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Stockholm Convention: “New POPs”

Screening Additional POPs Candidates

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1. Introduction

The Stockholm Convention targets 12 persistent organic pollutants (POPs) that threaten wildlife and people around the world. Placing these substances under global control is an important step in protecting the public and wildlife from harm. Envisioned by the international community to be a dynamic treaty, the Stockholm Convention provides a rigorous scientific process through which new chemicals with POPs characteristics can be added to the treaty. Several additional POP candidates await international attention; their expedited review, initially by the POP Review Committee (POPRC), will enable the Conference of Parties (COP) to address other dangerous chemicals sooner, rather than later.

Currently, approximately 80,000 chemicals (although the exact figure is unknown) are produced, marketed, used, and disposed of worldwide. Each year, hundreds of new chemicals are added to this ever-growing list. So far, very little is known about toxicity of these chemicals. Regulating these chemicals one-by-one will be a daunting and time-consuming effort. Over the longer term, relying solely on chemical-by-chemical regulation risks irreversible adverse effects to both human and wildlife health.

WWF applauds efforts of governments—at the national level, and through multilateral regimes—to address chemical groups such as polychlorinated biphenyls (PCBs) and dioxins (Stockholm Convention), or polycyclic aromatic hydrocarbons (PAHs) (United Nations Economic Commission for Europe /UNECE Protocol to the Convention on Long-Range Transboundary Air Pollution /LRTAP on POPs). The Stockholm COP and its POPRC should take the opportunity to seriously consider more chemical groups rather than individual chemicals for their inclusion as new POPs candidates. Substances and groups of chemicals that have similar chemical structures, properties, and/or potentials to harm, and those degrade to the Convention-regulated substances, all merit close scrutiny.

Screening Criteria for POPs Under the Stockholm Convention

The “Information Requirements and Screening Criteria” from the Stockholm Convention can be found in the Appendix. The criteria are summarized below:

Persistence: For the persistence requirement, the party nominating a chemical for listing in the Stockholm Convention should provide evidence that the half-life of the chemical in water is greater than two months, its half-life in soil is greater than six months, its half-life in sediment is greater than six months; or evidence that the chemical is otherwise sufficiently persistent to justify its consideration within the scope of the Convention.

Bioaccumulation: The bioaccumulation criteria requires evidence that the bioconcentration factor (BCF) or bioaccumulation factor in aquatic species for the chemical is greater than 5,000 or, in the absence of such data, that the log Kow is greater than 5; evidence that a chemical presents other reasons for concern, such as high bioaccumulation in other species, high toxicity, or ecotoxicity; or monitoring data in biota indicating that the bioaccumulation potential of the chemical is sufficient to justify its consideration within the scope of the Convention.

Potential for long-range environmental transport: To meet the long-range transport criteria, a nominating party must demonstrate measured levels of the chemical in locations distant from the sources of its release that are of potential concern; monitoring data showing that long-range environmental transport of the chemical, with the potential for transfer to a receiving environment, may have occurred via air, water, or migratory species; or environmental fate properties and/or model results that demonstrate that the chemical has a potential for long-range environmental transport through air, water, or migratory species, with the potential for transfer to a receiving environment in locations distant from the sources of its release. For a chemical that migrates significantly through the air, its half-life in air should be greater than two days.

Toxicity (Adverse Effects): The toxicity criteria requires evidence of adverse effects to human health or to the environment or toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.

Identifying New POPs

Identification of chemicals likely to meet the POPs criteria is hindered by the fact that data on persistence, toxicity, bioaccumulation, and long-range transport are available for very few chemicals. WWF urges the chemical industry to develop and disseminate this important information.

The following 20 chemicals or groups of chemicals are potential POP candidates meriting further investigation for possible early inclusion in the Stockholm Convention. Among the 20 new POPs candidates, 18 are suggested for addition to Annex A (A-1 to A-18) and 2 are suggested for addition to Annex C (C-1 and C-2), as shown in Box 1. The 18 chemicals suggested for addition to Annex A are clustered by their function and application. They are grouped as: 1) pesticides, insecticides, and other biocides; 2) brominated flame retardants; 3) perfluorochemicals; and 4) other chlorinated chemicals and chemical groups. Two chemicals suggested for addition to Annex C are unintentionally produced chemicals or chemical groups.

Box 1: New POP Candidates

Category	Cluster	New POP Candidates
A-1	Pesticides, Insecticides, Biocides, Fungicides	chlordecone
A-2		hexachlorocyclohexane (HCH) (includes lindane)
A-3		pentachlorophenol (PCP)
A-4		endosulfan
A-5		hexachlorobutadiene (HCBD)
A-6		dicofol
A-7		methoxychlor
A-8	Brominated Flame Retardants	hexabromocyclododecane (HBCD)
A-9		hexabromobiphenyl (Hexa-BB)
A-10		pentabrominated diphenyl ether (penta-BDE)
A-11		octabrominated diphenyl ether (octa-BDE)
A-12		decabrominated diphenyl ether (deca-BDE)
A-13	Perfluoro-chemicals	perfluorooctanyl sulfonate (PFOS)
A-14		perfluorooctanoic acid and its salts (PFOA)
A-15	Other Chlorinated Chemicals or Groups	pentachlorobenzene (penta-CB)
A-16		short-chained chlorinated paraffins (SCCPs)
A-17		polychlorinated naphthalenes (PCNs)
A-18		tetrachlorobenzene (tetra-CB)
C-1	Unintentionally Produced	ochtachlorostyrene (OCS)
C-2		polycyclic aromatic hydrocarbons (PAHs)

Four of the chemicals or chemical groups (A-1, 2, 9 and C-2) have been identified as POPs in the regionally-based LRTAP POPs Protocol. Nine chemicals or chemical groups (A-3~6, 10, 13, and 15~17) have been proposed for LRTAP listing after being evaluated by some European countries against screening criteria similar to that of the Stockholm Convention. Therefore, data are already available to suggest that these chemicals meet the UNEP POPs criteria. A-7 has been listed by the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention) in its OSPAR List of Chemicals for Priority Action because available data show that it is persistent, toxic, and bio-accumulative (OSPAR 2004). The EU has proposed eight chemicals (A-1, 2, 5, 9, 10, 11, 15, 17) to be added to the Annexes of the Stockholm Convention (EU 2004, EC 2004). Another four chemicals (A-8, 14, 18, and C-1) are listed because of concerns regarding their toxicity and detection in environments remote from the source of release. These 20 chemicals or chemical groups represent a selection of highly problematic chemicals that possess POP-like properties.

2. New POPs Candidates

A-1~7. Pesticides, Insecticides, etc.

These seven chemicals are commonly used as pesticides, insecticides, fungicides, fumigant, and biocides. Their ability to kill unwanted organisms also has the potential to harm wildlife and people.

A-1. Chlordecone

The insecticide chlordecone (Kepone) has already been banned in many countries. Its placement on the LRTAP POPs Protocol establishes its conformance with the UNEP POPs criteria, as these two international treaties have common criteria. Chlordecone is highly toxic to aquatic algae and invertebrate species and produces a range of health effects in mammals. These include reproductive impairment, liver damage, and neurological symptoms. It is also known to cause cancer in animals.

A-2. Hexachlorocyclohexane (HCH)

Also included on the LRTAP POPs Protocol, HCH is the predominant organochlorine chemical found in Arctic air and in the Arctic Ocean (AMAP 1997). It has also accumulated in humans and wildlife living in the Arctic. One form of HCH is lindane, which is neurotoxic and can adversely affect reproduction, the liver, and the immune system. Both “technical grade” HCH and lindane are used in wood treatments and as insecticides, and they are also used in the home and in forestry. The International Agency for Research on Cancer (IARC) has classified HCH isomers as possibly carcinogenic to humans.

A-3. Pentachlorophenol (PCP)

Used as a biocide and wood preservative, PCP was the subject of an International Declaration signed in 1998 by several countries party to the LRTAP POPs Protocol, including all EU countries, Iceland, Norway, and Switzerland. The Declaration states that these countries “maintain their belief in the need for pentachlorophenol use to be tightly controlled to minimize emissions to the environment and urge other Parties to the Convention on Long-Range Transboundary Air Pollution to adopt controls similar in effects to those in place in the European Community if they have not already done so” (ECE/EB.AIR/57 1998).

Toxicity: PCP is highly toxic and there is some evidence that it causes cancer in humans. The IARC has classified it as a possible carcinogen in humans, while the US Environmental

Protection Agency (US EPA) considers it to be a probable human carcinogen. It can also affect the immune and endocrine systems (ATSDR 1999). Disruption of thyroid hormone transport is a particular concern because PCP can bind to one of the thyroid hormone transport proteins, transthyretin, with twice the affinity of thyroxin (Sandau et al. 2000a). Free thyroxine levels in Nunavik placental cord plasma were negatively correlated with the sum of PCP and PCB hydroxylated compounds, suggesting that these chemicals are altering thyroid hormone status in newborns which could lead to neurodevelopmental effects (Sandau et al. 2002). The degradation products of PCP also raise concerns (AEA 1994). Pentachloroanisole, for example, has been found as a contaminant of Arctic air (Macdonald et al. 2000) and biota (Muir et al. 2001).

Persistence: PCP may not meet the UNEP POPs criterion for persistence, but it may be more recalcitrant to degradation under certain conditions, such as low sunlight, or when adsorbed on acidic soils (ATSDR 1999).

Bioaccumulation: PCP does not typically have high values for bioaccumulation but the criterion is met in some aquatic organisms (ATSDR 1999). PCP has also been reported to accumulate in human adipose tissue, particularly in testicular tissue (Wagner et al. 1991), although other sources state that the highest concentrations are found in the liver, kidney, and brain and that the potential for bioaccumulation is low (UNECE 2002a). Hydroxylated PCP has been detected in umbilical cord plasma in women from Quebec, including the Inuit from Nunavik, and was found at levels of 638-7680 pg/g wet weight (Sandau et al. 2002).

Potential for long-range environmental transport: Despite ongoing debate about PCP's ability to undergo long-range transport, PCP has been measured in the Arctic. Its half-life in air is estimated to be less than 2 days, but significant long-range transport might nonetheless occur when PCP is adsorbed onto particulates, as degradation in this form is likely to take occur more slowly. PCP has been found in the blood of polar bears and Inuit people (Sandau et al. 2000a).

A-4. Endosulfan

The insecticide endosulfan is structurally similar to chlordane and dieldrin. It is used on a wide variety of food crops including tea, coffee, fruits, vegetables, rice, cereals, maize, sorghum, and other grains. It is also widely used on cotton, and there is more limited application as a wood preservative and to control termites and tsetse fly. Use of endosulfan has declined in Europe, although elevated levels have been noted in certain foods such as peppers sold in the EU (EC 2001). In 1984, the World Health Organization estimated worldwide production at 10,000 metric tons. In the United States, it is no longer produced, but use continues, mainly on tobacco and fruit crops (ATSDR 2000). Technical-grade endosulfan contains at least 94% of two pure isomers, alpha and beta endosulfan, which are present in a ratio of 7:3.

Toxicity: Endosulfan has neurotoxic effects, as well as effects on the kidneys, testes, and liver. Endosulfan may lower the ability to fight infection. Experiments suggest that immune responses can be altered at dose levels that do not induce other overt signs of toxicity (ATSDR 2000). There are also concerns about human health in areas where spraying is conducted (Quijano 2002).

Endosulfan can act as an endocrine disruptor (BKH report 2000). Organisms treated with endosulfan exhibit toxic effects, such as developmental and reproductive changes that have been associated with endocrine disrupting chemicals (US EPA 2002a). In fish, effects on the onset of breeding behavior in juvenile male cichlid have been noted at 0.6 µg/l (Matthiessen and Logan 1984). Levels of 5µg/l have been shown to interfere with reproduction in the red-spotted newt, *Notophthalmus viridescens*, by disrupting the development of female glands that synthesize a pheromone used in female-male communication (Park et al. 2001). Other effects linked to its endocrine disrupting properties include: impaired development in amphibians; reduced cortisol secretion in fish; impaired development of the genital tract in birds; and altered hormone levels, testicular atrophy, and reduced sperm production in mammals (Herrmann 2002).

On the basis of standard tests, endosulfan is reported to be highly toxic for aquatic organisms, with, for example, a 96 hour LC_{50} value for the marine crustacean *Penaeus duorarum* of 0.04µg/l (Herrmann 2002). In the United States, a national database shows that during the 1980s, endosulfan was responsible for more fish kills in estuaries and coastal rivers than all other currently used pesticides (US EPA 2002a).

Persistence: Although endosulfan does not appear to meet the numerical UNEP POPs criterion for persistence in water, the criterion may be met in slightly acidic waters under anaerobic conditions. Similarly, the alpha and beta isomers both persist longer under more acidic soil conditions, with beta-endosulfan having a longer half-life as it is slowly converted to alpha-endosulfan. In many studies of soil and sediments it may not meet the criterion, although in sandy soils, the beta isomer can have a half-life greater than 6 months. Also, when considering degradation times in soils, if the persistent and toxic metabolite endosulfan sulfate is included, then the half-life of “total endosulfan” in soil exceeds 6 months in some cases (Herrmann 2002). Endosulfan could also arguably meet the non-numerical criterion, namely that it is sufficiently persistent to justify consideration within the scope of the Convention.

Bioaccumulation: Reported log Kow values suggest a high potential for bioconcentration, which is confirmed by laboratory data. For example, a BCF of 2,650 was reported for zebra fish exposed to 0.3µg/l for 21 days in a flow through system (ATSDR 2000), and one study has reported a BCF of 11,000 (Herrmann 2002). Also, endosulfan has been found in fish, crab, and mollusk samples, as well as in milk and vegetables. It is metabolized in mammals, so there is only limited biomagnification up the food chain, but endosulfan sulfate has been found in marine mammals (Muir 2001). Given reported BCFs of over 5000, and the presence of endosulfan and/or its metabolite in various biota, it could be judged to meet the bioaccumulation criterion (Swedish EPA 2002).

Potential for long-range environmental transport: The half-lives in air of alpha-endosulfan, beta-endosulfan, and endosulfan sulphate are respectively estimated at >2.7 days, >15 days, and >2.7 days (Herrmann 2002). Long-range transport is confirmed by monitoring data in the Arctic and elsewhere. For example, endosulfan has been identified in the Arctic atmosphere and in the Bering and Chukchi seas (Macdonald et al. 2000). It has also been found in Arctic biota, including ringed seals, beluga whales, and fish. Derek Muir of the Canadian National Water Research Institute in Ontario has also detected the metabolite, endosulfan sulfate, in fish and beluga whales from the Arctic (pers. comm.).

A-5. Hexachlorobutadiene (HCBD)

Russia has been reported to be one of the major users of HCBD, where it is applied as a fumigant on grape crops. HCBD has also been used to combat soil pests and is, or has been, used as a fumigant in France, Italy, Greece, Spain, and Argentina. In the United States, the largest use was for the recovery of “snift,” a chlorine-containing gas used in chlorine plants, but this use was discontinued. However, as of the early 1990s it was still imported for use as a chemical intermediate in the manufacture of rubber compounds and, to a lesser extent, as a solvent, laboratory reagent, heat-transfer liquid, hydraulic liquid, fluid for gyroscopes, and chemical intermediate in the manufacture of chlorofluorocarbons and lubricants (ATSDR 1994). In the EU in 1988, annual production was estimated at around 2000 to 4000 metric tons (NRA1995), but it is no longer produced in Western Europe or the United States (industry submission to EU PBT Group).

HCBD can also be inadvertently released during in the production of several other chlorinated chemicals, such as vinyl chloride, allyl chloride, epichlorohydrin, trichloroethylene, tetrachloroethylene, and carbon tetrachloride. In addition, HCBD can be released from incinerators, motor vehicle emissions, the manufacture of plastics (EC&HC 2000), and from waste dumps (UK COT 2000).

Toxicity: Based on results of animal laboratory studies, the kidney, and to a lesser extent the liver, appear to be the target organs of HCBD-induced toxicity. The US EPA has determined that HCBD is a possible human carcinogen. No studies were found on the effects of HCBD on the function of the human immune system and studies in animals seem to be limited to those showing lesions in lymphoid tissue, which occur at lethal doses (ATSDR 1994). With regard to environmental effects, HCBD is very toxic to aquatic organisms, with a "no observed effect concentration" (NOEC) for fish reported at 6.5µg/l (Swedish EPA 2002).

Persistence: HCBD biodegrades slowly in natural waters, with an estimated half-life of between 4 and 52 weeks, depending on the amount of organic matter (EC&HC 2000).

Bioaccumulation: HCBD accumulates in the tissues of freshwater organisms and BCFs of over 5000 have been reported in fish. It tends to be preferentially accumulated in the liver of the fish and a BCF of 10,000 has been reported for liver in dab (*Limanda limanda*). Once in the liver, polar metabolites can be formed and these may reach the kidneys to become nephrotoxic in fish. However, as HCBD is quite easily metabolized, it does not biomagnify through food chains (EC&HC 2000).

In a study reported in 1975, HCBD was found in the human liver at levels of 5.7-13.7ug/kg wet wt, and in adipose tissue at levels of 0.8-8ug/kg wet wt (ATSDR 1994).

Potential for long-range environmental transport: Research has suggested that HCBD can undergo long-range transport, with half-lives estimated at between 60 and 840 days. Monitoring data confirms this, and evidence for long-range transport of HCBD includes its detection in samples taken from various sediment depths in Canada's Great Slave Lake (EC&HC 2000). HCBD is also routinely found at low levels in Arctic biota, e.g., ringed seal blubber and Arctic char muscle, with levels *averaging* 0.07 ng/g in blubber of male and female ringed seal from the Hudson Strait area of northern Quebec. Levels are higher in juvenile seals aged less than one year, and have been found at approximately 0.11 ng/g, presumably due to transfer in mothers’ milk (D. Muir, pers. comm.).

A-6. Dicofol (Kelthane)

Dicofol is an organochlorine pesticide which is manufactured from DDT and DDE, although modern manufacturing processes can produce technical grade dicofol which contains less than 0.1% of DDT and related substances. It is used as an acaricide and mite-control agent on a wide variety of fruit, vegetables, and ornamental and field crops. In the EU, it is or was made in Spain and Italy (according to the database of the ECB) (Rasenberg 2003).

Toxicity: Dicofol has a high acute toxicity in the aquatic environment, with a LC_{50} of 15µg/l for eastern oyster and of 120µg/l for rainbow trout. In birds, it is a reprotoxic chemical which can affect eggshell quality, and in falcons, feminized male embryos have been found from females given 5mg/kg. It is also a suspected endocrine disrupting chemical. In mice, an increase in liver tumors has been reported, although in rats carcinogenicity was not found. IARC has classified it in category 3 (not classifiable as a human carcinogen) (Rasenberg 2003).

Persistence: The p,p-isomer which makes up about 80% of the formulation is more persistent than the o,p-isomer, which makes up approximately the other 20%. The p,p-isomer has a half-life in water greater than 2 months only in acid conditions, and in soil the half-life is considered to be shorter than the 6 months criterion. In sediments the primary degradation is rapid, but one of the degradation products, dichlorobenzylhydrol (DCBH), is reported to have a half-life of 197-429 days. Given that many lakes are already acidified, for example in Sweden and Norway, this chemical should be considered to meet the persistence criterion (Rasenberg 2003).

Bioaccumulation: Dicofol has a log Kow of around 5, and BCFs in fish are reported to range from 8,050 for the fathead minnow (*Pimephales promelas)* to 13,500 (Rasenberg 2003).

Potential for long-range environmental transport: Based on a low vapor pressure (less than 5.3 x 10^{-5}Pa) and a calculated atmospheric half-life of greater than 2 days, dicofol is considered to meet the criterion for long-range transport. However, data on levels in remote environments are sparse (Shaver 2003).

A-7. Methoxychlor

Methoxychlor has structural similarities with DDT, and has been used as an insecticide, a biocide, and a veterinary product. It was listed in the OSPAR List of Chemicals for Priority Action in 2000 (OSPAR Commission 2004).

Toxicity: Methoxychlor is extremely toxic to aquatic organisms, with an acute LC50 for rainbow trout of 52μg/l. The degradation products of methoxychlor are suspected endocrine disruptors (ATSDR 1994).

Persistence: Methoxychlor appears more persistent in aerobic conditions, but there is some uncertainty whether the persistence criterion is met. It has been reported that 6 months after the application of methoxychlor to the soil, 42% remained (ATSDR draft 2001). Therefore, it may be sufficiently persistent to merit inclusion. The half-life represents the calculated time for the loss of the first 50% of the substance, but the time required for the loss of the half that remains may be substantially longer.

Bioaccumulation: Methoxychlor has a log Kow of 4.7-5.08 and a reported BCF of 8,300 for fathead minnow (ATSDR draft 2001). In other fish species, however, quite different values have been reported, perhaps due to differences in metabolism and excretion. It has also been detected in the blubber and liver of harp seals (ATSDR draft 2001). Therefore, it can be considered to meet the criterion for bioaccumulation.

Potential for long-range environmental transport: Although its half-life in air is reported to be far less than the requisite 2 days, it has been detected in rain and snow in remote areas in Canada. Therefore, it appears that this substance may undergo long-range transport (ATSDR draft 2001). It has also been reported to be found in the Arctic (AMAP 1997).

A-8~12. Brominated Flame Retardants

The following four POP candidates belong to a family of commercially produced flame retardants known as brominated flame retardants (BFRs). Research has shown that certain BFRs exist in the environment far from the locations where they are produced and/or used and that the concentrations of some of the BFRs in both wildlife and humans in certain locations are increasing (Alaee and Wenning 2002).

A-8. Hexabromocyclododecane (HBCD)

HBCD is an additive flame retardant used mainly in polystyrene and in formulations for textiles. It may be found in a variety of articles including: upholstered furniture; automobile textiles and seat materials; interior textiles; insulation blocks in building and in transport vehicles; cable and textile coating; and electrical and electronic equipment (e.g., distribution boxes for electrical lines, video cassette recorder housings).

Production has increased dramatically since it was first marketed in the 1960s, and occurs in the EU, the United States, Japan, and probably elsewhere.

Trout and eels have been found contaminated with HBCD at levels of up to 6,758 and 9,432µg/kg, respectively (UK COT 2003). In addition to discharges from sites producing and processing HBCD, significant amounts of HBCD are likely to be released from articles in use, or when HBCD articles are put in landfills, where releases may prevail for a very long time, perhaps hundreds of years. Uncontrolled spreading of HBCD in the environment may also arise from products produced by using recycled expandable polystyrene. When HBCD is incinerated improperly, polybrominated dibenzofurans and dioxins may be released.

Toxicity: Daphnids exposed to 5.6 µg/l for 21 days had statistically significant reduced mean lengths. The lowest observed effect concentration (LOEC) was determined to be 5.6 µg/l. However, no statistical effects on survival, reproduction, or growth were observed in *Daphnia magna* exposed for 21 days to 3.1µg/l.

In mammals at relatively high doses (100mg per kg/day for 90 days in rodents), effects on liver weight and on the thyroid hormone system (T3↓ and TSH↑) have been noted. A recent study on behavioral effects has suggested that HBCD may cause developmental neurotoxic effects, including significant changes in spontaneous behavior, learning and memory defects, and a reduced number of nicotine receptors. (Eriksson et al. 2002). An indicative lowest observed adverse effect level (LOAEL) of 0.9 mg/kg/day can be deduced from this latter study. Data are lacking with regard to the potential carcinogenicity of HBCD.

Persistence: The levels found in biota and sediment indicate a high degree of persistence and laboratory tests show that HBCD is not readily biodegradable. There are also concerns about the persistence of the breakdown product, cyclododecatriene (EU RAR 2004).

Bioaccumulation: HBCD is considered to have a log Kow value of 5.625 and in fathead minnow a BCF of 18,100 has been reported. HBCD has been found in peregrine falcon eggs, and it has also been found in herring and guillemot in the Baltic, where the levels found show that biomagnification is occurring. Guillemot eggs from the Baltic, sampled between 1969 and 2001, showed an increase in HBCD levels over this time, although peak levels of HBCD were noted in the middle of the 1970s (Sellstrom et al. 2003).

HBCD has been detected in the breast milk of Swedish women at a maximum of 2.4 ng/g fat. HBCD has also been found in the breast milk of women from Mexico and it has been recorded in the serum of mothers from The Netherlands. HBCD was found in food samples, including the fat of pork, lamb, chicken, and beef, as well as fish, cows’ milk, and eggs (EU RAR 2004).

Potential for long-range environmental transport: HBCD has been found in air samples in the northernmost area of Scandinavia, supporting the assumption that long-range air transport can occur (for all data see EU draft RAR 2002).

A-9. Hexabromobiphenyl (Hexa-BB)

The flame retardant hexa-BB is also included on the LRTAP POPs Protocol and therefore meets the criteria of a UNEP POP. Hexa-BB is banned in Europe and production of Firemaster flame-retardant products (containing primarily hexa- and hepta-bromobiphenyl) ceased in the United States following a notorious incident in Michigan in 1973 when it was accidentally mixed into animal feed, causing widespread contamination of milk, meat, and eggs. It has also been found in wildlife, including seals from the Baltic and Svalbard. The effects of exposure to hexa-BB are similar to those from PCBs.

Although there is no known production of hexa-BB, inclusion in the Stockholm Convention would prevent any new production. Other polybrominated biphenyls (PBBs) include the commercial products octa- and deca-BB. These products are all mixtures to some extent. Production of octa-BB is considered to be very low. Deca-BB, because of its large size, is considered to have a low bioaccumulation potential, but this needs to be verified. Deca-BB was produced in Britain and is, or has recently been produced, by Atochem in France (Passivirta 2000). Concern about deca-BB may focus on its potential debromination to hexa-BB (KEMI 1999).

A-10~12. Penta-, Octa-, and Deca- Brominated Diphenyl Ethers

Pentabrominated diphenyl ether (penta-BDE), octabrominated diphenyl ether (octa-BDE), and decabrominated diphenyl ether (deca-BDE) are the names of the commercially-marketed polybrominated diphenyl ethers (PBDEs). Each is actually made up of a mixture of isomers, with the isomer which gives it its name, either dominating the mixture or representing the average bromine content. The total annual PBDE market demand worldwide in 2001 is about

67,440 metric tons, with penta-BDE at 7,500 metric tons, octa-BDE at 3,790 metric tons, and deca-BDE at 56,150 metric tons (BSEF website).

The marketing and use of both penta- and octa- BDE has already been banned in the EU (EU 2003). Penta-BDE has also been proposed to be listed in the LRTAP POPs Protocol. The similar characteristics of deca-BDE and penta- and octa-BDE merit their consideration as candidate UNEP POPs, although it may take some time for sufficiently persuasive data to be brought forward on deca.

The concerns related to these substances include their persistence and potential toxicity and there is evidence to suggest that highly brominated PBDEs such as deca- or octa-BDE may contain or degrade to more toxic, bioaccumulative, and persistent lower brominated PBDEs (Environment Canada 2004). The potential contamination of PBDEs with poly-brominated dibenzo-p-dioxins and furans is also a concern, as is the formation of these compounds during combustion (CSTEE 2002, Birnbaum and Staskal 2004).

Based on a time trend analysis of PBDE levels in Arctic ringed seals, Ikonomou et al. (2002) asserted that if present rates of bioaccumulation continue unchanged, PBDEs will surpass PCBs as the most prevalent organohalogen compound in Arctic seals by 2050. Moreover, the increasing incidence of PBDEs in Arctic biota provides increasing evidence for long-range atmospheric transport of these compounds (Stern and Ikonomou 2000). Wania and Dugani (2003) found that the atmospheric transport potential increases when the number of bromine ions in the PBDE decreases, i.e., the tetra-BDE showing the greatest and deca-BDE the lowest transport potential. They estimated a characteristic travel distance ranging from 608 to 1,349 km for penta-BDEs, and 480 to 735 km for deca-BDE.

A-10. Pentabromodiphenyl Ether (Penta-BDE)

Commercial penta-BDE is used as a flame retardant in a mixture that contains roughly 24-38% tetra-brominated diphenyl ether and 50-62% penta-brominated diphenyl ether. Used mainly in polyurethane foam filled furniture and car interiors, penta-BDE was also used in cot mattresses in the EU and in the production of packaging. Some printed circuit boards produced outside the EU, including perhaps some produced in Asia, may also contain penta-BDE. In the United States it is used in re-bond, a type of carpet underlay (EU RAR 2000, RPA 2000).

Toxicity: Experiments have shown that penta-BDE can alter thyroid hormone levels in mammals and can affect learning ability in mice. It may also adversely affect the immune system (Fowles et al. 1994, Darnarud and Sinjari 1996, Eriksson et al. 1998, Darnarud and Thuvander 1998). Penta-BDE is now found as a widespread contaminant in wildlife. The possibility of subtle impacts on brain development, as well as the potential interactive effects with other endocrine disrupting chemicals, should be sufficient to merit global control over the use of this substance. The EU has already agreed to take action, largely due to concern about the rising levels in breast milk. In Sweden, in the 25 years from 1972-1997, the concentration of polybrominated diphenyl ethers in mothers’ milk doubled every 5 years, with levels peaking in the late 1990s (Meironyte et al. 1998). However, much higher levels have since been found in UK breast milk (Betts 2003).

Persistence: Penta-BDE is very persistent and is not inherently biodegradable in the OECD Test (EU RAR 2000).

Bioaccumulation: Penta-BDE meets the UNEP POPs criterion for bioaccumulation. A log Kow of 6.57 and measured BCFs of well over 5000 have been reported (EU RAR 2000). In the Canadian Arctic between 1981 and 2000 there has been an exponential increase in the levels of this substance in biota (Ikonomou et al. 2002).

Potential for long-range environmental transport: Penta-BDE is a widespread contaminant in wildlife (EU RAR 2000) and has been found in many aquatic species including beluga whales in the Arctic (Stern and Ikonomou et al. 2000). It has also been measured in Arctic air (Muir et al. 1999), indicating that it can undergo long-range transport.

A-11. Octabrominated diphenyl ether (Octa-BDE)

The commercial octa-BDE includes some hepta- and hexa-BDE, and it is the hexa which is more bioavailable. Octa-BDE is used as an additive in polymers for use in plastic housings for office equipment and business machines, but since August 2004 it has been banned in the EU (EU 2003).

Toxicity: In the EU, octa-BDE was classified as toxic for reproduction and a study by Viberg et al. (2001) suggests that hexa-BED, one component of commercial octa-BDE, is a developmental neurotoxicant in mice (CSTEE 2002). Therefore, octa-BDE may also represent a possible risk of harm to the human fetus (Danish EPA 2000). Repeated doses of octa-BDE induced liver changes, indicative of an inducer effect.

Bioaccumulation: Octa has a reported log Kow of 6.9 (OSPAR 2002a). Furthermore, octa-BDE was detected (70-8,000 pg/g) in human adipose tissue selected from the US National Human Adipose Tissue Survey (FY 87 NHATS) Repository (Stanley et al. 1991). In addition, hexa-BDE a component of octa-BDE, has been measured in breast milk in several studies (EU RAR 2003). Bioaccumulation therefore seems to occur.

Potential for long-range environmental transport: Octa-BDE has a very low vapor pressure (6.59×10^{-6} Pa) (OSPAR 2002a). Combined with its persistence, octa-BDE could have the potential to undergo long-range transport.

A-12. Decabrominated diphenyl ether (Deca-BDE)

Deca-BDE is used as an additive flame retardant primarily in electrical and electronic equipment, as well as in textiles, where it is applied as a polymer backcoat to the fabric. Globally, deca-BDE has become the most used polybrominated diphenyl ether product, with production mostly concentrated in the Americas and Asia (BSEF website).

Emissions arise from production sites and from losses of the substance from flame-retarded products in use and after disposal. Such diffuse sources clearly occur and will be difficult to control without the phase-out of its use. For example, deca has been detected in sediments associated with effluents from waste dumps. It is also known to be present in indoor air and has been detected in household dust. Moreover, a number of studies show that deca-BDE is present in sewage sludge from waste water treatment plants (EU draft RAR R013_0405_env 2004), and it has been found in high concentrations at mg/kg level (dry weight) in North American sewage sludge (Environment Canada 2004). Deca-BDE has also been found in marine sediments and in a study around the Scheldt basin deca has been reported by de Boer et al. (2002) at levels of up to 700 µg/kg dry weight (EU draft RAR R013_0405_env 2004).

The combination of evidence of debromination with high accumulation of deca-BDE in the environment has led researchers to note that even slight and very long term degradation to lower brominated diphenyl ethers could have serious ecological consequences over periods spanning several decades. The overall persistence of deca and potential transformation to lower PBDEs that are persistent, toxic and bioaccumulative, and observed commercial and environmental trends, indicate environmental concerns (Environment Canada 2004).

However, the concern does not relate just to the potential debromination in the environment, but also to deca itself, because a study in mice has reported it to be a developmental neurotoxicant (Viberg et al. 2003). Indeed, in view of the concerns raised regarding the potential developmental neurotoxicity of deca-BDE, in 2005 the European Commission was proposing further testing for such effects.

Toxicity: Deca-BDE is reported to have low general toxicity comparing to penta- and octa-BDE. However, the concern is mostly focused on its potential developmental neurotoxicity and the toxicity of its lower brominated breakdown products. In addition, the International Agency for Research and Cancer (1990) has concluded it to be a Group 3 carcinogen, with limited evidence for the carcinogenicity in experimental animal and not classifiable as to its carcinogenicity to humans (EU draft RAR R013_0402_hh 2002). Thus, a 2 year deca-BDE exposure study in rats showed increased incidence of neoplastic nodules in the liver and in a 2 year deca-BDE feed study in mice, thyroid gland follicular cell hyperplasia was increased (Danish EPA 2000).

Persistence: Deca-BDE in natural sediments has been shown to be stable and resistant to biodegradation under anaerobic conditions for up to 2 years (de Wit 2000).

Bioaccumulation: Deca has a log Kow value of 6, but was formerly erroneously considered to be too large a molecule to cross biological membranes. However, deca has now been detected in human blood and breast milk and in many wildlife species.

For example, studies in Japan (Hori et al. 2002) and in Texas (Schecter et al. 2003) and in other USA states (Lunder and Sharp 2003) show that deca is a frequent contaminant of human breast milk, being found in approximately 30% of the Texan samples and in 80% of the samples in the Lunder and Sharpe study. Deca has also been detected in blood serum of workers, including hospital cleaners, clerks working full-time at computer screens, personnel at an electronics dismantling plant, and rubber workers. The highest blood serum deca-BDE concentrations were in rubber wire producers (maximum278 µg/kg fat). Deca has also been detected in blood serum samples from the general public, including Members of the European Parliament (MEPs), in 2 biomonitoring studies done by WWF at a median concentration of 83 µg/kg fat and 53 µg/kg fat, in those with positive results. A maximum concentration of 2400 µg/kg fat was found in the blood of one male participant, who testified that he had no known occupational chemical exposure, other than the use of a computer in a small office (EU draft RAR, 2004 and 2005 addendum, R013_0502hh and pers. comm. to Lyons 09-03-05).

Similarly, wildlife species, including fish, polar bears, and the eggs of predator birds have been found to be contaminated with deca-BDE and the extent of this contamination in birds of prey has become more widespread in recent years (EU draft RAR R013_0502hh 2004 and 2005 addendum).

Therefore, despite the absence of a bioconcentration factor in fish of greater than 5000, there is monitoring data in biota indicating that the bio-accumulation potential of the chemical is sufficient to justify its consideration within the scope of the Stockholm Convention

Potential for long-range environmental transport: A study by Muir and coworkers (2003) has detected deca-BDE in Arctic sediments. Deca-BDE was likely transported on particles to remote places such as Canadian Arctic due to its low vapor pressure (4.63x10-6 Pa) and high log Kow (OSPAR 2002b). The data appear to show an increasing trend in the concentration found in the samples taken, but with generally lower concentrations and a later date of first occurrence in the more northerly samples, which are considered to be consistent with transport to remote regions mainly on particulates. Detection of this substance in moss in relatively remote regions of Norway has also been attributed to long-range particulate transport and the substance has also been found in some birds in polar regions (EU draft RAR R013_0405_env 2004).

A-13, 14. Perfluorochemcials (PFCs)

Perfluorochemicals (PFCs) are non-polar, highly fluorinated compounds that are chemically and biologically inert. They are used in surface treatments to provide soil and stain resistant coatings, in paper treatments to provide oil, grease, and water resistance, and as performance chemicals in fire fighting foams, cosmetics, and cleaners. Some of PFCs including perfluorooctanyl sulfonate (PFOS) and perfluorooctanoic acid and its salts (PFOA) have proven to be persistent global pollutants.

A-13. Perfluorooctanyl sulfonate (PFOS)

(Note: Perfluorooctyl sulfonyl fluoride (POSF) and other chemicals that can degrade to Perfluorooctanyl sulfonate (PFOS) are included in this section.)

PFOS is a member of a large family of chemicals based on perfluorooctyl sulfonyl fluoride (POSF). POSF-based chemicals are used, or have been recently used, in many industrial and consumer applications including stain resistant coatings for fabrics, leather, furniture, and carpets; fire fighting foams; cleaning products; and commercial and consumer floor polishes.

Exposure may also result from perfluoro chemicals used in food wraps, particularly those used for moist or greasy fast food products. Perfluorooctyl sulfonic acid and its salts are used as surfactants in a variety of performance applications. Some salts of PFOS chemicals are also used as pesticides. Countries that produce PFOS include, or have included, the United States, Belgium, Japan, Italy, and possibly the Russian Federation, China, and Germany. The Minnesota Mining and Manufacturing Corporation (3M), once a dominant PFOS producer, has committed itself to the “phasing out of the perfluorooctanyl chemistry used to produce certain repellents and surfactant products,” (3M 2000). However, other chemical companies have been linked with chemicals of the “perfluoro” group, all of which need to be scrutinized with regard to their POPs characteristics.

Toxicity: PFOS is highly toxic to honey bees. Studies in rats and monkeys also raise serious concerns. Adverse signs of toxicity include increases in liver enzymes and other effects on the liver, gastro-intestinal effects, blood abnormalities, decreased serum cholesterol, and death. In a multigenerational study in rats, perinatal mortality was increased at PFOS doses of 0.8mg/kg/day and higher. Also, in subsequent tests on rats, at all the dose levels tested (0.4mg/kg/day and above) PFOS exposure caused reduced levels of the thyroid hormones T3 and T4. However, it is not yet clear whether this finding was connected to the underlying mechanism responsible for the perinatal mortality (US EPA 2001).

With regard to human health there is an association between exposure to PFOS and bladder cancer. Furthermore, there appears to be an increased risk of episodes of neoplasms of the male reproductive system, the overall category of cancers and benign growths, and neoplasms of the gastro intestinal tract (OECD 2002)

Persistence: PFOS and its salts are highly persistent in the environment and do not appear to degrade. Other substances based on POSF chemistry have the potential to degrade back to PFOS, although research is underway to try to improve the understanding of the breakdown of large molecules based on POSF chemistry. It is clear that substances that break down to PFOS could be judged to meet the UNEP POPs criterion for persistence.

Bioaccumulation: PFOS has an estimated half-life of 4 years in humans. Biological monitoring highlights that the bioaccumulation potential of this chemical is sufficient to justify its consideration within the scope of this Convention. Fish-eating birds appear to bioaccumulate PFOS to a considerable extent. PFOS has also been found in human blood samples, with concentrations in the parts per million range for exposed workers. In the general population, the levels in adults have been found to be in the parts per billion range (mean 30-44 ppb). Preliminary data suggest that children may have higher levels than adults; mean levels of 54 ppb were found in a small sample. Unlike many other bioaccumulating chemicals, PFOS does not accumulate in body fat but is found instead in the blood.

Potential for long-range environmental transport: Long-range transport is taking place. PFOS has been found at the parts per billion level in a wide variety of wildlife species around the globe, including seals from the Arctic and albatross from the Midway Atoll in the Pacific (Geisy and Kannan 2001).

A-14. Perfluorooctanoic acid and its salts (PFOA)

Perfluorooctanoic acid and its salts (PFOA) are another group of perfluorochemicals (PFCs). PFOA are fully fluorinated organic compounds that can be produced synthetically or through the degradation or metabolism of other PFCs. Perfluorooctanoic acid is primarily used as a reactive intermediate, while its salts are used as processing aids in the production of fluoropolymers such as polytetrafluoroethylene, a compound more commonly known as Teflon. Products made by using PFOA have been used in almost all industrial sectors, such as the automotive, defense, telecommunications, packaging, and textile industries. PFOA are not major ingredients in these commercial products. Instead, these products typically contain fluorochemicals that may degrade into PFOA. In recent years, about 600 metric tons of PFOA are manufactured per year in the United State, but other countries may also produce PFOA.

Toxicity: Toxicological studies have shown that PFOA could be carcinogenic, immunotoxic, and endocrine disruptive. For example, PFOA have been found to be carcinogenic and immunotoxic in rodents (US EPA 2002b). Also, PFOA exposure causes changes in body, liver, and kidney weight in animals (US EPA 2003) and causes Leydig cell (the cells that produce androgens) tumors in rats. PFOA directly modify the steroidogenic function of Leydig cells in vitro (Liu et al. 1996). Serum PFOA may change T3 hormone levels and increase cholesterol levels in humans (US EPA 2003).

Persistence: PFOA are persistent because of their long carbon chains saturated with fluorine atoms which are very resistant to physical, chemical, or biological attack. The very properties of PFOA that make them useful also make them problematic. There is no evidence that they ever fully degrade.

Bioaccumulation: PFOA have been detected in wildlife such as polar bears and fish in remote areas in the Canadian Arctic (US EPA 2002b, Ritter 2004, Kannan et al. 2002), and in both occupationally exposed workers and the general US population. PFOA distribute predominantly to the liver, plasma, and kidney and to a lesser extent the lungs, testis, and ovary (US EPA 2002b, Kudo and Kawashima 2003). The arithmetic mean PFOA levels in the serum of occupationally exposed workers ranged from 0.84 to 6.8 ppm, with the highest level at 81.3 ppm. Mean serum PFOA levels in general population range from 3 to 17 parts per billion (ppb), with the highest level in children at 56.1 ppb (US EPA 2003).

The biological half-life of PFOA in humans is 4.37 years (US EPA 2002b) and repeated exposure may result in accumulation of PFOA in humans and wildlife. The BCF of one of the PFOA salts (ammonium perfluorooctanoate) has been reported to be 56 (Giesy and Kannan 2002). Nevertheless, the monitoring data in biota indicate that the bioaccumulation potential of the chemical is sufficient to justify its inclusion in the Stockholm Convention.

Potential for long-range environmental transport: PFOA, a type of carboxylic acids, are often converted from other PFCs such as ployfluorinated alcohols that are a group of compounds known as telomers. Scientists from North America have found that fluorotelomer alcohols include $CF_3(CF_2)nCF_2CH_2CH_2OH$, where n=2, 4, or 6. These fluorotelomer alcohols can degrade to carboxylic acids such as PFOA (Ritter 2004). Studies of C_{10} (i.e., when n=6) fluorotelomer alcohol suggest that C_{10} fluorotelomer alcohol may stay in the air for as long as 20 days (Ellis et al. 2003). This is long enough for these potential PFOA predecessors to be transported to remote areas.

A 15~18. Other Chlorinated Chemicals and Chemical Groups

Individual and groups of chemicals that cannot be clustered are listed in this category.

A-15. Pentachlorobenzene (penta-CB)

Pentachlorobenzene is used, or has been used, as a dielectric fluid, a fungicide, and a flame retardant. It can also be produced by degradation of other organochlorine compounds, such as lindane and HCB, and is suggested to be a contaminant of HCB. Similarly, it is used as a starting material in the manufacture of the fungicide quintozene (pentachloronitrobenzene) and is a technical impurity in this compound. Other possible sources of chlorinated benzene contamination include use as chemical intermediates, as solvents in the manufacture of dyes, as lubricant and pesticides, and as transformer oils. It results as a byproduct or contaminant during the production of other chlorinated substances and is found in certain industrial effluents. It can be released from waste incinerators where it is produced during the combustion of plastics and chlorinated waste (US EPA 1999). In Canada, based on 1991 data, up to 200 metric tons of penta-CB were present in dielectric fluids in storage, destined for destruction (Rezek 1999). The UN ECE dossier concludes that penta-CB meets the POPs criteria (van de Plassche et al. 2002, UN ECE 2002).

Toxicity: The liver, kidney, adrenals, and thyroid appear to be the main target organs. No data were found concerning the toxicity of penta-CB on sediment and soil dwelling organisms, terrestrial invertebrates, birds, or wild mammals. In a 16-day EC_{50} (median effective concentration) test on the water flea (*Daphnia magna),* the most sensitive indicator of toxic stress was a reduction in productivity after exposure to 25µg/l. The most sensitive indicator of toxic stress during an early life stage toxicity test on fish was larval growth and a 28-day NOEC for survival hatching and growth of 34µg/l was noted for *Brachydanio rerio* (EC&HC 1993a). A NOEC for crustaceans of 10µg/l has been reported (van de Plassche et al. 2002).

Persistence: In surface water, the estimated half-life of penta-CB is reported to range from 194-1250 days, while the half-life for the anaerobic biodegradation of penta-CB in deeper waters is estimated to range from 776-1380 days. The half-life of penta-CB in soil has been calculated at 270 days and estimated at between 194-1250 days. Therefore, penta-CB meets the UNEP POPs criterion for persistence, as it appears to have a half-life in water of greater than 2 months, and a half-life in soil of greater than 6 months.

Bioaccumulation: The log Kow value is reported to be around 5. However, penta-CB undoubtedly meets the bioaccumulation criterion for a UNEP POP. For example, a whole body BAF of 20,000 has been reported for rainbow trout, and a BAF of 401,000 has been reported for earthworms (EC & HC 1993a).

Low levels have also been detected in human breast milk. In a study of Canadian women reported in 1987, an average concentration of 2 ppb (milk fat basis) was found in 17% of 18 samples taken from the indigenous population, and in 97% of the general population, penta-CB was found at an average of 3 ppb (US EPA 1999).

Potential for long-range environmental transport: The estimated half-life of penta-CB in air ranges from 45 days to over 1 year, which is sufficient to permit long-range transport (EC&HC 1993b). Long-range transport is confirmed by monitoring data provided by Muir, showing its presence in Arctic sea water and in the blubber of ringed seals from the Arctic (e.g., mean of 2.96ng/g wet wt in blubber from seals in Northern Labrador). In addition, penta-CB has been reported in air masses over the Pacific (EC&HC 1993a).

A-16. Short-chained chlorinated paraffins (SCCPs)

Short-chained chlorinated paraffins (SCCPs) are used in metal working fluids to cool and lubricate the tool/metal interface and to flush away the chips of cut metal. They are also used in paints and sealants, as flame-retardants in rubber and textiles, and in fat liquors in the leather working industry.

In 1998, SCCPs were the subject of an International Declaration in which EU countries, Iceland, Norway, and Switzerland shared "the objective of controlling and limiting the risks arising from the dispersive uses of short-chain chlorinated paraffins using appropriate national and/or international procedures" (ECE/EB.AIR/57 1998). Subsequently, in March 2003, the LRTAP Working Group reviewed the Draft II dossier of 3 March 2003 on SCCPs and their expert judgment based on the dossier was that SCCPs met the criteria for UNECE POPs (COM010_env_NI-LRTAP 2003). In 2004, the European Commission went on the record as wanting SCCPs to be included in the UNECE Protocol to restrict its uses (EC 2004).

Toxicity: The main concerns involve toxicity to aquatic invertebrates and the ability to cause cancer in rodents. In animal experiments, the principal signs of toxicity were effects on the liver and thyroid (EU RAR 2000). SCCPs also feature on Sweden's list of suspected endocrine disruptors (BKH report 2000).

Persistence: SCCPs are persistent in water. The available screening studies indicate that the half-life for mineralization is likely to be greater than 60 days in marine water and greater than 180 days in marine sediment (EU RAR 2000). In line with EU requirements, in 2005 industry was proposing to undertake further testing to verify whether or not the criterion for persistence was met.

Bioaccumulation: SCCPs meet the UNEP POPs criterion for bioaccumulation, as BCFs of over 5,000 have been measured in fish and in the common mussel (EU RAR 2000). SCCPs have also been found in three samples of breast milk taken from women living along the Hudson Straight at levels of 10.6-16.5ng/g lipid (EU RAR 2000).

Potential for long-range environmental transport: SCCPs are found in Arctic biota, including seals and beluga whales (with a mean of 142 ng/g wet wt in 6 whales from

Kimmirut in 1995), showing that long-range transport can occur (Muir et al. 1999 and 2001). This is confirmed by findings of SCCPs in fish at Ellasjoen, at a latitude of 74°N in the Norwegian Arctic, which is far from any point source (COM010_env_NI-LRTAP 2003). The half-life in air of SCCPs is estimated to be between 1.9 and 7.2 days, long enough for significant long-range transport to occur (EU RAR 2000).

A-17. Polychlorinated naphthalenes (PCNs)

PCNs were in use prior to PCBs as dielectric (insulating) fluids in electrical equipment and as heat-transfer fluids and plasticisers. In limited quantities, PCNs have also been used as lubricants, dye carriers in paints, and wood preservatives. They are also found as contaminants in PCB products. Stockpiles may still exist, for example in 1997, British Telecom was reported to have significant stocks (ENDS Report 1999). Putting these chemicals under global control could help to ensure their proper disposal. Recently, total PCN concentrations in digested sludge from 14 UK sewage treatment plants were found to range from 50 to 90μg/kg, suggesting numerous and ongoing diffuse sources (Stevens et al. 2003). Indeed, mono- through to octa-chlorinated naphthalenes have been measured in start-up, steady operation, and shutdown of flue gases and fly ash during different stages of a municipal incinerator and other incineration processes (Takasuga et al. 2004). Moreover, although PCNs are no longer used in most countries, production in developing countries cannot be ruled out; their manufacture is relatively simple.

Toxicity: Long-term exposure to PCNs has been associated with cancer and chronic liver disease in workers (Hayward 1998). Several of the 75 possible PCN congeners exhibit dioxin and PCB-like properties and have similar mechanisms of action, such that additive-type effects are possible. In wildlife, PCNs may account for around half of the dioxin-like toxicity exhibited (Kannan et al. 2000). Potential effects in porpoise are a concern (Ishaq 2000). PCNs are considered to have endocrine disrupting properties; they appear to cause an imbalance in vitamin A in wildlife (Swedish EPA 2002).

Persistence: PCNs are considered to be persistent chemicals, but only limited data are available.

Bioaccumulation: Some PCNs have been found to bioaccumulate to a significant extent, particularly in birds. Experimental BCF values in fish are greater than 5000 for di, tri, tetra, and pentachloronaphthalenes (Crookes and Howe 1993). The levels of PCNs in Swedish breast milk have declined, and were reported at 0.48ng/g lipid in 1992 (Noren and Meironyte 2000)

Potential for long-range environmental transport: PCNs are widespread global environmental contaminants. Elevated PCN levels in the remote Arctic have been attributed to air masses arising from Europe (Harner et al. 2001). PCNs have also been found in the Arctic and Antarctic marine food webs, with levels ranging from 1.5 pg/g in krill to 2550 pg/g in South polar skua on a wet weight basis. Lower chlorinated PCNs were the predominant congeners in most of the wildlife tested, except for skua and polar bears (Corsolini et al. 2002).

A-18. Tetrachlorobenzene (Tetra-CB)

Environmental releases of tetrachlorobenzene may result from direct usage, from its accidental production as a byproduct, and perhaps also from the degradation of pentachlorobenzene and hexachlorobenzene. There are several different isomers of tetrachlorobenzene. 1,2,4,5- tetra-CB has been produced and used as an insecticide and as an intermediate in the production of herbicides and defoliants. It is no longer produced in the Untied States or Canada, but releases to the environment occurring through various waste streams, including pulp mill effluents and the effluents of municipal waste incinerators. 1,2,3,4-tetra-CB is used as a component of dielectric fluids and as a chemical intermediate in the synthesis of pentachloronitrobenzene (quintozene). It is no longer produced in Canada, but was reportedly still produced in the United States, and presumably elsewhere. Based on 1991 data, in Canada alone there were 1,300 metric tons of tetra-CB in use in dielectric fluids (US EPA 1999, Rezek 1999, EC & HC 1993b).

Toxicity: The major target organs in mammalian species seem to be the liver, kidney, and thyroid. With regard to ecotoxicity, there is a lack of data on the effects of tetra-CB on benthic and soil dwelling organisms, despite the fact that tetra-CBs can persist under anaerobic conditions. Data are also lacking on the acute and chronic toxicity of tetrachlorobenzenes to terrestrial invertebrates, aquatic plants, birds, and wild mammals (EC&HC 1993b).

Persistence: The half-life of 1,2,4,5-tetra-CB in surface water is estimated to range from 28 to 417 days, while its half-life for anaerobic biodegradation in deeper waters is suggested to range from 120 to 720 days. The half-lives in soil of the tetrachlorobenzenes are estimated to range from 28 to 417 days. Also, 1,2,4,5- and 1,2,3,4-tetra-CB were not biodegraded after incubation in sewage sludge under anaerobic conditions for 32 days. The tetrachlorobenzenes are therefore expected to persist in sediments, and despite strongly adsorbing to sediment, some can be removed by re-suspension. The half-life for the biodegradation of 1,2,4,5-tetra-CB in sediment is estimated to range from 56 to 1250 days. These values suggest that tetrachlorobenzene meets the persistence criteria for a UNEP POP (EC&HC 1993b).

Bioaccumulation: The following BCF values have been reported for the various isomers in fish (ATSDR 1998):

1,2,3,4-tetrachlorobenzene	3,800-12,000
1,2,3,5-tetrachlorobenzene	1,800-3,900
1,2,4,5-tetrachlorobenzene	4,000-13,000.

This suggests that 1,2,3,4- and 1,2,4,5-tetra-CB would meet the UNEP criterion for bioaccumulation, despite quoted log Kow values of between 4.51 and 4.65 for the three isomers. The terrestrial food chain may also be at risk. For example, a BAF of 84,000 has been reported for earthworms (Eisenia andrei). 1,2,4,5-tetra-CB has also been found to biomagnify in the lichen-caribou-wolf food chains in the Canadian Arctic at Bathurst Inlet (Kelly and Gobas 2001).

In approximately one-third of 412 samples of Canadian breast milk taken in 1986, 1,2,3,4-tetra and 1,2,3,5-tetra were found. Maximum levels were 99ng/g milk fat and 138 ng/g milk fat respectively (Mes et al. 1993).

Potential for long-range environmental transport: 1,2,4,5-tetra-CB has been found as a contaminant in the Arctic terrestrial food chain by Kelly and Gobas (2001), demonstrating that this substance is able to undergo long-range transport. Similarly, monitoring data from the Arctic provided by Muir (pers. comm.) show that 1,2,3,4-tetra-CB and a range of other chlorobenzenes may be found in aquatic biota and sea water. Levels in the blubber of ringed seals from Northern Labrador were 1.52 ng/g wet weight (mean of 20 samples).

C-1, 2. Unintentional Production

The following two chemicals are generated unintentionally. WWF recommends that these chemicals be listed in Annex C of the Stockholm Convention.

C-1. Octachlorostyrene (OCS)

Octachlorostyrene is not commercially manufactured. Rather, it is an unwanted byproduct of processes that combine carbon and chlorine at high temperatures. These processes include chlorine production, magnesium production, commercial production of chlorinated solvents, and aluminium processes. OCS appears to be a ubiquitous contaminant, having been found in human breast milk (in Canada), in the eggs of little owls from Belgium (Jaspers et al. 2005), and in both Arctic and Antarctic biota.

Toxicity: Effects on the liver, thyroid, kidney, and blood have been noted in experimental animals exposed to OCS (OME & MDNR 2000). Also, 4-hydroxy-heptachlorostyrene, a suspected metabolite, has been shown by Sandau and co-workers to bind to the thyroid hormone transport protein, raising the possibility of thyroid hormone disrupting effects and effects on retinol transport (Sandau et al. 2000b). However, testing of OCS in Japan has not confirmed grounds for concern with regard to its endocrine disrupting properties (Hori 2003). The structural similarity of OCS and hexachlorobenzene (which is already designated as a UNEP POP) suggests that OCS has a similar toxicological profile.

Persistence: The structure of OCS indicates that it is likely to be persistent. However, there is a lack of persistence data for this substance in various media.

Bioaccumulation: Ochtachlorostyrene is very bioaccumulative, with recorded BCF values of over 5,000. It therefore meets the bioaccumulation criterion for a UNEP POP. It has also been found in 59% of 412 samples of breast milk taken from Canadian women. The mean level was 5.2 ng/g milk fat, with a maximum value of 191ng/g milk fat (Mes et al. 1993).

Potential for long-range environmental transport: The presence of OCS in the tissue of polar bears and Antarctic seabirds demonstrates that it can undergo long-range transport. 4-hydroxy-heptachlorostyrene, the suspected metabolite, is also found in the plasma of polar bears (Sandau et al. 2000a).

C-2. Polycyclic aromatic hydrocarbons (PAHs)

These substances are listed on the LRTAP POPs Protocol and thus meet the UNEP POPs screening criteria. PAHs are a group of chemicals released during the incomplete burning of oil, coal, gas, and other organic materials such as trees during forest fires. Significant sources of PAHs include domestic combustion; vehicles; the production sites of metals, coke, and asphal; and power stations. A survey of sludge samples from 14 UK sewage treatment plants found that total PAH (24 compounds) concentrations ranged from 67-370mg/kg dry weight;

all the samples would exceed the proposed EU limit for sludge used on land (Stevens et al. 2003).

Many PAHs have been designated by IARC as probable or possible human carcinogens and certain PAHs have also been linked to birth defects and reproductive problems in animals (ATSDR 1995). Some PAHs have endocrine disrupting properties and some have been shown to affect the immune system. In addition, recent studies have indicated that PAHs are more toxic in the presence of UV light, such that laboratory studies may underestimate their effects in the marine environment (MAFF 2000, Lyons 2002)

The LRTAP POPs Protocol requires, in Article 3(5), that each Party reduce its total annual PAH emissions from the levels recorded in any specified year between 1985 and 1995. Because PAHs are a group of over 100 different chemicals, four indicator compounds have been designated for the purpose of emission inventories: benzo(a)pyrene (BaP), benzo(b)fluoranthene, benzo(k)fluoranthen, and indeno (1,2,3-cd) pyrene.

3. Conclusion

The Stockholm POPs Convention is a historic, forward-looking agreement that was designed to respond to emerging scientific knowledge about chemicals beyond the initial 12. The adding mechanism is a key element of the treaty and Parties to the Convention should not hesitate to act when there is convincing evidence of a chemical’s toxicity, persistence, bioaccumulation, and long-range transport. WWF urges Parties to consider the 20 chemicals detailed in this paper for nomination to the POPs Review Committee.

4. Contact

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5. Appendix

If the screening criteria as laid down in Annex D to the Convention (reproduced below) are met, a risk profile must be drawn up based on the specifications in Annex E (also reproduced below). Although the toxicity criteria may seem rather onerous, it is clear that the potential for interactive effects, due to concurrent exposure to many pollutants, may be considered.

Extract from UNEP Stockholm Convention on POPs:

“Annex D

INFORMATION REQUIREMENTS AND SCREENING CRITERIA

1. A Party submitting a proposal to list a chemical in Annexes A, B and/or C shall identify the chemical in the manner described in subparagraph (a) and provide the information on the chemical, and its transformation products where relevant, relating to the screening criteria set out in subparagraphs (b) to (e):

(a) Chemical identity:
  (i) Names, including trade name or names, commercial name or names and synonyms, Chemical Abstracts Service (CAS) Registry number, International Union of Pure and Applied Chemistry (IUPAC) name; and
  (ii) Structure, including specification of isomers, where applicable, and the structure of the chemical class;

(b) Persistence:
  (i) Evidence that the half-life of the chemical in water is greater than two months, or that its half-life in soil is greater than six months, or that its half-life in sediment is greater than six months; or

  (ii) Evidence that the chemical is otherwise sufficiently persistent to justify its consideration within the scope of this Convention;

(c) Bio-accumulation:
  (i) Evidence that the bio-concentration factor or bio-accumulation factor in aquatic species for the chemical is greater than 5,000 or, in the absence of such data, that the log Kow is greater than 5;
  (ii) Evidence that a chemical presents other reasons for concern, such as high bio-accumulation in other species, high toxicity or ecotoxicity; or
  (iii) Monitoring data in biota indicating that the bio-accumulation potential of the chemical is sufficient to justify its consideration within the scope of this Convention;

(d) Potential for long-range environmental transport:
  (i) Measured levels of the chemical in locations distant from the sources of its release that are of potential concern;
  (ii) Monitoring data showing that long-range environmental transport of the chemical, with the potential for transfer to a receiving environment, may have occurred via air, water or migratory species; or
  (iii) Environmental fate properties and/or model results that demonstrate that the chemical has a potential for long-range environmental transport through air, water or migratory species, with the potential for transfer to a receiving environment in locations distant from the sources of its release.

For a chemical that migrates significantly through the air, its half-life in air should be greater than two days; and

(e) Adverse effects:
  (i) Evidence of adverse effects to human health or to the environment that justifies consideration of the chemical within the scope of this Convention; or
  (ii) Toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.

2. The proposing Party shall provide a statement of the reasons for concern including, where possible, a comparison of toxicity or ecotoxicity data with detected or predicted levels of a chemical resulting or anticipated from its long-range environmental transport, and a short statement indicating the need for global control

3. The proposing Party shall, to the extent possible and taking into account its capabilities, provide additional information to support the review of the proposal referred to in paragraph 6 of Article 8. In developing such a proposal, a Party may draw on technical expertise from any source.

Annex E

INFORMATION REQUIREMENTS FOR THE RISK PROFILE

The purpose of the review is to evaluate whether the chemical is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and/or environmental effects, such that global action is warranted. For this purpose, a risk profile shall be developed that further elaborates on, and evaluates, the information referred to in Annex D and includes, as far as possible, the following types of information:

(a) Sources, including as appropriate:
  (i) Production data, including quantity and location;
  (ii) Uses; and
  (iii) Releases, such as discharges, losses and emissions;

(b) Hazard assessment for the endpoint or endpoints of concern, including a consideration of toxicological interactions involving multiple chemicals;

(c) Environmental fate, including data and information on the chemical and physical properties of a chemical as well as its persistence and how they are linked to its environmental transport, transfer within and between environmental compartments, degradation and transformation to other chemicals. A determination of the bio-concentration factor or bio-accumulation factor, based on measured values, shall be available, except when monitoring data are judged to meet this need;

(d) Monitoring data;

(e) Exposure in local areas and, in particular, as a result of long-range environmental transport, and including information regarding bio-availability;

(f) National and international risk evaluations, assessments or profiles and labelling information and hazard classifications, as available; and

(g) Status of the chemical under international conventions.”

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