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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 (EA) and the Therapeutic Goods Administration (TGA), 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 (PECs).

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 PECs 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 PEC, 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, NOHSC, 92-94 Parramatta Road, Camperdown, Sydney, NSW 2050 (between 10 am and 12 noon and 2 pm and 4 pm each weekday). Summary Reports are published in the *Commonwealth Chemical Gazette*, which are also available to the public at the above address.

Copies of this and other PEC reports 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;
- subscription details for the NICNAS Handbook for Notifiers; and
- subscription details for the Commonwealth Chemical Gazette.

Information on NICNAS, together with other information on the management of workplace chemicals can be found on the NOHSC Web site:

http://www.nohsc.gov.au/nicnas

Overview

Acrylonitrile (CAS No. 107-13-1) was declared a Priority Existing Chemical for preliminary assessment on 7 April 1998 because of public concern about the health effects of the chemical. The focus of the assessment was on use and exposure in Australia.

Imports of acrylonitrile amount to approximately 2000 tonnes per year. Seventy per cent is used at a single site for the manufacture of a polymer, which is further compounded to plastic resins. Five companies process the remainder to polymer emulsions. About 13,000 tonnes of acrylonitrile-based plastic resins containing <0.005% residual acrylonitrile are imported per annum. Import figures were not available for acrylonitrile-based plastic articles or fibres and fabrics, which contain from 0.0001-0.005% residual acrylonitrile.

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

In Australia, acrylonitrile is classified as highly flammable; toxic by inhalation, in contact with skin and if swallowed; a skin irritant; and a carcinogen in Group 2 (substances regarded as if they are carcinogenic to humans). Recently, the European Communities have agreed to amend their classification to include irritation of the respiratory system, serious damage to the eyes, and skin sensitisation. Australia will adopt this amendment into the NOHSC List of Designated Hazardous Substances according to the usual process.

Acrylonitrile is readily to fairly degradable in water, soil and in the troposphere. Its toxicity to aquatic vertebrates and invertebrates, algae and aquatic plants is slight to moderate. Bioaccumulation is expected to be slight to negligible.

Industrial use of the chemical is tightly controlled by a number of national standards and codes and corresponding State and Territory legislation enforced through a system of conditional permits, licences and warrants.

Occupational exposure to acrylonitrile is minimised through rigid process isolation together with engineering controls to reduce emissions, waste streams and leaks from the closed system. Workers routinely use eye/skin protection and respiratory protection is deployed where isolation cannot be maintained. Safety measures and emergency plans aiming to reduce the likelihood and impact of fires, explosions and spills are in place at all sites storing bulk acrylonitrile.

Of 187 breathing zone air samples collected in 1991-99 during normal, fully enclosed transfer or processing operations, only two (1.1%) exceeded the national exposure standard of 2 ppm (8 h TWA). Sixty-eight per cent were <0.1 ppm, 95% <0.5 ppm and 97% <1 ppm. During sampling or maintenance work, short-term levels in the worker's breathing zone from 0.1-300 ppm have been recorded. However, in these situations workers wear respiratory protective equipment. In industries processing polymers containing only residual amounts of the chemical, exposure levels are expected to be <0.02-0.1 ppm.

In accordance with SUSDP, acrylonitrile must not be possessed, sold or supplied for domestic purposes. Consumer exposure to acrylonitrile from skin contact with acrylic fibres and from ingestion of foods contaminated with residual acrylonitrile in packaging materials is estimated at a maximum of 2.2 and 33 ng/kg/day respectively. Indirect exposure via the environment is likely to be less than 100 ng/kg/day. As such, total public exposure would be several orders of magnitude lower than the no observed adverse effect level for any toxicological end-point in laboratory animals.

There are no Australian data on acrylonitrile levels in air, water or soil. In a worst-case scenario, predicted environmental concentrations from acrylonitrile processing operations are 0.31 μg/L in effluents from sewage treatment plants and 0.00046 ppm in air at 100 meters from atmospheric emission sources. Overseas assessments and a crude comparison of the predicted environmental concentration in water and the effects on aquatic organisms suggest that acrylonitrile is of low concern for the environment.

Although occupational exposure levels are generally low, acrylonitrile is a possible human carcinogen and it is therefore recommended that industry continue to strive to improve their process and engineering controls and atmospheric monitoring programs. Other recommendations concern the revision of communication materials to comply with the impending amendment of the hazard classification of acrylonitrile, the inclusion of laboratory staff in training and monitoring programs, and the need to update the industry Code of Practice for the Safe Use of Acrylonitrile.

On the basis of the known hazards, assessed exposure information and current controls, NICNAS does not recommend a full (risk) assessment of acrylonitrile at this time.

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Abbreviations and Acronyms

ABS	acrylonitrile-butadiene-styrene
ACGIH	American Conference of Governmental Industrial Hygienists
ACN	acrylonitrile
ADG Code	Australian Code for the Transport of Dangerous Goods by Road and Rail
AICS	Australian Inventory of Chemical Substances
ANZFA	Australia New Zealand Food Authority
AS	Australian Standard
ASTER	Assessment Tools for the Evaluation of Risk database (US EPA)
bar	unit of pressure equal to 100 kPa or 0.987 atmosphere
BOC/COD	biochemical oxygen demand/chemical oxygen demand
C	centigrade
CAS	Chemical Abstracts Service
cm^3	cubic centimetre
CNEO	cyanoethylene oxide
CNS	central nervous system
DNA	deoxyribonucleic acid
EA	Environment Australia
E_bC_{50}	concentration leading to a 50% reduction in biomass
EC	European Communities
EINECS	European Inventory of Existing Commercial Chemical Substances
EPA	Environment Protection Authority (or, in the US, Agency)
E_rC_{50}	concentration leading to a 50% reduction in reproduction rate
EUSES	European Union System for the Evaluation of Substances
g	gram
GSH	glutathione
h	hour
IARC	International Agency for Research on Cancer
IPCS	International Program on Chemical Safety
ISO	International Standards Organization
IUPAC	International Union of Pure and Applied Chemistry
kg	kilogram
K_{oc}	partition coefficient to organic carbon
kPa	kilopascal
L	litre
LC_{50}	median lethal concentration

LD_{50}	median lethal dose
log	logarithm
m^3	cubic meter
mg	milligram
min	minute
ML	megalitre (1 million litres)
molec	molecule
MSDS	material safety data sheet
ng	nanogram
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NIOSH	National Institute for Occupational Safety and Health (USA)
NOEC	no observed effect concentration
NOHSC	National Occupational Health and Safety Commission
OECD	Organisation for Economic Cooperation and Development
PC	polycarbonate
PEC	predicted environmental concentration
$P_{o/w}$	octanol-water partition coefficient
ppb	parts per billion
PPE	personal protective equipment
ppm	parts per million
PVC	polyvinyl chloride
RTECS	Registry of Toxic Effects of Chemical Substances
s	second
SAN	styrene-acrylonitrile
SIDS	Screening Information Data Set
STEL	short-term exposure limit
STP	sewage treatment plant
SUSDP	Standard for the Uniform Scheduling of Drugs and Poisons
t	tonne
TGA	Therapeutic Goods Administration
TWA	time-weighted average
UN	United Nations
v/v	volume-volume
w/w	weight-weight
y	year
µg	microgram

1. Introduction

1.1 Declaration

The chemical acrylonitrile (CAS No. 107-13-1) was declared a Priority Existing Chemical for preliminary assessment under the *Industrial Chemicals (Notification and Assessment) Act 1989* on 7 April 1998. It was nominated by the public because of concerns about its human health effects.

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 for risk. If the findings indicate that there may be a significant risk of adverse health, safety or environmental effects, then a full (risk) assessment may be recommended.

1.3 Objectives

The objectives of this assessment were to:

- determine the likely uses of acrylonitrile in Australia;
- determine the extent of occupational, public and environmental exposure to acrylonitrile;
- characterise the properties of acrylonitrile;
- characterise the intrinsic capacity of acrylonitrile to cause adverse effects on persons or the environment; and
- determine whether or not the significance for risk of adverse health, safety or environmental effects is such that a full (risk) assessment should be undertaken.

1.4 Sources of information

Relevant scientific data were submitted by applicants and notifiers, obtained from the published literature, or retrieved from other sources. In particular, a great amount of information was obtained from the comprehensive, peer-reviewed Screening Information Data Set (SIDS) Initial Assessment Report prepared by the Health and Safety Authority of Ireland for the Existing Chemicals Programme of the OECD (HSA, 1998).

Data on atmospheric monitoring and releases to the environment and information on product specifications, labelling, use patterns and occupational and environmental control measures were made available by applicants and notifiers and obtained from site visits.

1.5 Peer review

During all stages of preparation, the report has been subject to internal peer review by NICNAS, Environment Australia (EA) and the Therapeutic Goods Administration (TGA). Dr Glenn Stanley of the Australia New Zealand Food Authority (ANZFA) reviewed sections of the report relating to acrylonitrile in foods. The report as a whole was peer reviewed by Dr Iona Pratt from the Hazardous Substances Assessment Unit under the Health and Safety Authority of Ireland.

2. Background

2.1 International perspective

Acrylonitrile was first prepared in 1893 but had no significant technical or commercial applications until the late 1930s when a synthetic rubber based on a co-polymer of butadiene and acrylonitrile was introduced in Germany (Langvardt, 1984). In USA, projects relating to nitrile rubber received special support during World War II because of their strategic importance and acrylonitrile became established as a monomer of commercial importance. Demand for acrylonitrile began to soar following the introduction of acrylic fibres in 1950. Today, acrylonitrile is an industrial intermediate used predominantly in the production of polymeric materials, with acrylic fibres accounting for 60% and plastics for 25% of world consumption (SRI, 1995). Other uses include the production of adiponitrile and acrylamide monomers and the co-polymerisation with other monomers to produce polymer emulsions, elastomers and nitrile rubber.

From the early 1940s to the mid-1960s, acrylonitrile was mainly manufactured by the dehydration of ethylene cyanohydrin produced from ethylene oxide and aqueous hydrocyanic acid. Nowadays, all acrylonitrile is produced by direct catalytic conversion of propene, oxygen (as air) and ammonia (SRI, 1995). Processes based on propane or ethylene have been developed and may become commercially viable in the future where propane or ethylene feedstock is readily available.

In 1995, global acrylonitrile capacity amounted to 4.5 million metric tonnes (t) (SRI, 1995).

2.2 Australian perspective

In Australia, importation of acrylonitrile began in the early 1960s (Huntsman, 1999). Initially, acrylonitrile was used exclusively for the production of polymer emulsion-based latex paints and coatings. Monsanto Australia Ltd commenced production of styrene-acrylonitrile (SAN) polymers in the late 1960s at its West Footscray, Victoria, site. SAN polymers continue to be manufactured today by the company, which became known as Chemplex Australia Ltd in 1988 and as Huntsman Chemical Company Pty Ltd in 1993. Acrylonitrile-butadiene-styrene (ABS) polymers were manufactured at the West Footscray site from the 1970s until 1994. Marbon Chemical Ltd (later known as Marplex Australia Ltd) also manufactured ABS at Dandenong, Victoria, from the late 1960s until mid-1997. Annual imports of bulk acrylonitrile peaked at 4500 t in the mid-1990s, but have subsequently declined to about 2000 t (Huntsman, 1999).

Acrylonitrile monomer, fibres, elastomers and nitrile rubber have never been produced in Australia. A plan has been put forward to construct a petrochemical plant in Western Australia to extract ethylene from liquefied natural gas (ACTED, 1997). The plant would also produce ammonia and it has been proposed that this could be reacted with ethylene to produce acrylonitrile.

Acrylonitrile was originally imported in drums but as demand increased, bulk importation in shipping tankers began in the late 1970s. Shipments were received at the chemical storage facility on Coode Island on Melbourne's waterfront, in close proximity to the plant at West Footscray. In 1991, an explosion occurred at Coode Island when a tank of acrylonitrile erupted, igniting other tanks containing benzene, butanol and methyl methacrylate monomer. It took more than 24 h to bring the fires under control. Monitoring conducted by the Victorian Environment Protection Authority (EPA) detected acrylonitrile and other hazardous chemicals in the air in the vicinity of the exploded tank and in the river adjacent to and immediately downstream of the facility, both during and after the fires (Coode Island Review Panel, 1991). There were no fatalities or serious injuries, although many firefighters complained of smoke or chemical exposure. Twenty-seven storage tanks and their contents were lost at an estimated cost of $50 million.

An inquiry was held to recommend an immediate action plan to minimise the risk associated with the Coode Island facility and review the longer term future of hazardous chemical bulk liquid storage in Victoria (Coode Island Review Panel, 1991, 1992). Many of the Panel's recommendations had an impact on the ways in which bulk acrylonitrile is stored and handled in Australia.

2.3 Assessments by other national or international bodies

Acrylonitrile has been assessed by several other national or international bodies involved in the review or evaluation of data pertaining to health and environmental hazards posed by chemicals. Of these, the most noteworthy are:

- the Advisory Committee to the German Chemical Society on Existing Chemicals of Environmental Relevance (Gesellschaft Deutscher Chemiker, 1995);
- the Agency for Toxic Substances and Disease Registry under the US Department of Health & Human Services (ATSDR, 1990);
- the Commission of the European Communities (EC, 1989, 1999);
- Environment Canada and Health Canada (Government of Canada, 1999);
- the International Agency for Research on Cancer (IARC, 1979, 1987, 1999);
- the International Programme on Chemical Safety (IPCS, 1983);
- the OECD SIDS Programme (HSA, 1998); and
- the UK Department of the Environment (DoE, 1993).

3. Applicants

Following the declaration of acrylonitrile as a Priority Existing Chemical, six importers and two formulators applied for assessment of the chemical. The applicants supplied information on the properties, import quantities and uses of the chemical. 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 corrections/variation phase of the assessment. Data for the assessment were also provided by five notifiers, including the company managing the bulk terminal on Coode Island and four businesses which purchase acrylonitrile in Australia and formulate it into various products or use it for analytical purposes.

The applicants were, as follows:

BASF Australia Ltd
500 Princes Hwy
Noble Park VIC 3174

Bio-Scientific Pty Ltd
28 Monro Ave
Kirrawee NSW 2232

Crown Scientific Pty Ltd
144 Moorebank Ave
Moorebank NSW 2170

Cytec Australia Holdings Pty Ltd
Suite 1, 7-11 Railway St
Baulkham Hills NSW 2153

Dow Chemical (Australia) Pty Ltd
541-583 Kororoit Creek Rd
Altona VIC 3018

Huntsman Chemical Company Australia Pty Ltd
Somerville Rd
West Footscray VIC 3012

Labax International Pty Ltd
23/199 Pacific Hwy
North Sydney NSW 2006

Sigma-Aldrich Pty Ltd
2114 Anella Ave
Castle Hill NSW 2154

4. Chemical Identity and Composition

4.1 Chemical name (IUPAC)

2-Propenenitrile

4.2 Registry numbers

Acrylonitrile is listed on the Australian Inventory of Chemical Substances (AICS) as *2-propenenitrile*.

CAS number	107-13-1
EINECS number	203-466-5
RTECS number	AT5250000
UN number	1093

4.3 Other names

Acrylonitrile monomer

Cyanoethene

Cyanoethylene

Propenenitrile

Vinyl cyanide

Vinylcyanide

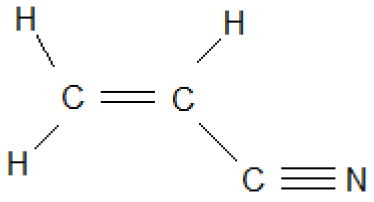
4.4 Trade names

Acrylonitrile inhibited

4.5 Molecular formula

C_3H_3N

4.6 Structural formula



4.7 Molecular weight

53.06

4.8 Composition of commercial grade product

The composition of acrylonitrile imported into Australia is >99.5% w/w acrylonitrile, 0.25-0.45% w/w water, and 35-50 ppm w/w hydroquinone methyl ether inhibitor to prevent polymerisation during storage and transport.

The following impurities have been reported to be present in commercial grade acrylonitrile: acetone and acetonitrile (300-500 ppm), aldehydes as acetaldehyde and propionitrile (30-50 ppm), acrolein, methanol, isopropanol and hydrogen cyanide (5 ppm), and trace amounts of iron and copper (HSA, 1998).

The purity of acrylonitrile is determined by gas chromatographic methods using flame ionisation detection or a nitrogen-specific detector. Characterisation of acrylonitrile is carried out spectroscopically using ultraviolet, infrared and mass spectrometry techniques (HSA, 1998).

5. Physical and Chemical Properties

5.1 Physical properties

Acrylonitrile is a clear, colourless liquid with a characteristic, weakly pungent, onion or garlic like odour (Gesellschaft Deutscher Chemiker, 1995). The odour threshold is reported to vary from 1.6-22 ppm (AIHA, 1989). Physical properties of acrylonitrile are given in Table 1.

Table 1: Physical properties of acrylonitrile

Property	Value	Reference
Melting point	– 88.55ºC	Gesellschaft Deutscher Chemiker (1995)
Boiling point	77.3ºC	Gesellschaft Deutscher Chemiker (1995)
Density		
• at 20ºC	0.8060 kg/L	Gesellschaft Deutscher Chemiker (1995)
• at 25ºC	0.8004 kg/L	
Vapour density	1.83 (relative to air = 1)	Langvardt (1984)
Vapour pressure		
• at 8.7ºC	6.67 kPa	Gesellschaft Deutscher Chemiker (1995)
• at 20.0ºC	12.4 kPa	
• at 23.6ºC	13.3 kPa	
• at 45.5ºC	33.3 kPa	
• at 50.0ºC	39.5 kPa	
Water solubility		
• at 0ºC	71.5 g/L	Gesellschaft Deutscher Chemiker (1995)
• at 20ºC	73.0 g/L	
• at 30ºC	75.1 g/L	
• at 40ºC	79.0 g/L	
• at 50ºC	84.1 g/L	
Henry's Law constant (20ºC, calculated)	9.0 Pa $\cdot$m^3/mole	Gesellschaft Deutscher Chemiker (1995)
Partition coefficient (log $P_{o/w}$)	0.00-0.30	Gesellschaft Deutscher Chemiker (1995)
	0.25 (recommended)	HSA (1998)
	– 0.92	Verscheuren (1996)
Sorption coefficient (K_{oc})	9 (calculated)	Kenega (1980)
	11.5 (measured)	Koch & Nagel (1988)
Flash point	Open cup: – 5 to 0ºC	Gesellschaft Deutscher Chemiker (1995)
Autoignition temperature	480-481ºC	Gesellschaft Deutscher Chemiker (1995)
Explosive limits		
• lower limit	2.8% v/v (62 g/m^3)	Gesellschaft Deutscher Chemiker (1995)
• upper limit	28% v/v (620 g/m^3)	

Conversion factors (at 25ºC):

1 mg/m^3 = 0.46 ppm *and* 1 ppm = 2.2 mg/m^3.

5.2 Chemical properties

Acrylonitrile is a very reactive compound due to the activation of the double bond by conjugation with the polar nitrile group.

It undergoes spontaneous, exothermic polymerisation and therefore must be inhibited during storage and transport. It is highly reactive with oxidative substances, alkalis and acids. Homo- and co-polymerisation of acrylonitrile takes place rapidly in the presence of anionic initiators or free radical producers such as peroxides, or on exposure to visible light.

Other reactions of the double bond include hydrogenation, cyanoethylation, hydrodimerisation and hydroformylation.

The most important reactions of the nitrile group are hydrolysis and alcoholysis. The products of hydrolysis are acrylamide in the first step and acrylic acid in the final step. Acrylic acid esters are formed during the acid-catalysed alcoholysis of acrylonitrile with primary alcohols.

Acrylonitrile is miscible with numerous organic solvents including acetone, benzene, diethyl ether, ethyl acetate, toluene and methanol. Its water solubility ranges from 71.5 g/L at 0°C to 111 g/L at 80°C. Acrylonitrile forms azeotropes with water and a number of organic solvents (for examples, see Langvardt (1984)).

Acrylonitrile is explosive and highly flammable. Combustion products include carbon dioxide, water vapour, nitrogen oxides and carbon monoxide. If incinerated under oxygen depletion, hydrogen cyanide can form and polymers may liberate monomeric acrylonitrile.

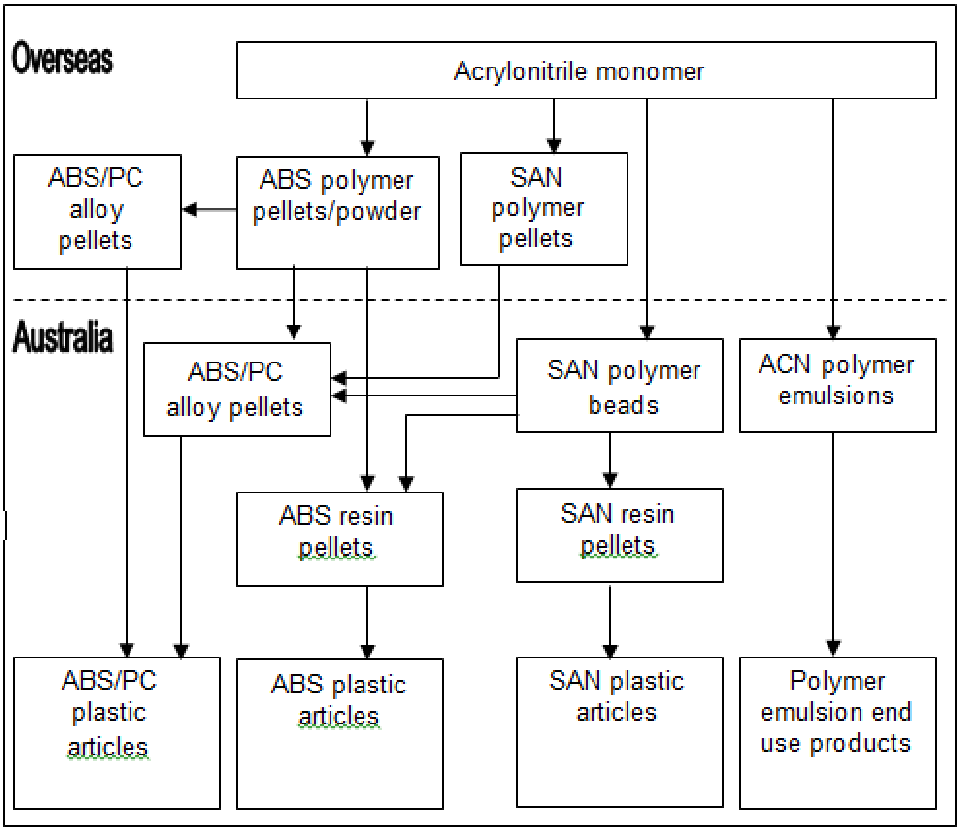
6. Manufacture, Importation and Use

6.1 Importation

Acrylonitrile is not manufactured in Australia, but imported as a raw material and as an impurity in ABS polymer pellets and powder, ABS/polycarbonate (PC) alloy pellets, and SAN polymer pellets. The flow of these materials into and within Australia is illustrated in Figure 1. The importation of acrylic fibres and fabrics is not considered in this assessment, except for their contribution to public exposure to acrylonitrile (see section 7.3.1).

Acrylonitrile is predominantly imported by one company, Huntsman Chemical. The predicted import volume for 1999 is approximately 2000 t. Acrylonitrile is imported in bulk shipping tankers and stored in a large storage tank at the bulk terminal. As required, it is transported directly to the site of use by dedicated road tanker. Huntsman expects to use approximately 1400 t acrylonitrile from the 2000 t imported for on-site manufacture of SAN polymer beads. The remaining 600 t acrylonitrile is onsold to 5 customers for the manufacture of polymer emulsions.

Figure 1: Flow of acrylonitrile monomer and polymers into and within Australia



ABS = acrylonitrile-butadiene-styrene
ACN = acrylonitrile
PC = polycarbonate
SAN = styrene-acrylonitrile

Other companies import reagent grade acrylonitrile in minor quantities (<10 kg per annum) for analytical or research use.

Residual acrylonitrile is present in SAN polymer pellets and beads at a concentration of approximately 2-50 ppm depending on grade and in ABS polymer pellets/powder and ABS/PC alloy pellets at 10-50 ppm (Huntsman, 1999). ABS polymer pellets and powder are not produced in Australia. In 1998, the total imports of SAN polymer pellets were 2100 t, whereas total imports of ABS pellets/powder and ABS/PC alloy pellets were 11,000 t (Huntsman, 1999). SAN polymer beads are imported in much smaller quantities, as local manufacture is able to meet most of the demand. The polymers are imported in 25 kg bags and 750 kg sacks.

6.2 Acrylonitrile processing

6.2.1 SAN polymer beads

In Australia, only Huntsman Chemical manufacture SAN polymer beads, using batch processing within a closed system. Liquid acrylonitrile and styrene monomers are charged with water and an appropriate catalyst to the reactor. Following charging the reactor is sealed and the mixture is heated at temperatures between 90 and 170^{0}C and at pressures of up to 6 bar to initiate the reaction.

When the reaction is finished, steam is introduced into the bottom of the reactor to strip out any non-converted monomers. The vapours are condensed and collected in a distillate receiver and recycled into the next batch to go into the reactor. The most dilute part of the distillate is discarded via a pipe into a covered effluent pit adjacent to the SAN plant before being pumped to the site biological effluent treatment plant.

The stripped polymer is transferred into a slurry tank and then pumped to a centrifuge system where the water is drained by centrifugal force to the effluent system. The wet SAN polymer particles then enter a hot rotary dryer and the resultant dry solid beads are airveyed to storage hoppers. The SAN polymer beads are transferred from the storage hopper for on-site use in the compounding and extrusion of SAN, ABS and ABS/PC alloy resin pellets or sold to local customers for compounding.

The plant produces approximately 4500 t of SAN polymer beads which contain approximately 30% w/w acrylonitrile in the polymer chains and 2-50 ppm residual acrylonitrile monomer depending on grade (Huntsman, 1999).

6.2.2 SAN, ABS and ABS/PC alloy resin pellets

Several companies produce SAN, ABS and ABS/PC alloy resin pellets in a wide range of grades and colours to fit a variety of application requirements. Depending on the desired colouration a number of pigments may be added to the beads, such as titanium dioxide, carbon black, iron oxides, copper phthalocyanine, cadmium sulphide/selenide and organic pigments. Other additives include various fatty acid esters and amides as lubricants, phenolic and phosphite antioxidants, and brominated or antimony oxide flame retardants. Additives may make up as much as 10% w/w of resin pellets that do not contain flame retardants and as much as 25% w/w of flame retardant-modified resin pellets.

SAN, ABS and ABS/PC alloy resin pellets are compounded from the respective polymers by blending and extrusion. The compounding and extrusion of SAN and ABS resin pellets at Huntsman Chemical is typical of this process. The SAN polymer beads are fed into a blender from a weigh hopper or added manually via a chute. The ABS polymer pellets/powder and PC powder are charged manually. To meet product specifications, a great deal of attention is paid to the weighing and addition of pigments and additives prior to manual charging by gravity into the blender. Following blending, the compound is fed into the heated barrel of an extruder and extruded continuously through uniform die heads. SAN and ABS polymers do not decompose at or near extrusion processing temperatures (≤230°C) under normal processing conditions (Radian Corporation, 1986). Volatile vapours from additives and residual acrylonitrile and styrene are removed from the die heads and extruder barrels by a vacuum system. The two vapour streams are combined and discharged from a vent. The hot resin strands are cooled through a water bath and pulled up through cutters. The resulting pellets are sifted to eliminate those of non-uniform size for disposal and sent to a hopper for bulk packaging into containers or bags. Dust is removed from the bead storage, weighing and blending and packaging areas by extraction and collected on a filter.

The further processing of resin pellets to plastic articles is described below. Some ABS resin pellets are exported to New Zealand for moulding.

6.2.3 Polymer emulsions

Approximately 600 t of acrylonitrile is used by 5 companies in the manufacture of polymer emulsions, also known as dispersions, synthetic latex or aqueous polymers.

Polymer emulsions are submicroscopic, spherical polymer particles of high molecular weight finely dispersed in water. They are made by dissolving an emulsifier in water until micelles are formed. As acrylonitrile and other hydrophobic monomers are mixed in, they migrate to the interior of the micelles where polymerisation occurs upon contact with the initiator. Emulsion polymerisation is always performed with water soluble free radical initiators, such as peroxides or persulfates.

In the manufacture of polymer emulsions, acrylonitrile may be co-polymerised with a number of other monomers, including *n*-butyl acrylate, 2-ethylhexyl acrylate, vinyl acetate, methyl methacrylate, styrene, ethyl acrylate, 1,3-butadiene, itaconic acid, acrylic acid, and *N*-methylolacrylamide. The concentration of acrylonitrile to other monomers ranges from 2-20% depending on the final product. In most cases, the specifications require that the concentration of residual acrylonitrile in the final product is <10 ppm, however, some require a level of <0.1 ppm (BASF, 1998). Each batch is tested for conformity with these requirements.

Acrylonitrile is delivered to the manufacturing sites in a dedicated road tanker. A discharge line is hooked up between the road tanker and a discharge pump for transfer of acrylonitrile into a sealed storage tank. The chemical is pumped directly to the reactor when required for production and the polymerisation process takes place under sealed conditions.

In the reactor, acrylonitrile is mixed with other monomers, aqueous emulsifier solution and other chemicals such as initiators, buffers and defoamers. Quantities in the reaction mixture are according to the specifications required in the final product. Some companies premix the emulsifier, water and other additives in a tank before being added to the reactor.

Polymerisation occurs in a stirred-tank enclosed reactor at temperatures between 20° and 130°C and depending on the components with or without pressure (up to 15 bar). Reactor cooling and further evaporative cooling if necessary reduces heat produced during the polymerisation process. The reaction is stopped at conversion levels of 80 to 99%. Steam stripping then removes vapours containing residual monomers from the reactor. The vapours from the steam are vented to an external caustic scrubber or an incinerator. During cooling, specific reagents may be added to scavenge any unreacted monomers in the emulsion. Following completion of the reaction, the polymer emulsion may pass through a coarse filter and is then transferred to a conditioning vessel, where final product adjustments are made to stabilise the mixture by adding preservatives, defoamers, plasticisers, thickeners and pH adjusters. If necessary, the product may be passed through a fine filter before being pumped into bulk product storage tanks or direct to packaging. The product is transported to the customer in road tanker, 1 t tanks (Schutz or collapsible Palecon containers), 200 kg drums or 20 L pails.

6.3 End use

6.3.1 SAN, ABS and ABS/PC alloy resin pellets

SAN, ABS and ABS/PC alloy resin pellets are used in the manufacture of plastic articles by injection moulding or extrusion and thermoforming.

Injection moulding starts with the heating and melting of SAN, ABS or ABS/PC alloy pellets. The melted plastic is then injected under pressure into the closed mould. After filling, the mould pressure is maintained on the injected material to prevent backflow and to compensate for the decrease in volume of the melted plastic during solidification. The moulded parts are cooled, the mould is opened, the rigid moulded parts are ejected and the mould is closed to restart the process.

Thermoforming starts with the heating, melting and sheet extrusion of ABS pellets. The sheet is then fitted along the contours of a mould, with pressure supplied by vacuum or another force, and is removed from the mould after cooling.

Neither SAN nor ABS polymers decompose at or near the maximum temperatures used in the above processes (200-240ºC) (Radian Corporation, 1986). ABS/PC alloys are stable up to the maximum moulding temperatures that are used (260ºC).

Three companies use ABS resin pellets containing <10 ppm acrylonitrile monomer for the manufacture of food packaging, primarily margarine container lids (Huntsman, 1999). ABS resin pellets containing <50 ppm acrylonitrile are used in the manufacture of components for telephones, computers, cars, air conditioners, refrigerators etc., predominantly by injection moulding. Extruded ABS resin is thermoformed to make refrigerator liners and automotive accessories.

ABS/PC alloy resin pellets containing <25 ppm acrylonitrile monomer are processed by injection moulding (Huntsman, 1999). Applications include automotive components such as wheel covers and dashboard inserts.

Only a small amount of SAN is used. SAN resin pellets containing <30 ppm acrylonitrile monomer are used in the manufacture of refrigerator dairy doors, bathroom fittings and some pen barrels by injection moulding (Huntsman, 1999).

6.3.2 Polymer emulsions

Polymer emulsions are used in a wide variety of applications that utilise their binding, coating and adhesive properties. They are generally blended with other ingredients at levels between 10-50%. End products containing polymer emulsions include paints, coatings, textiles, paper and adhesives.

In the paint industry polymer emulsions help to enhance the durability of paint and bind pigments and fillers in a homogeneous system for elastomeric and gloss paints. Interior, water-based gloss house paint contains approximately 50% w/w of polymer emulsion and is used and applied by contract painters and members of the public by brush or roller application. Elastomeric paints and coatings for waterproofing external surfaces contain approximately 50% w/w of polymer emulsion and are applied by brush, roller or spray by contractors and members of the public.

In the building industry polymer emulsions constitute approximately 30% w/w of clear coatings applied by roller or spray by contractors for waterproofing concrete or enhancing the appearance of masonry. Caulks and sealants for use in commercial and domestic buildings by tradespeople and the general public contain approximately 40% w/w of polymer emulsions as a binder.

In the textile and leather industry polymer emulsions bind pigments and auxiliary agents for coating and printing. Coatings for the backs of curtains and blinds contain approximately 60% w/w of the polymer emulsion. The polymer emulsion is whipped to foam, blended with other ingredients and applied to the textile by a coating machine. The coated textile runs through a drying oven to cure the coating and then passes through rollers applying pressure to crush the coating into the fabric. In textile printing, a pigment/polymer emulsion mix is extruded through patterned rollers. The fabric is run over the rollers and through an oven to heat-set the mix into the material.

In the paper industry polymer emulsions are used to bind fibres together during paper manufacture, impart whiteness and gloss to printing paper and as an ingredient in pigment slurries used for coating paper and board.

Polymer emulsions are an ingredient in the adhesive used to apply hessian backing on carpets and when laying PVC flooring. Commercial and domestic floor polishes contain 20-30% w/w polymer emulsions acting as binders for the other ingredients. Polymer emulsions also provide good surface tack, high peel strength and good cohesion to films used in the manufacture of pressure-sensitive adhesives for self-adhesive articles. The coatings and films are applied by machinery.

7. Exposure

7.1 Environmental exposure

7.1.1 Release

Of 2000 t imported bulk acrylonitrile, 1400 t will initially be processed at the Huntsman site at West Footscray in Melbourne to produce SAN polymer beads and, subsequently, SAN and ABS polymer resins. The remainder is processed to polymer emulsions at four sites in Victoria (Wangaratta, Geelong and two sites at Altona) and at one site in Sydney.

Transport and transfer

Acrylonitrile is transported to all manufacturing sites in a dedicated road tanker and pumped to on-site storage tanks in a closed vapour return system. Controls are in place to minimise leaks and spills (see section 10.1.1) and in the event of a major spill from the tanker, the sites have containment systems for any spillages to drains.

Release to the environment from these transporting and pumping procedures should be minimal.

SAN and ABS production

The formulating procedures are provided in section 6.2. Information on releases from the Huntsman West Footscray site has been provided and is summarised in Table 2.

In 1997, releases to air from the SAN plant came from carbon beds (0.02 g/min acrylonitrile for 72 minutes per day, 340 days per year) and the dryer (0.2 g/min acrylonitrile for 1152 minutes per day, 340 days per year). These releases total about 80 kg per annum from the SAN plant. Releases from the SAN/ABS resin pellet extruder are given as <0.4 g/min for 1440 minutes per day over 250 days per year. This indicates an annual release to air of 140 kg per annum.

In Europe, it is estimated that the production of ABS/SAN polymers releases in the order of 0.82 kg/t acrylonitrile to air, averaged over 13 producer companies (HSA, 1998). This rate is over 5 times higher than that reported for Australia.

The effluent produced is processed through a biological treatment plant prior to discharge to sewer. The feed to the activated sludge-type secondary treatment plant includes acrylonitrile at an average concentration of 5 mg/L. The discharge concentration is less than 0.1 mg/L. The effluent is discharged to a municipal treatment plant where the average dilution is 250:1. Huntsman have provided information on their discharge to sewer as 2.2 ML per day over 340 days per year.

According to further information provided by Huntsman, approximately 20 t/y of dried polymer waste containing an average of 50 ppm residual acrylonitrile is disposed of to a licensed chemical landfill. This would equate to around 1 kg of free acrylonitrile per annum.

Table 2: Expected release to the environment from the Huntsman site

	Concentration	Release per day	Release per year
Release to air			
• SAN polymer production	-	0.24 kg[a]	80 kg
• SAN/ABS resin pellet extrusion	-	0.56 kg[b]	140 kg
Release to water[c]			
• Inflow to company treatment plant	5 mg/L	11 kg	3740 kg
• From company treatment plant to sewage treatment plant	0.1 mg/L	0.22 kg	75 kg

[a] 340 days per year
[b] 250 days per year
[c] Assumes company has an outflow of 2.2 ML per day

Huntsman laboratory solvent residues containing <0.1% acrylonitrile are disposed of by incineration on site as boiler fuel. Additionally, semi-solid SAN waste containing <1% acrylonitrile in drums has previously been disposed of in an offsite incineration facility approved by EPA.

Polymer emulsion production

No relevant information was obtained from the Australian producers of polymer emulsions regarding release during their manufacturing operations. However, figures can be drawn from the European experience.

The SIDS Initial Assessment Report (HSA, 1998) indicates release to air during the production of nitrile rubbers of 1.2 kg/t acrylonitrile. Furthermore, based on the solubility and vapour pressure of acrylonitrile, the EC Technical Guidance Document (EC, 1996) estimates that five times more acrylonitrile will be released to air than water, giving a release estimate of 0.24 kg/t acrylonitrile released to water.

These values have been used as a surrogate for estimating the releases to air and water from manufacturers of polymer emulsions in Australia that are provided in Table 3. Daily releases assume production occurs on 300 days per year.

Table 3: Estimated releases from Australian polymer emulsion manufacturers

Location	Quantity of use (t/y)	Max. annual release (kg)		Max. daily release (kg)	
		Air	Water	Air	Water
Altona	1-10	12	2.4	0.04	0.008
Altona	260-400	480	96	1.6	0.32
Geelong	About 100	~120	~24	~0.4	~0.08
Sydney	No data	No data	No data	No data	No data
Wangaratta	About 200	~240	~48	~0.8	~0.16
Total	560-710	850	170	2.8	0.56

Injection moulding, extrusion and thermoforming

The majority of acrylonitrile imported is processed into polymer resins, which are then used to manufacture several end articles outlined in section 6.3.1, using manufacturing processes such as injection moulding or extrusion and thermoforming. Releases during these processes are considered minimal.

Residual acrylonitrile may be present in SAN, ABS and ABS/PC polymer powder and resin up to a concentration of 50 ppm. The total quantity of acrylonitrile-based powder or resin imported or manufactured in Australia for manufacture of plastic articles is in the order of 20,000 t/y (see section 6), which may contain a maximum of 1 t free acrylonitrile (at 50 mg/kg). This may be released from the end articles over their life, albeit in a highly diffuse manner.

End use of polymer emulsion product

Section 6.3.2 outlines several applications within the public domain where acrylonitrile, through the use of polymer emulsions, is likely to be released to the environment. Contractors and members of the public use paints containing the emulsions. As these paints are water based, it is likely that residues from buckets, rollers and brushes will be washed straight to the sewer when used by members of the public. There are no figures on quantities used in these areas, so realistic release estimates are not possible. The EC Technical Guidance Document (EC, 1996) estimates release to wastewater for products in the public domain to be 0.2%. If as a worst case it is assumed that 50% of the acrylonitrile processed to polymer emulsions (300 t per annum) is used in products likely to be in the public domain, then in the order of 600 kg per annum may be released to sewer around the country. This equates to around 1.6 kg per day as diffuse release around the country.

Additionally, in building and external painting, scope exists for paints to be sprayed which is likely to lead to releases through over-spray, although in this instance the products are expected to polymerise and not be mobile in the environment.

7.1.2 Fate

The level 1 MacKay fugacity model, as modelled by Assessment Tools for the Evaluation of Risk (ASTER) (US EPA, 1998), indicates that at equilibrium, 66.42% of released acrylonitrile will partition to air, 33.57% to water, and 0.01% to soil.

Aquatic fate

As there are no readily hydrolysable groups on the acrylonitrile molecule, hydrolysis is not expected to be an environmentally significant process. The hydrolysis of acrylonitrile to form acrylamide requires strong acid and elevated temperatures. Based upon measured acid- and base-catalysed hydrolysis rate constants, Howard et al. (1991) provides a first-order hydrolysis half-life for acrylonitrile at pH 7 of more than 1200 years.

Photooxidation of acrylonitrile in the presence of water has been reported as a further means of abiotic degradation, although it is not certain how relevant this process would be under normal environmental conditions as elevated temperatures were used in the study (HSA, 1998). Verschueren (1996) cites photooxidation by ultraviolet light in water at 50^{o}C as leading to 24.2% degradation to carbon dioxide after 24 h.

Half-lives of acrylonitrile in both surface and ground water have been estimated by Howard et al. (1991) by scientific judgement based on estimated aqueous aerobic biodegradation half-lives. They are summarised as follows:

Surface water	High:	552 h (23 days)
	Low:	30 h (1.25 days)

Ground water	High:	1104 h (46 days)
	Low:	60 h (2.5 days)

According to Mensink et al. (1995), these estimated half-lives indicate that acrylonitrile can be considered readily to fairly degradable in both surface water and ground water.

The vapour pressure of acrylonitrile puts it in the category of highly volatile chemicals (Mensink et al., 1995). However, the water solubility is also high. The Henry's Law constant can provide an indication of the volatility characteristics of compounds (Lyman et al., 1982). The characteristics of acrylonitrile indicate that although the volatilisation from aquatic systems is not rapid, it may be a significant removal process in the environment. Therefore, the high vapour pressure is mediated by the high water solubility. The volatilisation half-life of acrylonitrile in a typical pond, river and lake has been estimated at 6, 1.2 and 4.8 days respectively (Howard, 1989).

The US EPA has previously suggested that although acrylonitrile is quite volatile, large spillages of the substance could lead to groundwater contamination (DoE, 1993).

Atmospheric fate

Several studies of photooxidation of acrylonitrile by ozone and hydroxyl radicals indicate that the reaction with hydroxyl radicals will be the major loss process in the troposphere (Gesellschaft Deutscher Chemiker, 1993; HSA, 1998; DoE, 1993).

Reported rate constants for the reaction of acrylonitrile with hydroxyl radicals range from between 2 x 10^{-12} cm^3/molec/s to 4.9 x 10^{-12} cm^3/molec/s, leading to half-lives of approximately 5 days or less. It has been shown that the reaction of acrylonitrile with hydroxyl radicals is independent of temperature, although it is pressure dependent and the reaction constant rises slightly with increased pressure.

Half-lives determined from reaction with ozone are significantly longer, with rate constants reported between 0.14 x 10^{-18} and 1.38 x 10^{-19} cm^3/molec/sec. These constants suggest half-lives between 58 and 84 days.

The major product of the reaction of acrylonitrile with hydroxyl radicals has been identified as formaldehyde. Small amounts of carbon monoxide and hydrogen cyanide, formyl cyanide and formic acid have also been reported as degradation products.

According to the SIDS Initial Assessment Report (HSA, 1998), the estimated half-life of the reaction with hydroxyl radicals is sufficiently long to allow redistribution of acrylonitrile to the aqueous compartment and to soil, with associated exposure of populations in the vicinity of the emission source, but is unlikely to be long enough to allow redistribution to the stratosphere.

Terrestrial fate

The level 1 MacKay fugacity model, as modelled by ASTER, indicates that at equilibrium only 0.01% of released acrylonitrile will partition to soil.

This is likely to be the case for free acrylonitrile released through manufacturing or reformulation procedures. However, the main use of acrylonitrile in Australia is to make end articles such as latex products, refrigerator and car components, bathroom fittings and food packaging articles. Once incorporated into these products, the majority of acrylonitrile imported into Australia will eventually become associated with soils as landfill or discarded waste in a diffuse manner.

Polymerised acrylonitrile will not leach out from these end articles and, therefore, is not expected to be bioavailable.

Some free acrylonitrile may be present in end articles, which may lead to direct exposure of the terrestrial environment to this chemical through leaching. The partition coefficient for acrylonitrile to organic carbon (K_{oc}) is 9-11.5 (Table 1), which indicates that adsorption to soil will be insignificant (Howard, 1989). The high volatility and low K_{oc} suggest acrylonitrile will volatilise rapidly from soil and other surfaces.

The UK Department of the Environment (DoE, 1993) report that the US EPA stated that acrylonitrile is very strongly adsorbed by clays under hypohydrous conditions. However, in aquatic systems, the water molecules that would normally be associated with the clay’s structure can be expected to prevent any significant amount of the compound from becoming adsorbed onto the clay. Thus, sorption is not considered to be an important fate process for acrylonitrile under most conditions.

Howard et al. (1991) has provided a half-life range of 30-552 h (1.25-23 days) for acrylonitrile in soil, based upon aqueous aerobic biodegradation half-lives. This is in agreement with a study cited in the report from the German Chemical Society (Gesellschaft Deutscher Chemiker, 1993) and in the SIDS Initial Assessment Report (HSA, 1998). In this study, the aerobic degradability of acrylonitrile in surface soils was examined in the concentration range of 10-1000 mg/kg soil. Acrylonitrile in a concentration of 100 mg/kg was degraded in less than 2 days in sandy loam not previously exposed to acrylonitrile. More than 50% of the applied radioactivity was recovered as carbon dioxide during the 6 days after incubation. Degradation at 500 and 1000 mg/kg was relatively slow, which correlates with experimental evidence that these levels inhibit respiration of soil microbes.

Biodegradation and bioaccumulation

Ready biodegradation tests have provided conflicting results. The Ministry of International Trade and Industry (Japan) classified acrylonitrile as being readily biodegradable. However, one collection of data published by the Chemicals Inspection and Testing Institute in Japan showed a degradation rate of 41-75% measured for acrylonitrile at a starting concentration of 30 mg/L and at an activated sludge concentration of 100 mg/L which did not prove acrylonitrile to be readily biodegradable (HSA, 1998).

The SIDS Initial Assessment Report (HSA, 1998) claims that much of the earlier literature relates to experimental simulation tests, acclimation studies and biochemical oxygen demand/chemical oxygen demand (BOD/COD) tests, rather than assessment of biodegradability using current EC (Annex V) or OECD test methods. While two ready biodegradability tests conducted to EC guidelines showed acrylonitrile to be not readily biodegradable, a third test in sea water demonstrated almost 80% degradation over a 28 day period.

The majority of the earlier studies show extensive biodegradation by acclimated microbial populations and it can be expected that acrylonitrile is rapidly biodegradable in situations where an adapted microbial population is likely to exist, such as in an industrial waste water treatment plant.

The low log $P_{o/w}$ measures for acrylonitrile suggest bioaccumulation will not occur. An experimentally derived bioaccumulation factor of 48 for *Lempomis machrochirus* has been cited (Gesellschaft Deutscher Chemiker, 1993; HSA, 1998; DoE, 1993), which falls into the category of slightly concentrating (Mensink et al., 1995). However, according to the UK Department of the Environment (DoE, 1993), the US EPA reports that acrylonitrile may become accumulated as a result of the cyanoethylation of proteins. Acrylonitrile would react with the amino and sulphydryl groups of proteins and although the compound itself would not be accumulated, the reaction would lead to the accumulation of cyanoethylated proteins.

7.1.3 Predicted environmental concentrations (PECs)

Predicted concentrations in water

Section 7.1.1 describes expected releases to water through ABS, SAN and polymer emulsion production. In total, 0.78 kg per day would be expected to be released to sewage treatment plants from these operations. As a worst case, it can be assumed this daily release all occurs to a single sewage treatment plant (STP) with a daily output of 250 ML.

The $PEC_{effluent}$ is equivalent to the $PEC_{local(surface\ water)}$ divided by the dilution rate. Assuming a dilution rate of 10 and no removal from the STP, values for $PEC_{effluent}$ and $PEC_{local(surface\ water)}$ have been calculated as follows:

$PEC_{local(surface\ water)} = 3.1\ \mu g/L$; and

$PEC_{effluent} = 0.31\ \mu g/L$.

Comparison with measured values

No data were available on acrylonitrile levels in municipal or surface waters immediately downstream of any of the five acrylonitrile processing facilities in Victoria. Monitoring for contaminants was conducted by Sydney Water (details supplied through the NSW EPA) on STPs discharging to the Hawkesbury-Nepean River between June 1995 and June 1996, and for STPs discharging to the ocean during the second half of 1995. Ten STPs discharging to the ocean were monitored, with 207 observations conducted. A total of 343 observations were conducted from 17 STPs discharging to the Hawkesbury-Nepean River. With a detection limit of 5 µg/L, no acrylonitrile was detected during any of the sampling events. However, there is only one acrylonitrile processing plant in the Sydney region.

The following discussion on international levels in surface waters is taken from the SIDS Initial Assessment Report (HSA, 1998).

The presence of acrylonitrile in water systems has been reported by a number of investigators, particularly at sites of production or further processing.

Measurements carried out in the vicinity of production or processing facilities in 11 industrial areas in the US in 1978 detected concentrations ranging from 0-4300 µg/L.

High levels of 3500 µg/L and 4300 µg/L were only reported in the vicinity of two plants producing acrylic fibres and nitrile elastomers respectively, with levels in the vicinity of the remaining sites being 0-19.7 µg/L. The limit of detection was reported to be 0.1- 1.3 µg/L. A study in Italy in the late 1970s found levels of up to 25,000 µg/L in effluents from a nitrile elastomer production plant, before waste water treatment.

Information provided by industry on levels of acrylonitrile in water in the vicinity of European production and processing plants included influent into a waste water treatment plant, effluent from the site into a tidal estuary, and effluents from waste water treatment plants. Acrylonitrile could not be detected in the effluents from waste water treatment plants from a number of sites, at limits of detection ranging from 0.1 -100 µg/L.

In addition to studies carried out in the vicinity of production or processing facilities, several investigators have carried out measurements in municipal and surface waters, although little published information is available for European water courses. Levels of 0.07×10^{-3} µg/L have been reported in municipal water in Michigan, US, although the validity of this figure must be questioned, given the limit of detection of approximately 0.1 µg/L. Acrylonitrile was undetected in the Potomac River, West Virginia, US, at a detection limit of 10 µg/L. Acrylonitrile was also undetected using gas chromatography-mass spectroscopy in an examination of water from approximately 1800 wells in Wisconsin, US. The specific detection limit for acrylonitrile was not given, but a generally applicable limit of 0.1-3 µg/L was cited for the range of organic compounds under investigation. A survey carried out for the Japanese Environment Agency in 1987 did not detect acrylonitrile in 75 surface water samples at a limit of detection of 2 µg/L.

Australian monitoring did not use detection limits as sensitive as those overseas, and acrylonitrile is detected in significant concentrations in waste water from various industrial sites around the world. However, it appears to be removed from the waste water system readily and has not been detected in surface water samples from USA or Japan.

Predicted concentrations in the atmosphere

Table 2 indicates that 220 kg acrylonitrile will be released to air during production of SAN/ABS resins at the Huntsman Chemical site. Table 2 shows that up to 850 kg may be released to air during processing of bulk acrylonitrile into polymer emulsions.

A PEC_{local} for air via point source emissions from processing bulk acrylonitrile can be calculated, again using the methodology from the EC Technical Guidance Document (EC, 1996). As a worst case, it will be assumed that all emissions occur from a single point source over 300 days of a year. This means a total of 1,070 kg per annum, or approximately 3.6 kg per day being released to air.

C_{air} = Emission x $Cstd_{air}$

where:

C_{air} = concentration in air at 100 m from a point source (kg/m^3)

Emission = emission rate to air (kg/s)

$Cstd_{air}$ = standard concentration in air at source strength of 1 kg/s = 24×10^{-6} kg/m^3.

A daily release of 3.6 kg per day to the atmosphere equates to 4.2 x 10^{-5} kg/s. This gives a predicted acrylonitrile concentration at 100 m from the source of 1.0 µg/m^3 or 0.00046 ppm.

Comparison with measured values

There are no monitoring data available for atmospheric levels of acrylonitrile in Australia. The following discussion on international levels in air is taken from the SIDS Initial Assessment Report (HSA, 1998).

Measurements carried out in the vicinity of acrylonitrile production or processing facilities in 11 industrial areas of the US in 1978 found levels in air ranging from <0.1-325 µg/m^3 (detection limit 0.3 µg/m^3). The Japanese Environmental Protection Agency also monitored air emissions in the vicinity of Japanese plants and found levels of between 0.042-2.4 µg/m^3 (detection limit 0.04 µg/m^3). Measurements of acrylonitrile in air at different locations and during a range of activities within a number of French production or processing facilities found levels from 5-48.4 mg/m^3 in the vicinity of drains and tanks of ABS, ABS/SAN and nitrile rubber facilities. Loading and unloading of raw materials and products gave rise to levels of 4.1-6.1 mg/m^3 at an acrylonitrile production facility, while levels as high as 540 mg/m^3 were detected as a consequence of minor leaks.

It should be noted that the US and French data relate to emission levels pertaining to at least 15 years ago. Since that time, increasingly stringent controls on emissions have reduced reported atmospheric levels in the vicinity of production or processing facilities significantly. Information supplied by industry for an acrylonitrile and ABS/SAN polymer production site in Europe showed mean levels of 0.6 µg/m^3 acrylonitrile (but with a highest detected level of 240 µg/m^3). Comparable figures for an ABS plastics polymerisation facility were 0.2 µg/m^3 mean level (limit of detection), while no acrylonitrile was detected in fenceline monitoring carried out at an acrylonitrile fibre manufacturing facility in 1994. Monitoring carried out in the vicinity of two acrylonitrile production and processing facilities between May and October 1985 could not detect the chemical in 401 out of a total of 430 samples at a limit of detection of 1 µg/m^3. A mean level of 0.9 µg/m^3 was calculated, assuming a value of 0.5 µg/m^3 for those samples in which acrylonitrile was not detected.

In relation to the wider atmospheric environment, measurements of acrylonitrile in urban German air over the period 1977-84 showed levels ranging from 0.01-10.4 µg/m^3, while clean (rural) air contained <0.002 µg/m^3. No acrylonitrile was detected over a 6-month monitoring period of urbanised and industrialised air on the Gulf Coast of Texas (limit of detection 0.122 µg/m^3). The US EPA reported on a study of acrylonitrile levels in urban air in the US, in which the maximum level detected in Santa Clara County, California in October 1984 was 2.5 µg/m^3. Mean levels of 0.35-0.46 µg/m^3 were found in three cities in New Jersey in July-August 1981 and a mean level of 0.46 µg/m^3 was reported for Texas cities sampled between October 1985 and February 1986. Acrylonitrile has been detected in interstellar space with the source thought to be gas phase chemical reactions in interstellar clouds.

7.2 Occupational exposure

Occupational exposure in Australia may result from the direct handling or use of bulk acrylonitrile or from the manufacture or use of products that contain it. In this section, actual exposure levels in Australian workplace scenarios are assessed and compared to exposure levels reported from similar uses overseas. Air monitoring data were provided by applicants and notifiers and obtained from the international literature.

7.2.1 Methods of atmospheric monitoring

Personal monitoring is used to characterise workplace air levels for exposure control or compliance with relevant exposure standards. Area air monitoring is used to ensure the effectiveness of process isolation and engineering controls and to continuously monitor for leaks to prevent fires, explosions or acutely toxic concentrations of atmospheric contaminants.

Two sampling methods are commonly used in Australia for the measurement of airborne levels of acrylonitrile in the workplace.

For personal monitoring during full shifts or tasks, workers are equipped with a charcoal or other absorbent tube or badge placed in the breathing zone. For area monitoring, the tube or badge is placed at a fixed location in the workplace environment. Tubes are connected with a portable metering pump, whereas badges sample the air by diffusion. At the end of the sampling period, the tube or badge is sealed and transferred to a laboratory, where the chemical is eluted from the absorbent and quantified by gas chromatography. The result is expressed as a time-weighted average (TWA) concentration in ppm or mg/m^3 over the duration of the sampling period. The analytical detection limit varies according to the airflow across the absorbent and the duration of the sampling period. At Huntsman, for example, where a tube method is used, the detection limit is 0.03 ppm·L, or 0.006 ppm for a sample collected over 60 min at a pump speed of 80 mL/min. There is no significant difference between the overall accuracy of tube or badge sampling methods (Brown & Monteith, 1995).

‘Grab sampling’ or instantaneous measurement of acrylonitrile air levels is conducted with colourimetric detector tubes. These are glass tubes sealed at both ends with a graduated concentration scale etched into the outer surface. The tubes contain a carrier material covered with chemical reagents that react with acrylonitrile to produce a colour change whose end-point is read against the scale. Prior to use, the seals are broken, the tube is connected to a handpump and the pump is operated to draw a defined amount of air through the tube. The approximate air level can be read immediately, with a detection limit of approximately 0.1 ppm. Air can be sampled from the breathing zone (personal monitoring) or at fixed locations in the working environment (area monitoring).

In addition, one site conducts continuous area monitoring by pumping air collected at a number of fixed locations through an autoanalyser equipped with a gas chromatograph (see section 7.2.3). This method delivers readings for TWA as well as peak concentrations and has a limit of detection around 0.02 ppm.

7.2.2 Ship to shore transfer

Potential for exposure

Bulk acrylonitrile is delivered by ship 4-5 times a year. There is potential for exposure when making and breaking the line connections for ship to shore transfer. As the shore tank is vented to air through a carbon bed system, there is no potential for exposure to displaced vapours. The transfer requires a manning level of 2-3 operators. The time taken to connect, disconnect and pig[1] the lines is approximately 30 min and the transfer itself lasts from 5-10 h depending on the size of the cargo.

Monitoring data

Air monitoring data were available for two ship to shore transfers and are shown in Table 4. In all cases, the results were below the limit of detection (0.1 ppm).

Table 4: Air monitoring during ship to shore transfer of bulk acrylonitrile

Year	Monitoring	Description	Duration (min)	Result (ppm)
1998	Personal	Pigging operators (2)	17-35	<0.1
1997	Area	Storage tank surroundings (5)	1045-1105	<0.1
	Area	Storage tank rooftop (2)	1075-1110	<0.1
	Area	Wharf (1)	1145	<0.1

Numbers in brackets indicate the number of samples examined

7.2.3 Transport from bulk terminal to users

Potential for exposure

Acrylonitrile is transported by road tanker from the bulk terminal tank to smaller storage tanks or vessels at the users' sites. There is potential for exposure when making and breaking the connections between the storage tanks and the road tanker. As the road tanker and all storage tanks are equipped with a vapour return system, there is no potential for exposure from displaced air vented to the surroundings. Loading and unloading of the road tanker is usually carried out by the driver and 1-4 site operators. The road tanker is loaded/unloaded approximately 200 times per year. Individual drivers and site operators perform from 8-100 loading/unloading operations per year. The time taken to connect and disconnect the lines is approximately 40 min and the transfer itself lasts 1-2 h.

Monitoring data

Air monitoring data were available for unloading of the road tanker at 4 different sites and are shown in Table 5.

Table 5: Personal air monitoring during road tanker unloading

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[1] Pigging is the process of placing an object (called a pig) in a pipeline and propelling it through by liquid or gas pressure from behind to clean out the line.

Year	Site*	Description	Duration (min)	Result (ppm)
1993	E	Operator (1)	450	<0.005
1994	B	Operator (1)	120	<0.02
1995	E	Operator (1)	425	<0.005
1996	A	Drivers (2)	120	0.07 (1) 0.08 (1)
1996	E	Operator (1)	465	<0.05
1997	E	Operator (1)	30	<0.4
1998	D	Operators (5)	60-120	<0.018 (1) <0.24 (1) <0.26 (1) <0.45 (1) <0.46 (1)
1998	E	Operator (1)	110	<0.02

Numbers in brackets indicate the number of samples examined
* Site A manufactures SAN polymer beads and SAN and ABS resin pellets. Sites B-E manufacture polymer emulsions

At one polymer emulsion manufacturing site (F), there is continuous area monitoring of acrylonitrile levels at 8 points around the road tanker unloading bay, the storage tank, discharge pump and the reactor. The monitoring system is connected to an alarm set to activate at an acrylonitrile concentration ≥10 ppm. Monitoring data were not provided, but it was reported that most readings are below the limit of detection (0.02 ppm) and that there has been no alarm since 1996.

In summary, the exposure of workers and drivers involved with the transfer of bulk acrylonitrile from the road tanker to on-site storage tanks or vessels was <0.1 ppm in 2/13 samples and less than the limit of detection (0.005-0.46 ppm) in the remaining 11 samples.

7.2.4 Manufacture of SAN polymer beads

Potential for exposure

Approximately 1400 t/y bulk acrylonitrile is processed into SAN polymer beads in a dedicated plant at the Huntsman Chemical site. The process is fully enclosed, as described in section 6.2.1.

There are 5 SAN plant operators, who work 12 h shifts for 144 days/y. They run the process from a remote control room, with excursions outside for manual operations and instrument checks once or twice per shift. The plant technical leader and day co-ordinator may spend 2-4 h/day for 240 days/y in the SAN plant or control room to advise on production, maintenance and other matters. There are 5 site supervisors who are estimated to spend 1 h/day for 144 days/y in the SAN plant or control room. Five regular maintenance fitters and riggers may be called upon to open equipment containing acrylonitrile vapours or dilute mixtures of acrylonitrile, styrene and water and 4 instrument/electrical technicians may be required to work on instruments or electrically powered equipment containing trace amounts of the chemical. It is estimated that each of the 9 maintenance workers spends 2 h/day for 240 days/y doing tasks where there is the potential for exposure to acrylonitrile.

Monitoring data

Personal air monitoring data collected during normal plant operations and a variety of maintenance tasks are summarised in Table 6. The current reactor and control system were commissioned in 1994.

Table 6: Personal air monitoring during normal operation and maintenance of the SAN plant

Year	Description	Duration (min)	Result (ppm)
Normal operation			
1990	Operators (3)	225-425	<0.002 (2) <0.1 (1)
1991	Operators (9)	130-435	<0.003 (3) <0.1 (1) 0.10 (2) 0.11 (1) 0.12 (1) 0.17 (1)
1992	Operators (8)	320-645	<0.002 (4) <0.1 (2) 0.11 (1) 0.13 (1)
1996	Operators (3)	540	<0.001 (2) <0.05 (1)
1999	Operators (5)	720	<0.05
Maintenance			
1990	Dismantling of reactor (3)	170 225 230	<0.003 (1) 0.44 (1) 0.60 (1)
	Maintenance work (12)	3-485 105 23 21 11	<0.1 (8) 0.13 (1) 0.56 (1) 12.6 (1) 318 (1)

Numbers in brackets indicate the number of samples examined

Thirty-nine area and breathing zone air samples were collected by grab sampling during opening of the reactor and other equipment in a major maintenance overhaul in 1990. Of these, 11 showed air levels ≤0.5 ppm, 4 from 0.6-1 ppm, 7 from 2-10 ppm, 11 from 11-30 ppm, with one measurement at 40 ppm, one at 55 ppm and 4 indicating air levels >120 ppm.

In summary, during normal operation of the SAN plant, personal exposure to acrylonitrile was <0.01 ppm in 16/28 samples, <0.1 ppm in 21/28 samples and <0.2 ppm in 100% of the samples. By contrast, maintenance operations requiring the closed system to be opened resulted in some high to very high short-term air levels.

7.2.5 Manufacture of SAN, ABS and ABS/PC alloy resin pellets

Potential for exposure

Several companies process SAN, ABS or ABS/PC polymers to resin pellets as described in section 6.2.2. The content of residual acrylonitrile in the polymers is low (<50 ppm), the polymer chains do not decompose at or near normal extrusion temperatures (≤230°C), and volatiles are removed from the extruder barrels and die heads and discharged from a vent. As such, it is expected that the majority of workers in resin pellet extrusion plants have little opportunity for exposure.

Exposure data were available from one site only (Huntsman Chemical). At Huntsman, there are currently 9 SAN/ABS extrusion plant operators, who work 12 h shifts for 144 days/y. There is 1 pack-out worker in the plant for 8 h/day for 240 days/y. One technician, 1 day co-ordinator and 1 laboratory colour matcher each spends about 1 h/day in the plant for 240 days/y.

Monitoring data

Air monitoring data collected during normal running of the Huntsman extrusion plant are summarised in Table 7.

Table 7: Acrylonitrile air monitoring in a SAN/ABS resin pellet extrusion plant

Year	Monitoring	Description	Duration (min)	Result (ppm)
1986	Personal	Operators (8)	185-390	<0.01 (7) 0.27 (1)
1987	Personal	Operators (2)	415-425	0.03 (1) 0.40 (1)
1989	Personal	Operators (5)	17-400	<0.1 (4) 0.24 (1)
1996	Personal	Operators (1)	105	0.07
1987	Area	Near extruded resin lumps (1)	365	1.2
1996	Area	At or near die face (2)	5-100	<0.08 (1) 0.07 (1)
1996	Area	Near extruded resin lumps (1)	5	<0.08

Numbers in brackets indicate the number of samples examined

In an investigation by Huntsman Chemical of the effect of overheating on the emission of volatiles from ABS resin pellet extrusion, area air levels at the die face and near freshly extruded plastic lumps were measured by grab sampling. Concentrations of 10-20 ppm acrylonitrile were measured near lumps of a high rubber grade resin processed at 275-300°C compared to 1-4 ppm near lumps of a standard grade processed at the same temperatures. In recent years, however, production volumes for ABS resin pellets have declined, particularly grades that are prone to thermal degradation during abnormal processing situations.

In summary, personal exposure to acrylonitrile during SAN/ABS resin pellet manufacturing was <0.1 ppm in 13/16 samples and ≤0.4 ppm in all 16 samples. An investigation by Huntsman Chemical indicates that there is the potential for emission of acrylonitrile from extruded lumps of thermally degraded polymer if processing temperatures are abnormally high, particularly in the case of high rubber grade resins.

7.2.6 Manufacture of SAN, ABS and ABS/PC alloy plastic articles

Potential for exposure

ABS and ABS/PC alloy resin pellets are widely used in the manufacture of plastic articles by thermoforming or injection moulding, whereas the use of SAN resin pellets is limited. The resin pellets contain <50 ppm residual acrylonitrile and under normal operating conditions their processing into plastic articles would result in minimal exposure of workers to acrylonitrile vapours. However, fume emission is often noticeable during 'purging' when the extruder temperature is raised to remove the previous batch and a small amount of hot, molten plastic runs out of the die head, usually onto the floor.

Monitoring data

Australian data on the potential exposure to acrylonitrile from the manufacture of SAN, ABS or ABS/PC plastic articles were not available.

7.2.7 Manufacture of polymer emulsions

Potential for exposure

Five companies in Australia use acrylonitrile to manufacture polymer emulsions. The process is described in section 6.2.3. Prior to 1991-92, bulk acrylonitrile was delivered to some sites in drums and transferred manually to the reaction vessels, or in ISO containers[2] that were hooked up to the reactors. Currently, however, bulk acrylonitrile is stored in permanent tanks or vessels and pumped to the reactors in fixed pipework at all sites. The polymerisation process remains enclosed until all vapours have been removed and the content of acrylonitrile monomer in the emulsion has been brought down to a concentration <10 ppm. As such, the potential for exposure to acrylonitrile should be low, except during maintenance operations.

The maximum number of potentially exposed workers at any one plant is 16 operators, who work 12 h shifts for 144 days/y, and 13 daytime employees working 8 h/day for 240 days/y. Cleaning and maintenance may involve up to 25 regular workers who are potentially exposed to acrylonitrile for 2-12 h per year.

As the concentration of residual monomer in the end-product is <10 ppm, airborne exposure during the handling of polymer emulsions, or products containing polymer emulsions, is expected to be below the level of detection.

Monitoring data

Air monitoring data were available from all 5 polymer emulsion manufacturers and are summarised in Table 8.

At site D, the area around the reactor is grab sampled at 4-5 locations at 2 h intervals for the duration of every batch of polymer emulsion. In 1996-99, there were 4,936 readings relating to the production of 421 batches of polymer emulsion. Acrylonitrile was detected in 9 readings, 6 of which recorded air levels above 5 ppm. Five of the 6 readings above 5 ppm originated from a single batch.

In summary, since all sites converted to on-site storage tanks, personal exposure to acrylonitrile at polymer emulsion plants was <0.1 ppm in 80/122 samples, <0.2 ppm in 100/122 samples and <1 ppm in 118/122 samples, with levels from 1.2-12

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[2] Large, transportable stainless steel tanks that meet certain design standards laid down by the International Standards Organization (ISO).

ppm accounting for the 4 remaining cases. By contrast, maintenance operations requiring the closed systems to be opened resulted in some high short-term air levels of acrylonitrile.

Australian monitoring data on the potential exposure to acrylonitrile from the end use of polymer emulsions were not available.

Table 8: Personal air monitoring in polymer emulsion plants

Site	Year	Description	Duration (min)	Result (ppm)
B	1994	Operators (5)	480	<0.02
C*	1982-90	Operators (178)	480	≤0.20 (57) 0.21-1.0 (55) 1.1-2.0 (33) 2.1-10.0 (28) 10.1-200 (5)
	1991-98	Operators (35)	480	<0.01 (8) 0.01-0.05 (4) 0.05-0.1 (4) 0.1-0.2 (8) 0.2-0.5 (5) 0.5-1 (4) 1.7 (1) 12.0 (1)
D	1998	Operators (21)	240-480	<0.05 (7) <0.1 (10) <0.15 (2) 1.2 (1) 7.2 (1)
D	1998	Clean-up of spill (4)	NR	<0.05 (2) 0.074 (1) 0.089 (1)
E	1989	Operators (15)	125-480	<0.1 (12) 1.4 (1) 9.0 (1) 21.8 (1)
	1990	Operators (2)	20-75	<0.1
	1993	Operators (2)	435-470	<0.005
	1994	Operator (1)	340	<0.005
	1995	Operator (1)	420	<0.005
	1996	Operators (2)	465	<0.005 (1) 0.02 (1)
	1997	Operators (2)	180-365	<0.18 (1) 0.25 (1)
	1998	Operator (1)	155	<0.009
E	1989	Drumming (7)	200-390	<0.1
	1996	Drumming (1)	465	<0.005
	1997	Tanker loading (1)	40	<0.30
	1998	Drumming (1)	210	<0.009

Table 8: Continued

Site	Year	Description	Duration (min)	Result (ppm)
F†	1991	Operators (28)	580-690	<0.05
		Other plant staff (25)	415-670	<0.05 (20) <0.05-0.06 (5)

	1992	Operators (24)	270-660	<0.05 (11) <0.1-0.2 (8) <0.2-0.3 (5)
		Other plant staff (4)	495-540	<0.05
	1997	Operators (14)	615-690	<0.1
		Other plant staff (2)	440-495	<0.1
F†	1998	Drumming (3)	120-360	<0.2 (1) <0.4 (2)
	1999	Drumming (2)	210	<0.01 (1) <0.06 (1)
F†	1992	Maintenance work (20)	2-22	<0.5 (12) <0.5-1 (3) <1-2 (3) 9 (1) 35 (1)
	1997	Maintenance work (1)	15	<0.15
	1998	Maintenance work (5)	10-17	<0.2 (3) <0.3 (2)
	1999	Maintenance work (4)	6-16	<0.2 (1) <0.5 (3)

Numbers in brackets indicate the number of samples examined
* A permanent bulk storage tank was installed in 1991
† A permanent bulk storage tank was installed in 1992

7.2.8 Quality control sampling and laboratory use

Potential for exposure

Laboratory personnel are potentially exposed to acrylonitrile during the collection of samples from tanks and reactors for quality control purposes, during the handling of such samples, or during the use of reagent grade acrylonitrile for analytical or research purposes. At the sites where bulk acrylonitrile is handled and/or stored, the number of laboratory technicians potentially exposed to the chemical varies from 1-19, with an estimated exposure duration ranging from 1 h per year to 5 h/day for 240 days/y.

In addition, it is estimated that 1-2 health, safety and environment officers per site are potentially exposed to acrylonitrile for an average duration of 8 h/day for 15 days/y.

Monitoring data

Routine personal and area monitoring data were available from 3 sites and are summarised in Table 9.

Table 9: Air monitoring during quality control sampling and laboratory use of acrylonitrile

Year	Monitoring	Description	Duration (min)	Result (ppm)
1991	Personal	Laboratory assistant (4)	450-480	<0.05 (3) <0.06 (1)
1996	Personal	Sample collection at bulk terminal (1)	55	1.2
1998	Personal	Sample collection from	NR	<0.78

		polymer emulsion reactor (1)		
1996	Area	Quality control laboratory (6)	Grab testing	<0.5 (2) 0.5 (1) 1 (1) 2 (1) 40 (1)
1996	Area	Road tanker sampling point (1)	Grab testing	<0.5
1996	Area	Ship's pump room (1)	Grab testing	2.5

NR = not reported
Numbers in brackets indicate the number of samples examined

The high air levels recorded in grab samples from a quality control laboratory were from the zone immediately above a spectrophotometer containing open vials of test samples (1 ppm), the area outside a flammable liquids cupboard immediately after opening the door (2 ppm), and the air inside the cupboard (40 ppm). The source of the vapours was determined to be a number of sample bottles stored in the cupboard for an extended period of time.

The high reading in the shipping tanker's pump room related to the accidental spillage of approximately 1 L of acrylonitrile following the opening of a gate valve on a pressurised 1 inch line into a 750 mL bottle. This sampling method is no longer used.

In summary, the limited data that were available indicate that the average acrylonitrile level in the worker's breathing zone during collection of samples of the bulk chemical for analysis may exceed 1 ppm. Also, air concentrations of up to 40 ppm acrylonitrile can build up inside closed sample storage cupboards over prolonged storage periods due to vapour leakage from the sample bottles. Subsequent opening of such cupboards can lead to instantaneous exposures of up to 2 ppm even in a well-ventilated storage room.

7.2.9 Overseas air monitoring data

Most of the data in the published literature are based on exposure studies conducted in monomer or fibre production plants. As such, exposure levels for production workers are not comparable to Australian workplace scenarios, although measurements of the exposure of maintenance workers, laboratory staff and tank farm workers remain relevant.

At four acrylonitrile monomer production plants and three fibre mills in USA surveyed during 1977-1986, personal exposure levels (8 h TWA) ranged from 0.2-1 ppm for maintenance workers, 0.01-9.4 ppm for laboratory technicians, and 0.4-0.7 ppm during loading or unloading of tank trucks, rail cars or barges (HSA, 1998).

According to the same source (HSA, 1998), occupational exposure levels (8 h TWA) from 0.1-0.2 ppm appear to be representative for most industries that process bulk acrylonitrile into polymers of various types. Furthermore, in industries that handle polymers containing only residual amounts of acrylonitrile, exposure levels are generally an order of magnitude lower. For example, in Germany between 1991-95, 95% of all exposures were below the analytical detection limit of 0.02 ppm in industries such as the following: moulding of plastic articles (with and without exhaust ventilation), surface coating (spraying, brush application, roller application, filling, gluing), and paper and paper board manufacturing (with and without exhaust ventilation). Exposures above the detection limit occurred in individual cases during the production of resin pellets in work areas without exhaust ventilation.

In a laboratory degradation study of two grades of ABS and one grade of SAN polymer resins heated to 197-218°C for 10 min, a maximum of 25 μg acrylonitrile monomer/g of resin was liberated (Hoff et al., 1982). During ABS moulding in a Swedish factory, acrylonitrile was not detected above the analytical limit of 0.01 ppm during area air monitoring 50-100 cm away from the machine (Hoff et al., 1982). In a more recent British field study, air monitoring was conducted during ABS injection moulding at a process temperature of 245°C (Forrest et al., 1995). Air was sampled from the background area, the breathing zone of the operator, and the machine area under standard conditions as well as during purging. Acrylonitrile was not present above the analytical detection limit, which was approximately 0.00005 ppm, except during purging when a concentration of 0.01 ppm was measured in the machine area.

7.3 Public exposure

7.3.1 Consumer exposure

Acrylonitrile is an industrial chemical which is not sold to the public. However, members of the public will make contact with a variety of products made from acrylonitrile such as polymer emulsions (used in paints, printing inks, caulks, sealants and textile coatings) and ABS, ABS/PC and SAN plastic articles (food packaging such as margarine container lids; components for telephones, computers, cars, refrigerators and air conditioners; bathroom fittings, pens and toys). In addition, public contact with acrylonitrile will occur when wearing fabrics made from fibres containing residual acrylonitrile. According to the European industry (HSA, 1998), acrylic fibre is currently hardly used in carpets, especially domestic carpets, and inhalation of acrylonitrile released from carpets is therefore considered to be negligible. As such, the main routes of public contact will be dermal (for example, with fabrics) and oral (consumption of food packaged in materials containing residual acrylonitrile).

Dermal exposure from acrylic fibres and other products

According to the SIDS Initial Assessment Report (HSA, 1998), any residual acrylonitrile (generally <1 ppm) in acrylic fibres is tightly bound and its diffusion rate is low, even at elevated temperatures. If it is assumed that a consumer wears 1 kg of acrylic fibre (that is, 1 mg of residual acrylonitrile) in clothing and that all of the chemical is released over a period of 30 days, then the release per day would be 33 μg. It is estimated that most of this would evaporate to the ambient air, with only 0.4% being absorbed through the skin, corresponding to an average daily load of 0.13 μg or 2.2 ng/kg body weight/day for an adult woman weighing 60 kg.

Dermal exposure to acrylonitrile from other products such as polymer emulsions and plastic articles used by the general public is likely to be negligible because of the slow migration and low content of residual monomer (<50 ppm, usually <10 ppm) and the sporadic nature of the contact.

Oral exposure from food packaging materials

Foods may become contaminated with acrylonitrile as a result of the migration of the monomer from containers made from acrylonitrile polymers such as ABS (ANZFA, 1999). The ultimate level of acrylonitrile in the food depends on the contact time between the container and the food, the solubility of acrylonitrile in the food, and container parameters such as concentration of residual monomer, thickness and area exposed to the food, and is greater near the container walls than in the middle of the food. Acrylonitrile polymers are not used for the packaging of beverages in Australia (Huntsman, 1999).

Reported levels of acrylonitrile in some packaged foods are shown in Table 10.

Table 10: Levels of acrylonitrile in some packaged foods

Food	Acrylonitrile level in ppb (µg/kg)	Reference
Butter	11	Plastics Institute of Australia (1980)
Cold-pack cheese	24-29	Page & Charbonneau (1983)
Creamed coconut	<2.5	Page & Charbonneau (1983)
Honey butter	13-24	Page & Charbonneau (1983)
Luncheon meats	<2.5	Page & Charbonneau (1985)
Margarine	15	UK Government Survey (1982)
	24	Plastics Institute of Australia (1980)
	25	FDA (1984)
Peanut butter	12-35	Page & Charbonneau (1983)
Soft butter spread	<2.5	Page & Charbonneau (1983)

In a worst-case scenario, a consumer may have a daily food intake of 1 kg, of which 5% (50 g) is packaged in acrylonitrile-containing containers. According to Table 10, this food could contain up to 35 ppb acrylonitrile, or about 2 µg acrylonitrile. In relation to an adult man weighing 70 kg, this represents an intake of 30 ng/kg/day, for a 60 kg woman the intake would be 33 ng/kg/day, while for a 30 kg child it would be approximately 70 ng/kg/day. These estimates are conservative as according to ANZFA (1999) there is likely to be limited migration of the monomer from current packaging materials because food nowadays is packaged in vastly different, improved resins.

7.3.2 Exposure via the environment

Public exposure to acrylonitrile could also occur as a result of environmental release of the chemical from industrial sites.

The European Union System for the Evaluation of Substances (EUSES) is an empirical model used to deliver estimates for a standard exposure scenario for organic compounds where measured data are not available. For acrylonitrile, EUSES provides values of 2.8 µg/L for the concentration in drinking water, 0.071 µg/m^3 (0.00003 ppm) in air, 4.0 µg/kg in wet fish, 1.3 x 10^{-4} µg/kg in meat, 1.7 x 10^{-2} µg/kg in plant leaves, and 1.3 x 10^{-3} µg/L in milk (HSA, 1998). Based on these estimates, the following values are obtained for indirect exposure via the environment in the EUSES standard scenario:

- intake through drinking water: 8 x 10^{-5} mg/kg/day;
- intake through food consumption: 6 x 10^{-7} mg/kg/day;
- intake through inhalation: 2 x 10^{-5} mg/kg/day; and
- total intake: 1 x 10^{-4} mg/kg/day.

There are no Australian data on the levels of acrylonitrile in drinking water, unprocessed foods or ambient air. However, the predicted environmental concentrations discussed in section 7.1 indicate that the above estimates are very conservative, possibly with the exception of populations living in the immediate vicinity of a facility that emits acrylonitrile to the environment.

8. Health Effects and Hazard Classification

This section is limited to a brief overview of the health effects and classification of acrylonitrile and is intended as background information for the conclusions and recommendations that follow. It is based on the SIDS Initial Assessment Report prepared by the Health and Safety Authority of Ireland (HSA, 1998) and review articles by Léonard et al. (1999), Whysner et al. (1998), and Woutersen (1998).

8.1 Toxicokinetics and metabolism

Several studies in rats have shown that systemic absorption of acrylonitrile is fast and nearly complete by all routes of administration, with rapid distribution throughout the body and little accumulation in any particular organ.

In rodents, acrylonitrile undergoes extensive biotransformation by two pathways: direct reaction with glutathione (GSH) and oxidation by cytochrome P450 to yield the epoxide cyanoethylene oxide (CNEO), which also reacts with GSH. These routes produce distinct GSH conjugates, which are further metabolised to small, water-soluble, sulfur-containing molecules, including thiocyanate. Limited data on the disposition of acrylonitrile in humans indicate that both direct conjugation with GSH and metabolism via CNEO take place. The rate of spontaneous hydrolysis of CNEO is significantly increased by microsomes from human but not from rodent liver, apparently through catalysis by epoxide hydrolase. This is a detoxifying enzyme in liver, brain, and blood cells that hydrolyses a wide range of epoxides to the corresponding dihydrodiols. The dihydrodiol of CNEO is unstable and transformed to glycolate and thiocyanate.

In rats, the plasma half-life of acrylonitrile is 20-60 min. Elimination is predominantly by excretion of metabolites in urine (about 75%) and faeces (10%) and by exhalation as carbon dioxide (10%). A small fraction is eliminated unchanged through the lungs and in urine. The majority of GSH-derived metabolites are excreted within 24 h, but protein adducts may persist in the body for more than 10 days.

Acrylonitrile and CNEO have been shown to bind to proteins in the stomach, liver, blood, kidney, lung, skin and other organs. At high exposure levels, more than 25% of the chemical may form protein adducts. Both acrylonitrile and CNEO form DNA adducts *in vitro*, although acrylonitrile binding is limited in the absence of metabolic activation. The only DNA adduct identified *in vivo* is a CNEO-guanine reaction product found at very low levels in rat liver, which is not a target organ for acrylonitrile-induced tumours.

In humans, where the epoxide hydrolase pathway is active, proteins and DNA may be less likely to form CNEO adducts than in rodents.

8.2 Effects on experimental animals and *in vitro* bioassays

Acrylonitrile is acutely toxic by all routes of administration. In the rat, the LD_{50} is 72-186 mg/kg from oral and 148-282 mg/kg from skin exposure, and the 4 h LC_{50}

from inhalation is 138-558 ppm (0.47-1.2 mg/L). The acute toxicity is roughly similar in other species, including mice, guinea pigs, rabbits, cats and dogs. Irrespective of route or test species, a lethal dose causes central nervous system (CNS) excitation followed by paralysis and respiratory arrest. The target organs are the gastrointestinal tract (bleeding), adrenals (haemorrhagic necrosis), brain (oedema) and lungs (oedema).

Acrylonitrile is irritating to the skin and eyes. Repeated airborne exposure induces inflammatory and hyperplastic changes in the nasal mucosa, indicating a potential for irritation of the respiratory system. A guinea pig maximisation test for skin sensitisation was strongly positive. There are no data on respiratory sensitisation.

Repeated-dose toxicity studies involving inhalation, ingestion or subcutaneous or intraperitoneal injection of acrylonitrile for 1-12 months in rats, mice, guinea pigs, rabbits, cats, dogs and monkeys showed a narrow range between lethal and no observed adverse effect levels. The most consistently observed effects were decreased body weight gain, irritation of the respiratory tract, kidney damage and reversible ataxia or paralysis. Retching and vomiting, adrenal hyperplasia, increased liver weight, hyperplasia of the gastric mucosa and biochemical effects such as small reductions in haemoglobin, haematocrit and erythrocyte counts and small increases in alkaline phosphatase were observed in some studies.

In a 3-generation rat study, up to 35 mg/kg/day had no effect on fertility. In sub-acute studies in rats and mice, there was evidence of defective spermatogenesis at oral doses approaching acutely toxic levels, whereas several long-term studies found no abnormalities in male reproductive organs. In developmental toxicity studies in rats, hamsters, and rat embryos exposed *in vitro*, acrylonitrile showed some potential to cause foetal toxicity, but developmental effects *in vivo* occurred only at exposure levels associated with marked maternal toxicity.

The genetic toxicity of acrylonitrile has been investigated in numerous *in vitro* and *in vivo* test systems. *In vitro*, it was weakly positive in several bacterial, fungal and mammalian mutagenicity assays and mammalian and fungal cytogenetic tests, particularly in the presence of metabolic activation. Where CNEO was tested in parallel assays, it was mutagenic in the absence of metabolic activation. *In vivo*, acrylonitrile tested negative in several dominant lethal, micronucleus and chromosome aberration assays. Studies in *Drosophila* using various genetic markers gave positive results. *In vitro* and *in vivo* assays for DNA binding and unscheduled DNA synthesis yielded negative results in tests using the most reliable techniques. On balance, it appears that acrylonitrile has little affinity for DNA, whereas the metabolite CNEO is a direct-acting mutagen *in vitro*. It is conceivable that the lack of genotoxicity of acrylonitrile in several *in vivo* tests is due to limited formation and/or rapid degradation of CNEO in intact mammals.

The carcinogenic potential of acrylonitrile has been investigated in three strains of rats exposed to 5-80 ppm in air (2 studies), 1-500 ppm in drinking water (5 studies), or 0.1-10 mg/kg by gavage (2 studies). Exposure-related tumours were found in all studies. The most common forms were astrocytomas of the CNS and carcinomas of the zymbal gland[3], both of which rarely occur spontaneously in experimental animals. Tumours of the mammary gland, tongue, small intestine and forestomach (oral exposure only) were less consistent across studies. A 2-year

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[3] A sebaceous gland associated with the ear canal of certain rodent species.

bioassay in mice, where metabolism via CNEO plays a greater role than in rats, is currently underway within the US National Toxicology Program.

8.3 Human studies

In humans, short-term airborne exposure at >5 ppm (not otherwise specified) has been reported to cause eye, nose, throat and airway irritation, nausea, vomiting, headache, dizziness and limb weakness, whereas human volunteers exposed for 8 h to 2.4-5.0 ppm exhibited no deleterious effects. At higher concentrations, convulsions, unconsciousness and cardio-respiratory arrest have occurred. Skin exposure has resulted in one fatality and cases of irritant and allergic contact dermatitis. Chronic inhalation of concentrations from 0.3-5 ppm has been associated with headache, insomnia, irritability, fatigue and laryngitis, with mild anaemia and jaundice reported at levels >35 ppm.

In a poorly reported study, which did not account for concomitant exposure to other hazardous chemicals, vomiting and anaemia during pregnancy, preterm delivery and birth defects were increased in female workers exposed to levels up to 40 ppm acrylonitrile (Wu et al., 1995). There are no data on reproductive effects in men.

Two separate studies found no increase in chromosome aberrations or sister chromatid exchange in the lymphocytes of acrylonitrile workers.

Epidemiological studies of cancer rates include 21 retrospective mortality and/or incidence cohort studies with an average duration of follow-up of 30 years in 40,887 acrylonitrile workers. Whereas early studies pointed to lung cancer as a potential hazard, recent meta-analyses found no excess of all cancers or lung cancer (Collins & Acquavella, 1998; Rothman, 1994). In the mortality studies, all specific causes of cancer examined had meta-risk ratios near or below 1.0, except bladder cancer for which the excess was unrelated to exposure and limited to factories with aromatic amines. In the incidence studies, the relative risk of prostate cancer was slightly elevated, but most cases occurred when diagnostic techniques were less reliable and there was no trend with exposure level. The meta-analyses included many small studies with dubious exposure assessments. In the three most recent and well-conducted studies, overall findings indicated no elevation of risk for all cancers combined, cancers of the prostate and brain, or leukaemia. In the highest exposure groups (≥8 ppm-years) the relative risk of respiratory cancer was slightly elevated in two of the studies and there were 81 deaths from this cause against 75.5 expected in all three studies combined (Coggon & Cole, 1998).

8.4 Hazard classification

In Australia and the European Communities (EC) acrylonitrile is currently classified with the following risk phrases, in accordance with EC Council Directive 96/54/EC published in September 1996 (NOHSC, 1999):

R11	**Highly flammable**
R23/24/25	**Also toxic by inhalation, in contact with skin and if swallowed**
R38	**Irritating to skin**
R45(2)	**May cause cancer (Category 2)**

In March 1999, the European Commission Working Group on the Classification and Labelling of Dangerous Substances reached final agreement to amend the EC classification to include the following risk phrases:

R37	**Irritating to respiratory system**
R41	**Risk of serious damage to eyes**
R43	**May cause sensitisation by skin contact**

Acrylonitrile remained classified as a carcinogen in Category 2 as “based on current information and with no definitive contrary evidence acrylonitrile must be considered to [be] a genotoxic carcinogen” (EC, 1999).

This revised EC classification will be adopted by Australia according to the usual process when it has been laid down in an amendment to the EC Council Directive.

Acrylonitrile has also been evaluated by the International Agency for Research on Cancer (IARC). In 1979 and 1987, IARC concluded that there was limited evidence of carcinogenicity of acrylonitrile in humans and sufficient evidence of carcinogenicity in animals and therefore assigned the chemical to group 2A: agents that are *probably* carcinogenic to humans (IARC, 1979, 1987). In February 1998, all published literature on acrylonitrile was re-evaluated by an IARC working group comprising 30 experts from 12 countries. The group concluded that although additional studies confirmed that acrylonitrile is a potent multi-site carcinogen in rats, the combined epidemiological evidence did not support a credible association between acrylonitrile exposure and cancer. As such, IARC determined that there was inadequate evidence in humans but sufficient evidence in experimental animals for the carcinogenicity of acrylonitrile and re-classified the chemical in group 2B: agents that are *possibly* carcinogenic to humans (IARC, 1999).

9. Effects on Organisms in the Environment

The following results and discussion in this section of the report have been extracted from the SIDS Initial Assessment Report (HSA, 1998) and a report by the Advisory Committee to the German Chemical Society on Existing Chemical of Environmental Relevance (Gesellschaft Deutscher Chemiker, 1993).

9.1 Toxicity to fish

Data on the acute toxicity of acrylonitrile to fish are summarised in Table 11.

Table 11: Acute toxicity of acrylonitrile to fish

Species	**Test duration**	**Result (mg/L)**	
		LC_{50}	**NOEC**
Bitterling *(Rhodeus sericeus)*	48 h (nd)	25.7	
Bluegill sunfish *(Lepomis macrochirus)*	96 h (n; s)	10.0-11.8	10.0
Carp *(Cyprinus carpio)*	48 h (n)	24.0	
	96 h (n; ss)	19.64	
Carrassius sp.	48 h (nd)	40.0	
Fathead minnow *(Pimephales promelas)*	96 h (n; s)	14.3-18.1	
Gobius minutus	96 h (n; s)	14.0	
Golden orfe *(Leuciscus idus)*	No details	16-28	
Guppy *(Lebistes reticulatus (Fry))*	96 h (n; s)	33.5	
Leucaspius delineatus	48 h (nd)	22.7	
Perch *(Ctenopharyngodon idellus)*	96 h (n; ss)	5.16	
Phoxinus phoxinus	48 h (nd)	17.6	
Pinfish *(Lagadon rhomboides)*	24 h (nd)	24.5	
Rainbow trout *(Onchorhyncus mykiss)*	48 h (nd)	70	
	96 h (nd)	24	
Sheepshead minnow *(Cyprinodon variegatus)*	96 h (m; ss)	8.6	5.6
Zebrafish *(Brachydanio rerio)*	48 h (n; f)	15.0	
	48 h (nd)	25	

f = flow through
LC_{50} = median lethal concentration
m = measured concentration
n = nominal concentration
nd = no details available
NOEC = no observed effect concentration
s = static
ss = semi-static

Chronic toxicity of acrylonitrile to fish appears limited. A 30-day test to fathead minnow resulted in an LC_{50} = 2.6 mg/L, with a 100-day test on rainbow trout resulting in an LC_{50} =2.2 mg/L. A 30-day test in fathead minnow showed a significantly reduced survival rate at mean measured concentrations of ≥0.86 mg/L and significantly reduced growth rate at test concentrations of ≥0.34 mg/L. It is established from this test that a definite no observed effect concentration (NOEC) could not be measured, because effects were observed at all concentrations.

The report from the German Chemical Society (Gesellschaft Deutscher Chemiker, 1993) outlines two further studies. Roach (*Leuciscus rutilus*) was exposed to 40 and 30 mg/L and survived >6 days and >11 days respectively. Bleak (*Alburnus alburnus*) similarly were exposed to 40, 25 and 20 mg/L, resulting in survival of 47 h, 16 days and >20 days respectively. These results are somewhat inconclusive, as there is no indication of fish numbers, replicates, test conditions, or any sublethal effects.

A further study outlined in the SIDS Initial Assessment Report (HSA, 1998) examined the chronic toxicity and carcinogenicity of acrylonitrile in medaka (*Oryzias latipes*). The experimental procedure involved either continuous exposure to concentrations of 2.5 or 5 mg/L nominal acrylonitrile over a 28 day period or a multiple pulsing exposure to 8 mg/L once or twice per week for a 4-week exposure. The study revealed no evidence of carcinogenicity or significant chronic toxicity in the fish.

9.2 Toxicity to aquatic invertebrates

Data on the acute toxicity of acrylonitrile to aquatic invertebrates are summarised in Table 12.

Table 12: Acute toxicity of acrylonitrile to aquatic invertebrates

Species	Test duration	Result (mg/L)
Artemia salina	48 h (n)	EC$_{5}$ = 14.34
*Asellus aquaticus**	96 h (n)	LC$_{100}$ = 0.016
Chironomus sp.	48 h (n)	EC$_{5}$ = 14.21
Crangon crangon	24 h	LC$_{50}$ = 10-33
	96 h (n; f)	LC$_{50}$ = 6.0
Daphnia magna	48 h (n)	EC$_{50}$ = 8.7-10.0
	48 h	LC$_{50}$ = 7.6; NOEC = 0.78
Gammarus sp.	-	Survival time <22 h at 50 mg/L
Gammarus fossarum	96 h (n)	NOEC = 0.012
Limnodrillus hoffmeisteri	96 h (n)	EC$_{5}$ = 16.90
Ophryotrocha diadema	48 h	LC$_{50}$ = 10-33
*Radix peregra**	48 h (n)	LC$_{50}$ <0.04
	72 h (n)	LC$_{100}$ = 0.04
Radix pliculata	96 h (n)	EC$_{50}$ = 17.94

* Both the SIDS Initial Assessment Report (HSA, 1998) and the report from the German Chemical Society (Gesellschaft Deutscher Chemiker, 1993) claim the results for the freshwater isopod *Asellus aquaticus* and the freshwater mollusc *Radix peregra*, which have been taken from studies of which only English summaries were available, cannot be validated and are not suitable for risk assessment purposes. No data are given in the abstracts regarding test conditions.

EC$_{5}$ = concentration affecting 5% of population
EC$_{50}$ = concentration affecting 50% of population
f = flow through
LC$_{50}$ = median lethal concentration
LC$_{100}$ = concentration lethal to 100% of population
n = nominal concentration
NOEC = no observed effect concentration

The SIDS Initial Assessment Report (HSA, 1998) outlines two studies carried out at 14 and 21 days on *Daphnia magna*. The results were identical, with a NOEC for survival of 2 mg/L nominal, and a NOEC for reproduction of 0.5 mg/L. It is stated that the experimental data showed little or no dose response for both survival and reproduction in the concentration range used, making it difficult to establish how these values were derived. The SIDS Initial Assessment Report (HSA, 1998) also reports on a US EPA result where a no adverse effect level of 3.6 mg/L in a life cycle study (21 days) in *Daphnia* was determined. No further information on this study was available.

9.3 Toxicity to algae and aquatic plants

According to the SIDS Initial Assessment Report (HSA, 1998), the effect of acrylonitrile on cultivated seagrass (*Ruppia maritima*) showed that concentrations >100 mg/L completely inhibited photosynthesis and respiration, while lower acrylonitrile concentrations did not have any effect on these metabolic processes. When the number of leaves, roots and sprouts as well as the biomass were measured, lower concentrations of acrylonitrile (10-100 mg/L) were found to cause inhibition of growth rate. However, growth of roots was apparently stimulated at acrylonitrile concentrations below 1 mg/L. No firm conclusions were drawn from this test as further details were not available.

A green algae (*Scenedesmus subspicatus*) test resulted in a 72 h E_bC_{50} = 3.1 mg/L (nominal) and E_rC_{50} >7.1 mg/L (nominal). The calculated NOEC was 0.8 mg/L.

The effects of acrylonitrile on the growth of *Skeletonema costatum*, a unicellular chain forming marine diatom, were observed over a 72 h period. In this study, the 72 h E_bC_{50} = 1.63 mg/L (measured mean) and E_rC_{50} = 14.1 mg/L. The NOEC was 0.41 mg/L for effect on biomass and 3.0 mg/L for effect on growth rate.

9.4 Summary of environmental effects

Following the guidelines from Mensink et al. (1995), acrylonitrile can be described as moderately to slightly toxic to aquatic vertebrates and aquatic invertebrates based on acute exposure results. The available chronic studies for these two trophic levels indicate slight toxicity.

Similarly, for algae and aquatic plants, results for effects on biomass suggest acrylonitrile is moderately toxic, while results for effects on reproduction are indicative of slight toxicity.

10. Current Control Measures

In this section, measures currently employed in the management of human exposure, predominantly occupational, are described. It has been known for many years that acrylonitrile is a hazardous chemical and as such several control measures have been implemented to limit exposure. The key elements include workplace control measures, emergency procedures, hazard communication (including training and education), atmospheric monitoring and regulatory controls. Where appropriate, these measures are described separately for specific Australian workplace scenarios, that is, handling, storage and transport of bulk acrylonitrile, manufacture of acrylonitrile-based polymer beads, resin pellets and polymer suspensions, moulding of SAN, ABS or ABS/PC plastic articles, and handling of acrylonitrile in quality control and research laboratories.

Information on current control measures was obtained from importers and users of acrylonitrile and from site visits.

10.1 Workplace control measures

Workplace control measures include isolation, engineering controls, safe work practices and personal protective equipment (PPE).

Isolation as a control measure aims to separate employees, as far as practicable, from the chemical hazard. This can be achieved by distance (segregation) and/or enclosure. Engineering controls involve the design of plant, equipment and processes so as to minimise the generation of hazardous substances, suppress or contain hazardous substances, or limit the area of contamination in the event of spills or leaks. Safe work practices are administrative practices that require people to work in safer ways. PPE is used where other control measures are not practicable or do not provide adequate protection against hazards.

10.1.1 Bulk handling, storage and transport

Isolation

Bulk acrylonitrile is imported 4-5 times a year. The chemical is unloaded directly from the shipping tanker at the bulk terminal into a dedicated storage tank which is isolated from other tanks containing chemicals reactive with acrylonitrile. The ship to shore transfer is an entirely enclosed process employing sealed vessels and lines and is operated from a remote control point.

Transport of acrylonitrile from the bulk terminal to the users takes place in a dedicated 30 t capacity bulk road tanker. Bulk acrylonitrile is transferred from the storage tank to the tanker through a sealed loading line. The chemical is used at a total of 6 sites, where it is unloaded from the tanker into sealed storage facilities via enclosed lines.

Engineering controls

To minimise cleaning and the need for disposal of hazardous wastes, only dedicated hoses, pipes, pumps, vessels and tanks are used for road transport and for transfer and storage of bulk acrylonitrile at the bulk terminal and users' sites.

During unloading of acrylonitrile from the shipping tanker, non-return valves are used on the lines. Double block valves are used for sampling points on the lines. Piping is made from stainless steel with butt-welded fittings and drain valves at low points with the facility to contain and remove any acrylonitrile that is drained. To allow for liquid expansion, pressure relief valves are necessary with excess acrylonitrile returned to the system. A pigging breach at the bulk tank and the wharf eliminates the need to open the line and remove the pigs and allows for pigging in both directions.

To prevent leakage to the atmosphere, all pumps used in the ship to shore transfer are magnetic drive, hermetically sealed or equivalent.

The bulk terminal storage tank for acrylonitrile is bunded[4] and constructed from carbon steel, with a smooth interior surface, minimal interior framework where acrylonitrile vapours can accumulate, and sloping floors to aid drainage and prevent pooling inside the tank.

Fail-safe switches for emergency pump shutdown operate from the shipping tanker and at the wharf. Level indicators with automatic feed cut-off controls are installed in the tank to prevent overfilling and alarms operate away from the tank at the bulk terminal office and at the wharf. Displaced air is vented to the atmosphere through a carbon-bed fume extraction system.

The tank is equipped with a recirculation pump to ensure uniformity of the concentration of inhibitor, thus preventing polymerisation and the occurrence of potentially explosive conditions. Inhibitor levels are checked monthly and inhibitor is added as required. A thermometer gauge is present at the tank and also on a panel at the bulk site office. White paint is used for the exterior surface of the tank to minimise interior temperature increases. The tank is equipped with an external water deluge system to prevent overheating of the contents in case of a nearby fire. As a fire precaution, the tank is blanketed with nitrogen and any equipment likely to discharge are grounded to earth to prevent the accumulation of static electricity.

Road tanker filling at the bulk storage facility is fully enclosed in pipes using self-scaling couplings. The road tank vehicle is constructed in accordance with the standards published by Standards Australia (1985, 1986, 1990). A capacitance probe in the tanker prevents overfilling and the loading is metered by computer. The tanker is equipped with a vapour return system and discharge points on top of the tank including dry break fittings, preventing any release to the atmosphere. The tanker has specially designed and marked earthing points and is grounded to earth before any transfer of acrylonitrile takes place.

At the users' sites, bulk acrylonitrile is stored in smaller, sealed vessels or tanks constructed from stainless steel or concrete and fitted with high level and high temperature alarms. One larger tank is kept blanketed with nitrogen. To remove acrylonitrile vapours during tank breathing, the vessels and tanks are vented to a caustic scrubber or incinerator or fitted with a vacuum/pressure conservation vent

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[4] Placed in an area surrounded by a low wall to prevent spread of the chemical should any leakage occur.

with an activated carbon absorber tank. Upon arrival, the road tanker is directed to a bunded unloading bay, earthed and hooked up to a dedicated unloading pump. Bulk acrylonitrile is then pumped from the road tanker via top unloading to the storage vessel or tank and displaced acrylonitrile vapour is returned to the tanker in a closed system. To prevent leakage, magnetic drive pumps and dry break tanker-pump connections are used. There is a remote button for emergency pump shutdown.

Safe work practices

Safe work practices adopted at all sites where bulk acrylonitrile is handled and stored include the following:

- All entry points to areas where acrylonitrile is handled or stored are placarded with notices with “Entrance to carcinogenic area” or similar signal words.
- Access to such areas is limited to employees required to work there, with visitors and contractors required to sign in and out.
- Eating, drinking and smoking are prohibited in all areas where acrylonitrile is handled or stored.
- Records are kept of all procedures associated with the handling, storage and transport of bulk acrylonitrile.
- There are regular safety checks of tanks, drains, pumps and piping, hoses, housekeeping, level gauges, signs, lights and firefighting and first-aid equipment.
- The integrity of storage tanks is checked at regular intervals.

In addition, the following work practices apply at the bulk terminal and to the transport of acrylonitrile by road:

- There is a written procedure for ship to shore transfer of bulk acrylonitrile.
- At the wharf, lines are pigged or blown with nitrogen after use to clean out residual liquid and vapour.
- Written procedures exist for the loading and unloading of the road tanker.
- The road tank vehicle is inspected and hydraulically tested at intervals of not more than 5 years.

Personal protective equipment

During unloading of acrylonitrile from the shipping tanker and when loading the road tanker at the bulk terminal, workers wear helmets, safety glasses, nitrile rubber gloves, overalls, and covered shoes. In addition, self-contained breathing apparatus respirators are used while hoses are connected and disconnected.

During unloading of the road tanker, workers generally wear helmets, chemical goggles or safety glasses, rubber gloves, overalls or protective suits, covered shoes or safety boots, and face shields. The degree of respiratory protection used during unloading of the tanker depends on the requirements of the site receiving the chemical and varies from none in normal situations, to full-face organic vapour filter respirators used while the tanker-pump line is connected and disconnected, to the deployment of positive pressure air-supplied respirators throughout the entire unloading process.

10.1.2 Production of SAN polymer beads

SAN polymer beads are manufactured at a single site, using batch polymerisation of acrylonitrile and styrene monomers within a dedicated, closed system, as described in section 6.2.1. The SAN plant is operated from a remote control room, with occasional excursions outside for manual operations and instrument checks.

Engineering controls include the following:

- The bulk monomers are transferred from their storage tanks to the SAN reactor in dedicated pipes.
- During loading of the reactor, displaced vapours are vented through a dual carbon bed air emission system.
- All but the most dilute (≤50 ppm) acrylonitrile waste streams are recycled into the polymerisation process.
- Other liquid waste streams are piped to a covered pit and on to a biological effluent treatment plant.
- The reactor pressure relief vent is connected to a bunded emergency dump tank capable of holding the entire contents of the reactor. Any vapours vented from the dump tank would be entrained by water sprays and collected in the bund for transfer to the biological effluent treatment plant.
- SAN polymer beads are stored in closed hoppers in the SAN/ABS resin pellet plant (see below) or in bags in covered outdoor areas or well-ventilated warehouses.

Safe work practices at the SAN plant include placarding; limitation of access to employees required to work there, with visitors and contractors required to sign in and out; prohibition of eating, drinking and smoking; and written process operating procedures.

In normal situations, no special PPE is employed over and above the minimum required in all operating areas on the site, that is, helmet, safety glasses with side shields, disposable PVC or nitrile rubber gloves, long-sleeved shirts, long trousers and safety boots.

10.1.3 SAN, ABS and ABS/PC alloy resin pellets and plastic articles

Several companies produce SAN, ABS and ABS/PC alloy resin pellets in Australia by compounding and extrusion of polymer beads as described in section 6.2.2.

The blending step is carried out in an enclosed tank and the overall operation of the process is usually from a remote control room. During extrusion a vacuum system removes acrylonitrile and other volatile vapours from the die heads and extruder barrels. The vapour streams are combined and discharged to the atmosphere through a vent. Dust is removed from the bead storage, weighing/blending and pack-out areas by extraction and collected on a filter.

The safe work practices and PPE described above for the manufacture of SAN polymer beads also apply to the manufacture of SAN, ABS and ABS/PC alloy resin pellets.

Numerous companies manufacture plastic articles from SAN, ABS or ABS/PC alloy resin pellets by thermoforming or injection moulding as described in section 6.3.1. Apart from exhaust ventilation, no workplace control measures were identified that specifically aim to reduce exposure to vapours emitted from residual acrylonitrile in resin pellets during processing to plastic articles.

The concentration of residual acrylonitrile monomer in plastic articles made from SAN, ABS or ABS/PC alloy resin pellets is low (<50 ppm and usually <10 ppm, according to industry sources). Hence specific control measures for acrylonitrile exposure during workplace end use of these products are not considered necessary.

10.1.4 Polymer emulsions

Five companies manufacture polymer emulsions in Australia. The transfer of acrylonitrile from the on-site isolated storage vessel or tank to the reactor and the subsequent formation of polymer emulsions take place in closed systems and are usually operated from remote control rooms. The process is described in section 6.2.3.

Engineering controls commonly employed during the manufacture of polymer emulsions include the following:

- Reactor vessels have temperature monitoring devices, high temperature alarms, high level alarms with overfill cut-off controls and external water deluge systems to keep contents cool in the event of a building fire.
- Tanks and vessels are vented to an external caustic scrubber or an incinerator.
- Vapours generated during polymerisation are condensed and returned to the reactor.
- Exhaust ventilation systems remove any vapours that may escape from the reactors and prevent vapour pockets from forming.

Safe work practices observed during the manufacture of polymer suspensions include placarding of areas where acrylonitrile is stored or used; limitation of access to employees required to work there, with visitors and contractors required to sign in and out; prohibition of eating, drinking and smoking; and written process operating procedures.

In normal situations, no special PPE is employed over and above the minimum required in chemical plants in general, that is, helmet, chemical goggles or safety glasses, gloves, overalls or long-sleeved shirts and long trousers, as well as covered shoes or safety boots.

The concentration of residual acrylonitrile monomer in polymer emulsion end products is low (<10 ppm). Hence specific control measures for acrylonitrile exposure during workplace end use of these products are not considered necessary.

10.1.5 Cleaning and maintenance of closed systems

Dedicated acrylonitrile storage tanks and reactors are generally cleaned manually at intervals of one to several years. Non-dedicated reactors used for the production of polymer emulsions are boiled out between batches, in some cases with caustic soda. Tanks and reactors are permit-requiring confined spaces as defined in the Standards Australia/NOHSC *Joint National Standard for Safe Working in a Confined Space* (AS/NOHSC, 1995). Among others, this standard obligates the employer to ensure that no person enters a confined space until it has been demonstrated that atmospheric contaminants are reduced to below the relevant exposure standards or, where this is not practicable, unless he or she is equipped with suitable PPE.

Maintenance work on tanks, vessels, pipework and pumps necessitates temporary access to enclosed spaces and as such isolation is not an applicable control measure. Although engineering controls can minimise the need for maintenance through plant and process design and the deployment of suitable hoses, pipes, pumps and other equipment, protection of maintenance workers against exposure to acrylonitrile mainly relies on safe work practices and PPE.

Safe work practices commonly observed in connection with cleaning and other maintenance of acrylonitrile systems include:

- Access to a system is limited to personnel or contractors in possession of work permits and, where appropriate, confined space entry permits.
- Lines, vessels and tanks are cleaned with nitrogen, steam, hot water or caustic soda before any maintenance work.
- Movable equipment is high-pressure cleaned at a decontamination pad.
- Waste streams from cleaning are contained and recycled or disposed of in accordance with written operating procedures.

At one site, a standard procedure exists for breaking open and decontaminating lines, vessels or equipment known to or suspected of containing acrylonitrile. The procedure prescribes that after a line is opened, work cannot proceed until breathing zone air samples have been taken and analysed, and requires that air levels at the work site boundary and downwind are checked at regular intervals while the work is in progress. When a line is broken open, a full-face self-contained breathing apparatus, a protective suit, rubber gloves and rubber boots must be worn. Subsequently, chemical goggles, a protective suit, rubber gloves and boots must be worn if eye and skin contact with liquid acrylonitrile could occur.

The use of respiratory protection during maintenance work depends on the situation and the measured air level of acrylonitrile.

At all sites, respiratory protection is mandatory whenever the measured breathing zone air level is >1 ppm. Where the air level is between 1 ppm and 30-80 ppm, full-face organic vapour filter respirators must be used, whereas positive pressure air-supplied respirators are required if air levels exceed 30-80 ppm or are unknown.

10.1.6 Laboratory handling of acrylonitrile

Laboratory handling of acrylonitrile occurs during quality control of the bulk chemical and in a limited number of laboratories that use reagent grade acrylonitrile for analytical or research purposes.

Samples of bulk acrylonitrile are taken from shipping tankers during unloading and monthly from the shore storage tank for routine testing for appearance, refractive index and inhibitor level. Some users also test a sample from the road tanker before unloading begins and conduct regular quality tests on samples drawn from their own storage vessels or tanks. Samples are collected in accordance with written procedures that generally require the use of full-face organic vapour filter respirators, neoprene or butyl rubber gloves, protective suits and rubber or PVC boots during sampling. Contaminated protective clothing is flushed copiously with water before laundering. Contaminated gloves are disposed of by incineration.

Common safe work practices aimed at minimising laboratory exposure to acrylonitrile include the following:

- Written operating procedures for the purchasing, handling and storage of the chemical.
- During handling of acrylonitrile, all entry points to the laboratory and the fume cupboard where the chemical is manipulated are placarded with notices with "Caution: cancer causing agent in use" or similar signal words.
- Bottles containing acrylonitrile are stored in a locked flammable liquids/poisons cupboard in a ventilated storage room and transported in a covered container with a layer of absorbent vermiculite inside to contain any spills.
- All open containers with acrylonitrile are handled in flameproof fume cupboards that are checked for performance on a regular basis.
- Spill trays lined with absorbent paper are used to contain bottles/flasks in the fume cupboard.
- Acrylonitrile-containing waste is disposed of by incineration.
- Laboratory receipt, usage and disposal of acrylonitrile are recorded.

PPE used by laboratory personnel during handling of acrylonitrile includes facemasks, safety glasses, impervious gloves and fully buttoned laboratory coats.

10.2 Emergency procedures

All companies that handle or use bulk acrylonitrile have comprehensive written emergency response plans setting out how workers and emergency services should deal with on-site leaks, spills, releases, fires and explosions. These sites routinely handle or use a number of hazardous chemicals in large quantities and have on-site emergency squads that can be activated via alarm buttons posted throughout the site. Workers are trained to respond to emergencies by sounding the alarm, informing a manager and then promptly evacuating the incident area.

Three companies supplied separate procedures for certain emergencies involving acrylonitrile, including exposure procedures, first-aid procedures, spill/leak procedures and procedures for incident reporting to site managers and relevant authorities.

The exposure procedures include the following instructions:

- remove the exposed person from the area;
- in case of eye or skin contact, wash with plenty of water;
- report to company health centre for assessment of symptoms; and
- if necessary, transport exposed person to nearest hospital for medical attention.

The first-aid instructions comprise the following:

- protect yourself with gloves and respiratory equipment;

- remove patient from contaminated area;
- quickly take off contaminated clothing and wash contaminated body parts with plenty of water;
- if patient is not breathing, give expired air artificial respiration;
- if patient has no pulse, begin cardiac compressions;
- if patient has swallowed acrylonitrile and is conscious, do NOT induce vomiting but give a glass of water;
- if patient is conscious, administer oxygen while arranging for emergency transfer to nearest hospital or medical centre; and
- ensure emergency acrylonitrile hospital bag[5] is taken along.

The spill/leak procedures include instructions about PPE, evacuation, containment of spill, clean up, and disposal of waste streams.

The reporting procedures detail how, when and to whom incidents must be reported, including circumstances in which State occupational health and safety and environmental authorities must be notified.

10.3 Hazard communication

10.3.1 Labels

Under the NOHSC *National Model Regulations for the Control of Workplace Hazardous Substances* (NOHSC, 1994c) and the corresponding State and Territory legislation, suppliers or employers shall ensure that all containers of hazardous substances used at work are appropriately labelled in accordance with the NOHSC *Code of Practice for the Labelling of Workplace Substances* (NOHSC, 1994a).

In accordance with the NOHSC *List of Designated Hazardous Substances* (NOHSC, 1999b), labels for containers of acrylonitrile should contain the following risk and safety phrases:

R11	**Highly flammable**	**S45**	**In case of accident or if you feel unwell, seek medical advice immediately (show the label whenever possible)**
R23/24/25	**Also toxic by inhalation, in contact with skin and if swallowed**		
R38	**Irritating to skin**	**S53**	**Avoid exposure – obtain special instructions before use**
R45(2)	**May cause cancer (Category 2)**		

The EC have agreed to the following additional risk and safety phrases which will be adopted by Australia according to the usual process:

R37	**Irritating to respiratory system**	**S9**	**Keep container in a well ventilated place**

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[5] A kit containing a cyanide antidote, syringes, needles etc. and prescribing information for the attending doctor.

R41	**Risk of serious damage to eyes**	**S16**	**Keep away from sources of ignition - no smoking**
R43	**May cause sensitisation by skin contact**		

Bulk storage vessels and tanks must be labelled according to the appropriate State or Territory dangerous goods regulation, generally with an affixed hazard sign or placard similar to the one required for road tankers under the Australian Dangerous Goods (ADG) Code (see section 10.6). As a minimum, dedicated acrylonitrile lines and pipes must be labelled with the name of the chemical. Labels for reagent grade acrylonitrile for laboratory use were not available for assessment.

The above labelling requirements do not apply to mixtures or preparations containing <0.1% (<1000 ppm) free acrylonitrile, such as polymer beads, resin pellets or powder, moulded plastics or polymer emulsions.

10.3.2 Material Safety Data Sheets

Material Safety Data Sheets (MSDS) are the primary source of information for workers involved in the handling of chemicals. Under the NOHSC *National Model Regulations for the Control of Workplace Hazardous Substances* (NOHSC, 1994c) and the corresponding State and Territory legislation, suppliers of a hazardous chemical for use at work are obliged to provide a current MSDS to their customers. Employers must ensure that the MSDS provided by the supplier is readily accessible to employees with potential for exposure to the chemical.

Seven MSDS were available for assessment against the NOHSC *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC, 1994b). The following deficiencies were identified in several MSDS:

- no ‘statement of hazardous nature’;
- no Australian emergency telephone number; and
- no information on Australian regulations such as the national exposure standard, classification according to the ADG Code or the Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP).

One MSDS erroneously gave the national exposure standard as 0.3 mg/m^3, whereas the actual value is 2 ppm or 4.3 mg/m^3.

10.3.3 Education and training

All companies that handle or use the bulk chemical provide education and training in acrylonitrile hazards and safety procedures. In general, induction sessions lasting from 5 min to 1 h are held with all new staff, contractors and casual visitors, with annual or biannual refresher sessions for workers and contractors. Workers potentially exposed to acrylonitrile are trained in the proper use of respiratory protective equipment and first-aid officers are drilled in specific acrylonitrile procedures.

Some of the larger chemical companies that use bulk acrylonitrile have a community relations program that includes the distribution of newsletters to, and regular meetings with, the local residents about health, safety and environmental issues relating to the site and its neighbourhood.

10.4 Other workplace regulatory controls

10.4.1 Atmospheric monitoring

According to the NOHSC *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* (NOHSC, 1995a), exposure to Category 2 carcinogens such as acrylonitrile should be minimised to the lowest practicable levels and a program of routine air monitoring should be implemented to ensure the effectiveness of relevant control measures. In order to correctly assess the risks posed to workers from particular contaminants, airborne concentrations of such substances should be determined by personal monitoring, that is, by measuring the concentration in the breathing zone of the worker.

Current personal air monitoring programs reported by facilities handling or using bulk acrylonitrile are summarised in Table 13.

Table 13: Personal air monitoring and health surveillance programs reported by facilities handling or using bulk acrylonitrile (ACN)

Personal air monitoring for ACN	Health surveillance
Full-shift and task monitoring is conducted every 3-5 years.	Workers undergo regular medical examinations.
Monitoring is conducted on an annual basis.	Potentially exposed workers undergo annual medical examinations.
Monitoring is conducted 'on a routine basis' (not further specified).	Potentially exposed workers undergo medical examination pre-placement.
Monitoring is conducted annually for each task.	Potentially exposed plant and laboratory personnel undergo annual medical examinations.
Monitoring is conducted where potential for exposure is high. If a result is >50% of standard, formal investigation is launched. If any result is >10% of exposure standard, monitoring is repeated within 12 months, otherwise after 3 years, or earlier if process or equipment change.	Potentially exposed workers undergo medical examination pre-placement and at 3-year intervals.
Monitoring of plant and laboratory personnel is conducted twice yearly.	To be established.
Monitoring of plant workers is carried out on a monthly basis.	Exposed workers undergo pre-placement and annual medical examinations.

10.4.2 Occupational exposure standards

The current national occupational exposure standard for acrylonitrile in Australia is 2 ppm (4.3 mg/m^3) expressed as an 8 h TWA airborne concentration, Carcinogen Category 2, with a 'skin' notation (NOHSC, 1995a). The standard was adopted from documentation developed by the American Conference of Governmental Industrial Hygienists (ACGIH, 1986, 1991). The ACGIH recommended an 8 h TWA exposure limit of 2 ppm because of the consistent production of tumours in rats and the suspicion of cancer in humans raised by early epidemiological studies. The 'skin' notation implies that special measures are required to prevent absorption through the skin as the national standard only considers absorption via inhalation.

In Australia, there is no short-term exposure limit (STEL) for acrylonitrile. However, according to the NOHSC Exposure Standards (NOHSC, 1995a) a process is not considered to be under reasonable control if short-term exposures exceed three times the TWA exposure standard for more than 30 minutes per 8 h working day, or if a single short-term value exceeds five times the TWA exposure standard.

The NOHSC Exposure Standards also address the potential emission and/or production of toxic vapours and fumes from plastic resins such as ABS at or around normal melt processing temperatures. No exposure standard has been established, but it is recommended that exposure be kept as low as practicable.

Current occupational exposure standards for acrylonitrile in Australia and other countries are summarised in Table 14.

Table 14: National occupational exposure standards for acrylonitrile (from IARC (1999), HSA (1998) and RTECS (1998))

	Exposure limit	
Country	**8 h TWA**	**STEL**
Australia	2 ppm (4.3 mg/m^3)	-
Austria	2 ppm (4.5 mg/m^3)	-
Belgium	2 ppm (4.3 mg/m^3)	-
Denmark	2 ppm (4.0 mg/m^3)	-
Finland	2 ppm (4.3 mg/m^3)	4 ppm (9 mg/m^3)
France	2 ppm (4.0 mg/m^3)	15 ppm (32.5 mg/m^3)
Germany	3 ppm (7.0 mg/m^3)	-
Hungary	0.23 ppm (0.5 mg/m^3)	-
India	2 ppm (4.3 mg/m^3)	-
Ireland	2 ppm (4.5 mg/m^3)	-
Japan	2 ppm (4.3 mg/m^3)	-
Netherlands	4 ppm (9 mg/m^3)	10 ppm (22 mg/m^3)
Philippines	20 ppm (43 mg/m^3)	-
Poland	5 ppm (10 mg/m^3)	-
Russia	0.23 ppm (0.5 mg/m^3)	-
Spain	2 ppm (4.5 mg/m^3)	-
Sweden	2 ppm (4.5 mg/m^3)	6 ppm (14 mg/m^3)
Turkey	20 ppm (43 mg/m^3)	-
United Kingdom	2 ppm (4 mg/m^3)	-
USA (NIOSH)	1 ppm (2.2 mg/m^3)	10 ppm (22 mg/m^3)
USA (OSHA)	2 ppm (4.3 mg/m^3)	10 ppm (22 mg/m^3)

NIOSH = National Institute of Occupational Safety and Health (recommended limits)
OSHA = Occupational Safety and Health Administration (statutory limits)
STEL = short-term (15-min) exposure limit
TWA = time-weighted average

10.4.3 Health surveillance

Acrylonitrile is listed at Schedule 3 in the NOHSC *National Model Regulations for the Control of Workplace Hazardous Substances* (NOHSC, 1994c) as a hazardous substance for which health surveillance is required. Under the model regulation, employers must provide health surveillance for all employees whose health is at significant risk from exposure to the chemical. The surveillance of personnel exposed to acrylonitrile must include occupational and medical history, demographic data and records of personal exposure. Specific tests or examinations or other particulars of the surveillance are not prescribed.

As shown in Table 13, most facilities handling bulk acrylonitrile provide pre-placement and/or regular medical examinations for potentially exposed workers.

10.4.4 Scheduled carcinogenic substances

For certain carcinogenic substances the NOHSC *Model Regulations for the Control of Scheduled Carcinogenic Substances* (NOHSC, 1995b) impose requirements over and above the provisions of the NOHSC *National Model Regulations for the Control of Workplace Hazardous Substances* (NOHSC, 1994c).

Acrylonitrile is a scheduled carcinogenic substance under these regulations, listed in Schedule 2 as a notifiable carcinogenic substance. Requirements of the regulations include:

- notification to the relevant public authority of any proposed use of acrylonitrile and the quantity to be used per annum;
- a work assessment, including an assessment of potential exposure, to be carried out prior to its use;
- the keeping of records of employees likely to be exposed;
- the reporting of exposure incidents to the relevant public authority; and
- advising employees of any accidental exposure.

10.4.5 Control of major hazard facilities

Under the NOHSC *National Standard for the Control of Major Hazard Facilities* (NOHSC, 1996), acrylonitrile is one of 43 specifically identified chemicals that must be taken into account when determining whether a site is a major hazard facility. For acrylonitrile, the threshold quantity is 200 t. The purpose of this standard is to prevent, and minimise the effects of, major accidents and near misses by requiring the person in control of the facility to:

- identify and assess all hazards and implement control measures to reduce the likelihood and effects of a major accident;
- provide information to the relevant public authority and the community, including other closely located facilities, regarding the nature of hazards of a major hazard facility and emergency procedures in the event of a major accident;
- report and investigate major accidents and near misses, and take appropriate corrective action; and
- record and discuss the lessons learnt and the analysis of major accidents and near misses with employees and employee representatives.

10.5 Industry code of practice

A Code of Practice for the Safe Use of Acrylonitrile has been developed by the Acrylonitrile Users Group of the Australian Chemical Industry Council[6] (ACIC, 1992). The members of the group (BASF, Chemplex (now Huntsman), Dow, ICI-Valchem (now APS-Valchem), Rohm & Haas and Terminals Pty Ltd) represent all but one of the companies that currently handle, store or use bulk acrylonitrile in Australia.

The stated purpose of the code is to provide a uniform approach to the storage, handling, distribution, processing and disposal of acrylonitrile. Products manufactured from acrylonitrile such as SAN polymer beads, or SAN, ABS or ABS/PC alloy resin pellets, and acrylonitrile polymer emulsions are not covered by the code. The code contains a brief overview of the hazardous properties of the chemical and sets out guidance relating to training, assessment of health and safety risks, control measures, PPE, emergency procedures, atmospheric monitoring, health surveillance, labelling, storage and transport, waste management, security, laboratory handling and record-keeping. The code also contains a sample MSDS, a list of methods and equipment used for atmospheric monitoring, a guidance for medical practitioners involved in health surveillance examinations, a summary of the information which companies are required or advised to record and keep on file, and a directory of interested Victorian and New South Wales State government authorities.

Concerning training, control measures, health surveillance, labelling, storage and transport, waste management and laboratory handling the approaches laid down in the code do not deviate significantly from the current practices and procedures described above. The code recommends that the health and safety risks of any work involving acrylonitrile be assessed at intervals not exceeding 3 years. The assessment must include a determination of the degree of potential exposure established through air monitoring.

10.6 National transportation regulation

Under the ADG Code, inhibited acrylonitrile (UN Number 1093) is classified in Class 3, Subsidiary Risk Class 6.1, Packing Group I (FORS, 1998). Class 3 comprises flammable liquids. Acrylonitrile is assigned Subsidiary Risk Class 6.1 and Packing Group I because of its acute toxicity and high vapour pressure.

The ADG Code sets out various requirements relating to the transport of inhibited acrylonitrile by road or rail.

Road tankers must be placarded with class label 3 (‘flammable liquid’), the appropriate subsidiary risk label (‘toxic’) and an emergency information panel containing additional information such as the proper shipping name of the chemical (‘acrylonitrile, inhibited’), its UN Number, Hazchem Code and the name and telephone number of the consignor of the goods. The Hazchem Code for acrylonitrile is 3WE. The code reflects the initial emergency response recommended in case of fire, leakage or spillage. The number ‘3’ indicates that foam should be used for firefighting. The letter ‘W’ means that there is a risk of violent reaction or explosion; that emergency personnel should wear full protective clothing (breathing apparatus, protective gloves, appropriate boots and a chemical

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[6] Now the Plastics and Chemicals Industry Association (PACIA).

splash suit); and that any spillage should be contained so as to prevent the chemical from entering drains or water courses. The letter ‘E’ denotes that evacuation of people from the neighbourhood of an incident should be considered.

Under the ADG Code, road tankers used to transport inhibited acrylonitrile must be constructed in compliance with Australian Standards AS 2809.1, AS 2809.2 and AS 2809.4 (Standards Australia, 1985, 1986, 1990). Furthermore, they must be inspected externally and internally and hydraulically tested at intervals of not more than 5 years and carry a plate that attests to their compliance with the construction and testing requirements.

The dedicated road tanker used to transport bulk acrylonitrile from the storage tank at the terminal to the users of the chemical meets all of the above requirements.

The ADG Code also contains detailed provisions for the inner packaging and marking of packages containing small quantities of the chemical, such as bottles of reagent grade acrylonitrile distributed by road or rail.

10.7 Public health regulatory controls

Acrylonitrile is listed in Schedule 7 of SUSDP (Australian Health Ministers’ Advisory Council, 1998). Schedule 7 comprises poisons that require special precautions in manufacturing, handling, storage or use and which must not be possessed, sold, or supplied for domestic purposes. Furthermore, acrylonitrile is listed with a recommended condition in Part 2 of Appendix J that it is “not to be available except to authorised or licensed persons”. The labelling requirements for Schedule 7 substances include the statements ‘DANGEROUS POISON S7’, ‘NOT TO BE TAKEN’ and ‘KEEP OUT OF REACH OF CHILDREN’.

Controls are in place to limit public exposure to acrylonitrile released into food from packaging materials made from acrylonitrile polymers. According to the *Food Standards Code*, the proportion of acrylonitrile in any food shall not be greater than 0.02 mg/kg (that is, the limit of detection). This level was set by the National Health and Medical Research Council in 1980. A recent ANZFA review (ANZFA, 1999) proposes that the level of 0.02 mg/kg for acrylonitrile monomer migration in food be retained in the new Australia New Zealand Food Standards Code that is currently in preparation. This level is consistent with the EC limit of 0.02 mg/kg and with the recommendations by the Joint Food and Agriculture Organization of the United Nations/World Health Organization Expert Committee on Food Additives that human exposure to acrylonitrile in food as a result of its migration from food-contact materials should be reduced to the lowest levels technologically attainable (ANZFA, 1999). In addition, some States (New South Wales, Western Australia) have regulations that limit the quantity of acrylonitrile monomer in food packaging materials to 10 ppm.

10.8 Environmental regulatory controls

Most States and Territories have regulations which require any site using, storing or manufacturing acrylonitrile to possess a discharge licence issued by their State or Territory EPA. Each licence would be site-specific and include items such as operational restraints, monitoring requirements, measures to ensure maximum reductions of discharges to the environment and concentration limits on such discharges.

10.9 Applicable Victorian and New South Wales regulations

The NOHSC National Model Regulations, Codes of Practice and Exposure Standards, the ADG Code and the SUSDP are documents that aim to promote uniform regulation throughout Australia by inclusion in the relevant State and Territory legislation. As such, they have no legal standing other than that given to them by relevant legislation.

In general, the handling, storage and use of acrylonitrile are tightly controlled through State and Territory regulations pertaining to workplace health and safety, poisons, dangerous goods and protection of the environment.

In Victoria, where the bulk terminal and five of the sites using bulk acrylonitrile are located, the following regulations apply:

- Use of acrylonitrile is prohibited by a person unless they hold a warrant, granted under a Governer in Council Order of 27 April 1995 issued under *the Dangerous Goods Act 1985.* Application for a warrant must be made to the Victorian WorkCover Authority to use acrylonitrile in manufacturing or for laboratory purposes. Warrants are valid until cancelled or suspended. Under the warrant, access to areas where the chemical is present must be limited to the smallest possible number of persons, whose names must be recorded and who must be properly trained and kept informed of any exposure. Any incidents, accidents or other events that could increase exposure must be reported to the Authority and holders of warrants are inspected on an annual basis.
- Under the *Occupational Health and Safety (Hazardous Substances) Regulations 1999* (effective from 1 June 2000), acrylonitrile is regarded as a scheduled carcinogen. Under these regulations a person wishing to use acrylonitrile in a workplace other than a laboratory must obtain a licence prior to use while the use of the substance in a laboratory requires notification to the Victorian Workcover Authority.
- Under the *Drugs, Poisons and Controlled Substances Act 1981*, a person must apply in writing to the Secretary to the Department of Human Services for the issue of a permit to purchase acrylonitrile for industrial or research purposes and for a licence to manufacture and sell or supply the chemical by wholesale. A permit or a licence is valid for 12 months and the Secretary may require the premises of the applicant to be inspected. Permits and licences are issued on the condition that their holders maintain a poisons control plan which has been approved by the Department.
- Under the *Dangerous Goods (Storage and Handling) Regulations 1989*, the owner of a premise where more than a certain quantity of dangerous goods is stored must be licensed by the Victorian WorkCover Authority. Licences to store dangerous goods are usually valid for a maximum of 5 years.
- Under the *Environment Protection Act 1970*, the owner of a premise discharging acrylonitrile to the atmosphere must be licensed by the Victorian EPA. The licence stipulates discharge requirements (stack height), emission limits and monitoring frequency for each discharge point. It remains in force until revoked, suspended or surrendered.

One site using bulk acrylonitrile is based in New South Wales, where the pertinent regulations are as follows:

- Under the *Occupational Health and Safety (Hazardous Substances) Regulation 1996*, acrylonitrile is a hazardous substance for which health surveillance of exposed employees is required.

- Under the *Occupational Health and Safety (Hazardous Substances) Regulation 1996*, an employer must ensure that workers are not exposed to acrylonitrile in their breathing zone at a level greater than the national exposure standard.

- Under the *Occupational Health and Safety (Hazardous Substances) Regulation 1996*, acrylonitrile is a scheduled carcinogenic substance. As such, it must only be kept, stored or used by persons who hold a purchaser's permit. Among others, the permit holder must notify the WorkCover Authority of New South Wales of the stored quantity and intended use and disposal of the chemical. The permit is subject to conditions such as an obligation to notify the Authority of major incidents.

- Under the *Poisons and Therapeutic Goods Regulation 1994*, a person must not use acrylonitrile without holding an authority issued by New South Wales Health. The authority is issued on the condition that measures are taken to prevent public access to the chemical.

- Under the *Dangerous Goods Act 1975*, premises keeping dangerous goods must be licensed by the WorkCover Authority of New South Wales. Licences are issued annually and may be renewed for a maximum of 3 years.

- Under the *Protection of the Environment Operations Act 1997*, premises that are required to be licensed under the *Dangerous Goods Act 1975* or discharge hazardous waste including acrylonitrile must by licensed by the New South Wales EPA.

11. Discussion and Conclusions

11.1 Importation and use

Acrylonitrile is not manufactured in Australia but imported in bulk at about 2000 t per annum and as an impurity (residual monomer) in polymer-based intermediates and articles. Of the bulk, 70% is used at one site for the manufacture of a polymer, which is further compounded to plastic resins. Five companies process the remaining 30% to polymer emulsions. About 13,000 tonnes of acrylonitrile-based plastic resins containing <0.005% residual acrylonitrile are imported per annum. Import figures were not available for acrylonitrile-based articles or fibres and fabrics, which contain <0.005% and usually <0.001-0.0001% residual acrylonitrile.

11.2 Hazards

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

Acrylonitrile is a highly volatile, flammable and explosive liquid. It reacts violently with many other chemicals and may undergo spontaneous, explosive self-polymerisation unless stabilised by a chemical inhibitor and/or water.

In both laboratory animals and humans, acrylonitrile is readily absorbed by ingestion, by inhalation and through the skin. It is acutely toxic by all routes of exposure, causing convulsions followed by paralysis and respiratory failure. It is acutely irritating to the skin and eyes and may cause allergic contact dermatitis. Repeated exposure of workers to airborne acrylonitrile has been associated with respiratory tract irritation and functional disturbances of the CNS. Acrylonitrile is mutagenic *in vitro* and a potent multi-organ carcinogen in rats. Epidemiological studies involving large numbers of exposed workers and extensive follow-up periods have neither established nor ruled out a causal relationship between acrylonitrile exposure and cancer in humans.

Acrylonitrile is included in the NOHSC *List of Designated Hazardous Chemicals* based on the classification in EC Council Directive 96/54/EC. It is classified as highly flammable; toxic by inhalation, in contact with skin and if swallowed; a skin irritant; and a carcinogen in Group 2 (substances regarded as if they are carcinogenic to humans). In March 1999, the EC agreed to amend their original classification of acrylonitrile to include risk phrases for irritation of the respiratory tract, serious damage to the eyes, and skin sensitisation. Australia will adopt this amended classification via the NOHSC hazardous substances regulatory process.

The available environment data indicate that acrylonitrile can be characterised as exhibiting slight to moderate acute and slight chronic toxicity to aquatic vertebrates and aquatic invertebrates. Similarly, for algae and aquatic plants, results for effects on biomass suggest that acrylonitrile is moderately toxic, while results for effects on reproduction are indicative of slight toxicity.

11.3 Occupational controls

The storage, handling and use of acrylonitrile are tightly controlled by a number of national standards and codes. These include the ADG Code, the SUSDP and the NOHSC *List of Designated Hazardous Chemicals, Exposure Standards for Atmospheric Contaminants in the Occupational Environment, National Model Regulations for the Control of Workplace Hazardous Substances*, *National Model Regulations for the Control of Scheduled Carcinogenic Substances and National Standard for the Control of Major Hazard Facilities*.

In Victoria and New South Wales, almost all of the national provisions pertaining to acrylonitrile have been embodied in State legislation relating to occupational health and safety, drugs and poisons, or dangerous goods. The corresponding regulations are enforced through a system of permits, licences and warrants. These are issued on the condition that the holder supplies detailed information about health and safety control measures and can be withdrawn if it is found that the approved control plans are not adhered to in practice.

In the workplace, the principal method employed to control exposure to acrylonitrile is full enclosure and isolation together with engineering controls to minimise emissions, waste streams and leaks from the closed system. Access to areas where acrylonitrile is handled is limited to a minimum of people whose presence is absolutely necessary. In addition, all workers wear eye and skin protection. Respiratory protective equipment is used during the making and breaking of enclosed pipelines during ship to shore transfer and loading and unloading of the road tanker that transports acrylonitrile to the sites where it is processed.

In situations where isolation cannot be maintained because of emergencies or the need to enter the closed system to carry out sampling or maintenance, PPE deployed includes chemical goggles, a protective suit, rubber gloves and rubber boots. In addition, respiratory protection is mandatory in all situations where the breathing zone concentration (measured by grab sampling) is >1 ppm or unknown.

In laboratories handling neat acrylonitrile the main control measures are standard operating procedures and the confinement of all manipulations to a fume cupboard.

All sites storing bulk acrylonitrile have implemented control measures aimed at reducing the likelihood and impact of fires, explosions, spills and other accidents. These include isolation, chemical inhibition to prevent spontaneous polymerisation, nitrogen blanketing and bunding of storage tanks, the equipment of storage tanks and reactors with high temperature and high pressure alarms and deluge systems, and detailed on-site emergency plans.

Hazard communication includes MSDS, the labelling of containers of hazardous chemicals, and education and training of workers. Deficiencies were found in some of the MSDS provided for assessment. All companies handling the chemical in bulk provide training programs in acrylonitrile-related hazards and safety procedures.

Personal full-shift and/or task monitoring of potentially exposed workers is conducted by all companies that handle bulk acrylonitrile, although the exposure monitoring programs vary considerably from site to site. There was no indication of a consistent approach to strategic issues such as the selection of workers for personal monitoring, definition of sample sizes, data analysis or determination of the frequency of monitoring. The monitoring data provided for assessment indicate that the number of samples obtained for each similar exposure group has declined over the last decade. In recent years, several sites have relied on small samples, sometimes not exceeding 1-2 per assessment. This may not suffice to determine the level of exposure with a reasonable degree of confidence.

11.4 Occupational exposure

Table 15 summarises the available information about the number of potentially exposed workers, the frequency of exposure, principal control measures, PPE and personal air monitoring results of relevance to current control measures under normal operating conditions.

11.4.1 Transport and storage

The number of workers involved in ship to shore transfer and road transportation of acrylonitrile is limited, potential contact is relatively brief and infrequent and operations take place in the open air. Based on a limited number of samples, the overall exposure level can be characterised as probably low. The recorded range of <0.005 to <0.5 ppm is below the level of 0.4-0.7 ppm reported for workers loading or unloading tank trucks, rail cars or barges overseas.

11.4.2 Acrylonitrile processing

The potential for exposure at the Huntsman SAN plant and the five polymer emulsion plants is low as the processes are fully enclosed and highly automated and the end products contain low amounts of residual acrylonitrile.

Two older polymer emulsion facilities each had a single exposure value above the national standard of 2 ppm (8 h TWA) and one value in the 1-2 ppm range (Table 15). These plants also reported a higher frequency of monitoring (monthly and 6-monthly respectively) than the remaining sites and one of them conducts routine area monitoring (by grab sampling) around the reactor during each production run. Otherwise, exposure levels were comparable to those reported for similar activities overseas, that is, predominantly in the 0.1-0.2 ppm range.

Monitoring data for maintenance activities in the SAN plant were obtained in 1990 and relate to facilities and equipment which are no longer used. Short-term concentrations of up to 318 ppm were recorded in the worker's breathing zone. Personal monitoring data were also supplied for a small number of workers involved in maintenance work in one of the polymer emulsion facilities. Short-term concentrations of up to 35 ppm were recorded in the worker's breathing zone. However, maintenance workers routinely use respiratory protective equipment when air levels of acrylonitrile exceed 1 ppm or are unknown.

11.4.3 Processing and use of polymers containing residual acrylonitrile

There are several manufacturers of SAN, ABS and ABS/PC resin pellets in Australia, however, air monitoring data were available only for the Huntsman extrusion plant (site A). The overall exposure level at this plant was low, with most readings <0.1 ppm. Levels in the 0.01-0.02 ppm range have been reported for similar processes in Europe. It is not known whether these results are representative for other resin pellet manufacturing sites in Australia.

No Australian monitoring data were available for acrylonitrile exposure resulting from the manufacture of plastic articles from SAN, ABS or ABS/PC resins. Field studies from Sweden and Britain indicate that area and breathing zone levels are unlikely to exceed 0.01 ppm acrylonitrile.

Polymer emulsions are further processed into a variety of products such as paints, binders, coatings and adhesives. No Australian monitoring data were available for the use of such products in other industries. Given the low concentration of residual acrylonitrile in polymer emulsions (<10 ppm), the potential for exposure is likely to be very low. This is supported by data from Europe where exposure levels were consistently below the detection limit of 0.02 ppm in industries using polymer emulsions for surface coating or paper manufacturing.

11.4.4 Quality control sampling and laboratory use

Limited personal monitoring indicates that the collection of samples of bulk acrylonitrile may be associated with short-term breathing zone air levels above 1 ppm. However, workers routinely wear full-face organic vapour respirators during sampling.

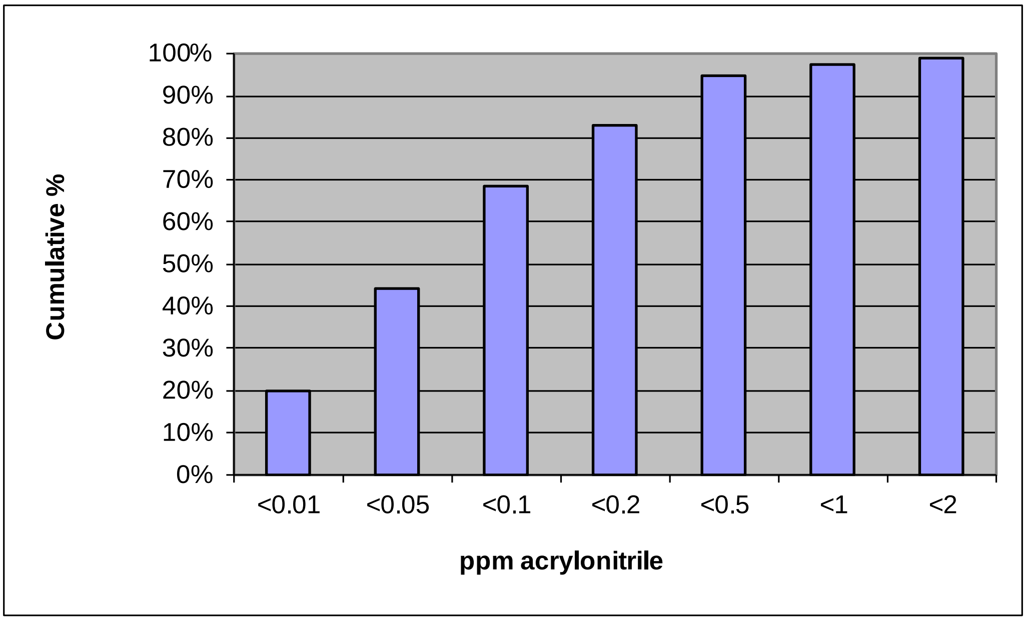
In one laboratory, limited task monitoring indicated the potential for instantaneous exposures of up to 2 ppm when opening a retention sample storage cupboard in a well-ventilated room. A concentration of 40 ppm inside the cupboard was due to leakage of acrylonitrile vapour from the sample bottles. Although the average 8 h workday exposures are expected to be low in this case due to the low frequency and short duration of the tasks, the number of potentially exposed workers (Table 15) and the high volatility of acrylonitrile emphasise the need to train laboratory personnel in acrylonitrile-related hazards and safety procedures and include them in the atmospheric monitoring program. This is confirmed by reports of personal exposure levels ranging from 0.1-9.4 ppm in laboratory technicians in monomer and fibre production plants in USA.

11.4.5 Summary of exposure findings

Excluding data of dubious relevance to current control measures, there were 187 data points for personal air monitoring during normal operations at all sites where bulk acrylonitrile is handled or used. Only two readings (1.1%) exceeded the national exposure standard of 2 ppm (4.3 mg/m^3) expressed as an 8 h TWA airborne concentration (Table 15).

The cumulative distribution of these measurements is shown in Figure 2. Sixty-eight per cent of measurements were <0.1 ppm, 95% were <0.5 ppm and 97% were <1 ppm. Short-term air levels of 0.1-318 ppm were recorded in the breathing zone of workers involved in maintenance or sampling activities. However, the use of suitable respiratory protection is mandatory at all sites when air levels exceed 1 ppm or are unknown.

Figure 2: Cumulative distribution of exposures to acrylonitrile during normal operations at 7 sites handling or processing the chemical in bulk (n = 187)



11.5 Conclusions

11.5.1 Occupational health and safety

Based on the findings discussed above, it can be concluded that workers in Australia are unlikely to be systemically exposed to acrylonitrile at or above the national exposure standard of 2 ppm (8 h TWA) and that the exposure can be expected to be <0.1 ppm in the majority of cases.

The SIDS Initial Assessment Report, which has been agreed by OECD, concludes that at present there is no need for further risk reduction measures beyond those that are already being applied overseas, as these have achieved exposure levels that typically are <1 ppm in acrylonitrile processing industries and <0.1 ppm in industries processing polymers containing only residual amounts of the chemical. This assessment has shown that similarly low levels of exposure are achieved in Australia under the currently practised workplace and regulatory control measures. Therefore, a full occupational (risk) assessment is not considered to be required at this time.

11.5.2 Public health

Acrylonitrile is not available to the general public as it is listed in Schedule 7 of SUSDP and must not be possessed, sold, or supplied for domestic purposes. The public may, however, be exposed indirectly via the environment or by ingestion of foods contaminated with residual acrylonitrile in packaging materials and to skin contact with residual monomer in acrylonitrile-based fabrics and other products such as paints, polishes and plastic articles.

The available evidence indicates that indirect exposure to acrylonitrile via the environment would be less than 100 ng/kg/day. The *Food Standards Code* sets a limit for acrylonitrile content in foods of 0.02 mg/kg (20 ppb) which ensures that the daily intake is unlikely to exceed 1 µg, representing a maximum of 14-33 ng/kg/day in persons weighing from 30-70 kg. There are no regulations pertaining to the content of residual acrylonitrile in other consumer products. However, the estimated maximum uptake of acrylonitrile from fabrics is 2.2 ng/kg/day for an adult woman weighing 60 kg and would be negligible from other products based on acrylonitrile polymers. Therefore, even in a worst-case scenario, total public exposure to acrylonitrile would not exceed 135 ng/kg/day. According to the SIDS Initial Assessment Report, which has been agreed by OECD, this is several orders of magnitude lower than the no observed adverse effect level for any toxicological end-point in laboratory animals. As such, it is considered that the risk of public health effects resulting from the current uses of acrylonitrile is unlikely to be significant and that a full public health assessment is not required at this time.

Similar conclusions were reached in a recent assessment report from Health Canada, although they also recommended additional investigation of the magnitude of airborne exposure of populations in the immediate vicinity of industrial point sources (Government of Canada, 1999). Compared to Australia, however, the Canadian acrylonitrile processing industry is four times larger and more concentrated in terms of location.

11.5.3 The environment

A crude comparison of the predicted environmental concentration in water and the effects known to cause impacts on aquatic organisms suggests that the expected risk to this compartment is low. Furthermore, all facilities storing or processing bulk acrylonitrile have measures in place to minimise transfer and process emissions and incidental releases such as spills and leaks. The premises must be licensed by the State EPA and are inspected at regular intervals for compliance with the conditions specified in the licence. As such, the findings in this preliminary assessment of acrylonitrile have not highlighted any significant concern for the environment and a full environment assessment is not considered to be necessary at this time.

12. Recommendations

NICNAS does not recommend a full (risk) assessment of acrylonitrile at this time. Nevertheless, given the findings discussed in the previous section, the following recommendations are made:

12.1 Hazard classification

It is recommended that suppliers and employers take note of the amended hazard classification agreed by the EC Working Group on the Classification and Labelling of Dangerous Substances in March 1999. The amendment will be taken up by the NOHSC *List of Designated Hazardous Substances* via the usual process, to provide the following classification:

R11	**Highly flammable**
R23/24/25	**Also toxic by inhalation, in contact with skin and if swallowed**
R37/38	**Irritating to respiratory system and skin**
R41	**Risk of serious damage to eyes**
R43	**May cause sensitisation by skin contact**
R45(2)	**May cause cancer (Category 2)**

The safety and first aid phrases agreed by the EC Working Group are:

S9	**Keep container in a well ventilated place**
S16	**Keep away from sources of ignition – no smoking**
S45	**In case of accident or if you feel unwell, seek medical advice immediately (show the label whenever possible)**
S53	**Avoid exposure – obtain special instructions before use**

MSDS, labels and training materials should be amended to provide appropriate information about the risks of irritation of the respiratory system, eye damage and allergic contact dermatitis.

12.2 Workplace control measures

The NOHSC *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* classifies acrylonitrile as a category 2 carcinogen in accordance with the criteria of that standard. It is recommended that companies handling bulk acrylonitrile continue to strive for further improvements in their workplace control measures, in accordance with the requirement of the NOHSC *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* that exposure to Category 2 carcinogens be minimised to the lowest practicable levels.

It is further recommended that all laboratory personnel be adequately trained in the hazards of the chemical and included in atmospheric monitoring programs, given the potential for high atmospheric levels from the evaporation of minute quantities of acrylonitrile during laboratory handling of the chemical.

12.3 Industry code of practice

It is recommended that the 1992 industry Code of Practice for the Safe Use of Acrylonitrile be updated with regard to the following issues:

- The overview of the hazardous properties of acrylonitrile should be revised to include the conclusions of recent international assessments such as the SIDS Initial Assessment Report and the latest IARC review of the carcinogenic potential of the chemical.
- The controls imposed by current NOHSC standards and codes of practice and State regulations should be addressed in detail.
- The sample MSDS attached to the code should be amended to include appropriate information about the risks of irritation of the respiratory system, eye damage and allergic contact dermatitis.

Given the inconsistency of current atmospheric monitoring programs for acrylonitrile, it is further recommended that industry develop practical guidelines that address the selection of acrylonitrile workers for personal monitoring, the definition of sample sizes, the analysis of exposure data and the determination of the frequency of exposure assessments.

13. Secondary Notification

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

- the function or use of acrylonitrile has increased, or is likely to change, significantly;
- the amount of acrylonitrile introduced into Australia has increased, or is likely to increase, significantly;
- manufacture of acrylonitrile has begun in Australia; and
- additional information has become available to the introducers as to the adverse health, safety or environmental effects of acrylonitrile, such as the results of the ongoing carcinogenicity study in mice.

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

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