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

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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

EC Number: 209-136-7

CAS number: 556-67-2

- It is proposed to identify the substance as persistent, bioaccumulative and toxic (PBT) according to Article 57 (d) of Regulation (EC) No 1907/2006 (REACH).
- It is proposed to identify the substance as very persistent and very bioaccumulative (vPvB) according to Article 57 (e) of Regulation (EC) No 1907/2006 (REACH).

Summary of how the substance meets the criteria set out in Article 57 of the REACH Regulation

The Member State Committee (MSC) provided an Opinion on the persistent and bioaccumulative properties of D4 and D5 at the request of the Executive Director of ECHA under Article 77(3)c of REACH (ECHA, 2015) during the process to restrict the use of these two substances. A weight-of-evidence determination according to the provisions of Annex XIII of REACH was used to form the Opinion. All available relevant information (such as the results of standard tests, monitoring and modelling, information from the application of the category and analogue approach (grouping, read-across) and (Q)SAR results) was considered together in a weight-of-evidence approach by the MSC. D4 was subsequently concluded by the Risk Assessment Committee (RAC) - based on the opinion of the MSC - to fulfil the criteria of Annex XIII of REACH as a PBT and vPvB substance (see RAC opinion on the restriction proposal: (ECHA, 2016; European Commission, 2018))[1].

<u>Persistence</u>

The Member State Committee (ECHA, 2015) concluded that:

> *With regard to the assessment of persistence, MSC concludes that the experimental observations in simulation and monitoring studies lead to the conclusion that both D4 and D5 meet the vP criterion as specified in REACH Annex XIII.*
>
> *MSC has evaluated non-degradation processes and concluded that these do not have a large impact on the sediment removal half-life, and thus cannot be used to refute the relevance of the sediment compartment in the assessment of persistence.*
>
> *Based on OECD TG 308 sediment simulation studies (Xu, 2009a; Xu, 2009b), D4 has an estimated degradation half-life of 365 days in anaerobic sediment and 242 days in aerobic sediment at 24°C, MSC concludes that D4 meets the Annex XIII criteria for a very persistent (vP) substance in*

[1] The restriction on D4 and D5 entered into force in 31.1.2018 (European Commission, 2018): http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2018.006.01.0045.01.ENG

sediment according to Regulation (EC) No 1907/2006.

After the MSC and RAC Opinion making processes, new studies have been published. The relevant studies have been summarised in this document. This new information supports the earlier conclusion.

Bioaccumulation

The Member State Committee (ECHA, 2015) concluded that:

With regard to the assessment of bioaccumulation, MSC concludes that D4 and D5 are very bioaccumulative based on high fish BCF values, supported by multiple lines of evidence on biomagnification in dietary studies, and elimination half-lives. In addition, the available field data provides evidence that bioaccumulation and trophic magnification have been shown to occur in certain food webs in the environment. The available information on biomagnification and trophic magnification factors (BMF/TMF) in the field, indicating that biodilution occurs in some food chains or in parts of some food chains, does not invalidate the other lines of evidence.

D4 meets the Annex XIII criteria for a very bioaccumulative (vB) substance according to Regulation (EC) No 1907/2006 based on the following studies:

- *A steady-state BCF of 12,400 L/kg for Fathead Minnow Pimephales promelas (Fackler et al., 1995) based on total 14C measurements.*
- *A steady state BCF for Common Carp Cyprinus carpio in the range of 3,000 – 4,000 L/kg (based on parent compound analysis) (CERI, 2007 and 2010a). The kinetic BCF in one of the studies was in the range 4,100 - 5,500 L/kg.*

After the MSC and RAC Opinion making processes new studies have been published. The relevant studies have been summarised in this document. The new information does not deviate from the diverse data available earlier on bioaccumulation. The new data do not provide any reason to change the conclusion that the substance is vB reached by MSC and RAC.

Toxicity

In its opinion on the UK proposal for a restriction on the use of D4 and D5 in wash-off personal care products (UK Health & Safety Executive, 2015), the Committee for Risk Assessment (ECHA, 2016) states that

D4 has a long-term NOEC of around 4 – 6 µg/L for rainbow trout (Oncorhynchus mykiss), although RAC notes that there is some uncertainty in this value, and a long-term NOEC of 7.9 µg/L for Daphnia magna survival. [...] Significant toxicity to invertebrates is also apparent in sediment organism studies.

The Committee for Risk Assessment (ECHA, 2016) concludes that

D4 meets the REACH Annex XIII criteria for toxicity based on both aquatic and mammalian end points.

New studies were published after the MSC opinion (ECHA, 2015) and RAC opinion (ECHA, 2016) were adopted. These studies were evaluated and taken into account for the overall weight-of-evidence determination. However, these studies are not considered to contest the conclusions on toxicity to fish and daphnids that were previously evaluated by the MSC and RAC. Hence, they do not change the overall conclusion on toxicity.

D4 is covered by index number 014-018-00-1 of Regulation (EC) No 1272/2008 in Annex VI, part 3, Table 3 (the list of harmonised classification and labelling of hazardous substances) and it is classified in the hazard class reproductive toxicity category 2 (hazard statement H361f "Suspected of damaging fertility"). Therefore, the criterion for toxicity of Annex XIII section 1.1.3 b) of REACH is fulfilled.

<u>Conclusion</u>

In its opinion on D4 and D5 (ECHA, 2015), the Member State Committee states that:

> *Based on the information presented by the DS and careful consideration of the comments received in the public consultation, MSC supports the opinion of the DS that D4 and D5 both meet the vPvB criteria in Annex XIII of REACH.*

The Committee for Risk Assessment (ECHA, 2016) concludes that:

> *D4 meets the REACH Annex XIII criteria for toxicity based on both aquatic and mammalian end points.*

In conclusion, D4 meets the criteria for a PBT and vPvB substance according to REACH Art. 57(d) and (e) by comparing all relevant and available information listed in REACH Annex XIII with the criteria set out in the same Annex, in a weight-of-evidence determination.

Registration dossiers submitted for the substance? Yes

PART I

Introductory note

The Member State Committee (MSC) provided an opinion on the persistent and bioaccumulative properties of D4 and D5 at the request of the Executive Director of ECHA under Article 77(3)(c) of REACH (ECHA, 2015) during the process to restrict the use of these two substances. D4 was subsequently concluded by the Committee on Risk Assessment (RAC) - based on the opinion of the MSC- to fulfil the criteria of Annex XIII of REACH as a vPvB substance (see RAC opinion on the restriction proposal: (ECHA, 2016). In March 2016, whilst evaluating the UK restriction proposal, the Committee for Risk Assessment (RAC) concluded that D4 meets the REACH Annex XIII criteria for toxicity based both on aquatic and mammalian endpoints (ECHA, 2016). The restriction of D4 and D5 entered into force in 31.1.2018 (European Commission, 2018).

Currently, a CLP proposal concerning the environmental classification of D4 is under scrutiny by RAC. It should be noted that the potential environmental classification of D4 (or lack of classification) would not change the overall conclusions of the PBT/vPvB assessment and hence it would not bring any changes to the needs for risk reduction at the EU level.

This dossier largely cites and refers to the respective documents from the Member State Committee, RAC and UK which have already been discussed and agreed upon. The cited text passages have been marked in *italics*.

Justification

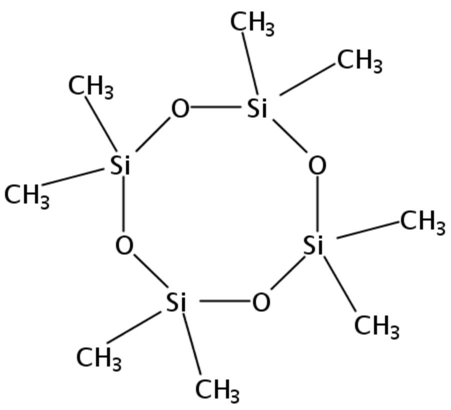
1. Identity of the substance and physical and chemical properties

1.1 Name and other identifiers of the substance

Table 1: Substance identity

EC number:	209-136-7
EC name:	Octamethylcyclotetrasiloxane
CAS number (in the EC inventory):	556-67-2
CAS number: Deleted CAS numbers:	
CAS name:	Cyclotetrasiloxane, 2,2,4,4,6,6,8,8-octamethyl-
IUPAC name:	Octamethylcyclotetrasiloxane
Index number in Annex VI of the CLP Regulation	014-018-00-1
Molecular formula:	$C_8H_{24}O_4Si_4$
Molecular weight range:	296.62 g/mol
Synonyms:	D4, cyclotetrasiloxane

Structural formula:



1.2 Composition of the substance

Name: Octamethylcyclotetrasiloxane

Description: -

Substance type: mono-constituent

Table 2: Constituents other than impurities/additives

Constituents	Typical concentration	Concentration range	Remarks
Octamethylcyclotetrasiloxane (EC no: 209-136-7; D4)		80 – 100 % w/w	

1.3 Identity and composition of degradation products/metabolites relevant for the SVHC assessment

The assessment of degradation/transformation products and/or metabolites is not the focus of this document.

1.4 Identity and composition of structurally related substances (used in a grouping or read-across approach)

Table 3: Structurally related substance(s) identity

EC number:	208-764-9
EC name:	Decamethylcyclopentasiloxane
SMILES:	C[Si]1(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O1
CAS number (in the EC inventory):	541-02-6
CAS number:	541-02-6
CAS name:	Cyclopentasiloxane, 2,2,4,4,6,6,8,8,10,10-decamethyl-
IUPAC name:	Decamethylcyclopentasiloxane
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	$C_{10}H_{30}O_5Si_5$
Molecular weight range:	370.77 g/mol
Synonyms:	D5, cyclopentasiloxane

Substance type: mono-constituent

Structurally related substance(s) formula:

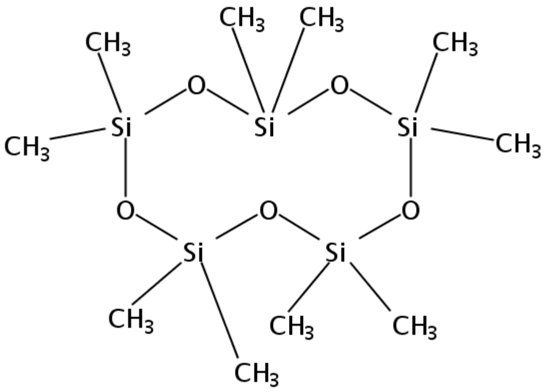
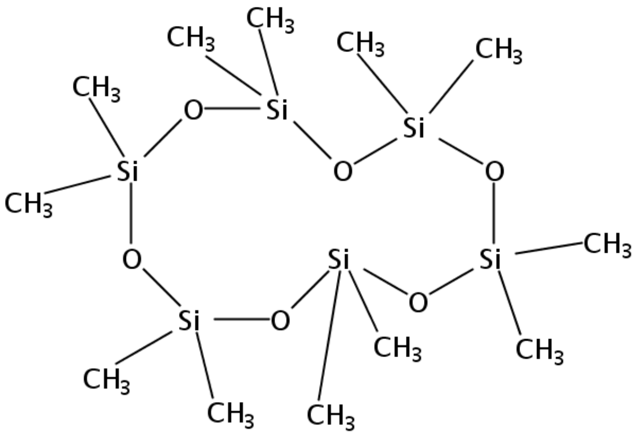


Table 4: Structurally related substance(s) identity

EC number:	208-762-8
EC name:	Dodecamethylcyclohexasiloxane
SMILES:	C[Si]1(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O1
CAS number (in the EC inventory):	540-97-6
CAS number:	540-97-6
CAS name:	Cyclohexasiloxane, 2,2,4,4,6,6,8,8,10,10,12,12-dodecamethyl-
IUPAC name:	Dodecamethylcyclohexasiloxane
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	$C_{12}H_{36}O_6Si_6$
Molecular weight range:	444.92 g/mol
Synonyms:	D6, cyclohexasiloxane

Substance type: mono-constituent

Structurally related substance(s) formula:



1.5 Physicochemical properties

Table 5: Overview of physicochemical properties

Property	Description of key information	Value [Unit]	Reference/source of information
Physical state at 20°C and 101.3 kPa	-	*liquid*	*Visual observation*
Melting/freezing point	*Handbook data*	*17.7 °C*	*J. Amer. Chem. Soc., 75, 2227*
Boiling point	*Handbook data*	*175 °C*	*J Amer. Chem. Soc., 68, 358*
Vapour pressure	*Handbook data*	*132 Pa at 25 °C*	*AIChE DIPPR Database*
Density	*Handbook data*	*0.95 g/cm³ at 25°C*	*AIChE DIPPR Database*
Water solubility	*Measured*	*0.0562 mg/L at 23 °C and pH ca. 7*	*Environmental Toxicology and Chemistry, Vol. 15, No. 8, pp. 1263–1265*
Partition coefficient n-octanol/water (log value)	*Measured*	*6.488 at 25.1 °C*	*OECD Guideline 123 (Partition Coefficient (1-Octanol / Water), Slow-Stirring Method)*

2. Harmonised classification and labelling

D4 is covered by Index number 014-018-00-1 in part 3 of Annex VI to the CLP Regulation as follows:

Table 6: Classification according to Annex VI, Table 3 (list of harmonised classification and labelling of hazardous substances) of Regulation (EC) No 1272/2008

Index No	International Chemical Identification	EC No	CAS No	Classification		Labelling			Spec. Conc. Limits, M-factors	Notes
				Hazard Class and Category Code(s)	Hazard statement code(s)	Pictogram, Signal Word Code(s)	Hazard statement code(s)	Suppl. Hazard statement code(s)		
014-018-00-1	octa-methyl-cyclo-tetra-siloxane	209-136-7	556-67-2	Aquatic Chronic 4	H413					
				Repr. 2	H361f ***					

The table above shows the current entry in Annex VI of CLP Regulation (Regulation (EC) No 1272/2008) for D4. In 2016, a proposal from the German CA has been submitted to change the current entry from aquatic chronic 4 to aquatic chronic 1.

3. Environmental fate properties

3.1 Degradation

3.1.1 Abiotic degradation

One relevant new study on abiotic degradation was identified after the MSC opinion.

3.1.1.2 Hydrolysis

Data on hydrolysis is described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, page 3 (ECHA, 2015).

3.1.1.3.1 Phototransformation in air

Data on phototransformation in air is described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, page 3 (ECHA, 2015).

After the UK-CA finalised its assessment of D4 and D5, a publication of Safron and co-workers (Safron et al., 2015) on the reaction of cyclic volatile methyl siloxanes with OH radicals became available. The authors applied the relative rate technique to study the kinetics of the reaction in a temperature range between 313 and 353 K. The Arrhenius equation was used to extrapolate from these results to a temperature of 298 K, yielding reaction rate constants of $1.9{\cdot}10^{-12}$ cm^3 $molecules^{-1}$ s^{-1} for D4, $2.6{\cdot}10^{-12}$ cm^3 $molecules^{-1}$ s^{-1} for D5 and $2.8{\cdot}10^{-12}$ cm^3 $molecules^{-1}$ s^{-1} for D6, respectively. These rate constants are within a magnitude but slightly greater than the values observed in two studies at 297 K which were described previously (ECHA, 2015; UK Environment Agency, 2013a; UK Environment Agency, 2013b). Consequently, the corresponding atmospheric half-lives would be slightly smaller.[2] While the study by Safron et al. (Safron et al., 2015) appears to be well-conducted, the extrapolation from higher temperatures to 298 K is expected to introduce some uncertainty. Therefore, the room-temperature data are preferred.

3.1.2 Biodegradation

No new relevant studies on biodegradation were identified after the MSC opinion.

3.1.2.1.2 Screening tests

Screening tests are described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, page 3 (ECHA, 2015).

3.1.2.1.3 Simulation tests (water and sediments)

Simulation tests are described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, pages 3-4 (ECHA, 2015) and in Annex 2a to MSC opinion on the persistency and bioaccumulation of D4 and D5, page 1 (ECHA, 2015).

[2] About 8.4 d for D4, 6.2 d for D5 and 5.7 d for D6, assuming an average atmospheric hydroxyl radical concentration of 5×10^5 molecules cm^{-3}.

3.1.2.2 Biodegradation in soil

Data on biodegradation in soil is described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, page 4 (ECHA, 2015).

3.1.3 Modelling data

Modelling data is described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, page 4 (ECHA, 2015).

Several new studies were published, or submitted for publication, after the adoption of the MSC opinion. These studies are discussed below.

A recently submitted manuscript questions the persistence of D4, D5 and other cyclic volatile methyl siloxanes based on multi-media modelling (Kim et al., 2017). In case of a cessation of emissions, modelling studies generally show a relatively fast initial reduction in concentrations, which is caused by the degradation of airborne siloxanes. However, these models also show that concentrations in sediment persist with half-lives exceeding the REACH Annex XIII trigger for persistence in sediments, a finding that is consistent with an earlier study of Xu and Wania (Xu and Wania, 2013). Consequently, these modelling results support the conclusion that D4 and D5 should be considered as persistent under REACH, rather than refute this conclusion.

In their PBT/vPvB and LRT analysis of cyclic volatile methyl siloxanes, Bridges and Solomon conclude that D4, D5 and D6 should not be regarded as persistent (Bridges and Solomon, 2016). However, while using largely the same data as the Member State Committee in its opinion (ECHA, 2015), their assessment methodology differs from the methodology applied under REACH. For D4, Bridges and Solomon (Bridges and Solomon, 2016) do not cite the Xu (Xu, 2009a) study on persistence in aerobic sediment previously cited by the UK and MSC that reports a degradation half-life of 242 days at 24°C and which was used to support a conclusion that D4 meets the vP criterion. Finally, the authors give a high weight to modelling studies on the overall persistence of cyclic volatile methyl siloxanes. According to these, the major (airborne) part of the siloxanes would be degraded within 3 months of the end of release. However, removal from sediment is predicted to take longer with half-lives of 1 year or more. As provided in Annex XIII of REACH and explained in ECHA Guidance on PBT/vPvB assessment (ECHA, 2017a), a substance should be considered persistent or very persistent if any of the compartment specific criteria are exceeded. REACH does not consider overall persistence as criterion for PBT/vPvB identification. The rapid removal of airborne cyclic volatile methyl siloxanes or consequent apparent low overall persistence cannot refute the PBT/vPvB concerns for sediment, and the paper hence acknowledges that the substances are very persistent in sediment and hence supports the MSC opinion.

3.1.4 Summary and discussion of degradation

In its opinion on the persistency and bioaccumulation of D4 and D5 (ECHA, 2015), the Member State Committee states the following:

> *MSC has evaluated non-degradation processes and concluded that these do not have a large impact on the sediment removal half-life, and thus cannot be used to refute the relevance of the sediment compartment in the assessment of persistence.*
>
> *Based on OECD TG 308 sediment simulation studies (Xu, 2009a; Xu,*

2009b), D4 has an estimated degradation half-life of 365 days in anaerobic sediment and 242 days in aerobic sediment at 24°C, MSC concludes that D4 meets the Annex XIII criteria for a very persistent (vP) substance in sediment according to Regulation (EC) No 1907/2006.

Among the new studies published after the MSC and RAC opinion making processes, three studies, summarised above, were identified to be relevant for the degradation assessment. These studies were evaluated and taken into account for the overall weight-of-evidence determination. These studies support the conclusion that the substance is very persistent in sediment.

3.2 Environmental distribution

3.2.1 Adsorption/desorption

Data on adsorption/ desorption is described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.2, page 5 (ECHA, 2015).

3.2.2 Volatilisation

Data on volatilisation is described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, pages 3-4 (ECHA, 2015).

3.2.3 Distribution modelling

Data on distribution modelling is described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, page 4 (ECHA, 2015).

3.2.4 Field data

Field data is described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, page 4 (ECHA, 2015).

Two new relevant studies were found after the MSC opinion:

Ahrens and co-workers examined temporal variations of siloxanes in the atmosphere (Ahrens et al., 2014). Samples of D4, D5, D6 and other volatile methylsiloxanes were generated with passive and active sampling techniques. These data show concentration gradients from north (less populated areas) to south (urban areas). Data showing seasonal trends and the influence of snowfall events were also raised. The seasonal trends can be explained with the increasing OH radical concentration during seasons with high solar radiation.

In a recent monitoring study, environmental contaminants in air and precipitation in Norway have been examined (Bohlin-Nizzetto P. and Aas W., 2016). The concentrations of D4, D5 and D6 in air were at the same level as in previous years. Results for cyclic volatile methyl siloxanes (cVMS) show an increase in summer and winter. The concentrations of cVMS are at the same levels as PAHs, and are three orders of magnitude greater than the concentrations of legacy POPs (i.e. PFAS). This suggests continuous emissions.

3.2.5 Summary and discussion of environmental distribution

In its opinion on the persistency and bioaccumulation of D4 and D5 (ECHA, 2015), the Member State Committee states that:

> *MSC has evaluated non-degradation processes and concluded that these do not have a large impact on the sediment removal half-life, and thus cannot be used to refute the relevance of the sediment compartment in the assessment of persistence.*

New studies were published after the MSC and RAC opinions. These studies were evaluated and taken into account for the overall weight-of-evidence determination. These studies are not considered to contest the overall conclusion on persistence as provided in MSC and RAC opinions.

3.3 Data indicating potential for long-range transport

Long-range transport properties are briefly described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.1, page 4 (ECHA, 2015).

A more detailed discussion is given in the UK proposal for a restriction on the use of D4 and D5 in wash-off personal care products (UK Health & Safety Executive, 2015). Furthermore, long-range transport was discussed in the RAC Opinion (ECHA, 2016). Several new relevant studies are available (Bohlin-Nizzetto P. and Aas W., 2016; Mackay et al., 2015a; Safron et al., 2015; Sanchis et al., 2015a; Sanchis et al., 2015b; Warner et al., 2015). The potential for long-range transport is not assessed in this dossier.

3.4 Bioaccumulation

3.4.1 Bioaccumulation in aquatic organisms (pelagic & sediment organisms)

Bioaccumulation studies are described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.3, pages 5-8 (ECHA, 2015) and in Annex 2a to the MSC opinion on the persistency and bioaccumulation of D4 and D5, pages 1-7 and 23–25 (ECHA, 2015).

A new publication has become available after the MSC opinion. In a recent publication, Domoradzki et al. examined the metabolism of D4 and D5 in rainbow trout (Domoradzki et al., 2017). ^{14}C-marked D4 and D5 were administered orally as a single dose. However, this study was submitted to the Member State Committee previously and is described and discussed in its opinion on D4 and D5 (ECHA, 2015), pages 16 to 17.

Furthermore, the registration dossier cites a study of Domoradzki and co-workers on Whole Body Autoradiography (WBA) that was conducted in conjunction with dietary bioaccumulation studies with radiolabelled D4 and D5 to assess distribution and metabolism in rainbow trout (ECHA, 2017b). The registrant concludes that the study indicates metabolism and elimination of D4 and D5 via the digestive tract over time. Only qualitative information is given, but the registrant considers that this study supports the findings of the feeding study mentioned above (Domoradzki et al., 2017). This study was already discussed by the Member State Committee (ECHA, 2015), which concluded the following:

> *[...] the observed half-lives in fish for D4 and D5 are consistent with the*

potential to bioconcentrate to high levels in aqueous bioconcentration studies and the potential to biomagnify in a dietary bioaccumulation study. The observed half-lives for D4 and D5 thus support the concern for bioaccumulation (B and vB) that arises from the aqueous and dietary laboratory bioaccumulation studies.

3.4.2 Bioaccumulation in terrestrial organisms (soil dwelling organisms, vertebrates)

Bioaccumulation studies in terrestrial organisms are described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.3, page 8 (ECHA, 2015).

3.4.3 Field data

Field data on bioaccumulation is described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.3, pages 7-11 (ECHA, 2015) and in Annex 2a to the MSC opinion on the persistency and bioaccumulation of D4 and D5, pages 7-23 (ECHA, 2015).

A review article was published after the MSC Opinion was agreed, which is largely based on the same data, but draws a different conclusion due to differences in the underlying bioaccumulation assessment approach:

- On request of industry, Bridges and Solomon conducted a quantitative weight-of-evidence analysis of the PBT/vPvB properties and the long-range transport potential of cyclic volatile methyl siloxanes (Bridges and Solomon, 2016). In the bioaccumulation part of their PBT/vPvB and LRT analysis of cyclic volatile methyl siloxanes, Bridges and Solomon conclude that D4, D5 and D6 are not bioaccumulative (Bridges and Solomon, 2016). While the high BCF values are considered reliable, the authors consider these values to be of little relevance. With respect to the fish dietary bioaccumulation studies, the difference in steady-state and kinetic BCF values is highlighted. The authors gave the greatest weight to field studies on trophic biomagnification. Hence, their conclusion that D4 and D5 are not bioaccumulative is based on biomagnification solely, and neglects bioconcentration completely. All of the discussed field studies have already been assessed by the UK Environment Agency and were considered in the Opinion of the Member State Committee in 2015 (ECHA, 2015). Furthermore, it should be noted that even if a conclusion was drawn on biomagnification solely, the authors omit that accumulation via the diet was shown in certain food webs.

However, the Dossier Submitter considers in agreement with the Opinion of the Member State Committee (ECHA, 2015), the following:

The available information on biomagnification and trophic magnification factors (BMF/TMF) in the field, indicating that biodilution occurs in some food chains or in parts of some food chains, does not invalidate the other lines of evidence.

New information on several field studies on trophic magnification became available after the MSC Opinion or – in the case of Jia et al. (Jia et al., 2015) – after the public consultation on the hazard assessment, but before the MSC Opinion. Due to the many underlying uncertainties of field studies, the Dossier Submitter considers that the results should be regarded with caution.

- Jia et al. studied the biomagnification of methyl siloxanes in a marine food web at Dalian Bay, China (Jia et al., 2015). Though relevant, this study is only briefly mentioned and not evaluated in the documents of the MSC Opinion, as it was published after the public consultation. It was hence mentioned in a footnote, but not completely included in the assessment. It is described for D4 in Annex 2 to MSC opinion on persistency and bioaccumulation of D4 and D5, section B.4.3, page 8 (ECHA, 2015), footnote.

  Care was taken to avoid cross-contamination of the samples and BDE-99 was analysed as a reference compound. A TMF of 1.77 was derived for D5, which was found to be significantly greater than 1 (95% confidence interval: 1.41−2.24, 99.8% probability of the observing TMF > 1). For D4 and D6, TMF values of 1.16 (0.94−1.44, 94.7%) and 1.01 (0.84−1.22, 66.9%) were determined, which were not significantly greater than 1. The TMF for BDE-99 was 3.27 (2.49−4.30, 99.7%). Gobas et al. (2015) reviewed this study with respect to D5 and recalculated a TMF of 1.39 (0.99−1.94) based on individual data instead of mean concentrations. This recalculated TMF is still greater than 1, but marginally exceeds the criterion for statistical significance ($p=0.054$, significant if $p < 0.05$). Furthermore, Gobas et al (Gobas et al., 2015) criticise the use of BDE-99 as a reference compound because in some cases, TMFs < 1 have been observed for this compound as well. On one hand, PCB-153 or PCB-180 would indeed be a better reference compound for determining biomagnification solely. On the other hand, TMFs > 1 have been observed for BDE-99 as well and as it is a POP substance, a comparison with BDE-99 is considered adequate when discussing bioaccumulation in general.

- Recently, a study was published on the bioaccumulation of cyclic volatile methylsiloxanes in a pelagic food web of Tokyo Bay (Powell et al., 2017). Data were evaluated with the bootstrap method and compared to the re-evaluated results of other field studies.

  These results had been submitted to the UK Competent Authorities before the MSC Opinion. They are described for D4 in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.3, page 9 (ECHA, 2015) and in Annex 2a to the MSC opinion on the persistency and bioaccumulation of D4 and D5, pages 13–17 and 22–23 (ECHA, 2015).

- Very recently, Powell and co-workers submitted a paper regarding the bioaccumulation of cyclic volatile methylsiloxanes in the aquatic marine foodwebs of Oslofjord (Powell et al., 2018). These results had also been previously submitted to the UK Competent Authorities and are already discussed for D4 in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.3, pages 8 - 9 and 10 (footnote) (ECHA 2015c) and in Annex 2a to the MSC opinion on the persistency and bioaccumulation of D4 and D5, pages 22-23 (ECHA 2015d).

- Woodburn et al. submitted a manuscript about the trophic dilution of cyclic volatile methylsiloxanes in Lake Pepin (Woodburn K., 2017). Samples for siloxanes were taken in September 2007 and May 2008. These results had been previously submitted to the UK Competent Authorities and are discussed ((Powell D.E., 2009)) for D4 in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.4.3, page 8 (ECHA, 2015) and in Annex 2a to the MSC opinion on the persistency and bioaccumulation of D4 and D5, pages 22–23 (ECHA, 2015).

  The new manuscript additionally includes data for the reference chemical PCB-180, samples of which were taken in May and July 2010. The calculated TMFs for D4, D5 and D6 (range 0.2 to 0.4) correspond to the findings that were already discussed in the documents mentioned above. Additionally, the TMF for the reference chemical PCB-180 was determined to be 2.2 ± 0.5. As samples for PCB-180 were taken later, the Dossier Submitter considers that they should not be used for benchmarking the siloxane TMFs.

- Siloxanes were measured by Ruus et al in a NIVA monitoring project at Inner Oslofjord (Ruus A., 2016). The area is an urban fjord neighboured by settlements, among them Oslo. Samples were analysed for several legacy and emerging contaminants, among them D4, D5 and D6.

  A TMF of 0.44 was calculated for D4. As D4 was not detected in blue mussel, this species was omitted from the regression. No TMF values were given for the other siloxanes. While some legacy POPs like PCB-180 yield a TMF larger than 1, a TMF of 0.53 was determined for SCCPs, which are considered as very bioaccumulative under REACH and which are also included in the Stockholm Convention. Furthermore, several relationships between biological variables and contaminant concentrations are analysed and discussed.

- Krogseth and co-workers conducted a research project on the fate of cyclic volatile methyl siloxanes in Lake Storvannet at Hammerfest, Norway (Krogseth, 2014; Krogseth et al., 2017a; Krogseth et al., 2017b), including both fate modelling and measurements. The applied models did not predict trophic magnification in Lake Storvannet. Based on the measured concentrations in fish muscle and sediment, BSAF values for fish were determined (Krogseth et al., 2017a): BSAF values for D4 were less than or equal to 6.2 for char and 1.5 ± 1.1 in sticklebacks. BSAF values for D5 were 1.0 ± 0.7 for char, 0.2 ± 0.1 for trout and 0.8 ± 0.7 for sticklebacks. For D6, the BSAF values were less than or equal to 1.0 for char and 0.2 ± 0.1 for sticklebacks.

- Sanchis et al. found unexpected high concentrations of the cyclic volatile methyl siloxanes D3, D4, D5 and D6 in Antarctic soils, vegetation, phytoplankton and krill (Sanchis et al., 2015b). Measured concentrations in krill were significantly greater than in phytoplankton, indicating biomagnification via the diet. The authors found an increase in BMF with increasing hydrophobicity and derived the following expression:

  $$\log BMF_{cVMS} = 0.51 \log K_{OW} - 1.12.$$

  The reliability of this study was questioned by two comments (Mackay et al., 2015a; Warner et al., 2015) and responded to by the authors (Sanchis et al., 2015a).

  While this study was not yet available at the time of the MSC opinion on D4 and D5, it was subsequently mentioned in the RAC opinion. It should however be noted that RAC considered this study with a focus on long range transport rather than bioaccumulation.

In summary, the new information on trophic magnification does not deviate from the diverse data available earlier.

Several new studies examined cyclic volatile methyl siloxanes in the environment. While the analytics of siloxanes are challenging and some environmental findings are influenced by point sources, the frequent detection of cyclic methyl siloxanes indicates that there is generally a background contamination of these substances:

- Wang et al. measured cyclic volatile methyl siloxanes in the blood of turtles, cormorants and seals from Canada (Wang et al., 2017). Sampling sites were chosen to include both places supposed to be contaminated and places expected to show background contamination only. D3, D4, D5 and D6 were detected in all samples. The observed concentrations varied with sampling site and species.

- In a monitoring study on predatory freshwater fish from Canadian lakes, all samples contained D4, D5 and D6 above quantification limits, with D5 being most abundant (McGoldrick et al., 2014).

- Sanchis and co-workers (Sanchis et al., 2016) examined the presence of volatile methyl siloxanes in market seafood and freshwater fish from different sites at the Xuque River in Spain. Cyclic volatile methyl siloxanes were detected in almost all freshwater samples at a concentration between pg/g and ng/g. Market samples showed a significant greater concentration, which is consistent with the expected contamination during storage and handling.

- Huber and co-workers examined the eggs of seabird species from remote Norwegian colonies for a broad range of legacy and emerging contaminants (Huber et al., 2015). Concentrations of cyclic volatile methyl siloxanes were below the limits of detection in the majority of eggs. The greatest concentrations of D5 and D6 were detected in eggs from common eider from Sklinna with 3.4 ng/g and 0.8 ng/g, respectively. D4 was not detected in any of the bird eggs.
- Lucia et al. studied the occurrence of several emerging contaminants in Arctic biota (Lucia M, 2016). Samples were collected in Svalbard, Norway at the west coast of Spitsbergen. The highest siloxane concentrations were found for D5 in glaucous gull eggs, ranging from 3.06 to 40.1 ng/g. The respective concentrations for D4 are lower and range from below the level of quantification up to 5.77 ng/g. D6 concentrations in these samples are generally below the level of quantification. In Arctic char and the eggs of black-legged kittiwakes, detected concentrations of D4, D5 and D6 were below the limit of quantification.
- Industry submitted two confidential draft interim reports (Powell D., 2015a; Powell D., 2015b) with first results of a long-term monitoring project in Inner Oslofjord for D4 and D5. Further details on these reports are summarised in the confidential annex.
- The Norwegian Institute for Water Research (NIVA) and the Norwegian Institute for Air Research (NILU) prepared a monitoring study on pollutants in Norwegian lakes that became available recently (Fjeld, 2016). Both NIVA and NILU have extensive experience in the analytics of cyclic volatile methyl siloxanes. The original report is in Norwegian and could therefore not be scrutinised. However, the summary and an extended abstract are available in English. Furthermore, the Norwegian Competent Authority gave a brief summary to the Dossier Submitter.

  In this study, cyclic volatile methyl siloxanes were analysed in fish from the lakes Mjøsa, Randsfjorden and Femunden and in the planktonic crustacean Mysis from Mjøsa (Fjeld, 2016). Generally, the greatest concentrations in fish were observed in Mjøsa, followed by Randsfjorden. The main sources for cyclic volatile methyl siloxanes in these lakes are expected to be local discharges via wastewater treatment plants. Samples from Femunden were below the quantification limits.

3.4.4 Summary and discussion of bioaccumulation

In its opinion on D4 and D5 (ECHA, 2015), the Member State Committee states that:

> *With regard to the assessment of bioaccumulation, MSC concludes that D4 and D5 are very bioaccumulative based on high fish BCF values, supported by multiple lines of evidence on biomagnification in dietary studies, and elimination half-lives. In addition, the available field data provides evidence that bioaccumulation and trophic magnification have been shown to occur in certain food webs in the environment. The available information on biomagnification and trophic magnification factors (BMF/TMF) in the field, indicating that biodilution occurs in some food chains or in parts of some food chains, does not invalidate the other lines of evidence.*
>
> *D4 meets the Annex XIII criteria for a very bioaccumulative (vB) substance according to Regulation (EC) No 1907/2006 based on the following studies:*
>
> - *A steady-state BCF of 12,400 L/kg for Fathead Minnow Pimephales*

promelas (Fackler et al., 1995) based on total 14C measurements.

- *A steady state BCF for Common Carp Cyprinus carpio in the range of 3,000 –4,000 L/kg (based on parent compound analysis) (CERI, 2007 and 2010a). The kinetic BCF in one of the studies was in the range 4,100 - 5,500 L/kg.*

New studies were published after the MSC and RAC opinions. These studies, summarised above, were evaluated and taken into account for the overall weight-of-evidence determination. However, these studies are not considered to contest the evidence of the studies on bioconcentration in fish and hence, they do not change the overall conclusion on bioaccumulation.

4. Human health hazard assessment

D4 is covered by index number 014-018-00-1 of Regulation (EC) No 1272/2008 in Annex VI, part 3, Table 3 (the list of harmonised classification and labelling of hazardous substances) and it is classified in the hazard class reproductive toxicity category 2 (hazard statement H361f “Suspected of damaging fertility”).

Therefore, the criterion for toxicity of Annex XIII section 1.1.3 b) of REACH is fulfilled.

5. Environmental hazard assessment

5.1 Aquatic compartment (including sediment)

5.1.1 Fish

5.1.1.1 Short-term toxicity to fish

Described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.7.1, page 11 (ECHA 2015c) and in the UK proposal for a restriction on the use of D4 and D5 in wash-off personal care products (UK Health & Safety Executive, 2015) section B.7.1, page 26.

In addition to the studies assessed by the UK Competent Authority (UK Environment Agency, 2009; UK Health & Safety Executive, 2015) registrants report in a 14 days short-term toxicity to fish study (ECHA, 2017b). This study is evaluated as a supporting study by the registrant. The test was performed according to OECD guideline 204. The test organism used was *O. mykiss*. Five concentrations (1.9, 3.4, 6.8, 13, 29 µg/L, means measured) of the test substance were tested. At the control 5 % lethal effects were detected after 14 days. No mortality was detected at 1.9, 3.4, and 6.8 µg/L. For the measured concentrations of 13 and 29 µg/L test substance a mortality of 25% and 90% was detected, respectively. In conclusion a 14-day LC50 value of 17 µg/L and NOEC of 6.8 µg/L have been determined for the effects of the test substance on mortality of *Oncorhynchus mykiss*.

5.1.1.2 Long-term toxicity to fish

Described in Annex 2 to MSC opinion on persistency and bioaccumulation of D4 and D5, section B.7.1, pages 11-12 (ECHA, 2015) and in the UK Restriction proposal (UK Health & Safety Executive, 2015) section B.7.1, page 26.

Additionally to the studies assessed by the UK (UK Environment Agency, 2009; UK Health & Safety Executive, 2015) as part of their restriction proposal a modelling approach, conducted by Mackay et al. was used to estimate critical body burden (CBR50, resulting in effects of 50 % of the test organism) for aquatic organisms (Mackay et al., 2015b). The authors reasoned the modelling to overcome difficulties of analysing volatile substance. Worth mentioning is that the use of a closed system is an approach that is e.g. recommended in the OECD guidelines 23 and 202. Nevertheless, Mackay and co-authors used for their modelling approach 1,2,4-Trichlorobenzene, Naphthalene and Di-n-Butylphthalate to validate the model used in their approach. For all substances of the validation data set, the calculated BCF underestimated the experimentally determined BCF values. The model was used to calculate e.g. the corresponding time to reach the CBR50 (3 mmol x m^{-3}). For aquatic organisms with an organism mass and lipid content ranging between 5 g and 5 % to 0.001 g and 1 % a corresponding time to reach CBR50 of 24.7 to 0.72 days was calculated for D4, respectively. Sousa et al. used *Oncorhynchus mykiss* with an average weight of 0.44 g in the prolonged acute toxicity test revealing a 14d-LOEC of 6.9 µg/L for D4 and a NOEC of 4.4 µg/L (Sousa et al., 1995). Therefore the results of the modelling approach by Mackay et al. are in line with results by Sousa et al. for a prolonged acute toxicity test (Sousa et al., 1995).

Although long-term toxicity tests including early life stage are preferred over prolonged acute toxicity tests (please refer to 5.1.1.1), the two tests did not overlap in the test substance concentrations. Therefore the true level of toxicity of D4 to fish over a long term remains elusive, but is in the range between 4.4 µg/L and 6.9 µg/L.

In their PBT/vPvB analysis of cyclic volatile methyl siloxanes, Bridges and Solomon conclude that D4 should not be regarded as toxic (Bridges and Solomon, 2016). However, valid studies on aquatic toxicity were rated irrelevant by the authors because the effect concentration was significantly larger than the maximum measured concentrations in surface waters receiving effluents. This maximum concentration was 0.02 µg/L for D4. Consequently, important studies for the aquatic toxicity of D4 were disregarded despite of high quality. This comparison of effect concentration and maximum realistic concentration is a key element of risk assessment, which is required under REACH as well. However, this method is not adequate for the PBT/vPvB assessment which focuses on the substance properties as such.

5.1.2 Aquatic invertebrates

5.1.2.1 Short-term toxicity to aquatic invertebrates

Described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.7.1, page 12 (ECHA, 2015) and in the UK Restriction Report (UK Health & Safety Executive, 2015) section B.7.1, page 26.

5.1.2.2 Long-term toxicity to aquatic invertebrates

Described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.7.1, page 12 (ECHA, 2015) and in the UK Restriction Report (UK Health & Safety Executive, 2015) section B.7.1, pages 26-27.

Recently, Fairbrother and Woodburn reviewed a previously assessed study by Sousa (Sousa et al., 1995) on toxicity to reproduction after 21 days on *Daphnia magna* (Fairbrother and Woodburn, 2016). The authors applied flow-through test system allowing a reproducible maximum concentration of 15 µg/L test substance. The following concentrations were used during the study: 0 (Control), 1.7, 1.8, 4.2, 7.9 and 15 µg/L. At the highest concentration the survival was significantly ($p \leq 0.05$) reduced to 77%. Therefore the 21d-$NOEC_{survival}$ is 7.9 µg/L. Fairbrother and Woodburn issued that survival rate (77%) at highest test concentration was only slightly below the allowable 80% survival rate for control. For the reproduction endpoint statistically significant differences (significantly higher) in the mean number of cumulative offspring per female were observed at a concentration of 7.9 µg/L. Differences between control response and treatment response were not statistically significant at the lower concentrations (1.7, 1.8, 4.2 µg/L). The overall 21 days NOEC for this study is therefore 7.9 µg/L based on survival.

5.1.3 Algae and aquatic plants

Described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.7.1, page 12 (ECHA, 2015) and in the British Restriction Report (UK Health & Safety Executive, 2015) section B.7.1, page 27.

5.1.4 Sediment organisms

Described in Annex 2 to the MSC opinion on the persistency and bioaccumulation of D4 and D5, section B.7.1, page 12 (ECHA, 2015) and in the British Restriction Report (UK Health & Safety Executive, 2015) section B.7.1, page 27.

The studies assessed by the UK Environment Agency (UK Health & Safety Executive, 2015) clearly demonstrate that D4 impacts the survival of all tested sediment dwelling organisms.

The risks of benthic organisms were further addressed by Woodburn et al. (Woodburn et al., 2018). The authors used probabilistic risk assessment (PRA) techniques to compare field sediment concentrations (95th centile) to effect level concentrations for D4, D5 and D6 in laboratory chronic toxicity tests with benthic organisms applying 5th benthic invertebrate fugacity biota NOEC values. The authors demonstrate the advantages of a probabilistic risk assessment techniques compared to classical risk quotient (PEC/PNEC). Thereby the authors excluded the study on the most sensitive organism *L. variegatus* from the PRA. The authors do not take into account, that the properties of a PBT/vPvB substance like D4 lead to an increased uncertainty in the estimation of risk to human health and the environment when applying quantitative risk assessment methodologies (ECHA, 2017a). Therefore the methodology used is not suitable to assess the hazard caused by D4 to benthic organisms.

5.1.5 Other considerations

Recent publications by Bridges and Solomon and Fairbrother and Woodburn do apply quantitative risk assessment methods to evaluate if D4 poses a risk to aquatic organisms (Bridges and Solomon, 2016; Fairbrother and Woodburn, 2016). Those assessments do compare environmental concentrations of D4, found in monitoring studies, e.g. in Canada (Wang et al., 2013), Scandinavia (Kaj et al., 2006) and Tokyo Bay (Powell et al., 2017) with experimentally derived toxicity values.
The purpose of this dossier is to identify D4 as a SVHC based on its PBT/vPvB properties. The PBT concept aims to protect all species. For PBT/vPvB substances, it is considered that a safe threshold does not exist. For that reason the studies done by Bridges and Solomon as well as Fairbrother and Woodburn are of benefit for an environmental risk assessment of D4, but are not suitable for a hazard characterisation, as needed for PBT/vPvB substances under REACH. For that reason these studies have not been further considered for the purpose of the PBT assessment.

5.2 Summary and discussion of the environmental hazard assessment

In its Opinion on the UK restriction proposal (UK Health & Safety Executive, 2015), the Committee for Risk Assessment (ECHA, 2016) states that

> *D4 has a long-term NOEC of around 4 – 6 µg/L for rainbow trout (Oncorhynchus mykiss), although RAC notes that there is some uncertainty in this value, and a long-term NOEC of 7.9 µg/L for Daphnia magna survival. [...] Significant toxicity to invertebrates is also apparent in sediment organism studies.*

The Committee for Risk Assessment (ECHA, 2016) concludes that

> *D4 meets the REACH Annex XIII criteria for toxicity based on both aquatic and mammalian end points.*

New studies were published after the MSC and RAC opinions. These studies, summarised above, were evaluated and taken into account for the overall weight-of-evidence determination. However, these studies are not considered to contest the studies on toxicity to fish and daphnids that were previously evaluated by the RAC and hence, they do not change the overall conclusion on toxicity.

6. Conclusions on the SVHC Properties

6.1 CMR assessment

Not relevant for the identification of the substance as SVHC in accordance with Article 57 (d) and (e) REACH.

6.2 PBT and vPvB assessment

6.2.1 Assessment of PBT/vPvB properties

The Member State Committee (MSC) provided an Opinion on the persistent and bioaccumulative properties of D4 and D5 at the request of the Executive Director of ECHA under Article 77(3)c of REACH (ECHA, 2015) during the process to restrict the use of these two substances. A weight-of-evidence determination according to the provisions of Annex XIII of REACH was used to form the Opinion. All available relevant information (such as the results of standard tests, monitoring and modelling, information from the application of the category and analogue approach (grouping, read-across) and (Q)SAR results) was considered together in a weight-of-evidence approach by the MSC. D4 was subsequently concluded by the Risk Assessment Committee (RAC) - based on the opinion of the MSC - to fulfil the criteria of Annex XIII of REACH as a PBT and vPvB substance (see RAC opinion on the restriction proposal: (ECHA, 2016; European Commission, 2018))[3].

6.2.1.1 Persistence

In its opinion on D4 and D5 (ECHA, 2015), the Member State Committee concluded that:

> *With regard to the assessment of persistence, MSC concludes that the experimental observations in simulation and monitoring studies lead to the conclusion that both D4 and D5 meet the vP criterion as specified in REACH Annex XIII.*
>
> *MSC has evaluated non-degradation processes and concluded that these do not have a large impact on the sediment removal half-life, and thus cannot be used to refute the relevance of the sediment compartment in the assessment of persistence.*
>
> *Based on OECD TG 308 sediment simulation studies (Xu, 2009a; Xu, 2009b), D4 has an estimated degradation half-life of 365 days in anaerobic sediment and 242 days in aerobic sediment at 24°C, MSC concludes that D4 meets the Annex XIII criteria for a very persistent (vP) substance in sediment according to Regulation (EC) No 1907/2006.*

New studies were published after the MSC and RAC opinions. These studies were evaluated and taken into account for the overall weight-of-evidence determination. This new information supports the earlier conclusion.

[3] The restriction on D4 and D5 entered into force in 31.1.2018 (European Commission, 2018): http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2018.006.01.0045.01.ENG

6.2.1.2 Bioaccumulation

In its opinion on D4 and D5 (ECHA, 2015), the Member State Committee concluded that:

> *With regard to the assessment of bioaccumulation, MSC concludes that D4 and D5 are very bioaccumulative based on high fish BCF values, supported by multiple lines of evidence on biomagnification in dietary studies, and elimination half lives. In addition, the available field data provides evidence that bioaccumulation and trophic magnification have been shown to occur in certain food webs in the environment. The available information on biomagnification and trophic magnification factors (BMF/TMF) in the field, indicating that biodilution occurs in some food chains or in parts of some food chains, does not invalidate the other lines of evidence.*
>
> *D4 meets the Annex XIII criteria for a very bioaccumulative (vB) substance according to Regulation (EC) No 1907/2006 based on the following studies:*
>
> - *A steady-state BCF of 12,400 L/kg for Fathead Minnow Pimephales promelas (Fackler et al., 1995) based on total 14C measurements.*
> - *A steady state BCF for Common Carp Cyprinus carpio in the range of 3,000 – 4,000 L/kg (based on parent compound analysis) (CERI, 2007 and 2010a). The kinetic BCF in one of the studies was in the range 4,100 - 5,500 L/kg.*

After the MSC and RAC Opinion making processes new studies have been published. The relevant studies have been summarised in this document. The new information does not deviate from the diverse data available earlier on bioaccumulation. The new data do not provide any reason to change the conclusion that the substance is vB reached by MSC and RAC.

6.2.1.3 Toxicity

D4 is covered by index number 014-018-00-1 of Regulation (EC) No 1272/2008 in Annex VI, part 3, Table 3 (the list of harmonised classification and labelling of hazardous substances) and it is classified in the hazard class reproductive toxicity category 2 (hazard statement H361f "Suspected of damaging fertility"). Therefore, the criterion for toxicity of Annex XIII section 1.1.3 b) of REACH is fulfilled.

In its opinion on the UK restriction proposal (UK Health & Safety Executive, 2015), the Committee for Risk Assessment (ECHA, 2016) states that:

> *D4 has a long-term NOEC of around 4 – 6 µg/L for rainbow trout (Oncorhynchus mykiss), although RAC notes that there is some uncertainty in this value, and a long-term NOEC of 7.9 µg/L for Daphnia magna survival. [...] Significant toxicity to invertebrates is also apparent in sediment organism studies.*

The Committee for Risk Assessment (ECHA, 2016) concludes that:

> *D4 meets the REACH Annex XIII criteria for toxicity based on both aquatic and mammalian end points.*

New studies were published after the RAC opinion. These studies were evaluated and taken into account for the overall weight-of-evidence determination. However, these studies are not considered to contest the studies on toxicity to fish and daphnids that were previously evaluated by the RAC and hence, they do not change the overall conclusion on toxicity.

6.2.2 Summary and overall conclusions on the PBT and vPvB properties

The Member State Committee (MSC) provided an Opinion on the persistent and bioaccumulative properties of D4 and D5 at the request of the Executive Director of ECHA under Article 77(3)c of REACH (ECHA, 2015) during the process to restrict the use of these two substances. A weight-of-evidence determination according to the provisions of Annex XIII of REACH was used to form the Opinion. All available relevant information (such as the results of standard tests, monitoring and modelling, information from the application of the category and analogue approach (grouping, read-across) and (Q)SAR results) was considered together in a weight-of-evidence approach by the MSC. D4 was subsequently concluded by the Risk Assessment Committee (RAC) - based on the opinion of the MSC - to fulfil the criteria of Annex XIII of REACH as a PBT and vPvB substance (see RAC opinion on the restriction proposal: (ECHA, 2016; European Commission, 2018))[4].

Persistence

The Member State Committee (ECHA, 2015) concluded that:

> *With regard to the assessment of persistence, MSC concludes that the experimental observations in simulation and monitoring studies lead to the conclusion that both D4 and D5 meet the vP criterion as specified in REACH Annex XIII.*
>
> *MSC has evaluated non-degradation processes and concluded that these do not have a large impact on the sediment removal half-life, and thus cannot be used to refute the relevance of the sediment compartment in the assessment of persistence.*
>
> *Based on OECD TG 308 sediment simulation studies (Xu, 2009a; Xu, 2009b), D4 has an estimated degradation half-life of 365 days in anaerobic sediment and 242 days in aerobic sediment at 24°C, MSC concludes that D4 meets the Annex XIII criteria for a very persistent (vP) substance in sediment according to Regulation (EC) No 1907/2006.*

After the MSC and RAC Opinion making processes, new studies have been published. The relevant studies have been summarised in this document. This new information supports the earlier conclusion.

Bioaccumulation

The Member State Committee (ECHA, 2015) concluded that:

> *With regard to the assessment of bioaccumulation, MSC concludes that D4 and D5 are very bioaccumulative based on high fish BCF values, supported by multiple lines of evidence on biomagnification in dietary studies, and elimination half-lives. In addition, the available field data provides evidence that bioaccumulation and trophic magnification have been shown to occur in certain food webs in the environment. The available information on biomagnification and trophic magnification factors (BMF/TMF) in the field, indicating that biodilution occurs in some food chains or in parts of some food chains, does not invalidate the other lines of evidence.*

[4] The restriction on D4 and D5 entered into force in 31.1.2018 (European Commission, 2018): http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2018.006.01.0045.01.ENG

D4 meets the Annex XIII criteria for a very bioaccumulative (vB) substance according to Regulation (EC) No 1907/2006 based on the following studies:

- *A steady-state BCF of 12,400 L/kg for Fathead Minnow Pimephales promelas (Fackler et al., 1995) based on total 14C measurements.*
- *A steady state BCF for Common Carp Cyprinus carpio in the range of 3,000 – 4,000 L/kg (based on parent compound analysis) (CERI, 2007 and 2010a). The kinetic BCF in one of the studies was in the range 4,100 - 5,500 L/kg.*

After the MSC and RAC Opinion making processes new studies have been published. The relevant studies have been summarised in this document. The new information does not deviate from the diverse data available earlier on bioaccumulation. The new data do not provide any reason to change the conclusion that the substance is vB reached by MSC and RAC.

Toxicity

In its opinion on the UK proposal for a restriction on the use of D4 and D5 in wash-off personal care products (UK Health & Safety Executive, 2015), the Committee for Risk Assessment (ECHA, 2016) states that

D4 has a long-term NOEC of around 4 – 6 µg/L for rainbow trout (Oncorhynchus mykiss), although RAC notes that there is some uncertainty in this value, and a long-term NOEC of 7.9 µg/L for Daphnia magna survival. [...] Significant toxicity to invertebrates is also apparent in sediment organism studies.

The Committee for Risk Assessment (ECHA, 2016; UK Environment Agency, 2009) concludes that

D4 meets the REACH Annex XIII criteria for toxicity based on both aquatic and mammalian end points.

New studies were published after the MSC opinion (ECHA, 2015) and RAC opinion (ECHA, 2016) were adopted. These studies were evaluated and taken into account for the overall weight-of-evidence determination. However, these studies are not considered to contest the conclusions on toxicity to fish and daphnids that were previously evaluated by the MSC and RAC. Hence, they do not change the overall conclusion on toxicity.

D4 is covered by index number 014-018-00-1 of Regulation (EC) No 1272/2008 in Annex VI, part 3, Table 3 (the list of harmonised classification and labelling of hazardous substances) and it is classified in the hazard class reproductive toxicity category 2 (hazard statement H361f "Suspected of damaging fertility"). Therefore, the criterion for toxicity of Annex XIII section 1.1.3 b) of REACH is fulfilled.

Conclusion

In its opinion on D4 and D5 (ECHA, 2015), the Member State Committee states that:

Based on the information presented by the DS and careful consideration of the comments received in the public consultation, MSC supports the opinion of the DS that D4 and D5 both meet the vPvB criteria in Annex XIII of REACH.

The Committee for Risk Assessment (ECHA, 2016) concludes that

> *D4 meets the REACH Annex XIII criteria for toxicity based on both aquatic and mammalian end points.*

In conclusion, D4 meets the criteria for a PBT and vPvB substance according to REACH Art. 57(d) and (e) by comparing all relevant and available information listed in REACH Annex XIII with the criteria set out in the same Annex, in a weight-of-evidence determination.

6.3 Assessment under Article 57(f)

Not relevant for the identification of the substance as SVHC in accordance with Article 57 (d) and (e) REACH.

Part II

According to Article 58(3) of REACH the three criteria regarding the substances to which priority for inclusion in Annex XIV to REACH shall normally be given are fulfilled. D4 is a substance with

(a) PBT or vPvB properties

(b) wide dispersive use

(c) high volumes.

Authorisation does, however, not address the main use of D4 and D5 as a chemical intermediate, which may lead to significant impurities of D4 and D5 in silicone polymers. Other uses in the scope of authorisation are expected to cease if the follow-up restriction on D4/D5 in other consumer/professional products under development by ECHA[5] would be adopted.

Once D4 and D5 are included in Annex XIV, they could no longer be subject to targeted restrictions, except for restrictions relating to imported articles. Therefore, the dossier submitter recommends not to include these substances in Annex XIV immediately after their identification as a SVHC.

[5] https://echa.europa.eu/registry-of-current-restriction-proposal-intentions/-/substance-rev/16310/term

7. Registration and C&L notification status

7.1 Registration status

Table 7 Registration status

From the ECHA dissemination site[6]	
Registrations	☒ Full registration(s) (Art. 10) ☐ Intermediate registration(s) (Art. 17 and/or 18)

7.2 CLP notification status

Table 8: CLP notifications

	CLP Notifications[7]
Number of aggregated notifications	38
Total number of notifiers	2985

8. Total tonnage of the substance

Table 9: Tonnage status

Total tonnage band for the registered substance (excluding the volume registered under Art 17 or Art 18)[8]	100 000 - 1 000 000 t/pa

[6] *https://echa.europa.eu/de/substance-information/-/substanceinfo/100.008.307 (accessed 11.12.2017)*
[7] C&L Inventory database, http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database (accessed 08.01.2018)
[8] *https://echa.europa.eu/de/substance-information/-/substanceinfo/100.008.307 (accessed 11.12.2017)*

9. Information on uses of the substance

Table 10: Uses[9]

	Use(s)	Registered use *(If not, specify the source of the information)*	Use in the scope of Authorisation
Uses as intermediate	Use as intermediate	Yes	No
Formulation or repacking	Use in the following products: leather treatment products, lubricants and greases, and dyes. Release to the environment of this substance can occur from industrial use: formulation of mixtures, in processing aids at industrial sites and as processing aid. Other release to the environment of this substance is likely to occur from: indoor use (e.g. machine wash liquids/detergents, automotive care products, paints and coating or adhesives, fragrances and air fresheners) and outdoor use as processing aid	Yes	Yes
Uses at industrial sites	Manufacture Release to the environment of this substance can occur from industrial use: manufacturing of the substance. Uses at industrial sites This substance is used in the following products: laboratory chemicals, non-metal-surface treatment products and semiconductors. This substance has an industrial use resulting in manufacture of another substance (use of intermediates). This substance is used in the following areas: formulation of mixtures and/or re-packaging and scientific research and development. This substance is used for the manufacture of: chemicals, rubber products, plastic products, mineral products (e.g. plasters, cement) and electrical, electronic and optical equipment. Release to the environment of this substance can occur from industrial use: as an intermediate step in further manufacturing of another substance (use of intermediates), for thermoplastic manufacture, as processing aid, in processing aids at industrial sites and in the production of articles. Other release to	Yes	No (research, intermediate) Yes (other)

[9] https://echa.europa.eu/documents/10162/13640/generic_exemptions_authorisation_en.pdf

	the environment of this substance is likely to occur from: indoor use.		
Uses by professional workers	Use in the following products: washing & cleaning products, cosmetics and personal care products, polishes and waxes and laboratory chemicals. Use in the following areas: formulation of mixtures and/or re-packaging, scientific research and development and printing and recorded media reproduction. Other release to the environment of this substance is likely to occur from: indoor use (e.g. machine wash liquids/detergents, automotive care products, paints and coating or adhesives, fragrances and air fresheners) and outdoor use as processing aid	Yes	Yes
Consumer uses	Use in the following products: Washing- and cleaning products, cosmetics, personal care products, polishes and waxes Other release to the environment of this substance is likely to occur from: indoor use (e.g. machine wash liquids/detergents, automotive care products, paints and coating or adhesives, fragrances and air fresheners) and outdoor use as processing aid	Yes	Yes
Article service life	Indoor use in long life materials with low release rate (e.g. flooring, furniture, toys, construction materials, curtains, foot-wear, leather products, paper and cardboard products, electronic equipment) substance can be found in products with material based on: paper (e.g. tissues, feminine hygiene products, nappies, books, magazines, wallpaper)	Yes	No

A detailed overview of uses is given in the current restriction report (UK Health & Safety Executive, 2015). The main points are summarised below:

The major use of D4 is as a feedstock for the production of silicone polymers which have a very wide range of uses (UK Health & Safety Executive, 2015). According to communication with industry, no direct intentional use of D4 in consumer and professional products is known. If such uses existed, they would be expected to cease if the restriction intended by ECHA would be adopted.

According to the UK restriction report, it is in principle not possible to reduce D4 to below 0.1% w/w in silicone polymers at the manufacturing stage (UK Health & Safety Executive, 2015). The economic and technical feasibility depends on the field of use of the polymeric products and also on the intended grade of D4/ D5 reduction.

According to personal communication with industry representatives during a national consultation meeting, the end products made from or containing silicone polymers would not contain D4 and D5 contents higher than 0.1%.

Industry representatives note that there is an enormous range of specialised applications for D4 and no detailed information on appropriate alternatives is currently available.

10. Information on structure of the supply chain

There is no information on the structure of the supply chain available.

11. Additional information

11.1 Alternatives

Both D4 and D5 can be used as substitutes for each other, and therefore, regulatory action should cover both substances at the same time. Furthermore, D4 usually contains impurities of D5 and vice versa.

Another alternative substance is D6 (EC 540-97-6, dodecamethylcyclohexasiloxane), which was assessed to be vPvB as well by the UK-CA (see also: Annex XV report (2018)). Further possible alternatives for the use as an intermediate in silicone production might be the respective linear siloxanes. However, octamethyltrisiloxane (EC 203-497-4, L3), decamethyltetrasiloxane (EC 205-491-7, L4) and dodecamethylpentasiloxane (EC 205-492-2, L5) are listed on the CoRAP as potential PBT/vPvB substances. Furthermore, silicone production from linear siloxanes would also lead to the formation of D4, D5 and D6 as residuals in the polymer.

11.2 Existing EU legislation

Harmonised C&L

The current entry for D4 (index number 014-018-00-1) in Annex VI of the CLP Regulation is:

- Repr. 2, H361f***
- Aquatic Chronic 4, H413

11.3 Previous assessments by other authorities

REACH restriction processes

A restriction dossier on D4 and D5 in wash-off personal care products was submitted by the UK (UK Health & Safety Executive, 2015). This proposal targets the use of D4 and D5 in wash-off personal care products which accounts for less than 5% of the total tonnage per substance. The restriction proposal on D4 and D5 in wash-off personal care products was agreed upon at the REACH Committee on May 10th 2017 and is now also available in the official journal:

https://echa.europa.eu/de/about-us/who-we-are/member-state-committee/opinions-of-the-msc-adopted-under-specific-echa-s-executive-director-requests

http://eur-lex.europa.eu/legal-content/DE/TXT/?uri=CELEX:32018R0035

In April 2017, ECHA submitted the intention to restrict the use of D4 and D5 in leave-on personal care products and other consumer/professional products not covered by the UK in the earlier restriction proposal:

https://echa.europa.eu/de/registry-of-current-restriction-proposal-intentions/-/substance-rev/16310/term?_viewsubstances_WAR_echarevsubstanceportlet_SEARCH_CRITERIA_EC_NUMBER=208-764-9&_viewsubstances_WAR_echarevsubstanceportlet_DISS=true

Harmonised C&L

On July 29th 2016, a proposal was submitted by the German CA to change the current entry for D4 (index number 014-018-00-1); the proposed future entry in Annex VI of the CLP Regulation is:

- Repr. 2, H361f***
- Aquatic Chronic 1, H410
- Aquatic Chronic 1, M-factor=10

(UNEP) Stockholm convention (POPs Protocol)

In April 2016, the European Commission has proposed to nominate D4 for regulation under the Stockholm Convention. Discussions on this Commission proposal are still ongoing.

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