14
Si
Silicon

Use of D4, D5 and D6 in industrial environments:

A TOOLBOX FOR MINIMISING ENVIRONMENTAL EMISSIONS

VERSION 1.0, JANUARY 2019

Table of Contents

Executive Summary

This toolbox is an interim document published under the direction of CES – Silicones Europe. It is an initial step, aimed at better informing downstream users of silicone products on the measures they may take to minimise emissions of volatile cyclic siloxanes, specifically focusing on D4, D5 and D6. In addition to promoting good product stewardship around the use of these substances, this document also aims to support the silicone industry's communication intentions to downstream users in the EU following the classification according to PBT/vPvB criteria under the EU REACH regulation. The future intent is to merge this information into a global living document, expanded to include additional siloxane substances.

Disclaimer

The information herein is offered without warranty, express or implied, as to merchantability, fitness for a practical purpose, and/or any other matter. Neither CES – Silicones Europe, nor any member company, assumes any liability or responsibility for any use, or the results of such use, of the information presented in this guide. All persons handling products containing D4, D5 and D6 have an independent obligation to assure that their actions are in conformity with all applicable laws and regulations, as well as company-specific policies and procedures.

CES – Silicones Europe may update this toolkit as significant new information becomes available. However, neither CES – Silicones Europe, nor any member company, assumes any responsibility to amend, revise, or otherwise update this guide to reflect information that may become available after its publication. While offered in good faith and believed to be correct, CES – Silicones Europe does not assume any liability for reliance on the information in this toolkit.

1 INTRODUCTION

1.1 Purpose of the document

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

In recognising 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 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 D4, D5, and D6 that may impact the effectiveness and selection of treatment methodologies for removal of D4, D5, and D6 from environmental emissions
4. Summarise global assessments of the environmental properties of these specific cyclosiloxanes 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 cyclosiloxanes, the silicones industry promotes minimisation of environmental emissions as part of good product stewardship. Recognising 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 D4, D5 and D6 from potential emissions.

1.2 Scope of the Document

This document provides information for all users of D4, D5 and D6 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 some professional products are typically seen to have a wide dispersive use and some can contain varying concentrations of D4, D5 and D6. 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 D4, D5 and D6

D4, D5, and D6 are often present concurrently in products and abatement technologies are similar for the three 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 three 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 CYCLOSILOXANES

2.1 Description of Substances

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.

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

D4, D5 and D6 have a distinct combination of properties compared to carbon-based PBT substances that makes their impact on the environment different from that produced by carbon-based substances. This unique combination of properties includes: 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 Annex 2.

2.3 Regional Environmental Assessment of Cyclosiloxanes Against PBT Criteria

Jurisdiction	D4	D5	D6
EU	**PBT /vPvB**	**vPvB**	**vPvB**
	Further information: section 8.1 and Annex 1. On EU Candidate List		
Canada	**PiT**	**Does not meet criteria for B or T**	**Does not meet criteria for B or T**
	PiT – Persistent and inherently Toxic Further information: section 8.1		
United States	D4 – risk review based on monitoring data ongoing. D5 & D6 – 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		
Japan	**PB**	**PB**	**PB**
	D4 & D6 - assessment ongoing. D5 assessment complete, no further action identified. Further information: section 8.1		

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

3 INDUSTRIAL AND PROFESSIONAL USE OF CYCLOSILOXANES

3.1 Use Summaries

The industrial and professional uses of cyclosiloxanes, 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 should 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 cyclosiloxanes. 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 cyclosiloxanes 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 cyclosiloxanes 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:

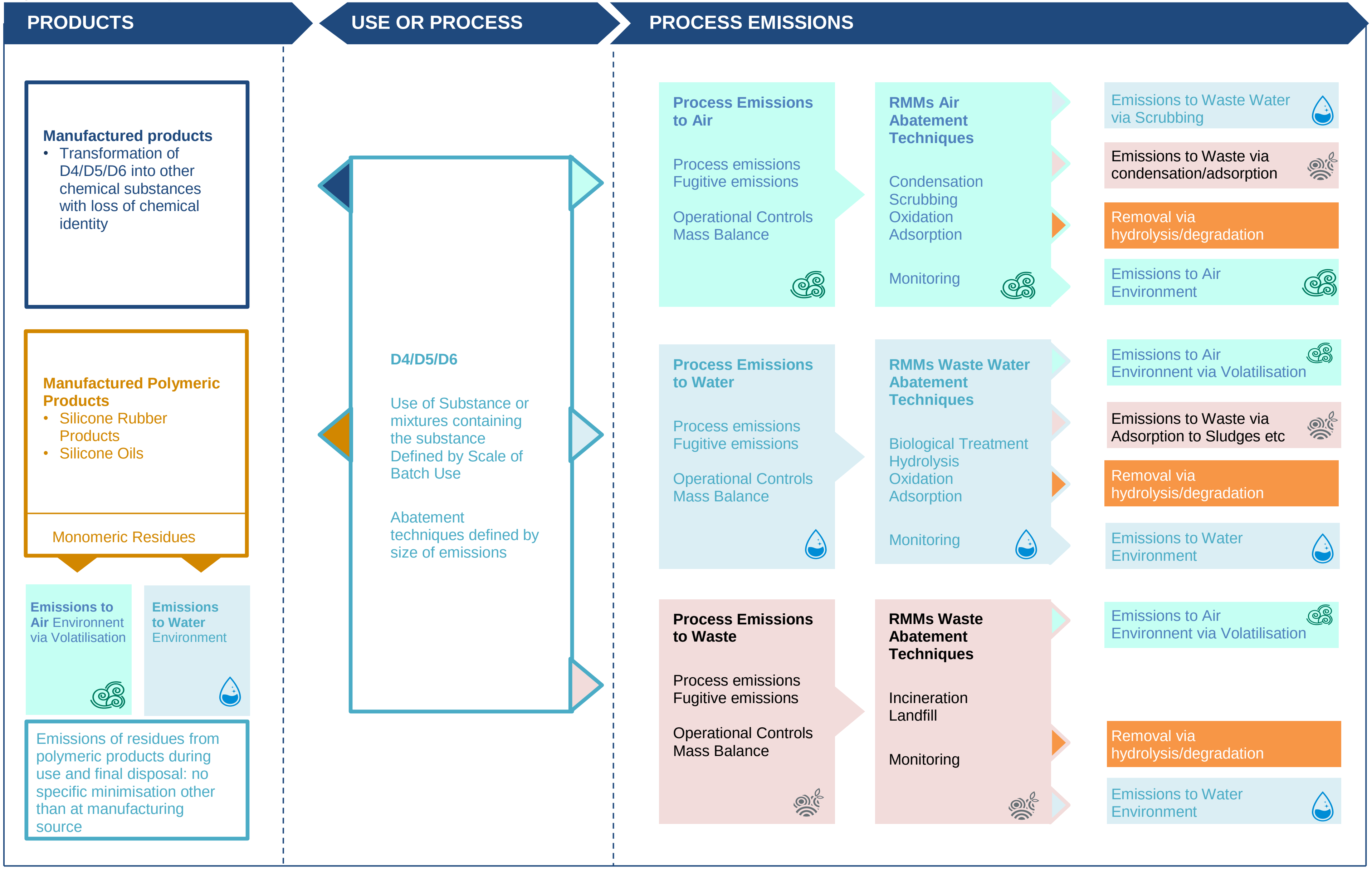
i. **Level 1 - Use of greater than 1000 kg per batch**: this is considered large-scale use at facilities which will typically have significant, dedicated engineering infrastructure to be able to handle the chemical or physico-chemical processes involving the cyclosiloxanes. Such industrial facilities 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

ii. **Level 2 - Use greater than 25 kg per batch but less than 1000 kg per batch**: the use of one drum or more of cyclosiloxanes 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

iii. **Level 3 - Use of less than 25 kg per batch**: the use of small quantities of cyclosiloxanes, most probably by professional users in formulated mixtures, where D5 and D6 are intentional ingredients, or in articles, where these cyclosiloxanes are present as residual monomers. This 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 cyclosiloxane 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 and D6 and formulated products.

Figure 1: Release pathways to the Environment for Cyclosiloxanes 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 Control[1] and Groundwater[2]) 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 cyclosiloxanes currently list PNECs for freshwater and marine water (D4 only) and for municipal sewage treatment plants (STPs) (D4, D5 and D6). The PNEC for municipal STPs is significantly higher than the solubility of these substances and will therefore not be attained under normal operational 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 D4, D5 and D6 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 cyclosiloxanes 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 a 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 cyclosiloxanes 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 cyclosiloxanes. Downstream users may wish to provide their staff with training on the behaviour of D4, D5 and D6 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:

- Optimise inerts in vent systems in order to maximise cyclosiloxane removal and recovery efficiency, whilst maintaining safe operational levels. E.g., excessive nitrogen in vent streams will adversely impact the cyclosiloxane removal efficiency (heat transfer coefficient) in vent cold traps and condensers.

- Lower temperature operations, if possible, to minimise volatilisation of cyclosiloxanes
- Condensation of cyclosiloxanes on process outlets. This can be effective but care needs to be taken to avoid temperatures at which cyclosiloxanes 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 Cyclosiloxanes at Source

Where it is not possible to prevent emissions within the process, it may be possible to recover cyclosiloxanes 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.

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 cyclosiloxanes. 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 cyclosiloxane products and the technology providers.

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.

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. Additionally, the ability to treat the scrubbing liquid will 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.

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 cyclosiloxanes being abated will not be able to sustain combustion without additional fuel.

Experience within the landfill gas management sector indicates that combustion of cyclosiloxanes can result in operational/maintenance issues for burner tips, downstream gas engines or other rotating equipment due to formation of SiO_2 (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%.

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 cyclosiloxane 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.

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.

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, cyclosiloxane 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 cyclosiloxanes in waste water but it is considered applicable at all levels of use (Levels 1 to 3).

Removal efficiency for D4, D5 and D6: Not known. No references to an industrial application of this technique for cyclosiloxanes 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 or hazardous 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 cyclosiloxanes 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.

6.3.4 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%.

6.4 Abatement of Emissions to Waste/Land

6.4.1 Thermal Oxidation

6.4.1.1 Incineration

Incineration of cyclosiloxane 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)

Cyclosiloxanes can be used as an alternative fuel source, where the cyclosiloxane 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 D4, D5 and D6: >99%.

6.4.2 Landfill

Disposal of cyclosiloxane 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 D4, D5 and D6: Not known

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 demonstrate (1) that the equipment is functioning as intended after the start-up period, and (2) that the equipment continues to provide the same efficiency of removal. Depending on the facility and RMMs, this may include emissions to air, water or wastewater, biological wastewater treatment sludge and wastes.

The type of monitoring and extent to which monitoring is sensible will typically depend on the individual scale and frequency of use. For example, it may be helpful to perform monitoring once to demonstrate the efficiency of the abatement techniques employed. Relevant costs and effort should be taken into account to ensure that monitoring is not disproportionate and it remains at the discretion of each company to decide on the extent of and necessity for their monitoring method and plan.

7.2 Emission Monitoring 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 in the EU to determine and define all of these procedures for air, water or wastewater, and wastes (See EPA, 2018 and JRC, 2017). Arespacochaga *et al* (2015) published a review of air sampling procedures and analytical procedures for environmental matrices. The Swedish Environmental Research Institute conducted a national screening programme that has information about sampling and analytical methods (Kaj *et al*., 2005).

The analysis of cyclosiloxanes in environmental emissions can involve complex and sophisticated analytical methods because of their very low water solubility. Therefore, a verified third party 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.

Third party laboratories may include commercial laboratories or laboratories at educational institutions. An important criterion is the experience of the laboratory in performing validated analyses for cyclosiloxanes.

7.2.1 Analytical Methodologies for Water

7.2.1.1 Analytical Methods Available

The aqueous solubility of cyclosiloxanes 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 this organic surface by gas chromatographic methods will confirm whether this is due to the presence of cyclosiloxanes above the water solubility limit.

Arespacochaga *et a*l (2015) describe a variety of methods for analysis of water samples:

- Purge and trap using helium followed by adsorption on a macroporous polymeric sorbent (i.e., XAD resins)
- Purge and trap followed by GC-MS, thermostatic bath and mechanical shaking before injection by headspace GC-MS
- Headspace-solid phase micro-extraction (HS-SPME) into the GC
- Ultrasound assisted dispersive liquid-liquid micro-extraction (USA-DLLME) into the GC

The authors also noted that GC–MS using single quadrupole mass spectrometry is the most common quantification technique and that some studies had used GC coupled to other detectors, such as flame ionisation detectors (FIDs), atomic emission spectroscopy (AES) or triple quadrupole MS instruments.

The following table indicates the concentration range reported by Arespacochaga et al (2015) for which the various techniques are applicable:

Table 7-1: Reported concentration limits of analytical methodologies for D4, D5 and D6

Method	[Cyclosiloxane]
Headspace-GC	>1 ppm
Purge and trap	>100 ppb
Ultrasound extraction	>100 ppb
High sensitivity method	>0.1 ppb

7.2.1.2 High Sensitivity Methodology

CES sponsored the development of an analytical method and sampling protocol for cVMS D4, D5 and D6 in wastewater (Knoerr, Durham and McNett, 2017). This is a fully validated method and sampling protocol.

The Knoerr, Durham and McNett (2017) method is unique in that it utilises 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 chromatogram (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. The procedure includes:

- Ensuring that the analytical equipment is not contaminated with cyclosiloxanes or using separate, dedicated instruments and equipment in the laboratory
- Preparing samples of all matrices by extraction with either hexane or tetrahydrofuran
- Analysing the sample extracts by using GC/MS-SIM
- Identifying cyclosiloxanes in samples by comparing the GC retention time and mass spectrum for the sample peak with known cyclosiloxanes reference standards
- Quantifying cyclosiloxanes by a stable isotope dilution technique, where the ratio of sample cyclosiloxanes responses to internal standards ($^{13}C_8$-D4, $^{13}C_{10}$-D5, $^{13}C_{12}$-D6) are used to minimise 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 6-2 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.

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

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 Air

Arespacochaga *et al* (2015) describe GC-MS as the most commonly used instrument for analysis of air samples. Other instruments, such as photoionisation detectors (PIDs), flame ionisation detectors (FIDs), and even direct analysis by atmospheric pressure ionisation and mass spectrometry (APCI-MS/MS) are also referenced.

7.2.3 Analytical Methodologies for Soil, Sludge and Sediment

Analytical techniques include solid–liquid extraction (SLE) and accelerated solvent liquid extraction (ASE), through mechanical vibration or sonication with an organic solvent, such as n-hexane, is a common technique. Sludge matrices have also been analysed through the purge and trap method and by solid-liquid extraction (Arespacochaga *et al*., 2015).

7.2.4 Quality Control Challenges in Monitoring D4, D5 and D6

Due to the ubiquity and volatile nature of cyclic volatile methylsiloxanes (cVMS), 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 cVMS 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 cVMS, 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 programme demonstrates that samples were handled and stored in a way to minimise contamination and analyte loss. QC samples utilised should include trip blanks, field blanks, field spikes, procedural blanks, and solvent blanks.

Personnel performing sample collection and analysis has to refrain from using any personal care products that may contain any of the cyclosiloxanes of concern while preparing for or conducting any field activities or laboratory analyses to minimise the possibility of contamination with cyclosiloxanes. 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 6-3 for a list of products and Table 6-4 for a list of potential ingredients containing cyclosiloxanes.
The samplers and laboratory analysts should be asked to use personal-care products that do not contain cyclosiloxanes, 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 cyclosiloxanes from car cleaning products used for detailing/cleaning cars. The cyclosiloxanes 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 cyclosiloxanes. 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 cyclosiloxanes via a review of the manufacturing materials. Hard hats and safety glasses with side shields do not contain cyclosiloxanes. Insect repellents that contain lotions have cyclosiloxanes; 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 personal care products which do not contain cyclosiloxane.

Table 7-3: Examples of personal care and make-up products that may contain D4, D5 and D6

Personal care and make-up products that may contain cyclosiloxanes			
Personal care products	Hand soap	Hand sanitiser	Sunblock
	Sunscreen	Hand lotion	Deodorant
	Antiperspirant	Hair shampoo	Conditioner
	Shaving creams containing lotions		
Make-up	Nail polish	Foundatio n	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 D4, D5 and D6 (either as an ingredient or as an impurity)

Ingredients that contain cyclosiloxanes
Amodimethicone, cyclomethicone, dimethicone, methicone, simethicone, trimethicone, dimethycone/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

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

ECHA (2018b) ECHA Registered Substances webpage, access to the D6 registration dossier

Denmark
Danish Ministry of the Environment, Siloxanes (D3, D4, D5, D6, HMDS)

United Kingdom
Environmental Risk Assessment Report: Octamethylcyclotetrasiloxane (2009)

Environmental Risk Assessment Report: Dodecamethylcyclohexasiloxane (2009)

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)

Silicones Europe (CES)

Whelan, M. and Kim, J. (2018) Application of Models in Understanding the Environmental Behavior 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

Arespacochaga, N. de, Valderrama, C., Raich-Montiu, J. Crest, M., Mehta, S., Cortina, J.L. (2015). Understanding the effects of the origin, occurrence, monitoring, control, fate and removal of siloxanes on the energetic valorization of sewage biogas – A review. Renewable and Sustainable Energy Reviews, **52:** 366-381. Summary Available

Bridges, J. and Solomon, K.R. (2016) Quantitative weight-of-evidence analysis of the persistence, bioaccumulation, toxicity, and potential for long-range transport of the cyclic volatile methyl siloxanes. Journal of Toxicology and Environmental Health, Part B, Critical Reviews: **19** (8)

EPA (2018). Air Emissions Monitoring Guidance Note (AG2), Rev. 4, Environmental Protection Agency Office of Environmental Enforcement (OEE), Wexford, Ireland, May 2018

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

JRC (2017). JRC Reference Report on Monitoring of Emissions to Air and Water from IED installations, European Commission, JRC IPTS EIPPCB

Kaj, L., Andersson, J., Palm Cousins, A., Remberger, M., Ekheden, Y., Dusan, B. and Brorström-Lundén, E. (2005). Results from the Swedish National Screening Programme 2004: Subreport 4: Siloxanes. Swedish Environmental Research Institute

Knoerr, S.M., Durham, J.A., and McNett, D.A. (2017) Development of collection, storage and analysis procedures for the quantification of cyclic volatile methylsiloxanes in wastewater treatment plant effluent and influent. Chemosphere **182**: 114-121

Mackay D, Powell D.E, Woodburn K.B. (2015). Bioconcentration and Aquatic Toxicity of Super-hydrophobic Chemicals: A Modeling Case Study of Cyclic Volatile Methyl Siloxanes. Environ. Sci. Technol. 49:11913-11922.

Nusz, JB; Fairbrother, A.; Daley, G.J.; Burton, A. (2018) Use of multiple lines of evidence to provide a realistic toxic substances control act ecological risk evaluation based on monitoring data: D4 case study. Elsevier, Science of the Total Environment, Volume 636, 15 September 2018, pages 1382-1395.

REACH Regulation (2006). Corrigendum to Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. December 2006

Redman, A. D.; Mihaich, E.; Woodburn, K.; Paquin, P.; Powell, D.; McGrath, J. A. & Di Toro, D. M. Tissue-based risk assessment of cyclic volatile methyl siloxanes *Environmental Toxicology and Chemistry, John Wiley & Sons, Inc.,* **2012***, 31*, 1911-1919.

Soreanu, G., Béland, M., Falletta, P., Edmonson, K., Svoboda, L., Al-Jamal, M. and Seto, P. (2011). Approaches concerning siloxane removal from biogas – a review. Canadian Biosystems Engineering, **53,** 8.1-8.18

9 LIST OF ACRONYMS

APCI-MS/MS	Atmospheric Pressure Ionisation and Mass Spectrometry
ARM:	Alternative Raw Material
ASE:	Accelerated Solvent Liquid Extraction
BAT:	Best Available Techniques
CA:	Competent Authority
CAS :	Chemical Abstracts Service
CES:	Centre Europeen Silcones
cVMS:	Cyclic Volatile Methylsiloxanes
D4:	Octamethylcyclotetrasiloxane
D5:	Decamethylcyclopentasiloxane
D6:	Dodecamethylcyclohexasiloxane
EC:	European Commission
ECHA:	European Chemicals Agency
EIPPCB:	The European IPPC Bureau
EU:	European Union
FID:	Flame Ionisation Detector
GC:	Gas Chromatogram
GCMS:	Gas chromatography Mass Spectrometry
GSC:	Global Silicones Council
HS-SPME	HeadSpace-Solid Phase Micro-Extraction
IED:	Industrial Emissions Directive
IPTS:	Institute for Prospective Technological Studies
JRC:	Joint Research Centre
LDPE:	Low Density PolyEthylene
MS:	Mass Spectrometer
PBT:	Persistent, Bioaccumulative and Toxic
PBiT:	Persistent, Bioaccumulative and Inherently Toxic
PID:	PhotoIonisation Detector
PNEC:	Predicted No Effect Concentrations
PPE:	Personal Protective Equipment
PTFE:	PolyTetraFluoroEthylene
QA:	Quality Assurance
QC:	Quality Control
REACH:	Registration, Evaluation, Authorisation and Restriction of Chemicals
RMMs:	Risk Management Measures
RPD:	Relative Percentage Difference
RSIA:	Regional Silicones Associations
RTVs:	Room-temperature vulcanising
SIM:	Selective Ion Monitoring
SiO_2:	Silicon Dioxide
SLE:	Solid-Liquid Extraction
SOP:	Standard Operating Procedure
STP:	Sewage Treatment Plant
vPvB:	Very Persistent and Very Bioaccumulative
USA-DLLME:	Ultra Sound Assisted Dispersive Liquid-Liquid Micro-Extraction
WWTP:	Waste Water Treatment Plant
%R:	Percent Recovery

10 ANNEX 1 – EU REGULATORY POSITION ON D4, D5, AND D6 AND CONSEQUENCES FOR MANAGEMENT OF SUBSTANCE EMISSIONS IN THE EU

10.1 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).

10.1.1 Silicones Industry Response to EU SVHC Candidate Listing

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 considers 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 Kow 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 for which an aquatic toxicity laboratory study demonstrated that it 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.

10.2 Specific Environmental Fate Data Relevant to the Assessment of D4, D5 and D6 as PBT Substances[1]

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 Criterion met	Biodegradation: 0.14% in 28 days Criterion met	Biodegradation: 4.5% in 28 days Criterion met
		Abiotic (hydrolysis): 3.9 days at pH 7 and 25°C Criterion not met	Abiotic (hydrolysis): 70.4 days at pH 7 and 25°C Criterion met	Abiotic (hydrolysis): 401 days at pH 7 and 25°C Criterion met
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 Criterion met	3 100 days at 25°C in anaerobic sediments Criterion met	3 100 days at 25°C in anaerobic sediments Criterion met
Degradation in soil (half-life)	*>120 days*	5.29 days at 25°C Criterion not met	12.6 days at 25°C Criterion not met	401 days at 25°C Criterion met
Bioaccumulation - B				
Bioconcentration factor (kinetic, lipid-normalised)	*>2 000 L/kg*	14 900 L/kg Criterion met	16 200 L/kg Criterion met	2 860 L/kg Criterion met
Toxicity – T				
Long-term NOEC or EC10 for aquatic organisms	*<0.01 mg/L*	≥0.0044 mg/L Criterion not met[2]	≥0.014 mg/L Criterion not met	≥0.014 mg/L Criterion not met
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 Criterion met	Not classified Criterion not met	Not classified Criterion not met
Classification as STOT RE 1, or STOT RE 2 based on chronic toxicity upon repeated dose exposure		Not classified Criterion not met	Not classified Criterion not met	Not classified Criterion not met

[1] Based on 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 the 93-day long study with D4, 0.0044 mg/L. However, to better define the potential NOEC, modelling (Mackay et al., 2015) to estimate fish critical body burden (CBB) levels and compare those CBB levels to those associated with a narcotic mode of action (MOA), under which the D4 and other volatile methyl siloxanes materials are proposed to operate (Redman et al., 2012, Mackay et al., 2015) was conducted. These results indicate that D4 dose levels up to 12 µg/l could have been successfully used in the D4 93-day trout ELS study without adverse effect.

10.3 Specific Environmental Fate Data Relevant to the Assessment of D4, D5 and D6 as vP/vB Substances[1]

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 Criterion met	Biodegradation: 0.14% in 28 days Criterion met	Biodegradation: 4.5% in 28 days Criterion met
		Abiotic (hydrolysis): 3.9 days at pH 7 and 25°C Criterion not met	Abiotic (hydrolysis): 70.4 days at pH 7 and 25°C Criterion met	Abiotic (hydrolysis): 401 days at pH 7 and 25°C Criterion met
Degradation in sediment (half-life)	*>180 days*	365 days at 25°C in anaerobic sediments Criterion met	3 100 days at 25°C in anaerobic sediments Criterion met	3 100 days at 25°C in anaerobic sediments Criterion met
Degradation in soil (half-life)	*>180 days*	5.29 days at 20°C Criterion not met	12.6 days at 20°C Criterion not met	401 days at 22°C Criterion met
Bioaccumulation - vB				
Bioconcentration factor (kinetic, lipid-normalised)	*>5 000 L/kg*	14 900 L/kg Criterion met	16 200 L/kg Criterion met	2 860 L/kg Criterion not met

[1] Based on ECHA (2018b) and Whelan, M. and Kim. J. (2018).

10.4 Classification of D4, D5 and D6 in the EU

The following table gives the current classification of these three substances

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

*H226 is not included in the harmonised classification of D4 but is included in the classification in the REACH registration dossier.

Neither D5 or D6 are currently classified under the CLP inventory.

10.5 Exposure Scenarios

The manufacturers of D4, D5 and D6 have registered these cyclosiloxane 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 substances.

The exposure scenarios are described by the sector of use (manufacture, formulation, industrial end use, professional end use and consumer end use) and provide detailed descriptions of the scale of use (in terms of quantity of cyclosiloxane 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).

10.6 Management of PBT/vPvB Substances under REACH

The ECHA PBT Expert Group indicates in general for substances that are considered PBT/vPvB the following[1]:

"*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] in their webpage, accessed on July 2018 (https://echa.europa.eu/pbt-expert-group): in their webpage, accessed on July 2018 (https://echa.europa.eu/pbt-expert-group):

10.7 Matching the exposure scenarios to the scale of operation

The following table lists the exposure scenarios based on generic scale of use:

Exposure Scenario Description	Scale of Use		
	D4	D5	D6
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
Formulation, household care products		Level 2	Level 2
Use of household products, industrial		Level 3	
Use of personal care products, professional			Level 3
Use of washing/cleaning products, professional, industrial		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
Use of rigid PU foam		Level 1	

11 ANNEX 2 – PHYSICO-CHEMICAL PROPERTIES AND ENVIRONMENTAL FATE INFORMATION RELEVANT TO MANAGEMENT OF ENVIRONMENTAL EMISSIONS

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 K_{ow})	6.98 at 25°C	8.09 at 25°C	8.87 at 25°C
Water solubility	0.056 mg/L at 23°C	0.017 mg/L at 23°C	0.0053 mg/L at 23°C
Vapour pressure	140 Pa at 25°C	33.2 Pa at 25°C	6 Pa at 25°C
Other environmental fate information			
Hydrolysis (half-life)	• 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	• 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	• >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	5.3 days	3.9 days
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} for adsorption)	4.22 at 25°C	5.17 at 25.6°C	6.03 at 25°C
Desorption coefficient (in terms of log K_{oc} for desorption)	4.3 at 25°C	5.34 at 25°C	not calculated

Sources: ECHA, 2018b and Whelan and Kim (2018)

The hydrolysis half-lives for D4 and D5 at pH 4 favour hydrolysis for removal of these two 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 three substances indicate rapid volatilisation from water. The adsorption coefficients suggest that removal via activated carbon beds may be an efficient treatment for D4, D5 and D6.

Any D4, D5 and D6 emitted to air is removed in a relatively short period via phototransformation; 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 D4, D5 and D6 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 minimise emissions. However, it is known that silica is formed during incineration, which has to be removed to avoid shortening the service time of incineration equipment. If the sludge is used as a fertiliser on agricultural fields, depending on the soil humidity, all three cyclosiloxanes would either rapidly volatilise 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 D4, D5 or D6 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.