



INSTITUTE OF ENVIRONMENTAL PROTECTION

PENTACHLOROPHENOL

Dossier prepared in support of a proposal of pentachlorophenol to be considered as a candidate for inclusion in the Annex I to the Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants (LRTAP Protocol on POPs)

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**RISK PROFILE
OF PENTACHLOROPHENOL**

document prepared by

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Extended Summary

General features of PCP in relation to the indicative criteria outlined in Executive Body Decision 1998/2
It can be concluded that PCP in relation to the indicative criteria has characteristics outlined in the table below.

Criterion	Quantitative criterion to be matched	Remarks based on the literature reviewed in the dossier
Potential long-range atmospheric transport	half-life ≥ 2 days	<ul style="list-style-type: none"> vapour pressure: 0.0070 – 0.213 Pa (at 25°C) half-life of 58 days for degradation by hydroxyl radicals photolysis degradation rate up to a factor of 10 higher estimated transport distances of 1500-3000 km
Persistence in water, soil and sediment	half-life ≥ 2 months half-life ≥ 6 months	<ul style="list-style-type: none"> Half-life in water: far below 2 months Half-life in sediment and soil: far below 6 months
Bioaccumulation	Log Octanol/water part. coeff. (Log Kow) ≥ 5 BCF > 5000	<ul style="list-style-type: none"> Log Kow between 1.3 and 5.86, but strongly pH dependent. Recommended values in Mackay et al. Are 5.12 and 5.18 BCF < 5000
Toxicity		<ul style="list-style-type: none"> pentachlorophenol is highly toxic when ingested by humans; the probable oral lethal dose is 50 to 500 mg/kg for a 70-kg person. acute inhalation exposure to pentachlorophenol in humans may result in death from effects on the circulatory system and accompanying heart failure. other effects noted from acute inhalation exposure in humans include effects on the cardiovascular system, blood, liver (jaundice), and eyes (visual damage and irritation). animal studies have reported effects on the cardiovascular system, blood, liver, immune system, and central nervous system (CNS) from acute oral exposure no reproductive effects and teratogenic effects nonmutagenic or weakly mutagenic considered a possibly carcinogen (group 2b IARC) dioxins and furans formed during incineration of materials containing PCP
Ecotoxicity		<ul style="list-style-type: none"> highly toxic to many species of fish (LC₅₀: 0.1 - 205 µg/l)

Conclusions

- It is seen that pentachlorophenol is:
 - highly toxic for human when ingested by humans;
 - moderate to highly toxic to many species of fish;

- nonmutagenic or weakly mutagenic;
 - possibly carcinogenic to humans
2. There are no reproductive effects and teratogenic effects of PCP confirmed. PCP is considered a possible human carcinogen. Current evidence is not sufficient to definitely assess the potential of PCP to cause carcinogenic effects in humans.
 3. Pentachlorophenol is moderately toxic via the:
 - inhalation route,
 - dermal route.
 4. Purified PCP also did not produce toxic effects such as liver damage and immune system alterations, which had previously been reported for the technical product. The chronic toxicity observed may depend in large measure on the proportion of chlorodibenzo-p-dioxins present in the mixture.
 5. Data from animal studies indicate that the major target organs for PCP are the liver, kidneys, and central nervous system.
 6. Pentachlorophenol has been detected in surface waters and sediments, rainwater, drinking water, aquatic organisms, soils, and food, as well as in human milk, adipose tissue, and urine.
 7. General population exposure may occur through contact with contaminated environmental media, particularly in the vicinity of hazardous waste sites. Important routes of exposure appear to be inhalation of contaminated air, ingestion of contaminated groundwater used as a source of drinking water, ingestion of contaminated food and soils, and dermal contact with contaminated soils or products treated with the compound.
 8. The actual concentrations to which workers have been exposed are seldom measured but, where they have been monitored, they have been predictably high.
 9. Pentachlorophenol does not meet some of the criteria of the Protocol on POPs concerning half lives in water, soils and sediments.
 10. With some exceptions the BCF's values are below the threshold criterion. However it must be recognized that when determining BCFs for degradable chemicals, such as pentachlorophenol, the average exposure affecting uptake is likely much greater than the final concentration, which tends to inflate the BCF.
 11. One of the major metabolic pathways is the methylation of pentachlorophenol to the methylether of PCP (pentachloroanisole), the characteristics of the metabolic products relative to the indicative values have not been evaluated in this risk profile
 12. From the available information it is clear that the reduction in use and significant restrictions of use patterns, levels of PCP and its derivatives in the environment have declined rapidly over the last decade. However:
 - pentachlorophenol is a major source of dioxin, furans and hexachlorobenzene;
 - there is a large body of evidence regarding the negative impacts of pentachlorophenol on the environment and human health;
 - pentachlorophenol treated products and pentachlorophenol treatment plants are known major sources of PCP and also emission of dioxins, furans and hexachlorobenzene into the environment;
 - it is not feasible from a technical or economical point of view to control and contain dioxins, furans and hexachlorobenzene emissions from treatment plants and treated wood poles;
 - the only realistic way to achieve zero discharge for pentachlorophenol treated wood industry is to stop the use, distribution and sale of pentachlorophenol;
 - pentachlorophenol is banned or severely restricted in at least 26 countries around the world;
 - there are readily available alternatives to the use of pentachlorophenol treated wood (recycled steel, fiberglass, cement made without burning waste)
 - it is hard to invent risk mitigation measures to reduce effectively the human health and environmental impacts of the use of pentachlorophenol because of the persistent and bio-accumulative nature of the micro-contaminants (dioxins, furans, hexachlorobenzene).

Based on the information provided in this risk profile we conclude that pentachlorophenol fulfills the indicative values for long range transport and toxicity. The fulfillment of the indicate values for bioaccumulation is doubtfull and the indicative values for persistence are not met. The vapour pressure and the estimated transport distances indicate that pentachlorophenol is transported over long distances. The high toxicity for aquatic organisms and the toxicity for man through inhalation and uptake through the skin indicate the toxic potentials of PCP. Furthermore pentachlorophenol is categorized as a category 2b carcinogen. LogKow meets the indicative value of 5 in a number of cases, but strongly depends on pH. Recommended Log Kow values are 5.12 and 5.18 respectively. However, the bioaccumulation factor (BCF) does not meet the indicative value of 5000. Pentachlorophenol does not meet the indicative values for persistence for water, sediment and soil. These conclusions are based on the substance pentachlorophenol. To provide a complete picture of the risks of pentachlorophenol the metabolites (e.g. pentachloroanisole) should be considered as well. Consideration of the impurities in technical pentachlorophenol (e.g. dioxins, furans and hexachlorobenzene) may lead to another conclusion in meeting the indicative values.

List of abbreviations

ATSDR	- Agency for Toxic Substances and Disease Registry
BAF	- Bioaccumulation Factor
BCF	- Bioconcentration Factor
CEG	- Criteria Expert Group
CNP	- chloronitrophen
EC ₅₀	- Concentration of a drug which induces a response halfway between the baseline and maximum
HCB	- hexachlorobenzene
HpCDD	- heptachlorodibenzo- <i>p</i> -dioxin
HxCDD	- hexachlorodibenzo- <i>p</i> -dioxin
IDLH	- Immediately Dangerous to Life or Health level
LC ₅₀	- Air concentration lethal to 50% of the test population
LD ₅₀	- Oral dose lethal to 50% of the test population
LOAEL	- Lowest Observed Adverse Effect Level
LOEL	- Lowest Observed Effects Level
NaPCP	- sodium pentachlorophenolate
NIOSH	- National Institute for Occupational Safety and Health
NOAEL	- No Observed Adverse Effect Level
NOEL	- No Observed Effects Level
OCDD	- octachlorodibenzo- <i>p</i> -dioxin
OCDF	- octachlorodibenzofuran
PCBs	- Polychlorinated biphenyls
PCDDs	- Polychlorinated dibenzo- <i>p</i> -dioxins
PCDFs	- Polychlorinated dibenzofurans
PCP	- pentachlorophenol
PCPL	- pentachlorophenyl laurate
pK _a	- dissociation coefficient
POPs	- Persistent Organic Pollutants
PTF	- Pentachlorophenol Task Force
TCDD	- Tetrachlorodibenzo- <i>p</i> -Dioxin
TDI	- Theoretical Daily Intake
TEF	- Toxic Equivalent Factors
TEQ concentration	- toxic equivalency concentration
TOC	- ratio of Total Organic Carbon
USEPA	- United States Environmental Protection Agency
WHO	- World Health Organization

Introduction

There exists a similarity in environmental toxicity, fate and behaviour profiles of Pentachlorophenol (PCP) and PCP's salt Sodium pentachlorophenate (NaPCP). Furthermore NaPCP degrades to PCP under favourable environmental conditions (depending on the acid-base status of the environment). At present the most extensive use of PCP is the production of PCP's ester Pentachlorophenyl laurate (PCPL). Therefore the document includes the assessment of PCP, NaPCP and PCPL.

A significant part of the information included in the report is extracted from the following comprehensive overviews on PCP and its salts:

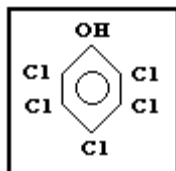
- IPCS - Inchem. International Programme on Chemical Safety, Environmental Health Criteria 71. Pentachlorophenol.
- Toxicological Profile for Pentachlorophenol Prepared By Syracuse Research Corporation for U.S. Department of Health And Human Services, Public Health Service Agency for Toxic Substances and Disease Registry, 1999.
- Draft OSPAR Background Document on Pentachlorophenol.
- FAO/U1NEP Joint Programme for the Operations of Prior Inform Consent. Prior Informed Consent Decision Guidance Document. Pentachlorophenol, 1996.
- Toxicological Profile For Pentachlorophenol, U.S. Department Of Health And Human Services; Public Health Service Agency for Toxic Substances and Disease Registry, 2001.
- WHO, Convention Task Force on The Health Aspects of Air Pollution. Health Risks Of Persistent Organic Pollutants From Long-Range Transboundary Air Pollution, 2003.
- Comments of E. John Wilkinson , Pentachlorophenol Task Force, 2002
- Kenneth M. Brooks, Ph.D. Aquatic Environmental Sciences for Western Wood Preservers Institute, Computer Model and Assessment of the Potential Environmental Risks Associated with Pentachlorophenol Treated Wood Products Used in Aquatic Environments, 2001.
- Brooks, Kenneth M. 2000. Assessment of the environmental effects associated with wooden bridges preserved with creosote, pentachlorophenol, or chromated copper arsenate. Res. Pap. FPL–RP–587. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 100 p.
- National Park Service Water Resources Divisions. Water Operations Branch. Environmental Contaminants Encyclopedia Pentachlorophenol (Pcp) Entry July 1, 1997.
- Borysiewicz M., Kolsut W. Institute of Environmental Protection. Draft Dossiert on PCP. Preliminary Risk Profile Pentachlorophenol, 2002.
- Assessment Report on Pentachlorophenol for Developing Ambient Air Quality Objectives prepared for Alberta Environment by WBK & Associates Inc., March 2004.

PART I. RISK PROFILE

A. IDENTITY

- Pentachlorophenol (PCP)

Chemical structure:



Formula: C_6Cl_5OH

CAS registry number: 87-86-5

CAS chemical name: pentachlorophenol

RTECS number: SM6300000

UN Number: UN2671, UN2762, UN2995, NA2020

Common Synonyms/ Tradenames Acutox; Chem-Penta; Chlon; Chlorophen; Cryptogil Oil; Cryptogil OL; Dow Pentachlorophenol DP-2 Antimicrobial; Dowcide 7; Dowicide 6; Dowicide 7; Dowicide 7 Antimicrobial; Dowicide EC-7; Dura Treet II; Durotox; EP 30; EPA Pesticide Chemical Code 063001; Forpen-50 Wood Preservative; Fungifen; GlazdPenta; Grundier Arbezol; 1-hydroxypentachlorobenzene; Lauxtol; Lauxtol A; Lioprem; Ontrack We Herbicide; Ortho Triox Liquid Vegetation Killer; Osmose Wood Preserving Compound; PCP; Penchlorol; Penta; Penta Concentrate; Penta Ready; Penta WR; Pentachlorophenate; 2,3,4,5-pentachlorophenol; Pentachlorophenol, Dowicide EC-7; Pentachlorophenol, DP-2; Pentachloropheno, Technical; Pentachlorophenol; Pentacon; Penta-kil; Pentasol; Penwar; Peratox; Permicide; Permagard; Permasan; Permatox DP-2; Permatox Penta; Permite; Prevenol; Prilttox; Santobrite; Santophen; Santophen 20; Sinithuo; Term-I-Trol; Thompson's Wood Fix; Watershed Wood Preservative; Weed and Brush Killer; Weedone; Witophen P; Woodtreat; Woodtreat A

Mode of action as pesticide:

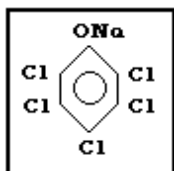
It is widely believed that pentachlorophenol affects uncoupling mitochondrial oxidative phosphorylation, thereby causing accelerated aerobic metabolism and increasing heat production. It causes loss of membrane electrical resistance.

Impurities in pentachlorophenol:

Technical PCP has been shown to contain a large number of impurities, depending on the manufacturing method. These consist of other chlorophenols, particularly isomeric tetrachlorophenols, and several microcontaminants, mainly polychlorodibenzodioxins (PCDDs), polychlorodibenzofurans (PCDFs), polychlorodiphenyl ethers, polychlorophenoxyphenols, chlorinated cyclohexenons and cyclohexadienons, hexachlorobenzene, and polychlorinated biphenyls (PCBs). Technical grade PCP is typically about 86% pure.

- Sodium pentachlorophenate (Na-PCP)

Chemical structure:



Formula: C_6Cl_5ONa ,
 $C_6Cl_5ONa \times H_2O$ (as monohydrate).

CAS registry number: 131-52-2 (Na-PCP),
27735-64-4 (Na-PCP monohydrate),

RTECS number: SM6490000

Common synonyms: penta-ate; pentachlorophenate sodium; pentachlorophenol sodium salt; pentachlorophenoxy sodium; pentaphenate; phenol, pentachloro-, sodium derivative monohydrate; sodium PCP; sodium pentachlorophenate; sodium pentachlorophenolate; sodium pentachlorophenoxide.

Registered trade names:

For 37% aqueous solution: Dow Dormant Fungicide; Dowicide G; Dowicide
For polymeric form: G-St; Mystox D; Napclor-G; Santobrite; Sapco25 Weedbeads

Physical and Chemical Properties

Pure pentachlorophenol consists of light tan to white, needle-like crystals and is relatively volatile. It is soluble in most organic solvents, but practically insoluble in water at the slightly acidic pH generated by its dissociation (pK_a 4.7). At room temperature, pentachlorophenol is a colourless crystalline solid with a phenolic odour [Kidd, H. and James, D.R.,1991]. Colour may vary from white to dark greyish brown, depending on the purity of the compound [Kidd, H. and James, D.R.,1991]; decomposes on heating in the presence of water, forming corrosive fumes (hydrochloric acid); not flammable and non-corrosive in unmixed; state; dissolved in oil, it causes deterioration of rubber. At the approximately neutral pH of most natural waters, PCP is more than 99% ionised.

Pentachlorophenate sodium can be in the form of tan powder, pellets, or briquettes with phenolic odour; decomposes on heating, forming toxic fumes (chlorides and sodium oxide).

Table I.A.1. Physical and Chemical Properties of Pentachlorophenol
 (Source: Assessment Report on Pentachlorophenol for Developing Ambient Air Quality Objectives prepared for Alberta Environment by WBK & Associates Inc., March 2004)

Property	Value	Reference
Molecular Weight	266.34	Lide, 2002
Physical state	White monoclinic crystalline solid Technical grade dark gray to brown	Verschueren, 2001
Melting Point	174 °C	Lide, 2002
Boiling Point	310 °C (decomposes)	Lide, 2002
Specific gravity (liquid)	1.978 (at 22°C)	Lide, 2002
Specific gravity (gas) (air =-1)	9.20	Verschueren, 2001
Vapour pressure	2 mPa (at 20°C) 0.0070 – 0.213 Pa (at 25°C)	Verschueren, 2001; Howard, 1991 Mackay et al, 2006
Solubility in water	Slightly soluble in water 0.13% (% weight at 25°C) 5 mg/l at 0°C 14 mg/l at 20°C 35 mg/l at 50°C 14 mg/l at 25°C	Lide, 2002 Lide, 2002 Verschueren, 2001 Mackay et al, 2006 recommended value IUPAC
Solubility	Soluble in benzene, very soluble in ethanol and ether	Lide, 2002
dissociation coefficient pK _a	4.60-5.30	Mackay <i>et al</i> , 1992
Henry's Law Constant	2.75x10 ⁻⁶ atm.m ³ .mol ⁻¹ 0.0248 to 0.284 Pa.m ³ .mol ⁻¹	Howard, 1991 Mackay <i>et al</i> , 1992
Octanol water partition coefficient (log K _{ow})	5.07 4.07; 5.01 5.18 5.12	Lide, 2002 Verschueren, 2001 Mackay et al 2006, recommended value Mackay et al 2006, recommended value
Organic carbon partition coefficient (K _{oc})	293 to 900 (at 0.0125 mg/l) 1000 (calculated) 3000 to 4000 (measured)	Verschueren, 2001 Howard, 1991 Howard, 1991
Flash Point	Not flammable	Weiss, 1986
Explosive limits	No data	ATSDR,2001
Autoignition temperature	Not flammable	Weiss, 1986
Odour threshold	0.857 mg/l at 30°C (in water) 12.0 mg/l at 60°C (in water)	Verschueren, Hoak cited in ATSDR, 2001
Conversion factors for vapour fat 25 °C and 101.3 kPa)	1 mg/m ³ = 0.09 ppm lppm= 11.1 mg/m ³	Verschueren, 2001

B. PCP CHARACTERISTICS

1. Potential for long-range atmospheric transport

Pentachlorophenol has been detected associated with particulate matter in air. This pentachlorophenol will be lost by gravitational settling. Vapour phase pentachlorophenol will be lost by photolysis and to a lesser extent, reaction with photochemically produced hydroxyl radicals. The loss from these process in noon-day summer sunshine is 6.2 and 1.5%hr, respectively.

Pilot calculations of PCP transport from Hungarian and United Kingdom emission sources were performed by EMEP. Fig. I.B.1.1. and I.B.1.2. present pilot calculations of PCP transport from Hungarian and United Kingdom emission sources [Shatalov et al., 2002]. PCP emissions are adapted from Berdowski et al. 1997. From these figures it can be seen that PCP is capable of being transported over considerable distances.

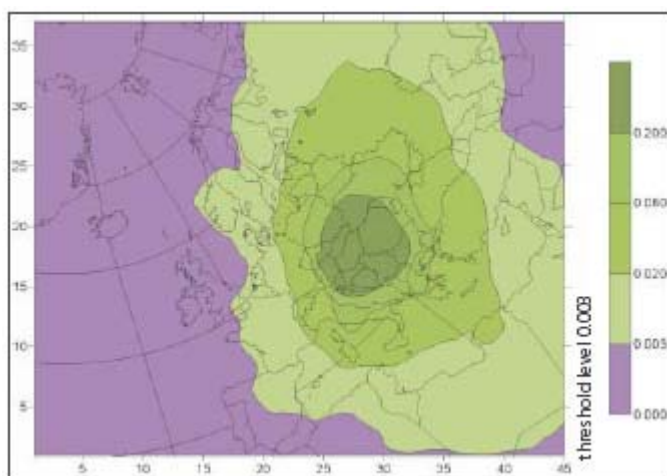


Fig. I.B.1.1. Spatial distribution of PCP air concentrations (ng/m³) from Hungarian emission sources for 1990 [Berdowski et al. 1997]. Violet means concentrations less than the 0.003 ng/m³ threshold level [Shatalov et al. 2002].

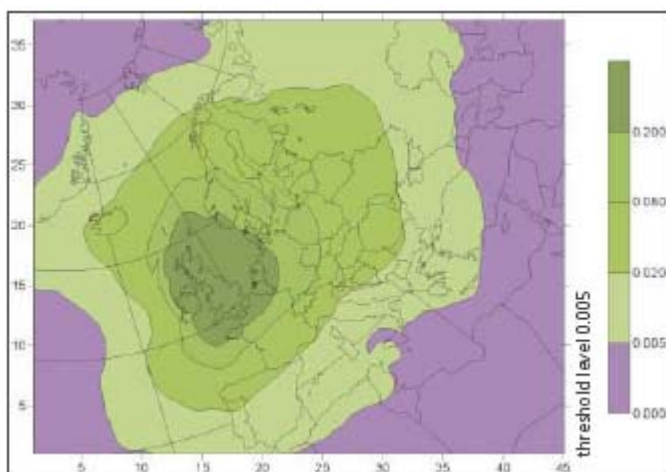


Fig. I.B.1.2. Spatial distribution of PCP air concentrations (ng/m³) from United Kingdom emission sources for 1990 [Berdowski et al. 1997]. Violet means concentrations less than the 0.005 ng/m³ threshold level.

Similar results were presented by Duchak et al (2002) at an OECD meeting on multimedia models for estimating overall environmental persistence. The model estimations resulted in transport distances of 1500-3000 km and an average half-life time in the environment equal to about 1.5 months.

From these calculations it can be seen that PCP is capable of being transported over considerable distances.

Concerning measurements in biota as evidence of transport to remote regions, the situation is complicated for two main reasons. On the one hand, PCP is metabolized into other molecules and therefore its absence in animal tissues is not conclusive; on the other hand, it is a major product of the metabolism of common pesticides in mammals, and therefore if it is found it does not mean it was taken up as such.

Infants from Inuit and local fishermen populations in Quebec are contaminated with PCP, [Sandau C.D. et al., 2002] indicating polluted marine food diets and/or ongoing HCB exposure and metabolism. Levels of PCP have been linked to fish consumption in Latvian and Swedish men [Sjoedin A. et al., 2000]. The first peer-reviewed scientific studies of PCP in sub-arctic wildlife came out in 2004 and showed contamination of the eggs of 4 Norwegian bird-of-prey species – golden eagles, ospreys, peregrine falcons, and white-tailed sea eagles. A breakdown product of PCP has been found in Canadian arctic snow [Welch H.E. et al., 1991] and lake sediments [CACAR II, 2003], indicating likely long-range transport of this chemical to remote regions.

2. Toxicity and Ecotoxicity

2.1. Toxicity

Acute Human Effects

The occupational IDLH value and acute effects concentrations for occupational exposures are presented in Table I.B.2.1.

Table I.B.2.1. Effects Associated with Acute Inhalation Exposure (Occupational) to Pentachlorophenol (Humans) (Source: Assessment Report on Pentachlorophenol for Developing Ambient Air Quality Objectives prepared for Alberta Environment by WBK & Associates Inc., March 2004)

Effects Reported	Exposure Period	Air Concentration mg/m ³ (ppm) ^a	Reference
Immediately dangerous to life and health	8 hour time-weighted average (occupational)	2.5 (0.2)	NIOSH, 1996
Severe effects on eyes and upper respiratory tract	8 hour time-weighted average (occupational)	1 (0.09)	Deichmann and Keplinger, 1981; ACGIH. 1986; NIOSH, 1996
Severe irritation to nose, throat and eyes	8 hour time-weighted average (occupational)	0.3 (0.03)	Deichmann and Keplinger, 1981; ACGIH. 1986; NIOSH, 1996

^a 1 ppm = 10.9 mg/m³. Based on PC MW of 266.32 and the formula: mg/m³ = ppm x (MW/24.45) for chemicals in air at 25°C and 101.3 kPa (760mmHg), [Plog *et al*, 1996].

Pentachlorophenol has been classified in the European Union as R24/25, toxic in contact with skin and if swallowed, R26, very toxic by inhalation and R36/37/38, irritating to eyes, respiratory system and skin (EC, 1993).

Acute and Sub-Acute Animal Effects

Animal data for the acute effects of inhalation exposure to pentachlorophenol were limited to two studies of lethal air concentrations (LC₅₀ values) for sodium pentachlorophenol in rats [Hoben *et al.* cited in WHO, 1987] and mice [Demidenko cited in WHO, 1987]. The available LC₅₀ values are presented in Table I.B.2.2.

Table I.B.2.2. Lethal Concentrations for Acute Inhalation Exposure to Pentachlorophenol (Experimental Animals). (Source: Assessment Report on Pentachlorophenol for Developing Ambient Air Quality Objectives prepared for Alberta Environment by WBK & Associates Inc., March 2004)

Effects Reported	Exposure Period	Air Concentration mg/m ³ (ppm) ^a	Species	Reference
Death (LC ₅₀)	45 minutes	14 (1.3)	Rats	Hoben <i>et al.</i> cited in ATSDR 2001.

Effects Reported	Exposure Period	Air Concentration mg/m ³ (ppm) ^a	Species	Reference
Death (LC ₅₀)	Not reported	355 (32.6)	Rat	Demidenko cited in WHO, 1987.
Death (LC ₅₀)	Not reported	225 (20.6)	Mouse	Demidenko cited in WHO, 1987.

^a 1 ppm = 10.9 mg/m³. Based on PC MW of 266.32 and the formula: mg/m³ = ppm x (MW/24.45) for chemicals in air at 25°C and 101.3 kPa (760mmHg) [Plog *et al.*, 1996].

Acute oral exposure studies reported LC₅₀ values ranging :

- from 80 to 120 mg/kg in rats, and
- from 117 to 177 mg/kg in mice,

[St. Omer and Gadusek cited in ATSDR, 2001; Borzelleca *et al.* cited in WHO, 1987; Renner *et al.* cited in ATSDR, 2001].

Age-related sensitivity was reported for rats with the lowest of the LD₅₀ ranges being:

- 50 mg/kg for preweaned rats,
- 80 mg/kg for adult rats, and
- 220 mg/kg for juvenile rats

[St. Omer and Gadusek cited in ATSDR, 2001].

Based on these results and the LC₅₀ identified for rats (14 mg/m³ or 11.7 mg/kg) by Hoben *et al.*, [cited in WHO, 1987], sodium pentachlorophenol is significantly more toxic via inhalation than ingestion [WHO, 1987].

Two studies on sub-acute effects in animals following inhalation were identified [Ning *et al.* cited in WHO, 1987; Demidenko cited in WHO, 1987]. The NOAELs and LOAEL's associated with the effects reported in these studies are presented in Table I.B.2.3.

Table I.B.2.3. NOAELs and LOAELs for Sub-acute Inhalation Exposure to Pentachlorophenol (Experimental Animals) (*Source*: Assessment Report on Pentachlorophenol for Developing Ambient Air Quality Objectives prepared for Alberta Environment by WBK & Associates Inc., March 2004)

Effects Reported	Exposure Period	Air Concentration mg/m ³ (ppm) ^a	Species	Reference
Haematological:				
LOAEL	4hr/d,	21.4 (1.9)	Rabbits	Ning <i>et al.</i> cited in WHO, 1987.
NOAEL	6d/wk,	3.1 (0.3)		
Increased serum-gamma-globulin, hyperglycaemia	4 mo			
NOAEL	4hr/d,	21.4 (1.9)	Rabbits	Ning <i>et al.</i> cited in WHO, 1987.
Increased alpha-globulin, beta-globulin or serum albumin	6d/wk, 4 mo			
LOAEL	4hr/d,	2.97 (0.3)	Rats and Rabbits	Demidenko cited in WHO, 1987.
Anemia, leukocytosis, eosinophilia, hyperglycaemia	4 mo			
Lung:				
LOAEL	4hr/d,	21.4 (1.9)	Rats and Rabbits	Ning <i>et al.</i> cited in WHO, 1987.
NOAEL	6d/wk,	3.1 (0.3)		
Increased lung weight	4 mo			

Effects Reported	Exposure Period	Air Concentration mg/m ³ (ppm) ^a	Species	Reference
Liver:				
LOAEL Increased liver weight	4hr/d, 6d/wk, 4 mo	3.1 (0.3)	Rabbits	Ning <i>et al.</i> cited in WHO, 1987.
LOAEL NOAEL Increased liver weight	4hr/d, 6d/wk, 4 mo	21.4 (1.9) 3.1 (0.3)	Rats	Ning <i>et al.</i> cited in WHO, 1987.
LOAEL Dystrophic processes in liver	4hr/d, 4 mo	2.97 (0.3)	Rats and Rabbits	Demidenko cited in WHO, 1987. ^b
Kidney:				
LOAEL NOAEL Increased kidney weight	4hr/d, 6d/wk, 4 mo	21.4 (1.9) 3.1 (0.3)	Rats	Ning <i>et al.</i> cited in WHO, 1987.
Adrenal gland:				
LOAEL NOAEL Increased adrenal gland weight	4hr/d, 6d/wk, 4 mo	21.4(1.9) 3.1 (0.3)	Rats	Ning <i>et al.</i> cited in WHO, 1987.

^a 1 ppm = 10.9 mg/m³. Based on PC MW of 266.32 and the formula: mg/m³ = ppm³ x (MW/24.45) for chemicals in air at 25°C and 101.3 kPa (760mmHg) (Plog *et al.*, 1996).

The World Health Organization (1987) has indicated that pentachlorophenol is more toxic via the inhalation versus oral route of exposure. Kunde and Bohme (cited in WHO, 1987) used the LOAEL concentration of 2.97 mg/m³ (liver and blood effects in rats and rabbits) reported by Demidenko (cited in WHO, 1987) to calculate an effective daily dose of 0.3 mg/kg body weight per day for rats (assuming 100% uptake and absorption). In a recent summary of sub-acute oral studies in rats (from 28 days to 8 months), the lowest comparable LOAEL value (for increased liver and kidney weights) was 2 mg/kg body weight per day for >99% pure pentachlorophenol given twice a week for 28 weeks [Blakley *et al.* cited in ATSDR, 2001], still nearly 10 times higher than the calculated dose received via inhalation.

Chronic Human Effects

Much research on PCP has been performed with poorly characterized technical material, and the chronic toxicity observed may depend in large measure on the proportion of chlorodibenzo-p-dioxins present in the mixture [Gasiewicz, T. A., 1991]. Pure PCP, and also technical PCP without dioxin contamination, produced only slight enlargement of livers and kidneys Gasiewicz, T. A., 1991]. Purified PCP also did not produce toxic effects such as liver damage and immune system alterations, which had previously been reported for the technical product.

In humans, the most common exposure to PCP is inhalation in the workplace. Abdominal pain, nausea, fever, and respiratory irritation, as well as eye, skin, and throat irritation, may result from such exposure [Wagner, S. L., 1981], while very high levels may cause obstruction of the circulatory system in the lungs and cause heart failure [Wagner, S. L., 1981]. Survivors of toxic exposures may suffer permanent visual and central nervous system damage [Wagner, S. L., 1981]. Persons regularly exposed to PCP tend to tolerate higher levels of PCP vapours than persons having little contact with these vapours [Wagner, S. L., 1981; U.S. Agency for Toxic Substance and Disease Registry, 1992].

PCP air concentrations (or ranges of concentrations) and effects reported following occupational exposures are summarized in Table I.B.2.4.

Table I.B.2.4. Effects Associated with Chronic Inhalation Exposure (Occupational) to Pentachlorophenol (Humans)
(Source: Assessment Report on Pentachlorophenol for Developing Ambient Air Quality Objectives prepared for Alberta Environment by WBK & Associates Inc., March 2004)

Effects Reported	Exposure Period	Air Concentration mg/m ³ (ppb) ^a	Reference
Liver Effects: Elevated activities of serum-aminotransferases and alpha-glutamyl transpeptidase	3 years (avg) 0.5 to 12 years (range)	2.4 (0.22) (avg) 0.3 to 8 (0.028 - 0.73) (range)	Zober <i>et al.</i> cited in WHO, 1987.
Hepatotoxic effects in humans	Chronic	0.8 (0.073)	Hassauer <i>et al.</i> cited in RIVM2001.
Neurological Effects: No effects on motor or sensory nerve conduction velocities	16 years (avg) 4 to 24 years (range)	0.3 to 180 (0.028 to 17) (range)	Triebig <i>et al.</i> , 1987
Genotoxic Effects: No effect on chromosomal aberrations or sister chromatid exchange	3 to 34 years (range)	1.2 to 180 (0.11 to 17) (range)	Ziensen <i>et al.</i> cited in HSDB, 2002.
^a 1 ppb = 10.9 mg/m ³ . Based on PC MW of 266.32 and the formula: mg/m ³ = ppm x (MW/24.45) for chemicals in air at 25°C and 101.3 kPa (760mmHg) [Plog <i>et al.</i> , 1996].			

Chronic Animal Effects

In the data reviewed, no chronic animal PCP inhalation studies were identified. Due to the lack of inhalation data, several key ingestion studies were identified. Examples of the lowest NOAELs and LOAELs for liver and kidney, endocrine, reproductive, developmental and carcinogenic effects are briefly summarized below in Table I.B.2.5. The use of pure or technical grade pentachlorophenol was documented where the information was provided.

Table I.B.2.5. Examples of NOAELs and LOAELs Associated with Chronic Ingestion of Pentachlorophenol (Experimental Animals) (Source: Assessment Report on Pentachlorophenol for Developing Ambient Air Quality Objectives prepared for Alberta Environment by WBK & Associates Inc., March 2004)

Effects Reported	Exposure Period	Dose Rate (mg/kg body weight/day)	Species	Reference
Liver and Kidney Effects:				
NOAEL	2 years	3 technical grade (90% pure)	rat	Schwetz <i>et al.</i> cited in ATSDR, 2001.
Increase in relative liver and kidney weights	28 day	2 (>99% pure)	rat	Blakley <i>et al.</i> cited in ATSDR, 2001.
Endocrine Effects:				
LOAEL Significantly decreased serum thyroxine concentrations	3 weeks prior to mating and throughout gestation and lactation	1	mink	Beard and Rawlings cited in ATSDR 2001.

Effects Reported	Exposure Period	Dose Rate (mg/kg body weight/day)	Species	Reference
Developmental Effects:				
LOAEL Delayed ossification of the skull	9 days (gestation)	5 (97.5% pure)	rats	Schwetz <i>et al.</i> cited in ATSDR 2001.
Reduced pup weight	70 days pre-mating through gestation and lactation	10	rats	Bernard <i>et al.</i> cited in ATSDR 2001.
Impaired development of reproductive system	70 days pre-mating through gestation and lactation	60	rats and rabbits	Bernard <i>et al.</i> cited in ATSDR 2001.
Reproductive Effects:				
NOAEL No histological alterations in reproductive tissues	2 years	30 (99% pure)	rats	Chhabra <i>et al.</i> , 1999, NTP cited in ATSDR, 2001.
NOAEL No significant reproductive effects	5 weeks prior to mating and throughout gestation & lactation	1	sheep	Beard <i>et al.</i> cited in ATSDR, 2001.
LOAEL Decreases in the proportion of mated females accepting a second mating and mink that whelped; increased severity of cystic uterine glands	3 weeks prior to mating and throughout gestation & lactation	1	mink	Beard <i>et al.</i> cited in ATSDR, 2001.
Carcinogenic Effects:				
LOAEL Significant increases in the incidence of hemangiosarcomas, liver adenomas and carcinomas, and adrenal gland pheochromocytomas	2 years	17.5 technical grade (90% pure)	mice	NTP cited in ATSDR, 2001.
LOAEL Mesotheliomas and nasal squamous cell carcinomas	52 weeks	60 (99% pure)	rats	Chhabra <i>et al.</i> , NTP cited in ATSDR, 2001.

Reproductive effects and teratogenic effects

The experiments carried with rats indicate that PCP does not cause reproductive effects [Gasiewicz, T.A., 1991]. They also indicate that it is unlikely that PCP has teratogenic effects in humans at normal exposure levels.

Mutagenic effects

PCP is not mutagenic in bacteria or houseflies, but is weakly mutagenic in mice and may be mutagenic in yeast [U.S. Agency for Toxic Substance and Disease Registry, 1992]. Weak mutagenic effects were seen in human lymphocyte cultures exposed to PCP [U.S. Agency for Toxic Substance and Disease Registry, 1992]. The evidence suggests that PCP is nonmutagenic or weakly mutagenic.

Carcinogenic effects

No convincing evidence of PCP's carcinogenic effects in humans is available [U.S. Agency for Toxic Substance and Disease Registry, 1992]. Current evidence is not sufficient to assess the potential of PCP to cause carcinogenic effects in humans. Studies of two formulated PCP products (Dowcide and Penta) showed increases in cancers of the spleen, liver, and adrenal gland in test mice or rats at doses of about 17 to 18 mg/kg/day [U.S. Agency for Toxic Substance and Disease Registry, 1992]. These findings were not replicated for Dowcide in mice in a second study [U.S. Agency for Toxic Substance and Disease Registry, 1992]. There have been reports of a possible association between occupational exposures to technical PCP and Hodgkin's disease, acute leukemia, and soft-tissue sarcoma, but confounding factors such as concurrent exposure to other substances makes interpretation of these data problematic [U.S. Agency for Toxic Substance and Disease Registry, 1992].

The European Union classified penta-chlorophenol as R40: limited evidence of a carcinogenic effect (EC, 1993). The International Agency for Cancer Research (IARC) considers pentachlorophenol possibly carcinogenic to humans (group 2b). This conclusion was based on the fact that there was inadequate evidence in humans, but sufficient evidence in experimental animals for the carcinogenicity of penta-chlorophenol [IARC, 1991].

2.2. Ecotoxicity

Effects on birds

The reported 5-day dietary LC₅₀ value in Japanese quail is greater than 5139 mg/kg [Hill et al 1975]. LC₅₀ values reported by Hill et al [1975] for northern bobwhite, pheasant and mallard duck varied between 3400 and 4500 mg/kg food. Reported acute oral LD₅₀ values for PCP are 380 mg/kg BW in mallard duck and 504 mg/kg BW in pheasant [Hudson et al., 1984]. Vermeer et al. [1974] found 50 dead snail kites (*Rostrhamus sociabilis*) after extensive application of Na-PCP as a molluscicide in Surinam rice fields. High PCP residues were found in the brain (mean, 11.3 mg/kg wet weight), liver (46.6 mg/kg), and kidney (20.3 mg/kg) of dead snail kites which had probably ingested Na-PCP contaminated snails.

Nesting of Canary (*Serinus canarius*) on straw containing 285 mg/kg PCP resulted in reduced hatch, high mortality of young during the first week and non surviving to the age of 3 months [Dorrestein and Zelle, 1979]. Sublethal effects occur at levels lower than those mentioned above. Poultry were fed graded levels (0, 1, 10, 100, and 1000 mg/kg) of pentachlorophenol (PCP) containing less than 0.0023% octachlorodibenzo-p-dioxin (OCDD) for 8 weeks. Kidney weights were significantly increased by the 100 mg/kg and 1000 mg/kg PCP diet. Weights of all other organs including the body weights were significantly lowered by the 1000 mg/kg PCP. Hatching of eggs was reduced by 50% at a dose of 50mg/kg egg and none hatched at 100 mg/kg diet [Stedman et al, 1980].

Pentachlorophenol toxicity in aquatic environments

Pentachlorophenol is known to uncouple oxidative phosphorylation, inhibiting ATP pathways important to respiration in both animal and plant cells. Moreland and Hilton (1976) described pentachlorophenol as a more general inhibitory uncoupler. They suggest that it has several sites of action, including photophosphorylation, protein synthesis and lipid biosynthesis [Morrod, 1976]. All of the mechanisms of penta's toxicity have not been precisely defined, but may generally involve the disruption of cellular membranes [Jayaweera, et al. 1982; Senger and Ruhl 1980; and Smejtek et al. 1983].

Toxicity data were provided in a report by Eurochlor for the Marine Environment [Eurochlor 1999]. Acute LC₅₀ values for fish species ranged from 20 µg/l to 600 µg/l pentachlorophenol. Acute LC₅₀ values for sensitive invertebrates including species of Daphnia, lymnaeid snails, and oligochaetes ranged from 240 µg/l to 2,000 µg/l. These data suggest that fish are somewhat more sensitive than invertebrates to pentachlorophenol. Acute (96-hour) EC₅₀ values for aquatic plants ranged from 80 µg/l to 7,000 µg/l. Lowest chronic NOECs in the

Eurochlor report varied between 2 µg/l and < 15 µg/l PCP with freshwater fish showing the lowest value [Eurochlor 1999]. These findings are supported by the data provided below.

Pentachlorophenol has been classified with the risk phrase R50/53, very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment, by the European Union (EC, 1993).

Acute toxicity

Pentachlorophenol interferes with the oxidative phosphorylation by uncoupling the production of adenosine triphosphate from adenosine diphosphate. As this process provides the energy source for cellular metabolism in most organisms, pentachlorophenol is a broad-spectrum biocide. A common measure of acute toxicity is the concentration of a toxicant that causes 50% mortality in a test population within some specified period of time (often 96 hours). This parameter is referred to as the 96-hr LC₅₀. Eisler (1989) summarized 96-hr LC₅₀ concentrations for aquatic organisms. For most freshwater species, the 96-h LC₅₀ varied between 100 and 2,000 µg penta/l. In general, Eisler's (1989) data suggest that freshwater vertebrates (fish) are more sensitive than invertebrates.

Table I.B.2.6. summarizes the lower LC₅₀ values provided by Eisler (1989) for salmonids and centrarchids. Salmonids of the genus *Oncorhynchus* appear most sensitive. In contrast, invertebrate LC₅₀ values are typically above 100 µg/l.

Table I.B.2.6. Acute toxicity of freshwater fish to pentachlorophenol (96-h LC₅₀) reported in Eisler (1989).

Species	Concentration (µg PCP/l)
<i>Oncorhynchus mykiss</i> (rainbow trout)	34 to 121
<i>Oncorhynchus nerka</i> (sockeye salmon)	63 to 68
<i>Oncorhynchus tshawytscha</i> (chinook salmon)	68 to 78
<i>Salvelinus fontinalis</i> (brook trout)	128
<i>Lepomis macrochirus</i> (bluegill)	120 to 350
<i>Micropterus salmoides</i> (largemouth bass)	136 to 287
<i>Salmo salar</i> (Atlantic salmon)	500

Chronic toxicity of pentachlorophenol in aquatic organisms

Pentachlorophenol can have more subtle effects that are important to the competitiveness of individuals in natural environments and to the sustainability of populations of organisms. Numerous endpoints are evaluated in assessing chronic effects (see table below). Most commonly, these endpoints involve reproduction and/or growth.

Table I.B.2.7. No Observed Effects Level (NOEL) and Lowest Observed Effects Level (LOEL) associated with pentachlorophenol in freshwater environments. All pentachlorophenol values are in µg PCP/l

Endpoint	Duration	Species	NOEL	LOEL	pH	Temp	EPA Chronic
Reproduction; number viable eggs	16	<i>Lymnaea stagnalis</i> (snail)	50	NR	8.0	18.3	46.5
Larval Survival and reproduction	10 – 28	American Flagfish	55	102	6.95	25	5.4
Biomass & mortality, eggs at 10°C alevins at 15 °C; fry at 20 °C	>28	<i>Oncorhynchus mykiss</i>	10.9	25	8.0	10-20	15.6
Hatchability, survival & growth	32	<i>Pimephales promelas</i>	16.5	34.6	6.5	25	3.5
Survival & growth (fry & juveniles)	90	<i>Pimephales promelas</i>	6	13	7.4	25	8.6
Survival & growth (fry & juveniles)	90	<i>Pimephales promelas</i>	36	85	7.4	25	8.6
Survival & growth (fry & juveniles)	90	<i>Pimephales promelas</i>	>130	>130	9.4	25	63.9
Early life stage hatchability, survival & growth	32	<i>Pimephales promelas</i>	44.9	73	7.55	25	10.0
Hatchability survival & growth	32	<i>Pimephales promelas</i>	63.7	125	8.5	25	25.9
Hatchability survival & growth	32	<i>Pimephales promelas</i>	27.6	58.2	7.5		9.5
Hatchability survival & growth	32	<i>Pimephales promelas</i>	32	75	8.0		15.6

Endpoint	Duration	Species	NOEL	LOEL	pH	Temp	EPA Chronic
Growth	56	<i>Chaetogammarus marinus</i>	100	NR	8.0	NR	15.6
Number of viable oocytes	18	<i>Oncorhynchus mykiss</i>	11	19	7.4	12	8.6
Number of viable oocytes	18	<i>Oncorhynchus mykiss</i>	12	22	7.5	12.5	9.5
Reproduction	21	<i>Daphnia magna</i>	180	320	8.0	20	15.6

Source: Kenneth M. Brooks, Aquatic Environmental Sciences for Western Wood Preservers Institute. Literature Review, Computer Model and Assessment of the Potential Environmental Risks Associated with Pentachlorophenol Treated Wood Products Used in Aquatic Environments, 2001

Pentachlorophenol toxicity to aquatic plants

Smith *et al.* (1987) investigated the toxicity of pentachlorophenol to *Selenastrum capricornutum* as a function of pH and found that the 96-h EC₅₀ was given by following experimental relationship:

$$96\text{-h EC}_{50} (\textit{Selenastrum capricornutum}) = \exp^{(0.847 \cdot \text{pH} - 4.28)}$$

The authors suggest that the toxicity of pentachlorophenol is primarily associated with the undissociated species of the compound.

Existing reference values

WHO has assessed PCP in order to establish water quality guidelines. In 1993 a TDI of 0.003 mg/kg bw was set and, although a subsequent risk assessment was conducted in 1998 based on neoplastic effects, it is noted that the resultant water quality guideline was the same (9 µg/l). A summary of existing reference values is presented in Table I.B.2.8.

Table I.B.2.8. Reference toxicological values for PCP

Source	Exposure route	Uncertainty factors used	Reference value	Year of evaluation
WHO	Oral		Provisional guideline for drinking-water quality: 9 µg/l	1998
ATSDR	Oral: acute	1000	MRL: 0.005 mg/kg per day	1994
ATSDR	Oral: subchronic	1000	MRL: 0.001 mg/kg per day	2001
ATSDR	Oral: chronic	1000	MRL: 0.001 mg/kg per day	2001
USEPA	Oral: chronic	100	RfD: 0.03 mg/kg per day	1999
USEPA	Oral	–	ERU _o : 1.2 × 10 ⁻¹ mg/kg per day	1991
USEPA	Oral	–	ERU _{water} : 3 × 10 ⁻⁶ mg/l per day	1993

Source: INERIS 2000.

3. Persistence

Atmospheric photodegradation

Pentachlorophenol (PCP) can be photo-oxidized in the atmosphere, mainly through reaction with OH-radicals and to a lesser degree by photolysis and reactions with other contaminating compounds, such as NO₂. As the chlorophenols, including PCP, absorb only little light at wavelengths above 300 nm, photolysis by sunlight is of minor importance. For PCP the rate of photolysis is estimated to range from 1.4% per h in winter to 6% per hour in summer (half-lives 12 to 44 h; clear weather conditions, mid-day) (Slooff *et al.*, 1989). This is considerably faster than the half-life for PCP in air based on reactions with OH-radicals is 19.43 days as calculated by the AOPWin (EPISUITE, US EPA, 2007).

Table I.B.3.1. includes various parameters describing persistence of PCP in air .

Table I.B.3.1. Persistence of PCP in air with t_{1/2} is the photo degradation half-life. *Blank cells indicate that no information is available.* (information provided by the Netherlands National Institute for Public Health and the Environment)

Compartment		Conc.	Temp	Light	Removal	T1/2	Remark	REF
AIR	Atmospheric			41°79' N		<24 h (summer) to 216 h (winter)	reaction with OH radical	Mackay et al citing Bunce 1991
AIR	Tropospheric			March 21, 43°N		4 d	with OH radical	Mackay et al citing Bunce 1991
AIR						6-58 d	based on estimated rate constant for vapour phase reaction with OH radicals	Howard 1991
AIR				noonday summer sunshine		6.5 h		Howard 1991
AIR	Atmospheric					>5 d		Mackay et al citing Kelly 1994
AIR	Atmospheric					19.43 d	Reaction with OH-radicals	EPIWIN AOP

Abiotic degradation

Both PCP and Na-PCP are subject to photochemical degradation. Degradation products are:

- tetra- and trichlorophenols;
- chlorinated dihydroxybenzenes (tetrachlororesorcinol and tetrachlorocatechol)
- non-aromatic fragments (dichloromaleic acid, CO₂ and chloride ions).

Biodegradation

Biological transformation, both aerobic and anaerobic has been demonstrated for PCP. Primary transformation as well as mineralization have been observed under natural conditions.

The major metabolic pathways are:

- methylation to yield the methylether of PCP (pentachloroanisole);
- acetylation of the hydroxyl group (PCP-acetate);
- dechlorination to tetrachlorophenols;
- hydroxylation to tetrachlorodihydroxybenzenes.

These metabolites are further transformed and a number of intermediates may arise. The limiting step is the ring fission to chlorinated aliphatic substances that are further dechlorinated and metabolized (WHO 1987).

Under anaerobic conditions and without adaptation, reductive dechlorination takes place at the ortho-position (Mikesell and Boyd 1986), but under sulfidogenic conditions, removal of chlorine from the para-position is observed whereas under methanogenic conditions the first attack is on the meta-position (Susarla et al 1997, 1998). The removal of ortho-chlorine is followed by the removal of para-chlorine (Masunaga et al 1996, Chang et al 1996). Bryant et al (1991) showed the preferred initial dechlorination from the para-position. As a result tetrachlorophenols are formed which are further dechlorinated to tri-, di- and mono-chlorophenols.

PCP shows aberrant degradability in various test systems in the sense that the degradation rates may vary considerable with half-lives from hours to many months. Many studies are available that illustrate the influence of environmental conditions on the degradation rate, e.g. the impact of pH, temperature, oxygen supply and redox potential, light, the concentration of PCP in the system and the degree of adaptation of the microflora.

Degradation in water

PCP is photomineralised by sunlight within a few days (Tamer 2006, Castillo et al 1997, Hwang and Hodson 1986, Crosby 1981). This effect is enhanced by adsorption on solid matter. However, at deeper layers in the water light is attenuated and thus photodegradation is limited to the upper layers in the water bodies. The degradation of phototransformation products is completed by micro-organisms.

An extensive study on the biodegradation rate in water showed the influence of the test concentrations and the inoculum (Ingerslev et al 1998, Ingerslev and Nyholm 2000). PCP is degraded by slowly growing specific degraders initially present in the test solution. During this so-called 'lag-phase' specific micro-organisms are growing but have not yet reached sufficient number to detect the removal of PCP. The duration of the lag-phase is variable and depends on the source of the test medium and microflora (river water, sediment, effluent). In unadapted systems, PCP is degradable only after considerable adaptation periods (lag phase 8 – 30 d in effluent-based systems and 14 – 85 days in river water tests). The adaptation period is eliminated by pre-exposure of the inoculum to PCP or lower chlorinated phenols (Ingerslev et al 1998, Ingerslev and Nyholm 2000). During pre-exposure, the specific microorganisms either grow in numbers or specific enzymes may be induced that are able to metabolise PCP. The biodegradation is enhanced by the presence of organic carbon or nutrients associated with sediment and thus the lag phase in river water in the presence of sediment solids is decreased.

The elimination time is the period needed after the lag phase to reach 50% of the final degradation (mineralization). The half-life for degradation is relatively short, in the order of 3 to 14 days for systems inoculated with effluent and 9 to 40 days in surface water systems. In a pre-exposed system the half-lives were reduced to 2 days.

At concentrations of PCP above 2.5 mg/l, PCP is toxic and thus studies at higher levels should generally not be taken into consideration. In adapted systems, however, PCP also tends to be less toxic. At very low concentrations, at 1 and 10 µg/l, there is a shift from growth-linked biodegradation to non-growth kinetics where PCP is degraded at a lower rate, as a secondary substrate along with other primary substrates (co-metabolism) (Ingerslev et al 1998, Ingerslev and Nyholm 2000).

The anaerobic degradation in groundwater was summarized by Aronson and Howard (1997). Half-life times varied from 9 to 36 days under nitrate reducing conditions. In other studies no rates were given. Toxicity may have affected the results.

Most of the studies listed in show biodegradation half-lives in the order of 1 to 4 weeks. The few cases with the longer half-life are explained either by high toxic levels of PCP or by extremely low levels where co-metabolism occurs.

Degradation in sediment

Normally, the major part of the sediment is generally anaerobic. The half-life of PCP for primary degradation under anaerobic conditions ranges from less than 13 days to less than 144 days. The relatively high value of circa 144 d was obtained with a high test concentration of 20 mg/l (Bryant et al 1991). It is not known whether a large lag-phase preceded the degradation phase which might be an indication for toxicity.

Literature reviews cite DeLaune et al (1983) and Baker et al (1980) with long high half-life times, 46 – 1520 d under aerobic and anaerobic conditions. In the article of DeLaune et al (1983) no kinetic data are presented, thus the extrapolation has been added by other readers by reading from the graphs. The test duration was 33 days and thus extrapolation far beyond a few months is highly speculative. As opposed to primary degradation in other tests, this test studied the complete mineralization of PCP under varying pH and redox potential. Mineralisation is a longer process involving many more specialized micro-organisms. Mineralisation (to CO₂) occurred rapidly under aerobic conditions and at pH above 6.5. In particular at the lowest redox levels, methane is formed and this has not been captured in this study. That is another reason why the mineralization rate cannot be derived for the tests at the lower redox levels.

The paper of Baker et al (1980) studied the degradation in water and aerobic sediment under low temperatures. No degradation was observed in water of 0 °C and 20 °C but the test was carried out at toxic levels (100 mg/l). In sediment removal was 24 and 29% after 30 days in 0 and 20 °C, respectively.

Under aerobic as well as under anaerobic conditions, evidence is available for relatively rapid primary degradation, both in aerobic and anaerobic sediment, under normal environmental conditions. The high values

for the half-life times cited in the literature are based on extreme extrapolations, due to toxicity or to a combination of unfavorable environmental conditions.

Table I.B.3.2. includes various parameters describing persistence of PCP in water and sediment.

Table I.B.3.2. Persistence of PCP in water and sediment with t1/2 is the half-life. *Blank cells indicate that no information is available (information provided by the Netherlands National Institute for Public Health and the Environment)*

Compartment		Conc.	Inoculum	Test Volume	Aerobic/ Anaerobic	Ph	Temp	Light	Oc ¹	Nutrients	Moisture	Duration	Lag Phase	Log Phase	Removal	K ²	T1/2 ³	Remark	REF
WATER	OECD 301E	0.01 - 74 mg/l	0.5 ml effluent/l	300 ml	aer		21	dark					30 d				3 to 8 d	toxicity above 2.5 mg/l	Ingerslev et al. 1998, Ingerslev and Nyholm 2000
WATER	OECD 301E variant	0.1 - 74 mg/l	0.3 ml SS (act sl)/l	300 ml	aer		21	dark					28 - 75 d				4 to 14 d	toxicity at/above 2.5 mg/l	Ingerslev et al. 1998, Ingerslev and Nyholm 2000
WATER	OECD 301A	0.01 - 74 mg/l	30 mg SS (act.sl.)/l	300 ml	aer		21	dark					15 d				4 - 30 d	toxicity above 2.5 mg/l	Ingerslev et al. 1998, Ingerslev and Nyholm 2000
WATER	OECD 301A		Pre-exposed , 30 mg SS (act.sl.)/l	300 ml	aer		21	dark					0.4 d				2 d	toxicity above 20 mg/l	Ingerslev et al. 1998, Ingerslev and Nyholm 2000
WATER	surface water	0.001 mg/l	polluted river	300 ml	aer		15	diffuse light	eutrophic				> 90 d				-	Cometabolism at low concentration	Ingerslev et al. 1998, Ingerslev and Nyholm 2000
WATER	surface water	0.001- 0.1 mg/l	poll river + 50 or 1000 mg SS from sediment	300 ml	aer		15	diffuse light	eutrophic				20 - 60 d				6 - 20d		Ingerslev et al. 1998, Ingerslev and Nyholm 2000
WATER	surface water	0.001- 0.1 mg/l	pristine river	300 ml	aer		15	diffuse light	humic rich				15 - 55d				7 - 20 d		Ingerslev et al. 1998, Ingerslev and Nyholm 2000
WATER	surface water	0.001- 0.1 mg/l	pristine river + 50 or 1000 mg SS from sediment	300 ml	aer		15	diffuse light	humic rich				15 - 25 d				7 - 64 d	Cometabolism at low concentration	Ingerslev et al. 1998, Ingerslev and Nyholm 2000
WATER	Freshwater	50 mg/l	400 ul of activ sludge sample in 6 ml mineral medium (~200 mg ds/l)	6 ml	aer	7	23			mineral medium		28 d			6 to 13%			Low biodegradation due to high test conc. (toxic)	Tamer 2006
WATER	Freshwater	50 mg/l	400 ul of activ sludge sample in 6 ml mineral medium (~200 mg ds/l)	6 ml	aer	7	23	after UV treatment, 40 h, 300 uW/cm2 at 15 cm, two 18W UV-blue lamps		mineral medium		28 d			100%, but photoproducts			Photodegradation; transformation products are then completely biodegraded	Tamer 2006
WATER	estuarine	40 µg/l	indigenous			8,1	ambient, 13 - 21 oC	ambient sunlight, 5.5h/d	2.4 mg TOC/l			7 wks				0.07 /d	< 2h	complete removal after 1 week	Castillo et al 1997
WATER	river	40 µg/l	indigenous			7,8	ambient, 13 - 21 oC	ambient sunlight, 5.5h/d	2.1 mg TOC/l			7 wks				0.08 /d	< 2h	complete removal after 1 week	Castillo et al 1997
WATER	ground water	40 µg/l	indigenous			7,4	ambient, 13 - 21	ambient sunlight,	0.4 mg TOC/l			7 wks				0.07 /d	< 2h	complete removal after 1 week	Castillo et al 1997

¹ Is organic Carbon content

² k is the degradation rate

³ t1/2 is the half-life

Compartment	Conc.	Inoculum	Test Volume	Aerobic/ Anaerobic	Ph	Temp	Light	Oc ¹	Nutrients	Moisture	Duration	Lag Phase	Log Phase	Removal	K ²	T1/2 ³	Remark	REF	
						oC	5.5h/d												
WATER	Estuarine	25 ug/l		60 ml	aer	7,7	21,7	Skidaway River, Georgia: 32°03'03 N 81°06'14 W. attenuation = 0.05 cm ⁻¹	4.8 mg/l	yes		up to 3 days					1 - 3h (photo) 6 - 14 d (mineralisation)	3 cm depth	Hwang and Hodson 1986
WATER	Distilled water		distilled water														2.4 h (photo)	3.8 cm depth	cited in Hwang and Hodson 1986
WATER	Freshwater		pond		aer												1.5-3 d (photo)	1 m depth	cited in Hwang and Hodson 1986
WATER	Marine			mesocosm	aer												22 d (photo)	5.5 m depth, marine	cited in Hwang and Hodson 1986
WATER	Freshwater				aer												625 d (photo)	40 cm, extrapolated, due to attenuation of light by dissolved and particulate matter.	cited in Hwang and Hodson 1986
WATER	Freshwater	50-100 ug/l				7.3-10.3	10-21										2-4.7 d		Mackay et al citing Crossland 1985 (abstract)
WATER	Freshwater					7.3											3.5 h		Mackay et al citing Wong 1981 (abstract)
WATER	Freshwater					3.3											100 h		Mackay et al citing Wong 1981 (abstract)
WATER	surface water		field study			ambient	ambient					> 3yr					15 d		Krieger 1989 (abstract)
SEDIMENT			field study			ambient	ambient					> 3yr			60%				Krieger 1989 (abstract)
SEDIMENT	freshwater	120 mg/kg dw	psychrotrophic	10 g		6,9	0 and 20		24 % OM	95% w/w	30 d				24 - 29 %			no large impact of temperature, circa 50% due to abiotic removal, toxic level	Baker et al 1980
WATER	river	100 mg/l	psychrotrophic	10 ml		7,1	0 and 20				40 d				1%			toxic level	Baker et al 1980
SEDIMENT	silty clay bottom sediment	20 mg/kg ds or 2 mg/l	14 d acclimation at redox and pH	1.8 L	- 250 MV (sulfidogenic)	6.5; 8	33		3 - 5%	87,50%		17 d					long	Mineralisation to CO ₂ , days read from graphs	DeLaune et al 1983
SEDIMENT	silty clay bottom sediment	20 mg/kg ds or 2 mg/l	14 d acclimation at redox and pH	1.8 L	- 250 MV (sulfidogenic)	9	33		3 - 5%	87,50%		> 35 d					long	Mineralisation to CO ₂ , days read from graphs	DeLaune et al 1983
SEDIMENT	silty clay bottom sediment	20 mg/kg ds or 2 mg/l	14 d acclimation at redox and pH	1.8 L	0 MV	5; 6.5; 9	33		3 - 5%	87,50%		17 - 21 d					long	Mineralisation to CO ₂ , days read from graphs	DeLaune et al 1983
SEDIMENT	silty clay bottom sediment	20 mg/kg ds or 2 mg/l	14 d acclimation at redox and pH	1.8 L	0 MV	8	33		3 - 5%	87,50%		17d					110 d	Mineralisation to CO ₂ , days read from graphs	DeLaune et al 1983

Compartment		Conc.	Inoculum	Test Volume	Aerobic/ Anaerobic	Ph	Temp	Light	Oc ¹	Nutrients	Moisture	Duration	Lag Phase	Log Phase	Removal	K ²	T1/2 ³	Remark	REF
SEDIMENT	silty clay bottom sediment	20 mg/kg ds or 2 mg/l	14 d acclimation at redox and pH	1.8 L	+250 MV (aerob)	5; 6.5	33		3 - 5%		87,50%		17 d				long	Mineralisation to CO ₂ , days read from graphs	DeLaune et al 1983
SEDIMENT	silty clay bottom sediment	20 mg/kg ds or 2 mg/l	14 d acclimation at redox and pH	1.8 L	+250 MV (aerob)	8; 9	33		3 - 5%		87,50%		17 - 21 d				45 - 48 d	Mineralisation to CO ₂ , days read from graphs	DeLaune et al 1983
SEDIMENT	silty clay bottom sediment	20 mg/kg ds or 2 mg/l	14 d acclimation at redox and pH	1.8 L	+500 MV (aerob)	5	33		3 - 5%		87,50%		17 d				long	Mineralisation to CO ₂ , days read from graphs	DeLaune et al 1983
SEDIMENT	silty clay bottom sediment	20 mg/kg ds or 2 mg/l	14 d acclimation at redox and pH	1.8 L	+500 MV (aerob)	6.5 - 9	33		3 - 5%		87,50%		17 - 21 d				25 - 47 d	Mineralisation to CO ₂ , days read from graphs	DeLaune et al 1983
SEDIMENT	silty clay bottom sediment	Serious contamination on site	Field observation						3 - 5%		87,50%	18 mnths			>>95%			almost complet removal in 18 mnths, residue < 5 µg/kg - 1.6 mg/kg	DeLaune et al 1983
SEDIMENT	estuarine	1 mg/l	contaminated sediment, sulfidogenic	5 ml	anaer	5,6	25					200d					2.1 d	formation of tetraCP, triCP, DCP and MCP	Masunaga 1996
SEDIMENT	sandy from freshwater lake	0.5 to 1 mg/l	sulfidogenic, no preexposure to CP	5 ml	anaer	6,9			<1%			1 yr	1d			0.07 /d	9.6 d	reduction at para position under sulfidogenic condition	Susarla et al 1997
SEDIMENT	sandy from freshwater lake	0.5 to 1 mg/l	methanogenic, no preexposure to CP	5 ml	anaer	6,9			<1%									reduction at ortho position under methanogenic condition	Susarla et al 1997
SEDIMENT	Pond	20 mg/l	indigenous	75 ml	anaerobic	?						144 d			55%			dechlorination	Bryant et al 1991
SEDIMENT	East River	20 mg/l	indigenous	75 ml	anaerobic	?						33 d	19 d		100%			dechlorination	Bryant et al 1991
SEDIMENT	Black Sea	20 mg/l	indigenous	75 ml	anaerobic	?						17 d	13d		100%			dechlorination	Bryant et al 1991
SEDIMENT	Freshwater															0.00074 /h	39 d	First order microbial degradation rate in sediment and water	Mackay et al citing Yoshida 1978 (abstract)
SEDIMENT					aer												23 d		Mackay et al citing Capel 1995 (abstract)
SEDIMENT					anaer												42 d		Mackay et al citing Capel 1995 (abstract)

Degradation in soil

The influence of environmental conditions on the anaerobic degradation in soil is illustrated by Chang et al (1996). No significant degradation was observed after 32 days in soil samples tested under anoxic conditions. However, this soil sample probably contained an aerobic microflora that does not immediately function as an anaerobic system when oxygen is eliminated. Next the soil was adapted to dichlorophenol under anaerobic conditions for 2 years and then PCP was degraded with half-lives ranging from 6 to 177 days.

Mikesell and Boyd (1988) showed that under anaerobic conditions, the PCP level was reduced by 45% after 56 days in natural soil with low pH 5.8. When anaerobic sludge was added 100% was degraded within 28 days. This system did not work under aerobic conditions. The amount of sludge used to achieve the enhanced PCP biodegradation is within the range of sludge application rates normally used in agricultural practices. Anaerobic conditions are induced by the sludge and by natural showers and flooding.

Indigenous microorganisms are successfully adapted to degrade PCP under aerobic conditions with $t_{1/2}$ of 60 days. The optimum pH was 7.0, and additional carbon and nitrogen sources had no significant effect (Cho et al 2000). However, low oxygen levels reduce the degradation rate. The moisture content in the soil affects the rate directly but also indirectly in two ways: (1) by agglomeration of the soil structure at higher moisture thus limiting the oxygen supply the degradation rate is reduced, and (2) by diluting the toxic levels of PCP, the rate may be increased.

According to Combrisson and Montrozier (1999), indigenous soil micro-organisms are capable of mineralizing PCP in 60 days without a lag phase. For the process to take place it is crucial that there is contact between the PCP molecules and the soil microorganism (location of micro-organisms, soil structure).

Thus, under normal environmental conditions the microflora will adapt and biodegrade PCP in soil less than 10 weeks. There are no studies reporting a half-life for PCP > 6 months.

Table I.B.3.3. includes various parameters describing persistence of PCP in soil.

Table I.B.3.3. Persistence of PCP in soil with t1/2 is the half-life. *Blank cells indicate that no information is available .(information provided by the Netherlands National Institute for Public Health and the Environment)*

Compartment		Conc.	Inoculum	Test Volume	Aerobic/Anaerobic	Ph	Temp	Light	Oc ⁴	Nutrients	Moisture	Duration	Lag Phase	Log Phase	Removal	⁵ K	T1/2 ⁶	Remark	REF
SOIL	sandy loam	10 mg/kg	natural	10 g	anaer	7,3	25	dark	1,40%		50%	32 d			4%			natural sample tested anoxic, no indication that anaerobic activity was present at all	Chang et al 1996
SOIL	clay loam	10 mg/kg	natural	10 g	anaer	6,6	25	dark	2,00%		50%	32 d			3%			natural sample tested anoxic, no indication that anaerobic activity was present at all	Chang et al 1996
SOIL	sandy loam	2 mg/kg	adapted (DCP, anaer)	10 g	anaer	7,1	25	dark	1,40%		50%	32d			100%		10.0 d		Chang et al 1997
SOIL	sandy loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	7,1	25	dark	1,40%		50%	32d			100%		12.5 d		Chang et al 1999
SOIL	sandy loam	50 mg/kg	adapted (DCP, anaer)	10 g	anaer	7,1	25	dark	1,40%		50%	32d			20%		44d	toxic level	Chang et al 1998
SOIL	sandy loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	7,1	25	dark	1,40%		50%	32d			100%		12.5 d		Chang et al 1999
SOIL	sandy loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	6	25	dark	1,40%		50%	32d			100%		86 d	low pH	Chang et al 1999
SOIL	sandy loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	7,1	20	dark	1,40%		50%	32d			100%		22 d		Chang et al 1999
SOIL	sandy loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	7,1	40	dark	1,40%		50%	32d			100%		10 d		Chang et al 1999
SOIL	sandy loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	7,1	25	dark	1,40%		10%	32d			100%		54 d	dried soil	Chang et al 1999
SOIL	clay loam	2 mg/kg	adapted (DCP, anaer)	10 g	anaer	6,7	25	dark	2,00%		50%	32d					20 d		Chang et al 1997
SOIL	clay loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	6,7	25	dark	2,00%		50%	32d					22 d		Chang et al 1999
SOIL	clay loam	50 mg/kg	adapted (DCP, anaer)	10 g	anaer	6,7	25	dark	2,00%		50%	32d					63 d	toxic level	Chang et al 1998
SOIL	clay loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	6,7	25	dark	2,00%		50%	32d					22 d		Chang et al 1999
SOIL	clay loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	6	25	dark	2,00%		50%	32d					103 d	low pH	Chang et al 1999
SOIL	clay loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	6,7	20	dark	2,00%		50%	32d					30 d		Chang et al 1999
SOIL	clay loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	6,7	40	dark	2,00%		50%	32d					20.5 d		Chang et al 1999

⁴ Is organic carbon content

⁵ k is the degradation rate

⁶ t1/2 is the half-life

Compartment		Conc.	Inoculum	Test Volume	Aerobic/Anaerobic	Ph	Temp	Light	Oc ⁴	Nutrients	Moisture	Duration	Lag Phase	Log Phase	Removal	⁵ K	T1/2 ⁶	Remark	REF
SOIL	clay loam	10 mg/kg	adapted (DCP, anaer)	10 g	anaer	6,7	25	dark	2,00%		10%	32d					177 d	dried soil	Chang et al 1999
SOIL	loamy sand	30 mg/kg	indigenous	60 kg	aer	6,5	30	dark	4,60%		11.5% (field moisture)	6 mnths		55d			57 d		Cho et al 2000
SOIL	sandy subsoil	30 mg/kg	contaminated	10 g	aer	7,9	15	dark	0,30%		60% of waterholding capacity (21%)	7 mnths			82% mineralised		toxicity at 100 mg/kg	Miethling and Karlson 1996	
SOIL	sandy loam	30 mg/kg	indigenous	10 g	aer	4,6	15	dark	0,70%		60% of waterholding capacity (21%)	7 mnths			no mineralisation		Low pH (4.6)	Miethling and Karlson 1996	
SOIL	alfisol, silty loam	22 mg/kg	pristine	30 g		6,9			2%		60% of water holding capacity	60 d			>50%		60d	50% mineralised	Combrisson and Monrozier 1999
SOIL	loamy fine sand	10, 20 or 30 mg/kg	indigenous		anaerobic	5,8			1,10%			56 d			45%		circa 60 d		Mikesell and Boyd 1988
SOIL	loamy fine sand	10, 20 or 30 mg/kg	anaerobic sludge, 5g/kg		anaerobic							28d			100%		14 - 45 d		Mikesell and Boyd 1988
SOIL	loamy fine sand	10, 20 or 30 mg/kg	indigenous		aerobic							80 d			10%				Mikesell and Boyd 1988
SOIL	loamy fine sand	10, 20 or 30 mg/kg	anaerobic sludge, 5g/kg		aerobic							56d			10%			Anaerobic system inhibited by O ₂	Mikesell and Boyd 1988
SOIL	undefined contaminated site		contaminated site									70 d			48 to 64% mineralisation		oxygen content 2-21%	Hurst et al 1997 (abstract)	
SOIL	slurry reactor		10% wt slurry	3 L	aerobic	7,8	21					15-30 d					9.8 d		Jerger et al 1992 (abstract)
AQUIFER	cobble, gravel, sand and groundwater			25 g, 1:4 solids/water	aer, anaer		10, 20					56d			16 to 26%			removal due to binding to soil	Mohammed et al 1998

Summarizing remarks

Photolysis is the fastest known mechanism of PCP degradation and can lead to total mineralization of PCP in water within hours of its release. In air and clean water this is the relevant mechanism. In waters where turbidity and depth prevent exposure to light, in sediment and in soil, biodegradation is the relevant process.

Under normal environmental conditions the microflora will adapt and biodegrade PCP in water with half-lives less than 4 weeks, in the sediment less than 20 weeks and in soil less than 10 weeks. Many studies discuss the degradation of PCP in terms of mineralization, with some of them showing a slow rate of mineralization. However, studies showing an incomplete mineralization do not imply that PCP is not completely removed. In fact, the rate of degradation of PCP in these studies, if not explicitly mentioned, can not be derived.

In water, the few cases with low rates of degradation are explained either by high toxic levels of PCP or by extremely low levels where co-metabolism occurs. In sediment, the high values for half-life cited in the literature are based on extreme extrapolations and concern mineralization, or are due to toxicity or to a combination of unfavorable environmental conditions.

4. Bioaccumulation

Log Kow is an indication of the bioaccumulation potential. The measured log Kow of PCP varies between 1.3 and 5.86 (Table I.B.4.1). Most of these values are retrieved from Mackay et al. (2006). Recommended values in Mackay et al. (2006) are 5.12 and 5.18 respectively. Several methods have been used for the determination of the log Kow, which explains some of the variation. The most widely accepted method for this type of compound is the shake flask method. The variation in log Kow values, however, is for the major part caused by the different dissociation of PCP at different pH (pKa of PCP is 4.7). Under acidic circumstances, PCP is undissociated and a comparable high log Kow is measured. With increasing pH, the dissociation of PCP also increases and the log Kow decreases. This is illustrated for example by the data of Nowosielski and Fein 1998 (Table I.B.4.1) who observed a decrease of logKow from 4.75 to 1 between pH of 5.5 and 8.

Table I.B.4.1 shows that in some studies a high log Kow >5 was observed for PCP. However, it should be taken into account that the bioaccumulation may be less than expected when a compound, as for example PCP, is subject to biotransformation (see for example Gates and Tjeerdema 1993).

BCF data expressed on dry weight or lipid weight that could not be converted to wet weight basis are not included in the evaluation. Also not included in the evaluation are BCF data measured in elimination collection organs. Examples are the studies by Statham et al 1976, who studied the occurrence of PCP in the bile of rainbow trout. In the previous study the ratio of concentration in bile/concentration in water is 5,360 for PCP. However, bile is the matrix in which degradation products are concentrated before elimination, and thus, it is not representative for BCF values. Moreover, in this study also degradation products of PCP (probably two) were included in the measurements. Studies in which concentrations in organs, such as the liver, are measured for estimating the BCF, e.g. Geyer et al 1987, were also not included in the comparison of BCF values.

The bioconcentration factor (BCF) of PCP is measured in *crustacea*, bivalves, aquatic and terrestrial worms and in fish. The data are summarized in Table I.B.4.2. As the table shows, the measured BCF data range from 18 – 640 in *crustacea*, 0.9 – 461 in bivalves, 71 – 3,830 in aquatic and terrestrial worms and 5 – 4,900 in fish. A large part of the variation is caused by the difference in lipid content of the organisms. The BCF also depends on the pH, with higher accumulation at lower pH values (Ineris 2005 citing Kobayashi et Kishino, 1980). At pH of 10, they determined a BCF in goldfish of 2, at pH 7 the BCF was 56 and at pH 5.5 the pH was 132. Also Stehly and Hayton 1990 and Fisher et al 1999 observed a pH dependence of the BCF. At a pH of 9 the BCF was 52.3, at pH 8 the BCF was 129 and at pH 7 the pH was increased to 607. The calculated BCF on wet weight basis is 696 (Stehly and Hayton 1990). As table 1.B.4.1 shows, high BCF values of 10,000 – 45,000 have been measured in a study with Zebra mussels *Dreissena polymorpha* (Gossiaux et al 1996). In another study with the same species the BCF was 429-1369 (Fisher et al 1999). Although both studies have been maintained in the table there is some doubt on the interpretation of the results as the radioactive label was measured and not the pure substance. Formation of metabolites within the organism may lead to overestimation of the BCF and this is not accounted

for in these studies. Furthermore, data on the pentachlorophenol concentration in the medium during the elimination period are not provided, which also hamper interpretation of the results.

Conclusion

Log Kow of PCP vary between 1.3 and 5.86 with recommended values of 5.12 and 5.18. However, in this particular case, log Kow is not a good indicator of bioconcentration as PCP is subject to biotransformation. Furthermore logKow is strongly pH dependent. The BCF in *crustacea*, bivalves, aquatic and terrestrial worms and in fish varies between 0.9 – 4900. There is one study with BCF > 5,000, which should be considered with the restrictions discussed above. Thus, it must be concluded that PCP does not meet the indicative value of BCF >5,000.

Table I.B.4.1: Reported log Kow values of pentachlorophenol.

log Kow	Method	Conditions	Reference	Year
5,01	Unknown	Na	Mackay et al. citing Leo et al.	1971
3,81	Unknown	Na	Mackay et al. citing Lu and Metcalf	1975
3,81	Lit. values	Na	Mackay et al. citing Hansch and Leo	1979
5,01	Lit. values	Na	Mackay et al. citing Hansch and Leo	1979
5,01	HPLC-RT correlation	Na	Mackay et al. citing Veith et al.	1979
5,12	Lit. values	Na	Mackay et al. citing Hansch and Leo	1979
5,86	Lit. values	Na	Mackay et al. citing Hansch and Leo	1979
4	Unknown	pH = 4	Mackay et al. citing Renberg	1981
5,1	HPLC-k' correlation	Na	Mackay et al. citing Butte et al.	1981
1,3	Shake flask-GC	pH = 10.5	Mackay et al. citing Kaiser and Valdmanis	1982
3,69	Unknown	Na	Mackay et al. citing Geyer et al; Schmidt-Bleek	1982
4,84	Shake flask-GC	pH = 1.2	Mackay et al. citing Kaiser and Valdmanis	1982
5,08	HPLC-k' correlation	Na	Mackay et al. citing Miyake and Terada	1982
5,15	Shake flask-GC	Na	Mackay et al. citing Saarikoski and Viluksela	1982
3,29	Unknown	Na	Mackay et al. citing Harnish et al.	1983
3,69	Shake flask OECD 1981	Na	Mackay et al. citing Geyer et al.	1984
3,81	Shake flask OECD 1981	Na	Mackay et al. citing Geyer et al.	1984
5,04	Shake flask-GC, HPLC -k'	Na	Mackay et al. citing Xie et al.	1984
5,08	Shake flask-GC, HPLC -k'	Na	Mackay et al. citing Xie et al.	1984
5,11	HPLC retention vol. Correlation-ALPM	Na	Mackay et al. citing Garst and Wilson	1984
5,24	Shake flask HPLC/UV	Na	Mackay et al. citing Schellenberg et al.	1984
5,12	Unknown	Na	Mackay et al. citing Hansch and Leo	1985
5,24	OECD guidelines	Na	Mackay et al. citing Leuenberger et al.	1985
4,71	RP-HPLC-RT	Na	Mackay et al. citing Chin et al.	1986
5,15	Shake flask-GC	Na	Mackay et al. citing Saarikoski et al.	1986
2,5	Unknown	pH=4.7	Mackay et al. citing Geyer et al.	1987
4,47	Centrifugal partition chromatography-RV	Na	Mackay et al. citing Tarada et al.	1987
4,84	Unknown	pH=1.2	EHC, 71	1987
3,56	Unknown	pH=6.5	EHC, 71	1987
3,32	Unknown	pH=7.2	EHC, 71	1987
3,86	Unknown	pH=13.5	EHC, 71	1987

log Kow	Method	Conditions	Reference	Year
5	Shake flask/batch equilibration-UV	Na	Mackay et al. citing Beltrame et al.	1988
5,04	HPLC-RT correlation	Na	Mackay et al. citing Shigeoka et al.	1988
5,06	COMPUTOX databank	Na	Mackay et al. citing Kaiser	1993
5,12	COMPUTOX databank	Na	Mackay et al. citing Kaiser	1993
5,18	LOGKOW databank	Na	Mackay et al. citing Sangster	1993
5,02	Shake flask-GC/ECD	Na	Mackay et al. citing Kishino and Kobayashi	1994
5,12	Unknown	pH=1.4	Mackay et al. citing Hansch et al.	1995
5,12	pH-metric method	Na	Mackay et al. citing Chamberlain et al.	1996
3,59	Shake flask-GC/HPLC	pH=8	Mackay et al. citing Nowosielski and Fein	1998
3,69	Shake flask-GC/HPLC	pH=7.2	Mackay et al. citing Nowosielski and Fein	1998
4,27	Shake flask-GC/HPLC	pH=6.1	Mackay et al. citing Nowosielski and Fein	1998
4,6	Shake flask-GC/HPLC	pH=5	Mackay et al. citing Nowosielski and Fein	1998
4,74	Shake flask-GC/HPLC	pH=2.1-3.1	Mackay et al. citing Nowosielski and Fein	1998

Table I.B.4.2: Reported BCF-values of pentachlorophenol

Species	Exp. Time	Exp. Conc. Lower	Exp. Conc. Upper	Unit	BCF (wet weight)	Reference	Year
CRUSTACEA							
<i>Daphnia magna</i> (waterflea)	1d	2.71	Na*	µg/L	165	US EPA Aquire citing Lu and Metcalf	1975
<i>Palaemonetes pugio</i> (shrimp)	0.5d	2000	Na	µg/L	18.5	US EPA Aquire citing Rao et al.	1981
<i>Daphnia magna</i> (waterflea)	1d	20	Na	µg/L	145-640	US EPA Aquire citing Kukkonen and Oikari	1988
<i>Gammarus pulex</i> (amphipod)	2d	70	Na	µg/L	51	Ashauer et al.	2005
BIVALVIA (bivalves/mussels)							
<i>Physa sp.</i> (pouch snail)	2d	2.71	Na	µg/L	121	US EPA Aquire citing Lu and Metcalf	1975
<i>Crassostrea virginica</i> (eastern oyster)	14-34h	3.7	11.3	µg/L	34-82	Schimmel and Garnas	1985
Bivalvia (bivalves/mussels)	1d	3	30	µg/L	160	US EPA Aquire citing Makela et al.	1989
<i>Anodonta anatina</i> (freshwater mussel)	4-16h	1.8	Na	µg/L	145-342	Makela and Oikari	1990
<i>Anodonta anatina</i> (freshwater mussel)	8d	6	56	µg/L	81-461	Makela et al.	1991
<i>Anodonta anatina</i> (freshwater mussel)	14d-252d	9.7	Na	µg/L	80.4-121	Makela and Oikari	1995
<i>Anodonta complanata</i> (freshwater mussel)	14d-252d	9.7	Na	µg/L	61.1-85.4	Makela and Oikari	1995
<i>Mytilus edulis</i> (mussel)	40h	1	100	µg/L	95.28	Jennings et al.	1996
<i>Dreissena polymorpha</i> (zebra mussel)	0.25d	0.00206	0.00328	µg/L	10000-45000	Gossiaux et al. ⁷	1996
<i>Corbicula fluminea</i> (freshwater bivalve)	1-3d	100	Na	µg/L	0.86-1.15	Basack et al.	1997
<i>Mytilus edulis</i> (common bay mussel/blue mussel)	8d	2	5	µg/L	390	US EPA Aquire citing Ernst	1997
<i>Dreissena polymorpha</i> (zebra mussel)	0.25d	0.05	5.3	µg/L	429-1369	Fisher et al. ⁷	1999
WORMS							
<i>Eisenia fetida andrei</i> (terrestrial earthworm)	14d	<771.4	Na	µg/L	426-634	Van Gestel and Ma	1988
<i>Lumbricus rubellus</i> (terrestrial earthworm)	14d	<771.4	Na	µg/L	476-996	Van Gestel and Ma	1988
<i>Haemopsis marmorata</i> (leech)	1d	10	Na	µg/L	71	US EPA Aquire citing Hall and Jacob	1988
<i>Nepheleopsis obscura</i> (leech)	7d	10	Na	µg/L	525-2508	US EPA Aquire citing Hall and Jacob	1988
<i>Lanice conchilega</i> (aquatic polychaete)	8d	2	5	µg/L	3830	US EPA Aquire citing Ernst	1997
FISH							
<i>Gambusia affinis</i> (western mosquitofish)	1d	2.71	Na	µg/L	296	US EPA Aquire citing Lu and Metcalf	1975
<i>Carassius auratus</i> (goldfish)	1d	200	Na	µg/L	475	US EPA Aquire citing Kobayashi et al.	1979

⁷ See remarks in the text on these studies

Species	Exp. Time	Exp. Conc.		Unit	BCF (wet weight)	Reference	Year
		Lower	Upper				
<i>Cyprinodon variegatus</i> (sheepshead minnow)	111d-133d	8	195	µg/L	5-48	US EPA Aquire citing Parrish et al.	1978
<i>Leuciscus idus</i> (Ide, silver or golden orfe)	3d	42	Na	µg/L	1100	US EPA Aquire citing Korte et al.	1978
<i>Pimephales promelas</i> (fathead minnow)	32d	11.1	Na	µg/L	770	US EPA Aquire citing Veith et al.	1979
<i>Salmo trutta</i> (trout)	1d	200	Na	µg/L	100	Hattula et al.	1981
<i>Fundulus similis</i> (longnose killifish)	4d-10d	57	100	µg/L	38-64	US EPA Aquire citing Trujillo et al.	1982
<i>Leuciscus idus melanotus</i> (carp)	3d	42	Na	µg/L	1050	US EPA Aquire citing Freitag et al.	1982
<i>Fundulus similis</i> (longnose killifish)	1-7d	57	610	µg/L	8-47	US EPA Aquire citing Trujillo et al.	1982
<i>Oncorhynchus mykiss</i> 1) (rainbow trout)	20d	0.04	Na	µg/L	200	Niimi et al.	1982
<i>Leuciscus idus</i> (Ide, silver or golden orfe)	3d	50	Na	µg/L	260	US EPA Aquire citing Freitag et al.	1984
<i>Pimephales promelas</i> (fathead minnow)	32d	3.1	327	µg/L	281-1066	US EPA Aquire citing Spehar et al.	1985
<i>Oncorhynchus gorbuscha</i> (pink salmon)	4d	0.8	3.11	µg/L	350-764	Stehly and Hayton	1988
<i>Oncorhynchus mykiss</i> (rainbow trout)	4d	5	Na	µg/L	193	Stehly and Hayton	1988
<i>Carassius auratus</i> (goldfish)	4d	5	Na	µg/L	52.3-607	Stehly and Hayton	1990
<i>Jordanella floridae</i> (flagfish)	28d	4.12	Na	µg/L	216	Smith et al.	1990
<i>Oryzias latipes</i> (Japanese medaka)	1d	100	Na	µg/L	1684	Tachikawa et al.	1991
<i>Oncorhynchus mykiss</i> (rainbow trout)	6d	91.2	Na	µg/L	411-482	US EPA Aquire citing Heuvel van de et al.	1991
<i>Trachurus novaezelandiae</i> (small rocky-reef fish)	40h	1	100	µg/L	283	Jennings et al.	1996
<i>Oryzias latipes</i> (japanese medaka)	60d	0.1	10	µg/L	2100-4900	Kondo et al.	2005
<i>Oryzias latipes</i> (Japanese medaka)	42d	3	Na	µg/L	39-198	NITE	1983
<i>Oryzias latipes</i> (Japanese medaka)	42d	0.3	Na	µg/L	(45)-224	NITE	1983

Na = not applicable

1) in this study under the old name *Salmo gairdneri*

* data by authors expressed on soil solution concentration. Expressed on dry soil basis, BCF values range from 3.4 and 5.3 for *Eisenia* (exposure concentration < LC50 of 140 mg kg dry soil) and from 4.0 and 8.0 for *Lumbriculus* (exposure concentration < 1100 mg/kg dry soil).

5. General population and occupational exposure

General population exposure may occur through contact with contaminated environmental media, particularly in the vicinity of hazardous waste sites. Important routes of exposure appear to be inhalation of contaminated air, ingestion of contaminated groundwater used as a source of drinking water, ingestion of contaminated food and soils, and dermal contact with contaminated soils or products treated with the compound.

Biotransformation of some chlorinated hydrocarbons (e.g., lindane, hexachlorobenzene) to PCP also contributes to the human body burden. The ambient air in urban areas typically contains several ng/m^3 .

Drinking-water concentrations of PCP rarely exceed several $\mu\text{g}/\text{l}$, even in highly industrialized regions, and most are less than 1 $\mu\text{g}/\text{l}$.

Fruits, vegetables, and other produce usually contain much less than 10 $\mu\text{g}/\text{kg}$, but may on occasion exceed this level. Most meats contain similar concentrations of PCP (10 $\mu\text{g}/\text{kg}$) but, a few samples, particularly liver, can contain over 100 $\mu\text{g}/\text{kg}$. Fish skeletal muscle typically contains PCP levels of 4 $\mu\text{g}/\text{kg}$ or less. Overall estimates of PCP intake from all foods, based on total diet samples in the USA and the Federal Republic of Germany, are remarkably similar, i.e., up to 6 $\mu\text{g}/\text{person per day}$.

Pentachlorophenol was used extensively in treating wood. Today, this use is restricted to the treatment of utility poles, railroad ties, and wharf pilings where it is widely used. Dermal exposure to pentachlorophenol by members of the general population may occur upon contact with these wood products. Pentachlorophenol is readily absorbed through skin representing a relevant route of low level exposure. Pentachlorophenol is known to volatilize from treated wood products at a rate that is temperature-dependent, and low level inhalation exposure may also occur with increased levels expected during the summer months.

PCP concentrations in indoor air can be expected to reach 30 $\mu\text{g}/\text{m}^3$ during the first month after treatment. Considerably higher levels, up to 160 $\mu\text{g}/\text{m}^3$, have been reported in houses with concomitant poor indoor ventilation.

Data have been collected on pentachlorophenol levels in human urine, blood, adipose tissue, and cerebrospinal fluid for both occupational and nonoccupational groups. While levels are much higher in occupationally exposed groups, tests on the general population consistently show evidence of low-level exposure.

Exposures of children

Children are likely to be exposed to pentachlorophenol via the same routes that affect adults. Small children are more likely than adults to come into intimate contact with yard dirt, lawns, and house (carpet) dust. Pesticide residues in carpets or on uncovered floors may present a relatively important exposure route for infants and toddlers through dermal contact and oral ingestion. It is possible that children may absorb pentachlorophenol dermally when exposed to soil contaminated with pentachlorophenol.

Percutaneous pentachlorophenol absorption from the pentachlorophenol used in the laundry can be a significant source of exposure to infants.

Occupational exposure

Occupational exposure to technical PCP mainly occurs through inhalation and dermal contact. Workers handling treated lumber or maintaining PCP-contaminated equipment would be exposed dermally to PCP in solution, and may take up from one-half to two-thirds of their total PCP burden through the skin. The actual concentrations to which workers have been exposed are seldom measured but, where they have been monitored, they have been predictably high. Airborne levels at PCP-production and wood-preservation facilities have ranged from several mg/m^3 to more than 500 mg/m^3 in some work areas. The outer layer of treated wood can contain up to several hundred mg/kg , though levels are usually less than 100 mg/kg . These exposures result in concentrations of PCP in the serum and urine that are 1-2 orders of magnitude higher than those found in the general population without known exposure.

Conclusion:

The BCF's values are below the threshold criterion except possibly for some species. However it must be recognized that when determining BCFs for labile chemicals, such as pentachlorophenol, the average exposure affecting uptake is likely much greater than the final concentration, which tends to inflate the BCF. It would appear that the

development of biologically meaningful BCFs should use some intermediate concentration of the contaminant. An appropriate protocol would necessarily require consideration of the dynamics of degradation in the ambient water integrated over time compared with the depuration and metabolism of the contaminant in the organism at question. The high value of BCF for pentachlorophenol may come from experiments which might not be designed adequately for the determination of bioaccumulation potential.

PART II. SUMMARY REPORT

A. EXTENT OF RELEASE TO THE ENVIRONMENT

1. Production

Manufacturing Processes

PCP is produced by one of two methods: direct chlorination of phenols and hydrolysis of hexachlorobenzene. The direct chlorination is carried out in two steps. First, liquid phenol, chlorophenol, or a polychlorophenol is bubbled with chlorine gas at 30 - 40 °C to produce 2,4,6-trichlorophenol, which is then converted to PCP by further chlorination at progressively higher temperatures in the presence of catalysts (aluminium, antimony, their chlorides, and others). The second method involves an alkaline hydrolysis of hexachlorobenzene (HCB) in methanol and dihydric alcohols, in water and mixtures of different solvents in an autoclave at 130 - 170 °C. In the Federal Republic of Germany, PCP is synthesized by means of stepwise chlorination of phenols. Na-PCP was produced until 1984 using hexachlorobenzene hydrolysis; now, it is produced by dissolving PCP flakes in sodium hydroxide solution [Umweltbundesamt, 1985]. In the USA, the general reaction used is the chlorination of phenols.

In addition to the formation of PCP, numerous by-products are generated, as reflected by analytical profiles in Table II.A.1.1. The chlorination procedure yields a technical product that usually contains a considerable amount of tetrachlorophenols (4 - 12%) due to incomplete chlorination reactions. The formation of microcontaminants is favoured by elevated temperatures and pressure. With both manufacturing methods, toxic by-products, such as chlorinated ethers, dibenzofurans, and dibenzo- *p*-dioxins, are formed. In addition, the alkaline HCB hydrolysis method can result in the presence of hexachlorobenzene in the resulting PCP.

Production Levels

No precise estimates can be made of the total world production of PCP and Na-PCP. According to the data profile of IRPTC (1983), 90 000 tonnes of PCP per year were produced globally. The Economist Intelligence Unit (1981) estimated world production to be of the order of 50 000 - 60 000 tonnes per year, based on the North American and European Community output. This production figure indicates can give only a rough idea of the true PCP market at that time. Recent restrictions on the use of PCP, a decline in the forestry industry, and the increasing use of alternative means of wood preservation have probably reduced the demand for PCP over the last few years.

The major PCP producers operating in 1980 are shown in Table II.A.1.2 together with the plant locations and their capacities. Some additional factories exist in which PCP is mixed or formulated to yield special end-use products. There are also chemical producers who sell pure, analytical grade PCP, but do not produce PCP for technical purposes. The Monsanto Company, which had a capacity of 11.8 kilotonnes in the USA, stopped PCP production in their plant at Saugeat, Illinois, in 1978. Dow Chemical closed down its manufacturing plant at Midland, Michigan in October 1980 [Jones, 1984]. Similarly, the only PCP producing plant in the United Kingdom, also operated by the Monsanto Company, was closed down in the same year [Economist Intelligence Unit, 1981], while Reichhold Chemicals Inc., at Tacoma, Washington, USA ceased PCP production in 1985. In the Federal Republic of Germany, the production of PCP and Na-PCP was stopped in 1986.

Table II.A.1.1. Results of Analyses of Impurities Present in the Pentachlorophenol Used in National Toxicology Program (NTP) Feeding Studies and the Types of Tumors they Induce (*Source*: Toxicological Profile for Pentachlorophenol Prepared By Syracuse Research Corporation for U.S. Department of Health And Human Services, Public Health Service Agency for Toxic Substances and Disease Registry)

Impurity	Technical grade	Dowicide EC-7	Pure	Tumor type	Species
Dichlorophenol	-	-	-	No data	
Trichlorophenol	100 ppm	70 ppm	100 ppm	Liver. leukemiase. lymphomas	Rat, mouse
Tetrachlorophenol	38.000 ppm	94.000 ppm	14.000 ppm	Not carcinogenic	Rat, mouse
Hexachlorobenzene	50 ppm	65 ppm	10 ppm	Liver Thyroid/ Parathyroid Adrenal Kidney Lymphosarcomas	Rat, hamster, mouse Rat Rat Rat Mouse
Tetrachlorodibenzodioxin	-	<0.04 ppm	<0.08 ppm	Liver. thyroid	Rat, mouse (both tumor types)
Hexachlorodibenzodioxin	10.1 ppm	0.19 ppm	<1 ppm	Liver	Rat, mouse
Heptachlorodibenzodioxin	296 ppm	0.53 ppm	-	No data	
Octachlorodibenzodioxin	1.386 ppm	0.69 ppm	<1 ppm	No data	
Pentachlorodibenzofuran	1.4 ppm	-	-	No data	
Hexachlorodibenzofuran	9.9 ppm	0.13 ppm	-	No data	
Heptachlorodibenzofuran	88 ppm	0.15 ppm	-	No data	
Octachlorodibenzofuran	43 ppm	-	-	No data	
Heptachlorohydroxydiphenyl ether	500 ppm`	-	100 ppm	No data	
Octachlorohydroxydiphenyl ether	19.100 ppm	900 ppm		No data	
Nanochlorohydroxydiphenyl ether	35.600 ppm	2.100 ppm		No data	
Hexachlorohydroxydibenzofuran	1.600 ppm	1.100 ppm		No data	
Heptachlorohydroxydibenzofuran	4.700 ppm	2.200 ppm		No data	

- = not detected; EC-7 = Dow Company chemical name

Table II.A.1.2. Major establishments producing PCP and their capacities in 1980

Country	Institutions	Location	Capacity (tonnes)	Notes
Germany	Dynamit Nobel	Rheinfelden	4000	Production ceased in 1986
France	Rhone-Poulenc	Pont-de-Claix	4500	
USA	Dow Chemical Company	Midland, Michigan	13 500	Closed in.1980
	Reichhold Chemicals Inc.	Tacoma, Washington	8 100	Production ceased in 1985
	Monsanto Company	Sanget, Illinois		Production ceased in 1978
	Vulcan Materials Company	Wichita, Kansas	9 000	
Canada	Uniroyal Chemical	Clover Bar, Alta	1800	

Production and Import of PCP, NaPCP and PCPL – EU Countries

Production of PCP and NaPCP ceased in the EU in 1992. After that these chemicals have been imported to the European market from the USA. There is unconfirmed information that additional NaPCP may be imported from South - East Asia. Currently no import of PCPL takes place but PCPL is synthesized from PCP by one plant in the UK [DG III/ERM 1998].

In 1996 total of 378 tonnes of NaPCP and 30 tonnes of PCP were imported to the EU. From 378 tonnes NaPCP imported 126 tonnes were imported to France, 108 tonnes to Portugal and 144 tonnes to Spain. From the 30 tonnes PCP imported in 1996 to the EU 28 tonnes were synthesized to 46 tonnes PCPL in the UK. Of the 46 tonnes PCPL produced, 5-10 tonnes were exported to France and a similar quantity was used in the UK. The rest was exported to countries outside the EU. Import of PCP and production of PCPL have slightly decreased during last few years. According to the only producer of PCPL in Europe they have purchased no more than 20 tonnes of PCP in 1999 for conversion into PCPL and their production of PCPL for 2000 is less than 30 tonnes.

Production of PCPL ceased in the European Union in 2000 since according to Commission Directive 1999/51/EC use of PCP and its compound is not permitted as a synthesizing and/or processing agent in industrial processes from 1 September 2000.

Import values of PCP and its sodium salt are detailed in Table II.A.1.3 (relating to imports from the US, although there may be some imports from other countries).

Table II.A.1.3. Imports of PCP and NaPCP in 1996 and 1999.

Substance	1996 (tpa)	1999 (tpa)	Countries
PCP	30	15	UK
NaPCP	378	324	France, Portugal, Spain

Of the 30 tonnes of PCP imported into the UK in 1996, this was all converted into 46 tonnes of PCP laurate (PCPL) of which 15 tpa was used in the UK and France and the remainder exported to outside the EU. PCPL is used in the preservation of textiles, which are subject to attack, by fungi and bacteria (for heavy duty military transport and tent textiles). The main use for NaPCP is in the treatment of wood as a sapstain control agent for freshly cut timber, pallet boards, construction timber and fencing panels (such use is restricted to industrial facilities).

Production in USA

Vulcan Chemicals, a division of Vulcan Materials Company (Wichita, Kansas), is the only current U.S. domestic manufacturer of pentachlorophenol [SRI, 1998]. Pentachlorophenol is produced by the stepwise chlorination of phenols in the presence of catalysts (anhydrous aluminium chloride or ferric chloride). Outside of the United States, it is also produced by the alkaline hydrolysis of hexachlorobenzene.

Typically, commercial grade pentachlorophenol is 86% pure. Contaminants generally consist of other polychlorinated phenols, polychlorinated dibenzo- p-dioxins, and polychlorinated dibenzofurans, which are formed during the manufacturing process. Pentachlorophenol has also been marketed in the past as a water-soluble sodium salt, a 5% emulsifiable concentrate, or a 3–40% solution in formulation with other chlorophenols, methylene bithiocyanate, or copper naphthenate [IARC, 1979].

Production volumes for 1983-1986 were as follows: 45 million pounds in 1983; 42 million pounds in 1984; 38 million pounds in 1985; and 32 million pounds in 1986 [Mannsville 1987]. About 24 million pounds were manufactured in 1987 by Vulcan Materials [HSDB, 1999b]. More recent production data are not available. [see also UNEP, 2002]. UNEP [2002] also reports production by KMG-Bermuth Inc with a production facility in Matamoros, Mexico. Production of both North American production facilities was estimated by the Pentachlorophenol Task Force to be 18.6 million pounds in 1996 [UNEP 2002]. A 1999 report from the Council of Great Lakes Industries reports an annual production of roughly 17 million pounds for both production facilities [Council of Great Lakes Industries, 1999].

The U.S. consumption of pentachlorophenol for 1986 was reported to be 28 million pounds [CMR 1987]. In 1982, 121,000 pounds of pentachlorophenol were imported to the United States (328,000 pounds were imported in 1980). In 1985, 3 million pounds of pentachlorophenol were exported, and in 1986, 2 million pounds were exported [Mannsville, 1987]. More recent data on the import/export volumes of are not available.

Other Countries of Major Production

According to the available data China produces about 5000 tonnes of Pentachlorophenol annually.

Pentachlorophenol was also produced in Poland, about 200 tonnes annually. A process of one-step chlorination of phenols was used. PCP was a component of preparations for wood preservation. The production ceased in the middle of nineties.

2. Uses

The main advantages of PCP and its derivatives are that they are effective biocides and soluble in oil (PCP) or water (Na-PCP). Few pesticides show a similarly broad efficiency spectrum at low cost. Therefore, PCP and its salts have a variety of applications in industry, agriculture, and in domestic fields, where they have been used as algacides, bactericides, fungicides, herbicides, insecticides, molluscicides, defoliant, germicide.

Major uses:

- in the preservation of starches, dextrans, glues;
- to inhibit fermentation in various materials;
- to maintenance of boats, trailers, station wagons, siding, fences, outdoor furniture and similar articles;
- in construction of boats and buildings;
- to mold control in petroleum drilling and production;
- in treatment of cable coverings, canvas belting, nets, construction lumber and poles;
- in paints, pulp stock, in pulp and paper, cooling tower water, hardboard and particle board;
- as wood preservative (applied as a 0.1% solution in mineral spirits, NO₂ fuel oil, or kerosene);
- in pressure treatment of lumber (at 5% concentration).

2.1. Previous Use of PCP, NaPCP and PCPL

The comprehensive report on the environmental health criteria for Pentachlorophenol published by ICPS in 1987 include information on use patterns of PCP, Na-PCP collected at the period of the report preparation. They can be summarized as follows.

Commercial use

Although PCP and its derivatives had many uses (see the Table II.A.2.1 in case of the United Kingdom and the USA), by far the major application was wood preservation.

In the USA, about 80% of PCP was used for commercial wood treatment, 6% was in use for slime control in pulp and paper production, and 3% accounts for non-industrial purposes, such as weed control, fence-post treatment and paint preservation [Crosby, 1981]; however, the last two cases imply wood treatment as well. The remaining 11% was converted to Na-PCP, which in turn was partly used for wood preservation, mainly sapstain control in waterborne conditions, e.g., for treating pressboard. Overall, some 95 – 98% of American PCP production was used directly or indirectly in wood treatment.

Data from Canada and the Federal Republic of Germany confirmed the main use of PCP as a wood preservative. In Canada, about 95% of the PCP was used for this purpose. Approximately 61% of the volume of PCP used in the Federal Republic of Germany in 1983 was used for wood preservation, while considerable amounts of PCP were used by the textile (13%), leather (5%), mineral oil (6%), and glue (6%) industries, respectively. No PCP was used in the paint or pulp industry whereas, in 1974, as much as 3% or 7%, respectively, were used in these branches. PCP used on textiles is usually in the form of the PCP ester rather than PCP or Na-PCP.

Pentachlorophenyl laurate (PCPL) was developed especially for application on fabrics. The estimates of PCPL use in the United Kingdom in Table II.A.2.1 are based on a publication from the year 1974. According to an unpublished note submitted to the IPCS by Catomance Limited, Hertfordshire, the sole manufacturer of pentachlorophenyl laurate in the United Kingdom, the usage pattern in the United Kingdom was not changed following the cessation of production of PCP in 1978. However, most of the PCP ester used there was for domestic timber preservation; the use of PCPL for textile preservation was mainly confined to tropical or semi-tropical countries.

In the USSR, PCP was used for the preservation of commercial timber, paints, varnishes, paper, textiles, ropes, and leather.

Na-PCP was also used to inhibit algal and fungal growth in cooling tower waters at electric generating plants; in 1976, about 30% of the Na-PCP used in Canada was for this purpose.

Table II.A.2.1. The use profile of PCP, PCPL and Na-PCP in the United Kingdom and the USA.

Use	Active ingredient
<i>United Kingdom</i>	
Anti-mildew agent in the wool textile industry	PCPL, Na-PCP
Mothproofing carried out by dyers and cleaners	PCPL
Wood preservation	PCP, PCPL,
Paint additives	PCP
Antimicrobial (slimicide) agents in paper and board	PCP
Antifungal agent in textiles other than wool (cotton, flax and jute fabric, ropes, cordage and tentage)	PCPL
Cable impregnation	PCPL
Anti-mildew agent in leather	ns
Fungicide in adhesives	Na-PCP
Bactericide in drilling fluids	ns
<i>USA</i>	
Microbiostat for commercial and industrial water cooling	Na-PCP
Microbiocide for leather	K-PCP, PCP
Microbiocide for burlap, canvas, cotton, rope, and twine	PCP
Microbiocide and insecticide for wood treatment	PCP, Na-PCP
Preservative for oil and water-based paint	PCP
Slime control for pulp and paper	PCP
Microbiocide for petroleum drilling mud and flood water	PCP
Fumigant for shipping-van interiors	PCP
Preservative for hardboard and particle-board	PCP

ns = not specified.

Agricultural use

Large quantities of PCP or its sodium salt were previously used in a number of agricultural applications:

- to prevent wood decay, in farm buildings, fences, and storage facilities,
- as a herbicide and desiccant for forage seed crops, a herbicide for non-food vegetation control, a biocide in the post-harvest washing of fruit,
- as an insecticide for use in beehives, seed plots, and greenhouses,
- as a herbicide in paddy and upland rice fields, particularly in Japan.

In various products, pentachlorophenol has been used as a herbicide, algicide, defoliant, wood preservative, germicide, fungicide, and molluscicide. As a wood preservative, it is commonly applied as a 0.1% solution in mineral spirits, NO₂ fuel oil, or kerosene. It is used in pressure treatment of lumber at 5% concentration. Weed killers contain higher concentrations. PCP is no longer available for over-the-counter sale in the USA. [Morgan D. P., 1989].

In addition, PCP and Na-PCP had been approved for a number of applications in the food industry, such as biocides in packaging materials and glues.

In the USSR, PCP was applied as a no selective herbicide and as a desiccant on cotton plants.

Domestic use

The largely uncontrolled use of PCP by private individuals was almost exclusively related to the treatment of wood, both outdoors and indoors. PCP was the main active ingredient in certain wood preservatives for home use, and is added to products such as stains and paints. Although this category of products played only a minor role in the overall PCP market, it was of particular concern, since cases of apparent PCP intoxication after indoor application in private homes have been reported. As a consequence of such incidents, the use of PCP for the preservation of interior timber was banned in Canada and the Netherlands. Since 1986, the use of PCP as a biocide for indoor application was forbidden in the Federal Republic of Germany by government regulatory action. The US EPA too limited in 1984 the use of PCP-containing wood preservatives in interiors to certain support structures. This was also true for the indoor use of PCP-treated wood. The sale and use of PCP was restricted to certified applicators.

Other reported applications of PCP included health-care products and disinfectants for use in the home, farms, and hospitals. PCP might also be contained in dental-care products, bactericidal soaps, laundry products, and medical products for the skin.

2.2. Today's Use of PCP, NaPCP and PCPL

Today the predominant use of pentachlorophenol containing chemicals is in the treatment of wood as a sapstain control agent for freshly cut timber. To protect the wood from fungi, which growth causes the wood to be stained, timber is either treated with chemicals like NaPCP or kiln dried. Drying of wood has been the predominant way of treatment for example in the Nordic countries in the 1990s. In 1996 almost 90 % of the total EU consumption of PCP, NaPCP and PCPL was through the use of NaPCP for sapstain control in France, Portugal and Spain. In Portugal three product types are treated with NaPCP: pallet boards, construction timber and fencing panels).

According to a survey carried out by the DG III and the Environmental Resources Management in 1998 [DG III/ERM 1998], no more than 2 tonnes of PCP was used for wood preservation in 1996. PCP, NaPCP and PCPL may be used in the remedial treatment of timber and as a surface biocide for masonry, particularly when timber in industrial or domestic premises becomes wet and stays wet, being susceptible to wood-rotting fungi. There might have been around 10 000 rot treatments carried out each year in the British Isles, a part of these could have used PCP-containing formulations (estimations by Building Research Establishment in 1982).

PCPL is used in the preservation of textiles, which are subject to attack by fungi and bacteria during storage and use. The majority of treatment in the UK and France is carried out for textiles used by military. These include wool,

cotton, flax and jute fabrics and yarns used in covers, tarpaulins, awnings, tents, webbing and netting and also sisal and manila ropes.

The import of treated wood products and textiles can be possible source of PCP, NaPCP and PCPL. In practice the control of this import is difficult. According to information from Umweltbundesamt (UBA) in 1994, no PCP levels above 5 ppm have been detected on textiles in this years within their monitoring programme [DG III/ERM 1998]. Imported leather and timber may also be treated with PCP, NaPCP or PCPL. However, according to UBA levels of PCP in these products are likely to be low [DG III/ERM 1998]. It has been found, that textiles and yarns imported into the UK for dyeing and finishing sometimes contain NaPCP, used as a fungicide in the maize or rice starch used to stiffen, or size, the yarn and this remains in the cloth after weaving. It is likely that some partly processed and finished leathers have been treated with PCP or NaPCP in their countries of origin. In addition, wood chips imported from South-America and wood imported from Africa to Finland have occasionally contained PCP.

The use of PCP, NaPCP and PCPL will cease by the end of 2008 in all EU Member States.

Denmark	prohibited 1979 not in use since 1980 pesticide not approved for use (last approval expired in 1981) all pesticides containing PCP were phased out in 1982 use of PCP and PCP-containing products is banned not used in forestry and timber processing industry
Estonia	banned 1999 not used in forestry and timber processing industry
Finland	use of PCP as antistain agent for treatment of wood ceased in 1984 by voluntary agreement PCP as such has not been produced in Finland restricted marketing and uses since 1993 (only three purposes) ban of use and placing on market of PCP and its salt and ester since 1 st March 2000 regulations not used in forestry and timber processing industry
Germany	complete ban of production and use in 1989 import of planting material containing the substance prohibited production and marketing as pesticide is prohibited completely banned for use in forestry and timber protection regulations No.
Latvia	no registration/licensing for plant protection use no info about use as industrial chemical banned for marketing and use: 01.01.2001 (except products, with cone. < 0.1 %) no use, no stockpiling not used in forestry and timber processing industry
Lithuania	no registration as pesticide import, production and use as pesticide is banned marketing restricted probably used in forestry and timber processing industry as wood preservative stockpiling: 553 kg in farms' storages
Poland	not registered and permitted for marketing and use as a pesticide since 1967 permits for trade/use in plant protection are not granted import not possible (except for scientific purposes) possible losses to the environment are not known no production and export not used in forestry and timber processing industry

Russia	banned in the Russian Federation not used in forestry and timber processing industry
Sweden	banned 1978 (not registered) no longer in use as a.i. in biocides no remaining uses are allowed not used in forestry and timber processing industry

Use in USA

Pentachlorophenol was one of the most widely used biocides in the United States. It was registered for use by EPA as an insecticide (termiticide), fungicide, herbicide, molluscicide, algaecide, disinfectant, and as an ingredient in antifouling paint [Cirelli, 1978], but it is now a restricted-use pesticide [CELDS 1992; EPA 1984]. The principal use of pentachlorophenol is as a wood preservative (registered by EPA as such). The treatment of wood for utility poles represents 80% of the U.S. consumption of pentachlorophenol [CMR 1987]. However, pentachlorophenol is no longer contained in wood preserving solutions or insecticides and herbicides available for home and garden use since it is a restricted-use pesticide.

Pentachlorophenol is used for the formulation of fungicidal and insecticidal solutions and for incorporation into other manufactured pesticide products. These nonwood uses account for no more than 2% of U.S. pentachlorophenol consumption [Mannsville, 1987]. This wide spectrum of uses was partially attributed to the solubilities of the nonpolar pentachlorophenol in organic solvents, and the sodium salt in water.

3. Discharges, emissions and losses

Emissions during Production

Some data are available concerning the loss of phenolic and nonphenolic compounds into the environment during the normal production of PCP or Na-PCP [Umweltbundesamt, 1985]. The following air emission concentrations (mg/m³) and mass flow values (g/h) were reported: PCP 0.7 mg/m³, 9 g/h; tetrachlorophenols 0.2 mg/m³, 0.8 g/h; trichlorophenols 0.02 mg/m³, 0.04 g/h; hexachlorobenzene 23.9 mg/m³, 12 g/h; pentachlorobenzene 2 mg/m³, 15.5 g/h; tetrachlorobenzene 2.8 mg/m³, 66.5 g/h; OCDD 0.05 mg/m³, 0.04 g/h; OCDF 0.02 mg/m³, 0.002 g/h.

The annual air emission values resulting from the production of approximately 2000 tonnes of PCP or Na-PCP, respectively, per annum are given in Table II.A.3.1.

Table II.A.3.1. Air emissions of phenolic and non-phenolic compounds during production (maximum values as reported in BUA (1986)).

Chemical compound	Annual air emissions (kg/year) during production of:	
	2000 tonnes PCP/year	2000 tonnes Na-PCP/year
PCP	18	65
Other chlorophenols	9	5
Hexachlorobenzene	-	105
Other chlorobenzenes	1	700
OCDD	0.2	0.2

While no waste water occurs during the production of PCP, the annual loss of various compounds resulting from Na-PCP production into the waste water was as follows: PCP, 60 kg; OCDD, 0.34 g; H₇CDDs, 0.1 g; H₆CDDs, 0.001 g; OCDF, 0.1 g; H₇CDFs, 0.026 g; H₆CDFs, 0.002 g [BUAS, 1986].

The volume of contaminated wastewater generated during the production of Na-PCP is small, because manufacturers and regulatory agencies have emphasized efficient process design.

During the production of approximately 2000 tonnes PCP/year, about 8 tonnes of washing methanol, 4 tonnes of activated charcoal, and 2 tonnes of other wastes occur. These wastes, as well as the filtration sludge resulting from Na-PCP production, contain considerable amounts of hazardous chemicals (Table II.A.3.2). They are generally disposed of by either storage in underground disposal sites (filtration sludge) or incineration at temperatures above 1200 °C [BUAS, 1986].

Table II.A.3.2. Phenolic and non-phenolic compounds in the combined wastes (PCP production) and filtration sludge (Na-PCP production) [BUAS In. Ges. Dt. Chemiker, 1986].

Compound	Combined wastes (kg/year)	Filtration sludge (kg/year)
PCP	1350	900
Other chlorophenols	0.7	ns
Hexachlorobenzene	ns	6000
Decachlorobiphenyl	ns	3400
Decachlorophenoxybenzene	ns	44
OCDD (OCDF)	0.98	0.67 (0.67)
H ₇ CDDs (H ₇ CDFs)	0.13	0.17 (0.045)
H ₆ CDDs (H ₆ CDFs)	0.013	0.092 (0.015)
P ₅ CDDs (P ₅ CDFs)	0.003 x 10 ⁻³	0.016 (0.005)
T ₄ CDDs (T ₄ CDFs)	0.002 x 10 ⁻³	0.007 (0.001)
2,3,7,8-T ₄ CDD	ns	0.001

ns = not specified

Pentachlorophenol has historically been estimated to volatilize from the surface of pentachlorophenoltreated wood products at an estimated rate of 760,000 pounds (344 metric tons) annually, or roughly 2% of the total amount of preservative applied. These estimates are representative of usage of the compound in those applications in the 1970s [EPA 1980f].

As much as 500,000 pounds annually (228 metric tons) of pentachlorophenol, used in cooling tower waters as an anti-fouling agent, have been released to the atmosphere through volatilization with heated water and steam in the past [EPA 1980f]. However, pentachlorophenol is no longer commonly used for this purpose [Vulcan Chemicals 1989].

According to the TRI, an estimated total of 1,306 pounds of pentachlorophenol, amounting to 1.3% of the total environmental release, was discharged to the atmosphere from manufacturing and processing facilities in the United States in 1999 [TRI99 2001] (Table II.A.3.3). The TRI data should be used with caution because only certain types of facilities are required to report.

Table II.A.3.3. Releases to the environment from facilities that produce, process, or use pentachlorophenol, reported in the USA (Source: U.S. Department Of Health And Human Services, Public Health Service Agency for Toxic Substances and Disease Registry. Toxicological Profile For Pentachlorophenol, September 2001)

State ^b	Number of facilities	Reported amounts released in pounds per year ^a						
		Air ^c	Water	Underground injection	Land	Total on-site release ^d	Total off-site release ^e	Total on and off-site release
AL	7	459	813	No data	0	1,272	331	1,603
AR	2	250	5	No data	No data	255	115	370
CA	2	5	No data	No data	No data	5	No data	5
FL	1	No data	No data	No data	2,000	2,000	No data	2,000
GA	2	13	5	No data	No data	18	122	140
ID	1	5	No data	No data	43,000	43,005	No data	43,005
IL	1	2	No data	No data	0	2	74	76
KY	1	10	No data	No data	0	10	250	260
LA	2	8	34	No data	No data	42	23	65
MD	1	No data	No data	No data	No data	No data	No data	No data
MN	1	1	No data	No data	No data	1	No data	1
MO	1	255	0	No data	No data	255	1	256
MS	4	10	112	No data	0	122	15	137
NC	2	3	3	No data	No data	6	1,480	1,486
NE	1	255	No data	No data	No data	255	No data	255
NJ	1	2	0	No data	0	2	15	17
NV	1	2	No data	No data	No data	2	No data	2
OH	1	2	1	No data	No data	3	5	8
OR	4	16	251	No data	26,793	27,060	14,654	41,714
SC	2	6	0	No data	11,911	11,917	8	11,925
SD	1	1	53	No data	No data	54	160	214
TX	2	0	0	5	No data	5	No data	5
UT	2	1	No data	No data	15,133	15,134	255	15,389
WA	4	No data	No data	No data	No data	No data	No data	No data
Total	47	1,306	1,277	5	98,837	101,425	17,508	118,933

^aData in TRI are maximum amounts released by each facility.

^bPost office state abbreviations are used.

^cThe sum of fugitive and stack releases are included in releases to air by a given facility.

^dThe sum of all releases of the chemical to air, land, water, and underground injection wells.

^eTotal amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

About 2 metric tons of pentachlorophenol used as a biocide in cooling tower waters were estimated to have been discharged to surface waters in 1978 [EPA 1979a]. In addition, industries such as leather tanning and textile factories may have released up to 4,400 pounds (2 metric tons) and 12,000 pounds (5.5 metric tons) of pentachlorophenol, respectively, in their waste water discharges to surface waters on an annual basis in the 1970s [EPA 1980f].

Pentachlorophenol is no longer used in these applications [Weinberg, 1997]. Total annual pentachlorophenol releases to municipal waste water treatment facilities were estimated to be 12,000 pounds (5.3 metric tons) [EPA 1980g]. Most of the pentachlorophenol removed from effluent streams by waste water treatment processes is adsorbed to sludge solids. Sludges from wood preservation industries historically have been estimated to contain up to 31,500 pounds (14.3 metric tons) of pentachlorophenol annually.

Pentachlorophenol in solid wastes from wood-treatment facility evaporation ponds was estimated to total an additional 133,000 pounds (60.2 metric tons) annually in the 1970s [EPA 1980f]. However, most wood-treatment facilities have closed, or are in the process of closing, on-site evaporation ponds [Vulcan Chemicals 1989].

According to Commission Directive 1999/51/EC, placing on the market and use of PCP is not permitted as a synthesising and/or processing agent in industrial processes from 1 September 2000. As a consequence the production of PCPL will eventually cease.

Formulation of substances

Products, which are used in wood treatment or in textile impregnation, may be ready-for-use products or may need some dilution, dissolution or addition of other (active) substances. Formulation of the treatment fluid may take place by the importer or the producer or the end user of the substance. In the absence of detailed information on products and preparations on the market at present, no quantitative emission estimation from formulation is possible to carry out. However, it could be assumed that the emissions will be probably lower during formulation compared to emissions during use of substances.

Wood treatment plants

At the wood treatment facility emissions to the environment (air, water and soil) may occur:

- during the dipping process (volatilisation to air);
- during transport from dipping to drying (runoff from wood surface to soil);
- during the drying process (volatilisation to air and leachates to soil);
- from leachates from treated wood stored outdoors (runoff from wood surface to soil);
- via evaporation from treated wood products (volatilisation to air);
- as wood waste from sawing and processing of treated wood;
- as solid waste, sludge from the bottom of dipping/treatment tank.

However, measured emission data or sufficient initial data to estimate emissions are not available.

In the production of pallet boards in South Europe, the dipping at the majority of sites takes place outdoors. Major releases may occur when the wood has just been removed from the dipping tank due to possible spillage or runoff of treatment fluid from the surface of wood to soil. In the past timber would have been allowed to drain directly onto the soil, but now at least in some plants timber is drained on impermeable, concrete pavements or on tables or worktops. If treated (and dried) wood is stored outdoors, it is difficult to prevent rainwater washing over it and then running into the soil or into surface water. Therefore potential for local soil contamination is high due to both runoff from wood surface after dipping and also during storage due to rainwater. As a water soluble substance (greater solubility than PCP), NaPCP is quite mobile and tends to migrate through soils with the potential to enter groundwater.

Releases as a solid waste may occur during sawing and processing of wood. Also sludge, consisting of sawdust and active substance, accumulated in the dipping tank may cause emissions if it is not treated in a proper way. According to a Finnish study at the beginning of the 1980s PCP-containing solid waste of about 0,3 litres per m³ treated wood was collected (Viitasaari 1988).

Use of treated wood

Emissions, discharges and losses of PCP and NaPCP are likely from wood in use. The volume of wood which was treated with PCP and NaPCP in the mid-1980s was much higher than in the mid-1990s or today. A part of this wood is probably still in use in buildings. However, it is unclear how much PCP/NaPCP this wood contains nowadays.

Rain may wash NaPCP from the surface of the treated pallets, leading to high local levels in soils where pallets and pallet boards are stored and used in the open [Hobbs *et al.*, 1993]. NaPCP may also reach the environment by volatilisation in spite of its low volatility. In a doctoral thesis PCP emission rates from NaPCP treated wood were measured. In this study, small pine wood blocks were treated by immersion in NaPCP for 18 hours and then dried for 3 weeks. PCP emissions were measured in a flux chamber. An average steady-state flux rate of 10,8 µg/m²/hour was observed after 96 hours, based on a loading rate of 5,4 m²/m³ (wood surface/chamber volume). Marchal observed that PCP emissions were strongly affected by both temperature and the loading rate. Wood treated with NaPCP showed lowest emissions to air ranging from 33 to 46 µg/m³ (but higher concentration with higher loading rate).

An estimate of PCP emissions to air from NaPCP treated wood can be derived from a doctoral thesis by Marchal (1996). Based on the flux rate from the Marchal thesis, emissions to air in Portugal are: 516 kg/a, in France 344 kg/a, in the UK 229 kg/a and in Spain 115 kg/a. Depending on the solvent, temperature, pH, and type of wood 30 – 80 % of PCP may evaporate within 12 months from dip- or brushtreated wood (WHO 1987).

PCP/NaPCP treated timber may exist in houses/buildings treated for remedial purposes. Dobbs *et al.*, (1979) estimated that an average whole house treatment involves about 1 kg of active ingredients. Where treatments are carried out against dry rot, the area treated is likely to be more localised and so smaller amounts of active ingredient may be used. No data on volumes of wood treated for this purpose are available. Emissions from the buildings are likely to be due to volatilisation, but it is not possible to predict the quantities of PCP/NaPCP released from this source.

In addition to emissions from ongoing production of treated wood or wood already in buildings or in products, some emissions may take place from treated wood which has been imported into Europe. Several studies on the PCP content of leather goods, wood and textiles have been carried out in the Federal Republic of Germany (UBA 1994). In 1992 and 1993 45 samples of wooden goods/articles (kitchen equipment, children's play equipment and fruit crates) were analysed. In all samples the PCP concentrations were below 2,5 mg/kg. A Swiss campaign was carried out in 1996 to study the market situation (i.e. import) of wood, textile and leather treated with PCP; 129 samples of wood were analysed and the highest PCP levels detected were in the range of 500 - 1 000 ppm. A limit value of 5 ppm was exceeded in 9,3 % of the samples (OFEFP 1998). In addition, wood chips imported from South-America and wood imported into Finland from Africa have occasionally contained PCP.

Impregnation of heavy-duty textiles and fibres

Pentachlorophenyl laurate (PCPL) is used in the treatment of fabrics and webbing, and also of yarns and ropes. PCPL is insoluble in water and so is applied either in solvent solution or, more normally, as a concentrated aqueous solution/emulsion. Releases to waste water may occur as not all textiles in the treatment plant are treated with PCPL and therefore the equipment has to be washed out. During treatment in a dyeing 80 % of the PCPL in the emulsion is adsorbed to the fibre or yarn. When textile-finishing operations include a highly alkaline wash the pH of the wastewater is high and when wastewater-containing PCPL is mixed with this water, PCPL is likely to undergo chemical hydrolysis, producing PCP in its ionic form.

According to Commission Directive 1999/51/EC, the impregnation of textiles and fibres with PCPL will cease by 31 December 2008 in France, Ireland, Portugal, Spain and the UK. In the other EU countries, where no national bans on PCP and its derivatives exist, this use ceased from 31 August 2000.

Use of textiles treated

Discharges to water and emissions to air are possible from the use of PCPL (and PCP) treated textiles. Textiles treated today in Europe are heavy-duty textiles for outdoor use where they may be in contact with rain, surface water or sea water. Textiles are used for transport lorries, public market trade stalls, army tents, awnings, ropes, sails and marine fabrics. No estimates are available of the volume of treated textiles, but the volume of PCPL used for treatment has ranged from 30 to 46 tonnes per year in the late 1990s. Releases during the user phase depend on the

type of textile, the environmental conditions and the application. PCPL is very insoluble in water and has a low vapour pressure. When treated tents and tarpaulins are exposed to the weather, PCPL may undergo photodegradation; no studies on this release have been reported. Also, when wet, PCPL will slowly de-esterify to produce PCP on its ionic form which washes out of the textile or is lost by vaporization.

In addition to textiles treated in Europe imported textile and leather are a source of releases. In practice the control of the import of treated wood products and textiles is difficult.

If imported hides and skins have also been treated with NaPCP in their countries of origin then it is possible that this is released during their further processing and tanning.

Dioxins and Furans and pentachlorophenol

→ *Amounts of dioxin and furan impurities in PCP*

Pentachlorophenol contains impurities of dioxins and furans. The concentrations have decreased after legal measures were taken in the US and Europe between 1987 and 1991.

Masunaga et al (2001a) studied the PCDD/F content of a number of Japanese agrochemicals. Three batches of PCP were produced between 1967 and 1971, whereas the production date from one batch was unknown. The total amount of PCDD/Fs varied between 14,000 and 24,000,000 ng/g a.i. In 1987 the US EPA established rules limiting the HxDD concentration per batch to a maximum of 4 ppm with a monthly average of 2 ppm (2,000 ng/g). In 1991 the EU restricted the use of PCP to formulations with a HxDD concentration below 4 ppm (EU directive 91/173/EEC). Due to these regulations PCDD/F concentrations have decreased considerably. Eduljee (1999) provide the results from measurements on the dioxin content in batches of PCP taken in 1992 and manufactured by Vulcan Chemicals. The HxCDD concentrations in these batches are roughly between 1000 and 2,300 ng/g. Eduljee (1999) citing Bingham (1991) mentions a total HxDD concentration of 9,700 ng/g in one sample of NaPCP and concentrations below 2,500 ng/g in three other samples. Eduljee (1999) cite data from the Penta Task Force (1996) who provided yearly average concentrations of 1,700 ng/g. These are also cited on the Eurochlor website.

In order to set these concentrations in a broader scope they have been compared them with the minimum limits for waste and the maximum limit to which storage in safe, deep, underground storages such as hard rock formations and salt mines is permitted within the EC. Above the a concentration of 15 µg/kg (15 ng/g) as laid down in EU Council regulation 1195/2006, amending Annex IV to Regulation (EC) No 850/2004 on persistent organic pollutants, waste should be handled according the relevant Community legislation⁸. According to EU Council regulation 172/2007 amending Annex V to Regulation (EC) No 850/2004 waste may be stored only in safe, deep, underground storages up to a concentration of 5 mg/kg (5,000 ng/g)⁹.

→ *Dioxin and furan formation*

Masanuga et al (2001) indicated that OCDD was the most common impurity formed during PCP production. From the congener profile it was deduced that dioxines were formed during the production of PCP through combination of two PCP molecules or between PCP and the most abundant secondary product 2,3,4,6 TeCP (Masunaga et al. 2001a). This process is also described by Ballschmiter & Bacher, (1996) as cited by Isoaari (2004). Kakimoto

⁸ COUNCIL REGULATION (EC) No 1195/2006 of 18 July 2006 amending Annex IV to Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants;

List of substances subject to waste management provisions set out in article 7 on waste management: Producers and holders of waste shall undertake all reasonable efforts to avoid, where feasible, contamination of this waste with substances listed in Annex IV. The Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) > 15 µg/kg (**)

⁹ COUNCIL REGULATION (EC) No 172/2007 of 16 February 2007 amending Annex V to Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants;

Up to a concentration of 5 mg/kg Polychlorinated dibenzo-p-dioxins and dibenzofurans(PCDD/PCDF) may be stored only in: — safe, deep, underground, hard rock formations, salt mines or a landfill site for hazardous waste (provided that the waste is solidified or partly stabilised where technically feasible as required for classification of the waste in subchapter 1903 of Decision 2000/532/EC) whereby the provisions of Council Directive 1999/31/EC (4) and Council Decision 2003/33/EC (5) have to be adhered to and whereby it has been demonstrated that the selected operation is environmentally preferable.

indicate that dioxins with a high chlorine content, HpDD and OCDD and HpCDFs are indicators of PCP contamination.

→ *Photochemical degradation*

Baker & Hites (2000a) carried out experiments in which PCP is converted to PCDDs under varying irradiation conditions. Their data suggest that available sunlight in the troposphere may convert environmental levels of PCP in the atmosphere to PCDD/F. The authors also cite a number of other experimental studies in which OCDD and in lesser amounts HpCDD were formed through photodegradation of PCP. Recent studies confirm the formation of PCDDs through photolysis of PCP (Liu et al., 2002).

→ *Releases from the Wood Preservation Sector –Case of Canada*

In the following tables data on emissions from the Wood Preservation Sector are given, basing on the recent comprehensive study carried out for developing strategic options for the management of toxic substances from the wood preservations sector in Canada. It should be noted, that the wood preservation sector in Canada comprises the preservative chemical manufacturers, the wood treating plants and the users of both industrial and consumer products. In 1995, 64 wood treating plants were reported as operational. In the study the Wood Preservation Sector was broken down into five wood preservative lifecycle steps:

1. chemical manufacturing;
2. wood treating;
3. in-service wood use;
4. out-of-service wood use;
5. contaminated sites.

Table II.A.3.4. Average Concentrations of Dioxin/Furan and HCB in Pentachlorophenol Wood Preservative used for Release Calculations (*Source: Strategic Options for the Management of CEPA-Toxic Substances from the Wood Preservation Sector, Volume I, July 1, 1999*)

Compound	TEF ^a	1997 Concentration ^b		Prior to 1987 Concentration ^c	
		(ppm)	TEQ (ppm)	(ppm)	TEQ (ppm)
Hexachlorobenzene	-	50		50	
TCDD (2,3,7,8)	1.0				
PCDD (2,3,7,8 isomer)	1.0				
HxCDD		1.51		10.1	
2,3,7,8 - HxCDD isomers (59%)	0.1	0.891	0.0891	5.96	0.596
HpCDD		61.3		296	
2,3,7,8 - HpCDD isomers (76%)	0.01	46.6	0.466	225	2.25
OCDD	0.0001	1420	0.142	1386	0.139
TCDF	0.1				
PCDF	0.5	0.005	0.0025	1.4	0.7
(assumes 100% 2,3,7,8 isomer)					
HxCDF		2.29		9.9	
2,3,7,8 - HxCDF isomers (13%)	0.1	0.298	0.0298	1.29	0.129
HpCDF		31.2		88	
2,3,7,8 - HpCDF isomers (27%)	0.01	8.42	0.0842	23.8	0.0238

Compound	TEF ^a	1997 Concentration ^b		Prior to 1987 Concentration ^c	
		(ppm)	TEQ (ppm)	(ppm)	TEQ (ppm)
OCDF	0.0001	303	0.0303	43	0.0043
Total Dioxin/ Furan			0.84		4.05

- a. World Health Organization - Europe 1997 Toxic Equivalent Factors (TEF). Note in particular revised OCDD and OCDF factors. These factors were reiterated in 1998.
- b.c. Dioxin/ Furan and hexachlorobenzene data was derived using: Weinberg Group^ Volatilization of Microcontaminants from Pentachlorophenol treated Utility Poles. May 28,1998. Report prepared for the Penta Task Force.
- b. The arithmetic mean is based on analysis conducted on pentachlorophenol samples taken between 1989 and 1997. The actual range of D/F TEQ concentration measured was 0.22 to 6.26 ppm.
- c. Technical grade (composite sample from Monsanto, Reichhold Chemicals, and Vulcan) concentrations were used from for samples analyzed prior to 1987. It was assumed that the concentrations of 2,3,7,8 isomers were found in similar proportion to the 1997 pentachlorophenol formulation.

Table II.A.3.5. Estimated Release of Dioxin/Furan and HCB from Wood Treatment Plants Utilizing Pentachlorophenol (Source: Strategic Options for the Management of CEPA-Toxic Substances from the Wood Preservation Sector, Volume I, July 1, 1999)

Reference Information	Activity	Release to Air (g/year)				Release to Water (g/year)				Waste Generation (g/year)			
		HCB		D/F TEQ		HCB		D/F TEQ		HCB		D/F TEQ	
Wood Preservation Plants	12 Plants	Per Site	Total	Per Site	Total	Per Site	Total	Per Site	Total	Per Site	Total	Per Site	Total
		2.76	33.1	0.147	1.76	0,006	0,076	$1.1 \cdot 10^{-4}$	0.0013	9	108	0.15	1.8

Notes on Estimate Calculation Methodology:

Air emissions based on US emissions data; water release data based on effluent volumes and known pentachlorophenol concentration in the effluent; Solid waste estimates based on 20 barrels/per year/per site with average PCP content of 3%. Solid waste is sent to incineration at Swan Hills or Laidlaw or to secure landfill at Thurso or Sarnia.

Table II.A.3.6. Estimated Annual Dioxin/Furan and Hexachlorohenzene Releases to Air and Soil from Penta Treated Wood In-service (Source: Strategic Options for the Management of CEPA-Toxic Substances from the Wood Preservation Sector, Volume I, July 1, 1999)

Product	Year Produced	Release to Air (g/year)				Release to Soil (g/year)			
		HCB		D/F TEQ		HCB		D/F TEQ	
		Per pole/tie	Total	Per Pole/Tie	Total	Per Pole/Tie	Total	Per Pole/Tie	Total
Utility Poles (6.8 million)	Post 1987 (20%)	$3.3 \cdot 10^{-4}$	446	$7.8 \cdot 10^{-9}$	0.01	$1.5 \cdot 10^{-5}$	100	$1.3 \cdot 10^{-6}$	9.0
	Pre-1987 (80%)	$3.3 \cdot 10^{-4}$	1784	$3.5 \cdot 10^{-7}$	1.89	1.5×10^{-5}		$1.3 \cdot 10^{-6}$	
Railway Ties (70,000 m ³)	Pre 1987 (100%)	Data not available; Modeling could not be performed				$5 \cdot 10^{-5}$	35.1	$4.4 \cdot 10^{-7}$	0.31

Notes on Estimate Calculation Methodology:

Utility Poles: Volatilization estimates based on Jury Model (Weinberg Group, May 1998); leaching estimates based on Monto Carlo analysis of Gurprasad and Lapointe data on concentration of contaminants surrounding poles.

Railway Ties: Assumes most PCP treated ties in service are treated with older pentachlorophenol formulation. Initial loading of 3.8 kg/m³ of wood was used. It was assumed that ties have similar release rates of HCB and D/F to soil as do poles. For utility poles losses were 9.2% of HCB and 1.0% of D/F over the lifetime of the pole. Assuming ties have a lifetime of 35 years this translates to a loss of 0.26%/year and 0.029%/year of HCB and D/F respectively. Railway ties for use in Canada have not been treated with pentachlorophenol since 1992.

Table II.A.3.7. Estimated Annual Quantities of Dioxin/Furan and HCB Landfilled with Penta Treated Wood (Source: Strategic Options for the Management of CEPA-Toxic Substances from the Wood Preservation Sector, Volume I, July 1, 1999)

Out-of Service Wood	Quantity	Contaminant Concentration in Landfilled Wood (e/year)	
		HCB	D/F TEQ
Landfilled Poles	4994 Poles	589	31,4
Landfilled Ties	287 m ³	54,5	4,4

Notes on Estimate Calculation Methodology:

Landfilled Poles: Approximately 1.9% of in-service poles removed from service annually; 53% are PCP treated poles and 4% of these are landfilled. Assumes 20% of poles were originally treated with new pentachlorophenol formulation; 80% of poles were treated originally with older pentachlorophenol formulation.

Landfilled Ties: Again initial loading of 3.8 kg/m³ of wood was used. Assumes 41% of the ties taken out of service are landfilled and that 2% > of 50%) of ties taken out of service are landfilled as only CN used pentachlorophenol treated ties and only for 1% of their tie service in eastern Canada and 2% of their tie service in the west.

→ *Waste management of treated material*

Releases from landfills are mainly in leachates. There are measurements available on PCP concentrations from landfill - in a 5-year field study conducted in Finland for 43 landfills in the during burning of PCP-, NaPCP- or PCPL-containing wastes the most severe emissions may arise from the formation of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). When waste is burned at a low temperature and low oxygen content like in open fire or on a small scale in households, PCP-treated wood may result in higher dioxin and furan emissions than from incineration under controlled conditions.

Pentachlorophenol (PCP) and its derivatives (NaPCP and PCPL) contain PCDD/Fs (predominantly Hp-CDD/Fs and OCDD/F) as impurities. Reported concentrations of 2,3,7,8-substituted congeners in technical PCP (1000 - 3000 µg TEQ/kg) are significantly higher than those reported in PCP products such as NaPCP (84 - 510 µg TEQ/kg). PCP-based textile preservatives (particularly associated with imported cotton textiles) probably represent an important PCDD/F source to sewage sludge. Chloranil and chloranil-based dyes and pigments can contain significant levels of PCDD/F impurities as predominantly OCDD. Associated dyes and pigment contain lower PCDD/F concentrations (2 - 200 µg TEQ/kg) than pure chloranil (300 - 2900 µg TEQ/kg). The use of water-based textile dyes containing chloranil in a given catchment could represent a significant source of higher molecular weight PCDD/F congeners to the resulting sewage sludge. In addition to sewage sludge, application of other types of organic amendments (e.g. farm yard manure), paper waste sludge and textile waste could represent important sources of PCDD/Fs to agricultural soils in the UK¹⁰.

→ *Emissions of dioxins as an impurity in PCP*

Dioxins (i.e. PCDDs) and furans (i.e. PCDFs) are formed as by-products during the manufacture of chlorinated phenols. Therefore PCP and its derivatives usually contain dioxins and furans at parts per million level. From 1 September 2000 the concentration of hexachlorodibenzoparadioxin (HCDD) in the PCP or in its derivatives may not exceed 2 ppm according to Commission Directive 1999/51/EC. The former limit value for dioxin was 4 ppm. The contribution of PCP and its derivatives to the PCDD/F loading to the aquatic environment is higher than to the atmospheric and terrestrial environment. PCP and its derivatives contain and emit the higher chlorinated PCDD/F congeners to the environment and do not contribute significantly to the burden of more toxic TCDD/F and PeCDD/F isomers, the contribution of PCP to the total I-TEQ (International Toxic Equivalents) of aquatic environmental samples is estimated to be in the order of 10%.

There is some evidence that CDD/Fs leaches from treated poles into the surrounding soils, but these studies do not allow for the calculation of a rate of release from this mechanism. Possible release mechanism is the volatilization of dioxins into the atmosphere. Bremmer, et al. estimated an annual release of 15-125 g of TEQ from PCP-treated wood in the Netherlands, based on estimates of dioxin in treated wood and a range of half-lives of dioxin in treated wood from 15 years to 150 years. In 1996, the United States (US) Environmental Protection Agency (EPA)

¹⁰ Alcock R. E., Jones K. C., Pentachlorophenol (PCP) and chloranil as PCDD/F sources to sewage sludge and sludge amended soils in the UK, Chemosphere, vol. 35, n°10, pp. 2317-2330, 1997

estimated that the use of technical grade pentachlorophenol (PCP) over the previous 25 years to treat wood was approximately 336,000 metric tons in the US and an associated 672 kg of dioxin toxic equivalents (TEQs; calculated using the international TEF scheme). Assuming a 3% replacement rate for treated wood, EPA estimated that 468 kg of TEQ could be present in inservice PCP-treated wood in 1996, and that most of it, about 80%, was in treated utility poles. If the above release assumptions were applied to the 468 kg estimate, the potential annual release in the US in 1996 would be 3 to 19 kg. If actual releases were of this magnitude, they would constitute a significant contemporary source. For these quantities of dioxin to be released to the environment from in-use poles requires that dioxin be able to migrate from the interior of a pole to a pole's surface.

Given that the mobility of the tetra and pentachlorophenol congeners has been established and their proximity to the environment enhanced, the hypothesis that utility poles can serve as a reservoir source for these congeners is strengthened as a result of this study of Dwain L, et al, (1999)¹¹. Likewise, for hepta and octa congeners, this study supports the hypothesis that most of the mass of these congeners remain in the pole through its useful life.

→ *Formation of PCP during the burning process*

There are a few indications that PCP emissions may also come from naturally occurring combustion processes like forest fires or from burning of wood. Ahling and Lindskog (1980) have analysed the flue gases of domestic fires. They considered the levels of PCP found (19-180 $\mu\text{g}/\text{m}^3$) to be too high to have been produced by contamination of the air stream prior to the fire. PCP has also been detected from sediment samples deposited many years ago. Salkinoja-Salonen *et al.*, (1984) measured significant concentrations of PCP in sediments deposited more than 50 years ago in a small lake in Finland. They calculated PCP was rained out from the air at an annual rate of 2-4 $\mu\text{g}/\text{m}^2$, compared with a current rate of 10-17 $\mu\text{g}/\text{m}^2$. In another Finnish lake, Paasivirta *et al.*, (1990) have analysed sediments as much as 300 years old. Annual deposition rates for these ranged from 0,1-0,8 $\mu\text{g}/\text{m}^2$ while, in sediments deposited since 1961, deposition was calculated to be 2,1 $\mu\text{g}/\text{m}^2$. It is unclear whether natural sources or burning processes form a significant part of PCP releases.

Formation of PCDD/F (dioxins and furans) during incineration of wastes is known in the presence of corresponding chlorinated precursors (such as PCBs, PCPs) by a homogenous gas phase reaction at temperatures between 300 and 800°C.

Model studies performed by Dickson L. C. et al. (1992)¹² to determine quantitatively the predominance of two proposed pathways of polychlorinated dibenzo-p-dioxin (PCDD) formation during municipal refuse incineration: surface-catalyzed reactions of precursors occurring on fly ash and de novo synthesis of PCDD and related compounds from reactions of particulate carbon. The relative yields of PCDD formed from the model precursor compound pentachlorophenol were 72-99000 times higher than PCDD formed from the reactions of activated charcoal, air, inorganic chloride, and Cu(II) as catalyst under identical reaction conditions.

Dioxins and furans emissions have reported to be high when PCP contaminated wood is burned. IPCS (1987) cite a few older studies on dioxin formation. A wide range of PCDD concentrations was observed in smoke from burning wood chips impregnated with a technical PCP formulation. Temperatures below 500 oC, oxygen deficit and lower gas retention time favored the formation of PCDDs (Jansson et al (1978) as cited by ICPS (1987). Vikelsee & Johansen (2000) studied the dioxin emissions from fires with various chlorinated substances (e.g. dichlorprop, chlorthalonil) and found extremely high yields of the congeners 1,2,3,4,6,7,8-HpCDD and OCDF and OCDD during burning of PCP. The precise pathways through which dioxins are formed have not yet been elucidated. In dioxin emission inventories PCP treated wood is generally taken into account. However, estimations are hampered by highly uncertain or lacking emission factors and corresponding activity rates (QuaB et al, 2000).¹³

→ *Contaminated sediments*

The most significant source of POPs in Finland today is the River Kymi, which also accounts for the largest single input of dioxins into the Baltic Sea. The total amount of contaminated sediments between Kuusankoski and the Gulf of Finland is approximately 5 million cubic meters. These sediments contain about 6,000 kg of PCDD/F (corresponding to 17 kg I-TEQ). Concentrations of PCDD/F up to 350 $\mu\text{g}/\text{kg}$ I-TEQ have been recorded in riverbed

¹¹ Matthew N. Lorber, A Field Study to Evaluate the Potential for the Release of Dioxins from Pentachlorophenol-Treated Utility Poles, *Organohalogen Compounds*, Volume 41:35-39

¹² Dickson L. C., D. Lenolr., and O.Hutzinger, Quantitative Comparison of de Novo and Precursor Formation of Polychlorinated Dibenzop-dioxins under Simulated Municipal Solid Waste Incinerator Postcombustion Conditions, *Environ. Sci. Technol.* 1992, 26, 1822-1828

¹³ Pentachloroanisole and dioxins/furans in relation to PCP, Memo of 24/02/08 prepared by the National Institute of Public Health and the Environment The Netherlands

sediments. The river also transports polychlorinated phenols (PCP, max. conc. 720 µg/kg) and polychlorinated diphenyl ether (PCDE, 500 µg/kg) into the Gulf of Finland.

Summary of discharges, emissions and losses

It is hard to determine exact volumes of releases to the environment from sources of PCP, NaPCP and PCPL. However, it can be estimated that the main emissions are from treatment of wood and textiles. The main use of these substances today is as a sapstain control agent for wood. Therefore it is very likely that emissions from this source are highest taking also into consideration several soil contamination cases.

In addition, treated products and material and especially imported cloth may cause significant emissions. Other sources of releases are production and formulation of substances, disposal of PCP containing wastes and burning processes. Although production and application of PCP have stopped in many countries, there is still a potential of PCP releases from reservoirs such as sediment, soil, sludges, wood constructions and landfills.

4. Pentachloroanisole¹⁴

Bioaccumulation

Pentachloroanisole is highly hydrophobic. The estimated log K_{ow} (KOWWIN v1.67) is 5.30. Opperhuizen and Voors experimentally assessed a log K_{ow} value of 5,45 (Opperhuizen & Voors, 1987). It can be assumed that the compound has a high bioaccumulation potential. From the many studies on polychlorinated aromatic ethers, only few address bioaccumulation of PCA. The results of these studies are summarized in Table II A.4.1.

Table II.A.4.1. BCF values for pentachloroanisole.

Species	Exp time	Exp	BCF kg _{ww} /L	Reference
Fish				
Oncorhynchus mykiss	35 d	0,9 ng/L	16000	Oliver, B.G. and A.J. Niimi, 1985
Oncorhynchus mykiss	50 d	0,9 ng/L	14000	Oliver, B.G. and A.J. Niimi, 1985
Oncorhynchus mykiss	75 d	0,9 ng/L	12000	Oliver, B.G. and A.J. Niimi, 1985
Oncorhynchus mykiss	96 d	0,9 ng/L	17000	Oliver, B.G. and A.J. Niimi, 1985
Oncorhynchus mykiss	35 d	10 ng/L	11000	Oliver, B.G. and A.J. Niimi, 1985
Oncorhynchus mykiss	50 d	10 ng/L	20000	Oliver, B.G. and A.J. Niimi, 1985
Oncorhynchus mykiss	75 d	10 ng/L	15000	Oliver, B.G. and A.J. Niimi, 1985
Oncorhynchus mykiss	96 d	10 ng/L	24000	Oliver, B.G. and A.J. Niimi, 1985
Poecilia reticulata	7 d	40 ng/L	9120	Opperhuizen, A and P.I. Voors (1987)

For fish BCFs range from approximately 11000 - 24000 L/kg. The values at 7 and 21 days were discarded as equilibrium was not yet reached (Oliver & Niimi, 1985, Opperhuizen & Voors 1987). Although the studies have not been extensively validated, BCF values appear to be significantly.

In two studies on the bioaccumulation of organochlorine compounds in earthworms, concentrations of PCA in the soil and earthworms were measured at a sawmill that was abandoned 28 years ago. In the soil PCA concentrations were found from 0,06-1 µg/g dry soil. PCA concentrations in earthworms varied from 0,09 – 8 µg/g fat (Haimi et al. 1992, Haimi et al. 1993). Estimated BCF's from these studies range from 5-40 kg fat/kg dry soil.

Apart from a few experimental studies, PCA has been detected in several biotic matrices, see Table II.A.4.2., confirming the suggestion of a high bioaccumulation potential.

¹⁴ Pentachloroanisole and dioxins/furans in relation to PCP, Memo of 24/02/08 prepared by the National Institute of Public Health and the Environment The Netherlands

Table II.A.4.2. Concentrations of pentachloroanisole in biotic matrices.

Year	Location	Species	Tissue	Concentration ng/kg	Reference
2004	Greenland	caribou	muscle	200 lipid weight	Vorkamp et al., 2004
2004	Greenland	Capelin; Cod	Mussle;liver	2300 lw	Vorkamp et al., 2004
2004	Greenland	Snow crab	Muscle;liver	660;450 lw	
2004	Greenland	King eider; thick billed murre	liver	360;220 lw.	Vorkamp et al., 2004
2004	Greenland	Harp seal; Narwhal;Beluga	muscle	80;540; 1100 lw	Vorkamp et al., 2004
1980-1984	Rivers US	fish	Whole body	100000 ww	Schmitt et al 1990
2006	Tanzania	cassave	Roots;leaves	600;2100 fresh weight	Marco et al., 2006
1988	Siskiwit Lake US	Lake trout; white fish	Whole body	360;650 lw	Swackhamer et al.,1988
1987	Finland	mussels	Whole body	25 ng/g lw	Herve et al 1988

The U.S. Fish and Wildlife Service periodically determines concentrations of organochlorine chemicals in freshwater fish collected from a nationwide network of 112 stations as part of the National Contaminant Biomonitoring Program. Schmitt et al.1990 analyses samples taken from 1970 up tot 1985. PCA was detected in 1980 an 1984 in fish samples from 30 % of the stations (Schmitt et al. 1990).

A study from Greenland shows bioaccumulation of PCA in range of species varying from aquatic invertebrates to fish, birds and mammals (Vorkamp et al. 2004). However, the concentrations of PCA found in these different trophic levels show no evidence for biomagnification.

Table II.A.4.3. Concentrations of pentachloroanisole in abiotic matrices.

Year	Location	Compartment	Concentration	Reference
1998-1999	Mississippi river, US	Sediment	Up to2700 ng/kg	Rostad et al, 1999
1988	Canadian Arctic	Snow	1230 pico gr/L	Welch et al, 1991
1998	Yangtze river China	water	0,6 ng/l	Jiang et al 2000
1998	Yangtze river China	Sediment	Up to 4800 ng/kg	Jiang et al 2000
1989	Finland	Soil	Up to 1000000 ng/kg	Haimi et al 1993
1985	South pacific ocean	Air	9000 ng/m3	Atlas et al, 1986
1985	New Zealand	Air	2100 ng/m3	Atlas et al, 1986

Persistence

Pentachloroanisole (PCA) can be photo-oxidized in the atmosphere trough reactions with hydroxyl (OH) radicals. The calculated half-life for PCA based on this reaction is 9.8 days, with a atmospheric (OH) concentration of 1.5E6 OH/cm3 (AopWin v1.92). No experimental data are available on atmospheric degradation but rather high concentrations of PCA detected in remote marine atmosphere, ranging from 2100 - 9000 ng/m3 (Atlas et al. 1986) may lead to the assumption that the actual half-life may be more than 9.8 days.

In soil pentachloroanisole is product from methylation of pentachlorophenol (PCP). Several bacteria and fungi may enhance this process (Walter et al. 2004, Okeke et al. 1997, Lamar et al. 1990 a, Lamar et al. 1990 b, Haggblom et al. 1988). The estimated soil adsorption coefficient (PCKOCWIN v1.66) is 1485.

In a laboratory experiment with PCA-contaminated soil concentrations of PCA have been measured over a period of 20 weeks. The PCA concentration of 0,38 µg/g, at the beginning was reduced in 5 weeks to 0,18 µg/g and after 20

weeks only of 0,05 µg/g PCA remained (Haimi et al. 1993). Under anaerobic conditions PCA is known to be demethylated to PCP (Murthy et al.1979). Some fungi are found to enhance mineralization of PCA (Lamer et al., 1990b). Volatilisation of PCA is also observed in some studies (Walter et al. 2004, Lamer et al. 1990b).

There are no data on the persistence of PCA in water. The Henry's Law constant for PCA is estimated as 1.94E-3 atm-m³/mole, using a group estimation method (HENRYWIN v 3.10). This value indicates that PCA will volatilize rapidly from water. Based on this Henry's Law constant, the volatilization half-life from a model river (1 m deep, flowing 1 m/sec, wind velocity of 5 m/sec) is estimated as 2.2 hours. The volatilization half-life from a model lake (1 m deep, flowing 0.05 m/sec, wind velocity of 0.5 m/sec) is estimated as 6.9 days. Volatilization of PCA from water has been argued to be the source of the rather high PCA concentrations measured in the air (Atlas et al. 1986).

Potential for Long range environmental transport

Calculation of the vapor pressure (MPBWIN v1.42) according to the modified grain method resulted in a vapor pressure for PCA of 0,0459 Pa at 25 °C.

Pentachloroanisole is one of the more abundant high molecular weight halocarbons in the remote marine troposphere. Levels of pentachloroanisole in the South Pacific ocean (American Samoa) in the northern hemisphere were on average 9000 ng/m³, while those in the southern hemisphere, New Zealand were 2100 ng/m³ (Atlas et al. 1986). Air samples collected on a cruise on the Atlantic Ocean between 50 °N and 50 °S had a mean concentration of 8799 ng/ m³ (Schreitmüller et al.1995). The presence of pentachloroanisole in the remote marine troposphere indicate that PCA is subject to long range transport.

Concentrations of PCA have also been found in fish in Siskiwit lake, a remote lake on Isle Royale in lake Superior (Swackhamer et al., 1988). It is argued that the atmosphere is the source of the found contaminants because Siskiwit Lake is remote and far from point sources. However, since PCA is a biodegradation product of PCP, it could be transported directly or it was formed after transport of PCP prior to uptake by fish.

In a study on distribution and transport of several anthropogenic lipophilic organic compounds associated with Mississippi River suspended sediment samples of sediment were taken from than 12 sites along the Mississippi River, and from some connected rivers. None of the sediment samples contained PCP, but in almost all of the samples PCA was detected. The PCA bound to the organic compounds of suspended river sediments results in transported amounts of PCA of 350 g/day to the Gulf of Mexico (Rostad et al. 1999).

Pentachloroanisole is an important metabolic product of the commonly used herbicide PCP, and therefore logically to be found all over the world. However, data of PCA concentrations in snow in the Canadian Arctic regions (Welch et al. 1991) and in animals in Greenland (Vorkamp et al. 2004) strongly suggest that PCA is subject to long range environmental transport.

5. Contribution of PCP in the total dioxin burden¹⁵

As PCP production and use have been forbidden in a number of countries, it is difficult to estimate the contribution of PCP in the total dioxin burden. However, various authors indicate that this contribution may be considerable.

Eduljee (1999) states that it is likely that the presence of higher chlorinated PCDDs in the atmosphere, such as HxCDD, HpCDD and OCDD may primarily be due to the use of PCP in the past. Baker & Hites (2000b) cites US EPA who observed a 75% decrease in PCDD/F emissions from combustion sources between 1987 and 1995. However, sediment concentrations only decreased by 20%. The authors suggest that de novo synthesis of PCDD/Fs from PCP in the atmosphere explains these data.

High concentrations of dioxins in sediment were also observed by various other authors. Several studies were carried out in Japan where PCP was widely used as paddyfield herbicides in the past. Masunaga et al (2001b) estimated the contribution of PCP in the dioxin content of Lake Shinji Basin sediment to be 68%. Chloronitrophenol (CNP), and combustion contributed for 16 and 16% in recent surface sediment. In Tokyo bay contributions of PCP, CNP and

¹⁵ Pentachloroanisole and dioxins/furans in relation to PCP, Memo of 24/02/08 prepared by the National Institute of Public Health and the Environment The Netherlands

combustion were estimated to be 76%, 15%, and 9%, respectively (Yao et al., 2002). Uchimiya et al (2007) estimated the contribution of PCP in the Ichihara Anchorage to be more than 90%.

Pentachlorophenol use in Japan peaked around 1967 and levelled out until 1986 (Yao et al., 2002). Masunaga et al (2001b) indicated that PCP and CNP were used extensively nationwide in Japan, and thus the situation described for the Lake Shinji Basin is expected to be ubiquitous throughout Japan. From the decreasing trend of dioxin deposition in Lake Shinji after phasing out these herbicides, the amount of dioxins that accumulated in the agricultural soil in the basin was estimated to have decreased by about 2%/yr or a half-life of about 35 yr, indicating that dioxin runoff from agricultural fields would continue for a long time.

B. ENVIRONMENTAL LEVELS AND BIOAVAILABILITY

The physical and chemical properties of PCP (water solubility, octanol/water partition coefficient, volatility) can lead to ubiquitous contamination of air, soil, water, sediments, and organisms in the environment. Depending on the soil type, PCP can be very mobile, potentially leading to contamination of ground water and hence, of drinking water. Photodecomposition and biodegradation processes may not be adequate to eliminate PCP from the different compartments. Unfavourable temperature, pH, and other environmental conditions may retard degradation of PCP allowing it to persist in the environment. Biological decomposition may also be limited in waste-treatment factories resulting in high concentrations in the final effluents.

However, the reduction in use and narrowing of use patterns, levels of pentachlorophenol in the environment have declined sharply over the last decade.

Monitoring data

PCP has been detected in air, soil, water and sediments as well as in a large number of aquatic organisms, sampled mainly near known discharges. Monitoring data exist only on PCP, but not on NaPCP or PCPL. This may be due to high volume consumption of PCP in the past, and an assumption that NaPCP turns into PCP in the environment.

The most current information on levels of pentachlorophenol in the marine environment has been compiled by Euro Chlor (1999). This assessment shows a sharp decline in the levels of PCP in European river waters since the early 1990 when the marketing and use restrictions under EU Directive 91/173 first took effect.

In the Euro Chlor Risk Assessment for the Marine Environment information from different sources has been gathered. From the North Sea, coastal waters and estuaries data are available for Germany, the Netherlands and the United Kingdom. All average/median PCP concentrations are below 1 µg/l, with a range of concentrations from non-detected to 0,79 µg/l. In estuary waters, average or median concentrations have generally shown a decreasing trend over time during the period from 1983 to 1997.

Considering all of the available monitoring data (covering the period 1983 to 1997) the typical concentrations for coastal and marine waters are estimated to be 0,07 µg/l (excluding the UK, where several higher concentrations were measured in 1991-1992).

Based on the data collected from 1990 to 1997 for the rivers in the Netherlands, Germany and Belgium, average PCP concentrations ranged from 0,01 µg/l to 0,17 µg/l [Euro Chlor, 1999]. From France only data from the Seine is available. This average concentration 0,03 µg/l from 1995 is at the same level as in rivers of the Netherlands, Germany and Belgium. An extensive river water monitoring in the United Kingdom in 1990-1992 shows somewhat higher concentrations. Most of the median levels of PCP were below 1 µg/l, although there were some large recorded values in industrial areas e.g. 40 µg/l in the Mersey (ACP 1994). The National Rivers Authority has identified textile industries as a major contributor to PCP levels in rivers. In more recent measurements from 1994 - 1996 carried out by the UK NRA and the Environment Agency, concentrations have been considerably lower: 0,15 µg/l in 1994, 0,20 µg/l in 1995 and 0,02 µg/l in 1996 (UK Department of the Environment, Transport and the Regions, 2000).

In the past PCP concentrations as high as 25 000–150 000 µg/l in industrial effluent were reported; at one time, 30–40 tonnes were calculated to be transported by the Rhine each year [WHO 1998]. Concentrations up to 10 500 µg/l have been reported locally in a river [Fontaine et al. 1976], but concentrations in water samples are usually below 10 µg/l [WHO 1987].

Monitoring data showed that PCP concentrations generally decreased (from 0.07–0.14 µg/l in 1988 to 0.01–0.02 µg/l in 1993) in the River Elbe after PCP production was stopped in Germany in 1986 and its use was banned in 1989. Such a trend was not seen in the Rhine and its tributaries, where concentrations were even higher in 1990–1991 than in 1980–1989 (maximum levels up to 0.23 µg/l); the cause is not known, but it indicates continuing environmental contamination.

The Fraunhofer Institut (1999) has gathered monitoring data from 1994 to 1998 on substances (including PCP) in EU Member States in the context of the EC Water Framework Directive. As a result of aggregation of monitoring data in the aquatic phase (fresh water) a median PCP concentration of 0,0706 µg/l (90-percentile 0,1351 µg/l) was detected. This contained 2 296 measurements from 85 sampling stations, from which 1527 measurements were higher than the detection limit. Aggregation of sediment monitoring data produced a median PCP concentration of 15,50 µg/l (90-percentile 62,30 µg/l). This was a result of 66 measurements from 20 sampling stations; 61 of the measurements were higher than the detection limit.

Recent monitoring data on the level of pentachlorophenol in drinking water are available from the USEPA's National Drinking Water Contaminant Occurrence Database:

- in drinking water derived from surface water over a range of 0.04 to 1 µg/l, with a mean of 0.4052 µg/l (N = 2.831) and a standard deviation of 0.4355 (USEPA 2001a),
- in ground water, range of 0.04 to 1.64 µg/l, a mean of 0.459 µg/l (N = 12.666), and a standard deviation of 0.444,
- a weighted mean for all systems (surface water and ground water) is 0.449 µg/l.

Limited information is available on the levels of PCP in ambient air. USEPA (1980) estimated atmospheric concentrations of PCP using air models. A cumulative concentration estimate based on all emission sources was 0.5–136 ng/m³. The lower end of this range coincides with the upper end of the range of computed air concentration estimates based on PCP concentrations in rainwater in Hawaii (0.002–0.063 ng/m³), where PCP has been used extensively as an herbicide and wood preservative. A Canadian study [Cessna et al. 1997] reported the amount of PCP in air in Saskatchewan (Regina and Waskesiu) and Northwest Territories (Yellowknife). The concentrations of PCP in the vicinity of Yellowknife ranged from 0.43 to 3.68 ng/m³ with a mean concentration of 1.53 ng/m³. At both the Regina and Waskesiu sites, the concentrations ranged from 0.06 to 0.58 ng/m³ with a mean value of 0.30 ng/m³ [ATSDR 2001];

Two background air sampling stations in the mountains above La Paz, Bolivia, at 5200 m measured 0.93 and 0.25 µg PCP per 1000 m³ of air, and four Antwerp (Belgium) samples varied from 5.7 to 7.8 ug PCP per 1000 m³ of air. The level of PCP in Burlington, Ontario, rainwater was 10 µg/l in 1982 (Warrington 1996).

C. SOCIO-ECONOMIC FACTORS

1. National and International Regulation

Recently, regulations to limit or even ban some uses of PCP have been established in a number of countries. In the following applicable laws in the various countries is overviewed in brief:

The European Union

Council Directive 67/548/EEC

Pentachlorophenol. classification and labelling, harmonized at Community level in accordance with Council Directive 67/548/EEC are as follows:

- classified as Category 3 carcinogenic;
- classified as very toxic by inhalation;
- classified as toxic by skin contact and by ingestion;
- classified as irritant to eyes, respiratory system and skin;
- classified as dangerous to the environment .

Council Directive 91/173/EEC

The uses of pentachlorophenol and its principal derivatives sodium pentachlorophenate (NaPCP) and pentachlorophenyl laurate (PCPL) in the European Union have been limited since the Member States adopted

Council Directive 91/173/EEC (21 March 1991). Council Directive 91/173/EEC amending the ninth time Directive 76/769/EEC prohibits the marketing and use of pentachlorophenol and its salts and esters in concentration equal to or greater than 0.1 % by mass in substances and preparations. However, four exceptions are given. The use of PCP and its compounds in industrial installations (not permitting the emission and or discharge of PCP in quantities greater than those prescribed by existing legislation) is permitted:

- i) in the treatment of wood;
- ii) for the impregnation of fibres and heavy-duty textiles not intended in any case for clothing or decorative furnishings;
- iii) as a synthesizing and/or processing agent in industrial processes;
- iv) for the *in situ* treatment of buildings of cultural and historic interest (subject to individual authorisation by the Member State concerned).

PCP used alone or as a component of preparations employed within the framework of the above exceptions must have a total hexachlorodibenzoparadiioxin (HCDD) content of not more than 4 parts per million (ppm). As from July 1992 all amateur uses of PCP-based formulations were revoked and these chemicals may not be sold to the general public.

Commission Directive 1999/51/EC

In May 1999 restrictions on use of PCP and its salts and esters were tightened by the Commission Directive 1999/51/EC of adapting to technical progress for the fifth time Annex I to Council Directive 76/769/EEC on the approximation of the laws, regulations, and administrative provisions of the Member States relating to restrictions on marketing and use of certain dangerous substances and preparations (tin, PCP and cadmium). Point 23 concerning pentachlorophenol and its salts and esters as an Annex to Directive 76/769/EEC was replaced by amended point 23 in Annex I to Directive 1999/51/EC.

According to Directive 1999/51/EC pentachlorophenol and its salts and esters shall not be used in a concentration equal to or greater than 0.1 % by mass in substances or preparations placed on the market. By way of derogation until 31st December 2008 France, Ireland, Portugal, Spain and the United Kingdom may choose not to apply this provision to substances and preparations intended for use in industrial installations not permitting the emission and/or discharge of PCP in quantities greater than those prescribed by existing legislation:

- a) in the treatment of wood; however, treated wood may not be used:
 - inside buildings,
 - for the manufacture and re-treatment of :
 - i) containers intended for growing purposes,
 - ii) packaging that may come into contact with raw materials, intermediate or finished products destined for human and/or animal consumption,
 - iii) other materials that may contaminate the products mentioned in i) and ii);
- b) in the impregnation of fibres and heavy-duty textiles not intended in any case for clothing or for decorative furnishings;
- c) by way of special exception, Member States may on a case-by-case basis, authorise on their territory specialized professionals to carry out *in situ* and for buildings of cultural, artistic and historical interest, or in emergencies, a remedial treatment of timber and masonry infected by dry rot fungus and cubic rot fungi.

In any case: PCP used alone or as a component of preparations employed within the framework of the above exceptions must have a total hexachlorodibenzoparadiioxin (HCDD) content of not more than 2 parts per million (ppm).

Member States shall adopt and publish the provisions necessary to comply with the Directive by the 29th February 2000 at the latest. They shall apply these provisions as from 1st September 2000. However, Austria, Finland and Sweden may apply these provisions from 1st January 1999 except where otherwise specified in the Annex.

Biocides Directive 98/8/EC

Biocide directive 98/8/EC will in future cover also those biocidal product types where PCP and its salts and esters are used. Wood preservatives and textile treatment preservatives have to be authorised by Member States. Only those products, which contain active substances, listed on the Annex I of the directive can be authorised. All existing active substances are to be evaluated and decided on the acceptance before May 2010.

Integrated Pollution Prevention and Control Directive

The Integrated Pollution Prevention and Control Directive (IPPC Directive) 96/61/EC controls emissions to air, water and land (including wastes) from medium-sized and large industrial installations, waste management installations and installations for the intensive rearing of poultry and pigs. For PCP and its derivatives there are several categories of industrial activities in the IPPC Directive which could cover the production and use of PCP, NaPCP and PCPL. Such categories are for example:

- Chemical industry (production);
- Plants for the pre-treatment or dyeing of fibres or textiles (where the treatment capacity exceeds 10 tonnes per day); and
- Installations for the surface treatment of substances, objects or products using organic substances, in particular for impregnating (with a consumption capacity of more than 150 kg per hour or more than 200 tonnes per year).

The OSPAR Convention

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the "OSPAR Convention") was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

PCP was included in 1998 in the OSPAR List of Chemicals for Priority Action. The action recommended by OSPAR was:

- urge the setting of stringent discharge limits for the remaining installations producing or using PCP or its compounds;
- support EC action to ban after 2008 the import of products containing PCP or its compounds;
- promote an information campaign by producers of products that contain, or used to contain, PCP or its compounds on the correct disposal of products containing PCP;
- consider an OSPAR recommendation on the clean-up of PCP-contaminated sites;
- develop a monitoring strategy for PCP;
- initiate reporting to OSPAR on the remaining use of PCP and its compounds, and on their levels in imported products, concentrations of them in the environment, and the clean-up of contaminated sites; and
- to ask other relevant international forums to take account of the background document.

Austria

Pentachlorphenolverordnung BGBl. Nr. 58/1991

Manufacturing, placing on the market and use of finished products, which contain PCP and PCP, salts or compounds in concentrations exceeding 5ppm are banned.

Belgium

Article 1 of the Royal Decree of 25 February 1996

Directive 91/173/EEC amending for the 9th time the parent Directive 76/769 and placing restrictions on the marketing and use of pentachlorophenol (PCP) and its salts and esters, was transposed in Belgian legislation via article 1 of the Royal Decree of 25 February 1996. PCP and its salts and esters shall not be used in a concentration equal to or greater than 0.1% by mass in substances or preparations placed on the market.

As in the European Directive, certain derogations are provided, i.e. for substances and preparations used in industrial installations for following purposes:

- the treatment of wood. Important to note is that wood treated with PCP may not be used in interiors of buildings, even not for decorative purposes,
- the impregnation of fibres and heavy duty textiles,
- as a synthesizing and/or processing agent in industrial processes,
- for the *in situ* treatment of buildings of cultural, artistic and historic interest.

For these derogations it is, however, still necessary to respect the legislation for biocidal products, i.e. the Royal Decree of 5 June 1975, which means that the products should have an allowance from the Minister of Public Health before being placed on the market.

Denmark

Statutory Orders

Denmark notified the Commission on 31 January 1995 of the following:

- a limit value of 1 ppm of dioxin in PCP (Statutory Order no.582 1977)
- a general ban on PCP and preparations containing PCP above 0.1% by mass (Statutory Order No 446, 1992)

Denmark has also notified a Statutory on PCP, which is in fact a consolidation of their legislation on PCP. The notification contained both the provisions notified under Art. 100A §4 and provisions relating to the free circulation of products containing PCP (Statutory Order No 420, 1996).

Finland

Exemption based on the Act of Accession. During a period of four years (until 31 December 1998) from the date of accession Directive 91/173 shall not apply for Finland. National regulations apply.

Germany

Appendix, section 15 ChemVerbotsV

§ 15 subparagraph 1 and appendix IV, No. 12 GefStoffV

Existing prohibition/restriction in law:

- Substances and preparations with a mass content of more than 0.01% as well as products, which are treated thereby (content greater 5 ppm) for example as wood preservatives.
- Directive for the evaluation and removal of Pentachlorophenol (PCP) -contaminated building materials and construction units in buildings (PCP Directive), Communication DIBt, in 1997, No. 1, P. 6-16; changed by Communication DIBt, in 1997, No. 3, P. 80
- Materials or products (indicative): Wood and wood based panels treated with biocides or made of waste wood.
- Textile floor covering, wall coverings treated with biocides

Poland

Since 1996 all uses and products are banned as a result of the regulation issued by the Ministry of Agriculture.

Sweden

Swedish National Chemicals Inspectorate's regulations

In the Act of Accession Sweden was exempted from EU legislation (Dir. 91/173). The total ban will continue for another three years (starting on 1 January 1999). The Swedish National Chemicals Inspectorate's regulations apply.

The Netherlands

Several legal acts:

- PCP emissions: Pesticides Act, Order on Environmental acceptance criteria for non-agricultural acceptance, Order on the classification, packaging and labelling of pesticides
Regulation governing Commodities act/Pentachlorophenol (Commodities act) Decree.
- PCP content: Regulation governing Commodities act/Pentachlorophenol (Commodities act) Decree.
- PCP/PAH content: Pesticides Act
- BaP, phenol, PCP content: Order on the classification, packaging and labelling of pesticides.
- Pentachlorophenol: Building materials decree.
- Chlorophenols (sum): Building materials decree.

USA

EPA's cost-benefit analysis of the heavy-duty wood preservatives as part of the Special Review process provided the agency with the principle argument for continued use of pentachlorophenol, creosote, and the inorganic arsenicals. In 1981, the agency concluded that: "The Agency is very concerned about reducing the apparently high risks to treatment plant workers. However, canceling a specific use or uses for each one of the three wood preservative chemicals is unlikely to alter the overall risk picture for that chemical, since the treatment plant applicator is likely to apply the chemical to another end-use product. Thus, in order to appreciably lower the risks from exposure, we would have to cancel all uses of that pesticide".

Prior to 1984, pentachlorophenol was used in a significant number of pesticide products to control fungi, mosses, weeds, insects and bacteria as well as in wood preservatives. The EPA began investigating pentachlorophenol in 1978 because of studies indicating its fetotoxicity and oncogenicity.

In 1984, the agency banned all uses of nonwood-preservative pesticide products containing pentachlorophenol and its sodium and potassium salts, except use as an anti-fungal agent in oil well flood waters and pulp and paper mill solutions.

EPA determined that the nonwood uses of pentachlorophenol posed a risk of fetotoxicity and, due to the presence of the contaminants polychlorinated dibenzo-p-dioxins (dioxins) and hexachlorobenzene (HCB), they also posed a risk of oncogenicity to applicators. Second, EPA's analysis of the benefits associated with the uses of pentachlorophenol revealed that for the majority of uses, viable, effective alternatives were available and in use. Therefore, EPA determined that the fetotoxic and oncogenic risks associated with most non-wood uses of pentachlorophenol outweighed the benefits.

In 1984, EPA did not ban the use of pentachlorophenol as a wood preservative because the economic benefits resulting from the use of the wood preservative chemicals exceeded the risks. According to EPA, several modifications to pentachlorophenol reduced environmental and health risks. These required modifications included: reducing the levels of several of pentachlorophenol's contaminants HxCDD and 2,3,7,8-tetrachlorodibenzo-p-dioxin; labels with information on protective clothing and equipment in the application of pentachlorophenol; participation of commercial wood treaters in a Consumer Awareness Program (CAP) for end users of the treated wood; and requirements for product formulations, registrant warnings, and applicator precautions.

Other countries

China

Since 1982 Pentachlorophenol has been banned for registration and production, sale and use as pesticide. Uses are only allowed as wood preservative. Use is still allowed as germicide on woods. However, areas and methods of approved application as stated in "Bulletin of Pesticide Registration" should be observed.

India

Banned since 1991.

Indonesia

Prohibited for all uses since 1980.

New Zealand

Since 1991:

- 1) All uses and products are banned
- 2) Agreement in principle to permit re-introduction in closed timber treatment systems at approved sites with specific conditions on disposal of waste. These conditions have not been met and therefore no products registered, no use permitted and no imports allowed.

Switzerland

Since 1988:

Totally banned chemical: manufacture, supply, import and use of the substance and of products, which contain the substance, are prohibited. (Applies to pentachlorophenol, its salts and pentachlorophenoxy compounds).

2. Substitutes of PCP and PCP Derivatives

Due to previously described characteristics, substitution of PCP, NaPCP and PCPL is hard to accomplish. Description of every usage of the substitutes is beyond the scope of this report. That is why only one section of substitution will be described, that is, the one which is linked to the wood preservation, in two issues:

- substitution in wood preservation indoors, especially in living quarters,
- substitution in preservation of wood used as a construction material, not intended for direct contact with humans.

Unlike as it may seem, the first one is much easier to accomplish, because wood elements, especially those intended for constant being among humans, work in conditions incomparably better than those wood elements exposed to outdoor conditions and atmospheric factors.

There is a wide assortment of preservatives, surface coating substances, paints, varnishes and stains in everyday use that is capable of substituting PCP with the restrictions of its usage in force. In addition to organic substances, inorganic substances may be used without concern about them being washed out of the materials that have been protected.

In the case of industrial wood preservation, the issue is a more complex one, because each substance is combined with the usage of, most frequently, two other preservatives to obtain the effect given by PCP or its by-products.

Now three groups of substances and preparations based on them are broadly used, and these are:

- preparations based on PCP as the active substance,
- preparations using creosote (a derivative of coal tars), where creosols are the active substance,
- arsenic preparations (chromated copper arsenate – CCA).

None of these preparations is faultless. As for now, with the clear restrictions of PCP usage, and difficulties with management of preserved wood wastes containing the PCP - as well as with the restrictions of creosote usage, it can turn out that wood preservation with CCA may to a great account be a substitute of PCP. The advantage of creosote and CCA over PCP is the fact, that they are polychloro dibenzodioxine and dibenzofourane free.

There are also many substances, which already have found usage as wood preservatives. Those are:

- 3-Iodo-2-propynyl butyl carbamate – is used in some preparations and pigmented stains,
- 2-(thiocyanomethylthio) benzothiazole (TCMB),
- Zinc naphthenate available in preparations with organic solvents as well in water soluble preparations,
- Copper-8-quinolinolate – effective concentrations range from 0.25 to 0.675 %,
- a mixture of bis(tibutylin)oxide and N-trichloromethylthio phthalimide in concentrations 0.5 – 1.0%

and many others. The above are given as examples. Many other substances are tested and used.

Another possibility could be to substitute elements, or wooden structures, by elements made of other materials. As an example there can be given the substitution of wooden electric and telephone line poles by concrete ones, which do not need preservation.

In the case of wood, the utility industry expects 40 to 50 total years of service (although it has been found that a bad batch of wood can yield less than 35 years of service). The steel, concrete, and fiberglass alternatives yield a lifespan of 80 to 100 years. There are differences in maintenance costs associated with different materials. For example, wood may require retreatment, which some utilities perform on a set cycle, while steel, concrete and fiberglass do not. In addition, disposal costs for chemicals used in wood treatment are high and growing, while steel is recycled.

However, the utility believes that steel provides long-term savings because its lifespan is nearly double that of wood and the use of steel eliminates the wood pole retreatment program that costs the utility \$30 to \$35 a pole.

Steel has been cited as the most common alternative utility pole material in a Swedish report. The same is true in the United States, although steel alternatives represent a small but growing alternative when compared with the use of treated wood utility poles.

The problem of sleepers was similarly solved, by changing the wooden ones to concrete sleepers. Although that process of such substitution may last long, but it completely would solve the problem.

Generally we should highlight the fact that as for now, there is no substance, that could compete with PCP and that is why this substance is still in use, despite the clear contraindications implied by the environmental safety.

Use of preservative-treated wood products faces increasing public and political pressure because of environmental concerns regarding the chemicals used to protect the wood. However, critics usually focus only on one single aspect of the whole life cycle of treated wood products, disregarding other environmental effects of timber utilization. To evaluate the ecological consequences of wooden utility poles (CCF/CCB impregnated roundwood and glulams) and their alternatives of reinforced concrete and steel, a life cycle assessment of the utility lines should be conducted with an account of cost-benefit analysis including factors such as varying life spans and maintenance costs for alternative pole materials. The next section attempts to outline relevant studies in this area.

3. Selecting Wood Preservatives¹⁶

A wide range of wood preservative treatments have been developed to protect wood and prolong its useful life. The U.S. EPA estimates that nearly 700 million pounds of wood preservatives are used annually in the United States [US EPA 1999a].

There is now a considerable body of scientific literature documenting the dislodging of surface residues and the leaching of preservative chemicals from treated wood of various types during its useful life. In addition, preservative chemicals can be released into the environment during processing and storage of treated wood, during sawing or other fabrication, and during or after disposal. The adverse environmental impacts from treated wood can be reduced by selecting the most appropriate material for the application (which may not be treated wood at all), mitigating impacts on site, and by proper disposal of construction materials and ultimately the structure itself.

In the U.S., the regulatory and political situation related to wood preservatives is highly volatile at the present time. There is rising concern about the arsenical preservatives, especially CCA. PCP and creosote are also being reviewed by EPA. Beyond Pesticides, formerly the National Coalition Against the Misuse of Pesticides, and several other groups are pursuing legal action against EPA to stop all uses of pentachlorophenol, creosote, and CCA [Feldman J., 2002]. Decisions may occur that would alter the allowed uses for these materials.

The San Francisco Department of the Environment contracted with the Washington Toxics Coalition to investigate factors or criteria that might be used to select preferred wood preservative treatments or alternative construction materials for city projects (Dickey, Ph., 2003).

The chemicals assessed included:

AAC	Alkyl ammonium compound
ACA	Ammoniacal copper arsenate
ACC	Acid copper chromate
ACQ	Ammoniacal (or amine) copper quat :ACQ-B: Ammoniacal copper quat, ACQ-D: Amine copper quat
ACZA	Ammoniacal copper zinc arsenate
CA-B	Copper azole
CBA	Copper boron azole
CC	Copper citrate (or ammoniacal copper citrate)
CCA	Chromated copper arsenate
CDDC	Copper bis(dimethyldithiocarbamate)
Creosote	
CuN	Copper naphthenate
Cu8	Copper-8-quinolinolate
IPBC	3-iodo-2-propynyl butyl carbamate
PCP	Pentachlorophenol
ZnN	Zinc naphthenate

The wood preservatives were assessed in terms of human health concerns (toxicity, routes of exposure, estimates of human health risk); environmental concerns (leaching, aquatic toxicity, aquatic risk, persistence and bioaccumulative characteristics); disposal; local regulations and policies. Based on the information presented in that report and in

¹⁶ Dickey, Ph., 2003, Guidelines for Selecting Wood Preservatives, , Washington Toxics Coalition, For the San Francisco Department of the Environment, September, 2003

consultation with the San Francisco Department of the Environment, a set of nine selection criteria were proposed for identifying acceptable wood treatments:

1. If a pressure treated product, treatment must be standardized by AWWA (American Wood Preservers Association) for the intended use. This requirement helps ensure that the treatment meets specifications to minimize leaching.
2. Product must not be used in ways that EPA prohibits or discourages.
3. Product or use must not violate state or local law, policy, or published best management practices.
4. Product may not result in the release or creation of dioxins during manufacture or disposal.
5. Product, constituents, or contaminants may not be listed on the EPA Priority PBT list or the EPA Waste Minimization Priority Chemicals list.
6. Product (or components) should not contain known, likely, or probable human carcinogens listed by EPA, NTP (National Toxicology Program), IARC (International Agency for Research on Cancer), or the State of California.
7. Product (or components) should not be listed as reproductive or developmental toxicants by the State of California.
8. For structures built in or over water, or where significant runoff is likely to occur, the use of copper should be minimized. If copper-based products are used, products with the lowest leaching potential should be chosen.
9. Product must not designate as a hazardous waste using criteria set by the State of California.

When applied to the wood treatments for which AWWA standards exists, these criteria eliminated pentachlorophenol, creosote, and arsenicals as acceptable wood treatments. Copper-8-quinolinolate and CDDC were also eliminated. The acceptable treatments have been presented in the form of a list indexed by use and cross referenced to the appropriate AWWA standards and use codes.

4. Factors relevant for utility line construction and maintenance affecting utility poles selection

The utility pole wars continue with suppliers of various materials making claims about their product being equal to or better than wood, followed by wood pole supplier countering the claims. To assess the relative cost position of wood and the alternative materials, Engineering Data Management inc. (EDMI), Fort Collins, Colo. was contracted to conduct an economic analysis of wood, light-duty steel, fiberglass and spun concrete poles. The study examined different factors contributing to the cost of building and maintenance of overhead power lines

The construction cost of a typical line is made up of the following factors; poles, 15 percent; engineering, 8 percent; right-of way preparation (including survey), 25 percent wire and insulators, 25 percent; lint and guy hardware, 7 percent; and construction labor (including foundations), 20 percent.

Pole prices are affected by several different factors including raw material cost and availability, supply and order quantity, delivery lead time, material-to-labor cost ratio and transportation.

For wood poles, West Coast species such as Douglas fir or western red cedar service a wide range of pole heights and load class demands and provide a sustainable supply of poles from 35-ft class 05 through 125-ft, dais H2 (ANSI classes).

Tools and procedures for field adaptation of wood poles are well established and are the standard against which the other materials are measured.

Final line engineering and survey costs are relatively independent of pole material selection. Only when pole configurations change or guying requirements differ between materials will cost variations be introduced.

Insulator costs are significant cost factors in the construction of an overhead line and usually represent more dollars than the poles themselves and show the greatest variation with the type of pole. Because wood itself is in insulator, less line insulation is required than would be for either steel or concrete poles. Many utilities do not size insulators based on pole type unless they are designing for higher voltage circuitry (230 kV and above).

Those utilities that consider pole material can save between \$1 and \$3 per insulator on a typical distribution line when using wood poles. Although different pole types utilize different hardware, then costs tend to be approximately the same and have no significant financial impact on pole material selection.

Installation labor costs

Generally, through-drilled hole are used for most line hardware connections. While wood poles are frequently furnished with pre-drilled framing holes, field drilling is often necessary. Because wood poles have been in use much longer than any of the other types have been, they are the most familiar and are normally considered the most user

friendly with regard to field drilling. Tools and procedures for field adaptation of wood poles are well established and are the standard against which the other materials are measured.

Fully predrilled poles are generally only practical when they are ordered for a specific project. The majority of projects utilize conventional construction techniques; line beds and/or cranes are used to lift and set poles. However, concrete poles typically require heavier equipment. In some instances aerial construction techniques are mandated and weight then has a significant impact on construction costs.

Years ago, pole climbing provided the only practical means of access to overhead lines for construction and maintenance operations and ease and safety in climbing were important issues. Wood poles were typically favored over other types because they were familiar and afforded versatility in climbing without added expense.

The other materials require added appendages to accommodate climbing and even then do not provide the same flexibility for worker positioning atop a pole. Consequently, climbing provisions often remain an added cost for steel, fiberglass, and concrete poles.

Purchase decisions of the past were sometimes based strictly on delivered cost of the product. Today there are post-construction cost factors that are also considered and occasionally alter the material selection. In general, the initial installation costs usually represent the largest portion of total expense, but in situations where comparison of installed costs between material types is comparable, differences in post-construction factors may influence the final selection of materials.

The frequency of line patrols and time spent in inspection are dictated by a line's importance. While no two utilities operate in the same way, on average, it appears that lines are patrolled and poles are inspected approximately once every five years.

The type of environment normally dictates pole maintenance requirements. Harsh environments can sometimes place strenuous demands on maintenance. However, an environment that is deemed particularly harsh for one material may not be for another.

The type and extent of maintenance will vary, but for the alternative material poles the maintenance generally relates to surface restoration. Should the galvanized finish or paint coatings, which are used to protect steel poles from corrosion, deteriorate or be damaged, repair or refinish work will be necessary, fiberglass poles also rely on protective coatings plus ultraviolet ray inhibitors to protect against resin decomposition and the subsequent blooming of glass fibers. Damage to any of these coatings needs to be repaired. Concrete poles must maintain good surface continuity so that the underlying steel it protected against exposure to the elements and consequent corrosion. Concrete poles that show signs of deterioration need to have cracks filled and their surfaces resealed.

While surface protection is of primary concern for the alternative material poles, the primary cause of wood degradation is biological attack. Most environments harbor multiple agents that are capable of causing damage to wood poles. Preservative treatment of wood is necessary to combat fungal, bacterial, and insect attacks. As poles age, the effects of initial treatments tend to diminish and remedial preservative treatments become necessary to prolong the life of the poles. The majority of wood poles in service today have received, or are scheduled to receive, remedial treatment.

Repair and replacement costs

Situations arise where more than simple maintenance activities are needed to prolong the useful life of a pole. Any of the pole types can become damaged beyond repair. Where damage to a pole diminishes its strength beyond an acceptable level, some type of corrective action becomes necessary. In the most extreme cases, pole replacement may be the best or only practical solution.

However, where reasonable caution is exercised and good inspection programs are in place during the life of the line, it is highly unlikely that any of the alternative material poles will warrant replacement as the result of progressive degradation. Catastrophic natural events, such as hurricanes or tornadoes, or forces beyond nature are the usual causes for alternative material poles needing to be replaced. Wood poles require replacement at the rate of 2 to 4 percent every year starting at 20 years.

When a line is decommissioned, materials are removed so that the land can be reclaimed for a new line or for another purpose. Old poles will either be reused or discarded. If discarded, several options exist for the material's final disposition. Steel is commonly recycled; in many instances new line applications can be found for the steel poles and they are returned to service on a different project.

When no new application is found, steel poles are typically sold for scrap and thus generate a small amount of revenue. Similarly, fiberglass and concrete poles are also candidates for reuse. When recycling is not viable, landfill disposal is normally used since these materials are not considered hazardous to the environment.

Wood poles removed from service are also candidates for reuse if they are still in sound condition. However, the disposal of wood poles is a slightly different issue. Because the vast majority of wood poles are treated with a chemical preservative, there is some concern for how to handle their disposal. Wood poles removed from service are often either given away, accompanied by a material safety data sheet, or used for fuel in certain types of power plants.

A few years ago, treated wood disposal practices were studied by various governmental agencies. There was concern that the waste might be reclassified as hazardous. However, after careful review by the governing environmental regulatory agencies, its classification as a solid waste remained unchanged.

The study of 1997 performed by Engineering Data Management, Inc. is one of several studies performed in the last decade. When evaluating the environmental costs and benefits of treated wood poles versus alternative materials, a full life cycle analysis should be undertaken, accounting for environmental factors such as the effects of producing the materials that go into the poles (e.g., wood, steel, concrete), water and air quality impacts, and factors such as varying life spans and maintenance costs for alternative pole materials.

These studies can be summarized as follows:

- **Kunniger and Richter Swiss Case Study:** In 1995, the Swiss Federal Laboratories for Materials Testing and Research published a life cycle analysis of utility poles [T. Kunniger and K. Richter, 1995]. This case study was conducted to better evaluate the ecological consequences of wooden utility poles and their alternatives of reinforced concrete and steel. Energy and material flows connected with utility poles and transmission lines in Switzerland were analyzed, using several evaluation criteria, including: (1) primary energy consumption, (2) global warming potential, (3) photochemical ozone creation, (4) acidification, (5) nitrification, (6) human toxicity, and (7) ecotoxicity.
- The entire life cycle of the poles was analyzed, including extraction and processing of raw materials, energy supply, pole production and setup, maintenance, dismantling, recycling, and disposal. All calculations were made for a service life of 60 years. The life cycle analysis showed that treated roundwood utility poles have several environmental benefits as compared to reinforced concrete and tubular steel, including low input of fossil energy, the positive aspects of wood as a material with a closed carbon cycle, and small contribution to the greenhouse effect. The report concludes that "treated wooden poles are fulfilling the resolution of the Earth Summit of Rio de Janeiro in 1992, where the reduction of greenhouse gases and an increased utilization of renewable resources was given priority".
- These findings are reiterated in a 2001 North American Wood Pole Coalition Technical Bulletin that examined recent domestic and international research comparing energy intensity and related global warming consequences of treated wood and its alternatives. [North American Wood Pole Coalition/Roger A. Sedjo, 2001]. The report concludes that: without exception, studies have found that total energy requirements associated with wood materials are considerably lower than those of commonly substituted materials. The substitution of high-energy-intensive materials for low-energy-using wood materials would contribute substantially to an overall increase in carbon dioxide emissions.
- **Erlandsson, Odeen, and Edlund Life Cycle Analysis:** This 1992 Swedish study examines the environmental life cycle analysis of treated wood, concrete, steel, and aluminum utility transmission poles, reporting their results in terms of "energy use" [Erlandsson M. et al., 1992]. The study found that a high energy use is often closely related to pollution by materials hazardous to the environment, which means that, in general, a product that needs a low energy use to produce can be assumed to have low environmental impact. The analysis showed that energy use for producing treated wood poles is significantly less than that required for steel, concrete, and aluminum poles—in some cases it was even found to be more than an order of magnitude lower.
- **Universal Forest Products, Inc. Energy Consumption Analysis:** This study compared the quantity of energy required to produce CCA-treated wood to that required to produce other alternative building materials (e.g., concrete and steel). [Conklin S. and Stalker I., 1996]. The report explains that although "total environmental impacts of using a particular material include resource issues such as depletion and renewability, solid waste generation, impacts to air and water quality, and the ultimate disposal of the

product, energy provides a common thread between many of these elements," and "energy efficiency is also widely recognized as an achievement in and of itself."

- The paper concludes also that "Treated wood is a superior building material from the perspective of energy efficiency"—the quantity of energy required to produce CCA-treated wood utility poles is as much as 13 times less than the energy required to produce alternative poles. Replacing CCA-treated wood with alternative materials would have a significant, negative, environmental impact, increasing annual carbon dioxide emissions by 6.2 billion kilograms.
- **NYSEG Wood, Concrete, and Steel Comparison Project:** Begun in 1988, explored the relative merits of steel, prestressed concrete, and laminated wood poles as a direct alternative to traditional treated roundwood poles.[NYSEG, July 1997]. The project evaluation covered: (1) total installed cost, (2) long-term durability, and (3) suitability for future use on the NYSEG transmission system.
- The project finds that " if pole materials were compared "...based solely on the cost of the material for the bulk of the transmission facilities constructed...the only decision which would be reached would be to use traditional, chemically treated, roundwood poles".
- **Wood Materials Used as a Means to Reduce Greenhouse Gases:** A 2002 report prepared by Roger Sedjo, Senior Fellow Resources for the Future, examined a number of studies, including some summarized above, comparing the total life cycle energy utilization of the use of wood products, including wood poles, with the use of substitute materials, such as steel, concrete, bricks and aluminum [Mitigation and Adaptation Strategies for Global Change 7: 191-200, 2002]. This report concludes that "Without exception all the studies found that the total energy requirements associated with wood materials are substantially lower than those of other commonly substituted materials."

The report found that the estimated effects of converting wood poles to steel poles in the U.S. "shows that, although the Green House Gas emissions associated with pole conversion were modest compared to the national total, they were nevertheless a significant portion of US annual emissions." The report concludes by stating that, these studies provide empirical confirmation of concepts developed in the IPCC, whereby the submission of high energy intensive materials for low-energy-using wood materials contributes substantially to the overall increase of CO₂ emissions through their overall higher energy requirements."

I should be emphasized that the above studies do not adequately account for the health and environmental burden caused directly by the emission of technical grade pentachlorophenol and its impurities to the environment.

5. Importance of wooden utility poles in the USA

In the USA the Utility Solid Waste Activities Group (USWAG) is an association comprised of the Edison Electric Institute (EEI), the National Rural Electric Cooperative Association (NRECA), the American Public Power Association (APPA), and approximately 80 energy industry operating companies. EEI is the principal national association of investor-owned electric light and power companies. APPA is the national association of publicly-owned electric utilities. NRECA is the national association of rural electric cooperatives. Together, USWAG members represent more than 85 percent of the total electric generating capacity of the United States, and service more than 95 percent of the nation's consumers of electricity.

The USWAG argues, that treated wood offers the most energy-efficient, functional, cost-effective and practical material for use by electric utilities in providing electrical services to the public. The re-registration of PCP, CCA, and creosote for use in treated wood transmission and distribution poles is considered by USWAG to be absolutely essential to the ability of electric utilities to continue to provide reliable electric power delivery services across the U.S. and maintain telecommunication services. The following evidence is used by USWAG to support its position:

- A 2002 USWAG Survey revealed that approximately 44 million treated wood poles currently are in service by those USWAG members (and electric co-operatives) responding to the Survey. When extrapolated out to reflect the entire electric power and telecommunication industries, USWAG estimates that there are approximately 130 to 135 million treated wood poles currently in service.
- Respondents to the USWAG Survey reported that they purchased approximately 719,000 new treated wood poles annually, either to provide electrical service to new service areas or to replace damaged poles in existing service areas. When extrapolated out, one can estimate that at least several million treated wood poles are

purchased annually in the U.S. by electric utilities alone.

- Less than 1% of electric utility distribution poles are preserved with alternative preservatives or manufactured with alternative materials. A slightly higher percentage of non-treated wood materials, primarily steel, are used for large transmission support structures, but even here a large number of the structures are treated wood. The treated wood represents the backbone of the electric distribution system in the U.S.
- The majority of support structures used by electric utilities for the distribution of electricity across the country, including both new construction and maintenance of existing plant, are comprised of treated wood poles.
- Treated wood structures also are used to support telecommunication services.
- Treated wood poles are preferred by utilities because they are more practical, functional, and economically acceptable than other alternatives—they are a natural and renewable resource.
- The three major preservatives currently used to treat utility poles, PCP, CCA, and creosote, have been in use for decades. During that period, poles treated with these preservatives have established a documented record of long-term performance and a reputation for safety and reliability throughout the industry. Treated wood poles manufactured from a sustainable natural resource that is both abundant and reasonably priced, and that commonly last for several decades in service, provide the most cost-effective alternative for modern electric utility construction and maintenance needs to an overall increase in carbon dioxide emissions.
- Without exception, studies evaluating the environmental costs and benefits of treated wood poles versus alternative materials, have found that total energy requirements associated with wood materials are considerably lower than those of commonly substituted materials. The substitution of high-energy-intensive materials for low-energy-using wood materials would contribute substantially.
- A switch to alternative material poles will require revisions to utilities' methods and practices addressing the installation, climbing, safety, maintenance, and replacement of poles by utility linemen, thereby increasing the expense of and complicating worker training.
- Over 700 of the electric utilities currently using treated wood are distribution cooperatives. These small utilities account for approximately one-third of all treated wood distribution poles currently in use in the country. Lack of readily available treated wood poles would be particularly severe and have a significant economic impact on these smaller entities, many of which are small businesses under Small Business Regulatory Enforcement Fairness Act.

Pentachlorophenol was one of the most widely used biocides in the U.S. prior to regulatory actions to cancel and restrict certain non-wood preservative uses of PCP in 1987. It now has no registered residential uses. Its commercial uses include: utility poles, fences, shingles, walkways, building components, piers, docks and porches, and flooring and laminated beams. Additionally, there are agricultural uses (which are sometimes referred to as "outdoor residential"), i.e., wood protection treatment to buildings/products, and fencerows/hedgerows. Prior to 1987, PCP was registered for use as a herbicide, defoliant, mossicide, and as a disinfectant, but now all these uses are cancelled.

The EPA has determined that PCP and its contaminants do leach out of treated wood utility poles. The EPA has noted that dioxins in treated wood appear to be the largest quantified flow of dioxins into the environment. The EPA calculated cancer risks for children as a result of their exposure to PCP. The EPA has noted that dioxins in treated wood appear to be the largest quantified flow of dioxins into the environment.

In the assessment of 1999 the agency found that children face a risk of cancer that is 220 times higher than levels deemed acceptable from exposure to soil contaminated with PCP treated wood poles; the same PCP treated wood poles that are planted in countless neighborhoods across the country. EPA recognized that the people that are exposed to PCP on the high risk of cancer. The risk faced by people retreating wood poles with liquid PCP; according to the EPA, they have a 100 percent chance of getting cancer. EPA recognizes that the people that are exposed to PCP on the job face high risk of cancer. The risk faced by people retreating wood poles with liquid PCP; according to the EPA, they have a 100 percent chance of getting cancer.

The recent preliminary risk assessment supporting the final reregistration eligibility document represents a significant reversal of the agency's assessment in 1999.

The agency's revision of its assessment is based totally on data provided to it by the Pentachlorophenol Task Force, a chemical industry group that as emphasized by the Beyond Pesticides has a vested economic interest in the continuing registration of PCP. The agency states, "The revision is based on EPA's receipt of a PCP-specific

exposure study from the Pentachlorophenol Task Force entitled 'Inhalation Dosimetry and Biomonitoring Assessment of Worker Exposure to Pentachlorophenol During Pressure Treatment of Lumber.'

Comments of the Beyond Pesticides¹⁷ on the EPA Preliminary Risk Assessment for Pentachlorophenol indicate reasons why the Industry Study and EPA's Risk Revisions are flawed. They concern changes in exposure description of scenarios and assumption made for assessments that according to Beyond Pesticides dismiss out of real world realities regarding common exposure to PCP-treated wood and its contamination.

The EPA's current reevaluation of the wood preservatives, starting with PCP motivated the Beyond Pesticides to carry out a survey of utility companies. The survey has provided real world numbers with which to measure risk assessment of PCP. What has been discovered is alarming. According to survey results utility companies, in general, prefer PCP treated wood utility poles to any other type. Most utility companies store treated wood utility poles on site. These stored poles represent large, concentrated reservoirs of PCP, and other wood preservatives, that leach out of the poles into soil and ground water. Many utility companies retreat their aging stock of wood poles to increase their lifespan. Retreating wood poles provides a fresh source of PCP to contaminate our environment and our bodies. Most alarming is the majority of utility companies that give away or sell their used treated wood poles to the public.

General conclusion and recommendation

1. It is seen that pentachlorophenol is:
 - highly toxic for human when ingested by humans;
 - moderate to highly toxic to many species of fish;
 - nonmutagenic or weakly mutagenic;
 - slightly toxic to practically non-toxic to bird species.
2. There are no reproductive effects and teratogenic effects of PCP confirmed. PCP is considered a possible human carcinogen. Current evidence is not sufficient to definitely assess the potential of PCP to cause carcinogenic effects in humans.
3. Pentachlorophenol is moderately toxic via the:
 - inhalation route,
 - dermal route.
4. Purified PCP also did not produce toxic effects such as liver damage and immune system alterations, which had previously been reported for the technical product. The chronic toxicity observed may depend in large measure on the proportion of chlorodibenzo-p-dioxins present in the mixture.
5. Data from animal studies indicate that the major target organs for PCP are the liver, kidneys, and central nervous system.
6. Pentachlorophenol has been detected in surface waters and sediments, rainwater, drinking water, aquatic organisms, soils, and food, as well as in human milk, adipose tissue, and urine.
7. General population exposure may occur through contact with contaminated environmental media, particularly in the vicinity of hazardous waste sites. Important routes of exposure appear to be inhalation of contaminated air, ingestion of contaminated groundwater used as a source of drinking water, ingestion of contaminated food and soils, and dermal contact with contaminated soils or products treated with the compound.
8. The actual concentrations to which workers have been exposed are seldom measured but, where they have been monitored, they have been predictably high.
9. Pentachlorophenol does not meet some of the criteria of the Protocol on POPs concerning half lives in water, soils and sediments.

¹⁷ Beyond Pesticides serves as a watchdog for federal and state agencies, which are institutionalizing "acceptable" levels of public exposure to harmful pesticides known to cause chronic health effects, such as cancer, neurological and immune system effects. Beyond Pesticides continuously sends comments on pesticide policies to the Environmental Protection Agency (EPA) and the United States Department of Agriculture (USDA), as well as, state and local agencies.

10. With some exceptions the BCF's values are below the threshold criterion. However it must be recognized that when determining BCFs for labile chemicals, such as pentachlorophenol, the average exposure affecting uptake is likely much greater than the final concentration, which tends to inflate the BCF.
11. From the available information it is clear that the reduction in use and significant restrictions of use patterns, levels of PCP and its derivatives in the environment have declined rapidly over the last decade. However:
 - pentachlorophenol is a major source of dioxin, furans and hexachlorobenzene;
 - there is a large body of evidence regarding the negative impacts of pentachlorophenol on the environment and human health;
 - pentachlorophenol treated products and pentachlorophenol treatment plants are known major sources of PCP and also emission of dioxins, furans and hexachlorobenzene into the environment;
 - it is not feasible from a technical or economical point of view to control and contain dioxins, furans and hexachlorobenzene emissions from treatment plants and treated wood poles;
 - the only realistic way to achieve zero discharge for pentachlorophenol treated wood industry is to stop the use, distribution and sale of pentachlorophenol;
 - pentachlorophenol is banned or severely restricted in at least 26 countries around the world;
 - there are readily available alternatives to the use of pentachlorophenol treated wood (recycled steel, fiberglass, cement made without burning waste)
 - it is hard to invent risk mitigation measures to reduce effectively the human health and environmental impacts of the use of pentachlorophenol because of the persistent and bio-accumulative nature of the micro-contaminants (dioxins, furans, hexachlorobenzene).

Accounting for:

- the known hazards, listed above;
 - data gaps and uncertainties of PCP characteristics, which cannot be used in favour of PCP acceptance;
 - the major metabolite Pentachloroanisole fulfills the POP-criteria
 - it is not feasible from a technical or economical point of view to control and contain dioxins, furans and hexachlorobenzene emissions from treatment plants and treated wood unless the parent substance is banned
 - overall trends of countries and international organizations to ban PCP production and uses,
- we recommend to include the pentachlorophenol on the POP's list requiring harmonized international actions with the ultimate goal to ban PCP and its salts production and uses.

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