

Overview of Occupational Exposures to Pentachlorophenol

Components, Contaminants , and Common Co-Exposures

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Background

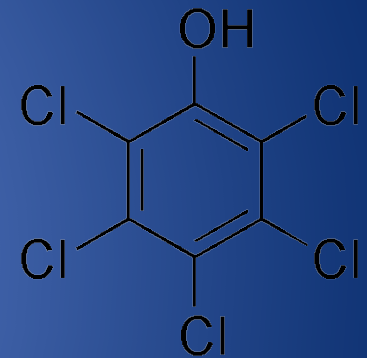
- PCP was produced in the United States primarily in four chemical plants, from 1936 to 2006
- PCP was widely used in herbicides, fungicides, and wood preservatives
- Currently used industrially as a wood preservative for utility poles, railroad ties, and wharf pilings

Background

- PCP was not restricted to its country of origin, some products were made during this time with PCP produced outside of the U.S.
- Currently there are no companies reporting production activities in the U.S., one facility in North America
- One known formulation facility in Tuscaloosa AL

Background

- PCP is classified by the International Agency for Research on Cancer as a possible human carcinogen (Group 2B)
- Use has been restricted to certified applicators in the U.S. since 1984
- Polychlorinated di-benzo dioxins and polychlorinated di-benzo furans are contaminants formed during the production of PCP



2,3,4,5,6-pentachlorophenol
(CAS 87-86-5)

Manufacturing

- All PCP manufactured in the United States was produced by the direct chlorination of phenol in the presence of various catalysts
- Phenol and chlorophenols were added to a chlorinator tank
- Chlorination was achieved with vaporized liquid chlorine until the Trichlorophenol stage is reached (60-65^o C)
- A catalyst was added, and temperature raised to 70-75^oC until a specific gravity of 1.670 was reached
- Batch temperature was then gradually increased until desired crystallization point of the completed Penta-Chlorophenol state is reached

Commercial Manufacturing

- PCP manufacturing contaminants included dioxins and dioxin-like compounds (Hepta-, Hexa, and octachloro di-benzo dioxins and furans), but not 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in significant levels
- PCP finishing options included-
 - Flake – 1930s to the 1960s
 - Prilling – 1960s (flaking and prilling offered greatest exposure scenarios)
 - Block molding – 1970s to present
- Production peaked in the late 1960s due to demands for NaPCP
- Most production facilities also made other chemical products

Common PCP contaminants

- From Technical Grade PCP analysis
 - Hexachlorodibenzo-*p*-dioxins (HxCDD)
 - Hexachlorodibenzofurans (HxCDF)
 - Heptachlorodibenzo-*p*-dioxins (HpCDD)
 - Heptachlorodibenzofurans (HpCDF)
 - Octachlorodibenzo-*p*-dioxin (OCDD)
 - Octachlorodibenzofurans (OCDF)
- Serum analyses of Human and animal populations use these same markers in determining exposures to PCP

Examples of Company Analysis of Technical Grade PCP Contaminants

Year	Sample Type	Analyte	Number of Samples	Mean $\mu\text{g/g}$
1976	PCP	2,3,7,8-TCDD	2	0
1965	PCP	HpCDD	1	110
		OCDD	1	140
1970	PCP	HxCDD	3	24.6
		HpCDD	3	24
		OCDD	1	15
1976	PCP	HxCDD	6	12.2
		HpCDD	5	100
		OCDD	6	283
1977	PCP	HxCDD	1	4.2
		OCDD	1	584

Modern Use Restricted

- Wood Preservatives
 - PCP has a long history of use as a wood preservative (restricted use since 1984)
 - May be used alone or in conjunction with other chemical substances such as
 - Creosote- can be wood creosote, coal tar creosote, coal tar pitch, or coal tar pitch volatiles
 - Chromated Copper Arsenate (CCA)

Wood Preservative Industry Exposures

- About 27000 workers in the PCP wood preservative industry as of 1991 (NIOSH National Occupational Exposure Survey)
- 2007 Census shows 13,369 workers in the wood preservative industry total. (U.S. Census)
- PCP treatment is still a common operation in the industry today
- Several studies report elevated HpCDD, HxCDD, and OCDD in blood serum samples from people living near active and former wood treatment facilities
- These blood serum markers are very similar to those found in PCP manufacturing workers, though not as high

Wood preservative process and exposure routes

- PCP and or other preservatives impregnated into wood stock at high temperature and pressure
- Wood is then stacked to air dry or kiln dried
- If air dried, evaporation into air or dripping of chemical mixtures onto the ground can occur
- Wood wastes could be burned, waste water often injected in boilers
- Often created chronic low level exposure to surrounding areas

EPA Toxic Release Inventory Data for PCP

TRI On-Site and Offsite Reported Disposed of or otherwise released (in pounds), for facilities in "NAICS 321-Wood Products, and NAICS 562Hazardous Waste/Solvent Recovery for PENTACHLOROPHENOL" CHEMICAL, U.S.				
Year	NAICS	Industry	On-site releases	Lbs Disposal or Other releases
2006	321	Wood Products	1307.2	1307.2
	562	Hazardous Waste/Solvent Recovery	1131.6	1131.6
2008	321	Wood Products	2965.9	2965.9
	562	Hazardous Waste/Solvent Recovery	2596.1	2596.1
2010	321	Wood Products	3940.1	3940.1
	562	Hazardous Waste/Solvent Recovery	328209	328209
2011	321	Wood Products	4785	4785
	562	Hazardous Waste/Solvent Recovery	89450	89450

Questions?

Selected References

Van der Zande A. 2010. Exploration of management options for Pentachlorophenol (PCP), Paper for the 8th meeting of the UNECE CLRTAP Task Force on Persistent Organic Pollutants, 22 March 2010.

Collins JJ, Bonder K, Aylward Lese L, Wilken M, Bonder C, 2009. mortality Rates Among Trichlorophenol Workers With Exposure to 2,3,7,8-Teterechlorodibenzo-*p*-dioxin. Am J Epidemiol 2009;170:501-506

Huwe JK, et al. ,2004. Levels of polychlorinated dibenzo-*p* –dioxins and dibenzofurans in cattle raised at agricultural research facilities across the USA and the influence of pentachlorophenol-treated wood. Food Additives and Contaminants 21(2):182-194

Collins JJ, Bodner K, Aylward LL, Wilken M, Swaen G, Budinsky R, Rowlands C, Bodnar CM. 2009. Mortality rates among workers exposed to dioxins in the manufacture of pentachlorophenol. J Occup Environ Med 51(10):1212-9.

Selected References

Karouna-Renier NK, Rao KR, Lanaza JJ, Davis DA, Wilson PA. 2007. Serum profiles of PCDDs and PCDFs, in individuals near the Escambia Wood Treating Company Superfund site in Pensacola, FL. Chemosphere.2007.05.028

Dahlgren J, et.al. 2008. Residential and biological exposure assessment of chemicals from a wood treatment plant. Chemosphere.2006.05.109

Marlow D, Fingerhut MA, Piacitelli L A,. 1997. Dioxin Registry Report of Monsanto Company Sauget, Illinois. CDC/NIOSH/DSHEFS/IWSB, Cincinnati Oh. 1997:Report number: 117.23