Polychlorinated Dibenzo-p-dioxin and Dibenzofuran Contamination of Sediments and Photochemical Decontamination of Soils

Pirjo Isosaari

National Public Health Institute
Department of Environmental Health
Laboratory of Chemistry
P.O. Box 95, FI-70701 Kuopio, Finland

and

University of Kuopio
Department of Environmental Sciences
P.O. Box 1627, FI-70701 Kuopio, Finland

ACADEMIC DISSERTATION

To be presented with the permission of the Faculty of Natural and Environmental Sciences of the University of Kuopio for public examination in lecture hall L21, Snellmania, University of Kuopio, on Friday 18th of June 2004, at 12 o'clock noon.

Author's address National Public Health Institute
                     Department of Environmental Health
                     P.O. Box 95, FI-70701 Kuopio, Finland
                     Phone   +358 17 201353
                     Fax   +358 17 201265
                     E-mail: pirjo.isosaari@ktl.fi

Supervisors   Professor Terttu Vartiainen, Ph.D.
                     National Public Health Institute
                     Kuopio, Finland
                     and University of Kuopio
                     Kuopio, Finland

                     Professor Tuula Tuhkanen, Ph.D.
                     Tampere University of Technology
                     Tampere, Finland

Reviewers   Heidelore Fiedler, Ph.D.
                     UNEP Chemicals
                     Châtelaine (GE), Switzerland

                     Professor Jussi Kukkonen, Ph.D.
                     University of Joensuu
                     Joensuu, Finland

Opponent   Professor Gunilla Lindström, Ph.D.
                     MTM Research Centre
                     Örebro University
                     Örebro, Sweden

ABSTRACT

The production and use of chlorinated chemicals is a significant source of polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) releases to soils and sediments. The manufacture of a chlorophenol formulation Ky 5 and vinyl chloride monomer between the 1940's and mid-1980's have been identified as potential sources of PCDD/F contamination in the Gulf of Finland sediments. Moreover, Ky 5 was widely used in sawmills as a fungicide, which resulted in leakages into soil and sediments. Proper management of these contamination problems and prevention of human exposure to PCDD/Fs requires in-depth knowledge of the concentrations and sources of pollution and development of appropriate techniques for environmental cleanup.

In this study, the concentrations and sources of PCDD/Fs in the Gulf of Finland were surveyed by analysing sediment samples. Lake sediments from an area with no known industrial sources were analysed to identify natural formation processes and pre-industrial sources of PCDD/Fs. In addition, experiments were carried out to investigate and develop a method for the removal and decomposition of PCDD/Fs in contaminated soils. The method was based on the use of vegetable oils and sunlight.

Sediment studies showed that the total amount of PCDD/Fs in the Gulf of Finland sediments was 16.4 kg, measured in toxic equivalents, WHO-TEQs. Fluvial transportation of PCDD/Fs that originated from the historical manufacture and use of the fungicide Ky 5 next to the Kymijoki River contributed 76% to the sedimentary PCDD/F load between 1960 and 1986 and still accounted for 58% between 1986 and 1997. Releases attributable to the manufacture of vinyl chloride monomer had negligible effect on the total PCDD/F load in the Gulf of Finland. The rest of the PCDD/Fs apparently originate from atmospheric background deposition. The most heavily polluted sediments were located within 12 km from the Kymijoki River inlet. However, the impact area of the Ky 5 releases extended over a distance of 75 km. The dominating congeners in the impact area were highly chlorinated dibenzofurans. The concentration of 2,3,4,7,8-pentachlorodibenzofuran, the main contributor to the WHO-TEQ content in Baltic herring, was relatively constant throughout the Gulf of Finland. Low concentrations of mainly highly chlorinated dibenzo-*p*-dioxins were detected in lake sediments that had been formed up to 8 000 years ago. The PCDD/F congener pattern in the old lake sediments was considered to give evidence of a natural formation mechanism.

When contaminated soil was mixed with vegetable oil (olive oil, for example), a more efficient dissolution of soil-bound PCDD/Fs was attained than by using the conventional analytical extraction method. Almost all (99%) of the PCDD/Fs transferred to the vegetable oil phase could be degraded during ultraviolet irradiation for 22 h. When a mixture of contaminated soil and vegetable oil was exposed to natural sunlight without a preliminary extraction step, the PCDD/F concentration declined by 48% in one month. Dechlorination of highly chlorinated PCDD/Fs during the treatment produced lower chlorinated and more toxic congeners. However, these reaction intermediates photodegraded rapidly. The type of the vegetable oil did have some influence on photodegradation. In the development of a cost-efficient treatment method, further studies should aim at optimising the type and amount of vegetable oil.

TIIVISTELMÄ (abstract in Finnish)

Kloorattujen kemikaalien valmistuksesta ja käytöstä aiheutuu merkittäviä polyklooratttujen dibentso-*p*-dioksiinien ja dibentsofuraanien (PCDD/F) päästöjä maaperään ja sedimentteihin. Kloorifenolivalmiste Ky 5:n ja vinyylikloridimonomeerin valmistusta 1940-luvun alusta 1980-luvun puoliväliin on pidettty mahdollisina Suomenlahden sedimenttien PCDD/F-lähteinä. Ky 5-valmistetta käytettiin lisäksi laajalti fungisidina sahoilla, mistä seurasi valumia maaperään ja sedimentteihin. Pilaantumisongelmien hoito ja ihmisen altistumisen estäminen edellyttää syvällistä PCDD/F-tasojen ja lähteiden tuntemusta sekä ympäristön puhdistamiseen soveltuvien tekniikoiden kehittämistä.

Tässä tutkimuksessa kartoitettiin PCDD/F-yhdisteiden pitoisuuksia ja lähteitä analysoimalla Suomenlahden eri osista kerättyjä sedimenttinäytteitä. Mahdollisten luontaisten muodostumisprosessien ja esiteollisten lähteiden selvittämiseksi analysoitiin järvisedimenttejä alueelta, jolla ei tiedetty olevan teollisuuslähteitä. Lisäksi tutkittiin ja kehitettiin kasviöljyjen ja auringonvalon käyttöön perustuvaa menetelmää PCDD/F-yhdisteillä pilaantuneen maan puhdistamiseksi.

Sedimenttitutkimusten perusteella PCDD/F-yhdisteiden kokonaismäärä Suomenlahden sedimenteissä oli 16,4 kg, mitattuna toksisina ekvivalentteina eli WHO-TEQ:ina. Kymijoen mukanaan tuomien, Ky 5:n valmistuksesta ja käytöstä peräisin olevien päästöjen osuus sedimenttien PCDD/F-kuormasta oli 76% vuosina 1960-1986 ja 58% vuosina 1986-1997. Vinyylikloridimonomeerin valmistuksen osuus oli vähäinen Suomenlahden kokonaiskuormituksen kannalta. Jäljelle jäävä osuus on oletettavasti peräisin ilmakehän kautta tulevasta taustalaskeumasta. Pahiten pilaantunut alue sijaitsi 12 km:n etäisyydellä Kymijoen suulta. Alue, jolla Ky 5-päästöjen vaikutus oli havaittavissa, ulottui kuitenkin 75 km:n etäisyydelle. Vaikutusalueella vallitsevat PCDD/F-kongeneerit olivat hepta- ja oktaklooratuja dibentsofuraaneja. Itämeren silakan tärkeimmän kongeneerin, 2,3,4,7,8-pentakloori-dibentsofuraanin, pitoisuudet olivat melko tasaisesti jakautuneet Suomenlahden eri osissa. Pieniä määriä lähinnä korkeasti klooratuja dibentso-*p*-dioksiineja havaittiin järvisedimenteissä, jotka olivat muodostuneet jopa 8000 vuotta sitten. PCDD/F-yhdisteiden kongeneerikoostumus viittasi luontaisiin muodostumislähteisiin.

Kun pilaantuneeseen maahan sekoitettiin kasviöljyä (esimerkiksi oliiviöljyä), saatiin maa-ainekseen sitoutuneet PCDD/F-yhdisteet liuotettua jopa tehokkaammin kuin yleisesti käytetyllä analyyttisellä uuttomenetelmällä. Kasviöljyyn uuttuneesta PCDD/F-määrästä (WHO-TEQ) hajosi 99%, kun uutetta säteilytettiin 22 h:n ajan ultraviolettivalolla. Kun pilaantuneen maa-aineksen ja kasviöljyn seos altistettiin luontaiselle auringonvalolle ilman esiuuttovaihetta, PCDD/F-pitoisuus aleni kuukaudessa 48%:lla. Käsittelyn aikana korkeasti kloorautuneiden PCDD/F-kongeneerien deklorautuminen tuotti alemmin kloorautuneita ja enemmän toksisia kongeneereja. Nämä hajoamisen välituotteet olivat kuitenkin nopeasti valohajoavia. Kasviöljyjen ominaisuudet vaikuttivat PCDD/F-yhdisteiden valohajoavuuteen. Kustannustehokkaan käsittelymenetelmän kehittäminen edellyttäisi öljyn valinnan ja annostelun optimointia.

Acknowledgements

Now that I have come this far in my career as a green scientist, I would like to express my gratitude to

ABBREVIATIONS AND DEFINITIONS

2,3,7,8-PCDD/Fs	2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans (toxic PCDD/Fs; 17 congeners)
d.w	dry weight
EDC	ethylene dichloride
f.w	fresh weight
HpDD/F	heptachlorodibenzo-*p*-dioxin/-dibenzofuran
HRGC	high-resolution gas chromatograph
HRMS	high-resolution mass-spectrometer
HxCDD/F	hexachlorodibenzo-*p*-dioxin/-dibenzofuran
I-TEQ	international toxic equivalent (NATO/CCMS, 1988; Ahlborg et al., 1994)
Nordic-TEQ	Nordic toxic equivalent according to Ahlborg et al., 1988
OCDD/F	octachlorodibenzo-*p*-dioxin/-dibenzofuran
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin
PeCDD/F	pentachlorodibenzo-*p*-dioxin/-dibenzofuran
PCDF	polychlorinated dibenzofuran
PVC	polyvinyl chloride
Safe-TEQ	toxic equivalent according to Safe, 1990
TCDD/F	tetrachlorodibenzo-*p*-dioxin/-dibenzofuran
TEF	toxic equivalency factor
UV	ultraviolet
VCM	vinyl chloride monomer
WHO-TEQ	toxic equivalent by the World Health Organisation (van den Berg et al., 1998). The WHO-TEQ for human and mammals, not including dioxin-like PCBs, is used in this dissertation.

The difference between I-TEQ, WHO-TEQ and Nordic-TEQ is mostly negligible. Where appropriate, I-TEQ and Nordic-TEQ have been recalculated as WHO-TEQ.

LIST OF ORIGINAL PUBLICATIONS

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

II   Isosaari, P., Kiviranta, H., Kohonen, T., Tuomisto, J., Vartiainen, T. 2000. Assessment of levels, distribution and risks of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the vicinity of a vinyl chloride monomer production plant. *Environ. Sci. Technol.* 34, 2684-2689.

III   Isosaari, P., Pajunen, H., Vartiainen, T. 2002. PCDD/F and PCB history in dated sediments of a rural lake. *Chemosphere* 47, 575-583.

IV   Isosaari, P., Tuhkanen, T., Vartiainen, T. 2001. Use of olive oil for soil extraction and ultraviolet degradation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *Environ. Sci. Technol.* 35, 1259-1265.

V   Isosaari, P., Tuhkanen, T., Vartiainen, T. 2004. Photodegradation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in soil with vegetable oil. ESPR – *Environ. Sci. & Pollut. Res.* 11, 181-185.

VI   Isosaari, P., Laine, O., Tuhkanen, T., Vartiainen, T. 2004. Photolysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) dissolved in vegetable oils: influence of oil quality. Submitted.

CONTENTS

1 INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) are formed in a multitude of industrial and non-industrial processes in which sources of chlorine, organic matter and sufficient energy are incorporated (Bumb et al., 1980; Fiedler, 1998; Rappe, 1993; Tuppurainen et al., 1998). Minor formation takes place in forest fires and other natural processes (Ferrario et al., 2000; Hoekstra et al., 1999). However, most of the PCDD/Fs are of anthropogenic origin: humans bear responsibility for their formation through combustion processes and the manufacture of chlorinated chemicals (Alcock & Jones, 1996; Breivik et al., 2004; Green et al., 2001). From these sources, PCDD/Fs are released into air, land and water. Despite the poor mobility of PCDD/Fs, their long half-live does facilitate transportation and redistribution between environmental compartments (Cole et al., 1999; Lohmann & Jones, 1998; Sinkkonen & Paasivirta, 2000). As PCDD/Fs accumulate from the abiotic environment into aquatic and terrestrial food chains, then they start to pose a risk to animals and humans can be at risk (Beck et al., 1996; Hites et al., 2004; Isosaari et al., 2002, 2004).

In certain human populations, the exposure to PCDD/Fs is close to the concentrations that potentially can cause adverse health effects (Alaluusua et al., 1999; Büchert et al., 2001; Johnson, 1995; WHO, 2000). Therefore, it is essential to identify the main sources of PCDD/Fs, including direct emissions and emissions from reservoir sources such as contaminated soils and sediments (Commission of the European Communitites, 2001). Improved identification and quantification of PCDD/F sources to air, land and water has been the objective of the recent inventories carried out in Europe and other continents. Inventories also aim to evaluate the efficiency of source control measures and try to predict future trends in emissions (Breivik et al., 2004; Fiedler, 2003; Hansen & Hansen, 2003; Quaβ et al., 2004; UNEP Chemicals, 1999). However, there is still much uncertainty over the quantity and development of emissions from some sources, particularly the sources of these compounds into land and water systems (Quaβ et al., 2000a; Wenborn et al., 1999).

One of the suspected sources of PCDD/Fs into the Gulf of Finland, a part of the Baltic Sea, has been the former production and use of a chlorophenol formulation, called Ky 5, next to the Kymijoki River (Malve et al., 2003; Verta et al., 2003). PCDD/F concentrations that

exceed the maximum limit set by the European Commission have been analysed from Baltic herring and salmon (Bjerselius et al., 2003; Isosaari et al., 2003; Kiviranta et al., 2003). Fish consumption is a significant pathway of PCDD/F exposure to the fish-consuming residents of the Baltic Sea region (Darnerud et al., 2003; Kiviranta et al., 2001, 2002). Hence, it is crucial to make an inventory of the PCDD/F sources into the Baltic Sea.

The manufacture and use of chlorinated chemicals have led to severe contamination of soil at industrial sites. Since Ky 5 and other chlorophenol formulations were used to treat timber, high concentrations of PCDD/Fs have been analysed at sawmill sites (Assmuth & Vartiainen, 1995; Kitunen & Salkinoja-Salonen, 1990; Persson et al., 2003; Troyanskaya et al., 2003). Remediation of soil has a high priority at sites that have been rezoned for residential use. However, the resources to remove and decompose PCDD/Fs are limited by the few techniques available and their high treatment costs (Jørgensen & Kalevi, 2002).

The following literature review compiles present knowledge of PCDD/F sources and concentrations in the Baltic Sea and its drainage area, particularly in Finland. Emphasis is placed on PCDD/F formation and releases attributable to the production and use of chlorinated chemicals. Techniques available for the destruction of PCDD/Fs in contaminated soils and sediments are also reviewed.

2 REVIEW OF THE LITERATURE

2.1 Sources of PCDD/Fs to land and water

2.1.1 Sources and emissions in Europe

Recent PCDD/F emission inventories have utilized an integrated approach to estimate emissions to the air, land and soil. The quantities of atmospheric emissions are best known. Emissions to land have also been quantified despite the scarcity of reliable data from most sources. Direct releases to water have only been qualitatively estimated (Quaβ et al., 2000a; Wenborn et al., 1999). The inventories suggest that emissions of PCDD/Fs to land, including landfills, may be as high or even higher than emissions into the air (Dyke et al., 1997; Hansen & Hansen, 2003; Haynes & Marnane, 2000; Wenborn et al., 1999).

A PCDD/F inventory that covered 17 European countries yielded a total annual emission of 38 kg I-TEQ/year to the land in 1994 (Wenborn et al., 1999). The greatest releases were attributed to the production and the use of organochlorine pesticides (Table 2-1). Pesticides and other chlorinated chemicals have an especially high potential of penetrating into water systems. There are many chlorinated chemicals that may contain PCDD/F impurities, which makes it extremely difficult to estimate the historical and current emissions. Even restricting to pesticides, 50 potentially PCDD/F-contaminated formulations have been listed (US EPA, 1994). PCDD/F impurities have also been detected in chemicals that have been synthesised from contaminated raw materials, for example, in Direct Blue 106 and Carbazole Violet synthesised from chloranil (Alcock & Jones, 1997). PCDD/F-containing chemicals have been used as pesticides, including fungicides, herbicides and insecticides (chlorophenols, chlorinated phenoxyacetic acids, hexachlorocyclohexane, chloranile, chloronitrofen), preservatives for wood, leather and textiles (chlorophenols), dry cleaning agents (tetrachloroethene), transformer oils and softeners (PCBs), raw materials for chemical syntheses (1,2-dichloroethene, chlorophenols, chlorobenzenes, chloranil), chemicals for drinking water purification (ferric chloride), dyes and pigments (chloranil, phthalocyanin), disinfection products (Irgasan DP 300, hexachlorophen) and coagulants in water treatment (ferric chloride) (Alcock & Jones, 1997; Ballschmiter & Bacher, 1996; Rappe et al., 1991; Masunaga & Nakanishi, 1999).

Other significant emissions to land and water have been attributed to accidental fires and treatment and disposal practices of municipal solid waste, combustion at old incineration plants in particular (Dyke et al., 1997; Quaβ et al., 2000a; Wenborn et al., 1999). Disposal of sewage sludge to land and sea represents a potential route of food-chain accumulation (Beck et al., 1996; Wenborn et al., 1999). In addition to the direct releases, PCDD/F concentrations in soils and sediments are affected by the atmospheric deposition. The most important source of PCDD/Fs into the atmosphere used to be municipal waste incineration; however, a recent European inventory proposes that iron ore sintering has become the biggest source (Quaβ et al., 2004).

TABLE 2-1. PCDD/F emissions to land and water from the EU countries in 1994 [a]

Source	Release to land		Release to water
	g I-TEQ	% of total release	potential (g I-TEQ)
production and use of chemicals			
pesticide production	13 000	34	high
pesticide use	1 600	4.2	high
chemical production			high
paper & pulp production			medium (8-27)
textile treatment			medium
combustion			
accidental fires	7 950	21	high
combustion of wood	650	1.7	
waste treatment and disposal			
incineration of MSW [b]	7 200	19	
disposal of MSW to landfill [b]	4 000	10	high
incineration of industrial waste			medium (0.3-16)
waste oil disposal			medium (1.8-7.9)
metal industry			
secondary Pb production	1 200	3.2	
secondary Cu production	390	1.0	
electric furnace steel plant	350	0.9	
secondary Al production	310	0.8	
metal industry [c]			medium

[a] Wenborn et al., 1999
[b] MSW = municipal solid waste
[c] Non-ferrous metal production, iron and steel industry, sinter plants: medium releases from each source

Releases from the production and use of chemicals and incineration of municipal solid waste and industrial waste are likely to continue their decreasing trend, whereas the patterns of other releases to land and water are less easy to predict (Quaβ et al., 2000b; Wenborn et al., 1999). With regard to air emissions, a 90% decrease was achieved in the emissions from

municipal waste incineration between 1985 and 2000 (Quaβ et al., 2004). However, significant reductions in PCDD/F emissions in the near future are deemed unlikely for all the other sources except for domestic coal combustion (Quaβ et al., 2000a). Therefore, it seems that the overall emissions in 1985 will not be cut by 90% until 2005, as intended in the 5th Action Programme of the European Commission (Commission of the European Communities, 2001; Quaβ et al., 2000a). Emissions from steel production in electric arc furnaces are even predicted to increase, due to an expanding activity in this field (Quaβ et al., 2000b, 2004). It is thought that non-industrial emissions will exceed industrial emissions in the near future, because they are more difficult to control (Quaβ et al., 2000a, 2000b).

2.1.2 Sources and emissions in the Baltic Sea region

The water basin of the Baltic Sea can be divided into several sub-basins. The commonly known main basins are the Gulf of Bothnia (Bothnian Sea and Bothnian Bay), the Gulf of Finland and the Baltic Proper. The catchment of the Baltic Sea covers parts of Finland, Sweden, Denmark, Germany, Poland, Belarus, Lithuania, Latvia, Estonia and Russia (Figure 2-1).
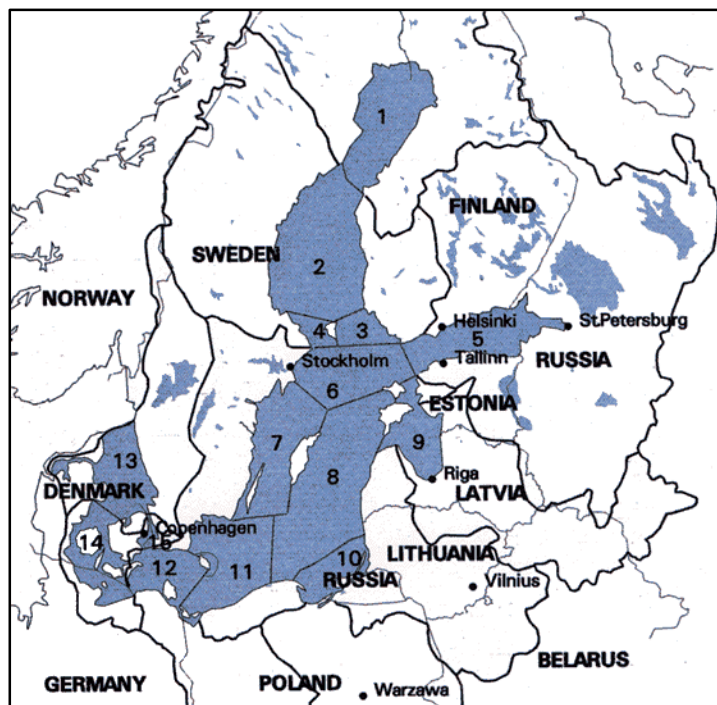

FIGURE 2-1. Map of the Baltic Sea and its catchment. 1 = Bothnian Bay, 2-4 = Bothnian Sea, 5 = Gulf of Finland, 6-12 = Baltic Proper, 13 = Kattegat, 14 = Belt Sea (HELCOM, 1993, 2003).

The availability of emission data from the countries in the Baltic Sea catchment varies. In those countries in which source-specific estimates have been made (Finland, Sweden, Denmark, Germany), the main sources of PCDD/Fs are the same as in the European countries in general. Waste treatment and disposal is estimated to be the greatest source to land, with the second largest being either the category "fires and other sources" or "industrial processes" (Wenborn et al., 1999). The emissions to land seem to be approximately 50 to 100-fold higher than the emissions to air in Finland, Sweden, Denmark and Germany, and of the same magnitude in the Baltic countries (Poland, Estonia, Latvia and Lithuania), assuming that residues (ash, dust, sludge) are disposed of to the land: at landfills or intosoil. However, the emissions from the Baltic countries may be underestimated because some subcategories have not been quantified (Table 2-2; Lassen et al., 2003).

TABLE 2-2. Estimates of PCDD/F releases to the land from the countries in the Baltic Sea drainage area [a]

Country	Min (g I-TEQ)	Max (g I-TEQ)	Best estimate (g I-TEQ)
Finland [b]	30	710	370
Sweden [b]	95	1 220	660
Denmark [b]	55	850	450
Denmark [c]	5.7	168	
Germany [b]	580	10 810	5 700
Poland [d]			6.6 + 530
Estonia [d]			0.12 + 15
Latvia [d]			0.24 + 32
Lithuania [d]			0.29 + 18
[a] Data from Russia not available [b] Situation in 1994 (Wenborn et al., 1999) [c] Situation in 2000-2002 (Hansen & Hansen, 2003) [d] Emissions to land + residues. Medium estimate in 2000 (Lassen et al., 2003)			

PCDD/F sources seem to have some distinct characteristics in each country. In Germany, the emissions from Hamburg are high and they may affect the pollution status of the Baltic Sea via atmospheric transportation. Potential industrial sources include emissions from hazardous waste incineration, production of copper, iron and steel and generation of aluminium (UNEP Chemicals, 1999). Previously, a manufacturing plant for the herbicide 2,4,5-T was also operating in Hamburg. In Estonia, Latvia and Lithuania, the amounts of waste that are incinerated are relatively low. PCDD/F releases to land and water are mainly assumed to occur from uncontrolled burning processes and discharge of municipal waste water (Jensen,

2003; Lassen et al., 2003). In Latvia, potentially PCDD/F-releasing industrial processes include municipal and hospital waste incineration, illegal processing of non-ferrous scrap and iron and steel production (Jensen, 2003; Quaβ et al., 2000a). Oil shale combustion and refining in Estonia does not seem to be a relevant emission source, although this statement should be viewed with caution until confirmed by more extensive measurements (Quaβ et al., 2000a). No data is available specifically relating to the PCDD/F emissions in the Baltic region of the Russia. Probable sources in Russia include biomass and waste combustion (Lassen et al., 2003). Heavily industrialised areas are located in the areas around St. Petersburg and Novgorod in which metal industry and production of chlorinated chemicals represent potential sources (Jensen, 2003). In Poland, releases to land and water are likely to occur from uncontrolled combustion, discharge of municipal waste water and spreading of sewage sludge onto the soil (Lassen et al., 2003).

A previous survey has examined industrial activities in the Baltic Sea drainage area in general. Potentially PCDD/F-emitting industries included pulp and paper plants that were located in several regions, iron and steel plants located near the Bothnian Bay and aluminium smelters located in Sundsvall (Bothnian Sea) and near St. Petersburg (Gulf of Finland). Several industrial plants for metal and chemical processing were operating in the southern and south-eastern parts of the Baltic Sea drainage area (HELCOM, 1993).

Chlorination processes in which PCDD/Fs have been formed include the chloralkali process, bleaching of pulp and manufacturing of chlorinated chemicals. The production of chlorine using the chloralkali process was a source of highly contaminated waste sludge until the 1980's, when most modern chloralkali plants discontinued the use of graphite electrodes (Rappe et al., 1991). A release estimate of 0.28 to 0.6 g Nordic-TEQ/year from the Swedish chloralkali plants to water was reported in 1993 (UNEP Chemicals, 1999). Chlorinated chemicals are not produced in Estonia, Latvia and Lithuania (Lassen et al., 2003). The production and use of chlorophenols and vinyl chloride monomer will be reviewed in Chapters 2.1.3 and 2.1.4.

The application of chlorine gas for pulp bleaching used to be a significant source of PCDD/Fs before its replacement with less hazardous forms of chlorine. In the 1980's, the releases of 2,3,7,8-TCDF from a single pulp mill are claimed to be as high as 60 g WHO-TEQ/year (MacDonald et al., 1998). It has been estimated that 30 000 t of total organic chlorine were

annually discharged into the Baltic Sea (Wulff et al., 1993). Today more than half of the pulp and paper in Europe is produced in Finland and Sweden (Leithe-Eriksen, 2001). The estimated releases from pulp and paper industry in 1994 were almost the same in Finland and Sweden, 1.2 to 83 g I-TEQ/year to land and 1.5 to 5.3 g I-TEQ/year to water (lowest to highest estimates) (Wenborn et al., 1999). In 2001, there were approximately one hundred paper mills in the Baltic Sea drainage area, with three of them using elemental chlorine for bleaching. These three paper mills were all located in Kaliningrad, Russia (Leithe-Eriksen, 2001). The production volumes of bleached pulp in the Baltic region increased by 56% during the 1990's (Leithe-Eriksen, 2001). However, PCDD/F releases are expected to undergo a continued decline (Quaβ et al., 2000b).

Statistics show that the use of PCDD/F-containing pesticides in Finland and Sweden has been low: in 1994, Finland and Sweden used 4.4 and 6.6% of the pesticide consumption of Germany, respectively. Pesticide consumption in Denmark has also been higher than in Finland and Sweden. No data is available pertaining to the consumption in other countries in the Baltic Sea region (Wenborn et al., 1999). However, production of chlorinated pesticides has been reported to take place in Poland (Lassen et al., 2003).

The future projections of atmospheric emissions in Sweden suggest that only a minor reduction in emissions will take place between 2000 and 2005. The slight increase in emissions from residential wood combustion, industrial combustion, secondary zinc production and electric furnace steel production will be compensated by a decrease in other emissions. The emissions from industrial sources were somewhat higher in Finland than in Sweden in 2000, and an increasing activity in electric furnace steel production and secondary zinc production is expected to play a bigger role in the development of emissions in Finland. No major changes are expected to occur between 2000 and 2005 in the overall emissions from Finland. In Denmark, PCDD/F emissions from all sources are expected to decline or at least remain unchanged. In Germany, emissions from the electric furnace steel production seem to be increasing, whereas other emissions are expected either to decline or to remain unchanged (Quass et al., 2000b).

In conclusion, there are a large number of industrial and municipal sources in the catchment of the Baltic Sea that have the potential to release PCDD/Fs directly to the air, land and water. These sources include combustion and chlorination processes as well as the metal processing

industry. The source reduction that may be achieved through improved emission control in the near future could be partially lost with increasing activity in some fields of industry.

2.1.3 Production and use of chlorophenols

Commercial chlorophenol formulations contain pentachlorophenol or its derivatives, sodium pentachlorophenoxide or sodium pentachlorophenyl laurate. Formulations with di-, tri- and tetrachlorophenols as the principal effective compounds have also been manufactured. The main applications of chlorophenols have been found in the timber industry, where they have been used to prevent freshly felled wood from staining and to protect wooden buildings and other constructions from the attack of fungi and insects. In addition, chlorophenols have been used for pest and weed control in agriculture, in the preservation of leather and textiles and synthesis of herbicides and other chemicals (Alcock & Jones, 1997; Ballschmiter & Bacher, 1996; Wild et al., 1992).

The large-scale manufacture of chlorophenols started in the 1930s. The most important manufacturing processes were alkaline hydrolysis from chlorobenzenes and catalytic chlorination of phenol. PCDD/Fs were formed in the process as a result of dimerisation of chlorinated aromatic compounds. In particular, pentachlorophenol formulations contained high amounts of PCDD/F impurities with OCDD being the main congener (Ballschmiter & Bacher, 1996). A Russian sodium pentachlorophenolate formulation contained exceptionally high proportions of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, 63 and 21% of I-TEQ, respectively (Troyanskaya et al., 2003). It has been estimated that the total amount of about 50 tonnes of PCDD/Fs in chlorophenol formulations were produced in the world (Ballschmiter & Bacher, 1996).

Most of the chlorophenol production in Europe had ceased by 1987, and PCDD/F concentrations in the formulations that have mainly been imported from the USA have been much lower than in pre-1987 formulations (Eduljee, 1999; Ballschmiter & Bacher, 1996). In 1991, strict restrictions were placed on the use of pentachlorophenol in the European Union (Council Directive 91/173/EEC).

At present, soils and other matrixes that became contaminated in the era of the large-scale use of chlorophenols still act as secondary sources of PCDD/Fs. In the UK, it was estimated at the

beginning of the 1990s that approximately 30 tonnes of pentachlorophenol might reside in soil at contaminated sites, and an additional pentachlorophenol burden of 50 tonnes might be associated with soil in the non-directly exposed environment (Wild et al., 1992). PCDD/F emissions from impregnated wood in the United Kingdom were estimated to be 1.2 g TEQ/year. The volatilisation rate from soils is less than 0.15 g TEQ/year (Duarte-Davidson et al., 1997).

In Finland, chlorophenols were used as fungicides in the sawmill industry between the 1930's and 1988 (Jørgensen & Kalevi, 2002). A technical chlorophenol formulation known by the trade name Ky 5 (also: Ky-5, KY-5) was manufactured and used on a large scale. The production amounted to approximately 24 000 tonnes between 1939 and 1984 (Malve et al., 2003; Suominen et al., 1999). It has been estimated that this amount contained about 1 530 kg of PCDD/Fs, or 20 kg I-TEQ (800 µg I-TEQ/kg). According to the manual of Kymi Kymmene Co from 1975, the manufacturing process included dissolution of phenols in carbon tetrachloride followed by a chlorination step, in which chlorine gas was applied in the presence of a ferric chloride catalyst. The synthesised chlorophenols, said to be mainly pentachlorophenol, were dissolved in lime to produce an aqueous solution of sodium pentachlorophenolate. This solution was press-filtered to remove solid impurities, then heated in a drum to produce dry Ky 5 flakes (Saatsi, 2002). The solid impurities that were formed in the process contained PCDD/Fs, and their disposal near the plant at the beginning of the manufacture is thought to be the main source of the contamination of the Kymijoki River by PCDD/Fs. An incident of accidental fire at the plant was another source of PCDD/F release (Malve et al., 2003; Suominen et al., 1999).

According to Vartiainen and co-workers (1995), the predominating chlorophenols in Ky 5 were 2,3,4,6-tetrachlorophenol (55%), 2,4,6-trichlorophenol (36%) and pentachlorophenol (7%); however, the composition varied to some extent. Tetrachlorophenols have actually been the most abundant chlorophenols found in some technical pentachlorophenol formulations (Alcock & Jones, 1997). The PCDD/F content in Ky 5 was 860 µg I-TEQ/kg (Vartiainen et al., 1995), which is close to the contents reported in pentachlorophenate (84-510 µg TEQ/kg) and in technical pentachlorophenol (1 000-3 000 µg TEQ/kg) (Alcock & Jones, 1997; UNEP Chemicals, 1999). The predominating PCDD/F congeners in Ky 5 were 1,2,3,4,6,7,8-HpCDF and OCDF (Assmuth & Vartiainen, 1995). High concentrations of 1,2,3,4,7,8-HxCDF have

also been reported, probably due to a misidentification of a non-toxic HxCDF (Assmuth & Vartiainen, 1995; Vartiainen et al., 1995). In pentachlorophenol, the predominating congener has always been OCDD. However, it appears that the exact composition changed during the production so that the relative contributions of HpCDFs and OCDF were much higher in the 1970's than in the 1990's (Alcock & Jones, 1997). Other impurities that have been analysed in Ky 5 include polychlorinated PCBs, diphenyl ethers (PCDE) and phenoxy anisoles (PCPA) (Humppi & Heinola, 1985; Vartiainen et al., 1995).

Ky 5 was mainly used at sawmill sites in Finland and Sweden (Persson et al., 2003) where to prevent fungal staining, timber was dipped into pools that contained an aqueous solution of Ky 5 (Kitunen & Salkinoja-Salonen, 1990). Timber piles were also sprayed with Ky 5. The mixture of sodium salts of chlorophenols was soluble in water, whereas the molecular form of pentachlorophenol was generally applied as an oily solution, for example in diesel fuel (Exner, 1987; Jackson & Bisson 1990).

In Denmark, the use of pentachlorophenol reached its maximum, 250 to 300 t/year, at the beginning of the 1970's. Despite the cessation of domestic use for wood preservation by 1978, it has been estimated that in 2000, 100 to 5 000 g I-TEQ was still present in the existing timber stock (Hansen & Hansen, 2003). There is no information available pertaining to the production and use of chlorophenols from other regions in the Baltic Sea drainage area.

2.1.4 Production and use of vinyl chloride

Vinyl chloride monomer (VCM) is produced from ethylene dichloride (EDC) by cracking. The EDC for this process is obtained by direct chlorination of ethene, and by oxychlorination, which is a process that recycles hydrogen chloride (HCl) that is formed in direct chlorination. (Carroll et al., 1998; Dyke et al., 1997; Khizbullin et al., 1998; Wenborn, 1999). The production of EDC, VCM and PVC can be accomplished at the same facility or at separate facilities. Most of the EDC produced in the USA and Canada is used for VCM production (Carroll et al., 1998).

PCDD/Fs are principally formed in the oxychlorination process. Solid and liquid waste arises from the purification of EDC and VCM, the disposal of spent oxychlorination catalysts and the treatment of effluent. Further emissions of PCDD/Fs may take place during the pyrolytic

cracking of EDC and the production of polyvinylchloride (PVC) resins (Carroll et al., 1998; Dyke et al., 1997; Khizbullin et al., 1998; Wenborn et al., 1999). The estimates of total emissions from the world VCM production at the beginning of the 1990's ranged from 2 to 1 800 g TEQ/year, depending on the source of information (Miller, 1993). A significant proportion of PCDD/Fs seems to be released to the land (Dyke et al., 1997; Miller, 1993).

Most of the data available on VCM production in Europe relates to the situation at the beginning of the 1990s. Germany was considered to be the biggest producer in Europe with a production volume of 6 000 kt/year of vinyl chloride in 1994. Data on the production volumes of EDC and VCM were virtually unavailable. Based on the production in Germany and the UK, the total releases in Europe represented more than one percent of all PCDD/F releases to land (Wenborn et al., 1999). German and Swedish VCM manufacturing plants that have been mentioned in the literature are not located next to the Baltic Sea (Miller, 1993). In Finland, vinyl chloride monomer was produced between 1973 and 1981 at one chemical plant that was located in Sköldvik, in the municipality of Porvoo. The manufacturing process included oxychlorination of EDC.

The use of PVC in several applications is being phased-out through international agreements and voluntary commitments (Greenpeace International, 2002, 2003).

2.1.5 Natural sources

Much attention has been recently paid on natural sources of PCDD/Fs owing to the detection of high concentrations of PCDD/Fs in certain clay minerals, some of which have been used as mineral supplements and anti-caking additives in animal feeds (Ferrario et al., 2000; Rappe & Andersson, 2000). Some clay samples have contained PCDD/Fs at concentrations up to thousands of pg/g. A similar congener profile has been found in clays that represent different regions and different ages, but a common geological process that could explain the formation of PCDD/Fs has not been identified (Ferrario et al., 2000; Rappe & Andersson, 2000).

Variable levels of contamination from unidentified sources have also been reported in soil and sediment samples from different regions and of different ages. For example, Hashimoto and co-workers (1995) found a PCDD concentration as high as 2 000 pg/g d.w in sediment slices that were one to ten million years old. The PCDD/F concentration analysed from Australian

sediment cores that represented the last 350 years was 2 500 pg/g d.w at its highest (Gaus et al., 2001). In rural lake sediments from the 1840s, a concentration of 100 pg/g d.w was analysed in the UK (Green et al., 2001). Müller and co-workers (2002) reported PCDD/F concentrations ranging from 3 to 33 pg I-TEQ/g d.w in Hong Kong sediments and Mai Po marshes. One characteristic of all these samples was a congener profile that was dominated by highly chlorinated PCDDs. The profile was different from known industrial sources.

The "trace chemistries of fire" theory helps explain the presence of PCDD/Fs in the environment before the manufacture of chlorinated chemicals started in the 1920's. The theory presented at the end of 1970's implied that PCDD/Fs are not only formed in industrial processes but also in domestic sources, including fireplaces, charcoal grills and cigarettes (Bumb et al., 1980). Whenever an organic material is burned, traces of chlorine are always present which give rise to the formation of organochlorine compounds.

Non-industrial combustion sources can be of purely natural or anthropogenic origin. Trees can be naturally set on fire but our ancestors also burned entire forests for heating and to clear land for cultivation. Judged by the low formation potential for PCDD/Fs that has been empirically demonstrated, forest fires as such are unlikely to cause significant contamination of soils (Hoekstra et al., 1999; Martínez et al., 2000; Prange et al., 2003). However, their role in PCDD/F redistribution from contaminated areas has been recently addressed (Prange et al., 2003).

Purely natural formation mechanisms have also been identified. These mechanisms require that suitable precursor compounds are available. Precursors can be produced naturally in small quantities (Gribble, 1994) but in some cases they are released in higher quantities from industrial sources. The formation of PCDD/Fs from chlorophenol precursors via enzyme-catalysed oxidative coupling has been demonstrated (Morimoto & Tatsumi, 1997; Silk et al., 1997; Svenson et al., 1989; Öberg & Rappe, 1992), and it is a possible formation mechanism mainly for OCDD and HpCDD congeners in digested sewage sludge and in composts (Klimm et al., 1998; Krauβ et al., 1994; Malloy et al., 1993; Stevens et al., 2003), for lower chlorinated PCDD/Fs in forest soils and peat bogs (Hoekstra et al., 2000; Silk et al., 1997), and for HpCDD and OCDD in incubated cow manure (Fries et al., 2002). Another formation pathway is photochemical dimerisation: formation of OCDD, OCDF and smaller amounts of lower chlorinated PCDD/Fs has been demonstrated after irradiating chlorophenols with UV

light (Lamparski et al., 1980; Liu et al., 2002; Skurlatov et al., 1997; Vollmuth et al., 1994). The proposed radical mechanism includes photolytic cleavage of the C-Cl or O-H bond which leads to the condensation of the radicals and the elimination of HCl (Piccinini et al., 1998; Skurlatov et al., 1997). In the atmosphere, pentachlorophenol is photochemically transformed to OCDD (Baker & Hites, 2000).

2.2 Contamination of soils

Guideline values have been set for PCDD/F concentrations in order to categorise soils as "clean" and "contaminated" or to define acceptable levels of contamination for certain land uses. In Finland, soils that exceed the level of 500 pg I-TEQ/g dry weight are recommended to be remediated (guideline value) with a target concentration of 20 pg I-TEQ/g dry weight (Jørgensen & Kalevi, 2003; Puolanne et al., 1994). In Germany, the Netherlands and Sweden, PCDD/F guidelines for soil depend on the use of land. In the most sensitive uses, soil is not allowed to contain more than 1 to 100 pg TEQ/g, whereas concentrations between 250 and 10 000 pg TEQ/g can be accepted for less sensitive uses (UNEP Chemicals, 1999).

The occurrence of exceptionally high levels of contamination in soils (and sediments) at so-called "hot spots" is usually attributable to the manufacture and use of chlorinated chemicals. For example, in the 1970's and 1980's, releases from the manufacture of 2,4,5-trichlorophenol and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) contaminated soil in Seveso (Italy), Hamburg (Germany) and New Jersey (USA) (Exner, 1987). In Poland, the production of 2,4,5-T, sodium pentachlorophenate, pentachlorophenol and 2,4,5-trichlorophenol was started in 1969 in Neratovice. Dumping of chemical wastes around the production facility led to soil contamination with 2,3,7,8-TCDD levels up to 29 800 pg/g being reported (Holoubek et al., 2000). Severe contamination of sawmill sites has been reported in Arkhangelsk district in northern Russia, with concentrations up to 224 000 pg I-TEQ/g d.w (Troyanskaya et al., 2003). In Japan, the annual emissions of PCDD/Fs from the herbicides pentachlorophenol and chloronitrofen (2,4,6-trichlorophenyl-4´-nitrophenyl ether) to agricultural land were more than 10 kg I-TEQ/year during the 1960's and early 1970's (Masunaga & Nakanishi 1999). PCDD/Fs have been found in at least 110 of 1 428 National Priorities List sites identified by the United States Environmental Protection Agency (Pohl et al., 1998).

Direct inputs of PCDD/Fs to land typically lead to local contamination in relatively small areas. Volatilisation, erosion, leakages to groundwater and transportation with surface runoff may result in a wider distribution in terrestrial, atmospheric and aqueous compartments. Therefore, any contaminated sites that are located within the drainage area of the Baltic Sea are potential sources of PCDD/F releases into the sea. A few cases of PCDD/F contamination in the drainage area of the Baltic Sea that originate from the production and use of chlorinated chemicals have received attention in the scientific literature. The use of Ky 5 has led to soil and sediment contamination by chlorophenols and PCDD/Fs at sawmill and waste disposal sites (Assmuth & Vartiainen, 1994; Assmuth & Vartiainen, 1995; Kitunen & Salkinoja-Salonen, 1990; Vartiainen et al., 1995). Concentrations of 2,3,7,8-chlorinated PCDD/Fs as high as 3 200 000 pg/g or 94 000 pg I-TEQ/g d.w have been reported in sawmill soil (Assmuth & Vartiainen, 1995). In Sweden, the maximum concentration of 2,3,7,8-chlorinated PCDD/Fs in samples collected from two sawmill sites has been 490 000 pg/g d.w (3 900 pg WHO-TEQ/g) (Persson et al., 2003).

Contaminated soils and sediments represent potential sources for food-chain accumulation of PCDD/Fs. Therefore, one of the tasks listed in the Dioxin Strategy of the Commission of the European Communities (2001) is to prepare a detailed survey of the locations of heavily contaminated soils and sediments.

2.3 Contamination of sediments

PCDD/F-contaminated sediments have been found in the vicinity of many industrial sites all around the world. The highest reported quantity emanates from magnesium production in Norway, where concentrations up to 18 000 pg Nordic-TEQ/g d.w have been analysed in the sediments of Frierfjord, giving rise to a total load of approximately 50 to 100 kg I-TEQ (Knutzen & Oehme, 1989). The manufacture and use of chlorine and chlorinated chemicals has been considered as the major source of severe sediment contamination in Tokyo Bay in Japan (Sakurai et al., 2000; Yao et al, 2002), Newark Bay (Passaic River) in New Jersey, USA (Bopp et al., 1991), Thunder Bay in Ontario, Canada (McKee et al., 1990), Arkhangelsk district in Russia (Troyanskaya et al., 2003), Venice Lagoon in Italy (Green et al., 1999; Jiminez et al., 1998), Lake Baikal in Hungary (Mamontov et al., 2000) and Hamburg harbour in Germany (Götz et al., 1990).

High PCDD/F concentrations have been analysed from fish living in the above-mentioned water systems. At the beginning of the 2000s, flounder caught from the Frierfjord still contained 28 pg WHO-TEQ/g fresh weight (f.w) (Knutzen et al., 2003), and striped bass caught from the Newark Bay contained 29 pg TEQ/g f.w (Litten et al., 2003). In Japan, PCDD/F concentrations up to 23 pg TEQ/g f.w have been analysed in tuna (Tsutsumi et al., 2003).

The pollution status of the Baltic Sea has been investigated both in coastal and offshore regions. However, we still do not have a consistent picture of the levels and time trends of PCDD/F deposition. Based on the sampling in 1988, Broman and co-workers (1991) estimated that the annual sedimentation of PCDD/Fs in the whole open Baltic Sea (near-coastal areas excluded) was 290 g Nordic-TEQ (37 kg of total PCDD/Fs). The highest concentrations in water samples, including particulate and dissolved fractions, were analysed in the Bothnian Sea.

Several sediment samples have been analysed from coastal regions of the southern Baltic Sea. In 1994, the mean concentration in 16 sediment samples from the estuary of the Warnow River, Bodden area, Mecklenburg Bight, Oder Bight and Arkona Basin was 8.53 ± 5.40 pg TEQ/g d.w. Concentrations of PCDDs were typically much higher than those of PCDFs, and the predominating congener was OCDD (Witt et al., 1997. The unit of measurement given in the original publication, ng/g, has been corrected to pg/g based on personal communication with Dr. Karl-Werner Schramm, 2004). Dannenberg and Lerz (1999) found 13-2 991 pg/g d.w. of PCDDs and 2.5-820 pg/g d.w. of PCDFs in sediment samples collected from approximately the same areas.

In the Bothnian Sea, sediment contamination has been identified in Hedesunda Bay (estuary of Dala River, multiple PCDD/F sources), and the vicinity of the Iggesund pulp mill, both located north of Stockholm. In Hedesunda Bay, the concentrations of 2,3,7,8-chlorinated PCDD/Fs were up to 190 000 pg/g (1 800 pg Nordic-TEQ/g) (Kjeller et al., 1990). Four kilometres away from the Iggesund pulp mill, the PCDD/F concentration was approximately 2 400 pg/g d.w. (Rappe et al., 1989). The PCDD/F concentrations decreased with increasing distance from Iggesund, being slightly elevated at a spot 29 km distant but only reaching the background level at a distance 150 km away from the pulp mill (Jonsson et al., 1993). The

concentration of 2,3,7,8-chlorinated PCDD/Fs in a sediment slice that was sampled from the area between Gotland and the Swedish coast in 1985 was low, 650 pg/g. The presence of alkyl-PCDFs, however, indicated releases from pulp mills (Kjeller & Rappe, 1995).

Little information on PCDD/F concentrations is available from the Bothnian Bay. In front of the city of Pietarsaari, PCDD/F concentrations of up to 350 pg Safe-TEQ/g d.w have been reported, which is equivalent to 63 pg WHO-TEQ/g d.w (Koistinen et al., 1995. Recalculation by Isosaari).

Contamination of Baltic fish species has also been surveyed. In a recent survey, fresh weight concentrations of PCDD/Fs as high as 17.4 pg WHO-TEQ/g were measured from pooled salmon samples from the Bothnian Sea, whereas the maximum in the Gulf of Finland was 9.7 pg WHO-TEQ/g. Pooled herring samples that were collected in spring contained up to 17.7 pg WHO-TEQ/g in the Bothnian Bay and 7.5 pg WHO-TEQ/g of PCDD/Fs in the Gulf of Finland (Hallikainen et al., 2004; National Food Agency Finland, 2004).

2.4 Remediation of contaminated soils and sediments

2.4.1 Available and emerging techniques

Only a few Finnish sawmill sites contaminated with chlorophenols and PCDD/Fs have been remediated. Remediation has usually been accomplished through mass transfer operations. Contaminated soils used to be treated by composting until the PCDD/F problem was recognised. The compost wastes or excavated soil that still contain high concentrations of PCDD/Fs have been transported to landfills, sometimes to special landfills. In a few cases, PCDD/Fs have been destroyed by high-temperature combustion. Less contaminated soils have been capped at the site. No degrading methods other than combustion have been used for the treatment of PCDD/Fs (Isosaari & Vartiainen, 2002; Jørgensen & Kalevi, 2002).

Combustion of soil and other PCDD/F-contaminated matrixes at temperatures higher than 1 000 °C is a conventional treatment technology that results in PCDD/F destruction efficiencies of 99.9% or more. Thermal desorption at 600 °C and afterburning of volatilised PCDD/Fs at temperatures higher than 1 000 °C is appropriate technology when the cleanup target is somewhat lower (Vis & Krijger, 2000).

Several emerging techniques for the removal and destruction of PCDD/Fs from soils and sediments have been presented in the literature. However, full-scale applications are not yet available. Soil extraction is one potential decontamination method. Dougherty and co-workers (1994) have studied the ability of a number of organic solvents, vegetable oils and solvent-oil mixtures to remove 2,3,7,8-TCDD from soil. With gentle periodical swirling, 13 to 14% of 2,3,7,8-TCDD could be dissolved in the investigated vegetable oils in 20 h, while 65 to 82% were dissolved in alcohols. The diffusivity of 2,3,7,8-TCDD in soil was highest in solvents with a low molecular weight and low viscosity, such as alcohols, and fairly low in ethyl oleate (Dougherty et al., 1991a; Overcash et al., 1991). In systems comprising oil, soil and water, a preferential partitioning of PCDD/Fs into mineral oils has been noted (Jackson & Bisson, 1990; Kapila et al., 1989). Even water can be used for the extraction. Extraction with water at elevated temperatures and sometimes also at elevated pressures has been termed subcritical water extraction. It also results in partial dechlorination of PCDD/Fs. Hashimoto and co-workers (2004) have reported a 99.4% reduction in PCDD concentration in soil after a 30-min water extraction at 350 °C, at atmospheric pressure.

Reductive dechlorination under alkaline conditions is an effective treatment for PCDD/F wastes. Peterson and Milicic (1992) have used potassium hydroxide in polyethylene glycolate (APEG-method) for the destruction of PCDD/Fs in contaminated sludge and activated carbon. DesRosiers (1989) has used the KPEG (potassium polyethylene glycolate) method, and Oku and co-workers (1995) have used sodium or potassium hydroxide in 1,3-dimethyl-2-imidazolidinone to degrade PCDD/Fs in liquid waste. In novel modifications of the technology, the use of organic solvents is no longer necessary: reductive dechlorination can be achieved through a mechanical treatment of PCDD/F-contaminated material in the presence of alkali metal salts, a process that is close to combustion because the intensive grinding creates high-temperature zones in the soil (Monagheddu et al., 1999). Other alternatives for chemical dechlorination of PCDD/Fs include the use a supported noble metal catalyst (typically palladium or platinum) and an alkaline hydrogen donor solution, for example, sodium hydroxide (NaOH) in propanol (Ukisu & Miyadera, 2003). Catalytic multiphase systems for the dechlorination of PCDD/Fs consist of a hydrocarbon solvent in which PCDD/Fs are dissolved, an aqueous phase, a phase-transfer agent, supported platinum or palladium catalyst and a source of hydrogen gas (Tundo et al., 2001). Solvated electrons have been generated for dechlorination purposes by dissolving alkali metals in anhydrous

ammonia (Getman, 2000). Reductive dechlorination multiphase processes can be operated at mild temperatures, at 30 to 50 °C.

Ionizing radiation in the form of a high-energy electron beam or γ radiation is also capable of dechlorinating PCDD/Fs. By irradiating spiked soil with γ rays, more than 92% of 2,3,7,8-TCDD has decomposed (Hilarides et al., 1994).

Ozonation has been successfully used to destroy PCDD/Fs when these agents are first adsorbed on a hydrophobic zeolite (Leichsenring et al., 1996). In soil suspension, ozonation at pH 10 and a temperature of 50 °C has destroyed 40% of 2,3,7,8-chlorinated PCDDs (Palauchek & Scholz, 1987). In seepage water from a landfill, probably containing precursors for PCDD/F formation, PCDD/F concentrations have started to increase during ozonation (Vollmuth & Niessner, 1995).

Using Fenton's reagent [Fe(II) and H_2O_2], Watts and co-workers (1991) have obtained 96% degradation in the OCDF content in sandy soil. In another study, Fenton's reagent has degraded 60 to 97% of pure PCDD/F congeners, but only 33% of PCDD/Fs were degraded in contaminated soil (Isosaari et al., 1997). Pignatello and Huang (1993) have used a combination of Fe^{3+}/ H_2O_2/visible light for the treatment of 2,4,5-T in water, and managed to decompose 66 to 100% of the PCDD/F impurities present in this herbicide. When contaminated soil slurry was pretreated with Fenton's reagent, up 99% of 2,3,7,8-TCDD were converted to biodegradable intermediates (Kao & Wu, 2000).

Biodegradation of non- to polychlorinated dibenzo-*p*-dioxins and dibenzofurans has been extensively investigated (Wittich, 1998). Microbes in PCDD/F-contaminated sediments exhibit some potential for dechlorination (Adriaens et al., 1995; Albrecht et al., 1999; Barkovskii & Adriaens, 1996; Bunge et al., 2003), however, the practical significance of natural processes in site cleanup appears to be low. The best results in PCDD/F bioremediation have been achieved with white rot fungus. In liquid-phase experiments in the laboratory, 40 to 76% of tetra- to hexachlorinated 2,3,7,8-PCDD/Fs were degraded in 10 days (Takada et al., 1996). In one application, 50-87% of tetra- to octachlorinated PCDD/Fs (chlorination patterns not given) were degraded in soil in 282 days (EarthFax, 2003). Another

potential remediation technique for 2,3,7,8-PCDD/Fs might be to use isolated bacterial enzymes in bioreactors (Ishii et al., 2003).

2.4.2 Photodegradation

Photodegradation mechanisms

PCDD/Fs have a strong UV absorption at wavelengths shorter than 270 nm; however, their absorption band extends into the wavelengths longer than 290 nm which makes is possible to use sunlight as a radiation source for PCDD/F photolysis (Choi et al., 2000; Choundry & Webster, 1989; Dulin et al., 1986; Tysklind et al., 1993; Wagenaar et al., 1995). Upon absorption of light, excitation of the PCDD/F molecule leads to the cleavage of either the C-Cl bond or the C-O bond. Cleavage of the C-Cl bond, dechlorination, accounts for less than 30% of the photodegradation products in isooctane and in aqueous solutions (Kieatiwong et al., 1990; Kim & O'Keefe, 2000; Rayne et al., 2002). In hexane, dechlorination yields have typically been higher: 50% from 2,3,7,8-TCDF (Dung & O'Keefe, 1994), 5 to 32% from OCDD and 35 to 68% from OCDF (Konstantinov & Bunce, 1996; Wagenaar et al., 1995). The relative yield of dechlorination products decreases with an increasing conversion of the original compound (Konstantinov & Bunce, 1996; Rayne et al., 2002).

Dechlorination reactions of PCDD/Fs, PCBs and other aryl chlorides (ArCl) are well established (Bunce, 1982; Chu & Kwan, 2002; Hawari et al., 1991; Konstantinov & Bunce, 1996). In the direct dechlorination mechanism (Eq. 1), absorption of UV light (hν) by the ArCl molecule leads to the formation of an excited singlet state that is converted to a triplet state via intersystem crossing (ISC). Homolytic dissociation of the triplet state into radicals then takes place readily.

$$\text{ArCl} \xrightarrow{[h\nu]} {}^1\text{ArCl} \xrightarrow{[ISC]} {}^3\text{ArCl} \rightarrow \text{Ar}\bullet + \text{Cl}\bullet \qquad \text{(Eq. 1)}$$
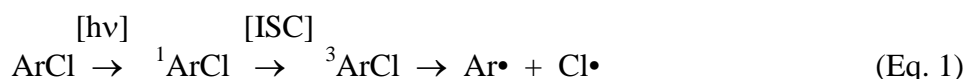
In the most typical form of an indirect or sensitised mechanism, an electron is transferred from an electron donor (don-H) to the excited state of aryl chloride (ArCl*) and an intermediate aryl radical anion is formed (Eq. 2).

$$\text{ArCl*} + \text{don-H} \rightarrow \text{ArCl}\bullet^- \rightarrow \text{Ar}\bullet + \text{Cl}^- \qquad \text{(Eq. 2)}$$
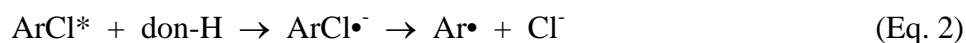
The generated aryl radicals (Ar•) are stabilised by hydrogen abstraction that yields the dechlorination product, ArH.

Cleavage of the C-O bond yields chlorinated dihydroxybiphenyls or hydroxydiphenyl ethers (the latter compounds are also known as chlorinated phenoxyphenols) (Friesen et al., 1996; Kieatiwong et al., 1990; Konstantinov et al., 2000; Rayne et al., 2002). As yet, the reaction mechanism involving the C-O bond cleavage and a complete mass balance have only been presented for the direct photodegradation of 2,3,7,8-TCDD in aqueous solutions: Rayne and co-workers (2002) demonstrated higher than 50% conversion of 2,3,7,8-TCDD into 2,2'-dihydroxy-4,4',5,5'-tetrachlorobiphenyl. The other degradation products were chlorinated phenoxyphenols and lower chlorinated dioxins. It was proposed that the yield of chlorinated hydroxydiphenyl ethers could be higher in better hydrogen-donor solvents. In isooctane, less than 10% of 2,3,7,8-TCDD has been found to be converted into 2,2'-dihydroxy-4,4',5,5'-tetrachlorobiphenyl and less than 10% into trichlorodibenzo-*p*-dioxin (Kieatiwong et al., 1990).

The ultimate aromatic photodegradation product of PCDDs appears to be hydroxybenzoic acid (Massé & Pelletier, 1987). Some researchers have also reported on the formation of PCDD/F-solvent adducts (Hung & Ingram, 1990; Kieatiwong et al., 1990) and chlorophenols (Konstantinov et al., 2000).

The data available on the influence of the chlorination degree and pattern of a PCDD/F molecule on photodegradation suggests that there is a more rapid photodegradation for lower chlorinated PCDD/Fs (Choundry & Webster, 1986; Friesen et al., 1996; Kim & O'Keefe, 2000; Koester & Hites, 1992; Nestrick et al., 1980; Niu et al., 2003; Yan et al., 1995). PCDFs degrade more rapidly than PCDDs (Konstantinov & Bunce, 1996; Niu et al., 2003; Ritterbush et al., 1994; Schuler et al., 1998; Wagenaar et al., 1995). It appears that 2,3,7,8-PCDD/Fs degrade more rapidly than non-2,3,7,8-PCDD/Fs on solid support and in the absence of photochemical sensitisers (Hosoya et al., 1995; Nestrick et al., 1980). When photochemical sensitisers are present, like in natural waters, chlorine substituents are preferably cleaved from positions 1, 4, 6 and 9, and 2,3,7,8-PCDD/Fs are more persistent (Friesen et al., 1990, 1996; Hung & Ingram, 1990; Konstantinov & Bunce, 1996).

Solvent and solid phase photodegradation

Photodegradation of PCDD/Fs has been investigated in natural and pure waters, surfactant solutions, acetonitrile-water solutions and organic solvents (Table 2-3). PCDD/Fs have also been photochemically degraded on solid surfaces, including soil, walls and vegetation (Table 2-4). Most of the research has been focused on photodegradation in the spectral range of sunlight.

Photodegradation rates are slow in soil (Kieatiwong et al., 1990; McPeters & Overcash, 1993; Wong & Crosby, 1978). Solvent additions are needed to overcome the strong binding of PCDD/Fs to solid surfaces and the shielding effect of particles (Kieatiwong et al., 1990; McPeters & Overcash, 1993; Wipf et al., 1978). They can also be used to extract PCDD/Fs from soil before irradiation (Botré et al., 1978; Namikaya et al., 2003). Selection of the solvent is a compromise between its environmental acceptability, its solubilising and diffusive properties as well as the UV absorption of the solvent. In strongly absorbing solvents, most of the UV light is absorbed within a few millimetres or even less. As an example, less than 1% of the original UV intensity penetrated beyond a depth of 2 mm in ethyl oleate (Dougherty et al., 1991b). In such a case diffusive and convective transport will determine whether any reduction takes place in deeper solvent layers or in solvent-amended soils (Dougherty et al., 1991c, 1993; Kieatiwong et al., 1990). Zhong and co-workers (1993) have stressed the importance of correct timing for new solvent additions to avoid downward migration of PCDD/Fs and to optimize photodegradation on the soil surface. The dosage is also crucial: low doses (0.1%) of ethyl oleate have even led to an increase in PCDD/F concentrations in soil due to an enhanced solubilisation of strongly bound pollutants (Miller et al., 1989).

Enhanced photodegradation of PCDD/Fs has been reported in solvents that act as hydrogen donors (Bertoni et al., 1978; Dung & O'Keefe, 1994; Hosoya et al., 1995; Tysklind & Rappe, 1991). The function mechanism of a hydrogen donor has been ascribed to the capability of hydrogen atoms to stabilise photolytically generated aryl radicals (Hung & Ingram, 1990). Radical stabilisation could also be an important mechanism in photodegradation pathways that involve homolytic cleavage of the C-O bond (Rayne et al., 2002).

TABLE 2-3. Compilation of photodegradation studies in solvent phase

PCDD/F congener	Solvent	UV source wavelength [a], power or intensity	Irradiation time	Degradation efficiency	t½, h	Reference
2378-TCDD	ethyl oleate-xylene	lamp: 20 μW/cm^2	5 d	100%	18.8*	Bertoni et al., 1978
2378-TCDD	surfactant methanol	lamp: 254-356 nm lamp: 254-356 nm	4.5 h 9 h	100% 88%	1.20 * 4.90 *	Botré et al., 1978
2378-TCDD	methanol	lamp: 100 μW/cm^2 sunlight	24 h 8 h	100% 100%	4.18* 1.81*	Crosby & Wong, 1971
2378-TCDD	hexadecane ethyl oleate	lamp: 290-320 nm lamp: 290-320 nm			0.43 4.99	Dougherty et al., 1991b
2378-TCDF 1278-TCDF	hexane pure water natural water hexane pure water natural water	lamp: 300 nm, 0.6 W/L [b] sunlight sunlight lamp: 300 nm, 0.6 W/L [b] sunlight sunlight			4.7-6.5 11 5.9-6.3 3.8-4.9 8.5 4.2-4.7	Dung & O'Keefe, 1994
2378-TCDF 23478-PeCDF 12347-PeCDD 1234678-HpCDD	natural water	sunlight	 5.25 d 10.2 d	 98% 94%	28.7 276 22.5 59.4	Friesen et al., 1990, 1996
OCDD	cyclohexadiene-hexane triethylamine-hexane cyclohexene-hexane hexane benzene-hexane benzophenone-hexane benzene acetonitrile-water	lamp: 295-350 nm, 1.2 W/L [c]			2.33 2.65 4.81 8.52 14.4 17.2 31.9 257	Hung & Ingram, 1990
2378-TCDD	isooctane	lamp: 310 nm	20 min		0.08	Kieatiwong et al., 1990

Table 2-3. Continuing

PCDD/F congener	Solvent	UV source wavelength [a], power or intensity	Irradiation time	Degradation efficiency	t½, h	Reference
1278-TCDD OCDD 1278-TCDF OCDF	pure water	sunlight			6.4 23 8.3 6.5	Kim & O'Keefe, 2000
OCDD OCDF	hexane	lamp: 285-335 nm	80 min 40 min		0.33 * 0.20 *	Konstantinov & Bunce, 1996
2378-TCDD 1478-TCDD 12378-PeCDD	hexane lab. wastes in isooctane	lamp: 254 nm, 4.6 W lamp: 254 nm, 4.6 W	20 min 24 h 24 h	98% 99% 100%	0.06 * 3.28 * 1.56 *	Konstantinov et al., 2000
2378-TCDD 1278-TCDD 1469-TCDD OCDD	n-hexadecane	lamp: 365 nm	60 min 555 min 1260 min -	52% 54% 10% 50%	0.95 8.18 140 24.3	Nestrick et al., 1980
OCDD OCDF	hexane	lamp: 254 and 313 nm	15 min	100% 100%	0.03 * 0.03 *	Ritterbush et al., 1994
2378-TCDD OCDD 2378-TCDF OCDF	tetradecane extract of fly ash	lamp: 300-400 nm, 3000 $\mu W/cm^2$			4.5 37.3 9.8 2.1	Tysklind & Rappe, 1991
2378-TCDD OCDD	decane-butanol	lamp: 313 nm, 0.09 W [d]			7.7 72.6	Yan et al., 1995

* Estimated from the data, based on 1st order degradation kinetics

[a] Wavelength range or wavelength of maximum intensity (λ_{max})

[b] Calculated based on the reported intensity of 1.48×10^{-6} einsteins L^{-1} s^{-1} and quantum energies from Leifer, 1988

[c] As above; reported intensity 3.13×10^{-6} einsteins L^{-1} s^{-1}

[d] As above; reported intensity 2.3×10^{-7} einsteins s^{-1}

TABLE 2-4. Compilation of photodegradation studies on surfaces and soil

PCDD/F congener	Matrix	Solvent	UV source wavelength [a], power or intensity	Irradiation time	Degradation efficiency	t½, 1/h	Reference
2378-TCDD	soil	ethyl oleate-xylene	sunlight	7 d	90%	1100*	Bertoni et al., 1978
PCDD/Fs	wall	no solvent	lamp: 254 nm, 12 W	48 h	90-99%	7.48-13.8*	Borwitzky & Schramm, 1991
2378-TCDD 1234-TCDD	C18-surface	2-propanol-water 2-propanol-water 2-propanol-water 2-propanol-methanol	medium-pressure Hg lamp: 450 W sunlight sunlight	5 min 20 min 4 d 6 d	100% 100%. 95% 100%	0.01 0.15 0.02 0.05	Hosoya et al., 1995
2378-TCDD 2378-TCDD OCDD	soil	hexadecane no solvent no solvent	lamp: 310 nm lamp: 310 nm sunlight	15 d	44-73% 16-41% 19-30%	191-429* 480-1990* 712-1190*	Kieatiwong et al., 1990
12389-PeCDF 123489-HxCDF OCDF 1234-TCDF 12347-PeCDD 123478-HxCDD OCDD	silica gel surface	no solvent	lamp: >290 nm, 450 W			3 5 9 88 92 140 270	Koester & Hites, 1992
2378-TCDD	glass surface		lamp: 20 µW/cm^2	42 h	87%	14.3*	Liberti et al., 1978a
2378-TCDD	floor/wall soil	ethyl oleate-xylene	lamp: 280-320 nm, 20 µW/cm^2 lamp: 2000 µW/cm^2	3 d 9 d	>78% 100%	<33* 143*	Liberti et al., 1978b
2378-TCDD	soil soil	tetradecane-1-butanol no solvent	sunlight	60 d	87% 70%	489* 829*	McPeters & Overcash, 1993

Table 2-4. Continuing

PCDD/F congener	Matrix	Solvent	UV source wavelength [a], power or intensity	Irradiation time	Degradation efficiency	t½, 1/h	Reference
OCDD	soil	no solvent	lamp: 310 nm	20 d	34-42%	614-804*	Miller et al., 1989
2378-TCDD 1278-TCDD 1469-TCDD OCDD	glass surface	no solvent	lamp: 365 nm	2.6 d 0.33 d 0.96 d -	20% 61% 59% 21%	140 5.83 13.8 815	Nestrick et al., 1980
2378-TCDD 12378-PeCDD HxCDDs [b] 1234678-HpCDD OCDD 2378-TCDF 23478-PeCDF HxCDFs [b] HpCDFs [b] OCDF	vegetation	(cuticular wax)	sunlight			55.5 57.8 76.2-91.2 83.5 105 45.9 55.0 70.7-78.8 84.5 100.5	Niu et al., 2003
2378-TCDD	vegetation	olive oil emulsion olive oil-cyclohexane no solvent	sunlight	9 d	77% 79% 57%	93.0* 69.6* 93.5*	Wipf et al., 1978
2378-TCDD	vegetation soil	(herbicide Agent Orange)	sunlight	6 h	70% 12%	3.45* 32.5*	Wong & Crosby, 1978

* estimated from the data, based on 1st order degradation kinetics

[a] Wavelength range or wavelength of maximum intensity (λ_{max})

[b] 2,3,7,8-chlorinated congeners

It is also possible to enhance photodegradation by using sensitising compounds. The role of photochemical sensitisers has been noted in natural waters, in which humic compounds and algal pigments play a significant role in PCDD/F photodegradation (Dung & O'Keefe, 1994; Friesen et al., 1990, 1996). Sensitisers have also been added to organic solvents to enhance the photodegradability of PCDD/Fs. Additions of hydrogen peroxide or azobis(isopropio-nitrile) shortened the half-life of OCDD in decane-butanol solution by 75% and 45%, respectively (Yan et al., 1995). Using triethylamine as a photosensitiser, 99% of OCDD had photolysed in 5 min in hexane (Konstantinov & Bunce, 1996). Photocatalytic treatment with titanium dioxide (TiO_2) has been effective for PCDD/Fs in solvents (Choi et al., 2000). In contaminated soils, a decline in the I-TEQ content by 21 to 34% has been noted after 12 weeks of sunlight exposure (Isosaari et al., 1998). However, in some experiments, no decline has been detected (Kobara et al., 2003).

3 AIMS OF THE STUDY

This dissertation aims to

- Make an inventory of the sources, concentrations and total amounts of PCDD/Fs in the Gulf of Finland sediments (I, II)

- Investigate the natural and pre-industrial background concentrations of PCDD/Fs in lake sediments (III)

- Study the photodegradation mechanisms of PCDD/Fs in vegetable oil-UV light systems (IV-VI)

- Assess the potential of photochemical decontamination of soils (IV-VI)

4 MATERIALS AND METHODS

4.1 Sediment sampling

Sediment samples were collected by specialists in geology and limnology from the University of Turku (II), Geological Survey of Finland (III), Finnish Institute for Marine Research and Finnish Environment Institute (I) between 1994 and 1999. Time dating of the sediments was carried out at the Radiation and Nuclear Safety Authority (I-III) and University of Turku (II). The methods used for the sampling and time dating are summarised in Table 4-1.

TABLE 4-1. Sediment sampling and dating methods used in original papers I-III

Sampling site	Depth	Sampling device	Dating method	Paper
Gulf of Finland	0-2, 0-5 cm	Limnos sampler		I
	0- ~50 cm	gravity corer	Cs-137, Pu-239, 240, Pb-210	I
Sköldvik	0-7 cm	Limnos sampler		II
	0-100 cm	freezing sampler	Cs-137, SCP [a]	II
Lake Ahmasjärvi	0-520 cm	piston corer	C-14	III
[a] Spheroidal carbonaceous particles				

One surface sediment sample or sediment core was collected per sampling point. The surface sediments were collected with Limnos-type samplers. The deeper sediment cores were obtained with different types of sampling devices that were designed for undisturbed sampling. The order of sediment layers was preserved either by slicing the sediment core onboard the research vessel as it was pushed out from the corer, layer by layer (I), by freezing the sediment profile immediately in the sea bed (II) or by transporting the core to the laboratory in closed sampling tubes and sectioning it there in the horizontal position (III). The sampling points of deep cores in studies I and II were located in echosounded accumulation areas of depositing material.

4.2 Photodegradation of PCDD/Fs

4.2.1 Light sources

The source of light in photodegradation experiments was either a set of two parallel blacklight lamps (IV, VI), fluorescent lamps (IV) or natural sunlight (V). Blacklight lamps emitted light in the UV-A and UV-B regions, between 300 and 400 nm. The intensity of the UV light was

50 W/m^2 (5 000 μW/cm^2) at the distance of the sample surface. Fluorescent lamps that emitted light in the visible region were used for the conventional lightning of the laboratory. The lamps were located approximately two metres above the samples. Under sunlight, the highest UV intensities measured at noon were between 30 and 35 W/m^2; however, a borosilicate glass cover above the soil samples restricted some of the incident light (V).

4.2.2 Vegetable oils

The vegetable oils used in the experiments included extra virgin olive oil (IV, VI), olive oil (V, VI), palm oil (VI) and rapeseed oil (VI). The classification criteria of olive oils have been established by the International Olive Oil Council, IOOC (www.internationaloliveoil.org). The vegetable oils were widely used food-grade oils that were purchased from a local supermarket or received directly from the distributor. The properties of the oils have been described in paper VI.

4.2.3 Photodegradation experiments in liquids

The purely liquid-phase photodegradation experiments were conducted in vegetable oils and organic solvents. Vegetable oil, hexane or toluene was spiked with 1,2,3,4,6,7,8-HpCDF (IV, VI), 1,2,3,4,6,7,8-HpCDD (VI) or a PCDD/F mixture that had been prepared by extraction from the Ky 5 wood preservative (IV). The concentration in oil or solvent was typically 6 000 pg/g of HpCDF, 60 000 pg/g of HpCDD or 66 000 pg/g of 2,3,7,8-chlorinated PCDD/Fs (900 pg WHO-TEQ/g) when congener mixtures were used.

For each photochemical experiment, a series of samples was prepared in sample vials with an inner diameter of 2.5 cm. The depth of the solvent was approximately 0.2 cm. The samples were irradiated under the light source and the entire contents of the vials were taken for PCDD/F analysis at defined time intervals.

4.2.4 Photodegradation experiments on soils

Photodegradation of PCDD/Fs was examined by using samples of sawmill soil that had become contaminated when the fungicide Ky 5 was used for wood preservation at least 20 years earlier (IV, V). The soil from Vääksy sawmill had been mixed with organic and inorganic supplements during a bioremediation trial intended to decompose the chlorophenols. At the end of the trial, a bucketful of soil with an unchanged PCDD/F

concentration was taken for photodegradation experiments (IV). The soil from Sikoniemi sawmill (V) had been excavated from its original location to temporary storage at a landfill site. The organic content, determined as ignition loss, was 14.7% in the Vääksy sawmill soil and 6.7% in the Sikoniemi sawmill soil. Both soils were sieved prior to the experiments. They were dried before usage, though not in the outdoor experiment (V).

Three modifications of photochemical soil decontamination were tested. Soil was either extracted with vegetable oil and the separated extract was irradiated in the laboratory (IV), or a soil-vegetable oil mixture was irradiated in a vial in the laboratory (IV) or on a Pyrex dish outdoors, under sunlight (V). Initial PCDD/F concentrations, vegetable oil to soil ratios and irradiation times were different in the experiments (see Results and discussion, Table 5-3).

4.3 Analytical methods

4.3.1 Extraction and pre-treatment of samples

Soil and sediment samples (1.5-4.0 g) were freeze-dried to complete dryness and the dry weight was determined from the weight loss. The samples were then homogenised with a spatula and extracted with toluene in a Soxhlet apparatus for 20 to 24 h (I-III, V). In a few photochemical studies, samples that contained soil and vegetable oil were extracted with 1:1 diethylether:hexane in an ultrasonic bath (IV). After extraction, the solvent was exchanged to hexane. The extracts were treated with concentrated sulphuric acid to decompose the vegetable oil.

Samples which comprised of spiked vegetable oils (without soil matrix) were not extracted. They were dissolved in hexane before decomposing the oil.

The pre-treatment of the sediments also included precipitation of elemental sulphur with activated copper powder and filter-removal of the precipitate (I-III).

4.3.2 Purification and quantification of samples

After the aforementioned pre-treatment steps, the vegetable oil, soil and sediment samples were purified over various solid-phase columns. The same column purification, gas-chromatographic separation and quantification methods were applied to all samples (I-VI). In

brief, the samples were eluted with organic solvents or solvent mixtures through a multi-layer silica gel column, activated carbon-Celite column and an aluminium oxide column. These columns were intended to remove decomposed lipids and other disturbing organic matter as well as compounds that would interfere with the identification and quantification of PCDD/Fs. For example, with an activated carbon-Celite column PCBs were separated in a different solvent fraction.

Samples that were concentrated to an approximate volume of 10 to 20 µl were injected into the column of a high-resolution gas chromatograph (HRGC) using the split-splitless technique. A high-resolution mass-spectrometric detector (HRMS) was used to record two mass per charge (*m/z*) values per each congener arriving at the detector. Quantification was based on the isotopic dilution method that compares the responses of native PCDD/Fs with those of spiked ^{13}C-labelled internal PCDD/F standards.

4.3.3 Analysis of degradation products

The methods that were used to determine the photodegradation products of PCDD/Fs included scanning of *m/z* values over a range 50 to 500 (IV), analysis of tetra- to heptachlorinated toxic and non-toxic dechlorination products (IV, VI), and analysis of tetra- to heptachlorinated hydroxy- and dihydroxybiphenyls and hydroxybiphenylethers (VI).

The samples that were run on the scan-mode were prepared by irradiating 114 ng of 1,2,3,4,6,7,8-HpCDF for 5 or 30 min. The purification of the samples was carried out as described in Chapter 4.3.2. One half of the purified sample was methylated with diazomethane and the other half was run in an unmethylated form (IV).

Dechlorination products of 1,2,3,4,6,7,8-HpCDF were determined from several samples that were taken during the experiments with initial 1,2,3,4,6,7,8-HpCDF concentrations ranging from 6 to 114 ng/g (IV, VI). Dechlorination products of 1,2,3,4,6,7,8-HpCDD (65 ng/g) were investigated after 10, 30 and 60 min of irradiation (VI). The identification of non-toxic PCDD/Fs was based on comparisons with previously run reference mass chromatograms (IV, VI).

Hydroxylated products of 1,2,3,4,6,7,8-HpCDD and –HpCDF were extracted from the vegetable oil samples with an alkaline alcohol and transferred into hexane after acidification. The samples were methylated with diazomethane, purified and analysed with HRGC-HRMS (VG 70-250 SE, resolution 10 000). The internal standard solution contained ^{13}C-labelled hydroxylated compounds with five to seven chlorine substituents (VI).

4.3.4 Quality control and assurance

Most of the experimental and analytical work in studies I-VI was carried out in a testing laboratory (No. T77 in Finland) that was accredited by the Centre for Metrology and Accreditation. In the first studies (I-IV), accreditation followed the standard SFS-EN 45001 and ISO/IEC Guide 25, and was then updated according to the standard ISO/IEC 17025 (V, VI). The basic quality control and assurance measures included participation in interlaboratory studies (I-VI), use of procedural blanks (I-VI), reporting of detection limits (III-VI), analysis of parallel samples (I, II, IV-VI) and replication of experiments (V, VI).

5 RESULTS AND DISCUSSION

5.1 PCDD/Fs in the Gulf of Finland sediments

5.1.1 Concentrations and spatial distribution

Investigations in the Gulf of Finland were focused on two regions. Most of the sediment samples were collected from the proximity of the Kymijoki River inlet, in front of the city of Kotka (I). This region was selected because transportation of PCDD/Fs from the Kymijoki River was anticipated in the light of previous studies (Koistinen et al., 1995; Verta et al., 1999a, 1999b). Another study area was located in front of Sköldvik (Kilpilahti), in the municipality of Porvoo, where the former manufacture of vinyl chloride monomer (VCM) could be considered as a potential source of PCDD/Fs into the sea (II). Depending on the availability of representative samples, investigations were also extended to other areas of the Gulf of Finland. Sampling was carried out in 1995-1996 in Sköldvik and in 1997-1998 in the other regions.

The PCDD/F concentrations in the investigated sediment samples can be divided into four categories: they represented the maximum pollution level in old (years 1960-1986) or recent (surface; years 1986-1997) sediment layers, or background contamination in old or recent sediment layers of the Gulf of Finland (Table 5-1). The most polluted sediments were located near the suspected coastal point sources: in front of Kotka (Kymijoki area) and in Sköldvik. In these areas, the sum concentrations of 2,3,7,8-PCDD/Fs exceeded the background concentrations by 80 to 1 100-fold in old sediments and by 63 to 76-fold in recent sediments. The background WHO-TEQ concentration was exceeded by 14 to 46-fold in polluted areas, including both old and recent sediment deposits.

The Finnish guideline value for PCDD/F contaminated soils, 500 pg I-TEQ/g d.w (Puolanne et al., 1994), was used as a rough estimate for contamination, because there are no guideline values for PCDD/F-contaminated sediments in Finland. However, it should be stressed that there is no regulatory or scientific basis for the application of the soil guideline value to sediments, because these matrices are different in many ways.

Table 5-1. Concentrations of PCDD/Fs (pg/g d.w) in the Gulf of Finland sediments

Region	Years	Classification	PCDD/Fs	2,3,7,8-PCDD/Fs	WHO-TEQ	n [a]	Ref.
Kymijoki area	1962-1971	old max. [b]	101 000	65 600	473 [c]		I
Sköldvik area	1970's	old max. [d]	914 000	901 000	1070 [e]		II
Kymijoki area	1997	recent max.	52 900	35 500	214		I
Sköldvik area	1995	recent max.	38 200	29 600	683 [e]		II
Gulf of Finland	1960-1986	old backgr. [f]	570-1 430	330-820	12-26	2	I
Gulf of Finland	1997	recent backgr.	430-810	250-470	10-15	4	I
Gulf of Finland /Sköldvik area	1996	recent backgr.	480-650	330-510	6.2-8.1 [e]	2	II
Gulf of Finland, near-coastal [g]	1997	recent range	800-2 200	460-1 240	14-26	6	I
[a] Number of sampling points [b] Sediment depth 25-31 cm [c] 479 I-TEQ [d] Sediment depth 65-68 cm [e] Recalculated as WHO-TEQ, based on the full-congener raw data [f] Sediment dept 5-8 cm [g] Northern coast of the Gulf of Finland, 0-15-km distance from coastline. Not influenced by the Kymijoki River discharges							

PCDD/F concentrations in sediments exceeded the Finnish guideline value for PCDD/F contaminated soils in a near-coastal sediment core from Sköldvik. Although the concentrations were lower in the surface layers than those measured deeper in the sediment core, the surface concentration was still higher than the guideline value. It is likely that the guideline was also exceeded in the near-coastal sediments in front of Kotka. Twelve kilometres away from the Kymijoki River inlet, the concentration was almost as high as the guideline value. Based on these considerations, the area within 12 km from the Kymijoki River inlet was classified as a highly polluted area (Fig. 5-1).

In the sediments that had been formed at the time of the maximum inputs of PCDD/Fs, the concentrations of 2,3,7,8-PCDD/Fs ranged from 330 to 820 pg/g d.w (12-26 pg WHO-TEQ/g d.w) in the area that was classified as "background". The background concentration was reached at about 75 km away from the two branches of the Kymijoki River, and therefore, the distance of 75 km was assigned as on the borderline of a slightly polluted area, or in other words, within the impact zone of the Kymijoki River (Fig. 5-1). In the Sköldvik region, the background was defined as an OCDF concentration of 200 pg/g d.w (II). The corresponding

sum concentrations have been presented in Table 5-1. In this area, the background concentration was reached only at 9 km from the point source. Hence, the forms and shapes of the coastline may effectively trap pollutants, preventing their transportation farther offshore.

FIGURE 5-1. A map of the Gulf of Finland, showing the impact area of the Ky 5 release from the Kymijoki River (I, Table 3) and the main sampling sites (I, II). Sampling sites for sediment cores have been named.

To expand the knowledge of PCDD/F concentrations and point sources in different parts of the Gulf of Finland, additional sediment samples were analysed from the southern coast, in front of Tallinn. The sediments had been sampled between 1993 and 1995 and analysed for extractable organic halogens (EOX) (Kankaanpää et al., 1997). The remaining sediment samples were kindly donated for PCDD/F analyses by Dr. Harri Kankaanpää from the Finnish Marine Research Institute. The samples were undated, 1-cm thick sediment slices from different depths of the sediment cores. PCDD/F concentrations in this area turned out to be among the lowest concentrations measured in the Gulf of Finland, ranging from 5.15 to 10.1 pg WHO-TEQ/g d.w (see Table 5-3).

A comparison of the highest PCDD/F concentrations in the Gulf of Finland with those that have been reported from the Kymijoki River, up to 350 000 pg I-TEQ/g d.w (Verta et al., 1999b), shows that PCDD/F concentrations declined significantly during the transportation in the river, and they were further diluted in the sea.

In the open sea, the measured PCDD/F concentrations did not differ from the background concentrations that have been reported from other background regions. In the Gotland deep, background concentrations of 24 and 27 pg WHO-TEQ/g d.w. (660 and 550 pg/g d.w. of 2,3,7,8-PCDD/Fs) have been found (Koistinen et al., 1995; Rappe et al., 1989). In two areas of the Mediterranean, the background levels ranged from 0.4 to 39 pg WHO-TEQ/g d.w (di Domenico et al., 1998; Eljarrat et al., 2001). Bonn (1998) reviewed the PCDD/F data available from lakes and rivers, and concluded that the background concentrations of PCDD/Fs in surface sediments are typically less than 1 000 pg/g d.w. The median concentration of 61 river sediments from rural areas of the USA was 9.9 pg TEQ/g d.w (Rappe et al., 1997). Finnish lake sediments seem to be cleaner. The median concentration was 0.65 pg Nordic-TEQ/g d.w in 18 lake sediment samples collected from central Finland (Koistinen et al., 1990), and concentrations in three northern lakes ranged from 1.4 to 4.2 pg I-TEQ/g d.w (Vartiainen et al., 1997a).

5.1.2 General time trends

Time trends in PCDD/F concentrations were studied from dated sediment cores. Time trends in front of the Kymijoki River inlet reflected the production history of Ky 5, whereas the trends in Sköldvik followed the production of VCM. The onset of Ky 5 production in 1939 was denoted by rapidly increasing concentrations in the sediments between the 1940's and 1960s-1970s (I, Fig. 2). The incidence of maximum concentrations seemed to be dependent on the distance from the coast: the farther the sampling point was located from the Kymijoki River, the later the concentration peak appeared. By the beginning of the 1980's, a rapid decrease was however noted at all the sampling stations. The PCDD/F sum concentrations in surface sediments were 24 to 66% of the maximum concentrations observed in the 1960s-1970s (excluding sampling station A1: 24-52%) and WHO-TEQ concentrations were 26 to 78% of the maximum concentrations (excluding A1: 26-50%) (I, Tables 1 and 2). If these trends are compared with the production history of Ky 5 (Verta et al., 1999a), it can be actually noted that PCDD/F concentrations in dated sediments already peaked at the time when the production volumes were increasing at their most rapid, and the concentrations started to decrease earlier than the production volumes declined. In contrast, the emission and concentration trends of mercury (Hg) (Verta et al., 1999a) suggest that transportation of pollutants from almost the same location (from the same industrial area in Kuusankoski) into the Gulf of Finland would take about 10 years. Hence, a delayed peaking of the PCDD/F

concentrations in the Gulf of Finland would have been expected. The observed discrepancies might have been caused by an exceptional PCDD/F release during an accidental fire in 1960 and an improvement in emission control and waste management practices as the manufacturing process developed (Malve et al., 2003; Suominen et al., 1999; Verta et al., 1999a). Another, less likely reason could be significant emission from sources other than the manufacture of Ky 5.

The production of VCM had a dramatic influence on the sediment concentrations in front of Sköldvik. A distinct peak in PCDD/F concentration seemed to conform to the production of VCM between 1973 and 1981, although the dating of the investigated sediment core did not reveal the exact years of the maximum inputs (II). In surface sediments, the PCDD/F concentration was 4.2% and WHO-TEQ was 64% of the maximum concentration in the same sediment core (Table 5-1).

The period of the highest PCDD/F concentrations was found to occur at the same time in background areas as in the areas that were directly impacted by the chemical industry, in the 1960s-1970s (I, Table 1). Similar time trends have been reported from several locations, both from rural and industrial areas: at that time the global emissions from industrial sources were at their highest (Alcock & Jones, 1996; Duarte-Davidson et al., 1997).

Due to a high sedimentation rate in coastal areas, particularly in Sköldvik, the most polluted sediments were buried under a layer of more recent, cleaner sediments that was up to 60 cm thick. However, the surface concentrations in the vicinity of the point sources were higher than in the background areas, which is indicative of continuing releases from the land. Since the manufacture of chlorinated chemicals no longer takes place, the origin of PCDD/Fs could be long-term leakages from contaminated sites or resuspension from the bottom of the Kymijoki River. Transportation and mixing of contaminated sediments in the Gulf of Finland might also lead to occasionally elevated concentrations in some locations.

The sedimentation rate of particulate matter in the Gulf of Finland varied with time and location (I, Fig. 3). The sedimentation rate affects the depositional fluxes of PCDD/Fs and therefore, the spatial and temporal comparisons of the pollution status cannot be properly evaluated on a concentration basis alone. In areas with a slow sedimentation rate, the past reservoir of PCDD/Fs is more susceptible to vertical mixing and transportation and better

available for biota than in areas in which a rapid burial takes place. Thus it is recommendedthat the concentration data should be supplemented with information on the sedimentation rates and origin of the sediment particles.

5.1.3 Congener-specific time trends

This chapter examines the history of PCDD/Fs in a congener-specific manner. The time trends of PCDD/F congeners were constructed using the data from the sampling stations K15, XV-1, LL3a, K20 and JML1b only (Table 5-2). Sampling station A1 was excluded because it was located near the coastline so that the concentrations were higher and peaked earlier than at the other stations. K19 was excluded for the reason that the decline in PCDD/F concentrations was much faster than at other sampling stations, which might indicate some instability in the sedimentation conditions. SL2s was excluded, as in paper I, because the concentrations were fairly constant throughout the sediment core. In addition to the decline percentages, the decline rates in PCDD/F concentrations were calculated to facilitate the comparisons between sediment cores and congeners.

TABLE 5-2. Concentration trends (± standard deviations) of selected PCDD/F congeners in the Gulf of Finland. For the maximum concentrations, n = 5; for the surface concentrations, n = 7

Congener	Surface concn., pg/g	Maximum concn., pg/g	year	Total decline, %	Decline rate % unit/year	pg/year
2378-TCDF	9.72 ± 1.93	25.0 ± 19.2	1980 ± 5	53.5 ± 16.1	3.52 ± 1.96	1.18 ± 1.59
12378-PeCDF	3.59 ± 0.46	8.28 ± 2.19	1978 ± 8	51.9 ± 12.0	2.86 ± 0.68	0.23 ± 0.04
23478-PeCDF	10.6 ± 2.4 [a]	20.9 ± 6.7	1976 ± 10	47.5 ± 16.6	2.43 ± 0.42	0.49 ± 0.10
234678-HxCDF	13.0 ± 8.7	41.1 ± 44.2	1975 ± 7	56.8 ± 14.0	2.61 ± 0.30	1.06 ± 1.14
1234678-HpCDF	2050 ± 2620	7490 ± 11800	1973 ± 5	61.3 ± 11.9	2.63 ± 0.29	188 ± 294
OCDF	1890 ± 2230	8900 ± 15080	1972 ± 7	62.3 ± 12.9	2.59 ± 0.31	212 ± 349
2378-TCDD	0.59 ± 0.38	1.95 ± 1.79	1982 ± 6	61.2 ± 14.3	4.76 ± 2.23	0.11 ± 0.12
12378-PeCDD	4.74 ± 2.90	19.7 ± 20.3	1978 ± 5	69.4 ± 8.8	3.72 ± 0.33	0.73 ± 0.72
123678-HxCDD	28.2 ± 25.1	159 ± 206	1974 ± 6	71.8 ± 9.7	3.25 ± 0.91	4.90 ± 5.84
1234678-HpCDD	42.9 ± 24.0	131 ± 123	1978 ± 8	57.4 ± 10.1	3.27 ± 1.16	3.98 ± 3.02
OCDD	108 ± 28.1	280 ± 235	1977 ± 7	49.4 ± 16.5	2.48 ± 0.55	7.19 ± 6.45
[a] With n = 22, the average concentration was 10.7 ± 2.7 (based on sampling sites from paper I, Table 2)						

It appears that the concentrations of lower chlorinated furans peaked later than the concentrations of higher chlorinated congeners and they also declined more rapidly towards the surface layer. One exception was 2,3,4,7,8-PeCDF that had the slowest decline rate. Interestingly, 2,3,4,7,8-PeCDF also has the slowest elimination rate among PCDFs in human

(Liem & Theelen, 1997). In general, PCDD inputs decreased faster than PCDF inputs; however, OCDD concentrations remained at a high level longer than OCDF concentrations. The stability of OCDD and the later peaking of 1,2,3,4,6,7,8-HpCDD and OCDD relative to the corresponding PCDFs reflected a shift towards the congener profile that was found in the background areas (see Fig. 5-2).

5.1.4 Congener patterns

The spatial (Chapter 5.1.1) and temporal (Chapter 5.1.2) distribution of PCDD/Fs in the Gulf of Finland sediments pointed to the existence of two major point sources of PCDD/Fs: the Ky 5 source in the Kymijoki River and the VCM source in Sköldvik. Further information of PCDD/F sources was obtained by examination of the percent distribution 2,3,7,8-PCDD/Fs (congener patterns) in the sediment samples. In the following chapters, the congener profiles obtained within the previous research projects (I, II) are presented and discussed in more detail.

Patterns based on absolute concentrations

Figures 5-2 and 5-3 illustrate the PCDD/F congener profiles in Ky 5 and VCM waste sludge as well as in sediment slices that had become contaminated by Ky 5 and VCM manufacture. These profiles are compared with the background profiles. Details of these samples are given in Tables 5-3 and 5-4.
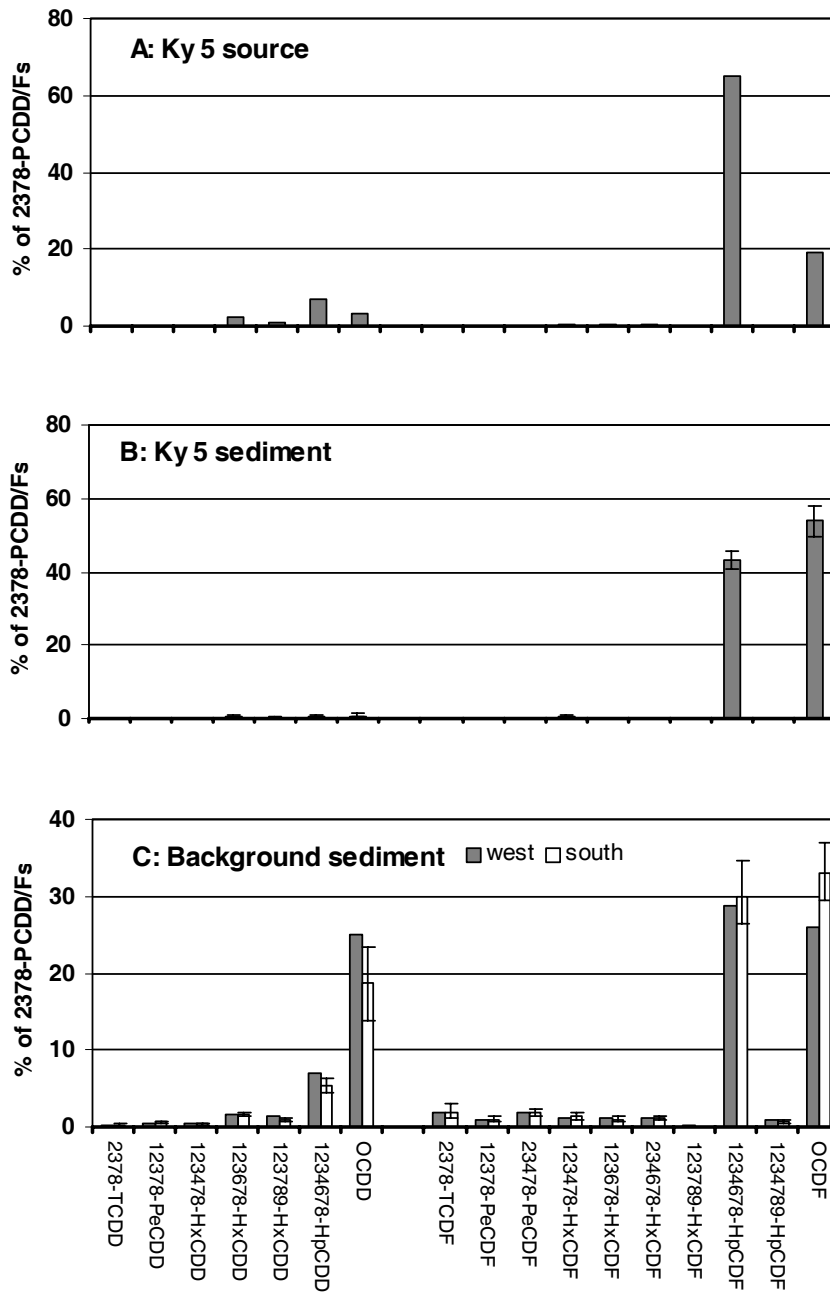
FIGURE 5-2. Congener patterns of 2,3,7,8-PCDD/Fs (± range) in A) Ky 5, B) sediment polluted with Ky 5, C) background sediment. See Table 5-3 for details of the samples.
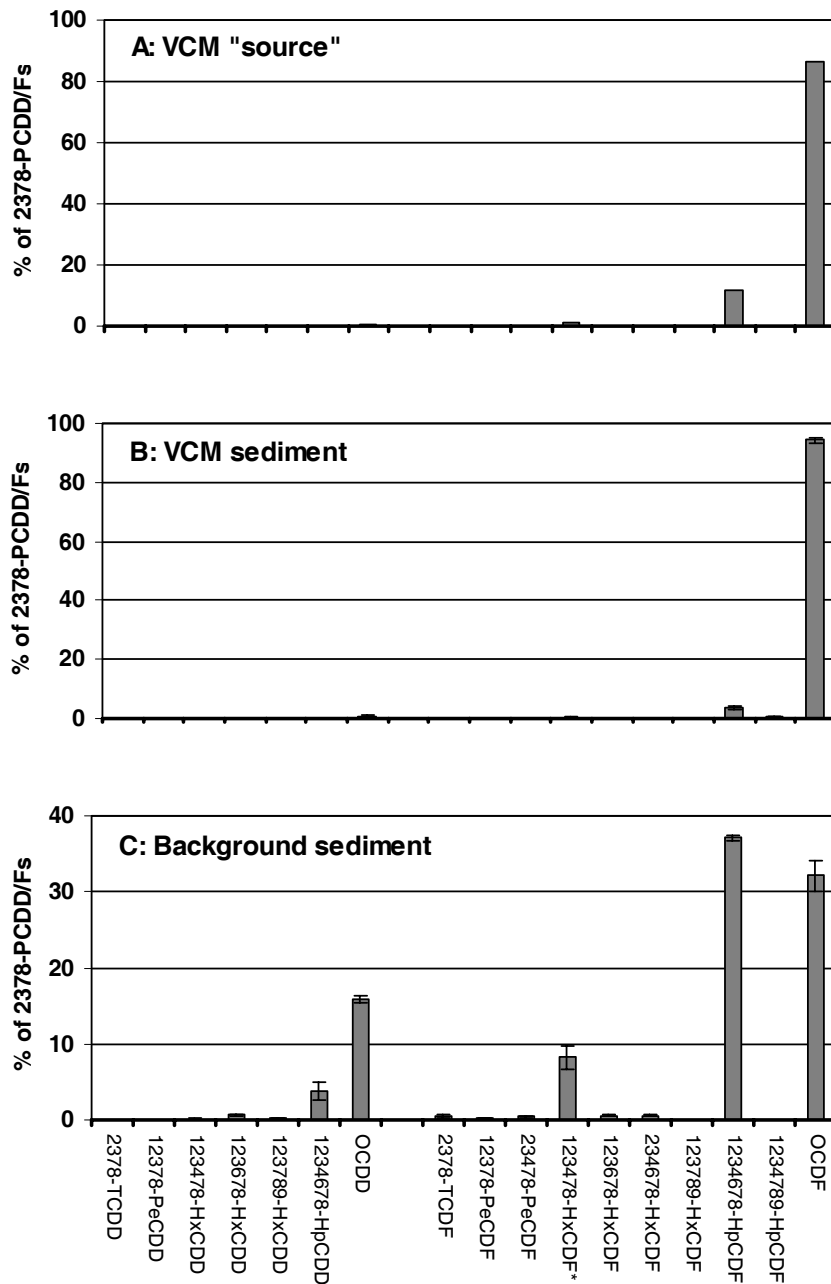
FIGURE 5-3. Congener patterns of 2,3,7,8-PCDD/Fs (± range) in A) the waste sludge from vinyl chloride monomer (VCM) manufacture B) sediment polluted by VCM manufacture C) background sediment. See Table 5-4 for details of the samples. *⁾ Possible artefact peak.

TABLE 5-3. Details of the sediment samples referred to in Figures 5-2 and 5-4

	Ky 5 source	Ky 5 sediment, n = 3	Background, west [a]	Background, south [b]
Reference	IV, Table 2	I, Table 1	I, Table 2	unpublished
Sampling site [c]	(Ky 5 extract)	A1, K15, K19	JML1b	Tallinn, n = 5
Distance from Kymijoki River		12-20 km	190 km	150 km
Depth		12-31 cm [d]	0-1 cm	3-15 cm
Years		1959-1980	1993-1996	not available
PCDD/Fs, pg/g d.w		22 300-101 000	610	217-652
2378-PCDD/Fs, pg/g d.w		14 900-65 600	365	137-416
WHO-TEQ, pg/g d.w		131-440	10.3	5.15-10.1
D/F ratio [e]	0.156	0.008-0.041	0.562	0.274-0.503

[a] Western Gulf of Finland
[b] Southern Gulf of Finland
[c] See I, Fig. 1 for a map
[d] Depth of maximum concentration at the sampling sites
[e] Ratio of 2,3,7,8-PCDDs to 2,3,7,8-PCDFs

TABLE 5-4. Details of the sediment samples referred to in Figures 5-3 and 5-5

	VCM source	VCM sediment, n = 3	Background, n = 2
Reference	II, Table 2	II, Table 2; Vartiainen et al., 1997b	Vartiainen et al., 1997b
Sampling site	(waste sludge)	see II, Fig. 1 [a]	see II, Fig. 1 [b]
Depth, cm		62.5-70.0	0-2.5
PCDD/Fs, pg/g d.w	25 900 000	396 000-914 000	482-651
2378-PCDD/Fs, pg/g d.w	22 000 000	389 000-901 000	330-510
WHO-TEQ, pg/g d.w	63 600	625-1 070	6.17-8.12
D/F ratio [c]	0.006	0.007-0.012	0.244-0.273

[a] In front of the cooling water tunnel; 3 slices from the same sediment core
[b] Freeze-corer samples with OCDF concentrations of 98 and 174 pg/g d.w
[c] Ratio of 2,3,7,8-PCDDs to 2,3,7,8-PCDFs

The predominating congeners in Ky 5 and polluted sediments from the Kymijoki River were 1,2,3,4,6,7,8-HpCDF and OCDF (IV, Table 2; Koistinen et al., 1995; Verta et al., 1999a, 1999b). In Ky 5, 1,2,3,4,6,7,8-HpCDF was more abundant than OCDF; however, in sediments close to the manufacturing site, OCDF was more abundant. At lower reaches of the river (Verta et al., 1999a) and in the Gulf of Finland (Fig. 5-2), the ratio of these congeners was close to 1:1. OCDF mostly predominated over 1,2,3,4,6,7,8-HpCDF in old and remote sediments which was thought to be an indication of the gradually lessening influence of the Kymijoki River discharges (I). This could be also due to a change in the PCDD/F composition in Ky 5 with time.

A significant contribution of sources other than Ky 5 in the Kymijoki River discharges seems unlikely due to the almost complete absence of any congeners other than these two dibenzofurans, and thus, PCDD/Fs in the Kymijoki River discharge can be primarily attributed to the production and use of Ky 5 adjacent to the river. Nonetheless, a contribution from other sources that produce almost exclusively PCDFs cannot be completely ruled out. One possible source of highly chlorinated dibenzofurans, but also of lower chlorinated dibenzofurans, could have been the production of chlorine by a chloralkali process taking place near the Ky 5 manufacturing site. The emission history of Hg from the chloralkali plant into the Gulf of Finland has been investigated by Verta and co-workers (1999a). According to Rappe and co-workers (1991), the PCDF profile in chloralkali sludge is dominated by almost equal proportions of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF and OCDF. Evers and co-workers (1993) associated the predominance of OCDF in sediments to the chloralkali industry and oxychlorination process during EDC manufacturing.

The congener pattern in VCM waste sludge was characterised by high concentrations of OCDF, lower concentrations of 1,2,3,4,6,7,8-HpCDF, and the almost complete absence of other PCDD/F congeners (Fig. 5-3). The occurrence of a similar congener pattern in sediments was evidence that the origin of pollution was VCM production.

The background PCDD/F patterns at the mouth of the Gulf of Finland ("western background") and in front of Tallinn ("southern background") were identical. The background pattern that was analysed in the frames of the Sköldvik case study contained a relatively high level of 1,2,3,4,7,8-HxCDF. This was probably an artefact caused by a non-toxic HxCDF that was not separated from the co-eluting 1,2,3,4,7,8-HxCDF when these samples were analysed.

Polluted sediments were easily distinguished from the background sediments by comparing the ratios of PCDDs to PCDFs. Owing to the large proportions of 1,2,3,4,6,7,8-HpCDF and OCDF in both Ky 5 and VCM sources, the PCDD to PCDF ratio in all polluted sediments was very low and clearly different from the background. In the background sediments, the proportions of 1,2,3,4,6,7,8-HpCDD and OCDD, in particular, were higher than in polluted sediments, although 1,2,3,4,6,7,8-HpCDF and OCDF still dominated.

Patterns based on WHO-TEQ

WHO-TEQ patterns were created by multiplying the absolute congener-specific concentrations by the toxic equivalency factors (WHO-TEFs) and then plotting the congener distributions. 1,2,3,4,6,7,8-HpCDF contributed most to the WHO-TEQ in both Ky 5 and VCM source profiles as well as in sediments that were contaminated via these sources (Fig. 5-4, Fig. 5-5). There were low concentrations of 2,3,7,8-TCDD in the most severely VCM-polluted sediment core, contributing between 4.1 to 14% to the WHO-TEQ at the depth of 62.5-70 cm. In the topmost layer of the sediment core, the relatively high concentrations of 2,3,7,8-TCDD (322 pg/g d.w) and 1,2,3,7,8-PeCDD resulted in a high WHO-TEQ sum concentration, and therefore, the decrease in WHO-TEQ was much slower than the decrease in 2,3,7,8-PCDD/F sum concentration (see Table 5-1). No literature data relating to the formation of 2,3,7,8-TCDD in VCM manufacturing was found. The current industrial activities carrief out in Sköldvik might affect the PCDD/F pattern.

In the background regions, 2,3,4,7,8-PeCDF was the dominating congener, followed by 1,2,3,7,8-PeCDD and 1,2,3,4,6,7,8-HpCDF. Together these congeners accounted for about 60% of the WHO-TEQ. With respect to the congener-specific analyses of sediments from the Baltic Proper, Gotland deep (Kjeller & Rappe, 1995; Koistinen et al., 1997), the predominance of 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD in the WHO-TEQ pattern appears to be a widespread phenomenon in the remote areas of the Baltic Sea, irrespective of the proportions of HpCDD/Fs and OCDD/F.
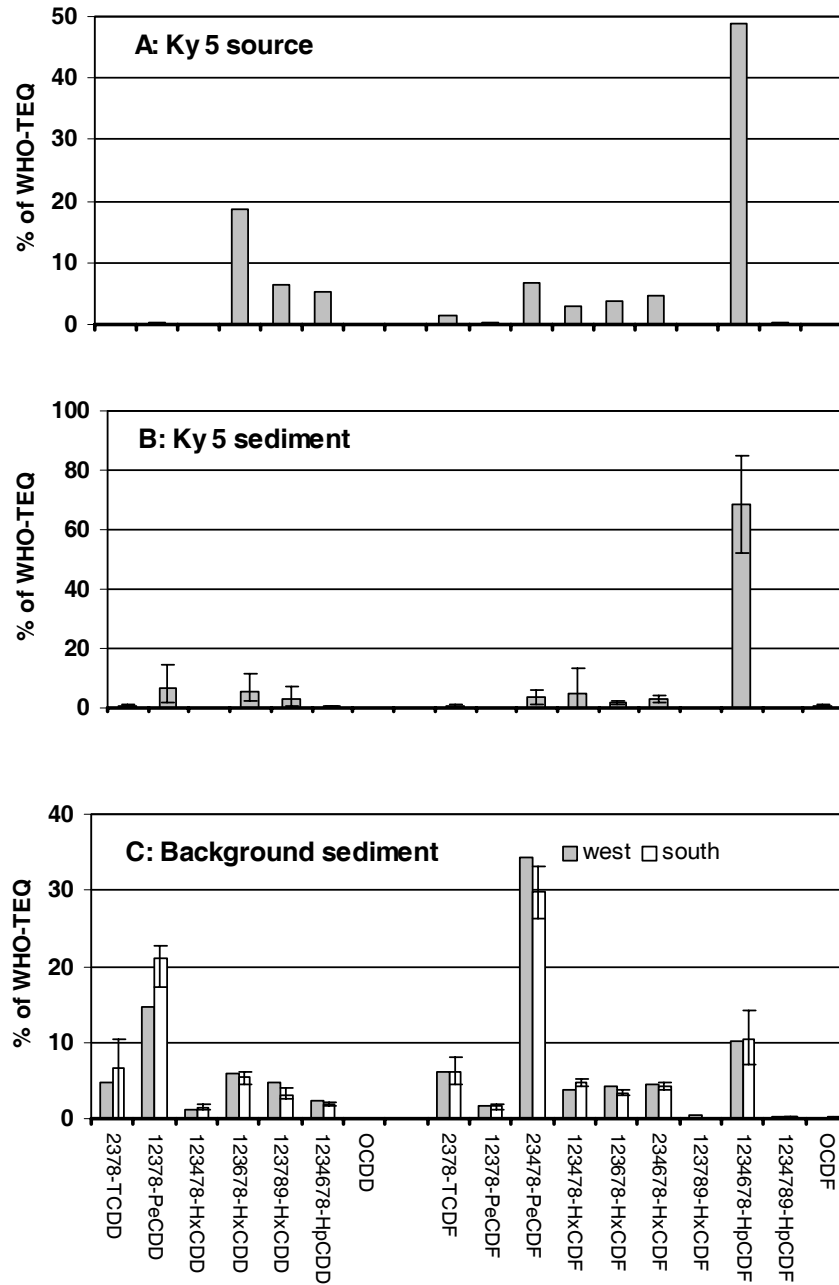
FIGURE 5-4. WHO-TEQ patterns of 2,3,7,8-PCDD/Fs (± range) in A) Ky 5, B) sediment polluted by Ky 5, C) background sediment. See Table 5-3 for details of the samples.
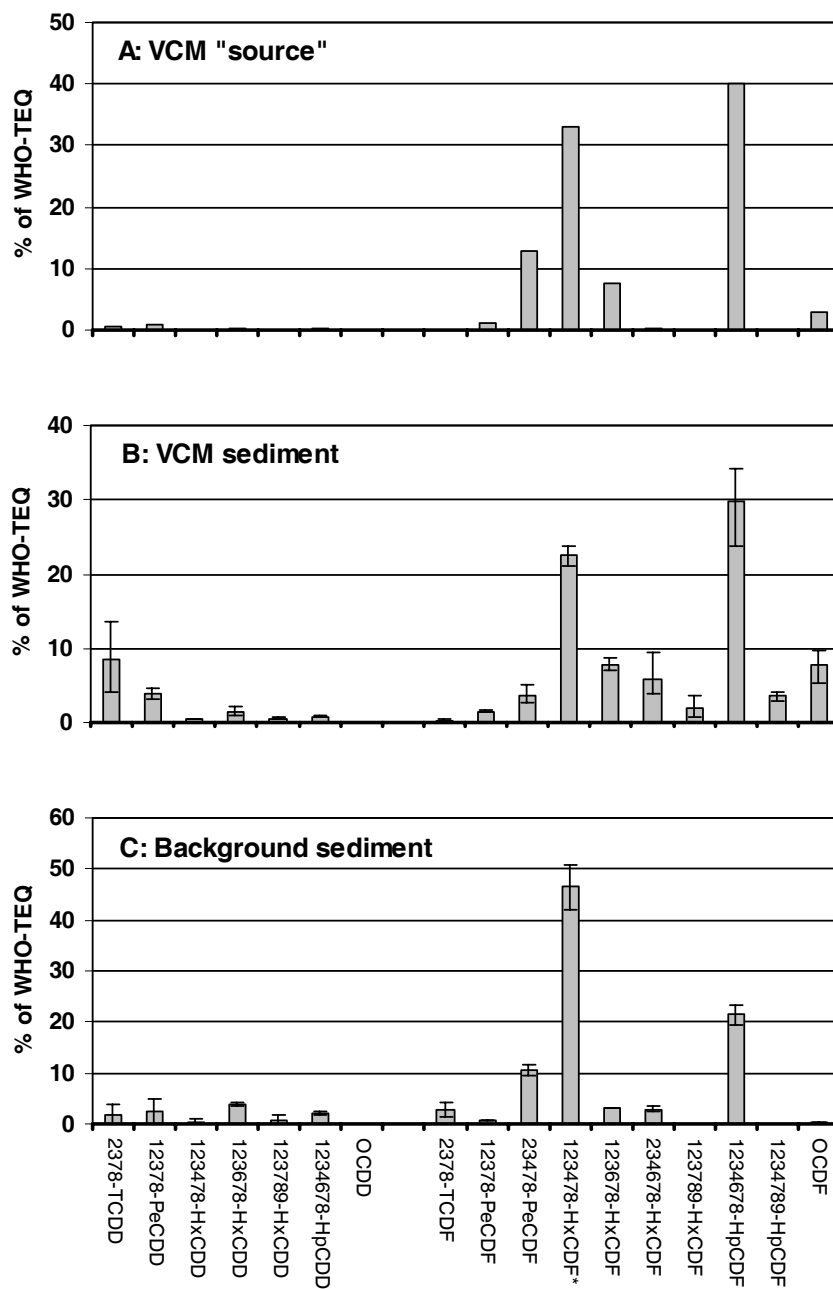
FIGURE 5-5. WHO-TEQ patterns of 2,3,7,8-PCDD/Fs (± range) in A) the waste sludge from vinyl chloride monomer (VCM) manufacture B) sediment polluted by VCM manufacture C) background sediment. See Table 5-4 for details of the samples. *) Possible artefact peak.

5.1.5 General inventory

According to the Ky 5 inventory (I, Table 3), 88% of the PCDD/F load and 76% of the WHO-TEQ load of the Gulf of Finland (years 1960-1997) could be attributed to the Ky 5 source. In the recent deposits, from the years 1986-1997, the influence of other sources was more pronounced and the contribution of the Ky 5 source was 79% of the PCDD/F load and 58% of the WHO-TEQ load. The VCM source had some local importance with regard to the pollution status, mainly in deep sediment layers. In view of the whole Gulf of Finland, its role was negligible. A compiled inventory from the Ky 5, VCM and background (atmospheric) sources that covers approximately the years 1960 to 1997 is presented in Table 5-5.

Table 5-5. Releases of PCDD/Fs into the Gulf of Finland in 1960-1997 (I, II)

Source, years	PCDD/Fs		WHO-TEQ	
	kg	%	kg	%
VCM manufacture [a]	11.4	0.6	0.011 [b]	0.1
Kymijoki River,				
1960-1986	1370	68	9.6	59
1986-1997	400	20	2.8	17
Atmospheric, [c]				
1960-1986	129	6.4	2.2 [d]	13
1986-1997	106	5.3	1.8 [d]	11
Total	2016	100	16.4	100

[a] Soft sediments from depths 0-50 cm or 0-100 cm, undated
[b] 0.032 I-TEQ
[c] Including the impact area of the Kymijoki River and the rest of the Gulf of Finland
[d] Calculated based on the average PCDD/F sum to WHO-TEQ ratio, 0.0173, at a remote sampling station (JML1b)

It was notable that the near-coastal (<12 km) sediments contributed to the total amount of PCDD/Fs in the Gulf of Finland by 24% in 1960-1986 and by 13% in 1986-1997, although the size of this highly polluted area was only 1.6% of the total area (I, Table 3). This highlights the importance of using a dense sampling net in the coastal zone to be able to identify the point sources and to quantify the releases that account for the majority of the PCDD/F reservoir in the seabed.

This inventory did not attempt to estimate the amount of PCDD/Fs in the pre-1960 sediments that contained some additional pollution. The post-1960 sediments were examined for the reason that the available sediment slices and dating methods reliably covered this period. The corresponding sediment slices were collected from the depths between 0 and 7-15 cm of the seabed in remote (offshore) areas and between 0 and 20-35 cm in coastal areas. As the depth

of the sediment deposits increases, the mobility and bioavailability of PCDD/Fs decreases, so that the risks associated with the uppermost sediments are definitely higher than those of the deep-buried sediments.

In the case of Sköldvik, the VCM production volumes and process history were well documented, and a previous estimate of 20 to 30 g I-TEQ in sediments (Vartiainen et al., 1997b) was consistent with the present estimate of 32 g I-TEQ that relied on the sediment analyses. The PCDD/F load from the Ky 5 source has also been estimated before, using the transportation data from the Kymijoki River. The estimate of 6 to 7 kg I-TEQ was somewhat lower than the present assessment (Verta et al., 1999a). The completion of the sediment studies required representative samples, careful time dating and knowledge of the sedimentation areas – on the other hand, these studies produced a great deal of new and confirmatory information that could not have been obtained by other means.

5.1.6 Inventory for tetra- and pentachlorinated PCDD/Fs

Although the absolute concentrations of tetra- and pentachlorinated PCDD/Fs were low in the Gulf of Finland, 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were shown to dominate in the WHO-TEQ profile of the background sediments (Chapter 5.1.4). As to the PCDD/Fs in Baltic fish, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF are the most abundant congeners in herring, salmon and sprat. 2,3,4,7,8-PeCDF contributes most to the WHO-TEQ content of these fish species (Kiviranta et al., 2003; Rappe et al., 1989; Vuorinen et al., 2002). According to Broman and co-workers (1991), 2,3,4,7,8-PeCDF appears to dominate in the WHO-TEQ patterns from the Scandinavian environmental samples in general. It was also a major congener in the fish that were analysed from the Sköldvik area: it contributed to the 2,3,7,8-PCDD/F concentration in perch by 50%, but in marine sediment by 0.01% only (II, Table 2).

Due to the importance of 2,3,7,8-substituted TCDD/Fs and PeCDD/Fs to fish concentrations, and consequently, to human exposure, their concentrations and distribution in the Gulf of Finland are examined in more detail in this chapter. The inventory is restricted to the sediments that had been deposited between the years 1986 and 1997, because only the recent PCDD/F deposition is relevant with respect to the current fish levels. The presented estimates contain a relatively high degree of uncertainty, indicated by the large standard deviations indicate (Table 5-6).

TABLE 5-6. Inventory of TCDD/F and PeCDD/F congeners in the Gulf of Finland sediments between 1986 and 1997

Congener	Area	Percentage of PCDD/Fs, average ± sd [a]	Load [b], kg from all sources	from Ky 5 (% of all)
2,3,7,8-TCDF	highly polluted	0.0730 ± 0.0664	0.26 ± 0.24	0.26 ± 0.24
	slightly polluted	0.1963 ± 0.0646	2.05 ± 0.24	0.76 ± 0.69 [c]
	background	1.3916 ± 0.5413	1.37 ± 0.53	
	Gulf of Finland, total		**3.68 ± 1.45**	1.02 ± 0.93 (**28%**)
1,2,3,7,8-PeCDF	highly polluted	0.0156 ± 0.0047	0.06 ± 0.02	0.06 ± 0.02
	slightly polluted	0.0679 ± 0.0372	0.71 ± 0.39	0.16 ± 0.05 [c]
	background	0.5943 ± 0.1568	0.58 ± 0.15	
	Gulf of Finland, total		**1.35 ± 0.56**	0.22 ± 0.07 (**16%**)
2,3,4,7,8-PeCDF	highly polluted	0.0312 ± 0.0181	0.11 ± 0.07	0.11 ± 0.07
	slightly polluted	0.1935 ± 0.0998	2.02 ± 1.04	0.33 ± 0.19 [c]
	background	1.2425 ± 0.2600	1.22 ± 0.26	
	Gulf of Finland, total		**3.35 ± 1.36**	0.44 ± 0.26 (**13%**)
2,3,7,8-TCDD	highly polluted	0.0071 ± 0.0059	0.03 ± 0.02	0.03 ± 0.02
	slightly polluted	0.0125 ± 0.0042	0.13 ± 0.04	0.07 ± 0.06 [c]
	background	0.1093 ± 0.0831	0.11 ± 0.08	
	Gulf of Finland, total		**0.26 ± 0.15**	0.10 ± 0.08 (**38%**)
1,2,3,7,8-PeCDD	highly polluted	0.0350 ± 0.0215	0.13 ± 0.08	0.13 ± 0.08
	slightly polluted	0.1066 ± 0.0264	1.11 ± 0.28	0.37 ± 0.22 [c]
	background	0.3864 ± 0.0656	0.38 ± 0.06	
	Gulf of Finland, total		**1.62 ± 0.42**	0.49 ± 0.30 (**30%**)

[a] Number of analysed PCDD/F congener profiles in highly polluted and background areas, 8; in slightly polluted areas, 17
[b] "Percentage of PCDD/Fs" multiplied by the PCDD/F load obtained from I, Table 3: 362 kg in highly polluted area, 1042 kg in slightly polluted area, 98.4 kg in background area
[c] Assuming the same "percentage of PCDD/Fs" as in highly polluted area

2,3,7,8-TCDF and 2,3,4,7,8-PeCDF were the most abundant congeners in sediments, which is directly reflected in the PCDD/F congener patterns of the Baltic fish. The low concentrations of HpCDD/Fs and OCDD/F in fish suggest that their bioaccumulation efficiency is very low, as also shown in feeding trials with farmed fish (Isosaari et al., 2004). The contribution of the Ky 5 source to the amounts of tetra- and pentachlorinated PCDD/Fs ranged from 13 to 38% (Table 5-6), being much lower than the estimate comprising the total PCDD/Fs, 79% (see Chapter 5.1.5).

The WHO-TEQ loads of tetra- and pentachlorinated PCDD/Fs in the background area (Fig. 5-6) confirm the presence of a common source of PCDD/Fs in the background sediments and in

Baltic herring. In the 1990's, PCDD/F congeners in herring that were caught from the Gulf of Bothnia and Gulf of Finland had the following median contributions to the WHO-TEQ: 2,3,4,7,8-PeCDF, 64%; 1,2,3,7,8-PeCDD, 21%; 2,3,7,8-TCDD, 7%; 2,3,7,8-TCDF, 3%; other congeners, $\leq$ 2% each (Kiviranta et al., 2003). The congener profiles and contributions of the different sources indicate that most of the PCDD/Fs in herring originated from the atmospheric background deposition rather than from the polluted sediments (or from the fluvial discharges that end up in the sediments). However, the differences in herring profiles between the Gulf of Finland, Gulf of Bothnia and the Baltic Proper have not been investigated in depth.
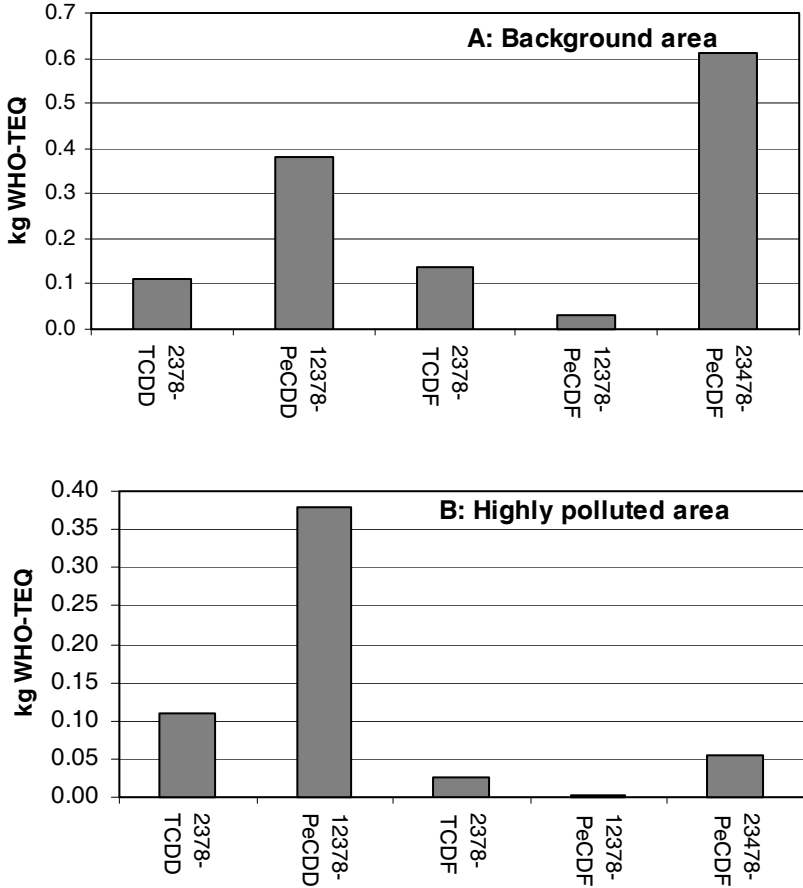

FIGURE 5-6. Loads of tetra- and pentachlorinated PCDD/Fs (as WHO-TEQs) in A) the background sediments B) in the highly polluted area of the Gulf of Finland. Illustration is based on Table 5-6.

The surface concentration of 2,3,4,7,8-PeCDF stated before, 10.7 ± 2.7 pg/g d.w (Table 5-2), was nearly constant throughout the Gulf of Finland, including coastal sediments. The only exception was a local peak concentration of 131 pg/g d.w in front of Sköldvik. Similar concentrations have been analysed in 14 coastal sediment samples from the North Sea, where the average concentration (± standard deviation) of 2,3,4,7,8-PeCDF was 9.4 ± 4.1 pg/g d.w in 1987-1990 (Evers et al., 1993). The concentration of 2,3,4,7,8-PeCDF in the Gotland deep was 16.4 pg/g d.w in 1985 (Kjeller & Rappe, 1995) and 17.0 pg/g d.w in 1993 (Koistinen et al., 1997), and a surface sample collected at the same time from the middle of the Gulf of Finland contained 9 pg/g d.w of 2,3,4,7,8-PeCDF (Koistinen et al., 1997).

The constant concentrations of 2,3,4,7,8-PeCDF in sediments do not correlate with the PCDD/F concentrations in Baltic herring that increase from south to north. The lowest concentrations in herring have been analysed in the southern Baltic Proper, and concentrations in the Gulf of Bothnia are higher than in the Gulf of Finland (Hallikainen et al., 2004; Jensen, 2003; Kiviranta et al., 2003; National Food Agency Finland, 2004; Rappe, 1993). Factors other than environmental PCDD/F concentrations probably affect accumulation in fish in the south-north direction.

There are several possible sources for 2,3,4,7,8-PeCDF. A brief review of the congener-specific data that has been published reveals that 2,3,4,7,8-PeCDF contributes to the WHO-TEQ concentration of a commercial PCB formulation Clophen A by 50%; stack gas from an aluminium smelter by 47%; chloralkali sludge by 40 to 48%; stove ash by 39%; zinc and copper oxide by 30 to 40%; and stack gas of a waste incineration plant by 27 to 30% (Ballschmiter & Bacher, 1996; Hosseinpour et al., 2003; Meneses et al., 2004; Rappe et al., 1990, 1991. WHO-TEQ calculations by Isosaari). In pentachlorophenol formulations and pulp-mill discharges, 2,3,4,7,8-PeCDF is not the main contributor to the WHO-TEQ profile (Ballschmiter & Bacher, 1996; Fouguet et al., 1990; Hutzinger & Fiedler, 1993; Jonsson et al., 1993; Rappe et al., 1989, 1990; Swanson et al., 1988. WHO-TEQ calculations by Isosaari).

5.2 Natural sources of PCDD/Fs

The analyses of PCDD/Fs from a deep sediment core from Lake Ahmasjärvi provided support for the hypothesis that there is a global background for PCDD/Fs in pre-industrial samples. The low concentrations of PCDD/Fs (0.24-1.70 pg WHO-TEQ/g d.w) in sediment slices that were up to 8 000 years old were not attributable to contamination from more recent sediment layers, sampling device, laboratory glassware or ambient air. A characteristic congener profile was found throughout the sediment core, with a decrease in concentrations occurring in the following order: OCDD > 1,2,3,4,6,7,8-HpCDD > 1,2,3,7,8,9-HxCDD > 1,2,3,4,7,8-HxCDD > 2,3,7,8-TCDD (III). Similar profile for at least the three most abundant congers has been reported in several other pre-industrial samples and samples with no known source of contamination (Ferrario et al., 2000; Gaus et al., 2001; Hashimoto et al., 1995; Müller et al., 2002; Rappe & Andersson, 2000).

The PCDD/F concentrations were at their lowest in sediment slices from the depths of 300 to 400 cm that were approximately 8 000 to 8 400 years old. The settlement and natural history of the investigated region was reviewed to try to find some explanation why the concentrations increased in approximately 3 400 to 4 400-year old sediments (III). One possible explanation could be the emergence of an anthropogenic source of PCDD/Fs such as wood burning or perhaps there had been a change in the prevailing environmental conditions which enhanced the formation of PCDD/Fs from natural precursors. Examination of the local history revealed that the first permanent settlement in the drainage area of Lake Ahmasjärvi arrived much later, in the middle of the 16th century, so that any possible anthropogenic PCDD/Fs must have been transported from a long distance. About 6 000 years ago, the ambient temperatures were at their highest, and there were some deciduous trees growing here that are no longer growing in that region. Physical analyses showed that the organic content of the sediments increased rapidly as the sediment depth decreased from 400 to 120 cm. No logical connection between these observations and the formation processes of PCDD/Fs was found.

Previous theories on the sources of PCDD/Fs in sediments have mainly been based on the assumptions that degradation and vertical transportation have negligible effect on PCDD/F concentrations and location in sediment cores. The observed concentrations and congener patterns should have existed in the environment at the time of the sediment formation, or their

formation should have taken place in the later sediments. Recent theories on the role of chlorophenols and other PCDD/F precursors in the formation of a natural dioxin profile could be more useful in explaining the presence of PCDD/Fs in the Lake Ahmasjärvi sediments. It has been proposed that the natural profile could result from the formation of OCDD from chlorinated chemicals, such as pentachlorophenol, followed by anaerobic dechlorination of OCDD in sediments (Gaus et al., 2002). Precursors in deep sediment layers could actually originate from the modern industrial sources, because these compounds are much more mobile than PCDD/Fs. If the dechlorination rate is fast enough, natural background could be observed in more recent sediments as well, provided that the other inputs are sufficiently low not to mask the natural source.

In the Gulf of Finland, the oldest sediment slices were about 100 years old (I). These sediments were not from the pre-industrial age, but they represented the time before the production and use of organochlorine chemicals. For a comparison with Lake Ahmasjärvi, the sediment data has been compiled in Table 5-7, and the congener patterns are presented in Figure 5-7.

If only PCDDs are examined, the main congeners were: OCDD > 1,2,3,4,6,7,8-HpCDD > 1,2,3,6,7,8-HxCDD = 1,2,3,7,8-PeCDD > 1,2,3,7,8,9-HxCDD > 2,3,7,8-TCDD (Figure 5-7). Still the pattern was not exactly the same as in Lake Ahmasjärvi. Another difference was the predominance of PCDFs instead of PCDDs in marine sediments, which implies that we can reject the hypothesis of identical sources for 100-year-old marine sediments and many thousand year old lake sediments.

TABLE 5-7. Details of the sediment samples referred to in Figure 5-7

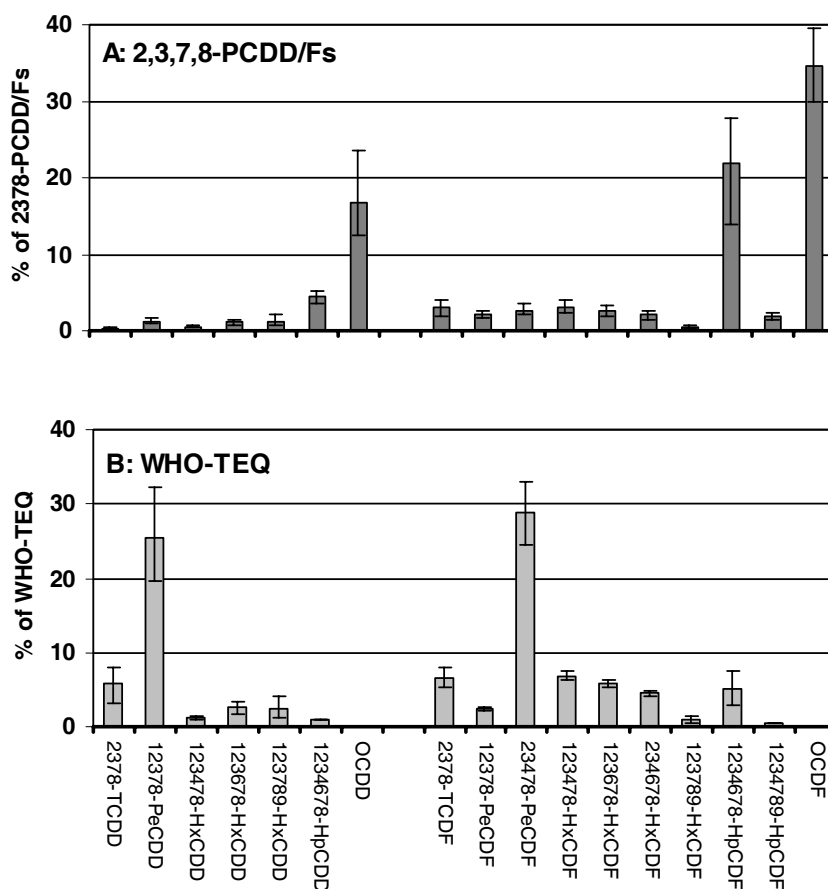|	K19 [a]	XV-1 [a]	JML1b [a]
Depth, cm	40-42	37-39	12-14
Years	1898-1904	1908-1915	1896-1917
PCDD/Fs, pg/g d.w	344	85.3	79.6
2378-PCDD/Fs, pg/g d.w	184	63.8	56.8
WHO-TEQ, pg/g d.w	6.75	3.30	2.81
D/F ratio [b]	0.243	0.391	0.491
[a] See I, Fig. 1 for the location of the sampling site [b] Ratio of 2,3,7,8-PCDDs to 2,3,7,8-PCDFs			

FIGURE 5-7. Congener patterns (± range) based on A) absolute concentrations, B) WHO-TEQ in sediment samples from the Gulf of Finland, from the years 1896-1917 (n = 3). See Table 5-7 for details of the samples.

Higher amounts of PCDDs with a natural congener pattern could probably be found in environments in which the direct deposition of PCDD/Fs has mainly consisted of OCDD. Another possibility is that the deposition of precursors, such as pentachlorophenol, has been much larger than direct PCDD/F deposition. In view of the extremely low concentrations of natural PCDDs in Lake Ahmasjärvi and the absence of a natural profile in the Gulf of Finland, it seems that such conditions were not met in the investigated sediments.

Actually, the congener pattern in the Gulf of Finland was similar to the recent background pattern (Fig. 5-2). It is also interesting that the only deviation from a sediment profile analysed from the Gotland deep (years 1882-1922, n = 3) was the smaller proportion of 1,2,3,4,6,7,8-HpCDD and OCDD in the Gulf of Finland (Kjeller & Rappe, 1995).

Summarising the WHO-TEQ pattern data (Fig. 5-4, 5-5, 5-7), 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were the main congeners in sediments from the background areas in the Gulf of Finland and in the Baltic Proper (Gotland deep), both in surface sediments and in sediments that represented the years 1882-1922. On the average, it seems that the WHO-TEQ concentrations have increased – however, the increase has been less than 5-fold.

The fact that the background WHO-TEQ pattern has remained unchanged implied that the contribution of 2,3,4,7,8-PeCDF to WHO-TEQ increased as the concentrations of 1,2,3,4,6,7,8-HpCDF and OCDF decreased either in the horizontal or vertical direction in the seabed, and consequently, the decrease in WHO-TEQ was not as large as the decrease in the absolute 2,3,7,8-PCDD/F concentration. This explanation also accounts for the previous observation that the WHO-TEQ concentration in polluted areas did not differ as much from the background as the 2,3,7,8-PCDD/F concentration (see Chapter 5.1.1).

5.3 Photodegradation of PCDD/Fs

5.3.1 Degradation products

Dechlorination to tetra- to hexachlorinated dibenzofurans accounted for less than one percent of the photodegradation of 1,2,3,4,6,7,8-HpCDF in some experiments and 28% at its highest (IV, VI, Table 5-8). The formation of dechlorination products decreased with irradiation time, probably because of the more rapid degradation kinetics of the lower chlorinated congeners than that of the original HpCDF (VI). If non- to trichlorinated dibenzofurans were formed, they could have easily decomposed further via dechlorination and benzene ring opening, to produce hydroxybenzoic acid (Massé & Pelletier, 1987).

TABLE 5-8. Formation of dechlorination products [a]

Congener and initial concn. in olive oil	Time, min	HpCDF/HpCDD degradation, %	Dechlorination [b] toxic, %	non-toxic, %	Ref.
1234678-HpCDF, 6 ng/g	15	66	0.47	1.34	IV, Fig. 1
1234678-HpCDF, 114 ng/g	30	98	0.15	0.15	IV [c]
1234678-HpCDF, 65 ng/g	30	61	0.92	0.73	VI
1234678-HpCDD, 65 ng/g	30	13	12.4	0.00	VI
1234678-HpCDF, 6 ng/g [d]	30	16	13.8	14.5	VI

[a] Additional data presented in VI, Figure 4
[b] Formation of dechlorination products relative to the amount of HpCDF/HpCDD degraded
[c] Exact data not published before
[d] In palm oil

The dechlorination products of 1,2,3,4,6,7,8-HpCDF included both toxic and non-toxic PCDD/Fs. When a large data set was examined, dechlorination from positions 1, 4 and 6 was found to be slightly favoured over positions 2, 3, 7 and 8, which resulted in an accumulation of small amounts of toxic PCDD/Fs at the end of the photolytic treatments (VI). When 1,2,3,4,6,7,8-HpCDD was irradiated, the yield of dechlorination products was 12% at 30 and 60 min. All the products were non-toxic (VI, Table 5-8). In previous studies, similar degradation patterns have been obtained when photodegradation has taken place via the direct mechanism. The direct photolysis yields non-toxic dechlorination products from the parent PCDDs, whereas both toxic and non-toxic dechlorination products are formed from PCDFs (Dobbs & Grant, 1979; Kieatiwong et al., 1990; Tysklind & Rappe, 1991; Wagenaar et al., 1996; Yan et al., 1995). The electron transfer mechanism in sensitised reactions enhances the formation of toxic PCDD/Fs (Hung & Ingram, 1990; Konstantinov & Bunce, 1996). The dechlorination patterns in the present study, with pure PCDD/F standards in particular, were indicative of direct rather than sensitised photolysis.

Humic compounds in soils could act as photochemical sensitisers (Kim & O'Keefe, 1998; Leifer 1988). It seemed that no accumulation of toxic dechlorination products occurred in the presence of soil: the residual PCDD/Fs at the end of the experiments were predominantly non-toxic (IV, V).

A nonchlorinated diphenyl ether was tentatively identified as a photodegradation product of 1,2,3,4,6,7,8-HpCDF by screening the mass spectra that were obtained by scan-mode analysis (IV). A semi-quantitative analysis showed that the amount of diphenyl ether increased by 1.4-fold between 5 and 30 min, corresponding to 87 and 98% degradation efficiency of

1,2,3,4,6,7,8-HpCDF. Other researchers have reported on the formation of hydroxylated products via C-O bond cleavage (Friesen et al., 1996; Kieatiwong et al., 1990; Konstantinov et al., 2000; Rayne et al., 2002). It seems likely that the detected compound was actually a hydroxylated diphenyl ether. However, polychlorinated hydroxybiphenyls (OH-PCBs), polychlorinated dihydroxybiphenyls (DOH-PCBs) and polychlorinated hydroxydiphenyl-ethers (OH-PCDEs) containing one to seven chlorine atoms were not detected in the irradiated HpCDF/HpCDD solutions (VI).

5.3.2 Influence of PCDD/F structure

The photodegradability of PCDD/Fs in vegetable oils was investigated using either single-congener solutions or mixtures that contained almost all the 17 toxic and a range of non-toxic PCDD/F congeners. In the mixtures, the degradation rates of the lower chlorinated congeners were influenced by the formation via the dechlorination of the HpCDD/Fs and OCDD/F that were much more abundant. Hence, the lower chlorinated PCDD/Fs (toxic and non-toxic) seemed to degrade more slowly than the highly chlorinated PCDD/Fs in this kind of situation (IV, V). Previous studies indicate that the degradation of lower chlorinated congeners is faster when degradation is not affected by their simultaneous formation (Nestrick et al., 1980; Niu et al., 2003) which rarely occurs in real contaminated matrices.

To compare the degradability of the toxic PCDDs with toxic PCDFs, results from these experiments and congeners (mostly OCDD and OCDF) were compiled that were unaffected by the dechlorination reactions of other congeners (Table 5-9). The degradation percentage of OCDD or 1,2,3,4,6,7,8-HpCDD was typically one sixth to one half of the degradation of OCDF or 1,2,3,4,6,7,8-HpCDF. Using long irradiation times (experiments C and D), high degradation percents were attained for PCDDs as well as PCDFs.

72

TABLE 5-9. Degradability comparison of PCDDs versus PCDFs

| Matrix [a], light source | Congener | Time | Degradation, % | | Ref. |
			PCDD	PCDF	
A) PCDD/F mixture, blacklight	OCDD/F	0.5 h	34	100	IV, Table 3-SI
B) PCDD/F mixture, fluorescent	OCDD/F	1 w 4 w	9.8 16	15 31	IV, Table 4b-SI IV, Table 2
C) soil extract, blacklight	OCDD/F	1 h 22 h	11 97	73 99	IV, Table 5a-SI IV, Table 3
D) soil, blacklight	OCDD/F	2.5 h 75 h	38 89	58 82	IV, Table 6-SI IV, Table 3
E) soil, sunlight	OCDD/F	28 d	31	65	V, Table 1
F) pure HpCDD/F, blacklight	1234678-HpCDD/F	0.5 h	13	61	VI
[a] All matrixes contained vegetable oil					

5.3.3 Influence of wavelength range

The results showed that PCDD/Fs were effectively photodegraded at wavelengths that are available from sunlight. Irradiation with blacklight lamps and sunlight both resulted in significant degradation of PCDD/Fs in contaminated soils (IV-VI). These light sources emitted light in the UV-A region (320-380 nm); however, the proportion of the more energetic UV-B light (280-320 nm) was very small. The maximum UV intensities measured under sunlight were 60 to 70% of the intensity of blacklight lamps (IV), but remained at this high level for less than four hours around noon. Exact comparisons of the light sources are not justified because the same matrices were not treated with the same light source.

The absence of UV wavelengths in fluorescent light made it ineffective for photodegradation. In four weeks, the reduction in WHO-TEQ content of a PCDD/F mixture in olive oil was only 13%, whereas blacklight irradiation reduced the WHO-TEQ content by 96% in 5 h (IV, Table 2. I-TEQ recalculated as WHO-TEQ). As photodegradation under the ambient lightning conditions in the laboratory was so slow, degradation would have some relevance pertaining to the sample storage and handling only. The results implied that OCDF concentration would drop to one half of the original in 52 days if oily PCDD/F samples were stored in open vessels. As a result of transformation of PCDD/Fs to lower chlorinated congeners, the congener profiles of PCDD/F samples would also be subjected to minor changes if the samples were stored unprotected for a long time. Studies conducted by Buser (1988) confirm that the half-lives of TCDD/F congeners under fluorescent light would also be long, at least 28 days.

A dark control proved that vegetable oil alone did not degrade PCDD/Fs but a light source was also needed. The concentrations of all congeners in a PCDD/F mixture remained unchanged when stored for four weeks in the dark at room temperature (IV). Furthermore, concentrations analysed in non-irradiated reference samples (IV, VI) were equivalent to the known amounts of PCDD/Fs that had been added to the samples. In the absence of vegetable oil, sunlight irradiation did not degrade PCDD/Fs (Isosaari et al., 1998).

The wavelength range effective for photodegradation was related to the UV absorption properties of PCDD/Fs. Although the absorbance of PCDD/F molecules is at its highest at wavelengths that are not present in the solar radiation that reaches the ground, they also absorb some UV light between 300 and 340 nm (Choi et al., 2000; Choundry & Webster, 1989; Tysklind et al., 1993; Wagenaar et al., 1995). In the solar light spectrum, the absorption maxima of PCDFs are located at 290-300 nm and 315-325 nm (Tysklind et al., 1993). The absorption bands slightly shift towards longer wavelengths as the chlorination degree increases. The molar absorptivity is lower for PCDDs than for PCDFs at wavelengths longer than 270 nm (Choudry & Webster, 1989; Podoll et al., 1986; Wagenaar et al., 1995). Experiments with photochemical sensitisers and catalysts do not indicate whether indirect photolysis of tetra- to octachlorinated PCDD/Fs could take place at longer wavelengths (Konstantinov & Bunce, 1996; Yan et al., 1995; Choi et al., 2000). At wavelengths longer than 340 nm, 2,7-dichlorodibenzo-p-dioxin degrades in the presence of TiO_2 but not without this catalyst (Pelizzetti et al., 1992).

In view of the UV spectral properties of vegetable oils and PCDD/Fs (VI), a wavelength range between 320 and 340 nm would be efficient for the direct photolysis of PCDD/Fs. In most vegetable oils and other solvents (toluene: VI) the advantage of a higher absorptivity of PCDD/F molecules is partially lost at wavelengths shorter than 320 nm, due to the strong shielding of the solvent. Using weakly absorbing vegetable oil, such as extra virgin olive oil, shorter wavelengths could probably be used.

5.3.4 Properties and functions of vegetable oils

Vegetable oils had three major functions in photolytic systems. They dissolved soil-bound PCDD/Fs, transported them towards the surface and acted as hydrogen sources for reductive

dechlorination. The solubilising effect was examined in aged sawmill soil (IV). The dissolution of PCDD/Fs was rapid during the first 30 min; however, residual PCDD/Fs were mobilised slowly. After rotating soil with extra virgin olive oil in a round-bottom flask for 24 h, 93% of WHO-TEQ (91% of I-TEQ) was transferred into the oil phase (IV, Table 1, Table 1a-SI, Table 1b-SI). Some congeners were even found at higher concentrations in oil than initially in soil. It was believed that a part of the apparent solubility of PCDD/Fs was due to the transfer of colloidial soil fractions into the vegetable oil phase. The binding of PCDD/Fs in these fractions probably explained why the residual 1% (29 ng) of OCDF in the separated soil extract degraded very slowly during the last 17 h of UV irradiation, irrespective of the constant and rapid degradation occurring during the first 5 h (IV).

The dissolution of PCDD/Fs affected the photodegradation rates in soil-vegetable oil mixtures. After a rapid initial photodegradation phase in the UV experiment, the dissolution rate of PCDD/Fs was faster than the photodegradation rate for quite some time. Thus, the PCDD/F concentration started to increase again. In sunlight experiments, mixing of the vegetable oil -amended soil during irradiation resulted in an enhanced solubilisation that doubled the OCDF concentration (Table 5-10).

TABLE 5-10. Observed solubilisation of PCDD/F congeners in olive oil –amended soils

Congener	Solubilisation, %	
	UV experiment [a]	Sunlight experiment [b]
OCDF	15	103
1234678-HpCDF [c]	31	45
non-toxic HpCDFs [c]	51	67
OCDD	13	-0.3 [d]
1234678-HpCDD [c]	27	26
non-toxic HpCDDs [c]	-3.8 [d]	25
[a] Vääksy sawmill soil, solubilisation between 17.5 and 67.5 h of irradiation (IV, Table 6-SI)		
[b] Sikoniemi sawmill soil, solubilisation after mixing with the second dose of olive oil (VI, Fig. 2)		
[c] Combined effect of solubilisation and formation via dechlorination		
[d] Degradation was faster than solubilisation or formation		

Thus it was assumed that the concentration analysed in soil after Soxhlet extraction in toluene would not represent the total concentration of PCDD/Fs, because it did not include a strongly bound fraction of PCDD/Fs intact in soil. Vegetable oils obviously penetrated into the soil matrix and desorbed PCDD/F molecules. The desorbing effect could be intensified by UV light, because it decomposes soil organic matter (Patel-Sorrentino et al., 2004), increases the

concentration gradient between soil and oil by degrading PCDD/Fs and accelerates the convective transport of PCDD/F molecules driven by evaporation (Dougherty et al., 1993; McPeters & Overcash, 1993; Overcash et al., 1991). The size of the strictly bound fraction is likely to vary according to the congener, soil properties and the age of contamination. PCDFs were found to dissolve faster than PCDDs, whereas we noted no influence of the chlorination degree on the dissolution rate (IV).

The convective upward transport of PCDD/Fs in vegetable oil solutions and soil-oil mixtures was not measured. It might have played a significant role in PCDD/F degradation. Otherwise it would be difficult to explain how it was possible to attain a more than 50% reduction in the PCDD/F sum concentration in 1-cm deep soil bed (V, Table 1) and in 1,2,3,4,6,7,8-HpCDF concentration in 2-cm deep olive oil solution (VI) without mixing. The formation of degrading radicals or electron-transferring species that could migrate into deeper layers and be stable for a sufficient time to reach the PCDD/F molecules is also unlikely.

On the basis of the photodegradation and diffusion experiments with 2,3,7,8-TCDD in ethyl oleate solutions under sunlight exposure, Dougherty and co-workers (1991b) have estimated that a theoretical maximum rate of soil decontamination would be 3.3 $ngh^{-1}cm^{-2}$. In the outdoor experiment with olive oil (V), the density of soil was 1.61 g/cm^2 (dry weight). Therefore the decontamination rate of 2,3,7,8-chlorinated PCDD/Fs was 0.87 $ngh^{-1}cm^{-2}$ during the first two weeks and 0.48 $ng\ h^{-1}\ cm^{-2}$ during the entire four-week period, which was relatively close to the theoretical maximum rate.

The hydrogen donor properties of vegetable oils made them better solvents for PCDD/F photodegradation in comparison with hexane and toluene. The hydrogen production in palm oil seemed to be suppressed by β-carotene that is an inhibitor of lipid photooxidation. In addition to the concentrations of β-carotene, the differences between vegetable oil qualities were attributable to their UV absorbance. A negative correlation was found between UV absorbance (at 290-310 nm) and photodegradation rate of 1,2,3,4,6,7,8-HpCDF (VI).

To understand better the action mechanisms of vegetable oils, either an experimental comparison with a wider range of vegetable oils or a more detailed mechanistic study will need to be performed.

5.3.5 Assessment of soil decontamination techniques

Assessment of the efficiency of two modifications of the vegetable oil-UV method for the treatment of PCDD/F-contaminated soils suggested that degradation results that are comparable to the blacklight lamp exposures in the laboratory could be obtained by using smaller amounts and cheaper types of vegetable oils and natural sunlight irradiation (V). However, this comparison was based on the initial stages of photodegradation that were more rapid than the subsequent stages. Extrapolation from the overall degradation rate reveals that the energy consumption required for 95% reduction in WHO-TEQ content would be higher under blacklight irradiation (experiment A) than under natural sunlight (experiment C) (Table 5-11).

TABLE 5-11. Comparison of three modifications of vegetable oil-UV light method

	A) Soil + blacklight	B) Soil extract + blacklight	C) Soil + sunlight
Reference	IV, Table 3	IV, Table 3	V, Table 1
WHO-TEQ, initial	44.4 ng/g	43.6 ng/g	2.07 ng/g
Organic content in soil	15%	15%	6.7%
Oil to soil ratio	2:1	1:1	0.4:1
Vegetable oil	extra virgin olive oil	extra virgin olive oil	olive oil
Treatment time	75 h	22 h (+24 h) [a]	28 d
UV consumption	13 kJ/g	1.9 kJ/g	2.4 kJ/g
WHO-TEQ, degradation	84%	99% (91%) [b]	48%
t½	28 h	3.3 h	30 d
k [c]	0.0244 h^{-1}	0.2093 h^{-1}	0.0233 d^{-1}
Treatment time, 95% [d]	123 h	14.3 h	129 d
UV consumption, 95% [d]	57 kJ/g	1.2 kJ/g	11 kJ/g
[a] Time used for soil extraction [b] Inclusive of the residual PCDD/Fs in extracted soil [c] First-order reaction rate constant [d] Estimated values required for 95% degradation in WHO-TEQ			

The lowest UV consumption was obtained by extracting the soil with olive oil and using blacklight irradiation for the decontamination of the separated olive oil fraction only (experiment B). Additional treatment costs of this modification arise from the extraction step. If the extraction is incomplete, PCDD/Fs remaining in the soil after extraction also impair the decontamination efficiency. Partial replacement of vegetable oils with low-molecular alcohols could enhance desorption of PCDD/Fs by accelerating the soil-wetting process (Dougherty et al., 1994).

A long-term treatment under sunlight (experiment C) offers certain advantages over the other treatment options, including efficient desorption of PCDD/Fs from soil matrix and a free UV source. Still, the treatment costs would be high. If 400 litres/ton of a low-grade olive pomace oil (see e.g., www.oliveoilsource.com) or rapeseed oil were used, the price of the oil would be approximately 800 euros/ton, that is approximately 200 euros/m^3 or if only a 1-cm layer were to be treated, 200 euros per one hundred square metres. It must be noted here that a realistic cost assessment would require experience from large-scale trials and should include all the associated costs, for example, the mechanical treatments. Process optimisation and oil recycling could help reduce the costs.

The most critical questions regarding the feasibility of the vegetable oil-UV treatment as a soil decontamination technique are related to the pre-treatment costs (sieving of soil, for example), vegetable oil quality and consumption, and the treatment time required to ensure that all the strictly bound PCDD/Fs have been desorbed and degraded. Further investigations should be carried out to find the lowest possible oil dose that could be used to maintain an appropriate dissolution and photodegradation rate. It might be useful to allow some time for vegetable oil to equilibrate with soil and to desorb PCDD/Fs prior to irradiation so that the light energy and hydrogen supply could be efficiently utilised for the degradation of dissolved PCDD/Fs. When the treatment time and vegetable oil dosage is sufficient, the technique is expected to produce soil that does not exhibit TCDD-like toxicity (IV, VI). Nonetheless, the soil might still need some post-treatment, for example, removal of vegetable oil by soil washing or microbial treatment.

In the experiments carried out with sawmill soil (V), 20% of olive oil mixed well with soil at 30% water content and no separate layers of soil, oil and water were formed. If dredged sediments were to be treated, the high water content could prevent vegetable oil from penetrating into the sediment particles. Therefore, treatability tests are recommended for soil and sediment matrices with different water and organic matter contents and particle size distributions.

6 CONCLUSIONS

Items A to D summarize the main results of the sediment studies (original papers I, II, III; Results and discussion, Chapters 5.1 and 5.2).

A) PCDD/F-contaminated areas in the Gulf of Finland

Two contaminated areas in the Gulf of Finland were identified: one in front of Kotka, where the Kymijoki River discharges into the sea, and the other in front of the municipality of Porvoo, Sköldvik (Kilpilahti). In these areas, the highest sediment concentrations exceeded the background concentration of 2,3,7,8-substituted PCDD/Fs by 80 to 1 100 -fold, and WHO-TEQ level in the background areas was exceeded by 63 to 76 -fold. The highly polluted area in front of the Kymijoki River inlet stretched out to a distance of 12 km away from the coastline. In areas that were located more than 75 km away from the Kymijoki River inlet or 9 km away from the coastal point source in Sköldvik, the sediments only contained low concentrations of PCDD/Fs that were representative of the general background contamination in the Gulf of Finland and other seas.

B) Sources and history of contamination

In both contaminated areas, the origin of PCDD/Fs was the former manufacture (and use) of chlorinated chemicals. Identification of the sources was based on the following lines of evidence: 1) decreasing concentration in sediments with an increasing distance from a coastal point of PCDD/F release, 2) congener pattern that was similar to the source and 3) concentration time trend in sediments that followed the production history of the chemical.

In front of Kotka, the time trends of PCDD/Fs in sediments reflected the years when the production and use of a chlorophenolic fungicide, Ky 5, was at its most extensive. At most of the sampling points, PCDD/F concentrations (2,3,7,8-PCDD/Fs and WHO-TEQ) in the surface sediments (years 1995-1997) were 24-52% of the maximum concentrations observed in the 1960s-1970s. Congener patterns in sediments were dominated by 1,2,3,4,6,7,8-HpCDF and OCDF, congeners which were also characteristic of Ky 5.

In front of Sköldvik, the sediments had become polluted by the manufacturing wastes of vinyl chloride monomer (VCM). A significant decrease in PCDD/F concentration was observed

after the cessation of the manufacture in 1983. Congener patterns in contaminated sediments were strongly predominated by OCDF.

There was evidence of a natural background concentration for PCDD/Fs in that traces of PCDD/Fs were detected in approximately 8 000 to 8 400 years old sediment layers from a remote lake. There was a characteristic congener pattern with the concentrations of OCDD > 1,2,3,4,6,7,8-HpCDD > 1,2,3,7,8,9-HxCDD > 1,2,3,4,7,8-HxCDD > 2,3,7,8-TCDD.

C) PCDD/F inventory

The total load of PCDD/Fs in sediments that had been deposited in the Gulf of Finland between the years 1960 and 1997 was 2 016 kg, or 16.4 kg WHO-TEQ. 1 770 kg (88%) of PCDD/Fs and 12.4 kg (76%) of WHO-TEQ were attributed to the Ky 5 source from the Kymijoki River. The contribution of this source has decreased, so that the respective proportions were 79% (PCDD/Fs) and 58% (WHO-TEQ) between 1986 and 1997. Of the tetra- and pentachlorinated congeners that are most abundant in Baltic herring, only 13-38% originated from the Ky 5 source at Kymijoki River.

The role of PCDD/F releases from the VCM manufacture in the total PCDD/F load in the Gulf of Finland was negligible. In the absence of significant point sources other than the Kymijoki River, the rest of PCDD/Fs are likely to be attributed to atmospheric background deposition.

D) Recent development in PCDD/F concentrations

At present, the production and use of Ky 5 is the only identified point source of PCDD/Fs in the Gulf of Finland. Kymijoki River continues transporting heavily polluted sediments towards the sea. Independently of the sources, PCDD/F concentrations were declining at approximately the same rate throughout the gulf. However, the decline rate was dependent on the congener: in general, the PCDD concentrations were declining faster than PCDF concentrations, and among the PCDFs, the decline was fastest for the lower chlorinated congeners. Congener patterns in the surface sediments were shifting towards the background pattern, in which the proportions of 1,2,3,4,6,7,8-HpCDD and OCDD increased relative to 1,2,3,4,6,7,8-HpCDF and OCDF, and 2,3,4,7,8-PeCDF had the largest contribution to WHO-TEQ.

When the development of PCDD/F concentrations in fish is assessed, it is important to pay attention to those individual congeners that are predominating in fish, especially of 2,3,4,7,8-PeCDF. The constant concentrations of 2,3,4,7,8-PeCDF throughout the Gulf of Finland and the slower reduction rate relative to other PCDD/F congeners suggest that multinational efforts are needed to achieve a faster reduction in the emissions of those congeners that contribute to significant human exposure.

The following conclusions (items E-G) can be drawn from the photochemical studies (original papers IV, V, VI; Results and discussion, Chapter 5.3).

E) Efficiency of the vegetable oil-UV method in soil decontamination

A rapid photodegradation of PCDD/Fs was demonstrated in vegetable oils. When contaminated sawmill soil was treated, the strong binding of PCDD/Fs to soil particles was the main barrier to photodegradation. This obstacle could be overcome by ensuring a proper solubilisation of PCDD/Fs, either by preliminary extraction of soil with vegetable oil or by using a longer contact time and periodical mixing of the soil-vegetable oil mixture.

The most effective (99% decline in WHO-TEQ content) and rapid (22 h) photodegradation was attained with a technique that utilised a preliminary extraction step with vegetable oil and artificial UV radiation from blacklight lamps. However, an outdoor treatment under natural sunlight could probably be accomplished at significantly lower costs.

The congener pattern of the soil affected the decontamination rate and efficiency. In soils that are predominantly contaminated with highly chlorinated furans, like Finnish sawmill soils, the required treatment time was ultimately determined by the dissolution rate of OCDF and the degradation rate of the lower chlorinated PCDD/Fs that were formed as dechlorination products.

F) Functions of vegetable oils

The degradability of PCDD/Fs was better in vegetable oils than in hexane or toluene. Vegetable oils desorbed soil-bound PCDD/Fs, transported them towards the soil or solvent surface and acted as hydrogen sources for reductive dechlorination. Vegetable oils were even capable of solubilising the strongly bound residual PCDD/Fs that could not be removed by

conventional analytical extraction methods. The excess solubilisation of PCDD/Fs prolonged the decontamination process.

The type of the vegetable oil had some influence on photodegradation. High concentrations of β-carotene and strong UV absorption of the oil retarded degradation. The photosensitising effect of α-tocopherol was noticed at concentrations higher than those naturally present in vegetable oils.

G) Degradation products

Dechlorination pathway that yields lower chlorinated PCDD/F congeners was the major photodegradation mechanism that was identified when heptachlorinated dibenzo-*p*-dioxins and dibenzofurans were irradiated in the wavelength range between 300 and 400 nm in vegetable oils. Photodegradation of PCDDs produced non-toxic (non-2,3,7,8-substituted) congeners whereas the formation of toxic products was slightly favoured for PCDFs. Mono- to heptachlorinated hydroxybiphenyls, dihydroxybiphenyls and hydroxydiphenylethers were not detected.

7 REFERENCES

Adriaens, P., Fu, Q., Grbić-Galić, D. 1995. Bioavailability and transformation of highly chlorinated dibenzo-*p*-dioxins and dibenzofurans in anaerobic soils and sediments. Environ. Sci. Technol. 29, 2252-2260.

Ahlborg, U.G., Håkanson, H., Wærn, F., Hanberg, A. 1988. Nordisk dioxinriskbedömning. Rapport från en nordisk expertgrupp. Statens Miljömedicinska Laboratorium (SML), Sweden.

Ahlborg, U.G., Becking, G.C., Birnbaum, L.S., Brouwer, A., Derks, H.J.G.M., Feeley, M., Golor, G., Hanberg, A., Larsen, J.C., Liem, A.K.D., Safe, S.H., Schlatter, C., Wærn F., Younes, M., Yrjänheikki, E. 1994. Toxic equivalency factors for dioxin-like PCBs; report on al WHO-ECEH and IPCS consultation. Chemosphere 28, 1049-1067.

Alaluusua, S., Lukinmaa, P.-L.,Torppa, J., Tuomisto, J., Vartiainen, T. 1999. Developing teeth as biomarker of dioxin exposure. Lancet 353, 206.

Albrecht, I.D., Barkovskii, A.L., Adriaens, P. 1999. Production and dechlorination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in historically-contaminated estuarine sediments. Environ. Sci. Technol. 33, 737-744.

Alcock, R.E., Jones, K.C., 1996. Dioxins in the environment: a review of trend data. Environ. Sci. Technol. 30, 3133-3143.

Alcock, R.E., Jones, K.C. 1997. Pentachlorophenol (PCP) and chloranil as PCDD/F sources to sewage sludge and sludge amended soils in the UK. Chemosphere 35, 2317-2330.

Assmuth, T., Vartiainen, T. 1994. Concentrations of 2,3,7,8-chlorinated dibenzo-*p*-dioxins and dibenzofurans at landfills and disposal sites for chlorophenolic wood preservative wastes. Chemosphere 25, 971-979.

Assmuth, T., Vartiainen, T. 1995. Analysis of toxicological risks from local contamination by PCDDs and PCDFs: importance of isomer distributions and toxic equivalents. Chemosphere 31, 2853-2861.

Baker, J.I., Hites, R.A. 2000. Siskiwit Lake revisited: Time trends of polychlorinated dibenzo-*p*-dioxin and dibenzofuran deposition at Isle Royale, Michigan. Environ. Sci. Technol. 34, 2887-2891.

Ballschmiter K., Bacher, R.1996. *Dioxine.* VCH Verlagsgesellschaft mbH, Weinheim, Germany. (In German)

Barkovskii, A.L., Adriaens, A.L. 1996. Microbial dechlorination of historically present and freshly spiked chlorinated dioxins and diversity of dioxin-dechlorinating populations. Appl. Environ. Microbiol. 62, 4556-4562.

Beck, A.J., Johnson, D.L., Jones, K.C. 1996. The form and bioavailability of non-ionic organic chemicals in sewage sludge-amended agricultural soils. Sci. Tot. Environ. 185, 125-149.

Bertoni, G., Brocco, D., Di Palo, V., Liberti, A., Possanzini, M., Bruner, F. 1978. Gas chromatographic determination of 2,3,7,8-tetrachlorodibenzodioxin in the experimental decontamination of Seveso soil by ultraviolet radiation. Anal. Chem. 50, 732-735.

Bjerselius, R., Aune, M., Darnerud, P.O., Andersson, A., Tysklind, M., Bergek, S., Lundstedt Enkel, K., Karlssson, L., Appelberg, M., Arrhenius, F., Wickström, H., Glynn, A. 2003. Study of dioxin levels in fatty fish from Sweden 2001-2002, Part II. Organohalogen Compounds 62, 193-196.

Bonn, B.A. 1998. Polychlorinated dibenzo-*p*-dioxin and dibenzofuran concentration profiles in sediment and fish tissue of the Willamette Basin, Oregon. Environ. Sci. Technol. 32, 729-735.

Bopp, R.F., Gross, M.L., Tong, H., Simpson, J., Monson, S.J., Deck, B.L., Moser, F.G. 1991. A major incident of dioxin contamination: Sediments of New Jersey estuaries. Environ. Sci. Technol. 25, 951-956.

Borwitzky, H., Schramm, K.-W. 1991. Reduction of dioxin concentrations on contaminated surfaces. Chemosphere 22, 485-493.

Botré, C., Memoli, A., Alhaique, F. 1978. TCDD solubilization and photodecomposition in aqueous solutions. Environ. Sci. Technol. 12, 335-336.

Breivik, K., Alcock, R., Li, Y.-F., Bailey, R.E., Fiedler, H., Pacyna, J.M. 2004. Primary sources of selected POPs: regional and global scale emission inventories. Environ. Pollut. 128, 3-16.

Broman, D., Näf, C., Rolff, C., Zebühr, Y. 1991. Occurrence and dynamics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons in the mixed surface layer of remote coastal and offshore waters of the Baltic. Environ. Sci. Technol. 25, 1850-1864.

Bumb, R.R., Crummett, W.B., Cutie, S.S., Gledhill, J.R., Hummel, R.H., Kagel, R.O., Lamparski, L.L., Luoma, E.V., Miller, D.L., Nestrick, T.J., Shadoff, L.A., Stehl, R.H., Woods, J.S. 1980. Trace chemistries of fire: a source of chlorinated dioxins. Science 210, 385-390.

Bunce, N.J. 1982. Photodechlorination of PCB's: current status. Chemosphere 11, 701-714.

Bunge, M., Adrian, L., Kraus, A., Opel, M., Lorenz, W.G., Andreesen, J.R., Gorisch, H., Lechner, U. 2003. Reductive dehalogenation of chlorinated dioxins by an anaerobic bacterium. Nature 421, 357-360.

Buser, H.-R. 1988. Rapid photolytic decomposition of brominated and brominated/chlorinated dibenzodioxins and dibenzofurans. Chemosphere 17, 889-903.

Büchert, A., Cederberg, T., Dyke, P., Fiedler, H., Fürst, P., Hanberg, A., Hosseinpour, J., Hutzinger, O., Kuenen, J.G., Malisch, R., Needham, L.L., Olie, K., Päpke, O., Rivera Aranda, J., Thanner, G. Umlauf, G., Vartiainen, T., van Holst, C. 2001. Dioxin contamination in food. ESPR – Environ. Sci. & Pollut. Res. 8, 1-5.

Carroll, W.F., Jr., Berger, T.C., Borrelli, F.E., Garrity P.J., Jacobs, R.A., Lewis, J.W., McCreedy, R.L., Tuhovak, D.R., Weston, A.F. 1998. Characterization of emissions of dioxins and furans from ethylene dichloride (EDC), vinyl chloride (VCM) and polyvinylchloride (PVC) manufacturing facilities in the United States. 1. Resin, treated wastewater and ethylene dichloride. Chemosphere 37, 1957-1972.

Choi, W., Hong, S.J., Chang, Y.-S., Cho, Y. 2000. Photocatalytic degradation of polychlorinated dibenzo-*p*-dioxins on TiO_2 film under UV or solar light irradiation. Environ. Sci. Technol. 34, 4810-4815.

Choundry, G.G., Webster, G.R.B. 1986. Photochemical quantum yields and sunlight half-lives of polychlorinated dibenzo-*p*-dioxins in aquatic systems. Chemosphere 15, 1935-1940.

Choundry, G.G., Webster, G.R.B. 1989. Environmental photochemistry of PCDDs. 2. Quantum yields of the direct phototransformation of 1,2,3,7-tetra-, 1,3,6,8-tetra-, 1,2,3,4,6,78-hepta- and 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin in aqueous acetonitrile and their sunlight half-lives. J. Agric. Food Chem. 37, 254-261.

Chu, W., Kwan, C.Y. 2002. The direct and indirect photolysis of 4,4'-dichlorobiphenyl in various surfactant/solvent-aided systems. Water Res. 36, 2187-2194.

Commission of the European Communities. 2001. Community strategy for dioxins, furans and polychlorinated biphenyls. Communication from the Commission to the Council, the European Parliament and the Economic and Social Committee. COM(2001) 593, final. Brussels, Belgium. (http://www.europa.eu.int/)

Council Directive 91/173/EEC. Amending for the ninth time Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations. 21 March, 1991. Official Journal L 085, 05/04/1991, 34-36.

Cole, J.G., Mackay, D., Jones, K.C., Alcock, R.E. 1999. Interpreting, correlating, and predicting the multimedia concentrations of PCDD/Fs in the United Kingdom. Environ. Sci. Technol. 33, 399-405.

Crosby, D.G., Wong, A.S. 1971. Photodecomposition of chlorinated dibenzo-*p*-dioxins. Science 173, 748-749.

Dannenberg, D., Lerz, A. 1999. Occurrence and transport of organic micro-contaminants in sediments of the Odra river estuarine system. Acta Hydroch. Hydrob. 27, 303-307.

Darnerud, P.O., Aune, M., Becker, W., Bjerselius, R., Glynn, A. 2003. Swedish consumption of fatty Baltic fish in relation to the total dioxin intake and the recommended TDI. Organohalogen Compounds 64, 378-381.

DesRosiers, P.E. 1989. Chemical detoxification of dioxin-contaminated wastes using potassium polyethylene glycolate. Chemosphere 18, 343-353.

Di Domenico, A., Baldassarri, L.T., Ziemacki, G., De Felip, E., La Rocca, C., Ferrari, G., Cardelli, M., Volpi, F., Ferri, F., Iacovella, N., Lupi, C., Rodriguez, F., D'Agostino, O., Sansoni, R., Settimo, G. 1998. Priority microcontaminants in sediment samples from the Venice lagoon: a selection of concentration data and predominant analytical features. Organohalogen Compounds 39, 205-210.

Dobbs, A.J., Grant, C. 1979. Photolysis of highly chlorinated dibenzo-p-dioxins by sunlight. Nature 278, 163-165.

Dougherty, E.J., Overcash, M.R., Carbonell, R.G. 1991a. Diffusivity of 2,3,7,8-tetrachlorodibenzo-p-dioxin in organic solvents. Hazard. Waste Hazard. Mater. 8, 43-53.

Dougherty, E.J., McPeters, A.L., Overcash, M.R. 1991b. Kinetics of photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin: theoretical maximum rate of soil decontamination. Chemosphere 23, 589-600.

Dougherty, E.J., Overcash, M.R., McPeters, A.L. 1991c. Estimated TCDD photodegradation in waste motor oil. Hazard. Waste Hazard. Mater. 8, 313-317.

Dougherty, E.J., McPeters, A.L., Overcash, M.R., Carbonell, R.G. 1993. Theoretical analysis of a method for in situ decontamination of soil containing 2,3,7,8-tetrachlorodibenzo-p-dioxin. Environ. Sci. Technol. 27, 505-515.

Dougherty, E.J., McPeters, A.L., Overcash, M.R., Carbonell, R.G. 1994. Sorption processes of 2,3,7,8-tetrachlorodibenzo-p-diozin on soil in the presence of organic liquids. J. Hazard. Mater. 38, 405-421.

Duarte-Davidson, R., Sewart, A., Alcock, R.E., Cousins, I.T., Jones, K.C. 1997. Exploring the balance between sources, deposition, and the environmental burden of PCDD/Fs in the U.K. terrestrial environment: an aid to identifying uncertainties and research needs. Environ. Sci. Technol. 31, 1-11.

Dulin, D., Drossman, H., Mill, T. 1986. Products and quantum yields for photolysis of chloroaromatics in water. Environ. Sci. Technol. 20, 72-77.

Dung, M.H., O'Keefe, P.W. 1994. Comparative rates of photolysis of polychlorinated dibenzofurans in organic solvents and in aqueous solutions. Environ. Sci. Technol. 28, 549-554.

Dyke, P.H., Foan, C., Wenborn, M., Coleman, P.J. 1997. A review of dioxin releases to land and water in the UK. Sci. Tot. Environ. 207, 119-131.

EarthFax. 2003. http://www.earthfax.com/WhiteRot/Dioxin.htm

Eduljee, G. 1999. Secondary exposure to dioxins through exposure to PCP and its derivatives. Sci. Tot. Environ. 232, 193-214.

Eljarrat, E., Caixach, J., Rivera, J., De Torres, M., Ginebreda, A. 2001. Toxic potency assessment of non- and mono-ortho PCBs, PCDDs, PCDFs and PAHs in northwest Mediterranean sediments (Catalonia, Spain). Environ. Sci. Technol. 35, 3589-3594.

Evers, E.H.G., Klamer, H.J.C., Laane, R.W.P.M., Govers, H.A.J. 1993. Polychlorinated dibenzo-p-dioxin and dibenzofuran residues in estuarine and coastal North Sea sediments: sources and distribution. Environ. Toxicol. Chem. 12, 1583-1598.

Exner, J. 1987. Perspective on hazardous waste problems related to dioxins. In Exner, J., ed. *Solving hazardous waste problems: learning from dioxins.* ACS Symposium Series 338, American Chemical Society, Washington, DC, USA. pp 1-10.

Ferrario, J.B., Byrne, C.J., Cleverly, D.H. 2000. 2,3,7,8-dibenzo-*p*-dioxins in mined clay products from the United States: evidence for possible natural origin. Environ. Sci. Technol. 4524-4532.

Fiedler, H. 1998. Thermal formation of PCDD/PCDF: a survey. Environ. Eng. Sci. 15, 49-58.

Fiedler, H. 2003. First results of release inventories of PCDD/PCDF under the Stockholm convention. Organohalogen Compounds 63, 1-4.

Fouquet, A., Messier, F., Colgan, D., Grondin, A. 1990. Investigation for presence of chlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in bleaching processes from pulp and paper industries. Chemosphere 20, 1707-1714.

Fries, G.F., Paustenbach, D.J., Luksemburg, W.J. 2002. Complete mass balance of dietary polychlorinated dibenzo-*p*-dioxins and dibenzofurans in dairy cattle and characterization of the apparent synthesis of hepta- and octachlorodioxins. J. Agric. Food Chem. 50, 4226-4231.

Friesen, K.J., Muir, D.C.G., Webster, G.R.B. 1990. Evidence of sensitized photolysis of polychlorinated dibenzo-*p*-dioxins in natural waters under sunlight conditions. Environ. Sci. Technol. 24, 1739-1744.

Friesen, K.J., Foga, M.M., Loewen, M.D. 1996. Aquatic photodegradation of polychlorinated dibenzofurans: rates and photoproduct analysis. Environ. Sci. Technol. 30, 2504-2510.

Gaus, C., Brunskill, G.J., Weber, R., Päpke, O., Müller, J.F. 2001. Historical PCDD inputs and their source implications from dated sediment cores in Queensland (Australia). Environ. Sci. Technol. 35, 4597-4603.

Gaus, C., Brunskill, G.J., Connell, D.W., Prange, J., Müller, J.F., Weber, R. 2002. Transformation processes, pathways, and possible sources of distinctive polychlorinated dibenzo-*p*-dioxin signatures in sink environments. Environ. Sci. Technol. 36, 3542-3549.

Getman, G.D. 2000. Solvated electron technology (SET): a process for remediation of recalcitrant materials. In Wickramanayake, G.B., Gavaskar, A.R., Gibbs, J.T., Means, J.L., eds. *Case studies in the remediation of chlorinated and recalcitrant compounds.* The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, California, May 22-25, 2000. Battelle Press, Columbus, Ohio, USA. pp 349-355.

Green, N.J.L., Wood, J., Alcock, R.E., Marcomini, A., Jones, K.J. 1999. PCDD/Fs and PCBs in sediment samples from the Venice Lagoon. Organohalogen Compounds 1999, 43, 339-342.

Green, N.J.L., Jones, J.J., Jones, K.C. 2001. PCDD/F deposition time trend to Esthwaite Water, U.K., and its relevance to sources. Environ. Sci. Technol. 35, 2882-2888.

Greenpeace International. 2002. Business as usual or 'Vinyl 2010', the voluntary commitment of the PVC industry. (http://www.greenpeace.org/international_en/reports/ ?campaign_id =3941).

Greenpeace International. 2003. PVC-free future: a review of restrictions and PVC-free policies worldwide. 9th edition. (http://www.greenpeace.org/international_en/ reports/ ?campaign_id =3941).

Gribble, G.W. 1994. The natural production of chlorinated compounds. Environ. Sci. Technol. 28, 310A-319A.

Götz, R., Schumacher, E., Kjeller, L.-O., Bergvist, P.-A., Rappe, C. 1990. Polychlorierte Dibenzo-*p*-dioxine (PCDDs) und polychlorierte Dibenzofurane (PCDFs) in Sedimenten und Fischen aus dem Hamburger Hafen. Chemosphere 20, 51-73. (in German)

Hallikainen, A., Kiviranta, H., Isosaari, P., Vartiainen, T., Parmanne, R., Vuorinen, P.J. 2004. Kotimaisen järvi- ja merikalan dioksiinien, furaanien, dioksiinien kaltaisten PCB-yhdisteiden ja polybromattujen difenyylieettereiden pitoisuudet. EU-KALAT. Elintarvikeviraston julkaisuja 1/2004. Edita Express, Helsinki, Finland. (Abstract in English)

Hansen, E., Hansen, C.L. 2003. Substance flow analysis for dioxin 2002. Environmental project no. 811. Danish Environmental Protection Agency, Danish Ministry of the Environment. (http://www.mst.dk/)

Hashimoto, S., Wakimoto, T., Tatsukawa, R. 1995. Possible natural formation of polychlorinated dibenzo-*p*-dioxins as evidenced by sediment analysis from the Yellow Sea, the East China Sea and the Pacific Ocean. Marine Poll. Bull. 5, 341-346.

Hashimoto, S., Watanabe, K., Nose, K., Morita, M. 2004. Remediation of soil contaminated with dioxins by subcritical water extraction. Chemosphere 54, 89-96.

Hawari, J., Demeter, A., Greer, C., Samson, R. 1991. Acetone-induced photodechlorination of Aroclor 1254 in alkaline 2-propanol: probing the mechanism by thermolysis in the presence of di-t-butyl peroxide. Chemosphere 22, 1161-1174.

Haynes, F., Marnane, I. 2000. Inventory of dioxin & furan emissions to air, land and water in Ireland for 2000 and 2010. Final report. Prepared for the Environmental Protection Agency by URS Dames & Moore, Dublin. Environmental Protection Agency, Co Wexford, Ireland. (http://www.epa.ie/)

HELCOM. 1993. The Baltic Sea Joint Comprehensive Environmental Action Programme. Balt. Sea Environ. Proc. 48. (http://www.helcom.fi/)

HELCOM. 2003. Fourth periodic assessment of the marine environment of the Baltic Sea area 1994-1998. Balt. Sea Environ. Proc. 82B. (http://www.helcom.fi/)

Hilarides, R., Gray, K., Guzzetta, J., Cortellucci, N., Sommer, C. 1994. Radiolytic degradation of 2,3,7,8-TCDD in artificially contaminated soils. Environ. Sci. Technol. 28, 2249-2258.

Hites, R.A., Foran, J.A., Carpenter, D.O., Hamilton, M.C., Knuth, B.A., Schwager, S.J. 2004. Global assessment of organic contaminants in farmed salmon. Science 303, 226-229.

Hoekstra, E.J., de Weerd, H., de Leer, E.W.B., Brinkman, U.A.Th. 2000. Natural formation of chlorinated phenols, dibenzo-*p*-dioxins and dibenzofurans in soil of a Douglas fir forest. Organohalogen Compounds 46, 5-8.

Holoubek, I., Kočan, A., Holoubková, I., Hilscherová, K., Kohoutek, J., Falandysz, J., Roots, O. 2000. Persistent, Bioaccumulative and Toxic Chemicals in Central and Eastern European Countries - State-of-the-art Report. TOCOEN Report No. 150a. Brno, Czech Republic.

Hosoya, K., Kimata, K., Fukunishi, K., Tanaka, N. 1995. Photodecomposition of 1,2,3,4- and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in water-alcohol media on a solid support. Chemosphere 31, 3687-3698.

Hosseinpour, J., Rottler, H., Malisch, R. 2003. Comparison of methods for extraction of PCDD/F from kaolinitic clays and copper oxide in view of European feedinstuff limits. Organohalogen Compounds 60, 13-16.

Humppi, T., Heinola, K. 1985. Synthesis and gas chromatographic–mass spectroscopic determination of polychlorinated dibenzo-*p*-dioxins and related compounds in the technical chlorophenol formulation Ky.5. J. Chromatography 331, 410-418.

Hung, L.-S., Ingram, L.L. Jr. 1990. Effects of solvents on the photodegradation rates of octachlorodibenzo-*p*-dioxin. Bull. Environ. Contam. Toxicol. 44, 380-386.

Hutzinger, O., Fiedler, H. 1993. From source to exposure: some open questions. Chemosphere 27, 121-129.

Ishii, K., Furuichi, T., Matsuda, Y. 2003. Degradation of dioxins using enzymes and sterilization of *Pseudallescheria boydii.* Organohalogen Compounds 63, 260-263.

Isosaari, P., Vartiainen, T. 2002. Dioksiini- ja furaanimaiden ympäristövaikutukset. Ympäristö ja Terveys 33 (9), 45-49. (in Finnish)

Isosaari, P., Vartiainen, T., Hallikainen, A., Ruohonen, K. 2002. Feeding trial on rainbow trout: comparison of dry fish feed and Baltic herring as a source of PCDD/Fs and PCBs. Chemosphere 48, 795-804.

Isosaari, P., Tuhkanen, T., Vartiainen, T. 1997. Dioxin degradation by Fenton's reagent. In *7th Nordic Symposium on Organic Pollutants*. Vartiainen, T., Komulainen, H., eds. Kuopio University Publications C. Natural and Environmental Sciences 68, Kuopio, Finland. pp 53-56.

Isosaari, P., Tuhkanen, T., Vartiainen, T. 1998. Photochemical degradation of dioxins in soil. In Wickramanayake, G.B., Hinchee, R.E., eds. *Designing and applying treatment technologies: remediation of chlorinated and recalcitrant compounds.* First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998. Battelle Press, Columbus, Ohio, USA. pp 213-218.

Isosaari, P., Kiviranta, H., Hallikainen, A., Parmanne, R., Vuorinen, P.J., and Vartiainen, T. 2003. Dioxin levels in fish caught from the Baltic Sea in 2001-2002. Organohalogen Compounds 62, 41-44.

Isosaari, P., Kiviranta, H., Lie, Ø., Lundebye, A.-K., Ritchie, G., Vartiainen, T. 2004. Accumulation and distribution of polychlorinated dibenzo-*p*-dioxin, dibenzofuran, and polychlorinated biphenyl congeners in Atlantic salmon *(Salmo salar)*. Environ. Toxicol. Chem., in press.

Jackson, D.R., Bisson, D.L. 1990. Mobility of polychlorinated aromatic compounds in soils contaminated with wood-preserving oil. J. Air Waste Manage. Assoc. 40, 1129-1133.

Jensen, A.A. Kortlægning af dioxinforurening samt kilder til dioxinforurening i Østersjøen. Miljøprojekt Nr. 796. Miljøstyrelsen, Miljøministeriet, 2003. 123 p. (http://www.mst.dk/)

Jiminez, B., Hernandez, L.M., Gonzales, M.J., Eljarrat, E., Rivera, J., Fossi, M.C. 1998. Congener specific analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in crabs and sediments from the Venice and Orbetello Lagoons, Italy. Environ. Sci. Technol. 32, 3853-3861.

Johnson, J. 1995. Dioxin risk: are we sure yet? Environ. Sci. Technol. 29, 24-29A.

Jonsson, P., Rappe, C., Kjeller, L.-O., Kierkegaard, A., Håkanson, L., Jonsson, B. 1993. Pulp-mill related polychlorinated organic compounds in Baltic Sea sediments. Ambio 22, 37-43.

Jørgensen, K.S., Kalevi, K. 2002. PCDD/F:lla pilaantuneet maat ja ongelman laajuus Suomessa. Ympäristö ja Terveys 33 (9), 40-44. (in Finnish)

Kankaanpää, H.T., Laurén, M.A., Saares, R.J., Heitto, L.V., Suursaar, Ű.K. 1997. Distribution of halogenated material in sediments from anthropogenic and natural sources in the Gulf of Finland catchment area. Environ. Sci. Technol. 31, 96-104.

Kao, C.M., Wu, M.J. 2000. Enhanced TCDD degradation by Fenton's reagent preoxidation. J. Hazard. Mater. 74, 197-211.

Kapila, S., Yanders, A.F., Orazio, C.E., Meadows, J.E., Cerlesi, S., Clevenger, T.E. 1989. Field and laboratory studies on the movement and fate of tetrachlorodibenzo-*p*-dioxin in soil. Chemosphere 18, 1297-1304.

Khizbullin, F., Muslymova, I., Khasanova, I., Chernova, L., Abdrashitov, J. 1998. Evaluation of polychlorinated dibenzodioxins and dibenzofuran's emission from vinylchloride-monomer production. Organohalogen Compounds 36, 225-227.

Kieatiwong, S., Nguyen, L.W., Hebert, V.R., Hackett, M., Miller, G.C, Miille, M.J., Mitzel, R. 1990. Photolysis of chlorinated dioxins in organic solvents and on soils. Environ. Sci. Technol. 24, 1575-1580.

Kim, M., O'Keefe, P.W. 1998. The role of natural organic compounds in photosensitized degradation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. Organohalogen Compounds 36, 377-380.

Kim, M., O'Keefe, P.W. 2000. Photodegradation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in aqueous solutions and in organic solvents. Chemosphere 41, 793-800.

Kitunen, V.H., Salkinoja-Salonen, M.S. 1990. Soil contamination at abandoned sawmill areas. Chemosphere 20, 1671-1677.

Kiviranta, H., Hallikainen, A., Ovaskainen, M.-L., Kumpulainen, J., Vartiainen, T. 2001. Dietary intakes of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and polychlorinated biphenyls in Finland. Food Addit. Contam. 18, 945-953.

Kiviranta, H., Vartiainen, T., Tuomisto, J. 2002. Polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and biphenyls in fishermen in Finland. Environ. Health Perspect. 110, 355-361.

Kiviranta, H., Vartiainen, T., Parmanne, R., Hallikainen, A., Koistinen, J. 2003. PCDD/Fs and PCBs in Baltic herring during the 1990s. Chemosphere 50, 1201-1216.

Kjeller, L-O., Rappe, C. 1995. Time trends in levels, patterns, and profiles for polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and biphenyls in a sediment core from the Baltic Proper. Environ. Sci. Technol. 29, 346-355.

Kjeller, L.-O., Kulp, S.-E., Bergek, S., Boström, M., Bergqvist, P-A., Rappe, C., Jonsson, B., de Wit, C., Jansson, B., Olsson, M. 1990. Levels and possible sources of PCDD/PCDF in sediment and pike samples from Swedish lakes and rivers (part one). Chemosphere 20, 1489-1496.

Klimm, C., Schramm, K.-W., Henkelmann, B., Martens, D., Kettrup, A. 1998. Formation of octa- and heptachlorodibenzo-p-dioxins during semi anaerobic digestion of sewage sludge. Chemosphere 37, 2003-2011.

Knutzen, J., Oehme, M. 1989. Polychlorinated dibenzofurans (PCDF) and dibenzo-*p*-dioxin (PCDD) levels in organisms and sediments from the Frierfjord, southern Norway. Chemosphere 19, 1897-1909.

Knutzen, J., Bjerkeng, B., Næs, K., Schlabach, M. 2003. Polychlorinated dibenzofurans/dibenzo-*p*-dioxins (PCDF/PCDDs) and other dioxin-like substances in marine organisms from the Grenland fjords, S. Norway, 1975-2001: present contamination levels, trends and species specific accumulation of PCDF/PCDD congeners. Chemosphere 52, 745-760.

Kobara, Y., Endo, S., Horio, T., Ishihara, S., Ohtsu, K. 2003. Photolysis of polychlorinated dibenzo-*p*-dioxins and enhanced detoxication by titanium dioxide photocatalyst on soils surface. Organohalogen Compounds 63, 256-259.

Koester, C.J., Hites, R.A. 1992. Photodegradation of polychlorinated dioxins and dibenzofurans adsorbed to fly ash. Environ. Sci. Technol. 26, 502-506.

Koistinen, J., Paasivirta, J., Särkkä, J. 1990. Organic chlorine compounds in lake sediments. IV. Dioxins, furans and related chloroaromatic compounds. Chemosphere 21, 1371-1379.

Koistinen, J., Paasivirta, J., Suonperä, M., Hyvärinen, H. 1995. Contamination of pike and sediment from the Kymijoki River by PCDEs, PCDDs, and PCDFs: contents and patterns compared to pike and sediment from the Bothnian Bay and seals from Lake Saimaa. Environ. Sci. Technol. 29, 2541-2547.

Koistinen, J., Stenman, O., Haahti, H., Suonperä, M., Paasivirta, J. 1997. Polychlorinated diphenyl ethers, dibenzo-*p*-dioxins, dibenzofurans and biphenyls in seals and sediment from the Gulf of Finland. Chemosphere 35, 1249-1269.

Konstantinov, A., Bunce, N.J. 1996. Photodechlorination of octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran in alkane solvents in the absence and presence of triethylamine. J. Photochem. Photobiol. A: Chem. 94, 27-35.

Konstantinov, A.D., Johnston, A.M., Cox, B.J., Petrulis, J.R., Orzechowski, M.T., Bunce, T.J., Tashiro, C.H.M., Chittim, B.G. 2000. Photolytic method for destruction of dioxins in liquid laboratory waste and identification of the photoproducts from 2,3,7,8-TCDD. Environ. Sci. Technol. 34, 143-148.

Krauβ, Th., Krauβ, P., Hagenmaier, H. 1994. Formation of PCDD/PCDF during composting? Chemosphere 28, 155-158.

Lamparski, L.L., Stehl, R.H., Johnson, R.L. 1980. Photolysis of pentachlorophenol-treated wood. Chlorinated dibenzo-*p*-dioxin formation. Environ. Sci. Technol. 14, 196-200.

Lassen, C., Hansen, E., Jensen, A.A., Olendrzyński, K., Kolsut, W., Żurek, J., Kargulewicz, I., Dębski, B., Skośkiewicz, J., Holtzer, M., Grochowalski, A., Brante, E., Poltimae, H., Kallaste, T., Kapturauskas, J. 2003. Survey of dioxin sources in the Baltic region. ESPR - Environ. Sci. & Pollut. Res. 10, 49-56.

Leichsenring, S., Lenoir, D., May, H.G., Kettrup, A. 1996. Catalytic oxidation of chloroaromatic trace contaminants adsorbed on Wessalith DAY by ozone. Chemosphere 33, 343-352.

Leifer, A. 1988. *The kinetics of environmental aqueous photochemistry, theory and practice.* ACS Professional Reference Book. American Chemical Society, Washington, DC, USA.

Leithe-Eriksen, R. 2001. Pulp bleaching around the Baltic Sea. Greenpeace report, April 2001. (http://www.greenpeace.org/international_en/reports/?campaign_id=3941)

Liberti, A., Brocco, D., Allegrini, I., Bertoni, G. 1978a. In Cattabeni, F., Cavallaro, A., Galli, G., eds. *Dioxin – toxicological and chemical aspects.* SP Medical & Scientific Books, a division of Spectrum Publications, New York, USA. pp 195-200.

Liberti, A., Brocco, D., Allegrini, I., Cecinato, A., Possanzini, M. 1978b. Solar and UV photodecomposition of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in the environment. Sci. Total Environ. 10, 97-104.

Liem, A.K.D., Theelen, R.M.C. 1997. Dioxins: Chemical analysis, exposure and risk assessment. Academic dissertation. Cip-Gegevens Koninklijke Bibliotheek, Den Haag.

Litten, S., McReynolds, D., Swart, J., Estabrooks, F., Hoover, D., Hamilton, C. 2003. Chlorinated dioxin/furans in New York harbor water, wastewater, biota, and sediments. Organohalogen Compounds, 62, 169-172.

Liu, P.-Y., Zheng, M.-H., Xu, X.-B. 2002. Phototransformation of polychlorinated dibenzo-*p*-dioxins from photolysis of pentachlorophenol on soils surface. Chemosphere 46, 1191-1193.

Lohmann, R., Jones, K.C. 1998. Dioxins and furans in air and deposition: a review of levels, behaviour and processes. Sci. Tot. Environ. 219, 53-81.

MacDonald, R.W., Ikonomou, M.G., Paton, D.W. 1998. Historical inputs of PCDDs, PCDFs, and PCBs to a British Columbia interior lake: the effect of environmental controls on pulp mill emissions. Environ. Sci. Technol. 32, 331-337.

Malloy, T.A., Goldfarb, T.D., Surico, M.T.J. 1993. PCDDs, PCDFs, PCBs, chlorophenols (CPs) and chlorobenzenes (CBzs) in samples from various types of composting facilities in the United States. Chemosphere 27, 325-334.

Malve, O., Salo, S., Verta, M., Forsius, J. 2003. Modeling the transport of PCDD/F compounds in a contaminated river and the possible influence of restoration dredging on calculated fluxes. Environ. Sci. Technol. 37, 3413-3421.

Mamontov, A.A., Mamontova, E.A., Tarasova, E.N., McLachlan, M.S. 2000. Tracing the sources of PCDD/Fs and PCBs to Lake Baikal. Environ. Sci. Technol. 34, 741-747.

Martínez, M., Díaz-Ferrero, J., Martí, R., Broto-Puig, F., Comellas, L., Rodríguez-Larena, M.C. 2000. Analysis of dioxin-like compounds in vegetation and soil samples burned in Catalan forest fires. Comparison with the corresponding unburned material. Chemosphere 41, 1927-1935.

Massé, R., Pelletier, B. 1987. Photochemistry of dibenzo-p-dioxin in organic solvents at 253.7 nm: GC/MS characterization of the phototransformation products. Chemosphere 16, 7-17.

Masunaga, S., Nakanishi, J. 1999. Dioxin impurities in old Japanese agrochemical formulations. Organohalogen Compounds 41, 41-44.

McKee, P., Burt, A., McCurvin, D. 1990. Levels of dioxins, furans and other organic contaminants in harbour sediments near a wood preserving plant using pentachlorophenol and creosote. Chemosphere 20, 1679-1685.

McPeters, A.L., Overcash, M.R. 1993. Demonstration of photodegradation by sunlight of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in 6 cm soil columns. Chemosphere 27, 1221-1234.

Meneses, M., Schuhmacher, M., Domingo, J.L. 2004. Health risk assessment of emissions of dioxins and furans from a municipal waste incinerator: comparison with other emission sources. Environ. Int. 30, 481-489.

Miller, A. 1993. Dioxin emissions from EDC/VCM plants. Environ. Sci. Technol. 27, 1014-1015.

Miller, G.C., Hebert, V.R., Miille, M.J., Mitzel, R., Zepp, R.G. 1989. Photolysis of octachlorodibenzo-*p*-dioxin on soils: production of 2,3,7,8-TCDD. Chemosphere 18, 1265-1274.

Monagheddu, M., Mulas, G., Doppiu, S., Cocco, G., Raccanelli, S. 1999. Reduction of polychlorinated dibenzodioxins and dibenzofurans in contaminated muds by mechanically induced combustion reactions. Environ. Sci. Technol. 33, 2485-2488.

Morimoto, K., Tatsumi, K. 1997. Effect of humic substances on the enzymatic formation of OCDD from PCP. Chemosphere 34, 1277-1283.

Müller, J.F., Gaus, C., Prange, J.A., Päpke, O., Poon, K.F., Lam, M.H.W., Lam, P.K.S. 2002. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in sediments from Hong Kong. Mar. Pollut. Bull. 45, 372-378.

Namikaya, K., Ishii, K., Yoshizaki, K., Furuichi, T. 2003. Solvent-washing of dioxin-contaminated soil and ultraviolet treatment of the extracted dioxins. Organohalogen Compounds 45, 423-426.

National Food Agency Finland. 2004. EU research project on dioxin in fish. Results of the dioxin project. http://www.elintarvikevirasto.fi/english/

NATO/CCMS. 1988. International toxicity equivalency factors (I-TEF) – method for risk assessment for complex mixtures of dioxins and related compounds. North Atlantic Treaty Organization/Committee on the Challenge of Modern Society, Report No. 176.

Nestrick, T.J., Lamparski, L.L., Townsend, D.I. 1980. Identification of tetrachlorodibenzo-*p*-dioxin isomers at the 1-ng level by photolytic degradation and pattern recognition techniques. Anal. Chem. 52, 1865-1874.

Niu, J., Chen, J., Henkelmann, B., Quan, X., Yang, F., Kettrup, A., Schramm, K.-W. 2003. Photodegradation of PCDD/Fs adsorbed on spruce (*Picea abies* (L.) Karst.) needles under sunlight irradiation. Chemosphere 50, 1217-1225.

Oku, A., Tomari, K., Kamada, T., Yamada, E., Miyata, H., Aozasa, O. 1995. Destruction of PCDDs and PCDFs. A convenient method using alkali-metal hydroxide in 1,3-dimethyl-2-imidazolidinone (DMI). Chemosphere 31, 3873-3878.

Overcash, M.R., McPeters, A.L., Dougherty, E.J., Carbonell, R.G. 1991. Diffusion of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in soil containing organic solvents. Environ. Sci. Technol. 25, 1479-1485.

Palauchek, N., Scholz, B. 1987. Destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans in contaminated water samples using ozone. Chemosphere 16, 1857-1863.

Patel-Sorrentino, N., Mounier, S., Lucas, Y., Benaim, J.Y. 2004. Effects of UV-visible irradiation on natural organic matter from the Amazon basin. Sci. Tot. Environ. 321, 231-239.

Pelizzetti, E., Minero, C., Carlin, V., Borgarello, E. 1992. Photocatalytic soil decontamination. Chemosphere 25, 343-351.

Persson, Y., Andersson, R., Öberg, L., Tysklind, M. 2003. PCDD/F contaminated soils in northern Sweden as an outcome of wood preservation with chlorophenols. Organohalogen Compounds 62, 448-451.

Peterson, R., Milicic, E. 1992. Chemical treatment of dioxin residues from wastewater processing. Chemosphere 25, 1565-1568.

Piccinini, P., Pichat, P., Guillard, C. 1998. Phototransformations of solid pentachlorophenol. J. Photochem. Photobiol. A: Chem. 119, 137-142.

Pignatello, J.J, Huang, L., 1993. Degradation of polychlorinated dibenzo-p-dioxin and dibenzofuran contaminants in 2,4,5-T by photoassisted iron-catalyzed hydrogen peroxide. Wat. Res. 27, 1731-1736.

Podoll, T.R., Jaber, H.M., Mill, T. 1986. Tetrachlorodibenzodioxin: rates of volatilization and photolysis in the environment. Environ. Sci. Technol. 20, 490-492.

Pohl, H. R., Holler, J., Fay, M., De Rosa, C. T. 1998. Focus on dioxins. Organohalogen Compounds 38, pp. 347-348.

Prange, J.A., Gaus, C., Weber, R., Päpke, O., Müller, J.F. 2003. Assessing forest fire as a potential PCDD/F source in Queensland, Australia. Environ. Sci. Technol. 37, 4325-4329.

Puolanne, J., Pyy, O., Jeltsch, U. 1994. Saastuneet maa-alueet ja niiden käsittely Suomessa. Ministry of the Environment, Helsinki, Finland. (In Finnish).

Quaβ, U., Fermann, M., Bröker, G. 2000a. The European dioxin emission inventory. Stage II. Volume 1. Executive summary. Prepared by the North Rhine Westphalia State Environment Agency on behalf of the European Commission, Directorate General for Environment (DG ENV). (http://www.europa.eu.int/)

Quaβ, U., Fermann, M., Bröker, G. 2000b. The European dioxin emission inventory. Stage II. Volume 3. Assessment of dioxin emissions until 2005. Prepared by the North Rhine Westphalia State Environment Agency on behalf of the European Commission, Directorate General for Environment (DG ENV). (http://www.europa.eu.int/)

Quaβ, U., Fermann, M., Bröker, G. 2004. The European dioxin air emission inventory project – final results. Chemosphere 54, 1319-1327.

Rappe, C. 1993. Sources of exposure, environmental concentrations and exposure assessment of PCDDs and PCDFs. Chemosphere 27, 211-225.

Rappe, C., Andersson, R. 2000. Concentrations of PCDDs in ball clay and kaolin. Organohalogen Compounds 46, 9-11.

Rappe, C., Bergqvist, P.-A., Kjeller, L.-O. 1989. Levels, trends and patterns of PCDDs and PCDFs in Scandinavian environmental samples. Chemosphere 18, 651-658.

Rappe, C., Glas, B., Kjeller, L.-O., Kulp, S.E., de Wit, C., Melin, A. 1990. Levels of PCDDs and PCDFs in products and effluent from the Swedish pulp and paper industry and chloralkali process. Chemosphere 20, 1701-1706.

Rappe, C., Kjeller, L.-O., Kulp, S.-E., de Wit, C., Hasselsten, I., Palm, O. 1991. Levels, profile and pattern of PCDDs and PCDFs in samples related to the production and use of chlorine. Chemosphere 21, 1629-1636.

Rappe, C., Andersson, R., Bonner, M., Cooper, K., Fiedler, H., Howell, F., Kulp, S.E., Lau, C. 1997. PCDDs and PCDFs in soil and sediment samples from a rural area in the United States of America. Chemosphere 34, 1297-1314.

Rayne, S., Wan, P., Ikonomou, M.G., Konstantinov, A.D. 2002. Photochemical mass balance of 2,3,7,8-TeCDD in aqueous solution under UV light shows formation of chlorinated dihydroxybiphenyls, phenoxyphenols, and dechlorination products. Environ. Sci. Technol. 36, 1995-2002.

Ritterbush, J., Lorenz, W., Bahadir, M. 1994. Determination of polyhalogenated dibenzo-p-dioxins and dibenzofurans in analytical laboratory waste and their decomposition by UV-photolysis. Chemosphere 29, 1829-1838.

Saatsi, K. 2002. Valobakteeritestin soveltuvuus dioksiinien määritykseen maanäytteistä. Dissertation. Häme Polytechnic, Environmental Engineering, Hämeenlinna, Finland. (In Finnish)

Safe, S. 1990. Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). Crit. Rev. Toxicol. 21, 51-88.

Sakurai, T., Kim, J.-G., Suzuki, N., Matsuo, T., Li, D.-Q., Yao, Y., Masunaga, S., Nakanishi, J. 2000. Polychlorinated dibenzo-p-dioxins and dibenzofurans in sediment, soil, fish, shellfish and crab samples from Tokyo Bay area, Japan. Chemosphere, 40, 627-640.

Schuler, F., Schmid, P., Schlatter, Ch. 1998. Photodegradation of polychlorinated dibenzo-p-dioxins and dibenzofurans in cuticular waxes of laurel cherry (*Prunus laurocerasus*). Chemosphere 36, 21-34.

Shelepchikov, A.A., Kluyev, N.À., Shenderyuk, V., Baholdina, L.P., Brodsky, E.F. 2003. Contamination of Russian Baltic fish by PCDD/F. Organohalogen Compounds 62, 152-156.

Silk, P.J., Lonergan, G.C., Arsenault, T.L., Boyle, C.D. 1997. Evidence of natural organochlorine formation in peat bogs. Chemosphere 35, 2865-2880.

Sinkkonen, S., Paasivirta, J. 2000. Degradation half-life times for PCDDs, PCDFs and PCBs for environmental fate modeling. Chemosphere 40, 943-949.

Skurlatov, Yu.I., Ernestova, L.S., Vichutinskaya, E.V., Samsonov, D.P., Semenova, I.V., Rod'ko, I. Ya., Shvidky, V.O., Pervunina, R.I., Kemp, T.J. 1997. Photochemical transformation of polychlorinated phenols. J. Photochem. Photobiol. A: Chem. 107, 207-213.

Stevens, J.L., Green, N.J.L., Jones, K.C. 2003. Fate of 1,2,3,4,6,7,8-heptachlorodibenzofuran and pentachlorophenol during laboratory-scale anaerobic mesophilic sewage sludge digestion. Chemosphere 50, 1227-1233.

Suominen, K., Saski, E., Puurtinen, R., Seppälä, A. 1999. Impact of contaminated sediment of river Kymijoki on land and water use – assessment and design for remedial actions. Final report. (Abstract in English).

Svenson, A., Kjeller, L-O., Rappe, C., 1989. Enzyme-mediated formation of 2,3,7,8-tetrasubstituted chlorinated dibenzodioxins and dibenzofurans. Environ. Sci. Technol. 23, 900-902.

Swanson, S.E., Rappe, C., Malmström, J., Kringstad, K.P. 1988. Emissions of PCDDs and PCDFs from the pulp industry. Chemosphere 17, 625-850.

Takada, S., Nakamura, M., Matsueda, T., Kondo, R., Sakai, K. 1996. Degradation of polychlorinated dibenzo-p-dioxins and dibenzofurans by the white rot fungus *Phanerochaete sordida* YK-624. Appl. Environ. Microbiol. 62, 4323-4328.

Troyanskaya, A.F., Rubtsova, N.A., Moseeva, D.P., Punantseva, E.A. 2003. Contamination of natural matrixes with persistent organic pollutants as a result of wood treatment in the northern regions of Russia. Organohalogen Compounds 62, 61-64.

Tsutsumi, T., Amakura, Y., Yanagi, T., Nakamura, M., Kono, Y., Uchibe, H., Iida, T., Toyoda, M., Sasaki, K., Maitani, T. 2003. Levels of PCDDs, PCDFs and dioxin-like PCBs in retail fish and shellfish in Japan. Organohalogen Compounds 62, 93-96.

Tundo, P., Perosa, A., Selva, M., Zinovyev, S.S. 2001. A mild catalytic detoxification method for PCDDs and PCDFs. Appl. Catal. B-Environ. 32, L1-L7.

Tuppurainen, K., Halonen, I., Ruokojärvi, P., Tarhanen, J., Ruuskanen, J. 1998. Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review. Chemosphere 36, 1493-1511.

Tysklind, M., Rappe, C. 1991. Photolytic transformation of polychlorinated dioxins and dibenzofurans in fly ash. Chemosphere 23, 1365-1375.

Tysklind, M., Lundgren, K., Rappe, C. 1993. Ultraviolet absorption characteristics of all tetra- to octachlorinated dibenzofurans. Chemosphere 27, 535-546.

Ukisu, Y., Miyadera, T. 2003. Hydrogen-transfer hydrodechlorination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans catalyzed by supported palladium catalysts. Appl. Catal. B-Environ. 40, 141-149.

UNEP Chemicals. 1999. Dioxin and furan inventories. National and regional emissions of PCDD/PCDF. Geneva, Switzerland. (http://www.chem.unep.ch/pops/)

US EPA. 1994. Estimating exposure to dioxin-like compounds. Volume II: Properties, sources, occurrence and background exposures. Review Draft EPA/600/6-88/005Cb, June 1994. Environmental Protection Agency of the United States.

Van den Berg, M., Birnbaum, L., Bosveld, A.T.C., Brunström, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., van Leeuwen, F.X.R., Liem, A.K.D., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tilitt, D., Tysklind, M., Younes, M., Wærn, F., Zacharewski, T. 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ. Health Perspect. 106, 775-792.

Vartiainen, T., Lampi, P., Tolonen, K., Tuomisto, J. 1995. Polychlorodibenzo-*p*-dioxin and polychlorodibenzofuran concentrations in lake sediments and fish after a ground water pollution with chlorophenols. Chemosphere 1439-1451.

Vartiainen, T., Mannio, J., Korhonen, M., Kinnunen, K., Strandman, T. 1997a. Levels of PCDD, PCDF and PCB in dated lake sediments in subarctic Finland. Chemosphere 34, 1341-1350.

Vartiainen, T., Kiviranta, H., Tuomisto, J., Kohonen, T., Salonen, V.-P. 1997b. Sköldvikin läheisen merialueen PCDD-, PCDF- ja PCB-määrät pohjasedimentissä. Loppuraportti. 30.4.1997. (In Finnish)

Verta, M., Ahtiainen, J., Hämäläinen, H., Jussila, H., Järvinen, O., Kiviranta, H., Korhonen, M., Kukkonen, J., Lehtoranta, J., Lyytikäinen, M., Malve. O., Mikkelson, P., Moisio, V., Niemi, A., Paasivirta, J., Palm, H., Porvari, P., Rantalainen, A.-L., Salo, S., Vartiainen, T., Vuori, K.-M. 1999a. Organoklooriyhdisteet ja raskasmetallit Kymijoen sedimentissä: esiintyminen, kulkeutuminen, vaikutukset ja terveysriskit. The Finnish Environment 334. Edita Ltd, Helsinki, Finland. (abstract in English)

Verta, M., Korhonen, M., Lehtoranta, J., Salo, S., Vartiainen, T., Kiviranta, H., Kukkonen, J., Hämäläinen, H., Mikkelson, P., Palm, H. 1999b. Ecotoxicological and health effects caused by PCPs, PCDEs, PCDDs, and PCDFs in River Kymijoki sediments, south-eastern Finland. Organohalogen Compounds 43, 239-242.

Verta, M., Salo, S., Malve, O., Kiviranta, H. 2003. Continued transport of PCDD/F contaminated sediments from River Kymijoki to the Gulf of Finland, the Baltic Sea. Organohalogen Compounds 61, 405-408.

Vis, P.I.M., Krijger, P. 2000. Full-scale thermal desorption of soil contaminated with chlorinated compounds. In Wickramanayake, G.B., Hinchee, R.E., eds. *Physical, chemical, and thermal technologies.* The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, California, May 22-25, 2000. Battelle Press, Columbus, Ohio, USA. pp 1-6.

Vollmuth, S., Niessner, R. 1995. Degradation of PCDD, PCDF, PAH, PCB and chlorinated phenols during the destruction-treatment of landfill seepage water in laboratory model reactor (UV, ozone, and UV/ozone). Chemosphere 30, 2317-2331.

Vollmuth, S., Zajc, A., Niessner, R., 1994. Formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans during the photolysis of pentachlorophenol-containing water. Environ. Sci. Technol. 28, 1145-1149.

Vuorinen, P.J., Parmanne, R., Vartiainen, T., Keinänen, M., Kiviranta, H., Kotovuori, O., Halling, F. 2002. PCDD, PCDF, PCB and thiamine in Baltic herring (*Clupea harengus* L.) and sprat [*Sprattus sprattus* (L.)] as a background to the M74 syndrome of Baltic salmon (*Salmo salar* L.). ICES Journal of Marine Science 59, 480-496.

Wagenaar, W.J., Boelhouwers, E.J., de Kok, H.A.M., Groen, C.P., Govers, H.A.J., Olie, K., de Gerlache, J., de Rooij, C.G. 1995. A comparative study of the photolytic degradation of octachlorodibenzofuran (OCDF) and octachlorobidenzo-*p*-dioxin. Chemosphere 31, 2983-2992.

Wagenaar, H., Boelhouwers, E., Olthof, H., de Kok, H., Govers, H., Olie, K. 1996. Instability of octachlorodibenzofuran during analysis. Organohalogen Compounds 27, 397-402.

Watts, R.J., Smith, B.R., Miller, G.C., 1991. Catalyzed hydrogen peroxide treatment of octachlorodibenzo-*p*-dioxin (OCDD) in surface soils. Chemosphere 23, 949-955.

Wenborn, M., King, K., Buckley-Golder, D., Gascon, J.A. 1999. Releases of dioxins and furans to land and water in Europe. Final Report Issue 2. Produced for Landesumweltamt Nordrhein-Westfalen, Germany, on behalf of European Commission, DG Environment. AEA Technology Environment, Oxfordshire, UK.

WHO Temporary Adviser Group. 2000. Consultation on assessment of the health risk of dioxins: re-evaluation of the tolerable daily intake (TDI): executive summary. Food Addit. Contam.17, 223-240.

Wild, S.R., Harrad, S.J., Jones, K.C. 1992. Pentachlorophenol in the UK environment I: a budget and source inventory. Chemosphere 24, 833-845.

Wipf, H.K., Homberger, E., Neuner, N., Schenker, F. 1978. In Cattabeni, F., Cavallaro, A., and Galli, G., eds. *Dioxin – toxicological and chemical aspects.* SP Medical & Scientific Books, a division of Spectrum Publications, New York, USA. pp 201-217.

Witt, G., Schramm, K.W., Henkelmann, B. 1997. Occurrence and distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediments of the western Baltic Sea. Chemosphere 35, 1465-1473.

Wittich, R.-M. 1998. Degradation of dioxin-like compounds by microorganisms. Appl. Microbiol. Biotechnol. 49, 489-499.

Wong, A.S., Crosby, D.G. 1978. In Cattabeni, F., Cavallaro, A., and Galli, G., eds. *Dioxin – toxicological and chemical aspects.* SP Medical & Scientific Books, a division of Spectrum Publications, New York, USA. pp 185-189.

Wulff, F., Rahm, L., Jonsson, P., Brydsten, L., Ahl, T., Granmo, Ä. 1993. A mass balance of chlorinated organic matter for the Baltic Sea - A challenge for ecotoxicology. Ambio 22, 27-31.

Yan, Q., Kapila, S., Sivils, L.D., Elseewi, A.A. 1995. Effects of sensitizers and inhibitors on phototransformation of polychlorinated dibenzo-*p*-dioxins (PCDDs). Chemosphere 31, 3627-3634.

Yao, Y., Masunaga, S., Takada, H., Nakanishi, J. 2002. Identification of polychlorinated dibenzo-*p*-dioxin, dibenzofuran and coplanar polychlorinated biphenyl sources in Tokyo Bay, Japan. Environ. Toxicol. Chem. 21, 991-998.

Zhong, Y., Overcash, M.R., McPeters, A.L. 1993. Near sunlight zone model for photodegradation of TCDD in soils containing organic solvents. Chemosphere 26, 1263-1272.

Öberg, L.G., Rappe, C., 1992. Biochemical formation of PCDD/Fs from chlorophenols. Chemosphere 25, 49-52.