Benzalkyl quaternary ammonium surfactants: Environment tier II assessment

01 July 2016

CAS Registry Numbers: 8001-54-5, 85665-42-5, 63449-41-2, 68989-00-4, 91080-30-7, 85409-22-9, 68424-85-1, 68391-01-5, 68607-20-5, 91080-31-8, 61789-75-1, 61789-72-8, 61789-71-7, 61789-74-0.

Preface

This assessment was carried out by staff of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) using the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework.

The IMAP framework addresses the human health and environmental impacts of previously unassessed industrial chemicals listed on the Australian Inventory of Chemical Substances (the Inventory).

The framework was developed with significant input from stakeholders and provides a more rapid, flexible and transparent approach for the assessment of chemicals listed on the Inventory.

Stage One of the implementation of this framework, which lasted four years from 1 July 2012, examined 3000 chemicals meeting characteristics identified by stakeholders as needing priority assessment. This included chemicals for which NICNAS

already held exposure information, chemicals identified as a concern or for which regulatory action had been taken overseas, and chemicals detected in international studies analysing chemicals present in babies' umbilical cord blood.

Stage Two of IMAP began in July 2016. We are continuing to assess chemicals on the Inventory, including chemicals identified as a concern for which action has been taken overseas and chemicals that can be rapidly identified and assessed by using Stage One information. We are also continuing to publish information for chemicals on the Inventory that pose a low risk to human health or the environment or both. This work provides efficiencies and enables us to identify higher risk chemicals requiring assessment.

The IMAP framework is a science and risk-based model designed to align the assessment effort with the human health and environmental impacts of chemicals. It has three tiers of assessment, with the assessment effort increasing with each tier. The Tier I assessment is a high throughput approach using tabulated electronic data. The Tier II assessment is an evaluation of risk on a substance-by-substance or chemical category-by-category basis. Tier III assessments are conducted to address specific concerns that could not be resolved during the Tier II assessment.

These assessments are carried out by staff employed by the Australian Government Department of Health and the Australian Government Department of the Environment and Energy. The human health and environment risk assessments are conducted and published separately, using information available at the time, and may be undertaken at different tiers.

This chemical or group of chemicals are being assessed at Tier II because the Tier I assessment indicated that it needed further investigation.

For more detail on this program please visit: www.nicnas.gov.au

Disclaimer

Acronyms & Abbreviations

Grouping Rationale

This Tier II assessment considers the environmental risks associated with industrial uses of fourteen benzalkyl quaternary ammonium salts. All chemicals in this group are mixtures of discrete benzalkyl quaternary ammonium salts, in the category of unknown or variable composition, complex reaction products or biological materials (UVCBs). Each salt contains an organic cation based on a quaternary nitrogen that is covalently bonded to a benzyl substituent, two methyl groups, and a single alkyl chain that has seven or more carbon atoms.

The quaternary ammonium salts in this group dissociate into their respective quaternary ammonium cations and chloride anions in water. These quaternary ammonium cations are surfactants that have biocidal activity. They have a wide range of potential domestic and industrial applications, many of which could lead to release of these chemicals into sewers. Therefore, there is a potential for the chemicals in this group to be emitted to the environment in treated effluents and biosolids produced by sewage treatment plants.

The Tier I assessment of the Stage One chemicals in this group identified concerns regarding their ecotoxicity and the potential for unreasonable risks to the environment from their emission to surface waters in treated effluents from sewage treatment plants. This Tier II assessment includes further refinement of the risk characterisation for these chemicals, together with an assessment of the environmental risks of other closely related benzalkyl quaternary ammonium salts listed on the Inventory.

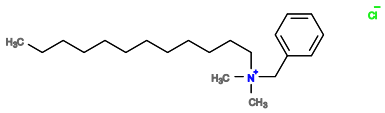
The IMAP Environment Tier II assessment of Mono- and Di-alkyl Quaternary Ammonium Surfactants (NICNAS, 2016) has been used as a reference assessment.

Chemical Identity

The proportions of the discrete chemical components in each UVCB in this group will depend on the chemical composition of the alkyl chain compounds used as precursors and the manufacturing process. Hence, the technical materials used industrially are expected to have varying proportions of the discrete chemicals identified as possible components of each UVCB in this group (Health Canada, 2008; US EPA, 2006b).

Representative chemical structure information is provided for benzalkonium chloride (CAS RN 8001-54-5). Representative chemical structure information is also provided for the main discrete chemical component of UVCBs that are derived from chemicals with biological origins, where composition information for the technical material is available. Only the CAS RN, chemical name and synonyms are presented for all other UVCBs in this group.

The substance represented by CAS RN 8001-54-5 is expected to be a mixture of discrete chemicals with alkyl chains of 12 to 18 carbons (US EPA, 2006a).

CAS RN	8001-54-5
Chemical Name	Quaternary ammonium compounds, alkylbenzyldimethyl, chlorides
Synonyms	benzalkonium chloride benzyl-$C_{12\text{-}18}$-alkyldimethylammonium chlorides
Representative Structural Formula	
Representative Molecular Formula	$C_{21}H_{38}ClN$
Representative Molecular Weight (g/mol)	340.00
Representative SMILES	C[N+](CC1=CC=CC=C1)(CCCCCCCCCCCC)C.[Cl-]

The substance represented by CAS RN 85665-42-5 is expected to be a mixture of discrete chemicals with alkyl chains of seven to 17 carbons (US EPA, 2006a).

CAS RN	85665-42-5
Chemical Name	Quaternary ammonium compounds, benzyl-C7-17-alkyldimethyl, chlorides
Synonyms	benzyl-C_{7-17}-alkyldimethylammonium chlorides

The substance represented by CAS RN 63449-41-2 is expected to be a mixture of discrete chemicals with alkyl chains of eight to 18 carbons (US EPA, 2006a).

CAS RN	63449-41-2
Chemical Name	Quaternary ammonium compounds, benzyl-C8-18-alkyldimethyl, chlorides
Synonyms	benzyl-C_{8-18}-alkyldimethylammonium chlorides

The substance represented by CAS RN 68989-00-4 is expected to be a mixture of discrete chemicals with alkyl chains of 10 to 16 carbons (US EPA, 2006a).

CAS RN	68989-00-4
Chemical Name	Quaternary ammonium compounds, benzyl-C10-16-alkyldimethyl,chlorides
Synonyms	benzyl-C_{10-16}-alkyldimethylammonium chlorides

The substance represented by CAS RN 91080-30-7 is expected to be a mixture of discrete chemicals with alkyl chains of 10 to 21 carbons (US EPA, 2006a).

CAS RN	91080-30-7
Chemical Name	Quaternary ammonium compounds, benzyl-C10-21-alkyldimethyl,chlorides
Synonyms	benzyl-C_{10-21}-alkyldimethylammonium chlorides

The substance represented by CAS RN 85409-22-9 is expected to be a mixture of discrete chemicals with alkyl chains of 12 to 14 carbons (US EPA, 2006a).

CAS RN	85409-22-9
Chemical Name	Quaternary ammonium compounds, benzyl-C12-14-alkyldimethyl,chlorides
Synonyms	benzyl-C_{12-14}-alkyldimethylammonium chlorides

The substance represented by CAS RN 68424-85-1 is expected to be a mixture of discrete chemicals with alkyl chains of 12 to 16 carbons (US EPA, 2006a).

CAS RN	68424-85-1
Chemical Name	Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl,chlorides
Synonyms	benzyl-C_{12-16}-alkyldimethylammonium chlorides

The substance represented by CAS RN 68391-01-5 is expected to be a mixture of discrete chemicals with alkyl chains of 12 to 18 carbons (US EPA, 2006a).

CAS RN	68391-01-5
Chemical Name	Quaternary ammonium compounds, benzyl-C12-18-alkyldimethyl,chlorides
Synonyms	benzyl-C_{12-18}-alkyldimethylammonium chlorides

The substance represented by CAS RN 68607-20-5 is expected to be a mixture of discrete chemicals with alkyl chains of 16 to 18 carbons (US EPA, 2006a).

CAS RN	68607-20-5
Chemical Name	Quaternary ammonium compounds, benzyl-C16-18-alkyldimethyl,chlorides

Synonyms	benzyl-C_{16-18}-alkyldimethylammonium chlorides

The substance represented by CAS RN 91080-31-8 is expected to be a mixture of discrete chemicals with alkyl chains of 16 to 22 carbons (US EPA, 2006a).

CAS RN	91080-31-8
Chemical Name	Quaternary ammonium compounds, benzyl-C16-22-alkyldimethyl,chlorides
Synonyms	benzyl-C_{16-22}-alkyldimethylammonium chlorides

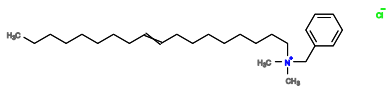
The remaining substances in this group are benzalkyl quaternary ammonium chloride salts that are derived from chemicals that have a biological origin.

Commercially available quaternary ammonium surfactants are often prepared indirectly from natural fats and oils. Natural fats derived from the fatty tissue of sheep or cattle, oil obtained from the kernel of the seed of *Cocos nucifera* (coconut), and seeds of *Glycine soja* (soybean) are used to prepare tallow alkyl-, coconut oil alkyl-, and soybean oil alkyl-ammonium compounds, respectively (Ash and Ash, 2004a; b). These surfactants have carbon chains with even numbers of carbon atoms, as fatty acid biosynthesis occurs mainly through addition of two carbon units in the form of acetyl-CoA (Voet and Voet, 1990).

The major process for transforming fats and oils of biological origins into oleochemicals is the hydrolysis of natural triglycerides into glycerine and mixed fatty acids (Corma, et al., 2007). Reaction of these fatty acids and ammonia followed by hydrogenation produces fatty amines (Corma, et al., 2007), which are then alkylated at the nitrogen atom by reaction with benzyl chloride (CAS RN 100-44-7) and chloromethane (CAS RN 74-87-3) (de Oude, 1992).

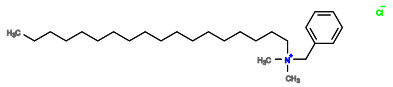
Representative chemical identity information for the remaining chemicals in this group is provided below for the discrete chemical that is expected to be most abundant in the technical mixture based on the reported composition of its respective fatty amine precursor (ECHA, 2011).

The substance represented by CAS RN 61789-75-1 is expected to be a mixture of discrete chemicals with saturated and unsaturated alkyl chains of 12 to 18 carbons derived from tallow.

CAS RN	61789-75-1
Chemical Name	Quaternary ammonium compounds, benzyldimethyltallow alkyl, chlorides
Synonyms	benzyl(tallow alkyl)dimethylammonium chloride
Representative Structural Formula	

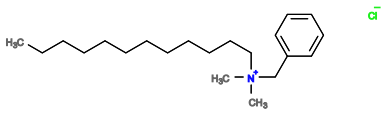
Representative Molecular Formula	$C_{27}H_{48}ClN$
Representative Molecular Weight (g/mol)	422.13
Representative SMILES	C[N+](CC1=CC=CC=C1)(CCCCCCCCC=CCCCCCCCC)C.[Cl-]

The substance represented by CAS RN 61789-72-8 is expected to be a mixture of discrete chemicals with alkyl chains of 12 to 18 carbons derived from hydrogenated tallow.

CAS RN	61789-72-8
Chemical Name	Quaternary ammonium compounds, benzyl(hydrogenated tallow alkyl)dimethyl, chlorides
Synonyms	benzyl(hydrogenated tallow alkyl)dimethylammonium chloride
Representative Structural Formula	
Representative Molecular Formula	$C_{27}H_{50}ClN$
Representative Molecular Weight (g/mol)	424.15
Representative SMILES	C[N+](CC1=CC=CC=C1)(CCCCCCCCCCCCCCCCCC)C.[Cl-]

The substance represented by CAS RN 61789-71-7 is expected to be a mixture of discrete chemicals with alkyl chains of eight to 18 carbons derived from coconut oil.

CAS RN	61789-71-7

Chemical Name	Quaternary ammonium compounds, benzylcoco alkyldimethyl, chlorides
Synonyms	benzyl(coconut oil alkyl)dimethylammonium chloride
Representative Structural Formula	
Representative Molecular Formula	$C_{21}H_{38}ClN$
Representative Molecular Weight (g/mol)	340.00
Representative SMILES	C[N+](CC1=CC=CC=C1)(CCCCCCCCCCCC)C.[Cl-]

The substance represented by CAS RN 61789-74-0 is expected to be a mixture of discrete chemicals with saturated and unsaturated alkyl chains of 16 to 18 carbons derived from soybean oil.

CAS RN	61789-74-0
Chemical Name	Quaternary ammonium compounds, benzyldimethylsoya alkyl, chlorides
Synonyms	benzyl(soybean oil alkyl)dimethylammonium chloride

Physical and Chemical Properties

Limited measured physical and chemical property data are available for the chemicals in this group. Information provided for benzalkonium chloride (CAS RN 8001-54-5) was retrieved from the scientific literature (Mukerjee and Mysels, 1971) and the databases included in the OECD QSAR Toolbox and the United States National Library of Medicine Hazardous Substances Data Bank (LMC, 2013; US NLM, 2013):

Physical Form	Solid

Melting Point	241°C (exp.)
Water Solubility	782 mg/L (C_{12}) (exp.) 16.6 mg/L (C_{16}) (exp.) 3.6 mg/L (C_{18}) (exp.)
Ionisable in the Environment?	Yes

The chemicals in this group are all salts of benzalkyl quaternary ammonium surfactants and are, therefore, expected to have low volatility (de Oude, 1992). The reported water solubility values are the measured critical micelle concentrations (CMCs) for discrete chemicals in this group (Mukerjee and Mysels, 1971). The CMCs decrease with increasing alkyl chain length as expected (Tezel, 2009).

The octanol-water partition coefficient (K_{OW}) for the chemicals in this group is not considered to provide a reliable indicator of the partitioning behaviour of surface-active substances in the environment (McWilliams and Payne, 2001; Shorts, et al., 2010) and, therefore, has not been reported.

Import, Manufacture and Use

Australia

Under previous mandatory and/or voluntary calls for information, three benzalkyl quaternary ammonium chloride compounds (benzyl-$C_{12\text{-}18}$-alkyldimethylammonium chlorides, benzyl-$C_{12\text{-}16}$-alkyldimethylammonium chlorides, and benzyl-$C_{12\text{-}14}$-alkyldimethylammonium chlorides) have been reported to be used domestically in cleaning and washing agents, and additives. The total volume introduced into Australia was between 100 and 1000 tonnes for each of these compounds (NICNAS, 2013b).

Benzalkyl quaternary ammonium surfactants are used in agricultural and veterinary chemical products (APVMA, 2016). It is reported that benzalkonium chloride is used in algaecides and sanitisers. However, use of these chemicals in pesticides or veterinary medicines and swimming pool applications is beyond the scope of this assessment, as such uses are not considered an industrial use under the *Industrial Chemicals (Notification and Assessment) Act 1989*.

No specific Australian use, import, or manufacturing information has been identified for other chemicals in this group.

International

Chemicals in this group are cationic surfactants that have a wide range of industrial applications reported internationally. They are used in cleaning and washing agents as well as in cosmetics, such as hair conditioners and deodorants (SYKE, 2014; US EPA, 2015). Due to their biocidal activity, they are used in agricultural and non-agricultural pesticides, disinfectants and preservatives (Nordic Council of Ministers, 2016; US EPA, 2015). There is also some indication of use as algaecides, indicating potential water treatment uses (US EPA, 2015; US NLM, 2013). However, algaecide use is beyond the scope of this assessment.

Environmental Regulatory Status

Australia

The use of the chemicals in this group is not subject to any specific national environmental regulations.

United Nations

The chemicals in this group are not currently identified as Persistent Organic Pollutants (UNEP, 2001), ozone depleting substances (UNEP, 1987), or hazardous substances for the purpose of international trade (UNEP & FAO, 1998).

OECD

A number of chemicals in this group (five substances) are listed as OECD High Production Volume (HPV) chemicals, indicating that more than 1000 tonnes of the chemicals are produced per year in at least one member country of the OECD (OECD, 2004; 2009).

The chemicals in this group have not been sponsored for assessment under the Cooperative Chemicals Assessment Programme (CoCAP) (OECD, 2013).

Canada

The chemicals in this group are not listed under Schedule 1 (the Toxic Substances List) of the *Canadian Environmental Protection Act 1999* (CEPA 1999) (Government of Canada, 2013b).

The majority of the chemicals in this group (eight substances) are listed on the Canadian Domestic Substances List (DSL) (Environment Canada, 2013). Four of the listed chemicals were categorised as Bioaccumulative (B) and Inherently Toxic to the Environment (iT_E) during the categorisation of the DSL. Three of the four B and iT_E chemicals are prioritised for further assessment under the Chemicals Management Plan (CMP) (Government of Canada, 2013a).

European Union

In the European Union, two chemicals in this group (benzyl-$C_{12\text{-}16}$-alkyldimethylammonium chlorides and benzyl-$C_{16\text{-}18}$-alkyldimethylammonium chlorides) are currently registered for use under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation (ECHA, 2015c). The remaining chemicals in this group have been pre-registered, but have not yet undergone the full registration process (ECHA, 2015b).

United States of America

Most of the chemicals in this group (nine substances) are listed on the inventory of chemicals manufactured or processed in the USA, as published under the *Toxic Substances Control Act 1976* (TSCA) (US EPA, 2014).

A number of chemicals in this group (four substances) are listed as United States High Production Volume (US HPV) chemicals, indicating that at least 454 tonnes of the chemicals are manufactured/imported into the United States of America per year (US EPA, 2010).

The United States Environmental Protection Agency (US EPA) has imposed Significant New Use Rules for benzyl(hydrogenated tallow alkyl)dimethylammonium chloride. Under the rule, new uses of the chemical require notification to the US EPA (United States Government, 2011).

Environmental Exposure

Chemicals in this group have widespread domestic and industrial uses, many of which result in eventual release of the chemicals into sewage treatment plants (STPs). Depending on degradation and partitioning processes of chemicals in STPs, some fraction of the quantity of chemicals in wastewater entering STPs can be emitted to rivers or oceans in treated effluent, or to soil through application of biosolids to agricultural land (Struijs, 1996; Zhang, et al., 2015).

Based on the partitioning properties of quaternary ammonium compounds, approximately 90% of the total volume of these chemicals entering a typical STP may be removed by adsorption to sludge (Boethling, 1984), which may be applied to land as biosolids. Hence, emissions of chemicals in this group to both environmental surface waters and soils are considered as part of this assessment.

The chloride counter ions of the chemicals in this group occur naturally in the environment, and the background concentration of chloride is unlikely to be perturbed by its use as counterions in the substances of this group. Hence, the environmental fate and effects of chlorides ions are not further considered in this assessment.

Environmental Fate

Dissolution, Speciation and Partitioning

The quaternary ammonium cations from substances in this group partition between water and sediment, or remain in soil when released from industrial uses.

If discharged into natural waters, the chemicals are expected to dissociate and release their quaternary ammonium cations and chloride anions. The quaternary ammonium cations can adsorb to clays and natural organic materials, such as humic substances (de Oude, 1992).

Adsorption coefficient values reported for the cationic surfactants in this group indicate strong adsorption and immobility in soil (Boethling and Mackay, 2000; LMC, 2013; US EPA, 2006b; Zhang, et al., 2015). The strong binding of benzalkyl quaternary ammonium surfactants to soil is attributable to the strong electrostatic attraction of cationic surfactants to soil (Boethling, 1984).

Degradation

The quaternary ammonium cations of substances in this group are biodegradable.

The degradation pathway for benzalkyl quaternary ammonium cations is considered to occur through *N*-dealkylation, followed by *N*-debenzylation and *N*-demethylation (Zhang, et al., 2015). Benzalkyl quaternary ammonium compounds with longer alkyl chains are relatively more persistent (Madsen, et al., 2001). Although benzalkyl chain quaternary ammonium compounds have decreased biodegradability compared to their mono- and di-alkyl chain analogues (Ivankovic and Hrenovic, 2010; Ying, 2006; Zhang, et al., 2015), they are nevertheless expected to be biodegradable in water (de Oude, 1992; Madsen, et al., 2001; Scott and Jones, 2000).

Benzalkyl chain quaternary ammonium compounds in this group are mixtures of compounds with linear alkyl chains made up of seven to 22 carbons. Information available for benzalkyl chain quaternary ammonium compounds with $C_{12\text{-}16}$ alkyl chains was used as representative data to characterise the biodegradability of the chemicals in this group. In a study conducted in accordance with OECD Test Guideline (TG) 301B, the biodegradation based on CO_2 evolution was determined to be 95.5% in 28 days (ECHA, 2015a). In a separate study conducted in accordance with OECD TG 301D, the biodegradation based on O_2 consumption was 63% of theoretical oxygen demand over 28 days (ECHA, 2015a).

This chemical is also degradable in sewage treatment plant sludge and in soil. In an aerobic sewage treatment plant simulation test conducted in accordance with OECD TG 303A, 100% dissolved organic carbon (DOC) removal from waste water was observed after 40 days with indications that removed substances were ultimately biodegraded (ECHA, 2015a). In soil, 64% biodegradation was observed after 70 days based on CO_2 evolution (ECHA, 2015a).

Bioaccumulation

The quaternary ammonium cations from substances in this group have low bioaccumulation potential in aquatic organisms.

Quaternary ammonium cations are surfactants and bioaccumulation for most classes of surfactants is generally below the level of concern (McWilliams and Payne, 2001). This is in agreement with experimental data available for the chemicals in this group.

Most surfactants tend to be retained on epithelial surfaces, rather than cross cellular membranes (de Oude, 1992; McWilliams and Payne, 2001). Reported bioconcentration factor (BCF) values are often overestimated as differentiating between parent compounds and metabolites or other breakdown products is difficult for experimental studies with radiolabelled compounds (McWilliams and Payne, 2001).

The reported BCF for benzalkyl chain quaternary ammonium compounds with C_{10-14} alkyl chains in the fish *Cyprinus carpio* was in the range of 0.2 to 5.9 L/kg at a test concentration of 0.5 mg/L and 1.8 to 8.6 L/kg at a test concentration of 0.05 mg/L (SYKE, 2014). The BCF for benzalkyl chain quaternary ammonium compounds with C_{12-16} alkyl chains in the fish *Lepomis macrochirus* was 79 L/kg (whole body wet weight) after 35 days of exposure at a test concentration of 0.076 mg/L (ECHA, 2015a).

Transport

The chemicals in this group are not expected to undergo long-range transport based on their low volatility, strong binding to soil and their rapid biodegradability in the environment.

Quaternary ammonium cations adsorbed to clays, sediment and soil containing organic carbon (de Oude, 1992; Ivankovic and Hrenovic, 2010) are strongly bound and immobile (Zhang, et al., 2015).

Predicted Environmental Concentration (PEC)

Predicted environmental concentrations for the chemicals in this group were estimated using standard exposure modelling.

No Australian environmental monitoring data were located for the chemicals in this group. According to overseas monitoring data, high removal efficiency of 90% or greater is obtained for quaternary ammonium surfactants in STPs (Boethling, 1984). Once removed, biodegradation occurs on sludge solids (de Oude, 1992). Based on standard Australian exposure modelling parameters (EPHC, 2009), and assuming 90% removal at the sewage treatment plant, the PEC in receiving waters is calculated to be 8.5 µg/L for chemicals with introduction volumes of 100 tonnes per annum (in accordance with the IMAP Framework (NICNAS, 2013a)). For chemicals that have reported introduction volumes higher than 100 tonnes (benzyl-C_{12-18}-alkyldimethylammonium chlorides and benzyl-C_{12-16}-alkyldimethylammonium chlorides), the PEC in receiving waters is calculated to be 85 µg/L based on introduction volumes of 1000 tonnes (the upper volume in the reporting band).

A recent review of environmental monitoring studies for quaternary ammonium compounds has reported the concentration of these compounds in sewage, sludge, surface water and sediment across a number of countries including China, Taiwan, Poland, Austria, Spain, England and the USA (Zhang, et al., 2015). The total concentration of benzalkyl chain quaternary ammonium compounds measured in a Taiwanese river was up to 65 µg/L. The measured concentration in other regions ranged from mainly below 1 µg/L (Austria) to 342 µg/L (Poland) (Zhang, et al., 2015).

Environmental Effects

Effects on Aquatic Life

The chemicals in this group have the potential to cause toxic effects in aquatic organisms across multiple trophic levels depending on the bioavailability of the surface-active quaternary ammonium cations.

Benzalkyl quaternary ammonium salts have increased toxicity to the aquatic invertebrate, *Daphnia magna,* compared to their mono-alkyl quaternary ammonium analogues (Ivankovic and Hrenovic, 2010). Aquatic invertebrates are also generally the most sensitive taxon with respect to toxic effects of chemicals in this group. Toxicity of quaternary ammonium compounds to aquatic

organisms is not due to bioaccumulation, but due to membrane surfaces being disrupted by the alkyl chains of cationic surfactants, which results in a loss of membrane integrity (McWilliams and Payne, 2001; Zhang, et al., 2015).

In general, laboratory-derived toxicity values are many times lower than field toxicity values (de Oude, 1992), which suggests that quaternary ammonium cations are largely sorbed to particulate matter and become less bioavailable under environmental conditions.

Acute toxicity

Due to insufficient toxicity data available for some of the chemicals in the group, data available for benzalkyl quaternary ammonium compound with C_{12-16} alkyl chains and those with C_{12-18} alkyl chains are presented as representative toxicity data for the chemicals in this group.

The following measured median lethal concentration (LC50) and median effective concentration (EC50) values for model organisms across three trophic levels were reported in the scientific literature (Madsen, et al., 2001), the databases included in the OECD QSAR Toolbox (LMC, 2013), the United States National Library of Medicine Hazardous Substances Data Bank (US NLM, 2013), and the New Zealand Chemical Classification and Information Database (EPA, 2015) for (a) benzyl-C_{12-16}-alkyldimethylammonium chlorides (CAS RN 68424-85-1) and (b) benzyl-C_{12-18}-alkyldimethylammonium chlorides (CAS RN 8001-54-5):

Taxon	Endpoint	Method
Fish	(a) 96 h LC50 = 0.064 mg/L	Experimental *Oncorhynchus mykiss* (Rainbow trout) Static
	(b) 96 h LC50 = 0.28 mg/L	Experimental *Pimephales promelas* (Fathead minnow) Static-renewal
Invertebrates	(a) 48 h EC50 = 0.037 mg/L	Experimental *Daphnia magna* (Water flea) Static
	(b) 48 h EC50 = 0.0059 mg/L	Experimental *Daphnia magna* (Water flea) Static

Taxon	Endpoint	Method
Algae	(a) 96 h EC50 = 0.67 mg/L	Experimental *Chlorella pyrenoidosa* (Green algae) Static
	(b) 96 h EC50 = 0.085 mg/L	Experimental *Scenedesmus pannonicus* (Green algae) Static

While the chemicals in this group also exhibit microbial toxicity, they are not expected to affect wastewater treatment processes at the concentrations found in STPs (Scott and Jones, 2000). Under environmental conditions, microbial populations are expected to be acclimatised to commonly used quaternary ammonium cations (Boethling, 1984; de Oude, 1992).

Chronic toxicity

The following no-observed adverse effect-concentration (NOAEC) and no-observed effect concentration (NOEC) values for model organisms across two trophic levels were reported in the databases included in the OECD QSAR Toolbox (LMC, 2013) and the New Zealand Chemical Classification and Information Database (EPA, 2015) for (a) benzyl-$C_{12\text{-}16}$-alkyldimethylammonium chlorides (CAS RN 68424-85-1) and (b) benzyl-$C_{12\text{-}18}$-alkyldimethylammonium chlorides (CAS RN 8001-54-5):

Taxon	Endpoint	Method
Fish	(b) 34 d NOAEC = 0.032 mg/L	Experimental *Pimephales promelas* (Fathead minnow) Static
Invertebrates	(a) 21 d NOEC = 0.00415 mg/L	Experimental *Daphnia magna* (Water flea) Renewal

Effects on Sediment-Dwelling Life

There are no suitable data available to evaluate the effects of these chemicals on sediment-dwelling organisms.

Effects on Terrestrial Life

There are no suitable data available to evaluate the effects of these chemicals on terrestrial life.

A similar toxicity range is observed between alkyl and benzalkyl chain quaternary ammonium compounds for aquatic organisms. The mode of toxicity is also expected to be similar between these two groups of chemicals. Based on the IMAP Environment Tier II assessment for Mono- and Di-alkyl Quaternary Ammonium Surfactants (NICNAS, 2016), benzalkyl chain quaternary ammonium compounds are considered to have some potential to cause toxic effects to terrestrial organisms depending on the bioavailability of the surface active cations in soil.

Predicted No-Effect Concentration (PNEC)

The aquatic PNEC for chemicals in this group was calculated based on the bioavailable fraction of each chemical estimated to be present in environmental waters.

Laboratory-derived toxicity values in clean test waters overestimate toxicity under environmental conditions as quaternary ammonium surfactants sorb to suspended solids and have a tendency to form complexes with anionic surfactants in natural waters (de Oude, 1992). As a result, the bioavailable fraction of quaternary ammonium surfactants in environmental waters is reduced by up to 95% (Landis, et al., 1993). To correct for this reduction in bioavailability under environmental exposure conditions, the measured ecotoxicity endpoints in laboratory tests (generally conducted in clean synthetic test waters) can be multiplied by a maximum mitigation factor of 20 (Landis, et al., 1993).

The PNEC for all chemicals in the group is taken to be equal to the PNEC calculated for benzyl-$C_{12\text{-}16}$-alkyldimethylammonium chlorides (CAS RN 68424-85-1). Aquatic invertebrates are the most sensitive taxon to toxic effects of the chemicals in this group, based on the available information. The PNEC for the chemicals in this group was, therefore, calculated to be 0.83 µg/L based on the 21 d NOEC of 0.00415 mg/L for *D. magna*. The laboratory chronic toxicity value for this aquatic invertebrate species was divided by an assessment factor of 100 to account for both interspecies variation and the relative lack of chronic aquatic toxicity data available for chemicals in this group. The value derived from this procedure was then multiplied by a factor of 20 to account for the 5% bioavailable fraction in environmental waters.

Categorisation of Environmental Hazard

The categorisation of the environmental hazards of the substances in this group according to domestic environmental hazard thresholds are presented below (EPHC, 2009; NICNAS, 2013a):

Persistence

Not Persistent (Not P). Based on results obtained from biodegradation studies, all chemicals in this group are categorised as Not Persistent.

Bioaccumulation

Not Bioaccumulative (Not B). Based on the available measured bioconcentration data, all chemicals in this group are categorised as Not Bioaccumulative.

Toxicity

Toxic (T). Based on available acute ecotoxicity values below 1 mg/L and chronic ecotoxicity values below 0.1 mg/L, all chemicals in this group are categorised as Toxic.

Summary

All chemicals in this group are categorised as:

- Not P
- Not B
- T

Risk Characterisation

Based on the PEC and PNEC values determined above, the following Risk Quotients (RQ = PEC ÷ PNEC) have been calculated for release of chemicals in this group into rivers:

Chemical	PEC (µg/L)	PNEC (µg/L)	RQ
benzyl-C_{12-16}-alkyldimethylammonium chlorides and benzyl-C_{12-18}-alkyldimethylammonium chlorides	85	0.83	102.4
All remaining chemicals in this group	8.5	0.83	10.2

An RQ of greater than one indicates that industrial uses of all chemicals in this group may pose an unreasonable risk to the environment, as environmental concentrations may exceed levels that cause harmful effects. It is noted that these RQ values are derived using reasonable worst case exposure scenarios and incorporate standard exposure mitigation factors which suggest up to 90% removal of benzalkyl chain quaternary ammonium cations from waste water in STPs through adsorption to sludge and biodegradation (EPHC, 2009).

International environmental monitoring data have been used in previous assessments to refine RQ values. In the IMAP Environment Tier II assessment for Mono- and Di-alkyl Quaternary Ammonium Surfactants (NICNAS, 2016), the cumulative surface water concentrations of mono- and di-alkyl quaternary ammonium surfactants in Taiwan suggested that these chemicals did not pose a high level of environmental concern.

However, these data also show concentrations of total benzalkyl quaternary ammonium compounds in a Taiwanese river water of up to 65 µg/L. If this value is used in place of the PEC for the chemicals in this group, the resultant RQ is 78 for Australian surface waters, which suggests that the concentration of benzalkyl chain quaternary ammonium in surface waters exceeds the level of concern. Therefore, industrial uses of all chemicals in this group are considered to potentially pose an unreasonable risk to the environment.

Key Findings

Based on available use and exposure information, chemicals in this group are widely used in a range of products including cosmetics, and cleaning and washing agents. Many of these use patterns can lead to release of the chemicals in this group into sewage treatment plants.

The chemicals in this group are highly toxic to aquatic organisms. While they are susceptible to rapid biodegradation in water and soil, have low bioavailability in soil, and have high removal rates in sewage treatment plants, estimated environmental concentrations in river water in Australia significantly exceed the level of concern for aquatic life. International environmental monitoring data show that benzalkyl chain quaternary ammonium substances can occur in river water at similar concentrations to those calculated in this assessment.

This assessment did not identify any Australian environmental monitoring data for benzalkyl chain quaternary ammonium compounds that could be used to refine the domestic risk characterisation.

The chemicals in this group are not PBT substances according to domestic environmental hazard criteria.

Recommendations

It is recommended that the benzalkyl chain quaternary ammonium substances in this group be considered for further assessment of environmental concerns at Tier III level under the IMAP framework.

The Tier III environmental risk assessment of these substances will focus on outstanding areas of uncertainty in the assessment, including the extent of environmental exposure resulting from industrial use in Australia and toxicity across various organisms under environmental conditions. Further clarification regarding these uncertainties will allow the exploration of appropriate risk management options.

Environmental Hazard Classification

In addition to the categorisation of environmental hazards according to domestic environmental thresholds presented above, the classification of the environmental hazards of (a) quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl,chlorides (CAS RN 68424-85-1) and (b) quaternary ammonium compounds, alkylbenzyldimethyl, chlorides (CAS RN 8001-54-5) according to the third edition of the United Nations' Globally Harmonised System of Classification and Labelling of Chemicals (GHS) is presented below (UNECE, 2009):

Hazard	GHS Classification (Code)	Hazard Statement
Acute Aquatic	(a) and (b) Category 1 (H400)	Very toxic to aquatic life
Chronic Aquatic	(a) Category 1 (H410)	Very toxic to aquatic life with long lasting effects
	(b) Category 2 (H411)	Toxic to aquatic life with long lasting effects.

The classification of the aquatic hazards posed by these chemicals has been performed based on the toxicity data presented in this assessment. The long-term aquatic hazard classification for both chemicals was determined based on the most stringent outcome method of the GHS, taking into account the rapid degradability of these substances and the available chronic ecotoxicity data (UNECE, 2007).

The remaining chemicals in this group are not classified for this assessment.

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