



Trisphosphates

***Priority Existing Chemical
Assessment Report No. 17***

June 2001

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Preface

This assessment was carried out under the National Industrial Chemicals Notification and Assessment Scheme (NICNAS). This Scheme was established by the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), which came into operation on 17 July 1990.

The principal aim of NICNAS is to aid in the protection of people at work, the public and the environment from the harmful effects of industrial chemicals.

NICNAS assessments are carried out in conjunction with Environment Australia and the Therapeutic Goods Administration, which carry out the environmental and public health assessments, respectively.

NICNAS has two major programs: the assessment of the health and environmental effects of new industrial chemicals prior to importation or manufacture; and the other focussing on the assessment of chemicals already in use in Australia in response to specific concerns about their health/or environmental effects.

There is an established mechanism within NICNAS for prioritising and assessing the many thousands of existing chemicals in use in Australia. Chemicals selected for assessment are referred to as Priority Existing Chemicals.

This PEC report has been prepared by the Director (Chemicals Notification and Assessment) in accordance with the Act. Under the Act manufacturers and importers of Priority Existing Chemicals are required to apply for assessment. Applicants for assessment are given a draft copy of the report and 28 days to advise the Director of any errors. Following the correction of any errors, the Director provides applicants and other interested parties with a copy of the draft assessment report for consideration. This is a period of public comment lasting for 28 days during which requests for variation of the report may be made. Where variations are requested the Director's decision concerning each request is made available to each respondent and to other interested parties (for a further period of 28 days). Notices in relation to public comment and decisions made appear in the *Commonwealth Chemical Gazette*.

In accordance with the Act, publication of this report revokes the declaration of this chemical as a Priority Existing Chemical, therefore manufacturers and importers wishing to introduce this chemical in the future need not apply for assessment. However, manufacturers and importers need to be aware of their duty to provide any new information to NICNAS, as required under section 64 of the Act.

For the purposes of Section 78(1) of the Act, copies of Assessment Reports for New and Existing Chemical assessments may be inspected by the public at the library of the National Occupational Health and Safety Commission (NOHSC). Summary Reports are published in the *Commonwealth Chemical Gazette*, which are also available to the public at the NOHSC library.

Copies of this and other PEC reports are available on the NICNAS website. Hardcopies are available from NICNAS either by using the prescribed application form at the back of this report, or directly from the following address:

GPO Box 58

Sydney

NSW 2001

AUSTRALIA

Tel: +61 (02) 9577 9437

Fax: +61 (02) 9577 9465 or +61 (02) 9577 9465 9244

Other information about NICNAS (also available on request) includes:

- NICNAS Service Charter;
- information sheets on NICNAS Company Registration;
- information sheets on PEC and New Chemical assessment programs;
- safety information sheets on chemicals that have been assessed as Priority Existing Chemicals;
- subscription details for the NICNAS Handbook for Notifiers; and
- subscription details for the Commonwealth Chemical Gazette.

More information on NICNAS can be found at the NICNAS Web site:

<http://www.nicnas.gov.au>

Other information on the management of workplace chemicals can be found at the website of the National Occupational Health and Safety Commission:

<http://www.nohsc.gov.au>

Overview

Trisphosphates were declared Priority Existing Chemicals for preliminary assessment on 7 March 2000, primarily due to concerns for potential bioaccumulation of these chemicals. The focus of this report is on the chlorinated members of this class of chemicals and their use and exposure in Australia.

The chlorinated trisphosphates assessed in this report are not manufactured in Australia, but are imported in bulk, total quantity around 410 tonnes per year. This is almost exclusively as the pure chemicals, apart from some resin products, which comprise around 1% of total imports. It is not known to what extent trisphosphates may be being introduced into Australia in other finished products or articles. The only chlorinated trisphosphates currently imported into Australia are tris (2-chloroethyl) phosphate (TCEP) and tris (1-chloro-2-propyl) phosphate (TCPP). Future imports will also include tris (1,3-dichloro-2-propyl) phosphate (TDCPP). Of the known imports, around 85% is used in the production of flexible and rigid foams, with the remainder used in the production of elastomers and specialist rubber materials (~6%), fibreglass resins and other moulded objects (~5%) and industrial paints, surface coatings and sealants (~4%). The use of these chemicals in these products is exclusively as flame retardants and/or plasticisers, typically in concentrations ranging from 5 to 20% depending on the product.

For this assessment, the physico-chemical, toxicological and environmental properties of chlorinated trisphosphates have been summarised from peer reviewed hazard assessments by international organisations, such as IARC, IPCS and OECD.

Release of trisphosphates into the environment can occur during the manufacture of products containing them or during the use of such products and their disposal. Release during manufacture of products is expected to be less than 1% of total usage and primarily sent to landfill. Trisphosphates are somewhat volatile and are likely to be slowly released to the atmosphere from the surfaces of solid articles containing these compounds during normal product use. Some may also be released to waste water during washing of fabrics containing the chemicals. The degradation of trisphosphates in the atmosphere occurs by hydroxyl radical attack resulting in the formation of hydrogen chloride, carbon dioxide, water and phosphoric acid. The trisphosphates examined here are not readily biodegradable under aerobic conditions and, due to their high water solubility, bioaccumulation is not expected.

TCEP and TCPP are slightly toxic to aquatic organisms at all trophic levels and TDCPP is moderately toxic to fish. All three compounds are slightly toxic to terrestrial species, aquatic green algae and are non-toxic to sewage bacteria.

Trisphosphates are absorbed dermally (TDCPP) and via inhalation (TCPP) with little evidence that these compounds are likely to accumulate in animal tissues. There are concerns with some trisphosphates about the neurotoxic effects (TCEP) seen in short-term studies and the carcinogenicity (TCEP, TDCPP) and reproductive health effects (TCEP) seen in chronic animal studies, with some effects being seen at relatively low doses (5 mg/kg/d) with TDCPP. Limited human data were available. At present, knowledge of long-term effects resulting from exposure to trisphosphates and their breakdown products is limited.

In Australia and the European Union, except for TCEP, none of the other trisphosphates considered in this assessment have been classified. TCEP is currently classified in Australia based on an EU classification, with the risk phrases R22 Harmful if swallowed and R36/38 Irritating to eyes and skin. However, this classification is no longer up to date. The current EU classification is R22 Harmful if swallowed and R40(3) Possible risks of irreversible effects, Carcinogen Category 3, although, this is now subject to further review and may be updated. However the classification should be upgraded by Australia in accordance with the NOHSC procedures as soon as possible.

Because the assessed chlorinated trisphosphates are apparently used in Australia almost interchangeably, occupational exposure to any one chemical may occur from any of the identified uses for trisphosphates.

It is estimated that overall, around 2000 workers may be employed nationwide in foam formulation/production. In general, exposures in foam production appear to be well controlled. Concerns were identified for some producers/ processes in rigid foam production and other uses where 'semi-closed' or 'open' conditions apply. It was reported that minimal protective measures were taken for some uses/processes with potential exposure to trisphosphates. In addition, application of certain surface coatings/sealants may be associated with some exposure to trisphosphates, particularly where application takes place under confined conditions.

Many plastics containing trisphosphates are widely used both in the home, office and in automobiles. No information on the volatilisation (from blooming) of these substances from articles in use was available for assessment. Exposures calculated for Europe were expected to be very low, with negligible inhalation exposure, and dermal exposure in the order of 0.006 mg/kg bw/day based on the use of TCEP in soft furnishings. It is considered that there is a potential for moderate exposure to trisphosphates for occupants of motor vehicles, particularly where internal car temperatures are high (summer) and where a recirculating air conditioner is installed. No monitoring of trisphosphate levels in vehicles or homes in Australia is currently available. There is widespread public contact with products containing trisphosphates in Australia, and a lack of information about exposure levels for the general public.

Due to the identified human health effects of concern with some trisphosphates and the lack of adequate data on others, the widespread public contact with products containing trisphosphates, and the potential for worker exposure, it is considered that a full (risk) assessment should be undertaken by NICNAS. This assessment should cover the AICS listed trisphosphates, irrespective of current imports, due to the potential for substitution. Measured emissions and exposure data will be required for this assessment. Industry data on representative measured worker exposures will be required for the occupational assessment to avoid the use of modelling methods which may over-estimate exposure and hence potential risk. A timeframe of 18 months is recommended for industry to provide emission and exposure data to enable public and occupational risk assessment to occur. Importers should coordinate this work in conjunction with their customers. NICNAS will work with industry in defining the data requirements for the assessment and will take into account any available overseas data that is representative of the Australian situation.

Although use and release of the two chlorinated phosphate esters (TCEP and TCPP) used in Australia is at reasonably high levels, neither of the two compounds is expected to be persistent in the environment and the overall environmental hazard is assessed as low. With the information available for this preliminary report it is concluded that no further environmental assessment is required at this time.

On the basis of the known hazards it is recommended that labels, MSDS and other hazard communication materials be revised to comply with the information on hazards available from international assessments and detailed in this NICNAS report. MSDS for the various triphosphates should include health hazard information relevant to the triphosphates concerned. If no data is available for a particular triphosphate then this should be stated on the MSDS.

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Acronyms and Abbreviations

ADG Code	Australian Code for the Transport of Dangerous Goods by Road and Rail
AICS	Australian Inventory of Chemical Substances
BDCPP	bis (1,3-dichloro-2-propyl) phosphate
bw	bodyweight
CAS	Chemical Abstracts Service
CO	carbon monoxide
CO ₂	carbon dioxide
CPSC	Consumer Product Safety Commission
d	day
DNA	deoxyribonucleic acid
EA	Environment Australia
EEC	European Economic Community
EHC	Environmental Health Criteria
EINECS	European Inventory of Existing Commercial Chemical Substances
EU	European Union
g	gram
HBr	hydrogen bromide
HCl	hydrogen chloride
IARC	International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
kg	kilogram
K _{oc}	partition coefficient to organic carbon
K _{ow}	octanol/water partition coefficient
L	Litre
LC ₅₀	median lethal concentration
LD ₅₀	median lethal dose
LOEC	lowest-observed-effect concentration
MDI	methylene di-para-phenylene isocyanate

mg	milligram
MITI	(Japanese) Ministry for International Trade and Industry
MSDS	Material Safety Data Sheet
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NOAEL	no-observed-adverse effect level
NOEC	no-observed-effect concentration
NOHSC	National Occupational Health and Safety Commission
NRC	National Research Council (USA)
NTP	National Toxicology Program (USA)
OECD	Organisation for Economic Cooperation and Development
OHS	occupational health and safety
PEC	Priority Existing Chemical
PVC	polyvinyl chloride
RNA	ribonucleic acid
RTECS	Registry of Toxic Effects of Chemical Substances
SIDS	Screening Information Data Set
STP	standard temperature pressure
TCEP	tris (2-chloroethyl) phosphate
TCP	tricresyl phosphate
TCPP	tris (1-chloro-2-propyl) phosphate
TDBPP	tris (2,3-dibromopropyl) phosphate
TDCPP	tris (1,3-dichloro-2-propyl) phosphate
TDI	toluene diisocyanate
TGA	Therapeutic Goods Administration
TMCPP	tris (2-chloro-1-propyl) phosphate
TPP	triphenyl phosphate
WHO	World Health Organization

1. Introduction

1.1 Declaration

The group of chemicals known as trisphosphates were declared as Priority Existing Chemicals for ‘preliminary assessment’ under the *Industrial Chemicals (Notification and Assessment) Act 1989* on 7 March 2000.

The main reason for the declaration was the potential for bioaccumulation, together with the wide variety of applications and sources of environmental exposure for this group of chemicals. It was agreed that Australian use information was needed to put the available hazard data on trisphosphates into perspective.

1.2 Scope of the assessment

The *Industrial Chemicals (Notification and Assessment) Act 1989* prescribes which matters may be taken into account and addressed in a preliminary assessment. Risk assessment and risk management are not covered in preliminary assessments. However, as an outcome of a preliminary assessment, the Act requires the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) to determine the significance of the assessment findings in terms of potential risk. For example, if the findings indicate significant environmental and/or human exposure together with a concern over intrinsic hazard(s) of a chemical, then a full (risk) assessment may be recommended.

At the commencement of this assessment, the non-halogenated trisphosphates were excluded from further consideration due to their lesser environmental persistence than other members of this class of compounds. The brominated trisphosphate, tris (2,3-dibromopropyl) phosphate is considered in the PEC assessment of polybrominated flame retardants.

This ‘preliminary’ PEC assessment, although focusing on trisphosphates as a single class of chemicals, acknowledges that the chemicals comprising this class are a structurally diverse group of chemicals. As such, trisphosphates do not necessarily have similar chemical, physical, toxicological or environmental properties. Every attempt has been made to clarify this issue, where relevant, in the body of the report. However, where data are either lacking or were not available for assessment, the default, by necessity, was to adopt a more generic approach.

The aim of a ‘preliminary’ PEC assessment is not to undertake a comprehensive evaluation of all available data (i.e., as required in a full risk assessment) or to recommend risk reduction measures beyond those that are currently enforced under relevant Australian regulations (e.g., NOHSC hazard classification) or initiated by international treaties or promulgated by expert international organisations (e.g. EU, OECD).

1.3 Objectives

As per the discussion in 1.2, the term trisphosphate in this section refers to chlorinated trisphosphates. The purpose of the assessment was to:

- Determine manufacture/importation volumes;
- Characterise applications and extent of use of trisphosphates in Australia;
- Determine the extent of environmental and human exposure to trisphosphates;
- Characterise the physicochemical properties of trisphosphates;
- Review and summarise the health and environmental effects; and
- Determine whether or not the significance for risk of potential health, safety and environmental effects is such, that a full (risk) assessment should be undertaken.

1.4 Sources of information

Information for the assessment was obtained from various sources.

Industry

Data were submitted by manufacturers and importers of trisphosphates and trisphosphate containing products. Information submitted included:

- Quantities imported in the past two years;
- Data on known usage, including product specifications;
- Material safety data sheet (MSDS) and labels; and
- A list of end users.

Importers/manufacturers on-sell trisphosphates and were unable to provide data on use patterns and exposure during use and disposal. An external consultant, Professor Ian Rae, was commissioned to facilitate data collection on use patterns and potential occupational, public and environmental exposure arising from use of trisphosphates in Australia.

Literature review

The major sources of information on the health effects of trisphosphates were the World Health Organisation (WHO) Environmental Health Criteria (EHC) monographs published under the International Programme on Chemical Safety (IPCS) covering tris (2-chloroethyl) phosphate, tris (1-chloro-2-propyl) phosphate and tris (1,3-dichloro-2-propyl) phosphate (IPCS, 1998); the Organisation for Economic Cooperation and Development (OECD) Screening Information Data Set (SIDS) report on tris (1-chloro-2-propyl) phosphate (OECD, 1998); the International Agency for Research on Cancer (IARC) monograph on tris (2-chloroethyl) phosphate (IARC, 1999) and the US National Academy of Sciences report on tris (1-chloro-2-propyl) phosphate, tris (2-chloro-1-propyl) phosphate and tris (1,3-dichloro-2-propyl) phosphate (National Academy Press, 2000).

In addition, a literature search was carried out for health effects data on the following chlorinated tris phosphate esters: tris (2-chloroethyl) phosphate (TCEP); tris (1-chloro-2-propyl) phosphate (TCPP); tris (1,3-dichloro-2-propyl) phosphate (TDCPP); tris (2-chloro-1-propyl) phosphate; tris (2,3-dichloro-1-propyl) phosphate and tris (3-chloro-1-propyl) phosphate. No additional data were identified for TCEP, TCPP or TDCPP. Available data were only identified for tris (2-chloro 1-propyl) phosphate with no data identified for tris (2,3-dichloro-1-propyl) phosphate and tris (3-chloro-1-propyl) phosphate.

1.5 Peer review

During all stages of preparation, this report has been subject to internal peer review by NICNAS, Environment Australia (EA) and the Therapeutic Goods Administration (TGA). External peer review was not undertaken because the primary sources of the hazard information have already been subjected to significant international peer review.

2. Background

Most of the early flame retardants were inorganic in nature, typically phosphate salts or metal compounds such as antimony trioxide. The earlier description of their function as 'flameproofing' has given way to a more modest description of such a substance as a 'flame retardant'.

The flame retardant properties of the inorganic phosphates are shared by organic phosphates, generally phosphate esters of aliphatic alcohols (trialkyl phosphates, $(RO)_3PO$) or their aromatic equivalents, like phenol or cresol (triaryl phosphates, $(ArO)_3PO$), and some phosphonates, $(RO)_2R'PO$. In addition, organic phosphates are good plasticisers (i.e. substances which lower the hardness or rigidity of polymers, making them more pliable). Simple phosphate esters such as triphenyl and tricresyl phosphates (TCP) are often employed in both lubricating and plasticising roles, and it is but a short step to incorporate halogens such as chlorine into the phosphate esters so as to combine flame retardancy with plasticisation.

These esters are soluble in, or readily miscible with, organic materials such as high molecular weight polymers. Use of plastics which incorporate these polymers has grown enormously in the second half of the twentieth century. They are found in fabrics and other clothing applications, in building and construction materials, and in a thousand kinds of articles from pens to musical instruments to computers.

Trisphosphates were introduced in the 1930s, but their main use began after World War II.

Trisphosphates are esters of phosphoric acid, whereby the hydrogen atoms of the hydroxy groups are each replaced by an organic moiety of the same structure, i.e. all 3 phosphoric acid hydrogen atoms are replaced/substituted (usually as a result of condensation/esterification reactions with phosphorus oxychloride and an alcohol) by 3 identical organic molecules (moieties), hence the term 'tris'. These moieties may be either aliphatic (allyl) or aromatic (aryl) and may contain other chemical groups, such as halogens, oxygen (e.g. ethers) and, in the case of aromatic moieties, aliphatic side chains.

Trisphosphates are used industrially, primarily as flame retardants, plasticizers and solvents. Some examples of commonly used aliphatic halogenated trisphosphates are TCEP, TCPP and TDCPP. For the chemical names and CAS Numbers of these compounds the reader is referred to Section 3.

Aromatic trisphosphates are primarily used in PVC-based plastics, but they are also used as lubricant oils for industrial air compressors and gas turbines, with miscellaneous use as pigment dispersants, additives in adhesives, lacquer coatings and wood preservatives (IPCS, 1997).

2.1 International perspective

The worldwide demand for flame-retardant chemicals in 1992 was estimated at 600,000 tonnes, including some 100,000 tonnes of phosphorous-based products. The market volume of phosphate esters (quantity of trisphosphates not stated) in

the US between 1986 and 1991 was steady, at around 20,000 tonnes per annum, with around twice as much halogenated to non-halogenated products. Consumption of halogenated and non-halogenated phosphate esters in Japan between 1986 and 1994 was also steady, at around 3,000 and 4,500 tonnes per annum, respectively (IPCS, 1997).

Phosphate ester chemicals containing chlorine and/or bromine represent about 20% of the worldwide production of flame-retardant chemicals and are one of the principle classes of flame retardants used in plastics and textiles. Triphosphate esters (allyl and aryl) are also excellent plasticizers and hence their extensive use in plastics manufacture.

Reportedly, the plastics industry is the largest consumer of flame retardants, estimated at 95% for the US in 1991. About 10% of all plastics contain flame retardants. The main applications are in building materials and furnishings (e.g. structural elements, roofing films, pipes, plastic insulation foams, furniture and wall/floor coverings), transportation (e.g. fittings for automobiles, trains, ships and aircraft) and in the electrical industry (cable housings and components for televisions, office machines, household appliances and lamination of printed circuit boards).

Some triphosphate chemicals have come under intense scrutiny by national and international regulatory bodies. A recent report (April 00) by the US National Research Council (NRC) recommended that further studies be carried out on a number of flame retardants potentially used in furniture upholstery, including TCPP, TDCPP and aromatic phosphate plasticizers (National Academy Press, 2000). The Council recommended that research be done to measure extraction of chemicals from treated fabrics into saline, volatilisation, and potential for chemicals to be released from treated fabric during wear that could lead to the generation of airborne particles that could contain the chemicals. For TCPP the Council identified data gaps in subchronic or chronic toxicity by all 3 routes of exposure, dermal absorption, reproductive toxicity and human exposure data. For TDCPP, data gaps identified are chronic toxicity by dermal and inhalation routes, dermal absorption, metabolism of TDCPP in animal or human system and human exposure data from treated furniture upholstery.

2.2 Australian perspective

Triphosphates are not listed in the *Standard for the Uniform Scheduling of Drugs and Poisons* (Australian Health Ministers' Advisory Council, 1997). TCEP is listed in the National Occupational Health and Safety Commission's (NOHSC) *List of Designated Hazardous Substances* (NOHSC, 1999). No Australian exposure standards have been established for any chlorinated triphosphates. The materials are not classified as dangerous goods according to the Australian Code for the Transport of Dangerous Goods by Road and Rail. There are no specific public, occupational or environmental regulatory controls in Australia.

The consumption of flame retardants in plastics and other combustible materials is closely linked to regulations covering fire precautions.

2.3 Assessment by overseas national or international bodies

Reviews of health and environmental effects of the various triphosphates have been carried out by the International Programme on Chemical Safety (IPCS, 1995; 1998); the International Agency for Research on Cancer (IARC, 1999), the US National Academy of Sciences (National Academy Press, 2000) and the Organisation for Economic Cooperation and Development (OECD, 1998).

3. Applicants

Following the declaration of trisphosphates as a PEC, seven introducers and one interested party applied for assessment of the chemical. The introducers supplied information on the properties, import quantities and use of a number of trisphosphate chemicals. In accordance with the *Industrial Chemicals (Notification and Assessment) Act 1989*, NICNAS provided the applicants with a draft copy of the report for comments during the statutory consultation phases of the assessment.

The applicants were as follows:

Akzo Nobel Chemicals

6 Grand Parade
Camellia
NSW 2142

Orica Australia Pty Ltd

Polyurethanes Section
Gate 3 Ballarat Road
Deer Park VIC 3023

Ariel Industries Pty Ltd

26 Kembla Street
Cheltenham
VIC 3192

Rhodia Australia Pty Ltd

*(formerly Albright & Wilson
Specialties Pty Ltd)*
313 Middlesborough Road
Box Hill, VIC 3012

Huntsman Chemical Company

Australia Pty Ltd
Sommerville Road
West Footscray VIC 3012

Swift Pty Ltd

PO Box 600
Abbotsford
VIC 3012

Australian Council of Trade Unions

393 Swanston St.
Melbourne
VIC 3000

Clariant (Australia) Pty Ltd

675-685 Warrigal Road
Chadstone
VIC 3148

4. Chemical Identity and Composition

The trisphosphates considered in this report include:

Chemical name	CAS Number	AICS Listing
Tris (2-chloroethyl) phosphate (TCEP)	115-96-8	Yes
Tris (1-chloro-2-propyl) phosphate (TCPP)	13674-84-5	Yes
Tris (1,3-dichloro-2-propyl) phosphate (TDCPP)	13674-87-8	Yes
Tris (2-chloro-1-propyl) phosphate	6145-73-9	Yes
Tris (2,3-dichloro-1-propyl) phosphate	78-43-3	No
Tris (3-chloro-1-propyl) phosphate	1067-98-7	No

The first three chemicals were specifically cited in the declaration notice and are listed in the Australian Inventory of Chemical Substances (AICS). A subsequent notice was published in the Chemical Gazette of October 2000 for tris (2-chloro-1-propyl) phosphate (CAS No. 6145-73-9) as no applicants had come forward. However, no importers or manufacturers indicated that the chemical was being imported into Australia. Trisphosphates not listed in the AICS were considered in this assessment as these chemicals may be imported under exempt categories or in articles.

It should be noted that a misuse of nomenclature was identified for tris (1-chloro-2-propyl) phosphate (CAS No. 13674-84-5) in this report. This chemical was incorrectly named by some applicants as either tris (2-chloro-1-propyl) phosphate or tris (2-chloro-2-propyl) phosphate. The latter chemical was also named in the declaration notice. However, although this chemical possesses a unique CAS number (16839-32-0), it appears to have been allocated in error due to a mistake in translating an old-fashioned nomenclature to the IUPAC and Chemical Abstracts nomenclature systems. Substances with chlorine and oxygen attached to the same aliphatic carbon are rare, and those that are known to exist such as chloromethyl ether are extremely reactive. The assigning of a CAS number to this (non-existent) substance can be traced to the abstracting of an article by van Netten et al. (1991). The abstractor appears to have taken the substance name in the title literally, and not checked the article in which it is clearly stated that it is tris (2-chloroisopropyl) phosphate (CAS No. 13674-84-5) also known by the trade name Fyrol PCF. Thus a CAS number already existed for this substance. NICNAS will refer this to CAS for consideration.

4.1 Chemical Identity

The chemical identities of the trisphosphates are listed in Table 1.

Table 1 - Chemical identity of trisphosphates

Chemical Identity	Tris (2-chloroethyl) phosphate	Tris (1-chloro-2-propyl) phosphate	Tris (1,3-dichloro-2-propyl) phosphate*	Tris (2-chloro-1-propyl) phosphate	Tris (2,3-dichloro-1-propyl) phosphate	Tris(3-chloro-1-propyl) phosphate
CAS No.	115-96-8	13674-84-5	13674-87-8	6145-73-9	78-43-3	1067-98-7
EINECS No.	204-118-5	237-158-7	237-159-2	228-150-4	201-117-1	NA
RTECS No.	KK2450000	NA	UB1473000	NA	NA	NA
AICS Listed	Yes	Yes	Yes	Yes	No	No
Synonyms	Tris (2-chloroethyl) phosphate Tri (2-chloroethyl) phosphate Tri (β-chloroethyl) phosphate Tri (chloroethyl) phosphate Tris (2-chloroethyl) orthophosphate Tris (chloroethyl) phosphate	Tris (2-chloro-1-methylethyl) phosphate 1-Chloro-2-propanol phosphate (3:1) Tris (1-chloro-2-propyl) phosphate Tris (1-methyl-2-chloroethyl) phosphate Tris (2-chloroisopropyl phosphate) Tris (chloroisopropyl) phosphate	Tris [2-chloro-1-(chloromethyl)ethyl] phosphate Tris (1,3-dichloro-2-propyl) phosphate 1,3-Dichloro-2-propanol phosphate (3:1) Tris (1,3-dichloro-2-propyl) phosphate Tris (1,3-dichloro-2-dichloroisopropyl) phosphate Tris (1-chloromethyl-2-chloroethyl) phosphate	Tris (β-chloropropyl) phosphate Tris (2-chloropropyl) phosphate 2-Chloro-1-propanol phosphate (3:1)	1-propanol, 2,3-dichloro-phosphate (3:1) Tris (2,3-chloropropyl) phosphate Tris (2,3-dichloro-n-propyl) phosphate	NA NA No

Table 1 - Chemical Identity of trisphosphates (Cont.)

Chemical Identity	Tris (2-chloroethyl) phosphate	Tris (1-chloro-2-propyl) phosphate	Tris (1,3-dichloro-2-propyl) phosphate*	Tris (2-chloro-1-propyl) phosphate	Tris (2,3-dichloro-1-propyl) phosphate	Tris(3-chloro-1-propyl) phosphate
Molecular Formula	$C_6H_{12}Cl_3O_3P_4$	$C_9H_{18}Cl_3O_3P_4$	$C_9H_{15}Cl_3O_6P_4$	$C_9H_{18}Cl_3O_4P_4$	$C_9H_{15}Cl_3O_6P_4$	$C_9H_{18}Cl_3O_4P_4$
Structural Formula	$(ClCH_2CH_2O)_3P=O$	$(CH_3(CH_2Cl)CHO)_3P=O$	$[(ClCH_2)_2CHO]_3P=O$	$(CH_3CHClCH_2O)_3P=O$	$(CH_2ClCHClCH_2O)_3P=O$	$(ClCH_2CH_2CH_2O)_3P=O$
Molecular Weight	285.5	327.5	431	327.5	431	327.5
Trade Names	3CF Amgard Antiblaze TCEP CEF CLP Disflamoll TCA Fyrol CEF Niax 3CF Niax Flame Retardant 3CF	Amgard TMCP Antiblaze 80 Fyrol PCF TCPP TMPP	Antiblaze 195 CRP FR 10 FR 10 (phosphate) Fyrol FR-2 PF 38 PF 38/3 TDCPP	Amgard TMCP Antiblaze 80 AP 33 Nolinen R 921 Peiron 9338 TMCPP	Celluflex FR.2 Fyrol 32B Peiron 9338	NA

* Tris (2,3-dichloro-1-propyl) phosphate is present as an impurity in the commercial product.
NA, not available

5. Physical and Chemical Properties

5.1 Physical and chemical properties

Trisphosphates are clear liquids or low-melting solids, with little or no odour. They:

- are denser than water, the density increasing with the number of chlorines in the molecule;
- have low vapour pressures, and as a consequence the boiling points are high, over 200 °C;
- cannot be distilled at atmospheric pressure without decomposition but can be distilled at reduced pressures;
- have high flash points,
- are soluble to a small extent in water, but readily soluble in ketone, alcohol and chlorinated hydrocarbon solvents;
- are incompatible with strong oxidisers and strong acid/bases;
- have moderate log K_{ow} values, increasing with increasing degrees of chlorination. The coefficient of partition between octanol and water, K_{ow} , is usually expressed in logarithmic form so as to avoid the use of exponents. Sometimes, the symbol p is used instead of K . The log K_{ow} value is often taken as a guide to biomagnification (being significant for substances with $K_{ow} > 3.8$) and bioaccumulation (when K_{ow} is > 4.5); and
- are hydrolysed to produce phosphoric acid and a chlorinated alcohol, but under the conditions of hydrolysis there may be some attack on the aliphatic chlorines to produce ethylene or propylene glycol or glycerol.

The physical properties of trisphosphates are provided in Table 2. These have been sourced from MSDSs provided by industry and available on the Internet, Aldrich-Sigma catalogue of organic chemicals and research articles identified through Chemical Abstracts (a on-line database). Additional sources are listed below:

- CRC Handbook of Chemistry and Physics. 79th edition (Lide, 1999);
- Beilstein's Handbuch der Chemie (1918-1984);
- Gardner's Chemical Synonyms and Trade Names. 9th edition (Pearce, 1987);
- Dictionary of Chemical Names and Synonyms (Howard & Neal, 1992);
- KEMI report (1994); and
- IPCS report (1998).

Table 2 - Physical properties

Property	Tris (2-chloroethyl) phosphate (TCEP)	Tris (1-chloro-2-propyl) phosphate (TCPP)	Tris (1,3-dichloro-2-propyl) phosphate (TDCPP)	Tris (2-chloro-1-propyl) phosphate	Tris (2,3-dichloro-1-propyl) phosphate
Molecule weight	285.5	327.6	430.9	NA	NA
Boiling point	145 °C (@66 Pa or 0.5 mm Hg)	NA	200 °C (@533 Pa or 4 mm Hg)	Decomposes @ 220 °C	NA
Melting point	NA (pour point approx. -70 °C)	-40 °C	27 °C	-65 °C	NA
Specific gravity	1.42	1.290 (@25 °C)	1.520 (@25 °C)	1.297 (@25 °C)	1.52
Water solubility	8 g/L (@20 °C) ⁺	1.6 g/L ⁺	0.11 g/L ⁺	1.2 g/L	0.053 g/L
Viscosity	38 mPa (@25 °C)	71 mPa (@25 °C)	1800 mPa (@25 °C)	NA	71 mPa (@25 °C)
Vapour pressure	8 Pa (@ 25 °C) [#] <1300 Pa ⁺	ND [#] <260 Pa ⁺	1.3 Pa (@ 30 °C) ⁺ [#]	< 13 Pa	NA
Henrys Law Constants [§]	0.285 Pa m ³ /mol	ND	5.1 Pa m ³ /mol	NA	NA
Partition coefficient to octanol/water (Log K _{ow})	1.7 ⁺	2.59 ⁺	3.8 ⁺	NA	2.67
Partition coefficient to organic carbon ^a (Log K _{oc})	2.3	2.8	3.4	NA	NA
Flash point [*]	252 °C	218 °C	252 °C	220 °C	NA

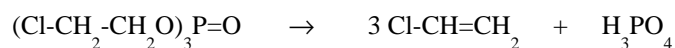
Values at 20 °C unless otherwise stated. * Cleveland open cup (C.O.C.)[#] source from Kerni report (1994) ⁺ source from IPCS report (1998)

[§] Henrys Law Constant (H) calculated from the measured vapour pressure (from Kerni, 1994) and water solubility using $H = MW \times \text{Vapour pressure in Pascals} / \text{Water solubility in grams/cubic metre}$.

^a Log K_{oc} estimated from Quantitative Structure Activity Relationship from equation 4-8 of Lyman (Lyman *et al*, 1996) i.e. $\text{Log Koc} = 0.544 \times \text{Log Pow} + 1.377$.
 ND, not detectable; NA, not available.

5.2 Thermal degradation

The most important route for thermal degradation of the trisphosphates is elimination of phosphoric acid, with consequent introduction of double bonds into the aliphatic moiety. For example, the thermal degradation of tris (2-chloroethyl) phosphate may be represented by:



Although the process no doubt occurs in stepwise fashion, producing a molecule of vinyl chloride at each stage.

In a real situation where oxygen is present, such as in combustion of material into which the trisphosphate has been incorporated, there will be many other products of thermal degradation and partial combustion, including hydrogen chloride, oxides of carbon and oxidised carbon compounds such as ketones. Notwithstanding this, experimental data show that the basic contention is true, since vinyl chloride is a major product of the thermal degradation of TCEP, and dichloro-propenes from TDCPP (Paciorek et al., 1978). The following substances were thermally degraded at 370 °C in the presence of air - tri-p-tolyl phosphate, tributyl phosphate, TCEP, TDCPP, but only the data for the halogenated substances are reported in Table 3.

5.3 Blooming potential

Blooming is defined as the migration (or more appropriately, diffusion) of an ingredient (e.g. plasticiser or flame retardant) in rubber or plastic material to the outer surface after curing. It is sometimes incorrectly referred to as 'leaching' or 'degassing'. Diffusion is generally considered to be a slow process.

Blooming has been identified as a source of potential exposure (human and environmental) to trisphosphate plasticisers/flame retardants. Although there appears to be a lack of data on the propensity for blooming for the chemicals reviewed in this report, other trisphosphates e.g. triphenyl phosphate (TPP) are the subject of current studies on this issue (Carlsson, 2000).

Trisphosphates are incorporated into polymers as 'additive' (i.e. not chemically bound to the polymer backbone) ingredients. Additive chemicals reside within the polymer matrix as discrete molecules, but may be subject to weak Van der Waals and electrostatic interaction both between trisphosphate molecules and the polymer backbone.

The degree (i.e. rate) to which blooming may occur is dependent on a number of factors, which include:

- size and shape of the trisphosphate molecule/polymer;
- geometric structure of the plastic matrix;
- stability of trisphosphate in the 'melt' i.e. compatibility of trisphosphate with plastic polymer;
- solubility (o/w partition coefficients) of the trisphosphate molecule/polymer;

- volatility (vapour pressure) of the trisphosphate molecule/polymer;
- temperature (generally increased temperature will increase blooming potential); and
- stability of polymer matrix in contact with solvents e.g., swelling.

The specific combination of these properties for a particular trisphosphate and polymer matrix will determine whether or to what extent blooming is likely to occur.

It is generally considered that high molecular weight compounds e.g. polymeric trisphosphates, will have a significantly lower potential for blooming than low molecular weight compounds (monomers, dimers etc.) due to the fact that the larger (long chain) structures will become more entangled (fixed) in the plastic polymer matrix.

A more contentious issue is the relationship of trisphosphate solubility and volatility to blooming potential. It appears that some confusion exists in relation to these properties, i.e. over the issues of potential for blooming and potential for movement/partitioning in environmental media. Although it is likely that trisphosphates that exhibit low solubilities in water will have a low propensity to be removed from the surface of the polymer, the effect of abrasion/movement during use/cleaning of the plastic may result in depletion of some trisphosphate (if present) at the material surface, thereby maintaining a 'concentration gradient', the net effect of which would be to propagate any blooming potential. Some applications requiring flame retardants are not subject to cleaning or abrasion during their entire useable life. Similarly, although leaching of sparingly soluble trisphosphates might be expected to be minimal from landfilled polymer materials, this would be dependent on the rate of 'flow' (i.e. quantity) of water across the polymer surface, which would provide a 'driving force' for migration of the trisphosphate. In addition, certain solvents may affect the stability of particular polymer matrices, causing swelling, which may facilitate trisphosphates migration. This would also apply to certain cleaning operations.

Increased temperature and high volatility are also associated with an increase in the rate of trisphosphate migration. In this regard, trisphosphates are known to bloom from car interior plastics, TVs and computer VDUs. Blooming may also occur during thermal processing (e.g. molding).

In summary, the potential for blooming of trisphosphates may be highly variable and related to a combination of physicochemical and structural parameters. However, no studies citing the degree of migration for trisphosphates were provided for assessment, and as such definitive conclusions on blooming potential are not possible.

Table 3 - Hazardous products of thermal degradation of some chlorinated trisphosphates

Degradation Product	TCEP (mg/g of trisphosphate)	TDCPP (mg/g of trisphosphate)
CO	19.3	1.82
CO ₂	8.72	5.10
HCl	25.3	146.0
Benzene	3.71	-
Toluene	0.29	-
Chloromethane	0.93	0.07
Chloroethane	0.44	0.16
Vinyl chloride	135.0	0.75
1,2-Dichloroethane	305.0	8.32
Chloropropenes	0.06	3.06
Dichloropropenes	-	312.0
1,2,3-Trichloropropane	-	116.0
2-Chloroethanol	8.03	0.02
1,3-Dichloro-2-propanol	-	0.18
Acetaldehyde	12.1	1.92
Acrolein	-	22.7
Chloroacetaldehyde	0.21	-
Chloroacetone	-	8.15
Bis(2-chloroethyl) ether	5.19	-
Bis(2-chloroethoxy) methane	2.49	-
Methyl formate	0.11	-
Methyl acetate	0.80	-
2-Chloroethyl acetate	1.24	-

6. Manufacture, Importation and Use

6.1 Manufacture and importation

Chlorinated trisphosphates are not manufactured in Australia. Trisphosphates are imported by a small number of companies who use them in formulations and/or on-sell them for formulation by client companies. The only chlorinated trisphosphates currently imported into Australia are TCEP and TCPP. A total volume of around 410 tonnes a year is imported in 200 L steel drums. The main sources of these compounds are Britain, Germany and Singapore. Approximately 20 to 40 tonnes of TDCPP are likely to be imported in the future. No examples were encountered of trisphosphates being imported as constituents of articles, unlike polybrominated flame retardants e.g. in casings of electronic equipment. However it is likely that where trisphosphates are incorporated into articles overseas, that similar articles containing trisphosphates are also imported. A small quantity of a trisphosphate is imported as a product. Table 4 provides details of current and predicted volumes of TCEP and TCPP imported into Australia.

Table 4 - Australian import data for chlorinated trisphosphates

Substance	Current Imports (tonne/yr)	*Future Imports (tonne/yr)
TCEP	120	90
TCPP	290	320

*Estimates provided by industry

Some users reported that TCEP was being phased out in favour of TCPP, and this is reflected in the above estimated future imports, but overall the total quantity of these closely-related trisphosphate esters remains relatively constant.

6.2 Uses and exports

6.2.1 Use in product formulation

The two main applications for trisphosphates in Australia are in the manufacture of polyurethane flexible and rigid foams, with smaller amounts used in production of polyurethane elastomers and for blending with alkyd or acrylic resins in the formulation of surface coatings and fibreglass resins. Concentrations of trisphosphates in finished products range from 2 to 15%. In flexible and rigid foams the concentration of the trisphosphate in the final product is typically around 7%. The two imported trisphosphates (above) are used almost interchangeably, with selection of the specific compound depending to varying degrees on cost, specific properties, and experience in the industry sector.

Flexible foams account for approximately 80% of the foam products and around 70% of total trisphosphate use in Australia. Several companies manufacture

flexible foams in Australia, with the majority being produced by two companies comprising around 35,000 tonnes per year. The trisphosphates are supplied to customers who use them at a few major locations to produce flexible foams, which are then dispatched to companies who incorporate/fabricate foam into finished products for retail sale. A sub-class of flexible foams are the semi-rigid foams, used, for example, in automobile interiors. However, one importer stated that to their knowledge TCEP and TCPP are not used in the automobile industry.

Rigid foams account for 20% of foam products and approximately 17% of trisphosphate use. Some changes are taking place in selection of flame retardants for particular uses, but as yet the total import volume remains unchanged. For example, TCPP is used by one company in rigid foam, where they had used decabromodiphenyl ether in the past, and one manufacturer is considering the advantages of less-volatile phosphorus compounds as substitutes for chloroalkyl phosphates.

In some cases, customers carry out a final formulation step prior to rigid foam production. Customers are provided with two components – a polyol to which has been added the trisphosphate, and an isocyanate which when combined with the polyol produces the rigid foam. One major supplier provides around 10,000 tonnes per year of such raw materials to customers, of which some 15% was exported to New Zealand. Most rigid foams do not require the addition of flame retardants, so the overall market for trisphosphates is much smaller than can be estimated from polyurethane foam use/production. It has been reported that about 10% of all plastics contain flame retardants (IPCS, 1997).

Other applications of trisphosphate flame retardants in Australia account for approximately 13% of the imported materials. These applications include surface coatings such as sealants and industrial paints (approximately 10 tonnes/year), resin reinforced with fibre-glass (> 4tonnes/year), moulded objects (10 tonnes/year), elastomers (> 7.5 tonnes/year) and specialist rubber-like materials (approximately 5 tonnes/year). TCEP is the major trisphosphate used in such formulations/products, and it is added to meet specific flame retardant regulatory requirements by the user. As with foams, these product types do not necessarily contain flame retardants.

6.2.2 End uses

Flexible foams are used almost exclusively in bedding and other furnishing applications e.g. plastic insulation foams, furniture and wall/floor coverings.

Semi-rigid foams containing TCPP were formerly used in automobile accessories, such as seating, crash pads, steering wheels, and sun-visors, but usage has declined in recent years so that foams incorporated into a typical car might contain only a few grams of flame retardant. Consumption of TCPP for use in sun-visors by one vehicle manufacturer in Australia is estimated at approximately 1 tonne per year.

A major use of rigid foams are in thermal insulation for hot water services. They are also used in applications such as buoyancy tanks in marine craft. Not all foam products have flame retardants added, but are specifically requested by certain customers. Mining companies, for example, require fire retardants and anti-static additives in equipment such as screens which are to be used underground. Other

moulded foam products reported to contain TCEP are panels, benches and containers (e.g. cherry picker baskets).

Recent concern has been expressed over potential exposure to organophosphate fire retardants in electrical products such as office machines and computer monitor casings, however no reports of the use of chlorinated trisphosphates appear in the available literature. It has been reported that triphenyl phosphate, a compound widely used as a flame retardant in the plastic of computer monitors and other products may be emitted when their temperature rises during normal operations (Carlsson, 2000). This chemical has not been considered in this assessment as it is not a chlorinated trisphosphate and not within the scope of the assessment. Other reported uses of plastics containing flame retardants in electrical products are cable housings and components for televisions and laminated printed circuit boards.

Resin reinforced with fibre-glass containing TCEP is used in Australia in the manufacture of structural materials used in the building industry such as sheeting and pipes and used in transport vehicle components.

Other reported uses (past and present) in Australia include: TCEP (3 to 8%) as flame retardant in acrylate and polyurethane preparations used to seal rock faces (sealing stoppings) in underground coal mines and incorporation into printing inks for applications where flame retardancy is required.

6.2.3 Exports

Export of components for production of rigid polyurethane foam to New Zealand (see section 6.2) accounts for approximately 3% of the trisphosphates entering Australia. No other instances of export have been identified.

7. Potential for Exposure

7.1 Environmental exposure

7.1.1 Release

Manufacturing of polymers and resins

Production of polyurethane foams entails mixing the required quantity of the flame retardant (TCPP) with the polyol component prior to mixing and reacting this with the isocyanate component. Apart from spills and leaks during transfer from the 200 L drums there is little possibility of release during these operations. It is estimated (Section 6.1) that release of the TCPP during primary manufacturing of polyurethane foams would be a maximum of 1% (ie. around 3 tonnes per annum) and that this would be placed into municipal landfill after absorption into saw dust or other absorbent materials.

Use of TCEP appears to be mainly in production of polyester resins, and again there is little possibility of release, with spillage again being placed into landfill. Assuming annual use of 100 tonnes of TCEP and 1% loss through spills, this amounts to release of 1 tonne per annum of this compound. In both polyurethane and polyester production small quantities of the material may be left in the empty 200 L drums, and this would be removed during drum re-conditioning and would most likely be recovered into waste industrial sludge at the recycling facilities and be either incinerated or be placed into landfill. If it is assumed that 0.5% of the esters are left in the drums (Section 6.1) then around 2 tonnes may be released in this manner.

Overall, a maximum of around 6 tonnes of the esters (1.5 tonne of TCEP and 4.5 tonnes of TCPP) may be released as a result of primary polymer and resin manufacturing. Most of the released material is expected to be placed into landfill, although possible release of some of this material to municipal sewers in aqueous waste from the polymer production facilities may also be possible.

Fabrication of end use products

Most polyurethane foam containing the flame retardant esters will be used in furniture production. In particular flexible foam is used in mattresses and upholstery while rigid foam is used for insulation in white goods such as electric water heaters and refrigerator lining. Some rigid foam is also used in vehicle interiors. Fabrication of these articles normally involves some cutting, and off-cuts would normally be collected and placed into landfill with solid waste. No figures are available, but a maximum wastage of 10% appears reasonable which amounts to a release of approximately 40 tonnes per annum. Again this would be placed into landfill with solid waste.

Releases during end use

The esters are incorporated into solid polyurethane or polyester masses and while not chemically bound to the polymer chains, the molecules are physically trapped in the matrices. However, in the IPCS report (IPCS, 1998) in studies from 1977 and 1979 it was indicated that significant quantities of TDCPP in polyester garments were released to waste water during washing (37% after 20 washings), and this suggests that while encapsulated in polymer masses, the compounds are appreciably mobile in these media. TDCPP is a close structural analogue of TCPP. Industry advised it was voluntarily taken out of the clothing market in 1978. This also suggests that release to the atmosphere by sublimation from the surfaces of the polyurethane or polyester articles is also possible.

The vapour pressure of the compounds is >1 Pa at ambient temperatures, and according to the scale provided by Mensink (Mensink et al, 1995) both of the chlorinated phosphate esters considered in this report are classified as volatile, and consequently some of the chemical is expected to be released to the atmosphere during the lifetime of the finished products (typically 10-20 years). Unfortunately no data are available to allow estimation of the likely quantities of the esters released to air in Australia, but TCPP and TDCPP have both been measured in air at Kitakushu in Japan at levels of 0.0053 and 0.0047 $\mu\text{g}/\text{m}^3$ respectively (IPCS, 1998). No data on measured atmospheric levels of TCEP was readily available during the preparation of this preliminary assessment.

Although release of the compounds to water from fabric has been observed (see above), the use patterns of the compounds within Australia seem to preclude this possibility. However, possible importation and local sale of polyester clothing articles containing these esters has not been addressed.

Some polyester fibreglass articles containing the esters (particularly TCEP) may be exposed to water in which case some release to this compartment is possible. It is not possible to make quantitative estimates of likely release, but any release is likely to be widespread and diffuse.

Overseas experience has demonstrated that some of the compounds will be released to the water compartment, and in particular TDCPP has been detected in sewage wastewater effluent's in Japan (IPCS, 1998) at levels up to 1.4 $\mu\text{g}/\text{L}$, while concentrations up to 5.6 $\mu\text{g}/\text{L}$ of TDCPP were found in domestic waste water – probably originating from washing articles containing the flame retardants. This compound has also been found at concentrations up to 3 $\mu\text{g}/\text{L}$ in effluent from Swedish waste water treatment facilities (IPCS,1998). TDCPP has also been detected in river water in Japan (IPCS, 1998) at levels between 0.02 and 0.14 $\mu\text{g}/\text{L}$, and in drinking water at levels up to 0.9 $\mu\text{g}/\text{L}$ (IPCS,1998). The IPCS report also cites other references to the presence of low levels of TDCPP (maximum 0.0046 $\mu\text{g}/\text{L}$) in Canadian drinking water.

TCEP has also been detected in both environmental (river and sea) waters and in drinking water in Japan and Canada, while this compound was detected in Rhine water from the Netherlands at concentration up to 1 $\mu\text{g}/\text{L}$ and in water samples from other European countries (IPCS, 1998).

Release after disposal of end use products

At the end of their useful lives articles containing the flame retardant esters would be discarded, and it is expected that articles containing flexible polyurethane foams (and hence containing TCPP) would be placed into landfill although some may be incinerated. Articles containing rigid polyurethane foam insulation (eg refrigerators and water heaters) are more likely to be reprocessed for recovery of the metal, although some would also be placed into landfill. Fibreglass articles produced from polyester containing TCEP are also likely to be placed into landfill.

In a landfill situation some of the contained chlorinated phosphate ester may be released to the atmosphere through sublimation, while as groundwater percolates through the landfill structure some leaching of the compounds is also possible. These release scenarios would become more important as the polyurethane or polyester masses into which the compounds are incorporated are broken down in the landfill by the slow biological and abiotic processes operative within these structures.

Summary of release scenarios

Ultimately both chlorinated phosphate esters used in Australia each year (total around 410 tonnes) will be released – primarily to the air and water compartments. Overall the release will be diffuse and Australia wide.

7.1.2 Fate/Disposal

This section provides information on TCEP, TCPP and TDCPP. Currently TCEP and TCPP are imported into Australia, however, information provided by industry indicates future importation of TDCPP.

Atmospheric fate

All three compounds have appreciable vapour pressures and are classified as volatile, and it appears likely that considerable quantities of TCEP and TCPP may enter the atmosphere (section 7.1.1). Once having entered the atmospheric compartment the compounds are expected to be destroyed through reaction with atmospheric hydroxyl radicals. For the present compounds the primary pathway for degradation in the atmosphere will be through hydrogen abstraction by OH radicals, and in OECD Environment Monograph 61 (OECD, 1992) methods for the calculation of reaction rate constants for compounds of known molecular structure (i.e. k_{abs}) are presented.

Assuming the accepted global average atmospheric concentration of hydroxyl radicals as 5×10^5 molecules/cm³, the atmospheric half-lives of the compounds can be estimated, and these data are reproduced in Table 5.

Table 5 - Atmospheric half lives

	TCEP	TCPP	TDCPP
$k_{\text{abs}} \times 10^{12}$ cm ³ /molecule/sec	3.74	10.89	11.58
$T_{1/2}$ (Hours)	102	35	37.6

Degradation of the compounds in the atmosphere is expected to lead to ultimate destruction with formation of HCl, water and carbon dioxide. The phosphorus component would most likely be converted to phosphoric acid and be precipitated (along with the HCl) to the surface with rain.

Aquatic fate

It is likely that some of the material will be released to the water compartment – primarily in landfill leachate resulting from degradation of polyurethane foam and polyester. All three compounds are appreciably soluble in water, with TCEP having the highest solubility of 8 g/L. Both TCEP and TCPP have only modest values of Log K_{ow} and Log K_{oc} (partition coefficient to organic carbon) (see Table 2) and are expected to remain in the water compartment. Even for TDCPP which is less water soluble than either TCEP or TCPP (solubility around 100 mg/L), and which also has a higher value of Log K_{ow} (3.4) the Simple Treat Model of the EU (European Union, 1996) indicates that only around 25% of the compound would become associated with sludge while 5% may be released to air and the remaining 70% would remain dissolved. While both the compounds used in Australia have significant vapour pressures and appear volatile from solids, this is not reflected in volatility from water due to the high water solubilities which give low values of H (the Henry's Law Constant). Both TCEP and TCPP have lower Henry's Law Constants than that of TDCPP for which H is 5.1 Pa m³/mol, and as indicated above the Simple Treat Model predicts only around 5% partitioning to the atmosphere from the water compartment for this analogue.

Biodegradation

Neither of the two chlorinated phosphate esters used in Australia is readily biodegradable according to OECD criteria, and after 4 weeks incubation with sewage sludge the KEMI report (KEMI, 1994), citing the Japanese Ministry for International Trade and Industry (MITI) List indicated 4% and 0% degradation for TCEP and TCPP respectively. The actual test regime used in these tests was not stated, although it was indicated that each of the test compounds was present in the media at 100 mg/L. However, in the IPCS report No 209 (IPCS, 1998) it was indicated that TCEP could be classified as ultimately biodegradable, while other tests cited in this report indicated that TCPP was 21% degraded after 28 days under the protocols of OECD TG 302C (the modified MITI test).

The conclusions from these abstracted data is that TCEP and TCPP are likely to be ultimately biodegradable under aerobic conditions, while the more heavily chlorinated TDCPP is probably not susceptible to aerobic biodegradation. No data on anaerobic degradation was available.

While refractory to aerobic bacterial biodegradation the compounds may be metabolised by higher organisms, and Sasaki et al (cited in IPCS, 1998) monitored the degree of degradation of TDCPP in water containing killifish (*Orzyias latipes*) or goldfish (*Carassius auratus*) and found the half life for the compound was 31 hours in the presence of the killifish and 42 hours for goldfish. No other details of the test conditions were indicated.

In respect of the refractory behaviour of TDCPP it is relevant to note that Ishikawa and co-workers (cited in IPCS, 1998) detected this compound in 5 sewage plant effluents at levels between 0.28 and 1.4 µg/L, while the raw sewage influent levels were between 0.33 to 1.6 µg/L. The similar levels in both sewage influent and effluent are in accord with the low tendency for removal into sludge (see above) and negligible aerobic biodegradation.

Abiotic degradation

Hydrolysis of the compounds in aqueous solution is likely to be slow in the normal environmental pH region where $4 < \text{pH} < 9$. However, at elevated temperatures and/or under extreme pH conditions hydrolysis of the C-Cl bonds may be more rapid (IPCS, 1998).

As indicated above, degradation through reaction with hydroxyl radicals in the atmosphere would lead to ultimate formation of HCl, water and carbon dioxide, while incineration of the compounds would produce the same compounds.

Bioaccumulation

The high water solubilities and modest values of Log K_{ow} indicate that none of the compounds has significant potential for bioaccumulation (Connell, 1989). Data cited in the KEMI report (1994) from the MITI List leads to similar conclusions, and measured bioconcentration factors for all three chemicals is low, with the largest bioconcentration factor of 49 found for killifish (*Orzyias latipes*) exposed to 0.08 mg/L of TDCPP over 32 days. Similar low values were found for TCEP, but in a separate study a BCF of 107 was found for killifish exposed to 0.3-1.2 mg/L of TDCPP over 96 hours. Nevertheless, on transfer of the fish to clean water elimination of the compound from fish tissue was rapid with a half life for elimination of TDCPP only 1.65 hours (IPCS, 1998).

Terrestrial fate

It is anticipated that much of chlorinated phosphate ester material will be released in landfill after degradation of old polyurethane and polyester articles, and so once released this is likely to become associated with the landfill soil. The QSAR estimated values for Log K_{oc} (see above) for all three compounds are > 2 (highest for TDCPP with estimated Log $K_{oc} = 3.4$) indicating that all have affinity for the organic component of soils and sediments and, according to the scale of Mensink (Mensink *et al*, 1995) are expected to have low mobility in these media. However, the high water solubility of all three compounds indicates that partitioning from the soil to the water phase is possible and that mobility in and from soil media may be quite high, and the presence of the compounds in leachate from landfills is likely. The presence of TCEP in municipal landfill leachate has been apparently been demonstrated (IPCS, 1998), although actual levels were not indicated in the article from which this reference was sourced.

TDCPP has been detected in sediments in Japan at levels of 9-17 µg/kg (IPCS, 1998), and while TCEP was also detected in river sediments, the levels were much lower being 0.013-0.028 µg/kg (IPCS, 1998).

TDCPP is the most likely of the three esters to become associated with soil and sediments, and given that it is apparently resistant to aerobic bacterial degradation it must be assumed that this compound will be persistent in aerobic soils and sediments. In the absence of viable anaerobic degradation mechanisms the compound would also be persistent in these environments, but no relevant data on this is available.

Summary of environmental fate

Release to the environment will be diffuse over the life of products containing the two chlorinated phosphate esters (TCEP and TCPP) imported into Australia, and significant release to the atmosphere through volatilisation is possible for all compounds. Some portion of these compounds may enter the water compartment through laundry and cleaning activities. Articles containing the compounds will be discarded at the end of their useful lives, with the majority being placed into landfill although some may be incinerated during activities directed at recycling steel.

Ultimately most of the chemicals used in Australia will be released, with much expected to enter the atmosphere and most of the balance being released to the water compartment. Nevertheless, use of articles containing the compounds is widespread and varied, and release will be diffuse.

On release to the atmosphere the compounds will be degraded through reaction with hydroxyl radicals. TCEP will have the longest half life (estimated as 102 hours) while TCPP and TDCP have significantly shorter atmospheric residence times. Ultimately all three compounds will be degraded to HCl, water and carbon dioxide. Destruction of articles containing the compounds through incineration (eg recycled white goods) will produce similar degradation products - but see Table 3.

On release to water the high solubility of all three compounds indicates that they will remain in this compartment although some TDCPP may become associated with sediments. All three compounds have been detected in wastewater and in surface waters during surveys in Japan, Canada and in Europe. None of the compounds is readily biodegradable although TCPP and TCEP may be ultimately biodegradable.

On the other hand TDCPP appears to be very refractory to aerobic biodegradation, and in the absence of other degradation mechanisms is expected to be persistent in the environment. However, studies in Japan have indicated that this compound is rapidly metabolised and degraded by fish.

7.2 Occupational exposure

In the following sections, occupational exposure is discussed for each of the main uses for chlorinated trisphosphates reported in Australia.

The intention of this preliminary report is to evaluate the available information on occupational use profiles, obtained from suppliers and users of trisphosphates and from site visits, in order to assess potential exposure from use of these chemicals in Australia. No exposure data was requested/sourced by NICNAS or made available for assessment by applicants. It is unlikely any Australian data exists, as there is no occupational exposure standard.

Occupational exposure to chlorinated trisphosphates in Australia may result from direct use of the trisphosphates per se, or products (e.g. resins) containing them, in the formulation or manufacture of finished products (e.g. foams, plastics, surface coatings). Other potential sources of exposure are during transport and storage of trisphosphate or products containing trisphosphates and during disposal of contaminated containers or certain waste products. Inhalation would be expected to be limited by the low vapour pressure of the chemicals under review. Being liquids, the potential for dermal absorption is considered greater for TCPP and TCEP. Dermal absorption is also likely with TDCPP, which although solid at standard temperature pressure (STP) is in a liquid under conditions of use.

7.2.1 Manufacture of foam products

It is estimated that overall, around 300 workers may be employed nationwide in the primary steps of foam formulation/production, with smaller facilities accounting for two-thirds of this figure. Many more workers are involved in foam fabrication and finishing - perhaps up to 1500 people.

Flame retardants are received in 200 L steel drums, the contents of which are pumped directly into formulation vessels (capacity ~ 80 L). Empty drums are managed by drum recyclers.

In the manufacture of flexible foams, the formulation of polyol, isocyanate, flame retardant and other components, such as pigments is carried out in a closed system. Typically, the flame retardant (8 parts by weight) is added to polyol (100 parts) and isocyanate (MDI or TDI) (50 parts), equivalent to a foam content of about 5% trisphosphate. Reaction mixtures usually commence 'foaming' on contact and 'set' within a few minutes to a near-final product (complete curing may take several days). At one formulation site inspected, TCPP was mixed with urethane components and extruded onto a paper-lined moving belt, casting a flexible foam slab up to 60 metres in length. This is then cut into defined sizes. TCPP comprised about 10% of the formulation. Approximately 190 tonne/year is used in this way by one company.

Another, reportedly older method, is to cast a slab in a static mould, then cut it to size. TCPP also exerts a beneficial effect in the foaming reaction by acting as scavenger of catalyst (dibutyl tin dilaurate), due to traces of free acid in the ester.

Because of the toxicity of isocyanates and methylene chloride, there is an extensive vapour collection system, preventing operators from exposure to these hazardous materials. Operators wear protective clothing, and any vapours (mainly solvents and isocyanates) are drawn away from the workers faces by extractor fans and trapped in vapour emission systems. Smaller operators, who might account for up to 10% of the market, generally do not possess the more sophisticated systems of the larger formulators, but OHS precautions associated with isocyanate use (see below) are likely to ensure minimal exposure to trisphosphates.

During foam cutting operations and in the curing warehouse, operators wear leather gloves and respiratory protection. Exposure to the flame retardant is minimised by these measures. The cured foam product is sliced into sections as specified by customers and dispatched for use largely in furnishing and bedding products. Limited amounts of fabrication and finishing are also performed by some end-users. Exposure to trisphosphates during fabrication and finishing would be expected to be significantly lower due to the fact that:

- the flame retardant is already incorporated (immobilised) into the foam matrix and only a very small proportion of it is accessible from “blooming” to anyone handling the material. Blooming is a process whereby the trisphosphate chemical may be released slowly from the surface of the foam product; and
- the upper limit of trisphosphate in foam materials is usually not more than 10% and neat substance is not handled.

Scraps and off-cuts from these operations are often shredded into small pieces and dispatched to manufacturers of simple furnishing items, futons and carpet underlay. There is therefore little waste to be disposed of from foam manufacture.

The manufacture of rigid foams involves a two-stage process. In the first stage the polyol and smaller quantities of additives, including the flame retardant, are blended before dispatch to customers. In this process, components are pumped into formulating vessels, typically of 2 tonne capacity or greater, and the contents are stirred for several hours before being transferred through closed systems into 200 L containers for dispatch. There is almost no loss during formulation because equipment is used repeatedly. Formulation processes typically occur over several hours and are conducted on a daily or near-daily basis. Customers mix the resultant polyol-plus-flame retardant with isocyanate to form a rapidly-setting foam. Systems employed are closed and exposure is strictly controlled according to measures/standards adopted for isocyanates. Scraps and unused solidified resin account for no more than 0.5% of product, containing approximately 4% trisphosphate and are disposed off as non-hazardous waste to landfill. Exposure to trisphosphates during end-use will be reduced due to encapsulation of the foam either in metal (e.g. in thermal insulating or buoyancy applications), or other materials (e.g. vinyl in automobile components).

In general, because of the use of isocyanates (MDI and TDI) in foam production, it is considered that measures currently employed for control of exposures to isocyanates will significantly reduce exposures (dermal and inhalation) to trisphosphates. The handling, transport and use of isocyanates are tightly controlled by a number of national standards and codes. These include the ADG Code (FORS, 1998) and the NOHSC hazardous substances regulations (in particular, Health Surveillance Schedule (NOHSC, 1995a), List of Designated Hazardous Substances (NOHSC, 1999) and Exposure Standard for Atmospheric Contaminants (NOHSC, 1995b)).

Site visits indicated that the potential for exposure (dermal and inhalation) to trisphosphates is greater in the case of rigid foams produced by smaller operators. Operators wearing minimal protective equipment cast rigid foam in moulds mainly in the production buoyancy or insulating material. In such cases, the two components (formulated polyester and isocyanate) are measured out by volume and mixed in open containers before the developing foam is transferred to the mould.

Overseas atmospheric monitoring data conducted at a flexible polyurethane foams plant using TDCPP was provided by industry (Unpublished, 2000). Nine static air samples were collected using automated thermal desorber (ATD) glass tubes and analyzed by a flame ionization detector for quantitative analysis and GC-MS system (gas chromatograph connected to a mass spectrometer) for peak identification and semi-quantitative analysis. The detection limit was 5 µg/m³. Sampling equipment was located at various places including polyether line (2 samples on mixing head, removing of paper and cutting point each) and one near the TDCPP filling tank, cooling down point after cutting and cutting into small layers point each. Sampling duration ranges from 3 to 20 minutes. Details on operation process and control measures were not reported. Monitoring results indicated that 7/9 samples were below the level of detection, 1/9 was 5 µg/m³ and one near the removal of the paper in the polyester line was 14 µg/m³.

7.2.2 Production of polyester resins

Both pure TCEP and mixtures containing TCEP are used as plasticizer/flame retardant in the production of polyester resins in Australia. The polyester resins, typically containing 4 to 20% of TCEP, are then supplied to fibreglass fabricators for use in the manufacture of fibreglass articles such as sheeting, panels, benches, containers, pipes for chemical plants and transport vehicle components.

In a typical polyester resins formulation operation, trisphosphate (TCEP) or products containing TCEP is received from importers in 200 L drums and stored in banded areas. In use, a drum is placed on a weighing scale, a lance is inserted through the drum bung hole and trisphosphate (TCEP) pumped into a blending tank. The line is then flushed with a solution containing an accelerator dissolved in mineral spirits, which becomes part of the formulated polyester resin. Formulation is carried out in a closed system and the resin mixture is dissolved in an olefinic solvent (usually styrene). At one site, this operation is performed approximately twice a month, with average trisphosphate (TCEP) charge of 150 kg. The polyester resin solution is delivered in drums or bulk to fibreglass fabricators where the resin solution mixed with organic peroxide catalyst is sprayed or hand-rolled onto a glass fibre mat.

Solidified waste material (typically 1 to 2%) is disposed of to landfill. Typically around 1% of resin is retained in drums, and is dealt with by drum recyclers. It is reported that TCEP used for this purpose is likely to be replaced by cheaper products in future or 'diluted' with other products e.g. antimony oxide.

Limited exposure is considered likely from the enclosed formulation process of polyester resins. In fibreglass fabrication workplaces, control systems vary depending on the fabrication process. Generally workers wear safety glasses, disposable rubber gloves and work clothing including boots. Half-face respirators are generally worn by operators when spraying. However, at some worksites no specific precautions, other than the wearing of normal work clothing, were taken by operators during mixing and spraying operations and a potential for both dermal and inhalation exposure exists.

7.2.3 Production of industrial paints and coatings

Smaller quantities of trisphosphates (TCEP) are used in formulation of industrial paints and resin components for paints and other coating products. The flame retardant is added only to meet specific flame retardant regulatory requirements by the user. TCEP is incorporated in standard closed industrial mixers with solvent and other components such as pigments and alkyd resins. One paint manufacturer reported that of the 100,000 L/week industrial paints they produced, only a small proportion (estimated at <5%) contain TCEP. Another company reported using between 5,000 and 10,000 kg TCEP per annum in production of surface coatings.

In use, many of these specialist paints are applied in automatic spray booths, from which a proportion of the 'dried' paint (perhaps 20%) is recovered as waste and landfilled. Operators wear protective clothing and breathing protection.

Limited exposure is considered likely from formulation or end-use paint operations. However, other applications for surface coatings may be associated with a risk of inhalation and/or dermal exposure.

7.2.4 Other potential occupational exposures

Other reported uses (past and present) in Australia include: TCEP (3 to 8%) as flame retardant in acrylate and polyurethane preparations used to seal rock faces (sealing stoppings) in underground coal mines. The liquid products are mixed in closed systems, pumped directly into drums, and transported to customers. They are then used in the mine without specific protective measures being taken.

A small proportion of the trisphosphate, perhaps 1%, is incorporated into specialist rubber-like materials. The components are blended in closed mixers and extruded or cast into final form.

In addition to formulation and product manufacture, potential for occupational exposure to trisphosphates exists during importation and transport of both the imported materials, blended formulation materials and finished products (e.g. surface coating resins). These products are distributed by road or rail in Australia in drums up to 200 L in capacity.

In addition to workers involved in the production/fabrication of foam products, there is also a possibility of extended low-level exposure to trisphosphates by occupants/cleaners of commercial premises from "blooming", due to the extensive use of foams in furnishing products.

Blooming of trisphosphates may also occur from articles containing the chemicals with potential for exposure.

7.3 Public exposure

Many of the plastics containing trisphosphates are widely used both in the home and in automobiles. Personal exposure to the trisphosphate component is limited in the case of the rigid foams, which are usually encapsulated in metal (for example, in thermal insulating or buoyancy applications), but others may be enclosed in vinyl material when used in automobiles and volatilisation of the trisphosphate may occur slowly.

Literature on the release (volatilisation) of trisphosphates is very sparse, but it is notable that one experiment in which volatiles from foam mattresses were examined failed to detect flame retardants although other components such as aromatics and limonene were detected (Anderson & Anderson, 2000). Exposures to TCEP in soft furnishings in Europe were expected to be very low, with negligible inhalation exposure, and dermal exposure in the order of 0.006 mg/kg bw/day based on the use of TCEP in soft furnishings (personal communications, 2000). The use of trisphosphates in the production of foams used in home furnishings may also increase exposure due to the release of the substances through 'blooming'. It is not clear at this stage how much of the initial material is released from the surface via this mechanism. No information on the amount of flame retardant remaining in the plastic, and thus the amount released to the environment, was available at this time. There is also potential for exposure to trisphosphates from their use in surface coating or paint products, however there was no information available on the levels of exposure from these sources.

Exposure to the public may occur when polyester clothing treated with trisphosphates is worn (IPCS, 1998). TDCPP is released from garments to waste water, and there may be potential for releases to air. This exposure is not able to be quantified for the Australian public, as no information is available on the importation of clothes treated with trisphosphates, including information on the levels of trisphosphates in the garments, or the types of clothes treated. The dermal exposure will vary depending on the type of clothing (ie outer garment or inner garment), while both inhalational and dermal exposure will vary depending on the how long the clothing is worn for. No information on the water levels of trisphosphates in Australia is available - overseas information indicates that trisphosphates may be found in waste water, with some information indicating that it is present in drinking water.

The use of trisphosphates in automobiles may result in high levels within the vehicle, particularly during summer when internal car temperatures may reach 80° C. There is the potential for moderate exposures when an individual re-enters the car, and if a recirculating air conditioner is used levels may not drop rapidly. Therefore there is potential for consumers to be exposed to relatively high levels for significant periods in their vehicles, depending on the degree of volatilisation of the substances. Current information indicates that the use of trisphosphates in automobile interiors has declined (see Section 6.3), and this exposure may be of a lesser concern in new vehicles. However, there is no monitoring data available to confirm this.

8. Health Effects

This section is limited to a brief overview of the health effects and classification of chlorinated trisphosphate chemicals, and is intended as background information for the conclusions and recommendations that follow.

Because of the use of chlorinated trisphosphates as flame retardants, the assessment of health hazards of thermal degradation products is of significance, particularly with respect to public health hazards. Hazardous degradation products identified for chlorinated trisphosphates include hydrochloric acid, acrolein, acetaldehyde, carbon monoxide and vinyl chloride (Paciorek et al., 1978). It is beyond the scope of this report to assess the health effects of degradation products, however the hazards of these substances are relatively well known.

The primary sources of data are monographs prepared by the International Programme on Chemical Safety, covering TCEP, TCPP, tris (2-chloro-1-propyl) phosphate, TDCPP and its brominated analogue, tris (2,3-dibromopropyl) phosphate (IPCS, 1995; 1998); the Organisation for Economic Cooperation and Development SIDS report on TCPP (OECD, 1998); the International Agency for Research on Cancer monograph on tris (2-chloroethyl) phosphate (IARC, 1999) and the US National Academy of Sciences report on tris (1-chloro-2-propyl) phosphate, tris (2-chloro-1-propyl) phosphate and tris (1,3-dichloro-2-propyl) phosphate (National Academy Press, 2000).

A literature search identified studies for tris (2-chloro-1-propyl) phosphate and these have been included in the report.

8.1 Tris (2-chloroethyl) phosphate (TCEP)

In mice, more than 70% of an oral dose of TCEP was excreted in urine within 8 h. Identified metabolites were bis (2-chloroethyl) carboxymethyl phosphate, bis (2-chloroethyl) hydrogen phosphate and bis (2-chloroethyl 2-hydroxyethyl phosphate glucuronide).

In rats, distribution of TCEP following single oral administration was seen to occur in a number of tissues, especially the liver and kidneys. However TCEP levels in the hippocampus (the site of major lesions), were no higher than in other brain tissues. Most of the dose was eliminated by 24 h, mainly via the urine and smaller amounts via faeces and expired air. The same urinary metabolites were identified as for mice.

In vitro studies with liver slices, indicate sex differences in metabolism of TCEP in rats, but not in humans.

Acute oral LD₅₀ values for TCEP range from 430 to 3600 mg/kg in rats. No data were available for acute dermal and inhalation studies. Clinical signs of acute toxicity include ptosis, ataxia, hyperactivity, respiratory distress and convulsions. No pathological lesions were reported. One of the studies, conducted according to the OECD Test Guidelines, reported that no clinical signs of toxicity were observed in surviving animals from day 4 onwards.

In studies carried out according to acceptable protocols, grade 1 skin (erythema) and eye irritation was observed on day 1 in 3/3 New Zealand White rabbits and eye irritation persisted in one animal on day 2. There were no signs of skin and eye irritation thereafter.

No information on sensitisation was available for TCEP.

The neurotoxic potential of TCEP has been investigated in standard tests in White Leghorn hens. No behavioural or histological evidence for delayed neuropathy was reported, although plasma cholinesterase and brain neuropathy target esterase were inhibited by 87% and 30% respectively, in hens administered 2 high doses at 3 week intervals, each of 14 g/kg TCEP. Female F-344 rats administered a single dose of 275 mg/kg TCEP by gavage, elicited convulsions within 90 minutes with extensive loss of CA1 hippocampal pyramidal cells, examined 7 days following dosing. Animals also exhibited impaired memory when trained and tested (reference memory test) 3 weeks after dosing, indicating long-term impairment of some brain functions. A further rat study using the same strain and dose, where convulsions were experimentally controlled, indicated that hippocampal lesions may be due to convulsions *per se* rather than TCEP tissue toxicity. Perturbations in cholinesterase activity and effects on brain pathology were also reported in repeated dose studies in rats (see below), but not in mice.

In a 90-day (80 d only for females) NTP gavage study in F-344 rats at doses from 22 to 350 mg/kg/d TCEP, the animals with the 2 highest dose levels were overdosed for 3 days in week 4 and consequently 2 females of each dose level died. Clinical signs of toxicity including ataxia and convulsions were observed in a few other animals. Additional 1/20 and 7/20 animals died in the 175 mg/kg group and high dose group during 90 days exposure, respectively. Relative liver and kidney weights were increased ($p \leq 0.01$) in females at and above 44 mg/kg and in high dose males. No gross lesions were observed, but necrosis of neurons in the hippocampus and thalamus was observed in 18/20 females in 175 and 350 mg/kg groups and in 2/10 males at 350 mg/kg. In addition, serum cholinesterase activity was decreased in female rats only, by a mean of 25% and 40% at and above 175 and 350 mg/kg groups respectively. Similarly, no gross lesions were observed in an 80-day NTP gavage study in mice, but mild cytomegaly and karyomegaly were observed in renal tubules in all animals (both sexes) at the highest dose (700 mg/kg). No Observed Adverse Effect Levels (NOAEL) reported for these studies were 22 and 88 mg/kg/d, in rats and mice, respectively.

In a NTP gavage study (103 weeks) in F-344 rats administered 44 and 88 mg/kg/d TCEP, non-neoplastic effects included degenerative lesions in the brain stem and cerebrum in 40% of females at the high dose (2% in controls) and dose-related kidney hyperplasia in both sexes, which occurred in 40% animals at the high dose. Benign neoplastic lesions were reported in kidney at 44 and 88 mg/kg/d TCEP ($p < 0.001$ in males, $p = 0.003$ in females at 88 mg/kg/d), and in brain of males at 88 mg/kg/d. Thyroid carcinomas were observed at both doses in females and in high dose males, with none in control animals.

Non-neoplastic effects seen in a NTP chronic gavage study (103 weeks) in B6C3F1 mice were an increased incidence of eosinophilic foci in liver and karyomegaly of proximal convoluted tubules at and above 175 mg/kg/d in both sexes. A slight increase in hepatocellular adenomas was seen at the same dose level with a single renal adenocarcinoma seen at 350 mg/kg/d.

Non-neoplastic effects seen in a chronic Slc/ddy mouse feeding (12 to 1500 mg/kg TCEP) study (18 months) included tubular karyomegaly in all treated animals and necrosis and interstitial fibrosis of kidneys at the high dose. An increase in renal adenomas was reported in males at and above 300 mg/kg/d and females (high dose) together with a significant increase in renal carcinomas in males (32/50 animals) at the high dose. An increase in hepatocellular adenomas was also seen in both sexes at the same dose levels.

NOAELs were not reported for any chronic animal studies.

The International Agency for Research on Cancer (IARC) has classified TCEP as a category 3 carcinogen under their classification system. However, only the NTP studies (rat and mouse) were included in their evaluation (IARC, 1999).

Another study in female Swiss mice reported no significant initiating or promoting activity for TCEP via skin testing. However, IARC concluded that the data was insufficient for the purpose of assessing TCEP as a complete carcinogen.

In a battery of *in vitro* and *in vivo* assays, TCEP produced equivocal evidence for clastogenicity *in vivo* and inconsistent results for mutagenicity *in vitro*. No other data were available for a mechanistic assessment of the observed tumours.

No developmental effects were reported in mice or rats administered TCEP between days 6-15 gestation by gavage up to maternally toxic levels of 940 mg/kg/d. Postnatal examination revealed normal development of the offspring.

In a fertility study, carried out according to a continuous breeding protocol, in Swiss CD-1 mice administered 175 to 700 mg/kg/d TCEP by gavage, adverse effects were reported on testes and all sperm end-points (density, motility, morphology) with significant effects on fertility (reduction in number of litter size and live pups) at all doses. Adverse effects on testes and sperm function/morphology, accompanied by decreased fertility, including increased pre and post-implantation loss, was also reported in rats at 1.5 mg/m³ TCEP in a 4-month whole body inhalation study (only males exposed). Decreased sperm density and motility have also been reported in other repeated dose studies with TCEP in rats and mice.

A single human case report was available (personal communication, 2000). The case report, however, has not been available for in depth review. A 5 year old girl developed neurological effects, later associated with repeated exposure to TCEP present in household timber (600 mg/kg wood). Clinical signs included weakness in arms and abdominal muscles and abnormalities in electromyogram and nerve conduction velocities. Following a further 9 months of exposure, the child was admitted to hospital with dystelectatic pneumonia where a diagnosis of spinal muscle dystrophy with tetraparesis was established. On cessation of exposure, neurological impairment was still evident after several months, despite an improvement in her health status. However, no functional abnormalities were reported at 2 years post exposure.

8.2 Tris (1-chloro-2-propyl) phosphate (TCPP)

Limited data were available on the uptake or metabolism of TCPP. In rats, the primary route of elimination is urine, with some excretion in faeces. Total body burden after 8 days was < 1% dose, indicating a lack of bioaccumulation. Bis [1-chloro-2-propyl (2-propionic acid)] phosphate was identified as the major metabolite, accounting for over 50% of dose recovered in urine and faeces.

Acute oral LD₅₀ values for TCPP range from 700 to 4200 mg/kg in rats with a dermal LD₅₀ of > 2000 mg/kg in rats and rabbits. The inhalation LC₅₀ in rats was > 5 mg/L.

TCPP is classified with R22 (Harmful if swallowed) by Clariant (Australia) and another company in their MSDS/label (dated May 1999 and August 1997 respectively).

Studies indicate that TCPP is slightly irritating to skin and eyes of New Zealand White rabbits. TCPP did not produce a skin sensitisation reaction in guinea pigs in a Magnuson and Kligman test.

The neurotoxic potential of TCPP has been investigated in standard tests in hens. No behavioural or histological evidence for delayed neuropathy was reported. No effects were reported in brain, plasma or erythrocyte cholinesterase activity in a 90-day rat feeding study with Fyrol PCF (~75% TCPP: ~25% 2-chloropropanol phosphate).

Minimal evidence of toxicity and no histopathological effects were reported in rats dosed for up to 14 days with up to 16 600 mg TCPP per kg food, although an increase in relative and absolute liver weights was reported.

In a 90-day feeding study with Fyrol PCF in rats (doses ranging from approx 800 to 20 000 ppm), no adverse clinical signs were noted, although increased relative and absolute liver weights were reported in all groups of males and at 7500 ppm for females. Absolute kidney weights were increased in males only, at 7500 ppm. Mild thyroid follicular cell hyperplasia was seen in both sexes in the highest dose group. NOAELs for Fyrol PCF in this study were reported as 800 and 7500 ppm for male and female animals, respectively.

No data on the carcinogenic potential of TCPP were available. Weight of evidence indicated that TCPP was non-genotoxic in a battery of *in vitro* and *in vivo* assays.

No developmental effects were reported in rats at dietary concentrations ranging from 0.01% to 1.0% TCPP during days 0-20 gestation. Postnatal examination revealed normal development of the offspring.

No data on the effects of TCPP were available for humans.

8.3 Tris (2-chloro-1-propyl) phosphate

Toxicity testing was carried out on commercial mixtures containing variable amounts of tris monochloropropyl phosphate isomers. The commercial mixtures contain tris (1-chloro-2-isopropyl) phosphate and tris (2-chloro-1-propyl) phosphate.

No information on the absorption, distribution metabolism or elimination of tris (2-chloro-1-propyl) phosphate was available.

In rats, acute oral LD₅₀ was determined to be 1276 mg/kg and a (four hour) inhalation LC₅₀ was > 5.05 mg/L for male and approximately 5 mg/l for female rats. Clinical signs during exposure included increased salivation, decreased activity and eye closure. In the follow up period, rats exhibited severe lethargy, reddish lacrimation, body weight depression, slight alopecia, convulsions and dyspnea. Rats exposed for one hour to an aerosol of tris (2-chloro-1-propyl) phosphate (nominal concentration 17.8 mg/L) produced clinical signs of decreased activity, partial eye closure, oedema of the eyelids and lacrimation. A number of rats exhibited excessive salivation and dry rales during the first four days post exposure. There were no deaths (Albright and Wilson, 1980).

The acute dermal LD₅₀ was determined for rabbits to be > 2 g/kg. Erythema and oedema were observed at the site of application at 24 h and by 72 h had returned to normal (Albright and Wilson, 1980).

Tris (2-chloropropyl) phosphate produced a negative result in eye (Albright and Wilson, 1980) and dermal irritancy tests (Albright and Wilson, 1980) conducted on rabbits conducted according to the Draize protocols. No information on sensitising potential was available.

No studies investigating chronic exposure, reproductive or developmental or carcinogenic effects following exposure to tris (2-chloro-1-propyl) phosphate were available.

Tris (2-chloro-1-propyl) phosphate tested negative in the Ames test. Negative results were obtained with the test substance at all amounts up to 2000 µg/plate with or without metabolic activation with 'S9 mix'. No *in vivo* genotoxicity studies were available (Albright and Wilson, 1980).

8.4 Tris (1,3-dichloro-2-propyl) phosphate (TDCPP)

In rats, TDCPP is absorbed via dermal and oral administration with rapid distribution throughout the body. Similar elimination profiles were seen from both exposure routes with greater than 95% of dose eliminated in urine (43%), bile, faeces (39%) and exhaled air (16%) within 7 d following oral dosing.

Evidence from studies on a structurally related chemical, tris (2,3-dibromopropyl) phosphate (TDBPP) (IPCS, 1995), indicated that skin absorption is greater in rabbits than in rats with greatest distribution to kidneys and liver. Studies in children have demonstrated skin absorption of TDBPP from TDBPP-treated clothing, where up to 9 µg/kg/day was absorbed from this source. TDCPP has been detected in human adipose tissue, up to 0.25 mg/kg and seminal fluid, up to 50 µg/L.

The major metabolites isolated from urine, bile and faeces were: 1,3-dichloro-2-propyl phosphate, bis (1,3-dichloro-2-propyl) phosphate (BDCPP), 1,3-dichloro-2-propanol and a dimethyl derivative of 1,3-dichloro-2-propyl phosphate. Biliary excretion and enterohepatic recirculation was identified as a major metabolic pathway for TDCPP.

Metabolism of TDCPP by an NADPH dependent microsomal mixed function oxygenase system and glutathione S-transferase to BDCPP, 1,3-dichloro-2-propanol, 3-chloro-1,2-propanediol and a postulated glutathione conjugate, has been demonstrated *in vitro*. Cytochrome P-450 dependent biotransformation has been demonstrated for TDBPP *in vitro* with the formation of the reactive metabolite, 2-bromoacrolein from oxidation of the parent compound at the propyl carbon-3 position. Glutathione conjugates of TDBPP have been detected *in vitro* and *in vivo*.

Binding of TDCPP to DNA, RNA and protein from liver, kidney and muscle was demonstrated in CD-1 mice following i.v administration. *In vitro* studies with TDBPP implicate the involvement of reactive ketones and aldehydes, including 2-bromoacrolein and a 2-bromoacrolein GSH adduct, in protein and DNA binding in kidneys and liver. The rate of *in vitro* microsomal formation of reactive TDBPP metabolites was greater in rodent than in human liver.

Oral and dermal LD₅₀ values for TDCPP are >2000 mg/kg in rats and mice with an LC₅₀ >5 mg/L (IPCS, 1998). The duration of exposure in these studies was not reported in the IPCS report. Clinical signs of acute toxicity include ataxia, hyperactivity, respiratory distress and convulsions.

In a study carried out according to acceptable protocols, TDCPP was a skin and eye irritant in New Zealand White rabbits.

No information on sensitisation was available for TDCPP, although immunological parameters, including delayed hypersensitivity and serum IgG, IgM and IgA concentrations, were normal in mice administered up to 25 mg/kg/d TDCPP by subcutaneous injection for 4 days.

The neurotoxic potential of TDCPP has been investigated in standard tests in hens. No behavioural or histological evidence for delayed neuropathy was reported in Leghorn hens, although one study in chickens (strain not stated), reported leg and wing weakness at and above 1.2 g/kg TDCPP per day, for 5 days.

No histopathological effects were reported in rats dosed for 10 days with 250 mg/kg TDCPP.

In a 90-day feeding study in Slc/ddY mice, at doses ranging from approximately 15 to 2000 mg/kg TDCPP per day, animals at the highest exposure exhibited emaciation and tremors and death within 1 month. Incidence of tremors was not reported. A significant increase in relative liver and kidney weights was reported at 62 mg/kg and 214 mg/kg/d, respectively. Slight liver necrosis was reported in females in the high dose group. NOAELs reported for this study were 15 mg/kg/d and 47 mg/kg/d with LOAELs of 62 and 171 mg/kg/d in females and males, respectively.

The IPCS monograph (1998) reported that non-neoplastic effects seen in a 2-year feeding study (unpublished) in Sprague-Dawley rats at doses of 0, 5, 20 and 80 mg/kg/d TDCPP, included a dose-related increase in kidney tubule hyperplasia in all treated groups and chronic nephropathy in the high dose group in both sexes; seminiferous tubule and seminal vesicle atrophy in all treatment groups with oligospermia and degeneration of seminal products in high dose group; parathyroid hyperplasia in both sexes of high dose groups. A dose-related increase in liver carcinoma and benign and malignant renal cortical tumours was observed in both

sexes. Other increased tumour incidence included benign testicular tumours at and above 20 mg/kg/d; benign brain tumours in males and thyroid and adrenal adenomas in females at the high dose. The report concluded that TDCPP is carcinogenic at all exposure levels tested, with the critical organ being the liver.

An article was published recently (Freudenthal and Henrich, 2000) based on the same study described in the IPCS report. An epigenetic mechanism was proposed for tumour formation, which exacerbated the spontaneously occurring tumour incidence but did not induce the transformation of benign tumours to a significant incidence of malignant neoplasm in any organ. The authors identified a NOAEL of 5 mg/kg/d for chronic toxicity and neoplastic activity.

TDCPP is classified with R40 (Possible risk of irreversible effects) by a company in their MSDS (dated Aug 1999) for Fyrol FR-2.

In a battery of *in vitro* and *in vivo* assays, weight of evidence indicated that TDCPP was mutagenic and clastogenic *in vitro*, but not *in vivo*. No other data were available for a mechanistic assessment of the observed tumours.

No developmental effects were reported in Wistar rats administered TDCPP by gavage up to maternally toxic levels, between days 6-15 gestation. Postnatal examination revealed normal development of offspring. In a 12-week fertility gavage study in male rabbits, no effects were seen on mating behaviour, sperm quality or quantity at doses up to 200 mg/kg/d TDCPP.

A retrospective cohort study examined mortality in 289 workers employed in the manufacture of TDCPP. A slight increase in cases of lung cancer was identified, which was not statistically significant. Historical air monitoring data was not available, but breathing zone samples, taken at the time of the study, all contained < 0.4 µg/m³ (7 ppb) of TDCPP. Health reports of 93 potentially exposed workers were compared to 31 non-exposed workers in the same factory. Chest X-ray results were similar between groups, however, exposed workers exhibited a 2-fold increase in the prevalence of abnormal electrocardiograms, despite a lower prevalence of reported heart disease in this group. There were no significant differences in clinical chemistry parameters investigated. Overall, the study did not reveal any significant increase in morbidity in exposed workers.

8.5 Health hazard classification

In Australia and the European Union, except for TCEP none of the other triphosphates considered in this assessment have been classified.

TCEP is classified with the following risk phrases, adopted by Australia (NOHSC 1999) from the EU Annex 1 classification:

R22 Harmful if swallowed

R36/38 Irritating to eyes and skin

However, the 25th adaptation (Dec 1998) of EU Directive 67/548/EEC revised their earlier classification as follows (EU 1998):

R22 Harmful if swallowed

R40(3) Possible risks of irreversible effects (Carcinogen Category 3)

This revised EU classification should be adopted by Australia in accordance with the NOHSC procedure as soon as possible. It is also noted that, TCEP is currently undergoing further consideration in the EU with respect to its classification, including carcinogenicity, therefore the Australian classification will need to be kept up to date when changes are made.

9. Effects on Organisms in the Environment

9.1 Aquatic toxicity

Very few data for aquatic toxicity have been found. However, for this preliminary assessment, international databases such as the USEPA's ECOTOX have not been interrogated. The following discussion on aquatic toxicity has been sourced from brief report summaries provided by IPCS and the Swedish authority (KEMI, 1994).

9.1.1 Toxicity to aquatic green algae

The IPCS report indicated that the EC₅₀ of TCPP against the green algae *Selenastrum capricornutum* is 47 mg/L, while that for TDCPP against the same species is 12 mg/L. These results indicate that both these chemicals are classified as slightly toxic to this species.

When *Scenedesmus subspicatus* was exposed to 10 mg/L of TDCPP no inhibitory effect on the growth of biomass was observed over 72 hours indicating at No Observed Effect Concentration (NOEC) of less than 10 mg/L.

The EC₅₀ for TCEP against *Tetrahymena pyriformis* was reported at 126 mg/L.

Together these results indicate that the compounds are at worst slightly toxic to algae.

9.1.2 Aquatic invertebrates

The IPCS report cites the (measured) 48 hour LC₅₀ for TCPP against *Daphnia* under static conditions as 131 mg/L. On the basis of behavioural abnormalities the (nominal) Lowest Observed Effect Concentration (LOEC) was found to be 33.5 mg/L. A 21 day chronic (reproduction) study on daphnia provided a 21 day NOEC of 32 mg/L.

The 48 hour acute LC₅₀ for TDCPP against *Daphnia* was reported as 4.6 mg/L with NOEC of 1.8 mg/L.

For TCEP, the LC₅₀ against *Moina macropoda* (a Daphnid) was determined as 1000 mg/L.

As with the fish studies, TCEP and TCPP appear to be practically non toxic to *Daphnia* while TDCPP is classified as moderately toxic.

9.2 Fish

The relevant acute toxicity data and references to the original papers/reports from the IPCS and KEMI reports are summarised in Table 6.

Table 6 - Environmental effects

Species	Compound	Result	Reference
Fathead minnow	T CPP	LC ₅₀ (48 h) = 98 mg/L NOEC = 9.8 mg/L	IPCS, 1998
Bluegill sunfish	T CPP	LC ₅₀ (48 h) = 180 mg/L NOEC = 9.8 mg/L	IPCS, 1998
Rainbow trout	TDCPP	LC ₅₀ (96 h) = 1.1 mg/L NOEC = 0.56 mg/L	IPCS, 1998
Killifish	TDCPP	LC ₅₀ (96 h) = 3.6 mg/L	IPCS, 1998
Goldfish	TDCPP	LC ₅₀ (96 h) = 5.1 mg/L	IPCS, 1998
Killifish	TCEP	LC ₅₀ (96 h) = 210 mg/L	IPCS, 1998
Goldfish	TCEP	LC ₅₀ (96 h) = 90 mg/L	IPCS, 1998
Killifish	TCEP	LC ₅₀ (96 h) = 251 mg/L	IPCS, 1998

All tests appear to have been conducted under static conditions. Although adherence to OECD test guidelines was not explicit, it is assumed that the test were conducted according to protocols at least the equivalent of OECD guidelines.

TDCPP appears to be moderately toxic to all fish species against which it was tested (LC₅₀ < 10 mg/L), while TCPP and TCEP appear to be slightly toxic to practically non toxic to fish.

In the study on killifish exposed to 3.5 mg/L of TDCPP for 24 hours it was noted that the fish developed spinal deformities, while similar effects were found for TCEP after 72 hours at exposure levels of 200 mg/L.

9.3 Toxicity to sewage micro-organisms

For TDCPP the LC₅₀ was reported (IPCS, 1998) as > 10,000 mg/L, while no data was available for TCPP. In the case of TCEP the LC₅₀ against the aerobic bacteria *Pseudomonas putida* was > 5000 mg/L.

This data indicates that none of the three chlorinated phosphate esters is toxic to aerobic bacteria.

9.4 Terrestrial toxicity

Little information on this aspect of environmental toxicology is available although the IPCS report provides a 14 days LC₅₀ for TDCPP against the earthworm *Eisenia foetida* as 130 mg/kg soil with a corresponding NOEC of 100 mg/kg. The corresponding values for TCPP were LC₅₀ = 97 mg/kg and NOEC = 32 mg/kg.

No data was available for the toxicity of TCEP against terrestrial organisms.

In so far as they go, the available data indicate that these esters are at worst slightly toxic to terrestrial species.

10. Discussion and Conclusions

10.1 Importation and use

The trisphosphates included in this report are not manufactured in Australia, but are imported in quantities of around 500 tonnes per year. They are imported almost exclusively as the pure chemicals. However, apart from resin products (1% of trisphosphate imports), it is not known to what extent trisphosphates may be being introduced into Australia in finished products or articles. Given the uses of trisphosphates in Australia, it is considered likely that similar products may be imported containing trisphosphates.

Of the known imports, around 85% is used in the production of the flexible and rigid foams, with the remainder used in the production of elastomers and specialist rubber materials (~6%), fibreglass resins and other moulded objects (~5%) and industrial paints, surface coatings and sealants (~4%). Five importers of chlorinated trisphosphates applied for this PEC assessment, with at least 30 companies identified as users of these products, either in formulation or further processing.

Trisphosphates are used to confer fire retardancy, and as plasticisers. Regulations require flame retardancy for certain articles/use situations as an essential safety feature to protect human health and property.

10.2 Environment

Approximately 410 tonnes total of both esters are used within Australia each year, and all will be released to the environment during the useful lives of products containing the chemicals or subsequent to their eventual disposal. However, due to the disperse nature of the use and disposal patterns of these articles, the release will be diffuse. The compounds are somewhat volatile and significant amounts of each are likely to be released to the atmosphere from the surfaces of articles into which they are incorporated (unfortunately this cannot be quantified), with the remainder released primarily to the aquatic compartment. Prolonged adsorption and residence in soils is considered unlikely.

On release to the atmosphere the compounds will be degraded through reaction with hydroxyl radicals, and the estimated atmospheric half lives are 102 and 35 hours for TCEP and TCPP respectively.

Both compounds are appreciably water soluble, and neither is readily biodegradable under aerobic conditions although both appear to be ultimately degradable. No data on biodegradation under anaerobic conditions is available.

The bioaccumulation potential of both chemicals is low due to the significant water solubilities.

No information is available on the amounts released to the environment. Assuming a worst case scenario, the total quantity imported is taken as being released. Using this conservative assumption, the various degradation mechanisms for the compounds in the atmospheric and aqueous compartments indicate that although significant quantities will be released (410 tonnes consumed each year) they are unlikely to be persistent in the environment.

TCEP and TCPP are at worst slightly toxic to aquatic organisms at all trophic levels, and both compounds are at worst slightly toxic to aquatic green algae, and are non toxic to sewage bacteria.

The limited data available indicate that these esters are at worst slightly toxic to terrestrial species.

Overall, despite the moderately high release levels, none of the compounds is assessed as presenting a hazard to the environment.

10.3 Health hazards

It is known the trisphosphates are absorbed dermally (TDCPP) and via inhalation (TCPP), although they appear to be rapidly eliminated in urine and faeces. There is little evidence from available pharmacokinetic data that these compounds are likely to accumulate in animal tissues. There are however concerns over both acute or short-term (neurotoxic) effects for TCEP and chronic (including carcinogenic for TCEP and TDCPP and reproductive for TCEP) health effects seen in animal studies, with some effects being seen at relatively low doses (5 mg/kg/d). Limited human data were available, such as an epidemiological study for TDCPP (negative findings) and a single case report for TCEP, where severe neurological effects were associated with repeated exposure (presumably vapours) to a coating product containing TCEP fire retardant. In addition, it is known that hazardous degradation products e.g. hydrochloric acid, carbon monoxide, carbon dioxide, vinyl chloride, acrolein and benzene are produced from pyrolysis of trisphosphates.

Current EU and industry classifications are risk phrase R22 (Harmful if swallowed) for TCEP, TCPP and TDCPP and risk phrase R40 (Category 3 Carcinogen) for TCEP and TDCPP. However the EU are reviewing the classification for TCEP. No data was available for tris (2,3-dichloro-1-propyl) phosphate and tris (3-chloro-1-propyl) phosphate.

The International Agency for Research on Cancer has classified TCEP as a category 3 carcinogen under their classification system.

10.4 Occupational health and safety

Levels of potential exposure to the trisphosphate flame retardants from formulation processes in Australia are unknown and may be highly variable depending on the process in which they are used. It would appear that the two compounds known to be used in Australia, TCEP and TCPP, may be used interchangeably, however, TCPP appears to be used in greater quantities in foam production, with TCEP used more frequently in other applications.

In general, exposures in foam production (major use) appear to be well controlled and no adverse health effects from trisphosphate exposure(s) are documented.

However the chronic effects seen in animals may only be detected in well conducted epidemiological studies. However, OHS concerns were identified for some producers/ processes in rigid foam production and other uses where 'semi-closed' or 'open' conditions apply. In this regard, it was observed from site visits (and reported from suppliers) that minimal protective measures were taken for some uses/processes with potential exposure to trisphosphates. In addition, application of certain surface coatings/sealants may be associated with some exposure to trisphosphates, particularly where application takes place under confined conditions. In this regard, a case report (non-occupational) exists where severe neurological effects resulted from exposure to a TCEP containing surface coating product.

Although it is considered that dermal/ocular exposure is the most likely route of exposure for processes utilising the two trisphosphates, TCEP and TCPP, inhalation exposure is also possible (particularly during processes undertaken at elevated temperatures), despite their low volatility.

Not all MSDS/labels provided for this assessment by suppliers of TCEP and TCPP reflected the available EU classification and available information on hazardous degradation products.

Without any monitoring data for these workplaces, it is difficult to make any conclusions regarding the potential risk to workers from exposure to trisphosphates. In addition, there are currently no national or international occupational exposure standards available for these chemicals and it is therefore likely that this data is not readily available. Such data would be a prerequisite to carrying out an OHS risk assessment.

The OECD report on TCPP concluded that the chemical is considered of low potential risk and low priority for further work. However this was on the basis that TCPP was not available from articles. New evidence on the blooming potential of trisphosphates indicates that this is no longer the case. Data on blooming from articles is needed to further characterise occupational risk. It also needs to be taken into account that no carcinogenicity studies were available for this chemical.

Data on blooming from articles used in the occupational environment is considered necessary to further characterise occupational exposure, and undertake a risk assessment.

The US NRC concluded that there are no data on subchronic or chronic toxicity of TCPP or tris (2-chloropropyl) phosphate for the dermal, inhalation or oral routes of exposure. No studies have been conducted on the effects on reproduction. Data on the dermal absorption of these chemicals as well as information on human exposure from treated upholstery are also not available. The subcommittee recommended that the potential for release of these chemicals' vapour into air and into saline from treated fabric be investigated.

10.5 Public health

It is not possible to clearly define the risk to the public from exposure to trisphosphates, as there is little information available on the amounts in articles used around the home or car, and no information was available on the amount of trisphosphate released from plastics over time. One importer stated that to their knowledge TCEP and TCPP are not used in the automobile industry. Exposure to

TCEP used in household timber at high levels (0.06%, or 600 mg/kg wood) was associated with reversible neurological deficits in a child; it is not clear how applicable to Australian conditions this case is. No monitoring of trisphosphate levels in vehicles or homes in Australia is currently available. The hazard information indicated that TCEP produced thyroid carcinomas in rats in a chronic study at 44 mg/kg bw/day and TDCPP produced pre-neoplastic effects at 5 mg/kg bw/day, the lowest doses tested. Given this information, and the lack of information about exposure levels for the general public, more Australian information is required, although the US work underway on trisphosphates in furniture products may address some of these concerns.

Exposure to the public may occur when polyester clothing treated with trisphosphates is worn. TDCPP is released from garments to waste water, and there may be potential for releases to air. This exposure is not able to be quantified for the Australian public, as no information is available on the importation of clothes treated with trisphosphates, including information on the levels of trisphosphates in the garments, or the types of clothes treated. Industry advised that TDCPP was voluntarily taken out of the clothing market in 1978. No information on the water levels of trisphosphates in Australia is available - overseas information indicates that trisphosphates may be found in waste water, with some information indicating that it is present in drinking water.

10.6 Further assessment

Due to the identified human health effects of concern with some trisphosphates and the lack of adequate data on others, the widespread public contact with products containing trisphosphates, and the potential for worker exposure, it is considered that a full (risk) assessment should be undertaken by NICNAS. This assessment should cover the AICS listed trisphosphates, irrespective of current imports, due to the potential for substitution. Measured emissions and exposure data will be required for this assessment. The recommendations at Section 11 address this.

Although use and release of the two chlorinated phosphate esters (TCEP and TCPP) used in Australia is at reasonably high levels, neither of the two compounds is expected to be persistent in the environment and the overall environmental hazard is assessed as low. With the information available for this preliminary report it is concluded that no further assessment is required at this time.

10.7 Data gaps

Data gaps identified in this assessment are:

- the fate of trisphosphates in disposal/recycling operations;
- air monitoring data representative of occupational processes utilising trisphosphates;
- levels of trisphosphates in indoor air (including estimates of “blooming” for furniture and officeware products/materials known to contain trisphosphates). Some research in this area is apparently being carried out in US (National Academy Press, 2000), however data representative for Australia is needed;
- levels of trisphosphates in the interior of automobiles (where components are known to contain trisphosphates). Trisphosphates are used in sun visors, a

portion of the car interior which may become hottest, and also is one relatively likely to be cleaned on a semi-regular basis, it is possible that there may be releases of trisphosphates from these. No information is available on the levels of trisphosphates in older cars which may contain significant levels of trisphosphates;

- levels of trisphosphate vapours arising from trisphosphates released from surface coatings;
- toxicology information for some trisphosphates. The US NAS has identified some of the data gaps for TCPP and TDCPP; and
- hazards from combustion or pyrolysis of trisphosphate products.

11. Recommendations

Recommendation 1 - Risk assessment

It is recommended that a full (risk) assessment of the trisphosphates is required, addressing the public and occupational exposures.

Data gaps in relation to emissions from articles and exposure from use of trisphosphates in workplaces must be filled by industry, to avoid use of modelling methods which may over-estimate exposure, and hence potential risk. A timeframe of 18 months is recommended for industry to provide the necessary data to enable the public and occupational risk assessments to occur. Importers should coordinate this work in conjunction with their customers. NICNAS will work with industry in defining the data requirements for the assessment and will take into account any available overseas data that is representative of the Australian situation.

For the fire retardant uses of the trisphosphates (there are other uses), the assessment will need to balance consideration of any adverse effects of these chemicals against the need for fire retardancy for certain articles and use situations to protect human health and property.

Recommendation 2 - Hazard classification

Only TCEP is classified by NOHSC (adopted from the European Union (EU)). However, the classification for TCEP was revised by the EU in 1998 as follows:

R22 - Harmful if swallowed

R40(3) Carcinogen (Category 3) - Possible risks of irreversible effects

It is recommended that NOHSC include this classification as soon as possible in the Designated List of Hazardous Substances. The EU is currently evaluating TCEP with respect to environmental and human health effects, including hazard classification and the Australian classification will need to be kept up to date. It is recommended that introducers/formulators of trisphosphates note the revised classifications.

Recommendation 3 - Hazard communication

It is recommended that MSDS, labels and training materials be updated with particular attention to the health effects information, the EU classification of TCEP and precautions based on the hierarchy of controls, including personal protective equipment, required for handling these compounds. MSDS for the various trisphosphates should include health hazard information relevant to the trisphosphates concerned. If no data is available for a particular trisphosphate then this should be stated on the MSDS.

It is also recommended that reference to tris (2-chloro-2-propyl) phosphate be amended to tris (2-chloro-1-propyl) phosphate (CAS No. 6145-73-9) or tris (1-chloro-2-propyl) phosphate (CAS No. 13674-84-5) as appropriate. NICNAS will bring this to the attention of the Chemical Abstracts Service which assigns CAS numbers.

Recommendation 4 - Substitution

Where trisphosphates are interchangeable in use, consideration should be given to using those compounds that are (currently) apparently less hazardous particularly with respect to neurotoxic, carcinogenic and reproductive effects.

12. Secondary Notification

Under Section 65 of the *Industrial Chemicals (Notification and Assessment) Act, 1989*, secondary notification may be required where an introducer of the existing chemical(s) becomes aware of any circumstances that may warrant a reassessment of its/their hazards and/or risks. Such circumstances include:

- a) the function or use of trisphosphate(s) has increased or is likely to change significantly;
- b) the amount of trisphosphate(s) introduced into Australia has increased, or is likely to increase;
- c) manufacture of trisphosphate(s) has begun in Australia;
- d) additional information has become available to introducers as to the adverse health, safety or environmental effects of trisphosphate(s), such as the revision of hazard classification(s) undertaken by the EU.

The Director (Chemicals Notification & Assessment) must be notified within 28 days of the supplier (manufacturer/importer) becoming aware of any of the above, or other circumstances prescribed under section 65 of the Act.

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