate HCB. In addition, the Nordic Chemical Group (Abildgaard, 2000) reports that Hexachloroethane may be used as a replacement for HCB for military pyrotechnics.

Aside from past pesticide use, the global burden of HCBs derives largely from the unintentional emissions of HCB as a by-product of industrial chemical processes involving chlorine, including the production of solvents such as perchloroethylene, trichloroethylene, and carbon tetrachloride.

Alternatives such as a new generation of petroleum solvents and water-based or mechanical cleaning methods will allow chlorinated solvents to be phased out. Dry cleaners, which constitute the largest use of perchloroethylene, can shift to multi-process wet cleaning or "GreenClean." Instead of chlorinated solvents, this process relies on a combination of heat, steam, vacuum, water, and natural soaps to clean clothing (WWF, 1999).

Finally, as HCB is often an impurity in pesticides, a reduction in the use of pesticides will reduce HCB emissions. Similarly, initiatives to reduce the emission of dioxins (developed in section 5.3) will have the added benefit of reducing HCB emissions (Abildgaard, 2000).

5. DIOXINS AND FURANS

5.1 Source characterisation

Neither dioxins nor furans are produced commercially, and they have no known use. Like unintentional emissions of PCBs and hexachlorobenzene, the main sources of dioxins are heating and combustion processes involving organic matter, chlorine compounds and a catalyst (usually copper). In reality, formation of trace concentration of dioxins may take place in any fire or combustion process based on natural or man-made organic materials, inclusive of fossil fuels. Dioxins are also by-products resulting from the production of other chemicals such as pesticides and other chlorinated substances, e.g. chlorophenols.

Sources of dioxins can be industrial or diffuse (inherent to the life cycle of products). Traditionally, municipal solid waste, medical waste and hazardous waste incineration were considered the major emission sources of dioxins and furans. However, according to OSPAR (OSPAR, 2002), diffuse sources and secondary sources have become the most important at present.

According to the Stockholm Convention, the following industrial source categories have the potential for comparatively high formation and release of dioxins and furans, PCBs and hexachlorobenzene unintentionally to the environment:

- Waste incinerators, including co-incinerators of municipal, hazardous or medical waste or of sewage sludge;
- Cement kilns firing hazardous waste;
- Production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching; and
- The following thermal processes in the metallurgical industry:
 - Secondary copper production;
 - Sinter plants in the iron and steel industry;
 - Secondary aluminium production; and
 - Secondary zinc production.

Furthermore, they may also be unintentionally formed and released from the following source categories:

- Open burning of waste, including burning of landfill sites;
- Thermal processes in the metallurgical industry not mentioned in Part II;
- Residential combustion sources;
- Fossil fuel-fired utility and industrial boilers;
- Firing installations for wood and other biomass fuels;
- Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil;
- Crematoria;
- Motor vehicles, particularly those burning leaded gasoline;
- Destruction of animal carcasses;
- Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction);
- Shredder plants for the treatment of end of life vehicles;
- Smouldering of copper cables; and

- Waste oil refineries.

As for incineration, currently two major mechanisms for PCDD/F (dioxins and furans) formation during incineration of wastes are known (UNEP, 2004):

- Formation of dioxins/furans in the presence of corresponding chlorinated precursors (such as PCBs, PCPs) by a homogenous gas phase reaction at temperatures between 300 and 800°C.
- De novo synthesis: The formation of PCDD/F takes place during cooling of the exhaust gas under the following conditions:
 - Temperature range between some 200 and 500°C and adequate residence time in this temperature range.
 - Presence of a chlorine source.
 - Presence of oxygen in the exhaust gas.
 - Presence of dust containing heavy metals and carbon which acts as catalyst.

Nevertheless, releases of dioxins and furans during thermal processes are not only affected by waste (or fuel) composition (dioxin precursors, chlorine, catalyst content) and combustion conditions (temperature, oxygen) but also by the cleaning process of the flue gases (filters, wet scrubbers, cooling) (OSPAR, 2002).

5.2 Effects on health and environment

5.2.1 Properties

Polychlorinated dibenzo para dioxins (dioxins) and polychlorinated dibenzofurans (furans) are two groups of planar tricyclic compounds that have very similar chemical structures and properties. They may contain between 1 and 8 chlorine atoms; dioxins have 75 possible positional isomers and furans have 135 positional isomers. At least twenty are considered highly toxic. The overall toxicity of a dioxin containing mixture is assumed to be the Toxic Equivalent (TEQ) of a stated amount of pure 2,3,7,8 - tetrachlorodibenzo-p-dioxin (TCDD), the most potent, hazardous and well-studied dioxin.

They are generally very insoluble in water, are lipophilic and are very persistent. The chemical properties of each of the isomers have not been elucidated, further complicating a discussion of their properties which vary with the number of chlorine atoms present (Ritter *et al.*, 1995).

5.2.2 Toxicity

There is substantial evidence to indicate that populations of wildlife species high on the food chain are suffering health damage caused by reproductive and developmental impairment due to background exposures to dioxins and related compounds. In the Great Lakes, exposure to dioxin-like compounds has been linked to large-scale hormonal, reproductive, and developmental impairment among numerous species of predator birds, fish and wildlife; these impacts are primarily transgenerational, affecting the offspring of the exposed organisms.

Approximately 90% of human exposure to dioxin comes from food, specifically in the form of beef, fish, and dairy products. Contamination in the food supply comes from dioxin particles that are deposited in water or soil and then proceed up the food chain through fish and livestock, ultimately reaching human tissues through the food we eat.

Dioxin bioaccumulates, becoming increasingly concentrated in living tissues as it moves up the food chain. Dioxins are known to be toxic at extremely low doses. Although on average Americans are exposed to only 1 to 3 picograms per kilogram of body weight per day (one picogram being one billionth of a gram), this level is comparable to doses used in laboratory studies resulting in adverse health effects in animals. Because a mother's milk is often highly contaminated, infants receive higher exposures. An average nursing infant receives 60 pg/kg/day of dioxin, not including dioxin-like PCBs. This is 10-20 times more than the average adult and, in the first year of life, 4-12 percent of his or her entire lifetime exposure. Daily exposure results in an accumulation of dioxins known as a body burden in oil soluble media such as lipids, breast milk, and blood.

A 1982 EPA study of dioxins in body fat from a representative sample of the U.S. population revealed an average body burden of 7,000 to 9,000 pg/kg of body weight (7-9 ppt). In most industrialized nations of the world, dioxin body burdens and exposures are in the same range, with levels assumed to be somewhat lower in developing nations, where little testing has been done. The U.S. EPA has found it difficult to define a safe dose of dioxin. The World Health Organization, however, recently lowered by more than half its tolerable daily intake. Fixed previously in 1990 at 10 picograms per kilogram of body weight for TCDD, the standard was reduced to 4 picograms based on the recognition that subtle effects may already occur in the general population in developed countries at levels of two to 6 picograms. Data on trends in dioxin contamination of human tissues are sparse, though one study found that levels might have decreased slightly in the 1980s following consistent increases during the preceding decades.

Chronic low-dose dioxin exposure can produce long-term health effects that permanently alter animal systems. Dioxins and furans have shown developmental and immuno-toxicity in animals, especially rodents. They have caused the alteration of estrogen, progesterone, testosterone, and thyroid hormone levels in several species, and have inhibited the action of estrogens in several species. They cause reductions in fertility, litter size, and uterine weights in mice, rats, and primates. In humans, there is evidence that high-level exposure to dioxins and furans can cause variations in serum lipid levels, microsomal enzyme induction, and gastrointestinal alterations. Other studies of high-level occupational exposure have found associations with some types of cancer, and have concluded that utero and lactational exposures to dioxins and furans are capable of affecting the hypothalamic/pituitary/thyroid regulatory system in human infants. According to the U.S. EPA, effects on humans, including hormonal and metabolic changes, have been documented at dioxin body burdens and exposures only slightly higher than those of the general population. A single cellular mechanism is thought to be responsible for the wide range of effects dioxin can have. It is believed that dioxins affect organisms by binding to pre-existing cellular receptors designed for hormones, entering the nucleus and then manipulating the on or off function of the gene. The genes affected by an imposter like dioxin contain codes for proteins, hormones, enzymes and growth factors, which collectively influence tissue development in the human body. This mechanism is the same in both humans and animals, allowing extrapolation from laboratory experiments involving dioxin effects on animals to a parallel human reaction (Orris *et al.*, 2000).

5.3 Development and use of substitutes

5.3.1 Reduction/substitution of materials with a high risk of unintentional POP formation

As dioxins and furans are emitted unintentionally, substitution is so often related to avoidance of those substances proved to lead to emissions of dioxins and furans during thermal processes involving chlorine, such as waste incineration. However, in most cases dioxins precursors are only avoidable through material sorting or pre-treatment because their

substitution is not feasible. In this case, these types of measures are considered as Best Environmental Practices rather than substitution.

The relevancy of chlorine content in waste, as well as its chemical form, in dioxin formation has been widely studied and discussed by different information sources. Most of them support substitution of dioxin precursors to avoid dioxin emissions:

1. The UNEP Database on POPs Alternatives (UNEP/POPs, 2004) supports substitution of chlorinated precursors as an alternative to avoid unintentional dioxins and furans. Technological alternatives and other best practices are also taken into account.
2. The Stockholm Convention on persistent organic pollutants establish (Article 5) the reduction of emissions of substances listed in annex C (dioxins and furans, hexachlorobenzene and PCBs) by applying Best Available Techniques (BATs) and Best Environmental Practices (BEPs). Among them, substitution of POPs known to be dioxin precursors and avoidance of elemental chlorine are highlighted.
3. The Nordic Chemical Group report (Abildgaard, 2000) recommends alternative measures based both on avoidance of dioxin precursors and Best Available Technologies (BATs) and practices to reduce dioxins and furans emissions, in particular:
 - Materials policy;
 - Substitution of materials producing dioxins and furans, e.g. chlorinated pesticides and chlorine-based materials;
 - Cleaner technology processes;
 - Avoiding the use of additives (e.g. flame retardant in plastic) containing chlorine or bromine;
 - Separation of waste before waste burning (remove chlorine-based materials from the waste); and
 - Waste reduction (recycling/reuse of materials).
4. The OSPAR report (OSPAR, 2002) states that higher chlorine content has a potential for the formation of more dioxins. However, the chemical form is not always so important if the substance concerned is not directly a dioxin precursor. The occurrence of precursors such as chlorophenols, chlorobenzenes, chlorodiphenyl ethers and PCBs are said to accelerate the dioxin formation.
5. The World Wildlife Fund (WWF, 1999) states that the manufacture, use, and destruction of PVC plastic are a major source of global dioxin emissions. PVC contributes to dioxin emissions from municipal waste incinerators, which is the largest dioxin source. The same source states that techniques developed to capture emissions from the stack do not eliminate dioxins as they shift the contamination to another part of the environment - from air to incineration ash or water discharge.
6. On the other hand, the World Chlorine Council (WCC, 1998) and a TNO report (Rijpkema, 1999) states that there is no significant relationship between PVC content and dioxins emissions; and Eurochlor (Eurochlor, 2003) states that there is no relationship between chlorine in incinerator feeds and dioxin emissions from waste incinerators, thus the only way to effectively control the dioxin emissions is to apply Best Available Techniques.
7. Furthermore, according to the *Club Español de Residuos* (Spanish Waste Club), research carried out by Holderbank and exposed during the recent International

Dioxin and Waste Conference, dioxins and furans emissions are not produced above detection limits (0.06 ng-ITEQ/m³ approximately) from pre-heaters and calcinators of clinker furnaces given an adequate operation. In addition, the type of fuel used (fossil or alternative) does not influence the formation or emission of dioxins and furans.

So, there is a lack of consensus on the effectiveness of preventing the dioxins precursors. However, on the basis of available information, the three main examples related to substitution of dioxins precursors by other type of substances that can be developed in more detail are: substitution of PVC plastics in incineration processes; substitution of elemental chlorine in pulp bleaching; and, substitution of Pentachlorophenol (PCP) in textile and leather finishing, which are described as follows.

5.3.1.1 Substitution of PVC in waste incineration

PVC has been indicated as a dioxins precursor in incineration processes. According to the World Wildlife Fund (WWF, 1999), PVC plastic can generally be replaced by other plastics that do not contain chlorine, such as the polyolefins PE and PP, the newly developed bioplastics, or more traditional materials such as wood, metal, paper, glass, and ceramics. Hospitals are a particularly large user of disposable PVC plastic; some of the specific alternatives for medical uses of PVC are listed in Table 8.

Table 8

Alternatives for medical use of PVC

Use	Alternative
Ambulatory assistance device	All steel frame
Breathing masks	Rubber, silicon
Examination gloves	PE and/or PE copolymers, nitrile
Film for collection bags	Polyolefin plastomer
IV bags	Polyolefins, EVA, glass
Mattress covers	Alternative plastic and rubber use only where necessary. Otherwise washable microfibre such as Kortex or Geritex.
Shoe covers	PP fabric line with PE film
Syringes	PE and PP, sometimes natural rubber, glass syringes for blood extraction

5.3.1.2 Production of pulp using chlorine for bleaching;

During the production of pulp using elemental chlorine, dioxins and furans are unintentionally produced. UNEP guidelines on Best Available Techniques and Best Environmental Practices (UNEP, 2004) reports the following primary measures, most of them related to dioxin precursors substitution, for eliminating and decreasing the formation of dioxins:

- Eliminate elemental chlorine by replacing it with chlorine dioxide (ECF bleaching) or with chlorine-free chemicals (TCF bleaching);
- Reduce application of elemental chlorine by decreasing chlorine multiple or

- increasing the substitution of chlorine dioxide for molecular chlorine;
- Minimise precursors entering the bleach plant by using precursor-free additives and thorough washing;
- Maximise knot removal; and
- Eliminate pulping of chips contaminated with polychlorinated phenols.

5.3.1.3 Textile and leather dyeing and finishing

So far, there is no strong evidence that the production processes in the textile and leather finishing industry are generators of new PCDD/PCDF. The occurrence of PCDD/PCDF in the textile and leather industries is due to:

- Use of chlorinated chemicals, specially PCP, to protect the raw material (cotton, wool or other fibres, leather, etc.);
- Use of dioxin-contaminated dye-stuffs, e.g., dioxazines (chloranil-based) or phthalocyanines; and, to a much lesser extend through
- Formation of PCDD/PCDF during finishing; and finally
- Formation of PCDD/PCDF may occur upon incineration of sludge.

Since the occurrence of PCDD/PCDF in the textile and leather industries are primarily linked to the use of dioxin-contaminated chemicals, such as pentachlorophenol and certain dye pigments, substitution of these chemicals by dioxin-free chemicals would be the alternative. For example, in Germany after the phase-out of PCP as a preservative, the following non-chlorinated chemicals were used:

- 2-(thiocyanomethylthio)benzothiazole (TCMTB; CAS Registry No. 21564-17-0, C9H6N2S3);
- o-Phenylphenol (oPP; CAS Registry No. 90-43-7);
- 4-Chloro-3-methylphenol (CMK; CAS Registry No. 59-50-7); and
- 2-n-Octyl-4-isothiazolin-3-one (OIT, CAS Registry No. 26530-26-1).

The abovementioned chemicals are assessed as less hazardous for the environment than PCP but they are by no means inherently safe.

5.3.1.4 Development of substitutes in other sources

The relative importance of several other notable sources of dioxin - wood burning, metal smelting, landfill fires, open burning, cement production, and others - varies around the world from region to region. A number of measures related to dioxins precursors' substitutes can prevent emissions from each of the following sources:

- Residential burning of wood: it is possible to avoid burning wood which has been treated with chlorinated wood preservatives;
- Emissions from cement kilns that now burn waste and which contain chlorine, can be decreased by sorting waste or switching back to conventional fuel;
- Emissions from landfill fires and open burning can be reduced through a sound materials policy, as is the case with municipal waste incineration;
- In the metal industry, dioxin emissions can be cut through pre-treatment of scrap metal prior to reprocessing. The sorting would exclude materials that contain chlorine or bromine; pre-treatment would strip plastic or PVC coatings.

Many other sources of dioxin can be reduced or eliminated by using similar methods.

5.3.2 Modification/substitution of processes (thermal- chemical) with a high risk of POP formation and use of Best Available Techniques

UNEP guidelines on Best Available Techniques (BATs) and Best Environmental Practices (BEPs), (UNEP, 2004) develop such types of alternatives for each of the source categories listed in Annex C of the Stockholm Convention. A review of BATs and BEPs proposed by UNEP for the different source categories is presented below.

5.3.2.1 Waste incinerators

Best Environmental Practices for Waste Incineration consists of well-maintained facilities. Well-trained operators, a well-informed public and constant attention to the process are all important factors in minimizing the formation and release of unintentional POPs from the incineration of waste. Furthermore, effective waste management strategies (e.g., waste minimization, source separation and recycling), to alter the volume and character of incoming waste, can also significantly impact releases.

In addition to applying best environmental practices to the incineration of MSW, hazardous waste and sewage sludge, there are a variety of demonstrated combustion engineering, flue gas cleaning and residue management techniques that are available for preventing the formation (or minimizing) the release of unintentional POPs.

Non-incineration and emerging technology options exist that may represent feasible and environmentally sound alternatives to incineration. Although most of them are not considered fully demonstrated on an industrial scale for the environmentally sound disposal of MSW, they warrant consideration and further study: pyrolysis and gasification, thermal depolymerization, plasma technologies and high temperature melting.

5.3.2.2 Medical waste incineration

General guidance:

- Segregation of waste;
- Alternate Processes; and
- Performance requirements for incineration plants (primary and secondary measures).

Firing technologies representing BAT:

- Pyrolytic incinerator;
- Rotary kiln;
- Incinerator with grate (municipal waste incinerator); and
- Fluidized bed incinerator.

Primary measures:

- Optimization of combustion conditions (standard for all activities).

Secondary measures:

- Dedusting (filters, cyclones, etc.);
- Reduction of unintentional POP emissions (catalytic oxidation, gas quenching, filters, wet and dry adsorption, fixed bed reactor, etc.); and
- Appropriate fly and bottom ash and waste water treatment.

Organizational measures: training, monitoring, maintenance, etc.

5.3.2.3 Cement kilns firing hazardous waste

The cement production process has an impact on the use of energy and air emissions and, for new plants and major upgrades, the best available technique for the production of cement clinker is considered to be a dry process kiln with multi-stage preheating and precalcination. For existing installations, considerable partial reconstruction is needed⁴.

Primary measures:

- Process optimization;
- Feed material preparation;
- Input controls; and
- Process modification.

Secondary measures:

- Further improvement of dust abatement and recirculation of dust;
- Activated carbon filter; and
- Selective catalytic reduction.

5.3.2.4 Pulp production

The following general measures are suggested:

- Substitution. The identification and substitution of potentially harmful substances with less harmful alternatives. Use of a detailed inventory of raw materials used, chemical composition, quantities, fate and environmental impact;
- Investment planning/cycles; coordination of process improvements to reduce technical bottleneck delays in the introduction of better techniques;
- Training; education and motivation of personnel. Staff training can be a very cost-effective way to reduce discharges of harmful substances;
- Process control monitoring and optimization. To be able to reduce different pollutants simultaneously and to maintain low releases, improved process control is required. Raw materials specification and monitoring of raw materials for precursor materials;
- Adequate maintenance. To maintain the efficiency of the process and associated abatement techniques at a high level, sufficient maintenance has to be ensured;
- Environmental management system. A system which clearly defines the responsibilities for environmentally relevant aspects in a mill. It raises awareness and includes goals and measures, process and job instructions, checklists and other relevant documentation. Incorporation of environmental issues in process change controls;
- Development of environmental monitoring and standard monitoring protocols; and
- Release monitoring for new facilities. Demonstrate the performance of combustion processes and releases to water.

⁴The dry process is only appropriate in the case of limestone as a raw material feed. It is possible to utilize preheater/precalciner technology to process chalk, with the chalk slurry dried in a flash drier at the front end of the process.

5.3.2.5 Thermal processes in the metallurgical industry

a) Secondary copper

Recommended process:

- The blast Furnace, mini-smelter, Top Blown Rotary Furnace, Sealed Submerged Electric Arc furnace, ISA Smelt, and the Pierce-Smith converter; and
- The reverberatory hearth furnace, the hearth shaft furnace and Contimelt process to treat clean copper scrap devoid of organic contamination.

Primary measures:

1. Pre-sorting of Feed Material

Methods to be considered are:

- Oil removal from feed (e.g., thermal de-coating and de-oiling processes followed by afterburning to destroy any organic material in the off-gas);
- Use of milling and grinding techniques with good dust extraction and abatement. The resulting particles can be treated to recover valuable metals, using density or pneumatic separation;
- Elimination of plastic by stripping cable insulation (e.g., possible cryogenic techniques to make plastics friable and easily separable); and
- Sufficient blending of material to provide a homogenous feed in order to promote steady-state conditions.

2. Effective Process Control

Secondary measures:

- Fume and gas collection;
- High efficiency dust removal;
- Afterburners and quenching; and
- Adsorption on activated carbon.

Emerging research:

- Catalytic oxidation.

b) Iron and steel industry

Alternatives:

- Alternate processes: FASTMET, direct reduction of iron, direct smelting; and
- Performance requirements: primary, secondary.

Primary measures:

- Stable and consistent operation of the sinter plant;
- Continuous parameter monitoring;
- Recirculation of waste gases;
- Feed material selection; and
- Feed material preparation.

Secondary measures:

- Adsorption/absorption and high efficiency de-dusting (BAT);
- Fine wet scrubbing of waste gases (BAT);
- De-dusting of waste gases; and
- Hooding of the sinter strand.

c) Secondary aluminium production/secondary zinc production/secondary lead production

Recommended process: Blast furnace, submerged electric arc furnace, injection of fine material via the tuyeres of a blast furnace reduces handling of dusty material.

Primary measures:

- Pre-sorting of feed material. The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion, or by de-novo synthesis; and
- Effective process control. Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation. PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls after having established optimum operating conditions for the reduction of PCDD/PCDF.

Secondary measures:

- Fume and gas collection. Effective fume and off-gas collection should be implemented in the capture of air emissions from all stages of the process;
- High efficiency dust removal. Particulate matter generated during the smelting process should be removed, as this material possesses large surface area on which PCDD/PCDF can adsorb. Proper isolation and disposal of these dusts will aid in PCDD/PCDF control;
- Afterburners and quenching. Afterburners should be used at temperatures of >950°C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250°C; and
- Adsorption on activated carbon. Activated carbon treatment should be considered as this material is an ideal medium on which PCDD/PCDF can adsorb due to its large surface area.

Emerging research:

Catalytic oxidation. Catalytic oxidation is an emerging technology which should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, carbon dioxide (CO₂) and hydrochloric acid using a precious metal catalyst.

d) Primary aluminium production

Alternate process:

- Inert anodes;
- Wettable cathodes;
- Vertical electrodes - low temperature electrolysis;

- Drained cell technology;
- Carbothermic technology; and
- Kaolinite reduction technology.

BAT recommended:

- Prebake technology.

Primary measures:

- Environmental management system, operational control and maintenance;
- Computer controlled process and monitoring; and
- Feed selection: Use of low sulphur carbon for anodes or anode paste.

Secondary measures:

- Feed preparation. Enclosed grinding and blending of raw materials. Use of fabric filters;
- Complete hood coverage of cells;
- Fume collection and treatment;
- Low NOx burners oxy-fuel firing;
- Alumina scrubber;
- Afterburner;
- Wet or semi-dry scrubbing; and
- Bio-filters.

e) Magnesium production

Primary measures:

- Alternate process:
 - Norsk Hydro's MgCl₂ brine Dehydration Process
 - Elimination of carbon source - replaces graphite with non-graphite anode;
- Feed quality; and
- Pre-treatment techniques.

Secondary measures:

- Treatment of the off-gases; and
- Treatment of effluent.

f) Secondary steel

New electric arc furnaces:

- Process design; and
- Performance requirements.

New and existing:

- General operating practices;
- Raw material quality; and

- EAF operation.

Primary measures:

- Off-gas conditioning; and
- Continuous parameter monitoring.

Secondary measures:

- OFF-GAS collection (BAT);
- Fabric filters (BAT);
- Post-combustion of off-gas (BAT);
- Adsorbent injection;
- Minimize solid waste generation; and
- Minimize waste water.

g) Primary metals

- New iron sintering plants.

Alternate processes:

Hydrometallurgical processes are a significant means to preventing emissions. Closed-loop electrolysis plants will contribute to prevention of pollution.

Primary measures:

- Use of hydrometallurgical processes;
- Quality control of (scrap) feed material;
- Effective process control; and
- Use flash smelting technology.

Other:

- Maximize SO₂ content for sulphur fixation.

Secondary measures (BATs):

- High efficiency gas cleaning and conversion of SO₂ to sulphuric acid;
- Fume and gas collection; and
- High efficiency dust removal.

5.3.2.6 Fossil fuel - fired utilities and industrial boilers

The best environmental practices described in this section are for general guidance, applicable to any kind of boiler regardless of its size or type:

- Identify key process parameters, either from site-specific investigations or research undertaken on similar facilities elsewhere;
- Introduce measures that enable control of key process parameters;
- Introduce monitoring and reporting protocols for key process parameters;
- Introduce and follow planning cycles, implement appropriate inspection and maintenance cycles;
- Introduce an environmental management system, which clearly defines

responsibilities at all levels;

- Ensure adequate resources are available to implement and continue best environmental practice;
- Introduce process improvements to reduce technical bottlenecks and delays;
- Ensure staff are appropriately trained in the application of the BEPs relevant to their duties;
- Define a fuel specification for key fuel parameters and introduce a monitoring and reporting protocol;
- When co-firing biomass or waste, the alternative fuels should not be added until the boiler furnace combustion conditions are stable and it has reached its operating temperature; and
- While the introduction of fuels containing POPs compounds or chlorine is possible, their proportion as co-fuel should be limited in order to allow proper destruction.

As discussed in Section 3, unintentional production of POPs compounds, such as PCDDs, PCDFs, PCBs and HCBs during the combustion processes, follows three general pathways:

- Undestroyed compounds originally present in the fuel;
- Gas-phase formation from precursors (e.g. polyhalogenated phenols, chlorinated aromatic compounds...) at temperatures higher than 500°C; and
- Reformation of POPs in the cooling flue gases.

In order to reduce the emission of POPs from fossil fuel-fired utility and industrial boilers, these three pathways must be minimized in the design and operation of the process. This will be effectively achieved by addressing:

- Fuel quality;
- Combustion conditions; and
- Installation of the most appropriate air pollution control devices (APCDs).

Primary measures:

- Fuel specification and monitoring; and
- Combustion conditions.

Secondary measures:

- Available methods; and
- Combination of techniques - efficiency measurements.

5.3.2.7 Firing installations for wood and other biomass fuels

Primary measures:

- Prevention of illegal incineration. Utilization of urban waste wood in conventional combustion systems has to be strictly avoided;
- Optimized combustion technology. Improved burn-out of gases and fly ash and reduction of dust content:
 - Reduction of excess air ratio to $\lambda \approx 1.5 - 2$;
 - Good mixing quality of gas and air (high turbulence);
 - Sufficient residence time in the hot zone;
 - Minimal disturbance of the glow bed and homogenous distribution of the primary air;

- Optional integration of SNCR for NO_x reduction.
- Measures in the boiler:
 - Minimal residence time in the temperature range between 180°C and 500°C and minimal dust deposition ability;
- Optimized plant operation:
 - Application of advanced combustion control technologies to ensure optimal burn out in practice;
 - Stationary operation, no on/off operation and prevention of rapid changes of heat the demand.

Secondary measures:

- Optimized gas cleaning:
 - Prevention of the temperature window of the de novo synthesis in filters (filter temperature < 120°C);
 - PCDD/PCDF separation in dust separators (electrostatic precipitators, fabric filters) in combination with sorbent injection (if necessary);
- Optional destruction of PCDD/PCDF by catalytic oxidation, i.e., in combination with SCR for NO_x reduction.

5.3.2.8 Chemical production processes

a) Oxychlorination process

The presence of heat, elemental chlorine, copper chloride catalyst and organic material makes the oxychlorination process a potential source of by-product POPs. Aromatics may be generated in high temperature processes and may also be present in feed materials, including HCl or air. Conditions in an oxychlorination reactor are in some ways similar to conditions in the areas of an incinerator downstream of the combustion zone, but may or may not contain similar amounts of soot-like elemental carbon or PAH's, which may contribute to *de novo* formation of PCDFs. By-product POPs created in this process, however, can be virtually completely removed from product and isolated in high-boiling materials (heavy ends) as a result of the distillation process.

Some by-product POPs will adhere to particles of catalyst. In the case of fixed bed systems, they can be a part of the spent catalyst that is removed from service. This material can be treated thermally to destroy adsorbed organics or placed in a secure landfill. In reactors, fluidized bed catalyst particles undergo size attrition and can become entrained in the vapour stream. These particles eventually show up in solid waste or in the biological solids removed at the end of water treatment.

Acetylene Process for Vinyl Chloride: Use of the balanced process for production of EDC, and subsequent cracking to vinyl chloride has, over the past 50 years, largely - but not entirely - superseded production of vinyl chloride via the acetylene route. In the acetylene process, calcium oxide and carbon are strongly heated together to produce calcium carbide. When CaC₂ is reacted with water, acetylene is produced. Vinyl chloride results from catalyst-mediated addition of HCl to acetylene. Due to the decreasing use of this process in the days of well-defined analytical procedures for detection of POPs, little is known of POPs generation and concentration in materials and wastes.

b) Other process contact with elemental chlorine

There is anecdotal evidence that contact of elemental chlorine with organic process equipment (seals, gaskets, fibreglass equipment), which may contain aromatics, PAHs or elemental carbon, can give rise to by-product POPs, usually PCDFs. In certain processes where high boiling material or condensate is separated from manufactured elemental chlorine and not

recycled in the process, by-product POPs can be found in solid or liquid effluent.

c) Titanium dioxide

The presence of coke, chlorine, metals and elevated temperature may give rise to dioxins and furans analogous to those generated in oxychlorination. PCDD/F, if formed, are expected to partition into stream(s) containing residual coke.

d) By-product destruction

There are three types of waste treatment: Hazardous Waste Combustion, Thermal Oxidation and Catalytic Oxidation, and some details of each are presented in the EDC/VCM Chapter of the EIPPCB BREF on Large Volume Organics. When heavy ends are burned, some by-product POPs are generated as in any hazardous waste combustion. EIPPCB is in the process of generating a BREF on waste combustion processes. However, there are legal requirements and best available technologies already in use in the US, the EU and Japan, among others.

The Catoxid process is a fluidized-bed catalytic process for oxidation of organics. It generates a stream of HCl and CO₂ that is sent in totality to the oxychlorination reactor for internal recycle.

e) Products

Many products of these processes have been analyzed for by-product POPs, specially PCDD/F. In general, products of the chloralkali-through-vinyl chloride chain are very low in such contamination. However, for these and other products, the POPs concentration may be a function of the efficiency of distillation or other purification.

Alternate processes to chlorination:

- Titanium Dioxide, Sulfate Process.

Primary measures of greater impact:

- Distillation and internal recycling of by-products;
- Elimination of carbon electrodes for chloralkali production;
- Elimination of alkali treatment of 1,2,4,5-Tetrachlorophenol and 2,4,5-Trichlorophenol;
- Elimination of Phenol route to Chloranil; and
- Modified production of Pentachlorophenol (PCP) and Sodium pentachlorophenate.

Primary measures of lesser impact:

- Use of Hydrogen in oxychlorination;
- Catalyst maintenance and temperature uniformity control; and
- Reduction in aromatic hydrocarbons in feeds to oxychlorination processes.

Secondary measures

- BAT for Waste Disposal Practices.

Summary of measures

Modify processes to reduce generation of by-product POPs. Incorporate steps that treat impurities in raw materials and use rigorous operational maintenance. Purify products

by distillation. Internally recycle inadvertently generated high molecular weight side-products as an integral part of the process.

5.3.2.9 Crematoria /destruction of animal carcasses

Recommended processes:

- Minimum 850°C, two second residence time in qualifying volume with sufficient air to ensure POPs destruction. Fit with APC equipment to minimise SO₂, HCl, CO, VOC, PM and POPs emission

Primary measures:

- Furnace design
- Pre-preparation of crematoria
- Effective combustion control
- Effective process control
- Operator training

Secondary measures:

- Fume and gas collection
- Air pollution control equipment

5.3.2.10 Shredder plants for treatment of end of life vehicles

Primary Measures:

On the basis of the above -mentioned knowledge, it can be concluded that PCB and some PCDD/PCDF emitted from shredder plants for the treatment of ELV are mainly derived from technical PCB mixtures or products contaminated with PCDD/PCDF entering the shredder plant with the objects to be shredded. The generation of new, unintentional POPs (mainly PCDD/PCDF and perhaps some PCB) seems to be much lower and may be due to thermal formation processes. Therefore, the following primary measures to prevent formation of unintentional POPs should be considered:

- Reduction of ASR generation by enforcing thoroughly pretreatment (dismantlement);
- Prohibition of mixing foreign materials into ELV to be shredded;
- Strict control of PCB management;
- Alternatives to shredding treatment (melting in electric furnace).

Secondary Measures:

- Advanced treatment of flue gas (bag filter, activated carbon filter to remove both gaseous and particle emissions);
- Avoidance of elevated surface temperatures to avoid by-product formation;
- Improved storage facilities for ASR;
- Advanced treatment of waste water, if any (activated carbon adsorption).
- Prevention measures on fire and explosion in the sense of preventing formation of by-products (?)

5.3.2.11 Smouldering copper cables

Alternate Processes:

- Cable chopping
- Cable stripping
- High temperature incineration for material unsuitable for chopping or stripping

5.3.3 Limit emissions on diffuse sources

5.3.3.1 Open burning of waste

Burning Process

Harmful emissions result from incomplete combustion. In the short term, where there are not realistic means to eliminate all open burning, practical process modifications that are likely to improve safety and reduce unintentional POPs generation include:

- Reduction in the amount of material discarded via open burning. Consistent with the convention, and its goal of elimination, this is the first line of improvement.
- Removal of non-combustibles, including glass and bulk metals, and materials of low fuel value.
- Removal of potential explosives (e.g. aerosol cans, partially full containers of flammable liquids).
- Removal of hazardous materials, especially those which should be destroyed under BAT described in other parts of the guidance
- Supply of sufficient air
- Steady burning or rate of mass loss
- Minimization of smoldering, possibly with direct extinguishment
- Small, actively turned, well-ventilated fires, rather than large poorly-ventilated dumps or containers

And with respect to the materials burned:

- Dry, not wet, waste combustibles of high fuel value
- "Homogeneous" or well-blended combustibles
- Low density; e.g. non-compacted waste
- Lower-probability techniques that may provide some reduction of PCDD/PCDF include:
 - Burning material in open piles rather than confined in burners
 - Avoiding burning waste that is exceptionally high in chloride content, noting that there is no apparent difference between inorganic chloride (salt) and organic chloride (PVC).
 - Avoiding burning waste that contains metals such as copper and iron, even in small amounts.

Handling After burning

Before burned waste can be handled or covered, it must be completely extinguished. Failure to do this can potentially ignite uncontrolled burning over large areas and or allow ongoing smoldering, which is shown to be the most polluting time in the life of a fire.

Intermediate Technologies

Devices known as “incinerators” are sold for the purpose of burning refuse. In some cases these devices may be as simple as steel drums or barrels which contain the waste but do not constitute BAT incineration. “Open burning” should be viewed as any form of combustion for waste disposal that does not meet the standards for BAT incineration of municipal, medical or hazardous waste, as defined by a party. In general, good incineration involves a combination of appropriate residence time in the flame zone, combustion gases reaching an elevated temperature of at least 800° C, in the presence of sufficient turbulence to avoid unburned material. In addition, BAT combustion will usually involve post-treatment of combustion gases to minimize the time that products of combustion spend in the temperature conditions conducive to formation of PCDD/F (ca. 250-450° C).

Other Considerations and Opportunities for Further Refinement of Methods

Research in open burning is hampered by irreproducibility of experiments, experimental scale (as in landfill fires) and control experimental conditions. On the other hand, these kinds of difficult to reproduce conditions are the hallmarks of open burning as actually practiced. Further research may define more precisely the impact of variables on the open burning process and allow development of better interim techniques for temporary use on the way to total elimination. For example, there may be processes that are analogous to those used for POPs reduction in controlled combustion.

Factors to be considered:

- Material composition
- Barriers to elimination; Remedies or Policy to remove barriers
- Strategies and Policy instruments to avoid, reduce or divert waste
- Alternatives, barriers to use and policy instruments to remove barriers
- Burning techniques and attributes, and means of improvement

5.3.3.2 Residential combustion sources

BAT for using biomass/wood for cooking and heating in developing countries

Biomass/wood stoves used in developing countries are not well designed. This leads to inefficient use of fuel during cooking and other heating purposes. In addition, it contributes to pollution of the atmosphere due to incomplete combustion, leading to many types of respiratory illnesses.

The simplest solution to the problem is to promote the so-called improved stoves. Some studies have indicated that improved designs save 50 to 80% fuel when compared to traditional ones. Possible designs for improved stoves would save fuel, reduce air pollution, be easy to manufacture/install and operate, yet would be affordable for rural users. There are many kinds of designs of improved stoves and it is difficult to recommend any one particular type in this document. Further research is needed in this area.

Best Environmental Practices

- Ventilation

To reduce indoor air pollution, a good supply of fresh outdoor air is needed. The movement of air into and out of residential places is very important. Normally, air comes through cracks around doors and windows and helps reduce the level of pollutants indoors. This supply of fresh air is also important to help carry pollutants up the chimney, stovepipe,

or flue to the outside. It also allows enough air for proper combustion and reduces the level of pollutants.

Use a hood fan, if using a range. Make sure that enough air is coming into the house when you use an exhaust fan. If needed, slightly open a door or window, specially if other appliances are in use. For proper operation of most combustion appliances and their venting system, the air pressure in the house should be greater than that outside. If not, the vented appliances could release combustion pollutants into the house rather than outdoors. If you suspect that you have this problem you may need the help of a qualified person to solve it.

- Correct Use of Appliances and Fuel

It is important to study the instructions in the manuals supplied with all appliances to understand how they work. Most importantly, the significance of using the recommended type of fuel for each particular appliance must be comprehended.

Only use water-clear ASTM 1-K kerosene for kerosene heaters. The use of kerosene other than 1-K could lead to a release of more pollutants. Gasoline is not to be used in a kerosene heater because it can cause a fire or an explosion.

Seasoned hardwoods should be used instead of softwoods in wood burning stoves and fireplaces. Hardwoods are better because they burn hotter and form less creosote, an oily, black tar that sticks to chimneys and stove pipes. Green or wet woods should be totally avoided. Never burn painted scrap wood or wood treated with preservatives because they could release highly toxic pollutants. Plastics, charcoal, and coloured paper, such as comics, also produce pollutants. Unfortunately, in developed countries people use plastics as fuel.

- Inspection and Maintenance

Combustion appliances should be regularly inspected and maintained to reduce exposure to pollutants. It is important to clean chimneys and vents, specially when changing heating systems.

5.3.3.3 Motor vehicles, particularly those burning leaded gasoline

Primary measures to reduce PCDD/PCDF emissions from motor vehicles may include the following:

- Prohibition of halogenated scavengers;
- Prohibition on the use of leaded gasoline;
- Installation of diesel particulate filters and/or catalytic converters; and
- Alternatives to gasoline engine (electricity, solar light, and fuel battery) However, it should be taken into consideration that the production of the alternative fuels may generate PCDD/PCDF, e.g., electricity generation, production of solar cells, etc.

Best practices may include:

- Separation of transport containers according to the fuel (e.g., not transport leaded gasoline containing halogenated scavengers in containers also being used for the transport of diesel or unleaded gasoline);
- Promotion of vehicles with low fuel consumption;
- Education to identify driving conditions that have low pollutant formation and release; and
- Maintain good vehicle maintenance practices.

6. FURTHER REGULATIONS

In this report, alternatives to avoid the use of the twelve POPs considered by the Stockholm Convention have been discussed. However, other hazardous substances that are presently, or will in the near future be prohibited/restricted by national or international regulations, should also be considered to anticipate their substitution and prevent them from becoming POPs alternatives.

6.1 European Union

According to Regulation EC 850/2004, production, marketing and use of substances included in Part A of Annex I are prohibited:

1. Aldrin
2. Chlordane
3. Dieldrin
4. Endrin
5. Heptachlor
6. Hexachlorobenzene
7. Mirex
8. Toxaphene
9. Polychlorinated biphenyls (PCBs) (exemption on articles in use)
10. DDT (exemption on production and use as intermediate of the production of dicofol until 1 January 2014)

Likewise, production, marketing and use of substances included in Part B of Annex I are prohibited:

11. Chlordecone
12. Hexabromobiphenyl
13. Hexachlorocyclohexane (exemption on specific pesticide uses until 1 January 2006 and as intermediate or public health insecticide (Lindane) until 31 December 2007)

Finally, release inventories for substances listed in Annex III of Regulation EC 850/2004 must be effected so as to reduce unintentional emissions:

- Dioxins and furans (PCDD/PCDF)
- Hexachlorobenzene (HCB)
- Polychlorinated biphenyls (PCBs)
- Polycyclic aromatic hydrocarbons (PAH)

6.2 Protocol to the 1979 Convention on long-range transboundary air pollution on POPs

Substances included in Annex I are subject to both prohibition and elimination (with some specific exemptions) by the Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on POPs:

14. Aldrin
15. Chlordane
16. Dieldrin
17. Endrin
18. Heptachlor
19. Hexachlorobenzene
20. Mirex

21. Toxaphene
22. Polychlorinated biphenyls (PCBs)
23. DDT
24. Chlordecone
25. Hexabromobiphenyl

The following substances, listed in Annex II, are subject to restrictions:

26. DDT
27. Hexachlorocyclohexane

The following substances, listed in Annex III, are subject to emissions reduction:

28. Dioxins and furans
29. Hexachlorobenzene
30. Polychlorinated biphenyls
31. Polycyclic aromatic hydrocarbons

6.3 Rotterdam Convention

The Rotterdam Convention establishes the principle that chemicals covered by the Convention may only be exported on the prior informed consent of the importing party. The Convention establishes a "Prior Informed Consent procedure," a means for formally obtaining and disseminating the decisions of importing countries as to whether they wish to receive future shipments of specified chemicals and for ensuring compliance with these decisions by exporting countries.

The Convention also contains provisions for the exchange of information among Parties about potentially hazardous chemicals that may be imported and exported.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted by the Parties for health or environmental reasons and which have been notified by the Parties for inclusion in the PIC procedure.

The initial list of the Convention includes the following 22 hazardous pesticides: 2,4,5-T, aldrin, captafol, chlordane, chlordimeform, chlorobenzilate, DDT, 1,2-dibromoethane (EDB), dieldrin, dinoseb, fluoroacetamide, HCH, heptachlor, hexachlorobenzene, lindane, mercury compounds, and pentachlorophenol, plus certain formulations of methamidophos, methyl-parathion, monocrotophos, parathion, and phosphamidon. It also covers five industrial chemicals: crocidolite, polybrominated biphenyls (PBB), polychlorinated biphenyls (PCB), polychlorinated terphenyls (PCT) and tris (2,3 dibromopropyl) phosphate.

Furthermore, 15 chemicals are candidates⁵ for inclusion in the Convention: binapacryl; toxaphene; ethylene dichloride; ethylene oxide; monocrotophos; DNOC and its salts; a severely hazardous pesticide formulation, dustable powder formulations containing a combination of benomyl at or above 7 per cent, carbofuran at or above 10 per cent and thiram at or above 15 per cent; actinolite asbestos; anthophyllite asbestos; amosite asbestos; tremolite asbestos; tetraethyl lead and tetramethyl lead; parathion; and chrysotile asbestos.

⁵ Press release: Up to 15 hazardous chemicals and pesticides to be added to trade "watch list"
<http://www.pic.int/>

6.4 Future amendments

A request for a Council Decision concerning proposals made on behalf of the European Community and the Member States, for amendments to Annexes I - III of the 1998 Protocol to the 1979 Convention on Long Range Transboundary Air Pollution on Persistent Organic Pollutants and to Annexes A - C of the Stockholm Convention on Persistent Organic Pollutants⁶ should be mentioned here:

Two of these substances have already been considered by Regulation EC 850/2004 (Chlordecone, Hexabromobiphenyl), but have yet to be regulated.

With respect to the Protocol to the 1979 Convention on long-range transboundary air pollution on POPs, the European Commission resolve is to:

- Add the following substances to Annex I:
Hexachlorobutadiene
Octabromodiphenyl ether
Pentachlorobenzene
- Add the following substances to Annex I and III:
Polychlorinated naphthalenes
- Add the following substances to Annex II:
Chlorinated paraffins (C10-C13)

Likewise, with respect to Stockholm Convention, the European Commission resolve is to:

- Add the following substances to Annex A:
Hexachlorobutadiene,
Octabromodiphenyl ether
Pentachlorobenzene,
Pentabromodiphenyl ether,
Chlordecone,
Hexabromobiphenyl,
Hexachlorocyclohexane (included Lindane);
- Add the following substances to Annex A and C:
Polychlorinated naphthalenes
- Add the following substances to Annex B:
Chlorinated paraffins (C10-C13)

⁶ Proposal for a Council Decision COM(2004) 537 Final. Brussels, 4.8.2004.

7. SUMMARY OF ALTERNATIVES

The alternatives identified in this document and the main related considerations are summarized in Table 9.

Table 9

Summary of identified alternatives to POPs

POPs	Alternatives	Considerations
Pesticide uses: Aldrin Chlordane Dieldrin DDT Endrin Heptachlor Hexachlorobenzene Mirex Toxaphene	<ul style="list-style-type: none"> Chemical substitutes: Organophosphorous Carbamates Synthetic Pirethroids Chlorinated hydrocarbons 	<ul style="list-style-type: none"> Toxic to aquatic organisms Adverse effects to human health and, frequently, to other plant and animal species Do require appropriate training and application control
	<ul style="list-style-type: none"> Integrated Management: Pests Vectors 	<ul style="list-style-type: none"> Highly specific according to local conditions
Hexachlorobenzene (Non pesticide uses)	<ul style="list-style-type: none"> Chlorinated solvents: wet cleaning 	<ul style="list-style-type: none"> Contrasted feasibility in most cases
	<ul style="list-style-type: none"> Aluminium: chlorine gas 	<ul style="list-style-type: none"> N.a.
	<ul style="list-style-type: none"> Pyrotechnics: hexachloroethane 	<ul style="list-style-type: none"> N.a.
	<ul style="list-style-type: none"> Graphite anodes: dimensionally stabilized anodes (DSA), 	<ul style="list-style-type: none"> N.a.
	<ul style="list-style-type: none"> Chemical intermediate: N.a 	<ul style="list-style-type: none"> None alternatives identified
	<ul style="list-style-type: none"> Wood preserving agent 	<ul style="list-style-type: none"> N.a.
	<ul style="list-style-type: none"> Unintentional emissions: see <i>Dioxins and Furans</i> 	<ul style="list-style-type: none">
PCBs	<ul style="list-style-type: none"> Mineral oils Silicone oils Phenxylylethane Vegetable oils 	<ul style="list-style-type: none"> Options already in use, proved feasibility

POPs	Alternatives	Considerations
	<ul style="list-style-type: none"> • Polychlorinated naphthalenes • Polychlorinated terphenyls • Alkylchlorodiphenyls • Biphenyls 	<ul style="list-style-type: none"> • Toxic to humans and environment
	<ul style="list-style-type: none"> • Material or design modification 	<ul style="list-style-type: none"> • Proved feasibility depending on each case
	<ul style="list-style-type: none"> • Unintentional emissions: see <i>Dioxins and Furans</i> 	<ul style="list-style-type: none"> •
Dioxins and Furans	<ul style="list-style-type: none"> • Chlorinated precursors avoidance/substitution 	<ul style="list-style-type: none"> • Lack of consensus on its effectiveness
	<ul style="list-style-type: none"> • Process modification/substitution (BATs) 	<ul style="list-style-type: none"> • Specific for each sector
	<ul style="list-style-type: none"> • Best Environmental Practices (BEPs) 	<ul style="list-style-type: none"> • Specific for each sector

N.a: Not available

PART B: Guidelines on Substitutes to be used as Alternatives to POPs

1. Stocks management

1.1 Obsolete pesticides

The actions outlined below should be taken to address the problem of obsolete pesticides worldwide, according to the OECD-FAO-UNEP workshop on obsolete pesticides (OECD-FAO-UNEP, 2000). Detailed measures on prevention and disposal of obsolete pesticides have been developed by the FAO, an extract of which is contained in Annex III.

1.1.1 Recommended actions

These general recommendations have been grouped by responsibility (OECD-FAO-UNEP, 2000).

Developing Countries

1. Assume leadership to address the country's problem of obsolete pesticide stocks.
 - designate an institution that will be dedicated to the issue and will serve as a promoter or catalyst for action; and
 - develop a national action plan for obsolete pesticide disposal and prevention, to include:
 - i. compilation and maintenance of a national inventory of obsolete and unwanted stocks
 - ii. identification and, to the extent possible, quantification of the risks associated with the country's obsolete pesticide stocks
 - iii. raising awareness within the country about problems associated with obsolete pesticide stockpiles.
2. Create an infrastructure for pesticide regulation and management to:
 - identify the country's need for "capacity development" to build an infrastructure for the regulation and management of pesticides;
 - develop policies and implement measures to ensure good chemical management from import or manufacture to storage, use, and disposal of pesticides and their containers; and
 - develop policies and implement measures to prevent the accumulation of pesticide stockpiles.
3. Co-ordinate and educate the relevant stakeholders to:
 - work with stakeholders to improve their understanding of the obsolete pesticide problem and its affects on socio-economic development. Stakeholders could include the responsible institution, the government authorities for pesticide regulation and hazardous waste management, pesticide producers, vendors, retailers and distributors, citizens, consumer representatives, and environmentalists;
 - bring the stakeholders together so they can work as a team. Create a committee that meets regularly to discuss the situation and decide how to proceed; and
 - organize training on pesticide stock management for pesticide vendors and recipients.

Pesticide Donor Countries and Aid Agencies

1. Recognize that prevention and disposal of obsolete pesticides is important to sustainable economic development. Include prevention and disposal of obsolete pesticides in wider development programmes, such as those for rural development, chemical management, public health, and waste management.
2. Give higher priority to provision of technical and capacity building assistance for pesticide management in developing countries. To the extent possible, fund and support relevant activities, including disposal of obsolete pesticides.
3. Follow the relevant guidelines and principles developed by the OECD DAC and FAO when responding to requests for pesticide donations.
4. Collaborate with others to:
 - identify an organization (possibly the FAO) that can facilitate regular interaction among donor countries on the issue of pesticide use and storage in developing countries;
 - develop close links with pesticide and waste management regulatory agencies in order to draw on their expertise and co-ordinate activities;
 - find ways to increase participation of less active donor countries in preventing and disposing of obsolete pesticide stocks; and
 - increase coordination and collaboration with other stakeholders by:
 - i. organising local meetings that bring together donors and other stakeholders
 - ii. forming a committee with representatives of the relevant government departments (agriculture, environment, public health, municipality)
 - iii. establishing expert centres, contact points, and a pool of experts with experience in pesticide management and obsolete pesticide prevention and elimination
 - iv. engaging the medical community and the World Health Organisation
 - v. making more use of NGOs and inter-governmental organisations.
5. Increase communication and exchange of information on the problem, and make the issues “transparent” through vehicles such as web sites, a newsletter and a clearinghouse.

Pesticide Industry (including the Global Crop Protection Federation, individual pesticide producers, retailers and distributors)

1. Take an active role in the effort to identify and dispose of existing stocks of obsolete and unwanted pesticides.
2. Contribute to the prevention of further obsolete stocks in the future:
 - develop products with an appropriate shelf life, clear labelling with expiry date, and appropriate packaging;
 - support the establishment of and compliance with good management practices for labelling, transport, handling and storage of pesticides;
 - explore ways to expand product stewardship, such as adopting a “return to vendor” policy for overstocked pesticides and empty containers; and
 - provide pesticide management training for vendors.

3. Take steps to ensure that the promotion of chemical pesticides does not undermine national, regional or local efforts to reduce reliance on pesticides and to promote alternatives to chemicals in pest management.

Non-Governmental Organisations

1. Raise awareness of the problem of obsolete pesticides at all levels of society, from the grass roots to government.
2. Develop educational programmes and encourage countries to develop strategies for the prevention of future accumulation of stockpiles.

All Organisations

1. Build a network for information sharing, coordination and collaboration on the problem of obsolete pesticides, drawing on lessons learned and focusing on the elimination of existing stockpiles and prevention of future accumulation.
2. Adhere to existing guidelines relevant to pesticide management, including those issued by the FAO, the OECD DAC, the WHO, the UNEP Chemicals Programme and SBC.
3. Take responsibility for ensuring that all pesticides supplied are used and managed properly.
4. Clarify the impact of pesticides on human health and livelihood and the environment. Identify the links between these impacts and socio-economic development.
5. Explore mechanisms, such as the POPs and Basel Conventions, for raising awareness and implementing solutions to the problem of obsolete pesticides.
6. Promote and strengthen existing training programmes on pesticide management and disposal and create more programmes wherever needed.
7. Highlight the issue internationally.

1.2 PCB containing equipment

1.2.1 Recommended actions

Various quantities of PCB-containing equipment is still in use in all countries. Therefore, measures must be developed to ensure its safe handling and consequential reduction in the release of PCBs.

In principle, the most sustainable measure would be to support the phasing out and complete destruction of all identifiable PCBs in an environmentally safe manner. This would also apply to all "uncontrolled" applications - products with a low concentration of PCBs (e.g., mineral oil contaminated with PCB) but marketed in large quantities and products with a small volume of pure PCBs (e.g., capacitors in strip light fittings). It would also cover the phasing-out of hazardous PCB-substitutes. However, a total ban on the ongoing use of all PCB containing materials, equipment and appliances, regardless of whether they constitute a serious source of PCB emissions, might be not a very cost-efficient measure.

Highest priority should be given to measures concerning existing equipment containing significant amounts of PCB (transformers and power capacitors). The main type of measures would, therefore, include (HELCOM, 2001):

- Carry out inventories (identification and labelling) of PCB-containing equipment and products;
- Guidelines, improved inspection, instructions and maintenance in order to prevent,

- avoid and discover accidents, abnormal operation conditions, leakage and spillage;
- Clean repair and decommissioning of equipment;
- Efficient decontamination and avoidance of reintroduction of PCBs via recycling of contaminated material;
- Establishment of safe collection and storage schemes;
- Proper/safe interim storage; and
- Safe destruction and environmentally sound disposal/incineration.

Inventories of PCB-containing equipment are an essential tool for a substitution programme, but experience has shown that it is not an easy or cheap measure.

The single identification of equipment suspected of containing PCB is not adequate. From this rough inventory, three main possibilities must be identified:

- Equipment containing PCB;
- Equipment on which PCBs have been fully replaced by other dielectric agent; and
- Equipment refilled with a variable amount (percentage) of non-PCB agents.

For the third case an analysis is necessary to identify the remaining concentration of PCB in order to decide the proper management procedure. The cost of such analysis is not trivial and becomes one of the difficulties along with the identification of PCB-containing equipment.

Similarly, measures could be identified for other main PCB sources (not in order of importance):

- Clean building renovation and demolition (covering open uncontrolled applications);
- Establishment of safe collection and storage schemes (covering closed, uncontrolled applications in small capacitors, e.g., in washing machines, CH circulation pumps, domestic fuel oil burners, strip light fittings, and in lights along motorways and municipal roads);
- Avoidance and control of unintended by-production;
- Avoidance of PCB emissions from incineration processes;
- Decontamination of PCB-contaminated sites and soils; and
- Land filling: to be carried out properly, otherwise it should be avoided.

Further, the following basic measures should be taken into account:

- Information campaigns and educational measures;
- Technology transfer and information exchange;
- Ban on the importation of PCB-containing products;
- Restricted transport; and
- Waste inventories.

2. AN APPROACH TO FIND THE BEST ALTERNATIVE

Applying alternatives requires a specific assessment of each substance/method for each specific situation. Following step-by-step approaches usually facilitates the process of finding the best alternative:

2.1 Substitution principle

Besides compliance with regulations, applying the substitution principle has significant benefits:

- To reduce the risk to human health and the environment represented by the use of products;
- To transfer more responsibility to people who handle products containing hazardous substances;
- To make users aware of how selection of the right products can help to prevent damage to health and the environment;
- To oblige all those who use products for occupational purposes to make systematic efforts to find substitutes for dangerous chemicals; and
- To replace hazardous chemicals with less dangerous substances and reduce the use of hazardous substances.

The substitution principle applies to all enterprises that use products containing hazardous substances and to chemicals used in the general running of a business, as well as those used as constituents of products. Competent authorities and industrial sectors should systematically evaluate the chemicals being used.

2.1.1 Step-by-step approach for the substitution process

There are various ways of going about the substitution process. These guidelines present one procedure, step-by-step. The process can of course be carried out in other ways, but it is important to ensure that all the steps presented here are carried out.

- 1.1 Obtain information on the existing product.
- 1.2 Set up an order of priority for further action.
- 1.3 Investigate whether alternatives are available. (This could mean other products or other production methods).
- 1.4 What risks are associated with the alternatives? What will happen if you choose one of the alternatives?
- 1.5 Compare risks. Compare the alternatives with each other and with the product or method you have been using or are planning to use.
- 1.6 Decide whether or not to make the change. Is the alternative a better choice?
- 1.7 Monitor developments and re-evaluate the situation at regular intervals-remember that substitution is a continuous process.

Governments in the Mediterranean Region should develop a national strategy or plan to deal with the substitution of POPs, taking the above steps into account and the involvement of all stakeholders.

2.2 Alternative methods

2.2.1 Steps in the process of change to pest and vector management

In the process of change towards more sustainable solutions several steps can be distinguished. Some steps may overlap in time (Mörner *et al.*, 2002).

1. Analysis of the present situation

As a first step it is important to analyse the current situation. Several issues need to be taken into account:

- Current policy framework. An assessment is required of policy issues related to pesticides, as well as what kind of strategies for management of pests and vectors are promoted by the existing policies;
- Current status and use of POPs pesticides. The identification of stocks of obsolete pesticides requires attention.
- Current practices for pest and vector control. For agriculture, it will be important to ascertain what knowledge base, analysis and procedures farmers use to decide on the application of pesticides, and what the actual use is at farm level. Similarly, an analysis of how decisions concerning vector control activities are made, to what extent vector ecology and biology are used as key criteria, and what the actual levels of pesticide use are.

2. Identification of alternative approaches

Analysis of the situation will be a starting point from where to further identify and discuss opportunities for change at policy level, as well as for alternative approaches for management of pests and vectors at field level.

- Policies may be changed in a number of ways to provide more support for alternative approaches and to make agricultural production systems and public health services less dependent on pesticides. The analysis is a point of entry point to identify and prioritise areas for change; and
- Current practice and management strategies used in the field will give insight into if and how IPM and IVM strategies can be used to improve decision-making and reduce reliance on pesticide use.

3. Developing National Action Plans

To reduce and/or eliminate POPs pesticides and to move towards more sustainable pest and vector management strategies, a national action plan will be needed.

Certain activities can be tested at pilot scale prior to scaling them up to implementation at the national level.

4. Pilot activities

Studies may be implemented at the policy level to gain a better insight into the policy framework. Workshops can be held with senior government officials to discuss the existing policy framework and to identify areas for change. Exchanges with other countries might provide ideas on how to implement change. Field visits can be made to pilot projects to familiarise policymakers with alternative approaches for pest and vector control.

Pilot projects can be set up at the field level to educate farmers and community members in the ecology of pest and vector species, and to involve them in the planning and design of IPM and IVM programmes. Data from these pilot activities should be made available to stakeholders. Field visits will help strengthen interest in IPM and IVM approaches. Monitoring and evaluation of these activities will yield important information to further improve pilot activities and to plan for action at national level.

3. CASE STUDIES

3.1 Pesticide reduction schemes in Europe

Concern over environmental contamination and loss of biodiversity in the 1980s prompted political decisions in several European countries to reduce the use of pesticides in agriculture.

Three countries in Northern Europe, Denmark, Sweden and the Netherlands, have mandated and made drastic cuts in pesticide use.

Although the preconditions were very different, a common feature of the three programmes was a combination of government measures and voluntary farmer involvement. All three countries have achieved significant reductions in pesticide use.

Key features of the programmes (Mörner *et al.*, 2002):

- A coherent strategy for achieving the target was set up;
- Specific taxes on pesticides were imposed (on value, amount active ingredient and/or differentiated according to hazard);
- Stricter registration and re-registration procedures were introduced, leading to restrictions and removal of less desirable products from the market;
- Training and certification of applicators was made mandatory. More hazardous pesticides are only sold to certified applicators;
- Certification of new application equipment was made mandatory and testing of existing equipment was subsidised;
- The use of pesticides in sensitive areas (e.g., along streams) was restricted;
- The keeping of records of pesticide applications and environmental effects of pesticides was made mandatory (or voluntary);
- Increased and targeted research on IPM, IPM components and the environmental fate of pesticides was funded;
- The plant protection extension service was strengthened to provide farmers with better decision support; and
- Ecological (organic) agriculture was given specific support.

3.2 From Law to Field: Pesticide Use Reduction in Agriculture - From pesticide residue analyses to action. Pesticide Action Network, Germany

The study "From Law to Field: Pesticide Use Reduction in Agriculture - From pesticide residue analyses to action", which was developed within the PAN Germany project "From Law to Field - How to put pesticide use reduction into practice", points out the importance of a crop specific approach and of the commitment of political and economic stakeholders as well as consumers for achieving a pesticide use reduction in Europe (PAN Germany, 2002).

Since patterns and modes of pesticides use, as well as the profile of unwanted side effects of chemical plant protection, differ from country to country and even from place to place, this study concentrates only on German research and data. However, the study provides a framework for analyses and action applicable to other crops and countries in the EU.

In November 1998, the German Federal Ministry of Agricultural constitutionally defined principles for good plant protection practice. This definition is quite general, however, and does not include crop specific guidelines. Therefore, the PAN Germany study worked out crop specific plant protection principles and additionally developed strategies for pesticide use reduction beyond the farm level. The study consists of 3 parts:

1. the documentation of pesticide residues in food and the environment (part 1: Residue Study);
2. the evaluation of these pesticide residues regarding their impact on human health and the environment (part 2: Risk Study), which allows the selection of priority crops for further investigation; and
3. the development of crop specific measures for pesticide use reduction for the priority crops apple and wheat (part 3: Apple and Wheat Case Studies).

3.2.1 Apple study: obstacles and the potential for pesticide reduction

Apple production in Europe is still typically an area with intensive use of pesticides, regardless of the important statement issued by the E.U. in 1993 aimed at a meaningful reduction by the year 2000. Great numbers of different pesticides against fungus, insects, mites, and weeds are sprayed at frequent intervals, according to the season. In the different climatic conditions of Europe's fruit growing regions, fungus or insect/mite pests make it essential to apply pesticides in quantity.

In Germany, the movement from conventional apple growing to the integrated system has been almost universal and has led to a reduction in the use of pesticides. Even integrated production characteristically makes intensive use of pesticides, though modern treatments require lower quantities. The range of different preparations is an indication of the extent to which their use is unavoidable in this kind of system. A further reduction in the use of pesticides in integrated production cannot be counted upon.

The organic system claims a much more extensive reduction in the use of insecticides and, in particular, of herbicides (fully banned) than the integrated. Since all synthetic chemical pesticides are excluded, the number of different treatments for pest control is significantly smaller than in either conventional or integrated farms. In cases of fungus infection the restrictions mean that sulphur or copper preparations have to be used, both of which have to be applied in large quantities. Copper is especially problematic because of its pollutant effects. Its use in organic farms is restricted and is used less widely than in integrated production. A full ban on copper would lead to unacceptable losses in the fruit varieties presently being cultivated.

The example of fungus infection makes it clear that further reductions in the use of pesticides cannot be achieved simply by the growers improving their methods; the potential for reduction lies outside the farms. In this context the excessively high standard for the skin quality of fruit can be cited - a standard that cannot be achieved without intensive use of pesticides. Another major problem is the reduction, enforced by the fruit trade, in the marketing of local varieties of apple which do well in agiven region and require less pesticide for their cultivation.

Consumers could be targeted through publicity to accept that organically grown apples cannot be produced at the same low prices as integrated or conventional apples. They could use their purchasing power to increase the demand for organic fruit and thus persuade more farmers to convert to the organic system. Conversion to organic methods is not enough in itself. They have to develop further to make the use of such substances as copper unnecessary. Here again, well-informed consumers could make a contribution by demanding disease-resistant varieties which would then be more widely grown. The local marketing initiative of the Finkenwerder Prinz provides an encouraging example of promotion of an apple which is relatively tolerant of scab, well suited to the conditions of its region ("Altes Land") and requires little fungicide treatment.

3.2.2 Wheat study: obstacles and the potential for pesticide reduction

Wheat is the most extensively cultivated crop in Europe and, in comparison to other cereals, the most intensively treated with pesticides. There are three systems of cultivation: organic, integrated and conventional. The greatest reduction in pesticide use is in the organic system, which uses no pesticides at all. At present only 2% of German farms are worked organically and few farmers are willing to convert to organic methods. The consumer demand for organic produce increases only slowly due to the high prices required. An increase in organic production can only come about if consumers are better informed. They should know how to identify genuine organic products and where to buy them locally. Additionally there should be awareness that in buying organic foodstuffs one is not only contributing to the conservation of the environment, but also to more humane treatment of animals and one's own health.

As far as marketing and processing are concerned, much more must be done to persuade firms to make organic products part of their stock list, so that they have a larger share of the market. Farmers will not have any incentive to turn to organic methods unless they are urged to do so by consumers, traders and food processors uniting to create the demand. Fruit producers have already made a noticeable advance towards integrated pesticide use.

The reality lags behind the practice in integrated pest control. For several years now different research projects have repeatedly confirmed that the adoption of integrated principles in agriculture can, among other advantages, lead to a reduction in pesticide use without financial loss. There has been official commendation of the integrated system since the Pesticide Act of 1986 but scarcely any sign of a change in attitude in German agricultural practices. The explanation lies in the economic climate, failures in marketing and, to some extent, a lack of conviction on the part of farmers and their advisors that integrated pest control is effective. It seems too many of them that chemical pesticides are easier to apply and carry less risk of economic loss. A major feature of integrated pest control is the expansion of crop rotation, but for economic reasons farmers tended to make rotations more one-sided. The economic risk could be avoided by careful implementation of the simple and straightforward methods of integrated production. They involve preventative measures such as late sowing dates, less use of nitrogenous fertilisers and the selection of resistant varieties of seed. These, together with observance of the economic injury level, should have wider recognition among farmers and their advisors. However, success will not be easily achieved without a greater share of the market. Advisors from the chemical industry and the "Landhandel" will continue to promote the use of their products on the land. The official advisory services and private advisory circles are not subject to this kind of "sales pressure" but they are under pressure to succeed in the sense of providing recommendations that lead to visible success for their clients. It is natural for them to want the farmers to continue to consult them, and confidence is best built up by recommending chemical pesticides with a certain outcome rather than preventative non-chemical measures. There would be wider acceptance of integrated pest control among farmers and advisors if there were

corresponding outlets in the processing industries and the markets. There would also be a need for much higher levels of inspection, and the logistics, finance and recruitment of personnel required make it unlikely that such a development will occur.

The greatest contribution to the reduction of pesticide use is in the organic system. For this reason it would be wiser to give it the highest level of incentives and support.

3.3 Vector management

No case studies on vector management within the Mediterranean or EU region have been identified. However, main observations extracted from six vector control case studies in different other regions have been taken from Mörner *et al.*, 2002:

1. Economic considerations are important when deciding on vector control programmes. Data must, therefore, be accurate and relevant. This includes opportunity costs of community participation and external benefits (such as commercial fish production linked to the production of larvivorous fish, or the gains from timber production where trees are planted to lower water tables).
2. Malaria transmission is often cyclical, following weather patterns. Vector ecology will also vary between areas. This must be considered when drawing conclusions from comparative studies on disease and vector management using conventional and innovative methods
3. Community participation will be sustainable if there is real economic benefit for a large segment of the local population. NGOs can play an important role in ensuring this. Building on existing socio-economic structures and traditions can lead to greater success. The introduction of "new" activities such as fish production, in areas where fish is not part of the traditional diet may be less sustainable and will need more coaching.
4. Strengthening the regulatory role of the health sector is an important prerequisite for the successful application of results from multi-disciplinary research.
5. Improved formulations and innovative applications of new pesticides may seem to be more expensive than older types, but can in fact reduce the costs of the vector control programme. This is particularly true where spraying programmes become better targeted and are supported by non-chemical interventions, as shown in the case of the Philippines (Mörner *et al.*, 2002).
6. The degree by which the decentralisation of malaria control programmes supports IVM with reduced costs and improved levels of protection should be carefully assessed.
7. Environmental management programmes are often more resilient and sustainable than service delivery programmes relying on regular spraying, case detection, drug treatment or vaccination. This is particularly important in times of social and political instability. An example: during the Iran-Iraq war, schistosomiasis was kept under control in Iran in irrigation schemes that included environmental modification measures, while it increased in schemes relying only on case detection and drug treatment, which were disrupted.

4. FACT SHEETS

ALDRIN

USEFUL DATA	
Synonyms	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-exo-1,4-endo-5,8-dimethanonaphthalene
Provisions in the Stockholm Convention and SAP	Production and use prohibited with specific exemptions in uses: Local ectoparasiticide and insecticide (Annex A Stockholm Convention) Phase out inputs of POPs pesticides by 2010 (SAP)
Main uses	Pesticide used to control soil insects such as termites, corn rootworm, wireworms, rice, water weevil, and grasshoppers. It has been widely used to protect crops such as corn and potatoes, and has been effective to protect wooden structures from termites [8].
Source of emissions	Aldrin-treated soil
MAIN ALTERNATIVES	
What alternatives exist:	
<i>Chemical substitutes</i>	
Crop	Pest
Maize	Soil pests
Tree nurseries	Termites
Grain storage	Microfungi
Sugarcane	Termites
Rice	Microfungi (several spp.)
Pine	Leafcutting ant
Wheat	Termites
	Alternatives
	Chlorpyrifos
	Carbaryl (carbamate)
	Carbosulfan (carbamate)
	Carbofuran (carbamate)
	Chlorpyrifos
	Cypermethrin
	Pirimiphos-methyl
	Pyrethrum
	Carbofuran (carbamate)
	Carbaryl (carbamate)
	Malathion
	Resmethrin
	Chlorpyrifos
	Endosulfan
<i>Alternative measures</i>	
Use	Alternatives
Crop protection	Sand
	Ashes
	Seed treatment
Control of termites	Concrete slabs
	Sheet materials
	Woven stainless steel mesh
	Graded stone articles
	Chemical soil barriers
	Biological barriers: use of Nematodes
	Treatment of infestations

Comments and considerations:

- Endosulfan and lindane have a potential for bioaccumulation, they are persistent in the environment and highly toxic to aquatic organisms. Lindane is known to cause cancer in animals according to U.S. EPA Office of Pesticide Programmes.
- Carbamates have low potential for bioaccumulation; they are not considered to be persistent in the environment but can be highly toxic to aquatic organisms. Carbaryl is possibly carcinogenic to humans according to U.S. EPA Office of Pesticide Programmes. Carbofuran has been classified as “very toxic” by the European Union.
- Chlorpyrifos and Malathion (organophosphorous) have lower potential for bioaccumulation than POPs, they are not persistent in the environment but highly toxic to aquatic organisms.

For more information:

- UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives
- Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996
- PAN Germany. Beyond POPs. Evaluation of the UNEP Chemical Substitutes of the POPs Pesticides Regarding Their Human and Environmental Toxicity. Hamburg, April 2001.
- UNEP. Johan Mörner, Robert Bos and Marjon Fredrix, Reducing and Eliminating the use of Persistent Organic Pesticides. Guidance on alternative strategies for sustainable pest and vector management, (Geneva, 2002). <http://www.pops.int/documents/guidance/Default.htm>
- UNEP/FAO/Global IPM Facility Expert Group on Termite Biology and Management. Finding Alternatives to Persistent Organic Pollutants (POPs) for Termite Management.
- Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000
- World Wildlife Fund. Successful, Safe, and Sustainable Alternatives to Persistent Organic Pollutants. Washington, D.C. September 1999

CHLORDANE

USEFUL DATA		
Synonyms	1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene 1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene	
Provisions in the Stockholm Convention and SAP	Production and use prohibited with specific exemptions in production and uses: Local ectoparasiticide; Insecticide; Termiticide; Termiticide in buildings and dams; Termiticide in roads; Additive in plywood adhesives (Annex A Stockholm Convention)	
Main uses	Phase out inputs of POPs pesticides by 2010 (SAP) A broad spectrum contact insecticide, it has been used on agricultural crops including vegetables, small grains, maize, other oilseeds, potatoes, sugarcane, sugar beets, fruits, nuts, cotton and jute. It has also been used extensively in the control of termites.	
Source of emissions	Chlordane has been released into the environment primarily from its application as an insecticide.	
MAIN ALTERNATIVES		
What alternatives exist:		
<i>Chemical substitutes</i>		
Use	Pest	
Alternative		
Sugarcane and maize	Termites	carbofuran (carbamate) chlorpyrifos (organophosphate) carbaryl (carbamate)
Eucalyptus	Termites	carbosulfan (carbamate) carbofuran (carbamate) phorate (organophosphate)
Building construction	Termites	bendiocarb (carbamate) carbaryl (carbamate) carbosulfan (carbamate) chlorpyrifos (organophosphate)
Wheat	Termites	chlorpyrifos (organophosphate)
Sugarcane	White grubs	carbofuran (carbamate) diazinon (organophosphate) fenthion (organophosphate)
Protection of buildings	Ants	petroleum oils endosulfan (organochlorine) (biological control using baculoviruses)

Alternative measures

Use	Alternatives
Crop protection	Cultural control aimed at increased plant vigour Using Titonia concoctions
Control of termites	Host plants resistance Concrete slabs Sheet materials Woven stainless steel mesh Graded stone articles Chemical soil barriers Biological barriers: use of Nematodes Treatment of infestations

Comments and considerations:

- Endosulfan and lindane have a potential for bioaccumulation, they are persistent in the environment and highly toxic to aquatic organisms. Lindane is known to cause cancer in animals according to U.S. EPA Office of Pesticide Programmes.
- Carbamates have low potential for bioaccumulation; they are not considered to be persistent in the environment but can be highly toxic to aquatic organisms. Carbaryl is possibly carcinogenic to humans according to U.S. EPA Office of Pesticide Programmes. Carbofuran has been classified as "very toxic" and Bendiocarb and Carbosulfan as "Toxic" by the European Union.
- Chlorpyrifos and Malathion (organophosphorous) have lower potential for bioaccumulation than POPs, they are not persistent in the environment but highly toxic to aquatic organisms. Phorate is classified as "extremely hazardous" by the WHO. Chlorpyrifos and Fenthion are classified as "Toxic" by the E.U.

For more information:

- UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives
- Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996
- PAN Germany. Beyond POPs. Evaluation of the UNEP Chemical Substitutes of the POPs Pesticides Regarding Their Human and Environmental Toxicity. Hamburg, April 2001.
- UNEP. Johan Mörner, Robert Bos and Marjon Fredrix, Reducing and Eliminating the use of Persistent Organic Pesticides. Guidance on alternative strategies for sustainable pest and vector management, (Geneva, 2002). <http://www.pops.int/documents/guidance/Default.htm>
- UNEP/FAO/Global IPM Facility Expert Group on Termite Biology and Management. Finding Alternatives to Persistent Organic Pollutants (POPs) for Termite Management.
- Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000
- World Wildlife Fund. Successful, Safe, and Sustainable Alternatives to Persistent Organic Pollutants. Washington, D.C. September 1999

DDT

USEFUL DATA	
Synonyms	Dichlorodiphenyltrichloroethane
Provisions in the Stockholm Convention and SAP	Production and use restricted (Annex B Stockholm Convention) to disease vector control and intermediate in production of dicofol. Phase out inputs of POPs pesticides by 2010 (SAP)
Main uses	DDT has been used on a variety of agricultural crops and for the control of disease vectors as well. It is still being produced and used for vector control.
Source of emissions	Because DDT has been sprayed on people, domestic animals, buildings, agricultural crops, and forests, it is now distributed widely in the environment.
MAIN ALTERNATIVES	
What alternatives exist:	
<i>Chemical substitutes</i>	
Use	Pest/disease
Crop pests	Termites
	Alternative
	Pyrethroids Organophosphates Carbamates
Public health sanitation	Malaria control
	Alphacypermethrin (synthetic pyrethroid) Bendiocarb (carbamate) Cyfluthrin (synthetic pyrethroid) <i>Lambda</i> -cyhalothrin (synthetic pyrethroid) Deltamethrin (synthetic pyrethroid) Etofenprox (synthetic pyrethroid) Fenitrothion (organophosphate) Malathion (organophosphate) Permethrin (synthetic pyrethroid) Pirimiphos-methyl (carbamate) Propoxur (carbamate)
Production of dicofol	N.a.
<i>Alternative measures</i>	
Use	Alternatives
Mosquito-borne viruses; Yellow fever and Dengue control Public health sanitation	Integrated Vector Management Water source reduction, good drainage Biological control using <i>Bacillus thuringiensis</i> Bio-repellents Netting on the houses and use of mosquito pyrethroid-treated bednets Introduction larvivorous fish

Comments and considerations:

- Lindane has a potential for bioaccumulation, it is persistent in the environment and highly toxic to aquatic organisms. Lindane is known to cause cancer in animals according to U.S. EPA Office of Pesticide Programmes.
- Carbamates have low potential for bioaccumulation; they are not considered to be persistent in the environment but can be highly toxic to aquatic organisms. Propoxur is known to cause cancer in animals according to U.S. EPA Office of Pesticide Programmes. Bendiocarb is classified as "Toxic" by the European Union.
- Malathion (organophosphorous) has lower potential for bioaccumulation than POPs, it is not persistent in the environment but highly toxic to aquatic organisms.
- Synthetic pyrethroids are toxic to aquatic organisms. Cyfluthrin and Lambda-cyhalothrin are classified as "Very Toxic" and Deltamethrin as "Toxic" by the European Union.

For more information:

- UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives
- Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996
- PAN Germany. Beyond POPs. Evaluation of the UNEP Chemical Substitutes of the POPs Pesticides Regarding Their Human and Environmental Toxicity. Hamburg, April 2001.
- UNEP. Johan Mörner, Robert Bos and Marjon Fredrix, Reducing and Eliminating the use of Persistent Organic Pesticides. Guidance on alternative strategies for sustainable pest and vector management, (Geneva, 2002). <http://www.pops.int/documents/guidance/Default.htm>
- UNEP/FAO/Global IPM Facility Expert Group on Termite Biology and Management. Finding Alternatives to Persistent Organic Pollutants (POPs) for Termite Management.
- Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000
- World Wildlife Fund. Successful, Safe, and Sustainable Alternatives to Persistent Organic Pollutants. Washington, D.C. September 1999

DIELDRIN

USEFUL DATA	
Synonyms	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-1,4-exo-5,8-dimethanonaphthalene HEOD
Provisions in the Stockholm Convention and SAP	Production and use prohibited, specific exemption for agricultural uses. (Annex A Stockholm Convention) Phase out inputs of POPs pesticides by 2010 (SAP)
Main uses	Control of soil insects and several insect vectors of disease.
Source of emissions	Former production and use as an insecticide. Dieldrin is also a degradation product of the insecticide aldrin, and the former use of aldrin has contributed to the occurrence of dieldrin in the environment.
MAIN ALTERNATIVES	
What alternatives exist:	
<i>Chemical substitutes</i>	
Use	Pest/disease
Crops	Locusts
	Alternative
	Chlorpyrifos
	Deltamethrin
	Fenitrothion
	Malathion
Grasslands	Termites
	Bromophos
	Endosulfan
Groundnuts	Termites
	Carbofuran
<i>Alternative measures</i>	
Use	Alternatives
Control of insects	Bacillus Thuringiensis
Control of termites	Concrete slabs
	Sheet materials
	Woven stainless steel mesh
	Graded stone articles
	Chemical soil barriers
	Biological barriers: use of Nematodes
	Treatment of infestations
Comments and considerations:	
<ul style="list-style-type: none"> • Endosulfan has a potential for bioaccumulation; it is persistent in the environment and highly toxic to aquatic organisms • Carbamates have low potential for bioaccumulation; they are not considered to be persistent in the environment but can be highly toxic to aquatic organisms. Carbofuran has been classified as "very toxic" by the E.U. • Malathion (organophosphorous) has lower potential for bioaccumulation than POPs; it is not persistent in the environment but highly toxic to aquatic organisms. • Synthetic pyrethroids are toxic to aquatic organisms. Deltamethrin and Chlorpyrifos are classified as "Toxic" by the European Union 	

For more information:

- UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives
- Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996
- PAN Germany. Beyond POPs. Evaluation of the UNEP Chemical Substitutes of the POPs Pesticides Regarding Their Human and Environmental Toxicity. Hamburg, April 2001.
- UNEP. Johan Mörner, Robert Bos and Marjon Fredrix, Reducing and Eliminating the use of Persistent Organic Pesticides. Guidance on alternative strategies for sustainable pest and vector management, (Geneva, 2002). <http://www.pops.int/documents/guidance/Default.htm>
- UNEP/FAO/Global IPM Facility Expert Group on Termite Biology and Management. Finding Alternatives to Persistent Organic Pollutants (POPs) for Termite Management.
- Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000
- World Wildlife Fund. Successful, Safe, and Sustainable Alternatives to Persistent Organic Pollutants. Washington, D.C. September 1999

ENDRIN

USEFUL DATA		
Synonyms		
Provisions in the Stockholm Convention and SAP	Production and use prohibited (Annex A Stockholm Convention) Phase out inputs of POPs pesticides by 2010 (SAP)	
Main uses	Foliar insecticide used mainly on field crops such as cotton and grains. It has also been used as a rodenticide to control mice and voles.	
Source of emissions	Former production and use as an insecticide, rodenticide and avicide has resulted in its widespread environmental release.	
MAIN ALTERNATIVES		
What alternatives exist: <i>Chemical substitutes</i>		
Use Crops (maize, rice, cotton and sugarcane)	Pest/effect Lepidopteran pest	Alternative Chlorpyrifos Carbaryl Endosulfan
<i>Alternative measures</i>		
Use Crops protection Public health sanitation (Mice and voles)	Alternatives Biological control; botanical pesticides Integrated Pest Management Anticoagulants in baits: CO, CO ₂ , traps	
Comments and considerations:		
<ul style="list-style-type: none"> • Endosulfan has a potential for bioaccumulation; it is persistent in the environment and highly toxic to aquatic organisms • Carbamates have low potential for bioaccumulation; they are not considered to be persistent in the environment but can be highly toxic to aquatic organisms. Carbaryl is possibly carcinogenic to humans according to U.S. EPA Office of Pesticide Programmes. • Synthetic pyrethroids are toxic to aquatic organisms. Chlorpyrifos is classified as "Toxic" by the European Union 		
For more information:		
<ul style="list-style-type: none"> - UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives - Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996 		

- PAN Germany. Beyond POPs. Evaluation of the UNEP Chemical Substitutes of the POPs Pesticides Regarding Their Human and Environmental Toxicity. Hamburg, April 2001.
- UNEP. Johan Mörner, Robert Bos and Marjon Fredrix, Reducing and Eliminating the use of Persistent Organic Pesticides. Guidance on alternative strategies for sustainable pest and vector management, (Geneva, 2002). <http://www.pops.int/documents/guidance/Default.htm>
- Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000
- World Wildlife Fund. Successful, Safe, and Sustainable Alternatives to Persistent Organic Pollutants. Washington, D.C. September 1999

HEPTACHLOR

USEFUL DATA	
Synonyms	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
Provisions in the Stockholm Convention and SAP	Production and use prohibited with specific exemptions for uses: Termiticide, Termiticide in structures of houses, Termiticide (subterranean); Wood treatment and in use in underground cable boxes (Annex A Stockholm Convention) Phase out inputs of POPs pesticides by 2010 (SAP)
Main uses	As a non systemic stomach and contact insecticide, used primarily against soil insects and termites. It has also been used against cotton insects, grasshoppers, some crop pests and to combat malaria.
Source of emissions	Its production and former use in termite control, seed/seed furrow treatment, and wood treatment did result in its direct release to the environment.
ALTERNATIVES	
What alternatives exist:	
<i>Chemical substitutes</i>	
Use	Pest/disease
Buildings	Termites
	Alternative
	bendiocarb (carbamate) carbaryl (carbamate) carbosulfan (carbamate) chlorpyrifos (organophosphate)
Crops, nurseries and forest plantations	Termites
	carbofuran (carbamate) chlorpyrifos (organophosphate) carbaryl (carbamate) phorate (organophosphate)
Crops	Cutworms
	Acephate Carbofuran Chlorpyrifos
<i>Alternative measures</i>	
Use	Alternatives
Crops protection	Botanical pesticides; Bacillus Thuringiensis Nematodes Using Titonia concoctions
Control of termites	Concrete slabs Sheet materials Woven stainless steel mesh Graded stone articles Chemical soil barriers Biological barriers: use of Nematodes Treatment of infestations Insect growth regulators

Comments and considerations:

- Carbamates have low potential for bioaccumulation; they are not considered to be persistent in the environment but can be highly toxic to aquatic organisms. Carbaryl is possibly carcinogenic to humans according to U.S. EPA Office of Pesticide Programmes. Carbofuran has been classified as “very toxic” and Bendiocarb and Carbosulfan as “Toxic” by the European Union.
- Chlorpyrifos (organophosphorous) have lower potential for bioaccumulation than POPs, they are not persistent in the environment but highly toxic to aquatic organisms. Acephate is possibly carcinogenic to humans according to U.S. EPA Office of Pesticide Programmes. Phorate is classified as “extremely hazardous” by the WHO. Chlorpyrifos is classified as “Toxic” by the E.U.

For more information:

- UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives
- Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996
- PAN Germany. Beyond POPs. Evaluation of the UNEP Chemical Substitutes of the POPs Pesticides Regarding Their Human and Environmental Toxicity. Hamburg, April 2001.
- UNEP. Johan Mörner, Robert Bos and Marjon Fredrix, Reducing and Eliminating the use of Persistent Organic Pesticides. Guidance on alternative strategies for sustainable pest and vector management, (Geneva, 2002). <http://www.pops.int/documents/guidance/Default.htm>
- UNEP/FAO/Global IPM Facility Expert Group on Termite Biology and Management. Finding Alternatives to Persistent Organic Pollutants (POPs) for Termite Management.
- Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000
- World Wildlife Fund. Successful, Safe, and Sustainable Alternatives to Persistent Organic Pollutants. Washington, D.C. September 1999

HEXACHLOROBENZENE

USEFUL DATA	
Synonyms	
Provisions in the Stockholm Convention and SAP	Production and use prohibited (Annex A Stockholm Convention) with specific exemptions: Intermediate; Solvent in pesticide; Closed system site limited intermediate. Reduction of the total releases from unintentional production derived from anthropogenic sources (Annex C Stockholm Convention) with the goal of their continuing minimization and, where feasible, ultimate elimination. Phase out inputs of POPs pesticides by 2010 (SAP) Reduce to the fullest possible extent inputs of unwanted contaminants (dioxins and furans and hexachlorobenzene) by 2010 (SAP)
Main uses	Seed dressing for crops such as wheat, barley, oats and rye to prevent fungi. Main non pesticide uses: wood-preserving agent; in the manufacture of pyrotechnics and tracer bullets; fluxing agent in the manufacture of aluminium; porosity-control agent in the manufacture of graphite anodes; peptizing agent in the production of nitroso and styrene rubber for tyres
Source of emissions	Waste incinerators; Cement kilns firing hazardous waste; Production of pulp using elemental chlorine; thermal processes in the metallurgical industry.
MAIN ALTERNATIVES	
What alternatives exist:	
Use/source	Alternative
Seed dressing for crops	Bitertanol Carboxin Fuberidazol Quazatine Biological control: Host plants resistance
Wood preserving agent	-
Pyrotechnics and tracer bullets	Hexachloroethane
Fluxing agent in manufacture of aluminium	Chlorine gas
Porosity-control agent in manufacture of graphite anodes	Dimensionally stabilized anodes (instead of graphite anodes)
Peptizing agent in production of rubber	-
By-product from industrial chemical processes involving chlorine (chlorinated solvents)	New generation of petroleum solvents Water-based methods Mechanical methods
Impurity in chlorinated pesticides	Avoidance of chlorinated pesticides
Thermal processes (unintentional)	See <i>DIOXINS and FURANS guidelines</i>
Comments and considerations:	
Chlorinated solvents are feasible to be successfully substituted in most cases by other methods	

For more information:

- UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives
- Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996
- PAN Germany. Beyond POPs. Evaluation of the UNEP Chemical Substitutes of the POPs Pesticides Regarding Their Human and Environmental Toxicity. Hamburg, April 2001.
- UNEP. Johan Mörner, Robert Bos and Marjon Fredrix, Reducing and Eliminating the use of Persistent Organic Pesticides. Guidance on alternative strategies for sustainable pest and vector management, (Geneva, 2002). <http://www.pops.int/documents/guidance/Default.htm>
- Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000
- World Wildlife Fund. Successful, Safe, and Sustainable Alternatives to Persistent Organic P ollutants. Washington, D.C. September 1999

MIREX

USEFUL DATA		
Synonyms		
Provisions in the Stockholm Convention and SAP	Production and use prohibited with specific exemptions in production and termiticide uses (Annex A Stockholm Convention) Phase out inputs of POPs pesticides by 2010 (SAP)	
Main uses	Stomach insecticide, mainly formulated into baits, for the control of ants, especially fire ants and harvester ants. As a flame-retardant.	
Source of emissions	Release into the environment has occurred via effluents from manufacturing plants and sites where mirex was utilized as a fire resistant additive to polymers and at points of application where it was used as an insecticide.	
ALTERNATIVES		
What alternatives exist:		
<i>Chemical substitutes</i>		
Use	Pest/disease	Alternative
Crops	Termites	Sulfuramid Carbaryl
Forest plantation, nurseries	Leafcutter ants	Diazinon Deltamethrin Diflubenzuron Sulfuramid
Flame retardant		Flame retardants can be substituted generally by: 1) Other flame retardant: <i>Organophosphorous</i> (Triphenyl Phosphate; Tricresyl Phosphate; Resorcinol bis(diphenylphosphate); Phosphonic acid, (2-((hydroxymethyl)carbonyl)ethyl)-, dimethyl ester) <i>Inorganic content</i> (Aluminium Trihydroxide; Magnesium Hydroxide; Ammonium Polyphosphate; Red Phosphorus; Zinc Borate) <i>Nitrogen content</i> (Melamine) 2) Replacing the plastic material 3) Replacing plastic material by another material
<i>Alternative measures</i>		
Use	Alternatives	
Crops protection	Insect growth regulators Using Titonia concoctions	

Control of termites	<p>Concrete slabs Sheet materials Woven stainless steel mesh Graded stone articles Chemical soil barriers Treatment of infestations</p>
Comments and considerations:	
<ul style="list-style-type: none"> • Carbamates have low potential for bioaccumulation; they are not considered to be persistent in the environment but can be highly toxic to aquatic organisms. Carbaryl is possibly carcinogenic to humans according to U.S. EPA Office of Pesticide Programmes. • Synthetic pyrethroids are toxic to aquatic organisms. Deltamethrin is classified as "Toxic" by the European Union. • Feasibility of flame retardant substitution by another type of flame retardant depends on technical and security requirements of the article. • Alternatives to flame retardants based on replacing the plastic material by other plastic material or replacing the plastic material by another type of material are feasible in most cases 	
For more information:	
<ul style="list-style-type: none"> - UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives - Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996 - PAN Germany. Beyond POPs. Evaluation of the UNEP Chemical Substitutes of the POPs Pesticides Regarding Their Human and Environmental Toxicity. Hamburg, April 2001. - UNEP. Johan Mörner, Robert Bos and Marjon Fredrix, Reducing and Eliminating the use of Persistent Organic Pesticides. Guidance on alternative strategies for sustainable pest and vector management, (Geneva, 2002). http://www.pops.int/documents/guidance/Default.htm - UNEP/FAO/Global IPM Facility Expert Group on Termite Biology and Management. Finding Alternatives to Persistent Organic Pollutants (POPs) for Termite Management. - Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000 - World Wildlife Fund. Successful, Safe, and Sustainable Alternatives to Persistent Organic Pollutants. Washington, D.C. September 1999 - OSPAR Commission. Certain Brominated Flame Retardants – Polybrominated Diphenylethers, Polybrominated Biphenyls, Hexabromo Cyclododecane. 2001 (2004 Update) - Danish Environmental Protection Agency. Brominated Flame retardants - Substance Flow Analysis and Assessment of Alternatives, Report No. 494, 1999. 	

TOXAPHENE

USEFUL DATA	
Synonyms	Chlorinated camphene (60%), camphechlor
Provisions in the Stockholm Convention and SAP	Production and use prohibited (Annex A Stockholm Convention) Phase out inputs of POPs pesticides by 2010 (SAP)
Main uses	Nonsystemic and contact insecticide that was used primarily on cotton, cereal grains fruits, nuts and vegetables. It has also been used to control ticks and mites in livestock.
Source of emissions	Its production and use as an insecticide has resulted in its direct release to the environment
ALTERNATIVES	
What alternatives exist:	
<i>Chemical substitutes</i>	
Use	Pest/disease
Cotton	Insects, boll weevil
Soybeans	Cassia obtusifolia
Vegetables	Sogartodes orizicola
	Alternative
	Dimethoate
	Chlorpyrifos
	Trifluralin
	Metribuzin
	Alachlor
	Dimethoate
	Chlorpyrifos
<i>Alternative measures</i>	
Use	Alternatives
Crops protection	Biological control: Alternaria cassiae Environmental management
Comments and considerations:	
<ul style="list-style-type: none"> Alachlor (chlorinated hydrocarbon) has been classified as "extremely hazardous" by the WHO. Organophosphorous (dimethoate) have lower potential for bioaccumulation than POPs, they are not persistent in the environment but highly toxic to aquatic organisms. Dimethoate is classified as possibly carcinogenic to humans by the U.S. EPA Office of Pesticide Programmes. Synthetic pyrethroids are toxic to aquatic organisms. Chlorpyrifos is classified as "Toxic" by the E.U. Trifluralin is classified as possibly carcinogenic to humans by the U.S. EPA Office of Pesticide Programmes 	
For more information:	
<ul style="list-style-type: none"> UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996 PAN Germany. Beyond POPs. Evaluation of the UNEP Chemical Substitutes of 	

the POPs Pesticides Regarding Their Human and Environmental Toxicity. Hamburg, April 2001.

- UNEP. Johan Mörner, Robert Bos and Marjon Fredrix, Reducing and Eliminating the use of Persistent Organic Pesticides. Guidance on alternative strategies for sustainable pest and vector management, (Geneva, 2002). <http://www.pops.int/documents/guidance/Default.htm>
- Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000
- World Wildlife Fund. Successful, Safe, and Sustainable Alternatives to Persistent Organic Pollutants. Washington, D.C. September 1999

POLYCHLORINATED BIPHENYLS

USEFUL DATA	
Synonyms	
Provisions in the Stockholm Convention and SAP	<p>Production and uses prohibited with the specific exemption of articles in use (Annex A Stockholm Convention). Reduction of the total releases from unintentional production derived from anthropogenic sources (Annex C Stockholm Convention) with the goal of their continuing minimization and, where feasible, ultimate elimination</p> <p>Collect and dispose all PCB waste in a safe and environmentally sound manner by 2005 (SAP)</p>
Main uses	<ul style="list-style-type: none"> • Dielectric fluids in transformers, capacitors, hydraulic oils, thermal oils, lubricating oils. • Plasticiser for rubber, synthetic resins • Solvent/support in carbonless copy paper, Adhesives, Paints, printing inks, sealants
Source of emissions	<ul style="list-style-type: none"> • Leakage and spillage from PCB containing equipment still in use or stored • Fires and accidents at sites where PCB containing equipment is still in use or stored • Inappropriate disassembling of PCB containing equipment • Improper waste disposal • Unintentional emissions: Waste incinerators, Cement kilns firing hazardous waste; Production of pulp using elemental chlorine; Thermal processes in the metallurgical industry: Secondary copper production; Sinter plants in the iron and steel industry; Secondary aluminium production; Secondary zinc production.
MAIN ALTERNATIVES	
What alternatives exist:	
Use	Alternative
Dielectric fluid in transformers	<p>Alternative design (e.g. encapsulated transformers)</p> <p>Mineral oils</p> <p>Silicone oils</p> <p>Tetrachlorobenzene</p> <p>Chlorinated diphenylethane</p> <p>Chloroalkylene</p> <p>Biphenyl</p>
Dielectric fluid in capacitors	<p>Mixture of methyl (phenylmethyl)benzene and methylbis (phenylmethyl) benzene</p> <p>Phenylxylene</p> <p>Alternative design for small capacitors</p>

Heat exchange fluid	Mineral oil Silicone oil Biphenyl Diphenyl oxide
Hydraulic fluids	A vegetable based oil (turnip oil)
Thermal processes (unintentional)	<i>See DIOXINS and FURANS guidelines</i>

Comments and considerations:

- Some reported substitutes such as Polychlorinated terphenyls (PCTs), alkylsubstituted chlorodiphenyls and polychlorinated naphthalenes (PCNs) and biphenyls have toxicological and ecotoxicological properties, which are similar to such of PCBs.
- Other chemical substitutes considered as hazardous are: Butylated monochlorodiphenyl ether; Chloralkylenes; Chlorinated benzenes; Chlorinated hydrocarbons.
- Mineral oils, Silicone oils, Phenylxylylethane, and Vegetable based oils are environmental and feasible options
- Changes of material or design are proved to be feasible in most cases

For more information:

- UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives
- Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996
- Abildgaard. A. Alternatives to Persistent Organic Pollutants. Final Report. COWI. Nordic Chemical Group. July 2000
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- Eurochlor Risk Assessment for the Marine Environment. OSPARCOM Region – North Sea. PCBs, DDT Dioxins. June 2002.

DIOXINS AND FURANS

USEFUL DATA			
Synonyms			
Provisions in the Stockholm Convention and SAP		Reduction of the total releases from unintentional production derived from anthropogenic sources (Annex C Stockholm Convention) with the goal of their continuing minimization and, where feasible, ultimate elimination. Reduce to the fullest possible extent inputs of unwanted contaminants (dioxins and furans and hexachlorobenzene) by 2010 (SAP)	
Main uses Source of emissions		No intentional uses Waste incinerators, Cement kilns firing hazardous waste; Production of pulp using elemental chlorine; Thermal processes in the metallurgical industry: Secondary copper production; Sinter plants in the iron and steel industry; Secondary aluminium production; Secondary zinc production.	
MAIN ALTERNATIVES			
What alternatives exist:			
Source	Avoidance/Substitution of precursors	Modification/substitution of processes	Alternate processes
Municipal Waste incineration:	Avoidance/substitution of chlorinated precursors e.g. PVC	Incinerator with grate	Pyrolysis and gasification Thermal depolymerization Plasma technologies High temperature melting
Medical waste incineration	Avoidance/substitution of chlorinated precursors e.g. PVC	Pyrolytic incinerator (BAT) Rotary kiln (BAT) Incinerator with grate (BAT) Fluidized bed incinerator (BAT)	
Cement kilns firing hazardous waste		Dry process kiln with multi-stage preheating and precalcination (BAT)	
Production of pulp using chlorine	Substitution of elemental chlorine for bleaching		
Secondary copper		Blast Furnace, mini-smelter, Top Blown Rotary Furnace, Sealed Submerged Electric Arc furnace, ISA Smelt, and the Peirce-Smith converter.	Catalytic oxidation (emerging research)
Iron and steel industry			FASTMET, direct reduction of iron, direct smelting
Secondary aluminium/zinc/lead production			Blast furnace, Submerged electric arc furnace
Primary aluminium production		Prebake technology (BAT)	Inert anodes Wettable cathodes Vertical Electrodes – Low Temperature Electrolysis Drained Cell Technology Carbothermic Technology Kaolinite Reduction Technology

Magnesium production	Elimination of carbon source-replaces graphite with non-graphite anode		Norsk Hydro's Mgcl2 brine Dehydration Process.
Secondary steel			Process design
Primary metals			Hydrometallurgical processes Closed-loop electrolysis plants
Fossil fuel – fired utilities and industrial boilers	-	-	-
Firing installations for wood and other biomass fuels			
Chemical production processes: Chlorination		Treatment of impurities in raw materials Distillation and internal recycling of by-products	Titanium dioxide, Sulphate process
Crematoria Destruction of animal carcasses		Minimum 850°C Residence time	
Textile and leather dyeing and finishing	Substitution of POP: 2-(thiocyanomethylthio)benzothiazole) o-Phenylphenol (oPP; 4-Chloro-3-methylphenol 2-n-Octyl-4-isothiazolin-3-one (OIT, CAS		
Smouldering copper cables			Cable chopping Cable stripping High temperature incineration Melting in electric furnace
Shredder plants for treatment of end of life vehicles			
Open burning of waste			Incinerators devices for burning refuse
Residential combustion			Design of improved stoves
Motor vehicles	Avoidance of halogenated scavengers and leaded gasoline		Electricity, solar light and fuel battery engines

Comments and considerations:

- Municipal waste incinerator: Non-incineration and emerging technology options may represent feasible and environmentally sound alternatives to incineration. Although most of them are not considered fully demonstrated on an industrial scale.

- Secondary copper: The reverberatory hearth furnace, the hearth shaft furnace and Contimelt process to treat clean copper scrap devoid of organic contamination
- Catalytic oxidation is an emerging technology which should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, carbon dioxide (CO₂) and hydrochloric acid using a precious metal catalyst.

For more information:

- UNEP/POPs. Information on POPs alternatives and approaches to replace and/or reduce the releases of POPs chemicals. Database on POPs alternatives
- Swedish National Chemicals Inspectorate Swedish Environmental Protection Agency. Alternatives to Persistent Organic Pollutants. The Swedish Input to the IFCS Expert Meeting on Persistent Organic Pollutants in Manila, The Philippines, 17-19 June 1996. May 1996
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- UNEP. Draft guidelines on best available techniques and provisional guidance on best environmental practices. July 2004.
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ANNEX I

WHO Resolutions on DDT

WHO position and recommendations on DDT use

The most recent recommendations of the World Health Organization concerning DDT give specific guidance on its proper use. A WHO Study Group (WHO, 1995) arrived at the following conclusions and recommendations:

- 1) the information does not provide convincing evidence of adverse effects of DDT exposure as a result of indoor residual spraying as carried out in malaria control activities.
- 2) there is, therefore, at this stage no justification on toxicological or epidemiological grounds for changing current policy towards indoor residual spraying of DDT for vector-borne disease control.
- 3) DDT may, therefore, be used for vector control provided that all the following conditions are met:
 - it is used only for indoor spraying;
 - it is effective;
 - the material is manufactured to the specifications issued by the WHO; and
 - the necessary safety precautions are taken in its use and disposal.
- 4) in considering whether to use DDT, governments should take into account the following additional factors:
 - the costs involved in the use of insecticides (DDT or alternatives);
 - the role of insecticides in focal or selective vector control, as specified in the Global Malaria Strategy;
 - the availability of alternative vector control methods, including alternative insecticides (... this was a departure from the long-held WHO position that considered DDT to be the insecticide of choice where effective ...);
 - the implications of insecticide resistance, including possible cross-resistance to some alternative insecticides; and
 - the changing public attitude to pesticide use, including public health applications.

The WHO outlook with respect to the future of insecticide use for vector control, and of DDT in particular, was clearly stated by the World Health Assembly in 1997.

The replacement of DDT should not be limited to alternative pesticides, but should consider alternative strategies and methods that allow an overall reduction of the reliance on pesticides. Excerpts follow:

FIFTIETH WORLD HEALTH ASSEMBLY (Geneva, 5-14 May 1997)

Excerpts from WHA Resolution 50.13: Promotion of chemical safety, with special attention to Persistent Organic Pollutants

The fiftieth World Health Assembly calls, inter alia, upon Member States:

- to involve appropriate health officials in national efforts to follow up and implement decisions of the UNEP and WHO governing bodies relating to the currently identified persistent organic pollutants;
- to ensure that scientific assessment of risks to health and the environment is the basis for the management of chemical risk;
- to continue efforts to establish or reinforce national coordinating mechanisms for chemical safety, involving all responsible authorities as well as non-governmental organizations concerned;
- to take steps to reduce reliance on insecticides for control of vectorborne diseases through promotion of integrated pest management approaches in accordance with WHO guidelines, and through support of the development and adaptation of viable alternative methods of disease vector control;
- to establish or strengthen government mechanisms to provide information on the levels and sources of chemical contaminants in all media, and in particular in food, as well as on the levels of exposure of the populations;
- to ensure that the use of DDT is authorised by governments for public health purposes only and that, in those instances, such use is limited to government-authorized programmes that take an integrated approach and that strong steps are taken to ensure that there is no diversion of DDT to entities in the private sector; and
- to revitalise measures for training and for increasing public awareness in collaboration with inter-governmental and non-governmental organizations, in order to prevent poisonings by chemicals and, in particular, pesticides.

Source, WHO, 2001

The WHO Action Plan for the reduction of reliance on DDT in disease vector control (WHO, 2001b), defines alternatives as use of alternative products for chemical and biological control, alternative methods for the application of chemical and biological control, environmental management and personal protection, and alternative strategies, i.e., integrated vector management based on scientifically sound criteria, cost-effectiveness analyses and delivery systems compatible with current trends in health sector reform. This reform may include decentralization, intersectoral action at the local level and subsidiarity in decision-making.

ANNEX II

Hazard classification and health risks of POPs pesticides

Pesticide	Type	Acute Toxicity (LD50)	PIC (a)	WHO (b)	USEPA (c)	IARC (d)	Other effects
Aldrin	Insecticide	83 (humans) 38	Yes	lb	B2	3	Immunotoxicity, chronic liver effect, male reproductive system impact
Chlordane	Insecticide	25 (humans) 250	Yes	II	B2	2B	Endocrine system impact, reproductive disorders
DDT	Insecticide	113	Yes	II	B2	2B	Immunotoxicity, interference with estrogenic system, possible endocrine disruption
Dieldrin	Insecticide	37	Yes	la	B2	3	Immunotoxicity, chronic liver effect, male reproductive system impact
Endrin	Insecticide	7		lb	-	3	
HCB	Fungicide	>10000	Yes	la	B2	2B	Effects on nervous, thyroid and reproductive systems
Heptachlor	Insecticide	147	Yes	II	B2	2B	Possible endocrine disruption, reproductive disorders
Mirex	Insecticide	306		-	B2	2B	Teratogenic
Toxaphene	Insecticide	30 (humans) 40		II	-	2B	Effects on nervous system

(a) Rotterdam Convention: www.pic.int

(b) Acute Toxicity – World Health Organisation (WHO)

- la Extremely hazardous
- lb Highly hazardous
- II Moderately hazardous
- III Slightly hazardous
- U Unlikely to present hazard in normal use

(c) Cancer Classification of the U.S. EPA

Category Description

Category A: Known to cause cancer in humans. Generally based on epidemiological data showing sufficient evidence to support a causal association between exposure to the substance and cancer.

Category B: Known to cause cancer in animals but not yet definitively shown to cause cancer in humans. These chemicals are designated “probable human carcinogens”. Category B is further split into pesticides for which some evidence exists that they cause cancer in humans (B1), and those for which evidence exists only in animals (B2).

Category C: Possible human carcinogens, where the data show limited evidence of carcinogenicity in the absence of human data.

Category D: This category is for chemicals for which the data are either incomplete or ambiguous and is labelled “cannot be determined”. This category is appropriate when tumour effects or other key data are suggestive, conflicting or limited in quantity and are thus not adequate to convincingly demonstrate carcinogenic potential for humans. In general, further chemical-specific and generic research and testing are required to be able to describe human carcinogenic potential.

Category E: Probably not carcinogenic, with no evidence of carcinogenicity in at least two adequate animal tests in different species in adequate epidemiological and animal studies. This classification is based on available evidence and does not imply that the agent will not be a carcinogen under any circumstances.

(d) International Agency for Research on Cancer - IARC

- | | |
|----------|--|
| Group 1 | The agent (mixture) is carcinogenic to humans |
| Group 2A | The agent (mixture) is probably carcinogenic to humans |
| Group 2B | The agent (mixture) is possibly carcinogenic to humans |
| Group 3 | The agent (mixture or exposure circumstance) is not classifiable as to its carcinogenicity to humans |
| Group 4 | The agent (mixture) is probably not carcinogenic to humans |

ANNEX III

Preventive measures to avoid accumulation of obsolete pesticides (FAO, 1997)

Cause of accumulation	Preventive measures
<p>Banning of product</p> <ul style="list-style-type: none"> • Residue after product banned 	<ul style="list-style-type: none"> • Formulate phasing-out clause when banning pesticides
<p>Inadequate storage capacity and poor stock management</p> <ul style="list-style-type: none"> • Insufficient storage capacity for pesticides • Staff not trained in stock management • Containers damaged through rough handling during transport • Unavailability of analytical facilities to determine product quality after prolonged periods of storage 	<ul style="list-style-type: none"> • Invest in new stores or upgrade old ones. Avoid procurement of pesticide quantities that exceed the storage capacity • Train staff in stock management, or at least provide them with copies of these and other relevant guidelines • Train staff in the proper handling of pesticides during transport. Shorten transit periods as much as possible. Request repackaging of material with each consignment • Make arrangements with a laboratory in or outside the country
<p>Donations or purchases in excess of requirements</p> <ul style="list-style-type: none"> • Inaccurate assessment of requirements • Lower than expected pest incidence • Overstocking of products with a short shelf-life • Excessive donations • Left over because of reduced demand as a result of removal of subsidies 	<ul style="list-style-type: none"> • Use checklists to determine requirements. Keep stocks as low as possible. Do not stock more than a one-season requirement • Keep stocks as low as possible. Purchase only when there is a direct need. Do not establish anticipatory stocks, but improve supply arrangements/systems instead • Do not stock large quantities of products with a short shelf life. Specify the desired product stability in tender documents or direct procurement orders to ensure that the minimum storage period is not longer than the expiry date of the product • Do not accept donations in excess of requirements. Aid agencies should not accept requests without satisfactory justification • Anticipate a drop in demand when planning requirements to cover a period when subsidies may be removed

Cause of accumulation	Preventive measures
<p>Unsuitable products</p> <ul style="list-style-type: none"> • Inappropriate active ingredient or formulation • Inappropriate package type or size • Missing or incomplete labels • Fraudulent practices of suppliers 	<ul style="list-style-type: none"> • Carefully determine requirements. Spell out product specifications in the tender document or direct procurement order. Do not accept donations of products that are considered unsuitable for the specific use intended • Carefully determine requirements. Spell out packaging specifications in the tender document or direct procurement order. Do not accept donations of products that are inappropriately packaged • Specify labelling requirements in the tender document or direct procurement order • Follow FAO guidelines on tender procedures for procurement of pesticides