

Cyclic volatile methyl siloxanes: Environment tier II assessment

16 June 2020

CAS Registry Numbers: 541-05-9, 556-67-2, 541-02-6, 540-97-6, 107-50-6, 69430-24-6.



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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

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Acronyms & Abbreviations

Grouping Rationale

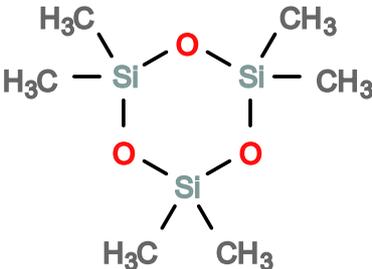
This Tier II assessment considers the environmental risks resulting from industrial uses of a group of six cyclic polyorganosiloxanes. The common structural feature of these industrially important silicones is a siloxane ring composed of alternating silicon and oxygen atoms where each silicon atom is also bonded to two methyl groups. The first five chemicals in this group comprise a homologous series of discrete cyclic dimethyl siloxanes in which there are from three to seven silicon atoms in the siloxane ring. The sixth member of this group is a mixture of these discrete cyclic dimethyl siloxanes.

The global production volume for some chemicals in this group is large. Globally, the majority of the production volume is consumed in the synthesis of a variety of polymeric silicones. However, the chemicals are frequently used in consumer products, including cosmetics and personal care products. The chemicals in this group are volatile and the majority of the quantity used in some consumer products are emitted to the atmosphere as a normal part of their use. Cyclic volatile methyl siloxanes present in some consumer products may also be released into domestic and industrial waste waters nationwide. Consequently, consumer uses of these chemicals will result in their environmental exposure through both direct emissions to the atmosphere and indirect emissions resulting from the treatment of waste water in sewage treatment plants (STPs).

There are concerns that some chemicals in this group have the potential to harm the environment based on their persistence and potential for bioaccumulation. This assessment will evaluate the currently available environmental hazard data for cyclic volatile methyl siloxanes and will seek to establish whether emissions of these chemicals to the environment in Australia pose a concern.

Chemical Identity

All of the chemicals in this group are cyclic oligomers. The repeating structural unit in these oligomers is a dimethyl siloxane moiety that is connected to the two adjacent dimethyl siloxanes in the ring through shared oxygen atoms. The dimethyl siloxane moiety is a di-functional chain extension unit and is given the symbol "D" in the nomenclature of silicone chemistry. As cyclic dimethyl siloxanes contain no end-groups, individual homologues can be distinguished simply by the number of dimethyl siloxane (or D) units in their structure. Hence, D3 is a commonly used synonym for the dimethyl siloxane cyclic trimer below, which contains three dimethyl siloxane units (Moretto, et al., 2012).

CAS RN	541-05-9
Chemical Name	Cyclotrisiloxane, hexamethyl-
Synonyms	D3 hexamethylcyclotrisiloxane
Structural Formula	
Molecular Formula	C ₆ H ₁₈ O ₃ Si ₃
Molecular Weight (g/mol)	222.47
SMILES	C[Si]1(C)O[Si](C)(C)O[Si](C)(C)O1

CAS RN	556-67-2
Chemical Name	Cyclotetrasiloxane, octamethyl-

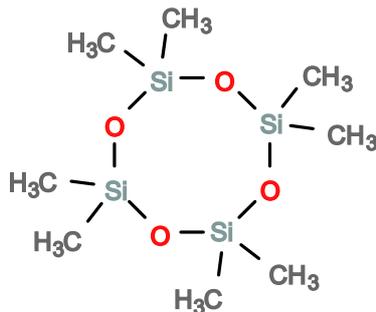
Synonyms

D4

octamethylcyclotetrasiloxane

cyclomethicone 4

Structural Formula



Molecular Formula

 $C_8H_{24}O_4Si_4$

Molecular Weight (g/mol)

296.63

SMILES

C[Si]1(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O1

CAS RN

541-02-6

Chemical Name

Cyclopentasiloxane, decamethyl-

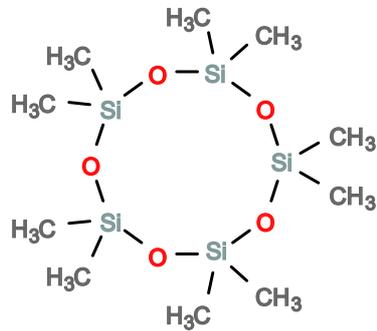
Synonyms

D5

decamethylcyclopentasiloxane

cyclomethicone 5

Structural Formula



Molecular Formula $C_{10}H_{30}O_5Si_5$

Molecular Weight (g/mol) 370.79

SMILES C[Si]1(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O1

CAS RN 540-97-6

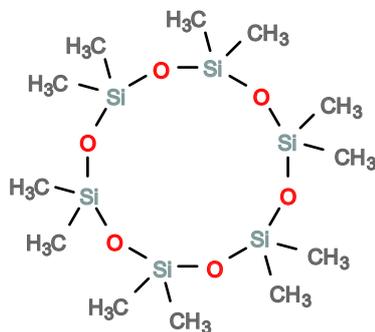
Chemical Name Cyclohexasiloxane, dodecamethyl-

D6

Synonyms dodecamethylcyclohexasiloxane

cyclomethicone 6

Structural Formula



Molecular Formula $C_{12}H_{36}O_6Si_6$

Molecular Weight (g/mol) 444.95

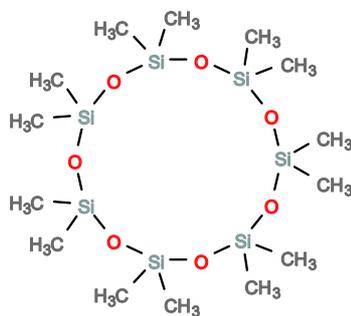
SMILES C[Si]1(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O1

CAS RN 107-50-6

Chemical Name Cycloheptasiloxane, tetradecamethyl-

Synonyms D7
tetradecamethylcycloheptasiloxane

Structural Formula



Molecular Formula $C_{14}H_{42}O_7Si_7$

Molecular Weight (g/mol) 519.11

SMILES C[Si]1(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O1

This substance is a variable mixture of the discrete cyclic dimethyl siloxane oligomers in this group (HSDB, 2018). In the past, D4 and D5 were the predominant constituents of this substance when it was used in the formulation of cosmetics and personal care products (Johnson Jr, et al., 2011). However, more recent analytical information on the chemical composition of cosmetic and personal care products on the market indicates that D5 is now the main cyclic volatile methyl siloxane present in these products, and D4 is presumed to be present only as an impurity (Dudzina, et al., 2014).

CAS RN 69430-24-6

Chemical Name	Cyclosiloxanes, dimethyl
Synonyms	cyclomethicone polydimethyl cyclic siloxanes

Physical and Chemical Properties

The chemicals in this group are volatile and very hydrophobic. This combination of properties has made it difficult to determine reliable experimental values for environmentally relevant properties of cyclic volatile methyl siloxanes including their water solubilities and octanol-water partition coefficients (K_{ow}). Measured values for the partitioning properties of D4, D5 and D6 used in this assessment have been selected from a recent critical review of the available environmental property data for this class of chemicals (Xu S, et al., 2014).

The description of the physical form and values for the melting and boiling points of these three chemicals are taken from the peer-reviewed records for each substance as listed on the Hazardous Substances Data Bank (HSDB) of the United States (US) National Library of Medicine (HSDB, 2018):

Chemical	D4	D5	D6
Physical Form	liquid	liquid	liquid
Melting Point	17.5°C	-38°C	-3°C
Boiling Point	176°C	210°C	245°C
Vapour Pressure	132 Pa (25°C)	23 Pa (25°C)	3 Pa (25°C)
Water Solubility	0.056 mg/L (23°C)	0.017 mg/L (23°C)	0.005 mg/L (23°C)
Ionisable in the Environment?	no	no	no
log K_{ow}	6.98 (25°C)	8.07 (25°C)	8.87 (24°C)

The three homologues D4, D5, and D6, are volatile or highly volatile liquids under ambient conditions. They are only very slightly soluble in water and have a very strong tendency to partition from water into octanol, which shows that all three chemicals are

very hydrophobic.

D3 is a solid (melting point 64°C) with a high (extrapolated) solid vapour pressure of 671 Pa at 25°C. It is also a reactive chemical and hydrolyses rapidly in water to form linear dimethyl siloxanes (OECD, 2008). Consequently, the water solubility and octanol-water partitioning of D3 are of limited relevance to the environmental fate of this chemical.

D7 is a volatile liquid with a vapour pressure of 1.49 Pa at 25°C (LMC, 2018). No reliable measured values were identified for the water solubility or K_{ow} of this chemical. However, D7 is expected to be the most hydrophobic member of this group based on the trend in measured water solubility and octanol-water partitioning for the lower molecular weight homologues in the series.

Cyclomethicone is a mixture of cyclic dimethyl siloxane oligomers and the properties of the substance depend on the blend of oligomers. The reported properties for commercial blends indicate that this substance is a colourless liquid that has low viscosity and is insoluble in water. It is also a volatile substance and the majority evaporates from surfaces, which is a functional requirement for some applications in cosmetics and personal care products (Andriot, et al., 2008; Johnson Jr, et al., 2011).

The chemicals in this group have low surface tension and they are, therefore, able to wet (spread across) a range of different surfaces (Johnson Jr, et al., 2011). This property is an important functional requirement for many commercial applications of these chemicals (Andriot, et al., 2008).

Import, Manufacture and Use

Australia

Both D4 and D5 were reported to have industrial uses under previous mandatory and/or voluntary calls for information conducted by NICNAS. The total volume of D5 introduced was reported to be low and to be for use in cosmetics or in site-limited industrial processes.

All chemicals in this group except D7 have reported uses in marine and automotive aftermarket products, and industrial products. The product types where these chemicals are reported to be used include sealants and adhesives (D4), cleaning products (D5 and D6), polishes (D4, D5, and D6), and waxes (D3, D4, D5, D6, and cyclomethicone).

No specific Australian use, import, or manufacturing information has been identified for D7.

Cyclomethicone is approved for use as an excipient in topical medicines (TGA, 2018). Non-industrial uses of cyclic volatile methyl siloxanes are outside the scope of this assessment.

International

The main industrial use for cyclic volatile methyl siloxanes is as intermediates in the manufacture of polydimethylsiloxane (PDMS) polymers. These polymers are the major constituent of a range of silicone fluids and they are also precursors to silicone elastomers. Silicone fluids and elastomers are produced in large volumes globally and they have a wide range of applications in products and articles (Andriot, et al., 2008; Colas, 2005; Moretto, et al., 2012). D4 is the most important cyclic dimethyl siloxane used in the manufacture of polydimethylsiloxanes which involves polymerisation of the oligomer in closed systems (Moretto, et al., 2012; Rich, et al., 1999). The sole use of D3 is as an intermediate in the manufacture of silicones in the United States of America (USA), Europe and Japan (OECD, 2008).

Most of the discrete chemicals in this group are known to have high global production volumes. In the USA, more than 138 000 tonnes of D4 and more than 43 400 tonnes of D5 were imported or manufactured in 2012 (HSDB, 2018). The production volume for D6 in the USA in 2007 was 7303 tonnes, which represented 61% of global production (OECD, 2009). In the European Union, 3221 tonnes of D3 was produced in 2001 (OECD, 2008). No global production information was identified for D7.

In addition to high-volume uses as industrial intermediates, chemicals in this group have multiple applications in cosmetics and personal care products (HSDB, 2018). They are solvents that function as volatile carriers of the active ingredients used in a range of spray-on and roll-on personal care products, including antiperspirants, deodorants and hair spray. In these applications,

the cyclic volatile methyl siloxane carrier readily evaporates from the skin surface leaving the active ingredients behind (Andriot, et al., 2008).

Cyclic volatile methyl siloxanes are also used in cosmetics such as liquid foundations, in other hair care products such as hair conditioners, and in various skin lotions including face creams and sun screens (Dudzina, et al., 2014; Horii and Kannan, 2008). They are used in skin care products to improve spreading of the liquid formulations across the skin surface (Andriot, et al., 2008).

The volume of cyclic volatile methyl siloxanes used in personal care products are significant. For example, it was estimated that the cumulative volume of D4, D5 and D6 used in the US personal care market in 2009 was more than 31 000 tonnes (Reisch, 2011).

There is a diverse range of other industrial applications for the chemicals in this group: D4 is used as a fuel additive, and is also used in washing and cleaning products, surface treatments, and paints; D5 is used as a dry cleaning solvent; D6 is used as a defoamer; and cyclomethicone has uses in glass and specialty cleaners, lubricants, and penetrating oils (HSDB, 2018).

Environmental Regulatory Status

Australia

The use of 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

All of the chemicals in this group except D7 and cyclomethicone are identified as high-production volume (HPV) chemicals by the OECD, which indicates that more than 1000 tonnes of each chemical are produced per year in at least one member country. The four HPV chemicals in this group have been sponsored for assessment under the cooperative Chemicals Assessment Programme by the USA (OECD, 2015).

The Screening Information Dataset (SIDS) Initial Assessment Reports (SIAR) for D3 and D6 have both been published (OECD, 2018). The conclusion of the SIAR for D3 is that this chemical has a low environmental hazard profile and that it is currently a low priority for further work (OECD, 2008). The conclusion of the SIAR for D6 is that there are sufficient data to characterise the environmental hazards of this chemical and that it has the potential to bioaccumulate. D6 is not toxic at the limit of its water solubility and on this basis it was concluded that the chemical does not possess properties indicating a hazard to the environment (OECD, 2009).

The assessments for D4 and D5 have not yet been published.

Canada

D4, D5, and D6 were all categorised as Persistent (P), Bioaccumulative (B) and Inherently Toxic to the Environment (iT_E) during the Categorization of the Domestic Substances List (DSL) (Environment Canada, 2013). All three chemicals were subsequently prioritised for screening assessments under the Challenge program.

The ecological screening assessment for D4 concluded that this substance is entering or may be entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity (ECCA, 2008a). D4 was subsequently added to Schedule 1 of the *Canadian*

Environmental Protection Act, 1999 (The List of Toxic Substances). The Government of Canada is developing measures to control the potential risks from uses of this substance. These include preventing or minimizing releases of D4 to the environment in industrial effluents, reassessing the use of D4 in pesticides, and ongoing monitoring of D4 in the environment (Government of Canada, 2014).

Following a scientific review of the screening assessment of D5, it was concluded that this chemical does not pose a danger to the environment in Canada. It was further concluded that projected future uses of this chemical will not pose a danger to the environment (ECCA, 2012). The Government of Canada has concluded that D5 is not entering the environment in a quantity or under conditions that constitute a danger to the environment (Government of Canada, 2012).

The ecological screening assessment of D6 concluded that this substance does not meet the criteria for persistence and bioaccumulation potential as set out in the *Persistence and Bioaccumulation Regulations* of the *Canadian Environmental Protection Act, 1999*. The chemical is being considered for environmental monitoring under the Chemicals Management Plan (ECCA, 2008b).

Cyclomethicone and D3 were both categorised as P, not B and iTE during the Categorization of the DSL (Environment Canada, 2013). Both chemicals have been prioritised for a screening assessment under the third phase of the Chemicals Management Plan (2016–2020) (Government of Canada, 2017).

D7 is not on the DSL.

European Union

All of the chemicals in this group are either registered (D3, D4, D5 and D6) or pre-registered (D7 and cyclomethicone) under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation (ECHA, 2016; 2017b).

The Member State Committee has adopted a decision that both D4 and D5 meet the criteria for very persistent (vP) and very bioaccumulative (vB) chemicals under Annex XIII of REACH (ECHA, 2015). Uses of D4 and D5 in wash-off cosmetic products are restricted under Annex XVII of REACH. Wash-off cosmetic products, which are defined as those that under normal conditions are washed off with water after application, are not to be placed on the market if they contain D4 or D5 at concentrations equal to or greater than 0.1% by weight (European Commission, 2018). An intent to register a restriction proposal has also been submitted which would limit the concentration of D4 or D5 to not more than 0.1% in leave-on personal care products and other consumer/professional products (such as dry cleaning, waxes and polishes, washing and cleaning products) (ECHA, 2017a).

D4, D5 and D6 have been the subject of informal hazard assessment and risk management option analysis under the substances of very high concern (SVHC) roadmap (ECHA, 2018b). Germany and the European Chemicals Agency have registered intentions to prepare Annex XV dossiers that would identify all three chemicals as SVHCs under REACH (ECHA, 2018a).

United States of America

All of the chemicals in this group except D7 are existing chemicals under the Toxic Substances Control Act (TSCA) (US EPA, 2018b).

D4 is on the list of chemicals in the 2014 update to the US Environmental Protection Agency (EPA) TSCA Work Plan for Chemical Assessment. This list identifies existing chemicals that the US EPA is considering for assessment (US EPA, 2014b). An Enforceable Consent Order under Section 4 of TSCA is also in place for this chemical. The Consent Order requires environmental testing for the presence of D4 in the influents, effluents, and biosolids of waste water treatment plants, and in the sediment, surface water, and biota (benthic and fish species) of surface waters that are receiving treated effluent. The testing is to be conducted at multiple sites including in the vicinity of facilities that are manufacturing and/or processing D4, which includes product formulators (US EPA, 2014a). Information provided for this assessment by Industry indicates that a final report on this monitoring program was submitted to the US EPA in September 2017.

D3, D4, D5, and D6 are listed on the US HPV Challenge Program Chemical List, which indicates that these chemicals are manufactured in or imported into the USA in amounts equal to or greater than one million pounds (454 tonnes) per year (US EPA, 2018a).

Japan

All of the chemicals in this group except D7 are existing chemical substances under the *Chemical Substances Control Law* and they all belong to the cyclic polyalkyl (C1–20) siloxane group (MITI Number 7-475) (NITE, 2017).

Environmental Exposure

All of the chemicals in this group are synthetic substances and their occurrence in the environment results exclusively from human activity.

Chemicals in this group are known to have multiple sources of emission to the atmosphere based on international air monitoring studies (Genualdi, et al., 2011). These emissions are positively correlated with population density and they are typically concentrated in urban areas (Janecek, et al., 2017). Emissions to the air compartment can be from diffuse sources such as uses of cosmetics and personal care products in domestic situations (Yucuis, et al., 2013). Diffuse emissions may also occur as a result of the thermal degradation of silicone fluids (Rich, et al., 1999), or from the release of residual cyclic dimethyl siloxane oligomers that are present in silicone products and articles (Rücker and Kümmerer, 2015). Emissions also occur from multiple point sources such as STPs and landfills (Wang, et al., 2015; Xu L, et al., 2017). All of these known emission sources are expected to be relevant to the environmental exposure of cyclic volatile methyl siloxanes in Australia.

Cyclic volatile methyl siloxanes are also washed down the drain into waste water from the use of some personal care and cleaning products in domestic situations. The subsequent treatment of this domestic waste water in STPs is a major pathway for the emission of these chemicals to surface waters, sediments and soil (Mackay, et al., 2015a; Rücker and Kümmerer, 2015). A recent study of the fate of D4, D5 and D6 in a secondary activated sludge waste water treatment plant in Canada showed that although typically >96% of the influent load of these chemicals was removed in the plant, up to 4% was released to surface waters in the effluent (Wang, et al., 2015). The removal of these chemicals was dominated by volatilization to the atmosphere and partitioning to sludge. In the case of D4, 78% of the total influent load was removed by volatilization. The less volatile and more hydrophobic D5 and D6 were principally removed by absorption to sludge: 55% of influent load for D5 and 59% for D6.

The majority of emissions from industrial uses of the chemicals in this group is expected to be to the air compartment in urban areas. Based on typical use patterns and emission pathways identified internationally, these chemicals are also expected to be released into waste water in Australia, predominantly from the use of consumer products in domestic situations. Cyclic volatile methyl siloxanes are known to be efficiently removed in secondary activated sludge waste water treatment plants through a combination of volatilization and partitioning to sludge. However, a small fraction of the load of these chemicals entering an STP will be discharged into receiving waters in treated effluent. They are also expected to be present as contaminants in dewatered and stabilised sewage sludge (biosolids), which is widely used as a soil conditioner on agricultural land in Australia (ANZBP, 2016). Hence, surface waters, sediments and soils in Australia are expected to contain the chemicals in this group, in addition to the air compartment which will receive the majority of emissions.

Environmental Fate

Partitioning

Chemicals in this group primarily partition to the atmosphere, but they also partition into sediments if they are released into water. Once in the atmosphere, transfer to other compartments is negligible.

Cyclic volatile methyl siloxanes rapidly evaporate from surfaces (including human skin) under ambient conditions. Consequently, most of the quantity of these chemicals used in some consumer products will partition into the atmosphere when they are used for their intended purpose (Mackay, et al., 2015a; Montemayor, et al., 2013). They also partition into the biogases produced during anaerobic digestion of sewage sludge and in landfills (Dewil, et al., 2006). Release of biogases from STPs and landfills is, therefore, another source of atmospheric emissions of these chemicals (Rücker and Kümmerer, 2015). In some waste disposal facilities, biogases are captured and burned to generate electricity. Contamination of these biogases with volatile organosiloxanes can pose significant operational issues as thermal degradation of organosilicon chemicals is known to foul gas engines and heat exchangers through the formation of abrasive silica residues (Dewil, et al., 2006).

The coefficients for partitioning between air and water (K_{AW}) for D4, D5 and D6 are high by comparison with many organic environmental contaminants: D4 (550 at 25°C); D5 (1445 at 25°C); and D6 (1023 at 24°C) (Xu S, et al., 2014). These uniformly high values indicate that all three chemicals are highly volatile from water and moist soil.

The coefficient for partitioning between octanol and air (K_{OA}) has also been determined for these three chemicals: D4 (log K_{OA} = 4.28 at 25°C); D5 (log K_{OA} = 4.94 at 25°C); and D6 (log K_{OA} = 5.86 at 24°C) (Xu S, et al., 2014). The K_{OA} parameter is an indicator of the tendency of a chemical to partition from the atmosphere to media which have a high proportion of organic carbon such as soils and aerosols. The K_{OA} values determined for D4, D5 and D6 are comparatively low (Kelly, et al., 2007). These chemicals are, therefore, expected to have a very low tendency to associate with aerosol particles and they are present predominantly in the gas phase in the atmosphere (Latimer, et al., 1998).

The chemicals in this group are very hydrophobic neutral substances. This would typically indicate a strong tendency to partition from water to organic carbon in soil or sediment. The high measured values for the organic carbon normalised adsorption coefficient (K_{OC}) for chemicals in this group are generally consistent with this expectation: D4 (log K_{OC} = 4.22); and D5 (log K_{OC} = 5.17) (Rücker and Kümmerer, 2015). However, as noted by Xu S, et al. (2014), these measured values are lower than would be expected for the partitioning to soil of neutral organic chemicals of comparable hydrophobicity. This may indicate a different mode of interaction between cyclic volatile methyl siloxanes and soil (or sediment) than occurs with neutral organic chemicals.

Chemicals in this group also partition from water to suspended organic matter and sediments. The coefficient for partitioning between suspended particles and water for D5 at 25°C is 29 582 L/kg and the coefficient for partitioning between sediment and water is 5916 L/kg (Mackay, et al., 2015a). The strong association between cyclic volatile methyl siloxanes and suspended solids and sediments contributes to the accumulation of these chemicals in the sediment compartment in the vicinity of outfalls from sewage treatment plants (Wang, et al., 2013). A level III fugacity calculation for the release of D5 in waste water from an STP in Canada found that 94% of the quantity of this chemical emitted to water in effluent would ultimately occur in the sediment compartment (Mackay, et al., 2015a).

Degradation

Chemicals in this group degrade slowly in the atmosphere and in sediments, but they degrade rapidly in dry soil.

The most important environmental degradation pathway for cyclic volatile methyl siloxanes is oxidation by hydroxyl radicals in the atmosphere (Xu S and Wania, 2013). The chemicals in this group undergo relatively slow indirect oxidation by hydroxyl radicals. According to a recent study, the atmospheric half-lives for D3, D4, and D5 at 25°C are 5.7 days, 4.5 days, and 4.2 days, respectively, assuming typical global average concentrations of hydroxyl radicals (Xiao, et al., 2015). These values are in generally good agreement with the established atmospheric half-lives for these three chemicals as determined in earlier studies (Rücker and Kümmerer, 2015). The atmospheric half-lives for all three chemicals determined in multiple studies all exceed the domestic criterion for persistence in the air compartment (half-life \geq 2 days).

No measured half-lives for the gas-phase oxidation of D6 and D7 were identified for this assessment. However, the rate of oxidation of cyclic volatile methyl siloxanes by hydroxyl radicals is known to increase as the number of oxidisable methyl groups increase (Xiao, et al., 2015). Accordingly, the half-life for oxidation of D6 in the atmosphere has been estimated as 3.3 days at 25°C by extrapolation from the recently remeasured half-lives for D4 and D5 (Panagopoulos and MacLeod, 2018). The estimated half-life for D6 also exceeds the categorisation criterion for persistence in air.

The oxidation of cyclic volatile methyl siloxanes in the atmosphere by hydroxyl radicals involves abstraction of hydrogen atoms from the methyl group (Xiao, et al., 2015). This initiates degradation of the parent chemical by chemical reactions which ultimately lead to the formation of silanols. These silanol transformation products are more polar than the parent cyclic siloxanes and they are removed from the atmosphere by wet deposition (i.e. removal in precipitation) (Janeček, et al., 2017).

D3 is hydrolytically unstable and has a short hydrolysis half-life of 23 minutes in water at neutral pH and 25°C. The hydrolysis of D3 is both acid and base-catalysed and the half-life of the chemical is significantly shorter under acid and alkaline conditions (e.g., < 1 minute at pH 9 and 25°C). The initial product of the hydrolysis of D3 is the linear trisiloxane, hexamethyltrisiloxanediol (CAS RN 3663-50-1). This primary hydrolysis product hydrolyses to the mononuclear dimethylsiloxane, dimethylsiloxane diol (DMSD; CAS RN 1066-42-8), which is the major degradation product in water at environmentally relevant concentrations (OECD, 2008).

The remaining discrete chemicals in this group also undergo hydrolysis in water although the rate of hydrolysis at neutral pH is slower than for D3 (Rücker and Kümmerer, 2015). For D4 and D5, the respective hydrolysis half-lives in water at pH 7 and 25°C

are 4.5 days and 66 days. The extrapolated half-life for hydrolysis of D6 is more than one year at pH 7 and 25°C. No hydrolysis half-life was identified for D7.

The chemicals in this group do not undergo significant aerobic microbial oxidation and this degradation pathway is not competitive with other dissipation pathways in water such as volatilization, hydrolysis and sorption to particulates (Rücker and Kümmerer, 2015).

Chemicals in this group undergo very slow degradation in sediments. The measured half-lives for D4 and D5 at 24°C are reported to be 242 days and 1200–2700 days, respectively, in aerobic sediments, and 365 days and 800–3100 days, respectively, in anaerobic sediments (ECHA, 2015). The extrapolated half-life for D6 in sediment is 5836 days (Panagopoulos and MacLeod, 2018). The long degradation half-lives for these three chemicals all significantly exceed the domestic categorisation criterion for persistence in the sediment compartment (half-life \geq 6 months).

The fate of cyclic volatile methyl siloxanes in soil is strongly dependent both on the mineralogy of the soil and soil moisture levels. In a highly weathered soil with a high clay content, the degradation half-lives for D4, D5 and D6 were all less than 2 days at the same relative humidity (32%; in a closed system). The rate of degradation was slower in soils with a lower proportion of different clay minerals. The relative importance of degradation as a dissipation pathway in soil decreases as the relative humidity increases. This is a result of the volatilisation of cyclic volatile methyl siloxanes from moist soils. For example, more than 80% of D4 applied to moist soil at 100% relative humidity was dissipated by evaporation in an open system as compared with less than 5% dissipation due to degradation under these exposure conditions (Xu S and Chandra, 1999).

The degradation of polyorganosiloxanes (including cyclic volatile methyl siloxanes) in soil is an abiotic process that is catalysed by clay minerals (Rücker and Kümmerer, 2015). In dry soils, the terminal organosilicon degradation product for D4, D5 and D6 is the mononuclear dimethylsiloxane, DMSD. The initial step in the degradation pathway involves hydrolytic cleavage of the siloxane ring to form the corresponding linear dimethylsiloxane diols, which are subsequently hydrolysed to the common degradant, DMSD. The ring-opening hydrolysis reaction is partially reversible and when the water content of soil increases self-condensation of linear dimethylsiloxane diols can reform cyclic volatile methyl siloxanes, such as D3 and D4 (Xu S, 1999). As discussed above, these chemicals are volatile from moist soil and they will tend to partition to the atmosphere. This provides another dissipation pathway (and source of atmospheric emissions) which will tend to limit the potential for accumulation of these chemicals or their likely degradation products in soil.

Bioaccumulation

D4, D5 and D6 can bioconcentrate in aquatic life.

A study on the bioaccumulation potential of D3 in aquatic life demonstrated some accumulation of the chemical in the tissues of rainbow trout (*Oncorhynchus mykiss*) after 14 days of continuous exposure to both the chemical and its hydrolysis products. A bioconcentration factor (BCF) for D3 of 100 ± 49 was derived based on the tissue content of the chemical measured at the conclusion of the exposure period (OECD, 2008).

D4 has a very high potential to bioconcentrate in fish under optimised exposure conditions (Fackler, et al., 1995). The steady state BCF for D4 in fathead minnows (*Pimephales promelas*) was determined to be 12 400 L/kg after 28 days continuous exposure to radiolabelled test material in soft water at 21–22°C in an enclosed flow-through system. This study did not identify any metabolites and the parent chemical was eliminated relatively slowly. The BCF value determined in this study significantly exceeds the domestic categorisation criterion for bioaccumulation (BCF \geq 2000 L/kg), which indicates that this chemical is an aquatic bioaccumulation hazard.

A recent review of the available studies on the bioconcentration of D5 in fish recalculated BCF values for this chemical in the range 1040 to 4920 L/kg wet weight (Gobas, et al., 2015). The review of these studies highlighted the fact that depuration of D5 in fish is more rapid than would be expected for a very hydrophobic organic chemical. The faster than expected elimination of D5 in fish is attributed to biotransformation of the chemical into polar metabolites.

The bioconcentration potential of D6 in aquatic life is moderate based on studies with fish and aquatic invertebrates (OECD, 2009). The steady state BCF for the chemical in the fathead minnow (*P. promelas*) is in the range 240–1160 L/kg based on total radioactivity taken up during a 49 day exposure phase; depuration of D6 was reported to be slow. The majority of the tissue content (79%) was parent chemical, although there was also an unidentified metabolite which accounted for 5% of the extracted radioactivity. The steady state BCF for the water flea, *Daphnia magna*, is approximately 2400 L/kg based solely on the uptake of the chemical.

No bioaccumulation data were identified for D7. This chemical is unlikely to be a bioconcentration hazard for aquatic life due to the expected low bioavailability of this very hydrophobic substance.

The chemicals in this group are all very hydrophobic neutral substances and there have been concerns that they will biomagnify in aquatic food webs. Multiple field studies on the fate of cyclic volatile methyl siloxanes in both freshwater and marine aquatic food webs have been conducted in order to determine whether these chemicals biomagnify (Gobas, et al., 2015). Trophic magnification of cyclic volatile methyl siloxanes has been demonstrated in some food webs, whereas in others trophic dilution occurs. These apparently contradictory findings have been attributed to the confounding effects of feeding by omnivorous itinerant organisms across food-chains (Powell, et al., 2018).

Hydrophobic organic chemicals that are not rapidly metabolised have a tendency to accumulate in air-breathing animals which may lead to biomagnification in mammalian food webs and the human food chain. However, it is also known that volatile chemicals which partition to the air compartment can be efficiently eliminated by exhalation in air-breathing animals. The potential for respiratory elimination by air-breathing animals is indicated by the magnitude of the K_{OA} parameters. Substances with a $\log K_{OA} < 6$ are not expected to bioaccumulate in air-breathing animals (Kelly, et al., 2007). The measured $\log K_{OA}$ values for D4, D5 and D6 are all less than 6 which indicates that they should not biomagnify in air-breathing animals. This expectation has been confirmed experimentally for D5 where respiratory elimination of this chemical in rats and humans has been demonstrated (Gobas, et al., 2015).

Transport

Chemicals in this group are transported over long distances through the atmosphere. Based on the partitioning properties of cyclic volatile methyl siloxanes they are not expected to deposit to terrestrial environments from the atmosphere. Transport of these chemicals through the atmosphere is, therefore, not anticipated to be a significant source of environmental exposure to terrestrial food chains.

Cyclic volatile methyl siloxanes are globally distributed atmospheric contaminants (Janecek, et al., 2017; R cker and K mmerer, 2015). Air sampling in the Arctic shows that D3 and D4 are the dominant oligomers present in these remote areas. The highest atmospheric concentrations for D3 and D4 were measured on the west coast of North America (including at high altitude sites), which may indicate atmospheric transport of these chemicals across the Pacific Ocean from emission sources in Asia. D3 and D4 were also both detected in air samples collected at the remote Cape Grim air monitoring station located in North West Tasmania, although the concentrations of these two chemicals at this site were low by comparison with concentrations measured in the Northern Hemisphere (Genualdi, et al., 2011).

The concentrations of some cyclic volatile methyl siloxanes in Arctic air are higher than the atmospheric concentrations of some semi-volatile persistent organic environmental pollutants that are managed globally under the *Stockholm Convention on Persistent Organic Pollutants* (Genualdi, et al., 2011; R cker and K mmerer, 2015; UNEP, 2001). It is currently uncertain whether the presence of cyclic volatile methyl siloxanes as atmospheric contaminants in remote areas has the potential to contaminate food chains. Calculations performed by Xu S, et al. (2014) taking into account the measured K_{OC} and K_{AW} values for D5 and the concentrations of this chemical in Arctic air suggest that partitioning from air to soil will make a negligible contribution to concentrations of the chemical in soil. Atmospheric transport of these chemicals from distant urban emission sources and deposition to land would, therefore, not be expected to make a significant contribution to their terrestrial concentrations in remote locations. Nevertheless, cyclic volatile methyl siloxanes have been measured in a diversity of biota in the Arctic and other remote areas, and it is unclear whether environmental exposure in these locations can be attributed solely to local emissions of these chemicals (R cker and K mmerer, 2015).

Predicted Environmental Concentration (PEC)

PECs were not calculated for the chemicals in this group.

No domestic environmental monitoring data for chemicals in this group were identified except for results from a single global atmospheric monitoring study conducted by Genualdi, et al. (2011). This study reported measured concentrations for D3 and D4 in air of 0.45 ng/m³ and 1.2 ng/m³, respectively, at Cape Grim in Tasmania. The concentrations of D5 in air at this site were below the detection limit. These results are not expected to be representative of urban air concentrations for cyclic volatile methyl siloxanes in Australia because the Cape Grim monitoring station is unaffected by local sources of pollution as it is used to collect clean air from the Southern Ocean (CSIRO, 2017).

Atmospheric monitoring at multiple sites around the world has confirmed that D5 and D6 are the dominant cyclic volatile methyl siloxanes present in urban air (Genualdi, et al., 2011; Janecek, et al., 2017). There is a significant correlation between the measured concentrations of these two chemicals in urban air, which suggests a common source of emission (Genualdi, et al., 2011). An air monitoring study conducted in central Chicago and surrounding suburban and rural areas in 2013 found that D5 was the dominant cyclic volatile methyl siloxane in both indoor and outdoor air. The maximum measured indoor air concentration for D5 was 56 000 ng/m³ and the maximum outdoor urban night time air concentration was 1100 ng/m³ (Yucuis, et al., 2013). The typical air concentrations for D5 measured in urban areas are significantly higher than the air concentrations measured in Arctic air which are in the range 0.5–4 ng/m³ (Mackay, et al., 2015a).

The air concentrations of these chemicals near waste treatment and disposal facilities such as STPs and landfills can be significantly higher than background levels. For example, a study of air emissions at waste water treatment plants and landfills in Canada determined the cumulative concentration of cyclic volatile methyl siloxanes (D3 to D6) to be more than 8000 ng/m³ above the aeration tank of a waste water treatment plant, and up to 7000 ng/m³ in air sampled onsite at a landfill. The measured onsite air concentrations were on average more than an order of magnitude greater than background concentrations. The cumulative emissions to air of cyclic volatile methyl siloxanes from both waste water treatment plants and landfills in this study were dominated by D5 (Cheng, et al., 2011). Very high concentrations of volatile methyl siloxanes (> 1 milligram per cubic metre (or > 10⁶ ng/m³)) have been measured in landfill and waste water treatment plant biogases at multiple sites around the world (Rücker and Kümmerer, 2015).

The levels of cyclic volatile methyl siloxanes present in treated waste water effluent and sludge from STPs have been monitored at multiple sites across several countries (Rücker and Kümmerer, 2015). A recent study conducted at a secondary activated sludge waste water treatment plant in Canada treating primarily domestic waste water determined the concentrations of these chemicals in effluents and sludge (Wang, et al., 2015). The measured concentrations of cyclic volatile methyl siloxanes in the final effluent from this plant were as follows: D4 (<0.009–0.026 micrograms per litre (µg/L)); D5 (0.192–0.242 µg/L); and D6 (0.012 to 0.015 µg/L). The highest average concentrations of these chemicals in sludge were found in waste activated sludge from the secondary settling tank: D4 (1.36 micrograms per gram dry weight (µg/g dw)); D5 (67.8 µg/g dw); and D6 (8.38 µg/g dw). The average concentration of D5 in Canadian biosolids has been estimated as 297 milligrams per kilogram dry-weight (mg/kg dw) based on measured concentrations for this chemical in sludge from an earlier study of the fate of cyclic volatile methyl siloxanes in Canadian waste water treatment plants (Mackay, et al., 2015a). The measured concentrations for D5 in biosolids amended agricultural soils in Canada are in the range < 0.007–0.221 mg/kg dw (Wang, et al., 2013). The concentrations of this chemical in biosolids-amended soil are less than expected from the levels in applied biosolids which is attributed to volatilization of the chemical immediately after application to agricultural land (Mackay, et al., 2015a).

Cyclic volatile methyl siloxanes are widely distributed in surface waters and biota at low concentrations (Rücker and Kümmerer, 2015). A recent review of measured concentrations for D5 from monitoring studies in multiple countries derived a median water concentration for this chemical of 0.06 µg/L with a 95th percentile value of 7.3 µg/L (Mackay, et al., 2015a). Cyclic volatile methyl siloxanes (D3 to D6) were measured in marine mammals from the Faroe Islands in the North Atlantic and in the livers of marine and freshwater fish from five Nordic countries. D5 was the dominant oligomer present in these samples. This oligomer was also found in all 10 seabird livers sampled from the Arctic Ocean archipelago of Svalbard (Norway). The measured concentrations in seabird livers were in the range 32 to 69 nanograms per gram wet-weight (ng/g ww) (Rücker and Kümmerer, 2015).

Sediments in the vicinity of outflows from sewage treatment plants are expected to be the most significantly impacted by release of cyclic volatile methyl siloxanes to surface waters. A number of environmental monitoring studies have been conducted to determine the concentrations of these chemicals in sediments near waste water treatment plants (Rücker and Kümmerer, 2015). A study of environmental compartments impacted by cyclic volatile methyl siloxanes in the effluents from waste water treatment plants in Canada measured the following sediment concentrations: D4 (<0.003–0.49 µg/g dw); D5 (0.011–5.84 µg/g dw); and D6 (0.004–0.371 µg/g dw). This study also showed that the concentrations of these chemicals in sediments near effluent discharge points were higher than the concentrations of cyclic volatile methyl siloxanes in agricultural soils amended with biosolids (Wang, et al., 2013).

Environmental Effects

The results of most standard short- and long-term aquatic toxicity tests available for the chemicals in this group show that they have no toxic effects on aquatic life up to the limit of their respective solubilities in water. Some toxic effects have been observed for D4 under optimised aquatic exposure conditions which indicate that these chemicals have a non-polar narcosis mode of toxic action in aquatic organisms.

Effects on Aquatic Life

The high volatility from water and the very high hydrophobicity of chemicals in this group has presented challenges for the conduct of standard short- and long-duration aquatic toxicity tests. In an attempt to ensure consistent exposures of test organisms to these chemicals, some aquatic toxicity tests have been conducted in fully enclosed systems with no head-space.

Acute and chronic toxicity

The acute toxicity of D3 has been investigated with standard freshwater fish, aquatic invertebrate and algal test species (OECD, 2008). No toxic effects were observed in rainbow trout (*O. mykiss*) exposed to the chemical for 96 hours in an open flow-through system at the nominal water solubility limit for D3 (1.6 mg/L). Similarly, no effects were observed in *D. magna* when water fleas were exposed for 48 hours under flow-through conditions. No biologically relevant effects on the growth of the green algae, *Pseudokirchneriella subcapitata*, were observed following exposure to D3 for up to 96 hours under static conditions in a closed system with no head-space. All of these studies involved exposure of the test organisms to an unquantified mixture of the parent chemical and its hydrolysis products.

The toxicity of D6 has also been investigated with standard freshwater fish, aquatic invertebrate, and algal test species (OECD, 2009). The toxicity of this chemical to fish resulting from extended exposures at the functional water solubility limit (4.4 µg/L) was evaluated from the bioconcentration study conducted with fathead minnow (*P. promelas*) described above. No acute or sub-acute effects in fish were observed after 49 days of exposure at the water solubility limit. The steady state tissue concentration at this exposure concentration was 1.06 mg D6/kg ww (based on total radioactivity). A full life-cycle test (21 days) with *D. magna* was conducted according to OECD Test Guideline (TG) 211 in sealed containers. No adverse effects on daphnids were observed in this test up to the functional water solubility limit for D6 in this system (4.6 µg/L). A static closed bottle test with *P. subcapitata* conducted according to OECD TG 201 showed no treatment related inhibition of growth and yield of green algae (relative to the solvent control) after 72 hours of exposure to D6 at the highest measured exposure concentration (2.0 µg/L).

Multiple aquatic toxicity tests on D5 have been described in unpublished study reports which were not available for this assessment. However, they have been reviewed by experts in other chemical regulatory agencies and in the scientific literature. The findings from these reviews (Gobas, et al., 2015) have, therefore, been adopted for this assessment: standard exposure length and extended exposure tests with fish (*O. mykiss* and *P. promelas*), aquatic invertebrates (*D. magna*), and algae (*P. subcapitata* and *Scenedesmus subspicatus*) do not show any evidence of adverse effects of D5 on aquatic life up to the water solubility limit for this chemical (17 µg/L); the majority of studies with fish were conducted under flow-through conditions.

Aquatic toxicity testing of D4 is difficult because this substance readily dissipates from water by a combination of volatilization, adsorption to surfaces and hydrolysis. A key study on the effects of this substance on fish and invertebrates was conducted using a fully enclosed continuous flow-through system with no head-space in order to achieve consistent exposure to the chemical (Sousa, et al., 1995). This study investigated the effects of D4 on two species of fish and two species of invertebrates: rainbow trout (*O. mykiss*); sheepshead minnow (*Cyprinodon variegatus*), a warm water marine fish, water fleas (*D. magna*); and mysids (*Mysidopsis bahia*), an estuarine shrimp. Acute toxicity tests with fish were conducted with extended exposure timeframes (14 days). In most cases, no effects were observed up to the functional water solubility limit of the chemical in the prevailing test medium. However, in the case of adult rainbow trout, mortality was observed at exposure concentrations below the solubility limit in the extended acute study and a median lethal concentration for the effects of D4 was calculated (LC50 = 10 µg/L). There was also some evidence of mortality in daphnids exposed to the chemical in a 21 day life cycle study at concentrations below the functional water solubility limit (No-observed effect concentration (NOEC) = 4.4 µg/L).

The study by Sousa, et al. (1995) was carefully conducted and the results were, therefore, considered reliable. However, more recent work suggests that the acute toxicity of D4 to rainbow trout may have been overestimated. An unpublished study described by Fairbrother and Woodburn (2016) indicates that D4 is not toxic to adult rainbow trout in an open flow-through system up to the functional water solubility limit (reported as 51.7 µg/L). The other extended acute studies on the effects of D4 on adult fish all consistently show no adverse effects up to the water solubility limit. This is also the consistent finding for all aquatic toxicity studies on the higher homologues D5 and D6. Based on the weight of evidence now available, the median lethal concentration derived for the effects of D4 on rainbow trout by Sousa, et al. (1995) is not considered to be representative of the likely toxic potency of this chemical to aquatic life.

Mode of action

The effects of cyclic volatile methyl siloxane on aquatic life are consistent with a non-polar narcosis (or baseline) mode of toxic action (Fackler, et al., 1995; Sousa, et al., 1995). These effects are, therefore, expected to be both reversible and dependent on the kinetics of uptake and elimination by aquatic life. The rate of uptake from water is known to be a significant factor influencing both the toxicity and bioconcentration of very hydrophobic neutral chemicals (Bruggeman, et al., 1984). Recent modelling of the uptake of cyclic volatile methyl siloxanes from water by fish suggests that the time required for adult fish to achieve the assumed narcotic critical body residue associated with a 50% effect on the organism ($CBR_{50} = 3$ millimoles per kilogram) is 24.7 days for D4, 101 days for D5 and 397 days for D6; these calculations assume continuous exposure at the respective water solubility limits for each chemical and no metabolism of the chemicals (Mackay, et al., 2015b). These findings are significant for ecological risk assessment as they suggest that significant acute toxic effects are unlikely to occur as a result of exposure to these chemicals in the water column because this would require unfeasibly long exposures at concentrations that are a significant fraction of the saturation concentration of each chemical. It also provides further evidence that exposure through aquatic food-chains will provide a more environmentally significant exposure pathway for these very hydrophobic chemicals.

Effects on Sediment Life

The chemicals in this group are expected to have low toxicity to benthic invertebrates.

Chronic toxicity tests on benthic invertebrates have been conducted for D4, D5 and D6 (Woodburn, et al., 2018). However, concerns have been raised regarding the reliability of some results based on the fact that most tests were conducted at concentrations in excess of the maximum sorptive capacity of the sediments (Fairbrother, et al., 2015). If this occurs, invertebrates will be exposed to the pure chemical as well as absorbed material, which will not replicate exposure conditions likely to be found in the environment. A re-analysis of laboratory sediment toxicity data for D5 by Fairbrother, et al. (2015) indicates that there is no toxicity to benthic invertebrates when the concentration of D5 does not exceed the sorptive capacity of the sediment.

Effects on Terrestrial Life

D4 and D5 have low acute inhalation toxicity.

Air breathing animals may be exposed to the chemicals in this group through inhalation. The inhalation toxicity of chemicals in this group to humans and model animals (rats, mice, rabbits, guinea pigs, and hamsters) was reviewed in the Human Health Tier II assessments of D4, D5 and D6 (NICNAS, 2018a; 2018b; 2018c). Based on the available data, it was concluded that both D4 and D5 have low acute inhalation toxicity to humans and rats. D5 may be a mild irritant in humans when repeatedly inhaled, and there is some evidence of species-specific carcinogenicity in female rats chronically exposed to the chemical through inhalation. Some non-reversible effects on the nasal tissues of rats exposed to D6 in the vapour phase were observed after 13 weeks of exposure (six hours per day, seven days per week). The no-observed adverse effect concentrations established for chronic inhalation exposure to D5 and D6 in model animals greatly exceed any exposure levels that are likely to occur in the environment and are, therefore, not considered ecologically relevant.

Predicted No-Effect Concentration (PNEC)

PNECs have not been calculated for the chemicals in this group.

Categorisation of Environmental Hazard

The categorisation of the environmental hazards of the chemicals in this group according to domestic environmental hazard thresholds is presented below (EPHC, 2009; NICNAS, 2017):

Persistence

D3

Persistent (P). Based on the half-life for degradation of this chemical in the atmosphere it is categorised as Persistent.

D4, D5, and D6

Persistent (P). Based on the half-life for degradation of these chemicals in the atmosphere and their long degradation half-lives in sediments they are all categorised as Persistent.

D7

Persistent (P). Based on the slow degradation in the atmosphere and in sediments of the immediate lower homologue, D6, this chemical is categorised as Persistent.

Cyclomethicone

Persistent (P). All three cyclic dimethyl siloxane oligomers typically present as constituents of this substance (D4, D5 and D6) are Persistent and mixtures of these substances are, therefore, also categorised as Persistent.

It should be noted that, due to partitioning behaviour, these chemicals do not persist in the water compartment.

Bioaccumulation

D3

Not Bioaccumulative (Not B). Based on the measured BCF for this chemical in fish and the rapid hydrolysis of the substance to polar metabolites it is categorised as Not Bioaccumulative.

D4 and D5

Bioaccumulative (B). Based on measured BCF values in fish, which are greater than 2000 L/kg, both chemicals are categorised as Bioaccumulative.

D6

Not Bioaccumulative (Not B). Based on a measured BCF value less than 2000 L/kg this chemical is categorised as Not Bioaccumulative.

D7

Not Bioaccumulative (Not B). Based on the measured BCF value for the immediate lower homologue (D6) this chemical is categorised as Not Bioaccumulative.

Cyclomethicone

Bioaccumulative (B). Two of the main cyclic dimethyl siloxane oligomer constituents of this substance (D4 and D5) are Bioaccumulative and mixtures containing one or both of these substances are, therefore, also categorised as Bioaccumulative.

Toxicity

D3

Not Toxic (Not T). Based on measured acute toxicity values for aquatic life that are greater than 1 mg/L and the rapid hydrolysis of the chemical into polar degradants it is categorised as Not Toxic.

D4

Uncertain (Uncertain T). The observed toxic effects of D4 on aquatic life below the water solubility limit for this chemical were obtained under exposure conditions which may not be relevant to the ecological hazards of this chemical. However, it is possible to induce toxic effects in some aquatic test species under certain exposure conditions at concentrations below the water solubility limit and the potential for adverse effects on aquatic life cannot be excluded. The toxicity of this chemical is, therefore, conservatively categorised as Uncertain.

D5 and D6

Not Toxic (Not T). Based on aquatic toxicity studies for D5 and D6 which demonstrate no toxic effects on aquatic life up to the respective water solubility limits of these chemicals they are both categorised as Not Toxic.

D7

Not Toxic (Not T). Based on the evidence that the immediate lower homologue, D6, is not toxic up to its water solubility limit and the expectation that D7 will be less bioavailable in water than lower molecular weight homologues it is categorised as Not Toxic.

Cyclomethicone

Uncertain (Uncertain T). The toxicity of this substance is categorised as Uncertain where the mixture contains D4 which is categorised as Uncertain Toxic.

Summary

Cyclotrisiloxane, hexamethyl- (D3) is categorised as:

- P
- Not B
- Not T

Cyclotetrasiloxane, octamethyl- (D4) and cyclodisiloxanes, dimethyl (cyclomethicone) are categorised as:

- P
- B
- Uncertain T

Cyclopentasiloxane, decamethyl- (D5) is categorised as:

- P
- B
- Not T

Cyclohexasiloxane, dodecamethyl- (D6) and cycloheptasiloxane, tetradecamethyl- (D7) are categorised as:

- P
- Not B
- Not T

Risk Characterisation

Three of the chemicals in this group (D4, D5 and cyclomethicone) have been categorised as persistent and bioaccumulative substances. This combination of hazard characteristics is of concern because it can increase the risk that environmental contaminants will become widely distributed in the environment and that they will contaminate aquatic food chains. The combination of hazard characteristics is complicated in the case of these chemicals by limited evidence of both persistence and bioaccumulation in any single environmental compartment. These concerns have been addressed for cyclic volatile methyl siloxanes by multiple studies of their environmental fate and effects, which includes monitoring of both their global atmospheric distribution and their accumulation in aquatic food webs.

The atmosphere is the environmental compartment most directly impacted by uses of cyclic volatile methyl siloxanes. It is now well established that the majority of the environmental emissions of these chemicals occur directly or indirectly into the atmosphere. Air monitoring studies have established that the highest emission intensity for these chemicals is in urban areas. The highest exposure concentrations are expected to occur in indoor situations and to be associated with domestic uses of cosmetics and personal care products. Outdoor air concentrations in urban areas are significantly lower than indoor air concentrations and air-breathing animals in the environment are expected to be exposed to lower air concentrations of these chemicals than are humans. Hence, there is unlikely to be a significant risk to terrestrial animals from inhalation exposure to background levels of these chemicals, even in urban areas.

Chemicals in this group are persistent in the atmosphere and they have become globally distributed atmospheric contaminants. Once in the atmosphere they are expected to be dissipated primarily by natural oxidation processes. Based on the partitioning properties of cyclic volatile methyl siloxanes they are not expected to deposit to terrestrial environments from the atmosphere. Transport of these chemicals through the atmosphere is, therefore, not anticipated to be a significant source of environmental exposure to terrestrial food chains. Nevertheless, there is uncertainty about the contribution of atmospheric transport of volatile cyclic methyl siloxanes to their occurrence as contaminants in water and biota in remote areas.

A small fraction of the total volume of cyclic volatile methyl siloxanes used in consumer products will be released into surface waters in the treated effluents from sewage treatment plants. There is currently no domestic environmental monitoring data available for chemicals in this group, although emissions are expected to be occurring based on the common use of these chemicals in multiple consumer products. Based on monitoring conducted overseas, D5 is expected to be the dominant oligomer present in waste water effluent. The measured concentrations for D5 in Canadian effluents were recently determined to be in the range 0.192 to 0.242 µg/L, and the median concentration for this chemical in water is 0.06 µg/L. No direct toxic effects on aquatic life would be expected if these values are representative of surface water concentrations of D5 in Australia as this chemical is not toxic up to its water solubility limit (17 µg/L).

A more significant concern for the aquatic environment is the accumulation of cyclic volatile methyl siloxanes in sediments. Chemicals in this group are expected to be very stable in sediments under both aerobic and anaerobic conditions, and they have the potential to accumulate in this compartment of the environment. Based on the findings from international environmental monitoring studies, concentrations of these chemicals in sediments are higher in the vicinity of outfalls from waste water treatment plants. Aquatic life living above or in sediments close to these emission sources may be at a potentially increased risk of exposure to cyclic volatile methyl siloxanes.

A recent comprehensive analysis of the ecological risks of D5 suggests that the risk of direct toxic effects on benthic invertebrates is low (Fairbrother, et al., 2015). The potential for accumulation of cyclic volatile methyl siloxanes in sediments in

the vicinity of sewage treatment plants is, therefore, not currently considered to be a priority for further investigation. However, monitoring of the sediment compartment may be relevant to consider in Australia to the extent there is evidence of accumulation of these chemicals in aquatic life. Sediments contaminated with cyclic volatile siloxanes may become a source of exposure for biota at the base of aquatic food-webs, such as benthic invertebrates and demersal fish.

Key Findings

Cyclic volatile methyl siloxanes have a wide range of industrial uses. They are high volume industrial intermediates in the production of silicone fluids and elastomers which have a wide range of applications in products and articles that are in use in Australia. They also have a wide range of applications in consumer products which include cosmetics and personal care products that are available on the market in Australia.

There is no information currently available on the environmental emissions of cyclic volatile methyl siloxanes in Australia. Based on detailed international assessments and global monitoring information, it is known that the majority of emissions of these chemicals from their use in consumer products are into the atmosphere. Emissions also occur through the release of residual cyclic volatile methyl siloxanes present in silicone products and articles, and through degradation of silicone fluids.

The chemicals in this group are persistent in the atmosphere and they are globally distributed atmospheric contaminants. Most members of this group are also known or expected to be persistent in the sediment compartment. Three members of this group (D4, D5 and cyclomethicone) have a high potential to bioconcentrate in fish, although they do not persist in the water compartment. There are inconsistent findings regarding biomagnification of these chemicals in aquatic food webs. Cyclic volatile methyl siloxanes are not considered likely to biomagnify in mammalian food webs and the human food chain because they are subject to respiratory elimination and biotransformation by air-breathing animals.

All of the chemicals in this group are very hydrophobic and, with the exception of D4, they have no toxic effects on aquatic life up to their respective water solubility limits. They have been categorised as Not Toxic. There is evidence that D4 can induce toxic effects in fish by a non-polar narcosis mode of action; however, the toxicity end points obtained under test conditions where this effect is observed are not considered suitable for a definitive categorisation of the aquatic hazards of this chemical and its toxicity is categorised as Uncertain.

A small fraction of the total environmental emissions of cyclic volatile methyl siloxanes will occur to surface waters in effluents from STPs. These chemicals are expected to dissipate rapidly from the water column by a combination of volatilization, hydrolysis and partitioning to suspended particulate matter and sediments. The direct risks to aquatic life from exposure to these chemicals at expected surface water concentrations are not likely to be significant. However, there is the potential for these chemicals to accumulate in sediments close to outfalls from waste water treatment plants based on their persistence in this compartment. This is not considered to be a priority for further investigation unless there is evidence that cyclic volatile methyl siloxanes are accumulating in aquatic food chains.

Recommendations

No further assessment is currently required under the IMAP framework.

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 cyclotetrasiloxane, octamethyl- (D4); cyclopentasiloxane, decamethyl- (D5); cyclohexasiloxane, dodecamethyl- (D6); and cyclosiloxanes, dimethyl (cyclomethicone) 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
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Hazard	GHS Classification (Code)	Hazard Statement
Acute Aquatic	Not classified	-
Chronic Aquatic	Category 4 (H413)	May cause long lasting harmful effects to aquatic life

D4, D5 and D6 are poorly water soluble, are not rapidly degraded, and have a tendency to bioaccumulate. Hence, according to the GHS guidance on classification of aquatic hazards, the long-term aquatic hazard of all three chemicals is classified as category Chronic 4 (i.e., the “safety net” classification) (UNECE, 2009). The long term aquatic hazard of cyclomethicone has been classified on the basis that this substance is composed of one or more discrete cyclic dimethyl siloxane oligomers which are all classified as Chronic Aquatic Category 4.

The aquatic hazards of cyclotrisiloxane, hexamethyl- (D3) and cycloheptasiloxane, tetradecamethyl- (D7) have not been classified for this assessment.

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