POLYCHLORINATED DIPHENYL ETHERS

July 2002

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME
GPO Box 58, Sydney NSW 2001, Australia www.nicnas.gov.au

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1. INTRODUCTION

1.1 Nomination reason

The chemical group polychlorinated diphenyl ethers (PCDEs) was nominated during the National Industrial Chemicals Notification and Assessment Scheme's (NICNAS) public call for nomination of chemicals of concern in February 1999.

The reason for nomination and selection of these chemicals for further work included concerns surrounding their potential to persist and bioaccumulate in the environment.

An initial call for information under Section 48 of the *Industrial Chemicals (Notification and Assessment) Act 1989 (Cwlth)* (the Act) was carried out for PCDEs in August 1999. No information was received by NICNAS as a result of this and a subsequent call for information was published in the *Chemical Gazette* of January 2002.

1.2 Objectives of report

The objectives are to identify the quantities of PCDEs or PCDE containing products imported into Australia, quantities manufactured and the uses of the products containing PCDEs. Amounts of PCDEs produced and/or released as by-products of processing and/or manufacture and uses were also investigated.

In addition to the uses and amounts, the report includes information on the physico-chemical characteristics of these chemicals and overseas regulatory initiatives pertaining to these chemicals.

2. SEARCH STRATEGY

2.1 Industry

In accordance with Section 48 of the Act, a notice was published in the *Chemical Gazette* of January 2002. Ten generic groups of PCDEs were identified and published in the call for information notice. The notice was directed at all persons who have manufactured or imported one or more of the chemicals or products containing the listed chemicals since August 1999. The information required in the Section 48 notice was:

- quantities imported and/or manufactured;
- amounts produced and/or released as by-products of processing and/or manufacture;
- products imported containing the chemicals and quantities of the chemicals in the products;
- uses of the chemicals or the products containing the chemicals.

It also encouraged any other persons with information on these chemicals including users, past importers or manufacturers to provide this information.

A total of 27 companies identified as being potentially involved with this group of chemicals were contacted. The companies are listed in Appendix 1.

Potential manufacturers and importers of these chemicals were identified from a search of:

- overseas use information;
- published literature (eg books, manuals and encyclopaedias);
- NICNAS Company Registration Database (NICNAS, 2002); and
- web site sources such as MSDSOnline (MSDSOnline, 2002), SciFinder (SciFinder, 2000) and TOMES Plus (TOMES Plus, 2002).

Throughout this process if information became available on a particular use, or, industry that may use, or be associated with the chemical, then further focused searching was conducted in that specific area.

2.2 Organisations

Organisations contacted included non-government organisations (NGO) such as industry associations and unions (see Appendix 2) and government agencies at the Federal, State and Territorial levels.

NGOs were identified from the Directory of Australian Associations (Current Contents, 2002).

In addition, agencies such as the United States Environmental Protection Agency (US EPA) and the European Chemicals Bureau were contacted for likely use information.

2.3 Literature sources

Chemical identity searching was conducted using a variety of databases to identify other chemicals within this group. SciFinder (2000) was used to identify chemicals with the same molecular structure, and chemical dictionaries and encyclopaedias were used to further identify the specific chemical constituents within the group of PCDEs.

3. CHEMICAL IDENTITY

PCDEs are a group of 209 halogenated aromatic compounds. They are also structurally related to polybrominated flame retardants (PBFRs).

Molecular formula

$C_{12}H_{10-(x+y)}OCl_{(x+y)}$ $(x+y = 1 \text{ to } 10)$

Chemical identification of the 10 generic groups of PCDEs are outlined in Table 1.

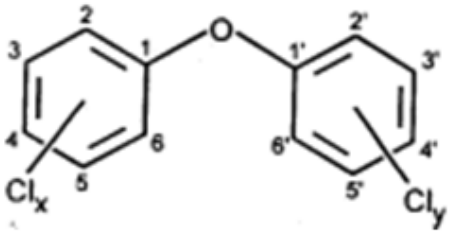
Table 1: Chemical identity of PCDE groups

PCDE	Molecular formula	Molecular weight
Mono	$C_{12}H_9OCl_1$	204.65
Di	$C_{12}H_8OCl_2$	239.10
Tri	$C_{12}H_7OCl_3$	273.54
Tetra	$C_{12}H_6OCl_4$	307.99
Penta	$C_{12}H_5OCl_5$	342.43
Hexa	$C_{12}H_4OCl_6$	376.87
Hepta	$C_{12}H_3OCl_7$	411.32
Octa	$C_{12}H_2OCl_8$	445.77
Nono	$C_{12}H_1OCl_9$	480.21
Deca	$C_{12}OCl_{10}$	514.66

(Adapted from Kurz and Ballschmiter, 1999)

The generic structure of PCDEs is outlined in Figure 1.

Figure 1: Generic structure of PCDEs



(Kurz and Ballschmiter, 1999)

4. CHEMICAL AND PHYSICAL PROPERTIES

PCDEs have physicochemical properties similar to those of polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). (Kurz and Ballschmiter, 1999; Nimi et al., 1994).

From the information outlined in Table 2 a relationship of increasing chlorination of the PCDEs correlating to decreasing vapour pressures is observed. Low vapour pressures and water solubility of PCDEs indicate that they are likely to be found at low concentration in the atmosphere and aqueous environmental compartments (Kurz and Ballschmiter, 1999). These authors conclude that the distribution between air and water expressed by the estimated Henry's law constants and the gas/water partition coefficients depends on the degree of chlorination, with the mono- to octa-chlorinated diphenyl ethers tending to accumulate in aquatic systems, whereas the nona- and deca-chlorinated ether have no preference. The high estimated water/octanol partition coefficients indicate that PCDEs may accumulate in the environmental compartments containing organic matter like biota, sediments and plants.

5. INTERNATIONAL PERSPECTIVES

5.1 Uses and emissions

Coupling reaction between diphenylidonium salts and chlorophenol is the most common route of synthesis of PCDEs in scientific research (Nevalainen and Kolstinen, 1994).

The sources of PCDEs are not well known but an identified use is the production of herbicides. While some PCDEs have antiseptic properties and others have heat transfer applications PCDEs are predominantly formed as accidental by-products. They have been found in fly ash from municipal incinerators, and as impurities in chemical products, transformer fluids, and wood preservatives (Nimi et al., 1994).

PCDEs have been identified in emissions from municipal waste incinerators (Nevalainen and Kolstinen, 1994). No emissions data is referenced for amounts, concentrations or related information.

PCDEs arise as impurities in technical chlorophenol preparations and chlorinated phenoxyacetic acids. Technical chlorophenol preparations include polychloroinated phenol, trichlorophenol (TCP) and pentachlorophenol (PCP). Between 100 and 1000 mg/kg of tetra- to octa-PCDEs have been identified in TCP formulations and hydroxylated octa- and nona-PCDEs were a major contaminant (8%) in technical PCP formulations (Nimi et al., 1994).

Analysis of used PCB transformer fluids indicated the presence of up to 51% PCDEs whereas others have 8% or none were measured in some PCB transformer mixtures (Nimi et al., 1994).

Table 2: Chemical and physical properties for PCDE groups

(Adapted from Kurz and Ballschmiter, 1999; and Ruelle and Kesselring, 1997)

PCDE	Vapour pressure (kPa)	Water solubility (ug/L)	-Log Kgw (@25°C)	Log Kow	Henry's Law ($Pa.m^3/mol$)
Mono	$4.37 - 5.37 \times 10^{-4}$	3396.35 - 12618.62	1.88 – 2.48	4.45-4.75	8.13-32.36
Di	$0.74 – 1.73 \times 10^{-4}$	722.07 - 5605.05	1.9 – 2.77	4.64-5.25	4.17-30.90
Tri	$1.38 – 5.50 \times 10^{-5}$	46.45 - 3069.17	1.35 – 3.04	4.96-5.88	2.24-112.20
Tetra	$0.26 – 1.02 \times 10^{-5}$	9.30 - 84.83	1.21 – 2.15	5.64-6.36	18.20-151.36
Penta	$0.50 – 2.19 \times 10^{-6}$	1.93 - 25.98	1.07 – 2.31	5.98-6.83	12.02-208.93
Hexa	$0.87 – 6.46 \times 10^{-7}$	0.43 - 4.97	1.09 – 2.31	6.47-7.11	12.02-199.53
Hepta	$0.38 – 1.20 \times 10^{-7}$	$0.94 - 5.30 \times 10^{-1}$	0.92 – 1.69	6.98-7.55	50.12-295.12
Octa	$1.59 – 3.16 \times 10^{-8}$	$1.26 - 3.54 \times 10^{-2}$	0.64- 1.02	7.63-7.84	234.42-562.34
Nono	6.92×10^{-9}	1.70×10^{-3}	0.01	8.07	1949.84
Deca	1.59×10^{-9}	5.77×10^{-5}	-0.76	8.16	14125.37

Log Kgw: gas/water partition coefficient
Log Kow: octanol/water partition coefficient

High concentrations of PCDEs were measured in the Kymijoki river in Finland. The source of contamination was attributed to a plant manufacturing wood preservatives, mainly polychlorinated phenols. PCDEs have been found as contaminants in the wood preservatives in PCPs (Nimi et al., 1994). Tetra- to hexa-PCDEs have also been measured in the low milligram per kilogram range in chlorophenol based wood preservatives (Nimi et al., 1994).

5.2 International initiatives

International attention for PCDEs has been limited. The closely related chemicals such as PCBs and PCDFs per se are subject to ongoing international regulatory actions.

6. AUSTRALIAN PERSPECTIVES

6.1 Uses and emissions

Ten companies (37%) and 2 associations/unions who were sent the Section 48 notice responded. In addition to that a further 11 companies responded directly to the Section 48 call for information. All responses indicated that no information was available on either the use of these chemicals or on measured concentrations in the environment.

Internationally municipal incineration facilities have been indicated as a current source of PCDE emissions to the environment. Currently, Australia has no municipal waste incineration facilities. The last municipal incineration facility in Australia closed in 1996 when the Sydney based Waverly-Woollahra Process Plant was shut. The closure occurred because of pollution and public health concerns (Lycos, 2000). Two new incineration facilities to deal with the municipal wastes in Western Australia and Tasmania have been granted environmental approvals by the relevant authorities. However, construction of these facilities has not begun because waste sources, cost of operation and remaining permits are still to be finalised. Municipal waste incineration facility approvals during this process must consider release of PCDEs.

Based on the international level of approximately 8% contamination of PCDEs in PCP formulations it is likely that PCDEs have entered Australia via this route. No records are held on volumes of PCPs used within Australia. The then Australia and New Zealand Environment Conservation Council (ANZEEC) published an Organochlorine Waste Management Plan (1999). This report states that six PCP containing products were still registered by the National Registration Authority (NRA) on the 18th of August 1997. The NRA grants approvals for Agriculture and Veterinary products including wood treatment and pesticide chemicals. However there are no currently registered PCP containing products approved for use by the NRA.

Internationally contamination of TCPs has been noted up to 1000 mg/kg by PCDEs (Nimi et al., 1994). 2, 4, 5-TCP was formerly used in Australia for the manufacture of 2,4,5-T, a pesticide. According to information held by Environment Australia, no stocks of 2, 4, 5-T or 2, 4, 5-TCP have been held in Australia from 1998. However, 2, 4, 6-TCP was being made in 1998 in Australia and would continue to be made (Environment Australia, 2002) . It is used as a fungicide in leather tanning and in a concrete formwork release agent.

The presence of PCDE impurities within PCB transformer fluids in Australia remains unknown.

6.2 Regulatory controls

PCDEs are not specifically listed in the:

- Australian Inventory of Chemical Substances (AICS), an inventory of chemicals used within Australia (AICS, 1999);
- National Occupational Health and Safety Commission's *List of Designated Hazardous Substances* (NOHSC, 1999);
- *Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP)* (NDPSC, 2001); and
- Australian Code for the Transport of Dangerous Goods by Road or Rail (FORS, 1998).

No specific tariff code was identified under the Australian Customs Service tariff code system for the specific chemicals or the PCDE groups.

PCPs are listed as scheduled wastes in a national Organochlorine Pesticide Waste Management Plan produced by the then ANZECC in 1999. This Management Plan outlines the safe disposal of PCPs. Therefore any PCDE contaminants in PCP formulations are likely to be destroyed at the same time as PCPs.

Regulation 4AB of the *Customs (Prohibited Imports) Regulations* 1956 prohibits import of PCBs and goods containing these, without the written consent of the Minister for Justice and Customs. In practice, where a request to import prohibited PCBs is received, the Australian Customs Service will seek advice from EA and NICNAS. A national PCB Management Plan exists in Australia. ANZECC prepared the Plan in 1996. The aims of the PCB Management Plan are the phasing out, disposal and destruction of PCBs within 13 years. The PCB Management Plan also includes a monitoring and sampling program to show trends of PCBs in the environment and general public. The controls in place for PCBs, particularly for capacitor fluid, may control further environmental or human exposure to PCDEs present as contaminants.

Various PCPs and TCPs are listed on the AICS.

7. CONCLUSIONS

The absence of PCDEs from the AICS indicates that from 1977 to present they were not used commercially within Australia. However, it is likely that they may be imported in products or articles made of substances contaminated with PCDEs.

Of the PCDEs within Australia, a significant source is likely to be from the use of polychlorinated phenols such as PCP, used as a timber preservative and the use of TCPs in the production of various pesticides. There are no current PCP registered products within Australia however they are listed on the AICS along with TCPs. Although this indicates that PCDEs may currently be imported or manufactured within Australia, it is expected that these will reduce over time as PCP products are removed from use (as is the case with NRA registrations of PCPs). The then ANZECC Organochlorine Pesticide Waste Management Plan outlining the safe disposal of PCPs would also be expected to control release of PCDEs occurring as contaminants in PCPs. Although this Waste Management Plan does not specifically cover TCPs, no stocks of 2,4,5,-T were present within Australia at 1998.

For the PCDEs present as contaminants in PCB mixtures, the PCB Management Plan is likely to cover the safe disposal of PCDEs occurring as contaminants in PCBs.

Currently Australia has no municipal waste incineration facilities. However, two facilities could be installed in the near future therefore potentially emitting PCDEs in contaminated fly ash from municipal incinerators.

8. FOLLOW-UP ACTION

There is currently no need for further action on PCDEs within Australia. This conclusion is based on:

1. the likelihood of PCDEs being present within Australia is very low because they are not listed in the AICS and therefore should not have been imported post 1977. However it is likely that they may be imported in products or articles made of substances contaminated with PCDEs; and

2. the limited potential sources of PCDEs as contaminants within Australia and the fact that Australia has already implemented Waste Management Plans to cover disposal of chemicals for which the greatest amount of PCDEs has been identified; and

3. the current regulatory regime prevents their availability for import or manufacture, and in the unlikely scenario that these chemicals were to be introduced, they would be subject to the NICNAS New Chemical assessment process.

APPENDIX 1: List of Companies Contacted

Alpha Chemicals (Australia) Pty Ltd

AS Harrison & Co Pty Ltd

Bostik Findlay Australia Pty Ltd

Bribros Australia Pty Ltd

Caltex Australia Limited

Chemlube Company Pty Ltd

Chem-Supply Pty Ltd

Ciba Speciality Chemicals Pty Ltd

Cognis Australia Pty Ltd

Dow Chemicals (Australia) Ltd

Du Pont (Australia) Ltd

Fuchs Australia Pty Ltd

HCA Colours Australia P/L

Houghton Australia Pty Ltd

Huntsman Corporation Australia Pty

International Chemicals Ltd

International Sales and Marketing

Lubrication Engineers Pty Ltd

Lubrizol Australia

Nufarm Coogee Pty Ltd

Oilchem Pty Ltd

Orica Australia Pty Ltd

Pennzoil Products Australia Company

Recochem Incorporated

Shoalhaven Mill

Sigma Aldrich Australia Pty Ltd

Swift and Company Limited

APPENDIX 2: List of Associations and Unions Contacted

Associations

AMIRA International Australian Mineral Industries Research Association Limited

Australian Consumer and Specialty Products Association

Australian Mines and Metals Association

Institute of Electrical Inspectors

Minerals Council of Australia

New South Wales Minerals Council Ltd

PACIA – Plastics And Chemicals Industries Association

Waste Contractors & Recyclers Association, NSW

Unions

Australian Council of Trade Unions

Australian Manufacturing Workers Union

Communications Electrical and Plumbing Union - Electrical Division

Construction Forestry Mining Energy Union - Construction and General

REFERENCES

AICS (1999) Australian Inventory of Chemical Substances (AICS). National Industrial Chemicals Notification and Assessment Scheme (CD ROM Issue 2).

Australia and New Zealand Environment Conservation Council (ANZEEC) (1999) Organochlorine waste management plan <http://www.ea.gov.au/industry/chemicals/swm/pubs/ocpplan.pdf>. Accessed May 2002.

Current Contents (2002) Directory of Australian Associations. March 2002-July 2002 **43**: Melbourne, Crown Content, p.945.

Environment Australia (2002) Personal communication to NICNAS.

Federal Office of Road Safety (1998) Australian code for the transport of dangerous goods by road and rail (ADG Code), sixth edition. Canberra, AGPS.

Kurz J, & Ballschmiter K (1999) Vapour pressures, aqueous solubilities, Henry's law constants, partition coefficients between gas/water (K_{gw}), n-octanol/water (K_{ow}) and gas/n-octanol (K_{og}) of 106 polychlorinated diphenyl ethers (PCDE). Chemosphere, **38:** pp 573-586.

Lycos (2000) Environment news service: Australian renewables legislation green lights incinerator - 12 December 2000 <http://ens.lycos.com/ens/dec2000/2000L-12-12-01.html>, Accessed 28 May 2002.

MSDSOnline (2002) http://www.msdsonline.com/Home/. Accessed April 2002.

NDPSC (National Drugs and Poisons Scheduling Committee) (2001) Standard for the uniform scheduling of drugs and poisons. **16** (Amendment 1-3). Woden, ACT, Commonwealth Dept of Health and Aged Care.

Nevalainen T, & Kolstinen J (1994) Synthesis, structure verification, and chematographic relative retention times for polychlorinated diphenyl ethers. Environmental Science and Technology, **28:** 1341-1347.

NICNAS (2002) National Industrial Chemicals Notification and Assessment Scheme Company Registration Database.

Nimi AJ, Metcalfe CD, & Huestis SY (1994) Chlorinated diphenyl ethers in Great Lakes fish and their environmental implication. Environmental Toxicology and Chemistry, **13**: pp 1133-1138.

NOHSC (National Occupational Health and Safety Commission) (1999) List of designated hazardous substances database : <http://www.nohsc.gov.au/OHSInformation/Databases/HazardousSubstances/>. Accessed April 2002.

Ruelle P, & Kesselring UW (1997) Aqueous solubility prediction of environmentally important chemicals from the mobile order thermodynamics. Chemosphere, **34:** pp 275-298.

SciFinder (2000) American Chemical Society.

TOMES Plus (2002) Klasco RK, Gelman CR, & Heitland G (Eds): TOMES® Plus System. MICROMEDEX, Greenwood Village, Colorado. Accessed via Thomson MICROMEDEX Corporate Solutions on the Internet Systems http://csi.micromedex.com/. Accessed April 2002.