



Use of Volatile Methyl Siloxanes (VMS) in industrial environments:

A TOOLBOX FOR MINIMISING ENVIRONMENTAL EMISSIONS

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Table of Contents

EXECUTIVE SUMMARY		4
DISCLAIMER	4	
1	INTRODUCTION	5
1.1	PURPOSE OF THE DOCUMENT	5
1.2	SCOPE OF THE DOCUMENT	5
1.3	APPLICABILITY OF THIS TOOLBOX TO VMS	5
2	ENVIRONMENTAL REGULATORY STATUS OF VMS	6
2.1	DESCRIPTION OF SUBSTANCES CONSIDERED IN THIS TOOLBOX	6
2.2	PHYSICO-CHEMICAL PROPERTIES RELEVANT TO THE MANAGEMENT OF ENVIRONMENTAL EMISSIONS	6
3	INDUSTRIAL AND PROFESSIONAL USE OF VMS	7
3.1	USE SUMMARIES	7
3.2	SCALE OF USE	7
4	WHAT DOES MINIMISATION MEAN?	9
4.1	PRINCIPLES OF MINIMISATION	9
4.2	CONTROLLING RELEASES OF VMS TO THE ENVIRONMENT	9
5	EMISSION MANAGEMENT THROUGH GOOD PRACTICE	10
5.1	UNDERSTANDING THE PROCESS – THE MASS BALANCE	10
5.2	MANAGEMENT THROUGH AWARENESS AND TRAINING	10
5.3	PROCESS INTEGRATED TECHNIQUES	10
5.4	RECOVERY OF VMS AT SOURCE	11
5.5	PRE-TREATMENT	11
5.6	FINAL TREATMENT	11
5.7	END-OF-LIFE OPTIONS	11
5.7.1	Polymer Recycling	11
5.7.2	Incineration with Energy Recovery	11
6	EXAMPLE EMISSION ABATEMENT TECHNIQUES	12
6.1	DISCLAIMER	12
6.2	ABATEMENT OF EMISSIONS TO AIR	12
6.2.1	Condensation	12
6.2.2	Scrubbing	12
6.2.3	Oxidation	13
6.2.4	Adsorption	13
6.3	ABATEMENT OF EMISSIONS TO WATER	14

6.3.1	<i>Biological treatment</i>	14
6.3.2	<i>Hydrolysis</i>	14
6.3.3	<i>Oxidation</i>	14
6.3.4	<i>Adsorption</i>	15
6.4	<i>ABATEMENT OF EMISSIONS TO WASTE/LAND</i>	15
6.4.1	<i>Thermal Oxidation</i>	15
6.4.2	<i>Landfill</i>	15
7	<i>DEMONSTRATING MINIMISATION BY MONITORING</i>	16
7.1	<i>MONITORING</i>	16
7.2	<i>EMISSION MONITORING PLANS & PROCEDURES</i>	16
7.2.1	<i>Quality Control Challenges in Monitoring VMS</i>	16
7.2.2	<i>Analytical Methodologies for Water</i>	18
7.2.3	<i>Analytical Methodologies for Air</i>	18
7.2.4	<i>Analytical Methodologies for Soil, Sludge and Sediment</i>	19
8	<i>WHERE TO FIND MORE INFORMATION</i>	21
8.1	<i>GLOBAL LEGISLATION</i>	21
8.2	<i>INDUSTRY INFORMATION</i>	22
8.3	<i>GENERAL REFERENCES</i>	22
9	<i>LIST OF ACRONYMS</i>	24
10	<i>PHYSICO-CHEMICAL PROPERTIES AND ENVIRONMENTAL FATE INFORMATION RELEVANT TO MANAGEMENT OF ENVIRONMENTAL EMISSIONS</i>	25
10.1	<i>DATA TABLES</i>	25
10.2	<i>DISCUSSION OF DATA</i>	27
	<i>ANNEX 1 – VMS REGULATORY STATUS (EUROPEAN UNION)</i>	28
	<i>EU DECISION</i>	28
	<i>SILICONES INDUSTRY RESPONSE TO EU SVHC LISTING OF D4, D5 AND D6</i>	28
	<i>ENVIRONMENTAL FATE DATA RELEVANT TO ASSESSMENT OF D4, D5 AND D6 AS PBT AND vPvB SUBSTANCES</i>	29
	<i>ENVIRONMENTAL FATE DATA RELEVANT TO ASSESSMENT OF L3, L4 AND L5 AS PBT AND vPvB SUBSTANCES</i>	31
	<i>CLASSIFICATION OF VMS IN THE EU</i>	32
	<i>EXPOSURE SCENARIOS</i>	33
	<i>MANAGEMENT OF PBT/vPvB SUBSTANCES UNDER REACH</i>	33
	<i>MATCHING THE EXPOSURE SCENARIOS TO THE SCALE OF OPERATION</i>	34
	<i>ANNEX 2 – VMS REGULATORY STATUS (OTHER COUNTRIES)</i>	35
	<i>ENVIRONMENTAL ASSESSMENT OF VMS AGAINST PBT CRITERIA IN OTHER COUNTRIES</i>	35



Executive Summary

This document is being published under the direction of the Global Silicones Council (GSC). This publication follows Version 1, which was launched in 2018 under the sponsorship of CES – Silicones Europe, and which had a scope limited to volatile cyclosiloxanes (cVMS) and the EU regulatory landscape. This document is aimed at further informing downstream users of silicone products on the measures they may take to minimize emissions of volatile methyl siloxanes (VMS), and is specifically focused on D4, D5, D6, L3, L4 and L5. In addition to promoting good product stewardship around the use of these substances, it is expected that this document will also support the silicone industry’s communication to downstream users globally.

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1 INTRODUCTION



1.1 Purpose of the Document

The Global Silicones Council (GSC), the Regional Silicone Industry Associations (RSIAs) and their member companies promote the highest stewardship standards in the manufacture and use of silicone products.

In recognizing the global public concern about the release of chemicals into the environment, the silicones industry continues to pro-actively address these concerns by providing voluntary guidance to downstream users of silicone products to:



1. Understand if there is potential for chemical emissions from the use of silicone products



2. Present a compendium of example Risk Management Measures (RMMs) that downstream users can review for minimising such potential emissions

This Toolbox is directed specifically at downstream users (DUs) of the cyclosiloxanes D4, D5 and D6 and the linear siloxanes L3, L4 and L5, all of which are volatile methyl siloxanes (VMS) and aims to:

1. Provide a set of Risk Management Measures (RMMs) to assist in the minimisation of emissions
2. Provide background information on monitoring procedures to generate data to evaluate/demonstrate the effectiveness of RMMs
3. Summarise the physico-chemical properties of VMS that may impact the effectiveness and selection of treatment methodologies for their removal from environmental emissions
4. Summarise global assessments of the environmental properties of specific VMS with respect to meeting the criteria of being Persistent, Bioaccumulative and Toxic (PBT) and/or very Persistent and very Bioaccumulative (vPvB)

Although most regulatory jurisdictions conclude that there are no elevated environmental risks from VMS, the silicones industry promotes minimisation of environmental emissions as part of good product stewardship. Recognizing the global public concerns about potential releases of chemicals into the environment the silicones industry wants to support practical steps. Therefore, the technical RMMs presented in this Toolbox will aim at minimising the levels of VMS from potential emissions.

1.2 Scope of the Document

This document provides information for all users of VMS in industrial and professional environments but does not include consumer use of formulations, mixtures or articles that may contain these substances and the use of which, therefore, may result in environmental emissions. Consumer and professional products are typically seen to have a wide dispersive use and some can contain varying concentrations of VMS. In the EU wash-off personal care products with higher concentrations of D4 and D5 are already subject to a restriction.

1.3 Applicability of this Toolbox to VMS

VMS are often present concurrently in products and abatement technologies are similar for VMS substances, although the specific efficiency of abatement may be different. Within the scope of this document, the described risk management measures do not distinguish between the six substances.

Due to the highly complex manufacture, processing and use patterns of silicone products, it is not intended for this document to be a complete and exhaustive description and should not be interpreted as such. The authors have attempted to assure the quality of information available in this Toolbox. However, before relying on it for a specific purpose, users should obtain advice relevant to their particular circumstances. This report has been prepared using a range of sources, including information from databases maintained by third parties and from data supplied by industry. For antitrust reasons, it is not possible to provide more detail on an Industry Association basis.

2 ENVIRONMENTAL REGULATORY STATUS OF VMS



2.1 Description of Substances Considered in this Toolbox

D4: octamethylcyclotetrasiloxane
EC 209-136-6, CAS 556-67-2

D5: decamethylcyclopentasiloxane
EC 208-764-9, CAS 541-02-6

D6: dodecamethylcyclohexasiloxane
EC 208-762-8, CAS 540-97-6

D4, D5 and D6 consist of four, five or six repeating units of dimethylated silicon atoms linked by the same number of oxygen atoms into cyclic ring structures. They are all odourless, colourless liquids and are used either as intermediate substances or as basic raw materials in the production of silicone rubbers, gels and resins. D5 and D6 are also used as an ingredient in mixtures for cosmetic applications, such as skin creams, deodorants and other personal care products.

L3: octamethyltrisiloxane
EC 203-497-4, CAS 107-51-7

L4: decamethyltetrasiloxane
EC 205-491-7, CAS 141-62-8

L5: dodecamethylpentasiloxane
EC 205-492-2, CAS 141-63-9

L3, L4 and L5 consist of one, two or three repeating units of dimethylated silicon atoms linked together in a linear structure with oxygen atoms and capped at each end by trimethylated silicon atoms. They are all odourless, colourless liquids and are used either as intermediate substances or are present as residual impurities in some siloxane polymers and the resulting products produced using such polymers. L3, L4 and L5 are also found as ingredients in personal care products.

2.2 Physico-chemical Properties Relevant to the Management of Environmental Emissions

VMS have a unique combination of physico-chemical properties compared to carbon-based substances that makes their impact on the environment different from that produced by carbon-based substances. The unique combination of properties include: high octanol-water partition coefficient, low water solubility, high vapour pressure, fast indirect phototransformation by hydroxyl radicals in air, high Henry's law constant, and high adsorption and desorption. The specific values are presented in Section 10.

3 INDUSTRIAL AND PROFESSIONAL USE OF VMS



3.1 Use Summaries

The industrial and professional uses of VMS, and the potential for environmental emissions, are described generically in Figure 1. The individual uses of the substances can be described in detail to define:

- Where the substance is used
- The scale at which it is used and the operational conditions
- RMMs downstream users could take to ensure safe use of these substances and minimise environmental releases

In the EU, for example, these use summaries are referred to as exposure scenarios and this information is communicated to downstream users in the (extended) safety data sheets for the substances or mixtures containing VMS. This toolbox provides information on example techniques that are available to users of the substance to help minimise environmental emissions.

3.2 Scale of Use

For the purposes of this Toolbox, example techniques for the minimisation of environmental emissions from the industrial and professional uses of VMS are considered in relation to the different levels of scale at which these substances are used, when defined by quantity used per batch operation. Scale of use will typically inform:

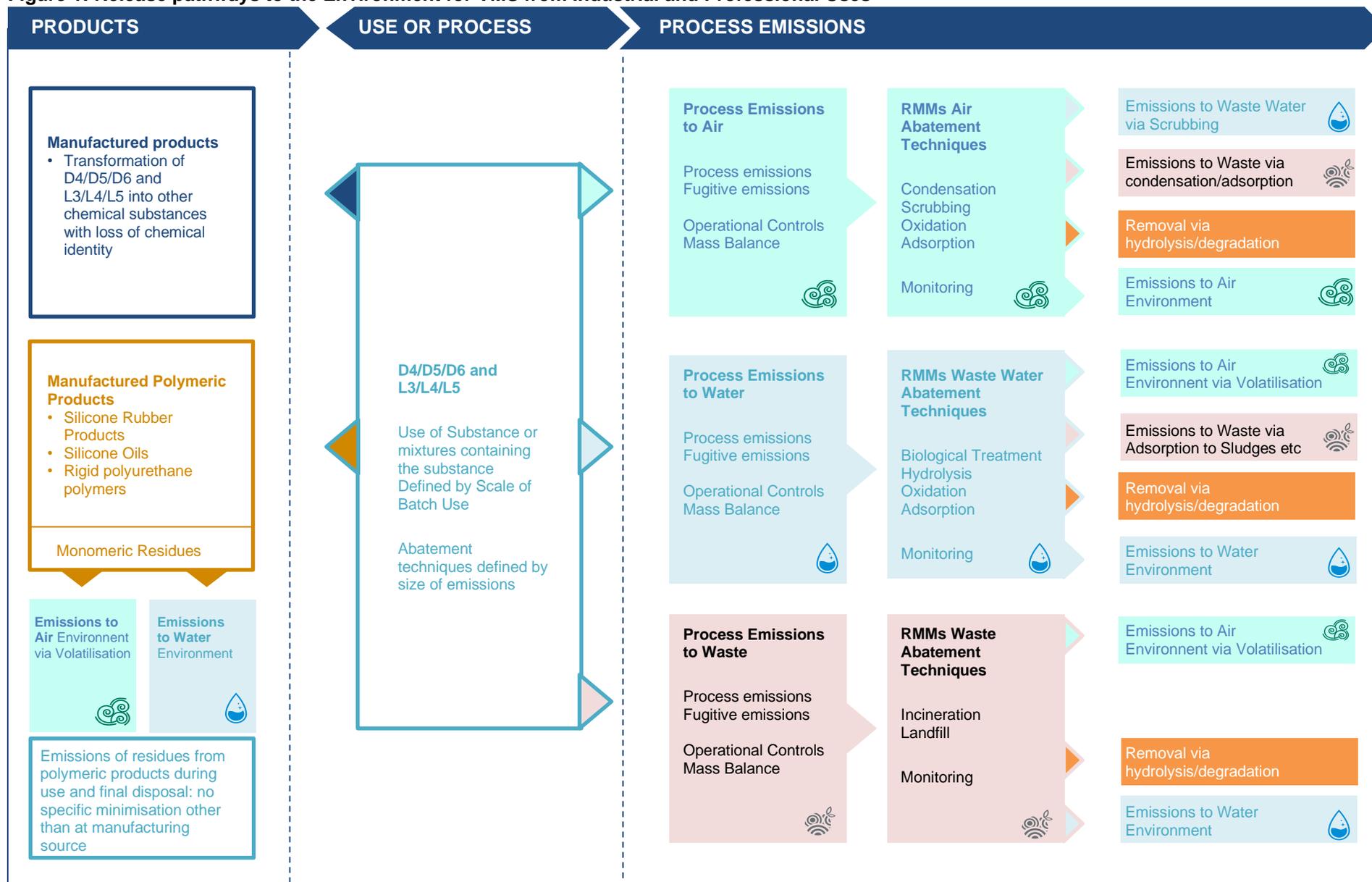
- The extent of engineering control in place to control the risk of exposure to the substance hazards
- The type of abatement techniques that would be appropriate to a) the production environment and b) the scale of potential release

From a detailed review of the exposure scenarios described in the latest chemical safety reports for the individual cyclic and linear siloxanes prepared for the registration of these substances in the EU, the following boundaries are considered appropriate for framing the subsequent discussion of example techniques for the minimisation of environmental process releases:

- Level 1 - Use of greater than 1000 kg per batch:** this is considered large-scale use at facilities which will typically have significant, dedicated engineering infrastructure to be able to handle the chemical or physico-chemical processes involving the VMS. Such industrial facilities will typically already be subject to industrial process permitting and may be able to consider and implement more complex, capital-intensive abatement techniques if they do not already exist within their current infrastructure
- Level 2 - Use greater than 25 kg per batch but less than 1000 kg per batch:** the use of one drum or more of VMS in manufacturing or formulation processes suggests a degree of engineering sophistication may be in place on site which, whilst not as capital intensive as Level 1, suggests that the user may be able to consider and implement management and engineering solutions to minimise emissions to the environment
- Level 3 - Use of less than 25 kg per batch:** The use of small quantities of VMS, most probably by professional users in formulated mixtures, where the VMS are intentional ingredients, or in articles, where these volatile siloxanes are present as residual monomers, is taken to indicate that the use may not be in settings where there is typically any significant extent of engineered abatement for either air or water emissions and that the minimisation of emissions will likely be primarily achieved by management techniques in understanding the potential for emission and segregation of waste streams for off-site disposal options

This approach allows information to be provided to the downstream user on the management and abatement of VMS emissions to the environment. Downstream users in the EU should also consult the specific exposure scenarios in the chemical safety reports and the (extended) safety data sheets for D4, D5, D6, L3, L4 and L5 and formulated products.

Figure 1: Release pathways to the Environment for VMS from Industrial and Professional Uses



4 WHAT DOES MINIMISATION MEAN?



4.1 Principles of Minimisation

Minimisation of emissions to the environment is a systematic approach to the reduction of emissions at source through understanding and changing activities to either prevent or reduce such emissions. Mapping of the conditions of use and subsequent fate of the substance in a particular use can identify and prioritise applicable risk management measures.

Published guidance documents in other sectors (e.g. EU Integrated Pollution Prevention and Control¹ and Groundwater²) discuss the implementation of all 'necessary and reasonable' measures in the prevention of the discharge of substances to the environment and provide a clearer definition of what minimisation means in this context, recognising that there is a practical limit to what can be realistically achieved.

Any assessment of the measures to prevent or reduce environmental emissions should be preceded by an investigation to determine the pathways by which such emissions are or may be occurring and is therefore site-specific. Such precautionary measures can be described as follows:

- Technically feasible, not disproportionately costly and within the control of the operator
- A combination of source control, alteration of discharge mechanisms or routes and treatment of discharges
- Should not result in a net environmental disbenefit
- Cost benefit is not a factor in deciding whether measures should be implemented but can be taken into account in the determination of which measures should be implemented
- The assessment of whether costs are proportionate or not is therefore dependent on local operator circumstances and cannot be generically prescribed

For many substances, discharge limits can be set based on the known environmental effects of those

substances. For example, in the EU Predicted No Effect Concentrations (PNECs) are used within chemical risk assessments to determine the use specific risks of environmental emissions.

The EU REACH registration dossiers for these VMS currently list PNECs for freshwater and marine water (D4 only) and for municipal sewage treatment plants (STPs) (D4, D5, D6, L3, L4, and L5). The PNEC for municipal STPs is significantly higher than the solubility of these substances and will therefore not be attained under normal operation circumstances. However, it should be noted that, when substances are considered to be PBT or vPvB, as defined by the REACH Regulation in the EU, it is believed that no such numeric limits can be set, and the PNECs calculated for the purposes of registration cannot be relied upon for demonstration of regulatory compliance. This logic does not apply in other countries where risk assessments have been completed on these substances.

4.2 Controlling Releases of VMS to the Environment

It is considered good product stewardship practice to minimise chemical emissions to the environment where possible. This toolbox is designed to assist downstream users in identifying an appropriate methodology for doing so based on the scale of use.

Whilst the exact behaviour and fate of VMS in the aqueous environment is interpreted differently in different jurisdictions, and may trigger varying regulatory obligations, it is still prudent to take appropriate steps to manage emissions to the environment. All downstream users should therefore understand the use and fate of these substances in the products they manufacture, formulate or use.

¹ <http://ec.europa.eu/environment/industry/stationary/ied/legislation.htm>

² <http://ec.europa.eu/environment/water/water-framework/groundwater/framework.htm>

5 EMISSION MANAGEMENT THROUGH GOOD PRACTICE



5.1 Understanding the Process – the Mass Balance

In order to be able to manage emissions of a substance, a clear understanding of how that substance moves through the process and where it has the potential to enter the environment is good practice and can be achieved through an evaluation of the process mass balance.

A mass balance is one useful tool that enables the user to record inputs and outputs to the process, and thus account for and quantify any losses. Such an approach will help to identify and prioritise the source and nature of any process emissions but will not, necessarily, be of sufficient accuracy to account for the complete substance inventory.

The balance is inputs versus outputs:

Inputs:

- The quantity of the substance (or quantity in mixtures) that is used as an input to the process
- The quantity of any recycled or recovered amounts of the substance from previous batches or emissions management

Outputs:

- Quantity in product (as component part)
- Quantity in product (as a residue/impurity)
- Substance consumed or lost in chemical or physical reactions
- Quantity destroyed or captured by abatement systems
- Emissions to air (point sources)
- Fugitive emissions to air (non-point sources)
- Emissions to water
- Quantity in solid wastes

The mass balance can also take into account other losses, where appropriate, such as releases that may occur through maintenance activities.

It may be the case that not all of the outputs are quantifiable, e.g. fugitive losses, however if the rest of the inputs and outputs are known, then these losses may be estimated by calculation.

All levels of use of VMS will likely benefit from a detailed examination on the mass balance of the particular process.

5.2 Management through Awareness and Training

The importance of understanding the mass balance should be communicated to all staff who manage or operate the process involving VMS. Downstream users may wish to provide their staff with training on the behaviour of VMS in the environment, the reasons for specific controls being applied and the importance of maintaining them. Wherever possible staff should be encouraged to suggest improvements to the process that could reduce emissions.

5.3 Process Integrated Techniques

As a general principle, prevention or reduction of emissions within the process is considered an appropriate technique to prevent or reduce emissions to the environment.

The method(s) by which reduction of emissions might be achieved are dependent on the process involved but are applicable to all scales of use and may include:

- Minimisation of excess reagents in reaction chemistry
- Minimisation of potential emission points (point source or fugitive emissions)
- Efficient conversion chemistry, either through refinement of reaction temperatures and pressures or through recirculation of reagents
- Robust maintenance programmes to minimise process breakdown or failed batches

Emissions can be minimised by optimising process conditions and are especially relevant for large and medium scale uses (Levels 1 and 2). Process options that can be considered include:

- Optimisation of inerts in vent systems in order to maximise VMS removal and recovery efficiency, whilst maintaining safe operational

levels. For example, excessive nitrogen in vent streams will adversely impact the VMS removal efficiency (heat transfer coefficient) in vent cold traps and condensers.

- Lower temperature operations, if possible, to minimise volatilisation of VMS
- Condensation of VMS on process outlets. This can be effective but care needs to be taken to avoid temperatures at which VMS freeze, because this can cause equipment and pipework blockage, leading to the risk of overpressure scenarios. Alternatively, freeze/thaw technology can be effective, if designed correctly, to manage the resulting solids and the subsequent liquid upon melting

5.4 Recovery of VMS at Source

Where it is not possible to prevent emissions within the process, it may be possible to recover VMS prior to their release to the environment by instituting recycle, recovery or re-use loops. These may include:

- Recovery (extraction, condensation, distillation) of the substance of concern from the product stream, with the recovered substance being recycled in the process
- Counter-current reaction processes to maximise reaction efficiency

Such recovery and recycle options are applicable to large-scale uses (Level 1 and larger scale Level 2).

5.5 Pre-treatment

Pre-treatment techniques may be used to abate, combine, or concentrate substances or otherwise pre-treat the waste stream to aid the final treatment. Pre-treatment can be carried out at the source or in combined streams. Typical examples include:

- Equalisation
- Neutralisation
- Physical separation, e.g. screening, grit separation, grease separation or settlement

5.6 Final Treatment

Final treatment techniques are the final stage of control before the substances are emitted or discharged into the environment. Typical examples of treatment techniques are presented in detail in Section 6.

5.7 End-of-Life Options

5.7.1 Polymer Recycling

There are currently some recycling methods for polymers that aim at generating siloxane raw materials for further manufacturing of silicone products.

5.7.2 Incineration with Energy Recovery

The preferred method for end-of-life of VMS is incineration with energy recovery. This method leads to generation of energy and transforms the VMS substances into SiO_2 and CO_2 .

6 EXAMPLE EMISSION ABATEMENT TECHNIQUES



6.1 Disclaimer

The following sections describe a variety of example techniques that may be applicable to the minimisation of environmental releases of VMS. Any methodology selected should be subject to a risk management assessment and its implementation would need to be consistent with all applicable local/national permits and laws. Further information can be obtained from the suppliers of the VMS products and the technology providers.

Each VMS substance has a specific set of properties that make it more effective than other VMS substances for specific products or applications. Therefore, the operating procedures or parameters for emission abatement purposes may need adjustments if one substance has to be targeted preferentially over the others because of its higher concentrations in the emissions.

6.2 Abatement of Emissions to Air

6.2.1 Condensation

Condensation is a technique that helps eliminate solvent vapours from a waste gas stream by reducing its temperature below its dew point. There are different methods of condensation, depending on the operating temperature range.

Condensation is carried out by means of direct cooling (i.e. contact between gas and cooling liquid) or indirect cooling (i.e. cooling via a heat exchanger). Indirect condensation is preferred because direct condensation needs an additional separation stage. Recovery systems vary from simple, single condensers to more complex, multi-condenser systems designed to maximise energy and vapour recovery (European Commission, 2016).

Applicability: The type of condensation will depend on the other substances present in the waste gas stream, the relative vapour pressures, dew points and the temperature of the waste gas stream. This technique is considered to be applicable to large and medium scale uses (Levels 1 and 2).

Removal efficiency for D4, D5 and D6:

Appendix B to the ECHA D4 and D5 background document (ECHA, 2016) indicates that condensation is a potential abatement technique for waste gases containing cyclosiloxanes and that removal efficiencies may be up to 90%.

A study (Soreanu *et al.*, 2011) reviewing options for cyclosiloxane removal from digester gas indicated that up to 95% removal efficiency might be achieved at temperatures around -30 °C or 15-30% at temperatures around 2-4 °C.

Removal efficiency for L3, L4 and L5: Although there are no specific studies documenting removal efficiency via condensation for the linear VMS, given the similarities in physico-chemical properties to the analogous cyclic species, similar removal efficiencies could be anticipated if the appropriate operating procedures or parameters for the specific target VMS are used.

6.2.2 Scrubbing

Wet scrubbing (or absorption) is a mass transfer between a soluble gas and a solvent – often water – in contact with each other. Physical scrubbing is preferred for chemical recovery, whereas chemical scrubbing is restricted to removing and abating gaseous compounds. Physico-chemical scrubbing takes an intermediate position. The compound is dissolved in the absorbing liquid and involved in a reversible chemical reaction, which enables the recovery of the gaseous compound (European Commission, 2016).

A variety of scrubber types exist with differing means of maintaining contact between the gas and the scrubbing liquid. These include:

- Fibrous packing scrubbers
- Moving-bed scrubbers
- Packed bed scrubbers
- Impingement bed scrubbers
- Spray towers

Applicability: The scrubbing liquid should be selected based on the substance to be removed. The scrubbing liquid pH and temperature should also be set to maximise recovery. The ability to treat the scrubbing liquid will also affect the choice of this abatement technique over other options. This technology is considered to be applicable to all scales of use (Levels 1 to 3).

Removal efficiency for D4, D5 and D6: Appendix B to the ECHA D4 and D5 background document (ECHA, 2016) indicates that mist filtration may be a potential abatement technique for waste gases containing cyclosiloxanes and that removal efficiencies can be up to 99%.

A study (Soreanu *et al.*, 2011) reviewing options for cyclosiloxane removal from digester gas indicated that 99% removal efficiency might be achieved with gas-liquid adsorption.

Removal efficiency for L3, L4 and L5: Although there are no specific studies documenting removal efficiency via scrubbing for the linear VMS, given the similarities in physico-chemical properties to the analogous cyclic species, similar removal efficiencies could be anticipated if the appropriate operating procedures or parameters for the specific target VMS are used.

6.2.3 Oxidation

Thermal oxidation (also often referred to as 'incineration', 'thermal incineration' or 'oxidative combustion') is the oxidation process of combustible gases and odorants in a waste gas stream by heating a mixture of contaminants with air or oxygen above its auto-ignition point in a combustion chamber and maintaining it at a high temperature for sufficient time to complete combustion to carbon dioxide and water (European Commission, 2016).

Applicability: The incoming waste gas stream will determine what contaminants are present in the discharge gas from the thermal oxidiser. These final waste gases are likely to be subject to environmental controls. The residence time, temperature of the combustion and the oxygen content are all important parameters in the operation of an effective thermal oxidiser. Heat recovery options for thermal oxidisers are available. This technology is typically considered to be applicable to large scale (Level 1) uses.

Energy usage is likely to be a consideration for the selection of this abatement option as the VMS being abated will not be able to sustain combustion without additional fuel.

Experience within the landfill gas management sector indicates that combustion of VMS can result in operational/maintenance issues for burner tips, downstream gas engines or other rotating equipment due to formation of SiO₂ (Soreanu *et al.*, 2011).

Removal efficiency for D4, D5 and D6: Appendix B to the ECHA D4 and D5 background document (ECHA, 2016) indicates that thermal oxidation may be a potential abatement technique for waste gases containing

cyclosiloxanes and that removal efficiencies can be up to 99.9%.

Removal efficiency for L3, L4 and L5: Although there are no specific studies documenting removal efficiency via thermal oxidation for the linear VMS, given the similarities in physico-chemical properties to the analogous cyclic species, similar removal efficiencies could be anticipated if the appropriate operating procedures or parameters for the specific target VMS are used.

6.2.4 Adsorption

Adsorption is a heterogeneous reaction in which gas molecules are retained on a solid or liquid surface (adsorbent also referred to as a molecular sieve) that prefers specific compounds to others and thus removes them from effluent streams. When the surface has adsorbed as much as it can, the adsorbed content is desorbed as part of the regeneration of the adsorbent. When desorbed, the contaminants are usually at a higher concentration and can either be recovered or disposed of (European Commission, 2016). Major types of adsorption are:

- Fixed bed adsorption
- Fluidised bed adsorption
- Continuous moving-bed adsorption
- Pressure swing adsorption

Adsorbents include:

- Activated carbon
- Zeolites
- Polymers
- Silica gel
- Sodium aluminium silicate

Applicability: Fixed bed adsorption processes are widely used and are readily scalable. It is therefore considered applicable to all scales of use (Level 1 to Level 3). In order to be able to operate continuously, multiple beds may be required to allow regeneration or replacement of the adsorption media. The rate of replacement or regeneration of the adsorption media may determine the applicability of this type of abatement, normally dictated by the concentration of the VMS and other contaminants in the waste gas. This abatement technique is commonly coupled with waste gas combustion to protect rotating equipment, for example in landfill gas engines.

Removal efficiency for D4, D5 and D6: Appendix B to the ECHA D4 and D5 background document (ECHA, 2016) indicates that adsorption may be a potential abatement technique for waste gases containing cyclosiloxanes and that removal efficiencies can be up to 95%.

A study (Soreanu *et al.*, 2011) reviewing options for cyclosiloxane removal from digester gas indicated that 97-99% removal efficiency might be achieved with liquid

adsorption and 90-99% removal efficiency with solid adsorption.

Removal efficiency for L3, L4 and L5: Although there are no specific studies documenting removal efficiency via adsorption techniques for the linear VMS, given the similarities in physico-chemical properties to the analogous cyclic species, similar removal efficiencies could be anticipated if the appropriate operating procedures or parameters for the specific target VMS are used.

6.3 Abatement of Emissions to Water

Because of the low aqueous solubility of these substances and their propensity to volatilise, bind to particles and hydrolyse in aqueous environments, they can be relatively easily removed from water by application of elevated temperatures and/or mixing and injection of air. The primary route of process emissions to the wastewater is via saturation of process waters or spills to process sewers.

6.3.1 Biological treatment

Aerobic treatment is the biological oxidation of dissolved organic substances with oxygen using the metabolism of microorganisms. In the presence of dissolved oxygen – injected as air or pure oxygen – the organic compounds are converted (mineralised) into carbon dioxide, water or other metabolites and biomass (i.e. the activated sludge). Toxic waste water content can inhibit the biological process. The acclimation of the bacterial community is an important factor and can affect the threshold inhibiting concentration (European Commission, 2016). Common aerobic biological treatment techniques are:

- Complete mix activated sludge process
- Membrane bioreactor process
- Trickling or percolating filter process
- The expanded-bed process
- Fixed-bed biofilter process

Applicability: Studies of behaviour of cyclosiloxanes in WWTPs indicate that volatilisation and adsorption to sludge are important contributing factors to the ability of this abatement technology to remove cyclosiloxanes from waste water (ECHA, 2016). Large and medium scale users (Level 1 and 2) may operate their own on-site waste water treatment plants and these should be effective in minimising off-site emissions. Small scale users may consider discharge to municipal WWTPs as permitted by the laws of the applicable jurisdiction.

Removal efficiency for D4, D5 and D6: Studies of the removal of D4 and D5 from waste waters using biological treatment in WWTPs indicate that removal efficiencies for D4 are of the order of 96% and for D5 are of the order of 95%.

Although removal rates might be lower or higher at individual WWTPs, these values were considered to be broadly representative.

Removal efficiency for L3, L4 and L5: Although there are no specific studies documenting removal efficiency from WWTPs for the linear VMS, given the similarities in physico-chemical properties to the analogous cyclic species, similar removal efficiencies could be anticipated if the appropriate operating procedures or parameters for the specific target VMS are used.

6.3.2 Hydrolysis

Hydrolysis is a destructive technique. It is a chemical reaction in which organic and inorganic substances react with water, breaking them into smaller compounds. Downstream treatment of the chemically hydrolysed stream is generally required, e.g. in a central biological WWTP (European Commission, 2016).

Applicability: Under laboratory scale testing, VMS hydrolysis proceeds more quickly at high temperature and at low or high pH values (see further detail in Annex 2). However, no references have been found of industrial scale applications of this technique to abate VMS in waste water but it is considered applicable at all levels of use (Levels 1 to 3).

Removal efficiency for VMS: Not known. No references to an industrial application of this technique for VMS have been found.

6.3.3 Oxidation

Chemical oxidation is the conversion of substances by agents other than oxygen/air or bacteria into similar but less harmful compounds and/or to short-chained and more easily degradable or biodegradable organic compounds.

Applicability: The choice of oxidant, pressure and temperature is critical to the abatement efficiency. The use of, for example, halogenated oxidants may require further treatment steps to treat the resultant waste water. Chemical oxidation treatments are scaleable and therefore considered applicable to all levels of use (Levels 1 to 3).

However, it should be noted that siloxanes are resistant to most forms of chemical oxidation.

Removal efficiency for D4, D5 and D6: Despite the resistance of cyclosiloxanes to chemical oxidation, Appendix B to the ECHA D4 and D5 background document (ECHA, 2016), indicates that chemical oxidation may be a potential abatement technique for waste waters containing cyclosiloxanes and that removal efficiencies may be up to 90%. However, no references to an industrial application of this technique for cyclosiloxanes have been found.

6.4.1 Thermal Oxidation

6.4.1.1 Incineration

Incineration of VMS containing wastes, either in sludges, solid wastes or liquids should be carried out in an appropriately licensed waste incinerator.

6.4.1.2 Alternative Raw Material (ARM)

VMS can be used as an alternative fuel source, where the VMS waste is blended with other high calorific wastes to be used as alternative fuels in cement manufacture.

Applicability: Incineration technology is considered applicable to large scale users (Level 1) for on-site operation but for the majority of uses will likely be accessed via external waste contract facilities. ARM is considered applicable to large and medium scale users (Levels 1 and 2).

Removal efficiency for VMS: >99%.

6.4.2 Landfill

Disposal of VMS containing wastes in landfill should typically only occur where no other option higher up the waste hierarchy is available and where the waste is confirmed to meet waste acceptance criteria for the landfill.

Applicability: Not appropriate

Removal efficiency for VMS: Not known

Removal efficiency for L3, L4 and L5: Although there are no specific studies documenting removal efficiency via chemical oxidation for the linear VMS, given the similarities in physico-chemical properties to the analogous cyclic species, similar removal efficiencies could be anticipated if the appropriate operating procedures or parameters for the specific target VMS are used.

6.3.4 Adsorption

Adsorption is the transfer of soluble substances (solutes) from the waste water phase to the surface of solid, highly porous particles (the adsorbent). The adsorbent has a finite capacity for each compound to be removed. When this capacity is exhausted, the adsorbent is 'spent' and has to be replaced by fresh material. The spent adsorbent either has to be regenerated or incinerated and should be managed/disposed of consistent with applicable laws.

Adsorbents include:

- Activated carbon
- Lignite coke
- γ -Aluminium oxide
- Adsorber resins

Adsorption processes are divided into:

- Mixing, usually used for batch-wise treatment
- Percolation, applicable to continuous treatment, normally with a fixed-bed adsorber packed in two columns that are alternately on duty and undergoing backwashing
- Pulse-bed or moving-bed process, as continuous percolation with waste water and adsorbent led countercurrent through the column (European Commission, 2016)

Applicability: The efficiency of adsorption processes varies widely with waste water composition and feed concentration, which should be borne in mind when references to achievable emissions or removal efficiencies are cited. The technologies are scaleable and therefore may be applicable to all levels of use (Levels 1 to 3).

Removal efficiency for D4, D5 and D6: Appendix B to the ECHA D4 and D5 background document (ECHA, 2016) indicates that adsorption is expected to have a removal efficiency of up to 95%.

Removal efficiency for L3, L4 and L5: Although there are no specific studies documenting removal efficiency via thermal oxidation for the linear VMS, given the similarities in physico-chemical properties to the analogous cyclic species, similar removal efficiencies could be anticipated if the appropriate operating procedures or parameters for the specific target VMS are used.

6.4 Abatement of Emissions to Waste/Land

7 DEMONSTRATING MINIMISATION BY MONITORING



7.1 Monitoring

Once RMMs have been selected for a downstream user's facility, a demonstration that the emissions have been minimised may be conducted through the collection and analysis of emission samples.

Monitoring of the emissions may be used to help demonstrate (1) that the equipment is functioning as intended after the start-up period, and (2) that the equipment continues to provide expected removal. Depending on the facility and RMMs, this may include monitoring air, water, or waste releases.

The type of and extent to which monitoring is sensible will typically depend in part, on the individual scale of operation and frequency of use. For example, it may be helpful to perform monitoring once to demonstrate the efficiency of the abatement techniques employed.

7.2 Emission Monitoring Plans & Procedures

Emission monitoring involves preparation of a sampling plan (to include the monitoring location, sampling frequency, sample collection and sample handling procedures), analytical methods, quality control (QC) samples and any other information that has to be collected at the time of sampling to be able to calculate the releases (such as volume or flowrate of water or air, or type of processes used or products generated).

For example, guides are available to determine and define all of these procedures for air, water or wastewater, and wastes (See EPA, 2018 and JRC, 2017).

The analysis of VMS in environmental emissions can involve complex and sophisticated sampling and analytical methods because of their very low water solubility (less than 0.1 mg/L) and potential for contamination and generation of sampling and analytical artefacts. VMS have different requirements in terms of mass spectra, solvent used for extraction, need for more cleaning of laboratory instrument and equipment, or other requirements. Therefore, a qualified laboratory should be commissioned to undertake such analyses, especially for medium and small scale users (Levels

2 and 3) who may not have the in-house capability to undertake such laboratory analysis.

Available laboratories may include commercial laboratories or laboratories at educational institutions. An important criterion is the demonstrated (meeting quality acceptance criteria) experience of the laboratory in analyses for VMS.

7.2.1 Quality Control Challenges in Monitoring VMS

Due to the ubiquity and volatile nature of VMS, it is important to implement a QC program to ensure sample integrity from collection to analysis. Potential problems faced when analysing for trace levels of VMS in environmental media samples are contamination from the environment, analyst, equipment, and tools, so the sample collection equipment and analytical instrumentation needs to be assessed for the presence of siloxanes.

Additionally, since many personal care products contain VMS, personnel collecting and processing samples must refrain from the use of these products. Analyte loss during collection, transfer, and sample preparation can also be a problem. In order to assess potential problems, a QC program demonstrates that samples were handled and stored in a way to minimize contamination and analyte loss. QC samples utilized should include trip blanks, field blanks, field spikes, procedural blanks, and solvent blanks.

Personnel performing sample collection and analysis must refrain from using any personal care products that may contain any of the VMS of concern while preparing for or conducting any field activities or laboratory analyses to minimise the possibility of contamination with VMS. If a list of ingredients is not available, the product should not be used. As most make-up products do not include a comprehensive list of ingredients, they should be avoided completely. See Table 7-3 for a list of products and Table 7-4 for a list of potential ingredients containing VMS.

The samplers and laboratory analysts should be asked to use personal-care products that do not contain VMS, or no personal care products at all, for

at least one day before as well as during the sampling and analysis activities, respectively.

Rental or personal vehicles used by the monitoring crews must be vacuum cleaned only; vehicles used for field sampling must not be detailed to avoid contamination of VMS from car cleaning products used for detailing/cleaning cars. The VMS in those products may go from the cars to the samplers, thus contaminating the samples collected. Other products to avoid include window treatment, silicone lubricating spray, silicone tubing, and greases and oils.

Similarly, the sampling equipment must not contain VMS. Equipment made of stainless steel or polytetrafluoroethylene (PTFE or "Teflon") can be used, as well as glass sample jars with Teflon lined lids and Teflon-wrapped threads for closure; in addition, sampler seals and other components must be non-silicone; low-density polyethylene can also be used. Proper decontamination of equipment using a final hexane rinse is required.

Personal protective equipment that can be used include nitrile coated nylon gloves, nitrile outer chemical gloves (disposable, powderless nitrile), and rubber-soled footwear; each of this PPE should be confirmed not to contain VMS via a review of the manufacturing materials. Hard hats and safety glasses with side shields do not contain VMS. Insect repellents that contain lotions may have VMS; therefore, a different type of repellent should be used.

Due to potential sample contamination issues, no physical contact (i.e., handshakes, etc.) should be allowed by non-project related personal prior to or following entry into the work zone and non-project personal should not be allowed in the vicinity of the work zone unless wearing non-VMS containing personal care products.

Sample manipulation for solid samples especially in open air near potential air emission points (both outdoors or indoors) should be avoided or minimized as much as possible. Common sample processing such as homogenization in open air may also promote sample/air exchange; solid sample drying may also promote volatilization and degradation of VMS.

Most of the methods reported in the literature are for the analysis of samples for concentrations of the cyclic siloxanes, Octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5), and Dodecamethylcyclohexasiloxane (D6); however, the precautions, sampling procedures and methods described here can be utilized for the linear siloxanes as long as the proper validation is conducted.

The validation procedure should include:

- Ensuring that the analytical equipment is not contaminated with cyclosiloxanes by using separate, dedicated instruments and equipment in the laboratory
- Ensuring that labware and equipment (vials, caps, syringes, pipets, tubing, septa, liners, columns, etc.) do not contain silicones
- Ensuring that the processing or reagents utilized in the method will not induce re-arrangement by incorporating individual quality control samples containing only one analyte at a time while analysing all analytes of interest during the validation stage
- Analysing the sample extracts by using GC/MS-SIM
- Identifying siloxanes in samples by comparing the GC retention time and mass spectrum for the sample peak with known siloxanes reference standards
- Quantifying siloxanes by a stable isotope dilution technique, where the ratio of sample siloxanes responses to internal standards (¹³C-labelled analogs) are used to minimize matrix effects. A minimum of five points are used in all the calibration curves

Strict laboratory and field quality assurance/quality control is needed to ensure the analysis is valid. Table 7-2 lists the requirements. A critical requirement is the analysis of up to seven procedural blanks for each analytical run of field samples. The average of the procedural blanks for each cyclosiloxane is subtracted from the analytical result obtained as indicated above. Method detection limits should be measured using matrix to include any potential variability introduced by the matrix and method and not just determined based on solvent.

Table 7-2: Analytical method QA/QC requirements per batch of samples

Requirements	Evaluation (based on method validation)
Instrument tuning	Must meet requirements in the Standard Operating Procedure (SOP)
Initial calibration (as needed)	Must meet requirements in the SOP
Continuing calibration	Must meet requirements in the SOP
Relative retention time	Must meet requirements in the SOP
Response factor	Must meet requirements in the SOP
Internal standards	Must meet requirements in the SOP
Surrogates	Must meet requirements in the SOP
Procedural blanks (included with each preparation batch)	Subtract the average of the procedural blanks results from the sample results provided by the GC/MS
Method blank	Concentration must be less than the quantitation limit
Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD)	Must meet the percent recovery (%R) and relative percent difference (RPD) specified in the SOP
Field matrix spike (MS) and field matrix spike duplicate (MSD)	Must meet the %R and RPD specified in the SOP or the quality assurance field plan
Field blank	Concentration must be less than the quantitation limit
Field duplicates	Must meet the %R specified in the SOP or the quality assurance field plan

7.2.2 Analytical Methodologies for Water

7.2.2.1 Analytical Methods Available

The aqueous solubility of VMS is very low (Annex 2) and initial screening for a surface sheen in the sample may indicate their presence above this solubility limit. Sampling and semi-quantitative analysis of any surface sheen by gas chromatographic methods will confirm whether this is due to the presence of VMS above the water solubility limit.

In addition to VMS having very low aqueous solubilities, their air/water partition coefficients (K_{aw}) are relatively high especially in comparison to organic compounds of similar size, indicating a strong tendency to partition to the air. They also have relatively high water-organic carbon partition coefficients (K_{oc}), thus if the volatilization path is reduced, they will readily partition from water to organic matter (Xu *et al.*, 2014). Several methods for the analysis of water for concentrations of VMS have been reported in the literature that take advantage of these physical chemical properties.

- Purge and trap with adsorption on a solid phase extraction sorbent (i.e., Sep-Pak plus PS-2) followed by GC-MS (Horii *et al.*, 2017)
- Headspace extraction with GC-MS (Sparham *et al.*, 2008)
- Liquid-liquid extraction with low density polyethylene (LDPE) sample stabilization by GC-MS (Knoerr *et al.*, 2017)

7.2.2.2 Liquid-Liquid Extraction with LDPE

CES sponsored the development of the liquid-liquid extraction with LDPE analytical method and sampling protocol for cVMS (D4, D5 and D6) in wastewater (Knoerr *et al.*, 2017). This is a fully validated analytical method and validated sampling protocol, and has been successfully utilized in two large monitoring programs, one in the U.S. for D4 in surface water, effluent and influent, and one in Europe for D4, D5 and D6 in influent.

The Knoerr (2017) method is unique in that it utilizes low density polyethylene (LDPE) to inhibit loss of cVMS during sampling and transport to the laboratory. The samples are then processed with a simple solvent extraction.

The analytical method involves the use of a capillary-column gas chromatograph (GC) with mass spectrometer (MS) detection using electron-impact ionisation equipment operated in a Selective Ion Monitoring (SIM) mode (GC/MS-SIM). Validation of the analytical method must be performed before analyses can start to ensure the correct procedure is followed during analysis.

7.2.3 Analytical Methodologies for Air

Hayward *et al.*, 2011 describes a collection and analytical method for the analysis of air samples for

D4, D5 and D6 utilizing XAD-2 sorbent. This method was subsequently used for passive air sampling and compared to a method utilizing Isolute ENV+ sorbent (Krogseth et.al. 2013a). Air methods for siloxane analysis must be carefully validated to ensure that the chosen sorbent does not catalyze equilibration of the siloxanes during collection or processing into a mixture of siloxanes while the sorbent must also be proven to be efficient in capturing the siloxanes from the air without breakthrough. For example, ENV+ sorbent was initially determined to be a good sorbent for efficiently capturing the siloxanes from air in the environment, but subsequently was shown to convert D5 present in a sorbed air sample to hexamethylcyclotrisiloxane (D3), D4 and D6 (Krogseth et.al., 2013b and Kierkegaard *et.al.*, 2013). The presence of D3 was unexpected due to its short aquatic half-life (23 minutes) and its use patterns. In order to ensure that a chosen sorbent collection method produces accurate results for each siloxane, validation must include individual fortification of samples for each siloxane separately while analyzing for all the siloxanes. It is preferable to fortify sorbent tubes in the gaseous form similar to how the samples will be collected to ensure the validation of the collection method as well as the analytical method. The sorbent method is valid if the individual analyte fortified samples only show the fortified analyte through processing, does not produce other siloxanes within the method and can capture siloxanes from air appropriate for the application (e.g. passive or active sampling).

7.2.4 Analytical Methodologies for Soil, Sludge and Sediment

One of the most important aspects in analysing solids such as soil, sludge and sediment for VMS is the minimization of sample handling in the presence of air as mentioned previously to avoid the potential for contamination and/or degradation. A collection and analytical technique described by Nusz et.al. 2018 for the analysis of D4 in sludge and sediment was validated and utilized for the U.S. waste water treatment plant monitoring program. For example, the field processing method for sediment minimizes sample handling in the field, by collecting the sample in a LDPE bag for homogenization with aliquots transferred by squeezing a portion through a hole cut in the LDPE bag into glass jars for shipment back to the analytical laboratory. When the samples are received in the laboratory, the sample processing should be conducted within a clean fume hood where the air passes through filters designed to remove volatile materials prior to coming in contact with the samples. Extraction of the solid samples is done with Hexane and with Acetonitrile as a wetting aid in the same extraction step without drying or lengthy homogenizing. This method works well for soils and also for both linear and the other cyclic siloxanes.

Table 7-3: Examples of personal care and make-up products that may contain VMS

Personal care and make-up products that may contain VMS			
Personal care products	Hand soap	Hand sanitizer	Sunblock
	Sunscreen	Hand lotion	Deodorant
	Antiperspirant	Hair shampoo	Conditioner
	Shaving creams containing lotions		
Make-up	Nail polish	Foundation	Eye shadow
	Antiperspirant	Hair shampoo	Conditioner
	Concealer	Facial powder	Lipstick
	Eye cream	Eye liner	Mascara
	Acne treatment		

Table 7-4: Examples of ingredients that contain VMS (either as an ingredient or as an impurity)

Ingredients that contain VMS
Amodimethicone, cyclomethicone, dimethicone, methicone, simethicone, trimethicone, dimethicone/Isobutyl PPG-20 crosspolymer, and hundreds of other ingredients with dimethicone as part of the name
Polydimethyl siloxane, polysiloxanes, polysilicone
Cyclotetrasiloxane, cyclopentasiloxane, cyclohexasiloxane
Polyquaternium 22
Organo-modified siloxane copolymer
Silicone antifoams
Silicone fluids
Silicone polymers
Silicone volatiles
Room-temperature vulcanising (RTVs) silicones

8 WHERE TO FIND MORE INFORMATION



8.1 Global Legislation

AUSTRALIA

[Australian Regulatory Assessment D4/D5/D6: Environment Tier II](#)

CANADA

[Government of Canada, Siloxane D4 \(Cyclotetrasiloxane, octamethyl-\)](#)

[Government of Canada, Siloxane D4: P2 notice performance report](#)

[Government of Canada, Siloxane D5 \(Cyclopentasiloxane, decamethyl-\)](#)

[Government of Canada, Cyclohexasiloxane, dodecamethyl- \(D6\)](#)

EUROPE

European Union (General) and [European Chemicals Agency \(ECHA\)](#)

[EC Candidate List](#)

ECHA (2016) Background document to the Opinion on the Annex XV dossier proposing restrictions on Octamethylcyclotetrasiloxane (D4) and Decamethylcyclopentasiloxane (D5), including non-confidential appendices, June 2016

ECHA (2017a) Guidance on information requirements and chemical safety assessment, Part C: PBT Assessment, June 2017

ECHA (2017b) Guidance on Information Requirements and Chemical Safety Assessment Chapter R.11: PBT/vPvB assessment, Version 3.0, June 2017

ECHA (2018a) Annex XV report, Proposal for identification of a substance of very high concern on the basis of the criteria set out in REACH Article 57 - Substance Name: Dodecamethylcyclohexasiloxane [D6], EC Number: 208-762-8, CAS Number: 540-97-6, Submitted by: European Chemicals Agency (ECHA) at the request of the European Commission, Date: February 2018

ECHA (2018b) ECHA Registered Substances webpage, access to the D4 registration dossier; <https://echa.europa.eu/registration-dossier/-/registered-dossier/15289>

ECHA (2018b) ECHA Registered Substances webpage, access to the D5 registration dossier;

<https://echa.europa.eu/registration-dossier/-/registered-dossier/14807>

ECHA (2018b) ECHA Registered Substances webpage, access to the D6 registration dossier; <https://echa.europa.eu/registration-dossier/-/registered-dossier/15811>

ECHA (2018b) ECHA Registered Substances webpage, access to the L3 registration dossier; <https://echa.europa.eu/registration-dossier/-/registered-dossier/16055>

ECHA (2018b) ECHA Registered Substances webpage, access to the L4 registration dossier; <https://echa.europa.eu/registration-dossier/-/registered-dossier/5665>

ECHA (2018b) ECHA Registered Substances webpage, access to the L5 registration dossier; <https://echa.europa.eu/registration-dossier/-/registered-dossier/5714>

[ECHA \(2018c\) Persistence, bioaccumulation and toxicity assessment, accessed on 25 November 2018](#)

ECHA (2018d) C&L Inventory; https://echa.europa.eu/information-on-chemicals/cl-inventory-database?p_p_id=disclinventory_WAR_disclinventortoryportlet&p_p_lifecycle=0&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=1&p_p_col_count=2

Denmark

[Danish Ministry of the Environment, Siloxanes \(D3, D4, D5, D6, HMDS\)](#)

United Kingdom

[Environmental Risk Assessment Report: Octamethylcyclotetrasiloxane \(2009a\)](#)

[Environmental Risk Assessment Report: Dodecamethylcyclohexasiloxane \(2009b\)](#)

JAPAN

[Cyclosiloxanes Information Center Summary](#)

OECD

[OECD SIAM 29 \(2009\): D6](#)

UNITED STATES

[Maine Chemicals of Concern](#)

[Oregon Priority Pollutant List](#)

[Minnesota Chemicals of High Concern List 2016](#)

[Use of multiple lines of evidence to provide a realistic toxic substances control act ecological risk evaluation based on monitoring data: D4 case study](#)

UNITED NATIONS

[UN Persistent Organic Pollutants Review Committee, August 24th 2014: Review of D4, D5 and D6.](#)

8.2 Industry Information

ORGANISATIONS

[Cyclosiloxanes Information Center:](#)

On-line repository of scientific data on D4, D5 and D6

[Global Silicones Council](#)

See also

<http://www.siliconesinfo.com/>

<https://siliconesbenefits.com/>

[FAQ – D4 & D5: Europe, North America and Japan. GSC \(2015\)](#)

[CES-Silicones Europe](#)

[Whelan, M. and Kim, J. \(2018\) Application of models in understanding the environmental behaviour of volatile methylsiloxanes: Fate, transport, and bioaccumulation. CES – Silicones Europe, March 23, 2018.](#)

[The addition of D4, D5 and D6 to the Candidate list under REACH is disproportionate and endangers critical beneficial uses](#)

[Silicone Research, An Industry Commitment. GSC \(2016\)](#)

[Does D4 meet PBT or vPvB Criteria? Regulation in the context of developments in science. CES \(2015\)](#)

[Does D5 meet PBT or vPvB Criteria? Regulation in the context of developments in science. CES \(2015\)](#)

[Silicone Industry Association of Japan](#)

[Workshop of the Latest Development on the Evaluation Method of PBT \(Persistent Bioaccumulative Toxic\) Chemicals— Focusing on the Environmental Fate, Bioaccumulation, and Safety Assessment of Cyclic Siloxane \(2017\)](#)

[Silicones Environmental, Health and Safety Council of North America \(SEHSC\)](#)

COMPANIES

Evonik

[Addition of D4, D5 and D6 to the SVHC Candidate List. FAQ \(2018\)](#)

8.3 General References

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European Commission (2016). Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector, Joint Research Centre for the European Commission, 2016

German CA (2018a) Annex XV report, Proposal for identification of a substance of very high concern on the basis of the criteria set out in REACH Article 57 - Substance Name: Octamethylcyclotetrasiloxane, D4, EC Number: 209-136-7, CAS Number: 556-67-2, Submitted by: German CA, Date: 01.03.2018

German CA (2018b) Annex XV report, Proposal for identification of a substance of very high concern on the basis of the criteria set out in REACH Article 57 - Substance Name: Decamethylcyclopentasiloxane; D5, EC Number: 208-764-9, CAS Number: 541-02-6, Submitted by: German CA, Date: 01.03.2018

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9 LIST OF ACRONYMS



APCI-MS/MS	Atmospheric Pressure Ionization and Mass Spectrometry	LDPE:	Low Density PolyEthylene
ARM:	Alternative Raw Material	MS:	Mass Spectrometer
ASE:	Accelerated Solvent Liquid Extraction	MSCA	Member State Competent Authority
BAT:	Best Available Techniques	PBT:	Persistent, Bioaccumulative and Toxic
CA:	Competent Authority	PBiT:	Persistent, Bioaccumulative and Inherently Toxic
CAS :	Chemical Abstracts Service	PID:	Photolonisation Detector
CES:	Centre Europeen des Silicones	PNEC:	Predicted No Effect Concentrations
cVMS:	Cyclic Volatile Methylsiloxanes	PPE:	Personal Protective Equipment
D4:	Octamethylcyclotetrasiloxane	PTFE:	PolyTetraFluoroEthylene
D5:	Decamethylcyclopentasiloxane	QA:	Quality Assurance
D6:	Dodecamethylcyclohexasiloxane	QC:	Quality Control
EC:	European Commission	REACH:	Registration, Evaluation, Authorisation and Restriction of Chemicals
ECHA:	European Chemicals Agency	RMMs:	Risk Management Measures
EIPPCB:	European Integrated Pollution Prevention and Control (IPPC) Bureau	RPD:	Relative Percent Difference
EU:	European Union	RSIA:	Regional Silicones Associations
FID:	Flame Ionisation Detector	RTVs:	Room-temperature vulcanising
GC:	Gas Chromatogram	SIM:	Selective Ion Monitoring
GCMS:	Gas chromatography Mass Spectrometry	SiO ₂ :	Silicon Dioxide
GSC:	Global Silicones Council	SLE:	Solid-Liquid Extraction
HS-SPME	HeadSpace-Solid Phase Micro-Extraction	SOP:	Standard Operating Procedure
IED:	Industrial Emissions Directive	STP:	Sewage Treatment Plant
IPTS:	Institute for Prospective Technological Studies	VMS	Volatile Methyl Siloxanes
JRC:	Joint Research Centre	vPvB:	Very Persistent and Very Bioaccumulative
L3:	Octamethyltrisiloxane	USA-DLLME:	Ultra Sound Assisted Dispersive Liquid-Liquid Micro-Extraction
L4:	Decamethyltetrasiloxane	WWTP:	Waste Water Treatment Plant
L5:	Dodecamethylpentasiloxane	%R:	Percent Recovery

10 PHYSICO-CHEMICAL PROPERTIES AND ENVIRONMENTAL FATE INFORMATION RELEVANT TO MANAGEMENT OF ENVIRONMENTAL EMISSIONS



10.1 Data tables

Table 10-1: Physico-chemical Properties and Environmental Fate Information Relevant to the Management of Environmental Emissions of D4, D5 and D6 ¹

Substance	D4	D5	D6
Physico-chemical properties			
Boiling point	175°C	210°C	245°C at 101.3 kPa
Density	0.95 g/cm ³ at 25°C	0.96 g/cm ³ at 20°C	0.98 g/cm ³ at 20°C
Octanol-water partition coefficient (in terms of log Kow)	6.98 at 25°C	8.09 at 25°C	8.87 at 25°C
Water solubility	0.056 mg/L	0.017 mg/L	0.0053 mg/L
Vapour pressure	140 Pa at 25°C	33.2 Pa at 25°C	6 Pa at 25°C
Environmental fate information			
Hydrolysis (half-life)	<ul style="list-style-type: none"> • 16.7 days at pH 7 and 12°C • 3.9 days at pH 7 and 25°C • 1.8 h at pH 4 and 25°C • 0.9 - 1 h at pH 9 and 25°C 	<ul style="list-style-type: none"> • 365 days at pH 7 and 12°C • 70.4 days at pH 7 and 25°C • 9.3 h at pH 4 and 25°C • 24.8 to 31.6 h at pH 9 and 25°C 	<ul style="list-style-type: none"> • >1 year at pH 7 and 12°C • 401 days at pH 7 and 25°C • 42 h at pH 4 and 25°C • 125 h at pH 9 and 25°C
Phototransformation in air (half-life)	7.2 days at 25°C	5.3 days at 25°C	3.9 days at 25°C
Henry's law constant (in terms of log K _{AW})	2.74 at 25°C	3.16 at 25°C	3.01 at 25°C
Adsorption coefficient (in terms of log K _{oc})	4.22 at 25°C	5.17 at 25°C	6.03 at 25°C
Desorption coefficient (in terms of log K _{oc})	4.3 at 25°C	5.34 at 25°C	Not calculated

¹ Sources: ECHA (2018b) and Whelan, M. and Kim, J. (2018)

Table 10-2: Physico-chemical Properties and Environmental Fate Information Relevant to the Management of Environmental Emissions of L3, L4 and L5 ¹

Substance	L3	L4	L5
Physico-chemical properties			
Boiling point	152.4°C at 101.3 kPa	194°C at 101.3 kPa	229 to 232°C at 101.3 kPa
Density	0.82 g/cm ³ at 20°C	0.854 g/cm ³ at 20°C	0.875 g/cm ³ at 20°C
Octanol-water partition coefficient (in terms of log K _{ow})	6.79 at 25°C	8.14 at 25°C	9.41 at 25°C
Water solubility	0.0345 mg/L	0.00674 mg/L	0.0000704 mg/L
Vapour pressure	535 Pa at 25°C	58.1 Pa at 25°C	6 Pa at 25°C
Environmental fate information			
Hydrolysis (half-life)	<ul style="list-style-type: none"> • 13.7 days at pH 7 and 25°C • 5.09 h at pH 5 and 25°C • 9.76 h at pH 9 and 25°C 	<ul style="list-style-type: none"> • 30.3 days at pH 7 and 25°C • 14 h at pH 5 and 25°C • 21.1 h at pH 9 and 25°C 	<ul style="list-style-type: none"> • 41.5 days at pH 7 and 25°C • 14 h at pH 5 and 25°C • 21.1 h at pH 9 and 25°C
Phototransformation in air (half-life)	5.4 days at 25°C	3.6 days at 25°C	2.7 days at 25°C
Henry's law constant (in terms of log K _{AW})	3.06 at 25°C	3.45 at 25°C	3.95 at 25°C
Adsorption coefficient (in terms of log K _{oc})	4.34 at 25°C	5.16 at 25°C	5.68 at 25°C
Desorption coefficient (in terms of log K _{oc})	4.35 at 25°C	5.33 at 25°C	Not calculated

¹ Sources: ECHA (2018b) and Whelan, M. and Kim, J. (2018)

10.2 Discussion of Data

The hydrolysis half-lives for D4 and D5 at pH 4 and L3, L4 and L5 at pH 5 favour hydrolysis for removal of these six substances. The hydrolysis half-life for D6 is less favourable; however, hydrolysis can be accelerated by increasing the temperature and lowering the pH. The Henry's law constants for the six substances indicate rapid volatilization from water. The adsorption coefficients suggest that removal via activated carbon beds may be an efficient treatment for all six substances.

Any VMS emitted to air is removed in a relatively short period via indirect phototransformation by hydroxyl radicals in air; therefore, air emissions are not as much of a concern, although any minimisation measure would help.

Based on the low water solubilities and biodegradation rates, and the high log Kow and adsorption coefficients, typical aerobic biological wastewater treatment systems remove VMS as part of a normal load of organic carbon via air emissions and adsorption to sludge. Incineration of the off-gas and the sludge of wastewater treatment plants would be the best option to minimize emissions.

However, it is known that silica is formed during incineration and has to be removed to avoid shortening the service time of incineration equipment. If the sludge is used as a fertilizer on agricultural fields, depending on the soil humidity, all six VMS would either rapidly volatilize to air in high humidity soil, which will result in their removal from the soil in a short period, or degrade rapidly in dry soil.

In biological wastewater treatment systems, the substances can also adsorb to organic solids suspended in the wastewater and then settle into the sediments of the receiving water; however, a large fraction of the substances would partition to air and only a small portion would partition to the sediments. Spills of VMS would result in emissions to waste water and air and, therefore, spills should be either prevented or removed with dry absorbents to reduce the amount that reaches the waste water.

ANNEX 1 – VMS REGULATORY STATUS (EUROPEAN UNION)



EU Decision

According to the EU authorities:

D4 (octamethylcyclotetrasiloxane, EC 209-136-6, CAS 556-67-2),

D5 (decamethylcyclopentasiloxane, EC 208-764-9, CAS 541-02-6) and

D6 (dodecamethylcyclohexasiloxane, EC 208-762-8, CAS 540-97-6)

are Persistent, Bioaccumulative and Toxic (PBT) and Very Persistent and Very Bioaccumulative (vPvB) substances.

These three cyclosiloxanes were placed onto the ECHA Candidate List of substances of very high concern (SVHCs) on June 27, 2018.

The latest documents that discuss the reasons for the classification of D4, D5 and D6 as PBT/vPvB substances were issued by Germany for D4 and D5 on 1st March 2018 (Germany CA, 2018a and 2018b, respectively) and by ECHA for D6 in February 2018 (ECHA, 2018).

The linear VMS covered by this document (L3, L4 and L5) are currently under evaluation by a Member State Competent Authority (MSCA) to determine whether or not they meet PBT or vPvB criteria. Some of the dossiers still have testing proposals that have not been approved. The results of that evaluation will not be available until the studies are completed and added to the dossiers by the registrants, and the dossiers evaluated by the MSCA.

Silicones Industry Response to EU SVHC Listing of D4, D5 and D6

The silicones industry has published a robust analysis of the application of the criteria used by the European regulator in prioritising D4, D5 and D6 onto the Candidate List. Based on a weight of evidence approach from a robust evaluation of all the current available scientific literature, the industry

maintains that cyclosiloxanes should not be considered PBT/vPvB.

Based on studies performed in water, which are designed to determine bioconcentration factors using fish, the EU decided to classify the substances as B and vB, despite the fact that exposure to aquatic organisms will occur primarily via the diet. A weight of evidence determination using expert judgement indicates that the depuration rate constants obtained from the bioconcentration factor (BCF) in water and the biota-sediment accumulation factor (BSAF) studies are considered to be the most applicable metric for assessing the bioaccumulation potential of substances like D4, D5 and D6, which have log K_{ow} values greater than 6. The depuration rates found for all three substances are indicative of substances that do not bioaccumulate, and it is concluded that D4, D5 and D6 are not B or vB. Depuration occurring faster than diffusion alone is consistent with a fugacity ratio less than 1. TMF data for D4, D5 and D6 also support the conclusion of not B or vB.

P and vP were determined based on water and sediment half-lives, but ignoring the fact that D4, D5 and D6 are readily degraded in air and that most of the concentrations of these substances discharged to water or soil partition to air. A small fraction, when discharged to water, partitions to the sediments via adsorption to particulates.

The EU determined that only D4 met the T criterion, based on a CMR Cat.2 classification due to toxicity to reproduction in rodents that is species specific, and on an aquatic toxicity laboratory study that demonstrated that toxicity happens at concentrations that cannot be achieved in the environment (Bridges and Solomon, 2016). However, the EU applied the T criterion to D5 and D6 on the basis that all occurrences of these substances would have more than 0.1% of D4 as an impurity (which is not the case), despite the fact that studies conducted with D5 and D6 have not shown the same toxicity to reproduction in rodents found for D4.

Further information can be found in the links provided in Section 8.2.

Environmental Fate Data Relevant to Assessment of D4, D5 and D6 as PBT and vPvB Substances

Annex 1, Table 1: Environmental Fate Data Relevant to Assessment of D4, D5 and D6 as PBT Substances¹

Classification Criteria		D4	D5	D6
Persistence – P				
Degradation in water (criteria in half-life, data in % biodegraded and days to achieve it or in half-life for hydrolysis)	>60 days in marine water	Not available	Not available	Not available
	>40 days in fresh or estuarine water	Biodegradation: 3.7% in 29 days	Biodegradation: 0.14% in 28 days	Biodegradation: 4.5% in 28 days
		Abiotic (hydrolysis): 3.9 days at pH 7 and 25°C	Abiotic (hydrolysis): 70.4 days at pH 7 and 25°C	Abiotic (hydrolysis): 401 days at pH 7 and 25°C
Degradation in sediment (half-life)	>180 days in marine water	Not available	Not available	Not available
	>120 days in fresh or estuarine water	365 days at 25°C in anaerobic sediments	3 100 days at 25°C in anaerobic sediments	3 100 days at 25°C in anaerobic sediments
Degradation in soil (half-life)	>120 days	5.29 days at 25°C	12.6 days at 25°C	401 days at 25°C
Bioaccumulation - B				
Bioconcentration factor (kinetic, lipid-normalised)	>2 000 L/kg	14 900 L/kg	16 200 L/kg	2 860 L/kg
Toxicity – T				
Long-term NOEC or EC10 for aquatic organisms	<0.01 mg/L	≥0.0044 mg/L	≥0.014 mg/L	≥0.014 mg/L
Classification as carcinogenic (category 1A or 1B), germ cell mutagenic (category 1A or 1B) or toxic for reproduction (category 1A, 1B or 2)		Toxic for reproduction Category 2	Not classified	Not classified
Classification as STOT RE 1, or STOT RE 2 based on chronic toxicity upon repeated dose exposure		Not classified	Not classified	Not classified

¹ Sources: ECHA (2018b) and Whelan, M. and Kim, J. (2018).

² The substance had no chronic effects on fish up to the highest concentration tested in a 93-day long study with D4, 0.0044 mg/L.

Annex 1, Table 2: Environmental Fate Data Relevant to Assessment of D4, D5 and D6 as vP/vB Substances¹

Classification Criteria	D4	D5	D6	
Persistence – vP				
Degradation in water (criteria in half-life, data in % biodegraded and days to achieve it or in half-life for hydrolysis)	>60 days	Biodegradation: 3.7% in 29 days	Biodegradation: 0.14% in 28 days	Biodegradation: 4.5% in 28 days
		Abiotic (hydrolysis): 3.9 days at pH 7 and 25°C	Abiotic (hydrolysis): 70.4 days at pH 7 and 25°C	Abiotic (hydrolysis): 401 days at pH 7 and 25°C
Degradation in sediment (half-life)	>180 days	365 days at 25°C in anaerobic sediments	3 100 days at 25°C in anaerobic sediments	3 100 days at 25°C in anaerobic sediments
Degradation in soil (half-life)	>180 days	5.29 days at 25°C	12.6 days at 25°C	401 days at 25°C
Bioaccumulation - vB				
Bioconcentration factor (kinetic, lipid-normalised)	>5 000 L/kg	14 900 L/kg	16 200 L/kg	2 860 L/kg

¹ Sources: ECHA (2018b) and Whelan, M. and Kim, J. (2018).

Environmental Fate Data Relevant to Assessment of L3, L4 and L5 as PBT and vPvB Substances

Annex 1, Table 3: Environmental Fate Data Relevant to Assessment of L3, L4 and L5 as PBT Substances ¹

Classification Criteria		L3	L4	L5
Persistence - P				
Degradation in water (criteria in half-life, data in % biodegraded and days to achieve it or in half-life for hydrolysis)	>60 days in marine water	Not available	Not available	Not available
	>40 days in fresh or estuarine water	Biodegradation 0% in 28 days Abiotic (hydrolysis) 13.7 days at pH 7 and 25°C	Biodegradation 0% in 28 days Abiotic (hydrolysis) 30.3 days at pH 7 and 25°C	Biodegradation 0% in 28 days Abiotic (hydrolysis) 41.5 days at pH 7 and 25°C
Degradation in sediment (half-life)	>180 days in marine water	Not available	Not available	Not available
	>120 days in fresh or estuarine water	365 days at 25°C	420 days at 25°C	912 days at 25°C
Degradation in soil (half-life)	>120 days	4.54 days at 25°C	7.6 days at 25°C	16.5 days at 25°C
Bioaccumulation - B				
Bioconcentration factor (kinetic, lipid-normalised)	>2 000 L/kg	27 600 L/kg	6 910 L/kg	4 260 L/kg
Toxicity - T				
Long-term NOEC or EC10 for aquatic organisms	<0.01 mg/L	≥ 0.0094 mg/L	≥ 0.0022 mg/L ²	≥ 0.000047 mg/L ³
Classification as carcinogenic (category 1A or 1B), germ cell mutagenic (category 1A or 1B) or toxic for reproduction (category 1A, 1B or 2)		Not classified	Not classified	Not classified
Classification as STOT RE 1, or STOT RE 2 based on chronic toxicity upon repeated dose exposure		Not classified	Not classified	Not classified

¹ Sources: ECHA (2018b) and Whelan, M. and Kim, J. (2018).

² NOEC is close to the solubility limit of 0.007 mg/L.

³ NOEC determined in test media prepared at a nominal concentration that corresponded with the water solubility of the substance (70 ng/l).

Annex 1, Table 4: Environmental Fate Data Relevant to Assessment of L3, L4 and L5 as vP/vB Substances ¹

Classification Criteria		L3	L4	L5
Persistence – vP				
Degradation in water (criteria in half-life, data in % biodegraded and days to achieve it or in half-life for hydrolysis)	>60 days	Biodegradation 0% in 28 days	Biodegradation 0% in 28 days	Biodegradation 0% in 28 days
		Abiotic (hydrolysis) 13.7 days at pH 7 and 25°C	Abiotic (hydrolysis) 30.3 days at pH 7 and 25°C	Abiotic (hydrolysis) 41.5 days at pH 7 and 25°C
Degradation in sediment (half-life)	>180 days	365 days at 25°C	420 days at 25°C	912 days at 25°C
Degradation in soil (half-life)	>180 days	4.54 days at 25°C	7.6 days at 25°C	16.5 days at 25°C
Bioaccumulation – vB				
Bioconcentration factor (kinetic, lipid-normalised)	>5 000 L/kg	27 600 L/kg	6 910 L/kg	4 260 L/kg

¹ Sources: ECHA (2018b) and Whelan, M. and Kim, J. (2018).

Classification of VMS in the EU

Annex 1, Table 5: Classification of VMS in the EU ¹

Substance	CAS	EC	H-Phrase	H-Phrase Description
Octamethylcyclotetrasiloxane (D4)	556-67-2	209-136-7	H226 ²	Flammable liquid and vapour
			H361f	Suspected of damaging fertility of unborn child
			H411	Very toxic to aquatic life with long lasting effects
Decamethylcyclopentasiloxane (D5) ³	541-02-6	208-764-9		
Dodecamethylcyclohexasiloxane (D6) ³	540-97-6	208-762-8		
Octamethyltrisiloxane (L3)	556-67-2	209-136-7	H226 ²	Flammable liquid and vapour
Decamethyltetrasiloxane (L4)	541-02-6	208-764-9	H226 ²	Flammable liquid and vapour
Dodecamethylpentasiloxane (L5) ³	540-97-6	208-762-8		

¹ Sources: ECHA (2018b) and CLP inventory.

² H226 is not included in the harmonised classification of D4, L3 or L4 but is included in the classification in the respective REACH registration dossier.

³ D5, D6, and L5 are not currently classified under the CLP inventory.

Exposure Scenarios

The manufacturers of D4, D5, D6, L3, L4 and L5 have registered these VMS substances under the EU REACH Regulation. As part of this registration the individual uses of the substances are described in exposure scenarios, which provide detail on where the substance is used, the scale at which it is used and the operational conditions and risk management measures downstream users are required to take to ensure safe use of these substances and minimise environmental releases. These exposure scenarios evaluate the risk arising from environmental exposure and this information is communicated to downstream users in the (extended) safety data sheets for the substances or mixtures containing these substance.

The exposure scenarios are described by the sector of use (manufacture, formulation, industrial end use, professional end use and consumer end use) and provided detailed descriptions of the scale of use (in terms of quantity of VMS used each day in each use) and the corresponding expected releases of these substances to air and to water prior to the implementation of RMMs.

This document does not seek to replace these detailed exposure scenarios and downstream users in the EU have an obligation under REACH to ensure that their use is either covered by these exposure scenarios or by their own exposure scenario submitted as part of an individual downstream user Chemical Safety Report (CSR).

Management of PBT/vPvB Substances under REACH

The ECHA PBT Expert Group indicates in general for substances that are considered PBT/vPvB the following¹:

"Substances that persist for long periods of time in the environment and have a high potential to accumulate in biota are of specific concern since their long-term effects are rarely predictable. After entering the environment once, the exposure to these substances is very difficult to reverse by the cessation of emission. Protection of pristine remote areas from PBT/vPvB substances is particularly difficult as these substances do not degrade near emission sources but may be gradually transported into remote areas. For PBT/vPvB substances a

"safe" concentration in the environment cannot be established using the methods currently available. A particular concern with vPvB substances is that even if no adverse effects can be demonstrated in laboratory testing, long-term effects might be possible since high but unpredictable levels may be reached in humans or the environment over extended time periods."

The latest version of the ECHA Guidance on Information Requirements and Chemical Safety Assessment Chapter R.11: PBT/vPvB Assessment, Version 3.0, June 2017 provides guidance on the information requirements for the effective management and control of PBT/vPvB substances:

- Section 6.5 of Annex 1 to the REACH Regulation requires that 'for substances satisfying the PBT and vPvB criteria the manufacturer recommends for downstream users RMMs which minimise exposures and emissions to workers and the environment'
- DUs have to implement the recommended RMMs or prepare their own DU CSR
- Descriptions of the implemented or recommended RMMs and OCs in an ES need to be sufficiently detailed to demonstrate rigorous control of the substance and to allow examination and assessment of their efficiencies by authorities
- The level of detail communicated in the ES attached to the SDS must permit DUs to check that their own use(s) are covered by the ES developed by their supplier and that they have implemented the recommended RMMs and OCs correctly

¹ ECHA PBT Expert Group webpage, accessed on July 2018 (<https://echa.europa.eu/pbt-expert-group>).

Matching the Exposure Scenarios to the Scale of Operation

Annex 1, Table 6: Exposure Scenarios Based on Generic Scale of use

Exposure Scenario Description	Scale of Use					
	D4	D5	D6	L3	L4	L5
Offsite Monomer or Intermediate Use	Level 1	Level 1	Level 1			
Monomer, emulsion polymerisation	Level 1					
Rigid polyurethane manufacture		Level 1				
Formulation, pharmaceuticals		Level 2	Level 2			
Formulation, personal care products		Level 1	Level 1	Level 2	Level 2	Level 2
Formulation, household care products		Level 2	Level 2	Level 2		
Use of household care products, industrial		Level 3		Level 2		
Use of personal care products, professional			Level 3	Level 3	Level 3	Level 3
Use of washing/cleaning products, professional		Level 3	Level 3			
Use of polishes and waxes, professional		Level 3				
Use of dry cleaning products, professional		Level 2				
Use as a laboratory reagent	Level 3	Level 3	Level 3	Level 3	Level 3	Level 3
Use of rigid polyurethane foam		Level 1				
Formulation, non-metal surface treatment products					Level 3	
Use as a non-metal surface treatment agent – 'in situ' treatment (industrial)				Level 2	Level 3	Level 2
Formulation, coatings				Level 3		
Use in coatings (industrial)				Level 3		
Formulation, adhesives and sealants				Level 2		
Use of adhesives, sealants (industrial)				Level 3		
Formulation, healthcare products				Level 3		
Use of heat transfer fluids (industrial)				Level 3	Level 3	
Formulation, automotive care products				Level 2	Level 3	
Use of automotive care products (professional)				Level 3	Level 3	
Formulation, lubricants, greases – release products					Level 3	
Use of lubricants, greases – release products					Level 3	
Formulation, polymer preparation - formulation of release agent						Level 2
Polymer preparation - use as release agent						Level 2
Use in semiconductor and electronics manufacture (industrial)					Level 3	

ANNEX 2 – VMS REGULATORY STATUS (OTHER COUNTRIES)



Environmental Assessment of VMS Against PBT Criteria in Other Countries

Jurisdiction	D4	D5	D6	L3	L4	L5
 Canada	PiT	Does not meet criteria for B or T	Does not meet criteria for B or T	PBiT		
	PiT – Persistent and inherently Toxic. Further information: section 8.1.			PBiT – Persistent, Bioaccumulative and inherently Toxic	L4 and L5 – Assessed with no further action identified	
 Australia	Assessed in 2018 with no further action identified for D4, D5 and D6. Further information: section 8.1.					
 United States	D4 – risk review based on monitoring data ongoing.	D5 & D6 – Assessed with no further action identified.		Not currently under review		
 China	Environmental assessment expected to be completed in Q1 2020 based on risk, combining hazard and exposure data	No information on plans for evaluation of D5 and D6		Not currently under review		
 Japan	PB	PB	PB			
	D4 & D6 - assessment ongoing. D5 assessment complete, no further action identified. Further information: section 8.1.			Not currently under review		

Note: The individual criteria to classify substances as (very) persistent (P/vP), (very) bioaccumulative (B/vB) and toxic (T) may differ between jurisdictions.