

**This is an updated version of the D4 RMO that has been previously circulated, updated with further information that has been provided since the original RMO.**

## **Analysis of the most appropriate risk management options for D4**

**Substance name:** Octamethylcyclotetrasiloxane  
[Referred to as D4 in this document]

**EC number:** 209-136-7

**CAS number:** 556-67-2

**Submitted by:** United Kingdom

**Date:** June 2015<sup>1</sup>

### **1. Background**

Two cyclic volatile methylsiloxane (cVMS)<sup>2</sup> substances (referred to as D4 and D5) were included in Commission Regulation (EC) No 465/2008 to clarify their PBT properties. Industry submitted data in compliance with the Regulation in November 2009, and a final evaluation report for each substance was submitted by the UK rapporteur to ECHA in October 2010 (EA, 2010a & 2010b). The conclusion was that D4 meets the PBT and vPvB criteria, and that D5 meets the vPvB criteria of Annex XIII. In parallel, the UK published detailed environmental risk evaluation reports (RERs) for both substances in 2009, along with a third related substance (D6) (EA, 2009a, 2009b & 2009c).

The purpose of this RMO analysis is to summarise what evidence is available to support any additional regulatory action required to minimise the release of D4 to the environment and the form that this regulatory action should take. This RMO analysis only considers measures to protect the environment and does not consider measures to protect human health. D4 has not been identified as an SVHC on human health grounds and a detailed review of other human health risks has not been performed for this RMO paper. The Scientific Committee on Consumer Safety (SCCS) published its opinion that cyclomethicone (D4, D5) does not pose a risk for human health when used in cosmetic products (SCCS, 2010).

### ***Regulatory Action Outside the EU***

#### ***Canada***

D4 was included in Batch 2 of the Challenge initiative under the Canadian Chemicals Management Plan. The final screening assessment report concluded that D4 met the criteria in paragraph 64 (a) of the Canadian Environmental Protection Act, 1999 (CEPA), i.e. it is (or may be) entering the environment in a quantity or a concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. The Proposed Order to add D4 to Schedule 1 of CEPA was published on 16 May 2009<sup>3</sup>. This triggered a legal obligation to develop an instrument under CEPA to reduce release of D4 to the environment within two years. The proposed environmental objective is to prevent or minimize release of D4 to the aquatic environment.

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<sup>1</sup> This RMO is an updated version of one that has been previously circulated in 2011, taking into account further information that has been provided and including an annex on additional uses identified.

<sup>2</sup> Cyclomethicone is a general term used when mixtures of D4, D5 and D6 are used.

<sup>3</sup> <http://canadagazette.gc.ca/rp-pr/p1/2009/2009-05-16/html/reg1-eng.html>

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In June 2012 the requirement to produce and implement Pollution Prevention Plans in respect of D4 in industrial effluents was published. The requirement applies to any person who owns or operates an industrial facility that manufactures or uses D4 or a mixture containing D4, where the total quantity of D4 used or manufactured is equal to or greater than 100 kg during a calendar year, and, as a result of manufacturing or use, the effluent at the final discharge point(s) of the facility contains D4.

### ***USA***

The US Environment Protection Agency (US-EPA) has entered into an Enforceable Consent Agreement (ECA) for D4<sup>4</sup>. The effective date was 4th April 2014 and a study plan should now have been submitted to the EPA. Testing should commence in early 2015 and will take place over a period of one year. The final report is due to be submitted to the US EPA in June 2016 and is expected to be released to the public in 2016 or 2017<sup>5</sup>.

Regulatory agencies in a number of individual states are assessing the PBT profile of D4. The assessments are at different stages and are proceeding along individual timelines

### ***Japan***

CES (personal communication) has indicated that the Japanese regulatory authorities have expressed concern about D4 and D5 in relation to their national PBT criteria, although they are not yet considering specific risk management activities. They have conducted their own bioconcentration study for D4 (these are new data that have not been evaluated in the EU), and requested an additional assessment of biomagnification for both D4 and D5, including laboratory studies with Japanese carp and field monitoring.

The European manufacturers/suppliers have indicated a preference for consistent global approaches to managing the risks of D4.

## **2. Objectives for (further) risk management**

The key concern for D4 is its PBT/vPvB properties and therefore its possible long-term effects on release to the environment from products in which it is contained and/or industrial waste. REACH calls for minimisation of emissions and exposures of SVHCs as far as technically and practically possible (recital 70). The aim for further regulatory action on D4 is therefore to minimise its release to the environment.

The timing of any intervention is potentially important in terms of its connection with any regulatory action on D5, which is a possible major substitute for D4. An RMO paper is also being put forward for D5. Considering regulatory action for both D4 and D5 at the same time should prevent any major reformulation from taking place that would have potentially higher costs in the longer-term to the industry.

If the level of D4 is above 0.1% w/w in any other substances, this would make them PBT-containing substances, regardless of their own PBT/vPvB profile.

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<sup>4</sup> <http://www.epa.gov/opptintr/chemtest/pubs/eca.html>

<sup>5</sup> <http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPPT-2012-0209-0067>

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Therefore, any further regulation of D4 will also need to take account of its presence in higher homologue substances<sup>6</sup>, which might be potential alternatives in some applications. This is considered further below (and is also discussed in the separate RMO document prepared for D5).

### **3. Available information**

#### **3.1 Current information on environmental hazard and risk**

##### **3.1.1. Issues around substance identity**

This information is taken from EA (2009a) and EA (2010a). The purity of D4 is between >96 % and >99 % w/w. The major impurity is D5, which is present at a concentration of less than 5 % w/w. No additives are present in the commercial substance.

##### **3.1.2 Hazard evaluation**

###### **3.1.2.1 Classification**

The harmonised classification for D4 under the CLP Regulation is Repro. 2 (H361f) and Aquatic Chronic 4 (H413). The implementation of the 2<sup>nd</sup> ATP to the CLP Regulation will produce a more stringent environmental classification as the lowest reliable aquatic NOEC is around 4.4 µg/l (equivalent to Aquatic Chronic 1). Some companies who have made notifications under the CLP Regulation also propose additional classifications (Flam. Liq. 3, Acute Tox. 4).

###### **3.1.2.2 PBT assessment**

Full details are provided in EA (2010a).

**Persistence:** Although it is expected to hydrolyse relatively quickly in water, D4 has a very long degradation half-life in sediment, in the order of 242 days at 24 °C under aerobic conditions and 365 days at 24 °C under anaerobic conditions. The half-life at lower temperatures (e.g. 12 °C) would be expected to be longer than these values. D4 therefore meets the Annex XIII criteria for a very persistent (vP) substance. Persistence in sediment is also supported by the sediment core data from Lake Pepin in the USA.

**Bioaccumulation:** A steady state fish bioconcentration factor (BCF) of 12,400 l/kg has been determined for D4 and so it clearly meets the Annex XIII criteria for B and vB. Monitoring studies show that it is detectable in biota in the environment, particularly in areas close to sources of release, but also in some samples from more remote regions. Biomagnification factors above 1 have been observed in some feeding relationships, and the trophic magnification factor could be greater than 1 for the fish studied in Lake Pepin.

**Toxicity:** D4 has a long-term fish NOEC of around 4.4 µg/l and a long-term NOEC of 7.9 µg/l with *Daphnia magna*. In addition, it is classified as toxic to reproduction category 2. Therefore, it can be concluded that D4 meets the Annex XIII criteria for toxicity (T) based on both aquatic and mammalian end points.

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<sup>6</sup> For example, D5 (CAS no. 541-02-6), dodecamethylcyclohexasiloxane (D6) (CAS no. 540-97-6) and tetradecamethylcycloheptasiloxane (D7) (CAS no. 107-50-6).

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**Summary:** D4 meets both the PBT and vPvB criteria of Annex XIII. This has since been confirmed by an opinion from the Member State Committee, issued in April 2015.<sup>7</sup>

### 3.2 Overview of uses for D4 and availability of alternative substances

The UK risk evaluation report (EA, 2009a) was based on the total European tonnage that was known about at the time of its preparation. Industry has confirmed that the use pattern has remained broadly consistent (personal communication), and so unless otherwise stated the rest of the information in this section is taken from EA (2009a).

Four companies produced or supplied D4 in the EU in 2004. The actual quantities are confidential. The main uses of D4 can be divided into four areas:

- Use as a site-limited chemical intermediate at the site of production.
- Use as an off-site chemical intermediate for the production of silicone polymers and synthetic amorphous silica.
- Use in personal care products.
- Use in household products.

In 2004, around 8,866 tonnes were used as an off-site intermediate for the production of silicone polymers and 579 tonnes were used in personal care products. The other uses are much smaller in scale (the amounts are confidential).

Production of D4 in the UK has shown an increasing trend over recent years, but the use in personal care products and household products shows a generally decreasing trend in both the UK and the EU. However, this analysis is based on relatively few data points (in some cases only two years).

Reasonable worst-case regional and continental emissions for each use based on EA (2009a) are presented in Table 1.

**Table 1 Summary of environmental release estimates for D4**

Scenario	Emission (kg/year)	
	Regional	Continental
Production and on-site use as an intermediate – UK site	Confidential to air 23.4 to surface water	Not quantified
Chemical intermediate – off-site – polymers – wet process (also covers dry processes)	Confidential to air Confidential to wastewater	Confidential to air Confidential to wastewater
Chemical intermediate – off-site – silica – UK and EU sites	Confidential to air 0 to wastewater	Confidential to air 0 to wastewater
Personal care products – formulation – UK sites	10.5 to air 52.1 to wastewater	92.7 to air 459 to wastewater
Personal care products – formulation – generic site (non- UK)	-	-
Personal care products – use	25,200 to air 2800 to wastewater	485,100 to air 53,900 to wastewater
Household products – formulation	Confidential to air Confidential to wastewater	Confidential to air Confidential to wastewater

<sup>7</sup> <http://echa.europa.eu/about-us/who-we-are/member-state-committee/opinions-of-the-msc-adopted-under-specific-echa-s-executive-director-requests>

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Scenario	Emission (kg/year)	
	Regional	Continental
Household products – use	Confidential to air Confidential to wastewater	Confidential to air Confidential to Wastewater
Residual monomer in polymers	104,840 to air	943,560 to air

The release estimates are based on assumptions about percentage losses from different scenarios and are not necessarily measured data. The most significant release to wastewater is expected to arise from use in personal care products. Smaller releases to wastewater are expected from (in order of declining magnitude): use of household products, formulation of personal care products, production and on-site use as an intermediate, off-site chemical intermediate for polymer production (wet processes), and formulation of household products. Monitoring data (summarised in EA (2009a) and EA (2010a)) demonstrate that environmental exposure in aquatic ecosystems is widespread. Although the sources of that exposure are not always apparent, the levels are highest downstream from municipal WWTP and industrial areas.

Siloxanes (both cyclic and linear) are well known components of landfill gas, and can cause mechanical problems in pumping engines due to the build up of silica deposits (EA, 2010c). A further emission of 44,875–78,000 kg/year of D4 to air is estimated from the possible degradation of silicone polymers in soil and landfills in the EU, although this is subject to a large uncertainty. This amount is small compared to other sources of emission to air and so has not been considered further.

D4 is highly volatile (the Henry's law constant is around  $1.21 \times 10^6$  Pa m<sup>3</sup>/mol at 25 °C), which has a significant influence on its environmental fate and distribution. Release to water can lead to accumulation in sediments, where it has a long dissipation half-life. Transport through the marine environment is unlikely given D4's overall volatility, low water solubility and hydrolytic instability at normal pHs of the marine environment.

Release to air can lead to long-range transport. The available experimental and modelling studies indicate that once in the atmosphere, D4 is present almost entirely in the vapour phase and has a low potential for wet and dry deposition (EA, 2009a & 2010a). Monitoring shows that D4 is present in some biota samples from remote regions, generally at very low concentrations (close to the limit of detection). The possibility of local sources of D4 even in remote locations means that the interpretation of these data in terms of long-range transport potential is difficult.

It is therefore proposed that the aim for regulatory action should be to limit release into the aquatic environment in the first instance, since its presence in the atmosphere is not expected to lead to significant exposure of the aquatic or terrestrial environments.

### **3.2.1 Use as a chemical intermediate**

By far the major use of D4 is as a monomer in the manufacture of silicone polymers. The equilibrium concentration of cVMS in polydimethylsiloxane (PDMS) is thought to be around 18 % by weight with D4, D5, and D6 making up >95 % of the total cyclic fraction. CVMS can also be reformed through thermal degradation of the polymer. Similarly, modified PDMS polymer and silicone

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elastomer products may contain small amounts of cVMS as impurities (at levels that are currently unclear).

The polymers have a very wide range of uses in consumer and industrial applications:

- anti foaming agents in oil processing;
- flow and/or gloss improvers in alkyd paints and varnishes;
- lubricants in polishes and maintenance products;
- anti-adhesion/anti-adherence coatings and mould-release agents;
- hydraulic, dielectric, and heat-transfer fluids and in diffusion pump oils;
- barrier creams and lipsticks;
- pharmaceuticals;
- lubricants for motors, instruments, and precision bearings;
- silicone emulsions used as antifoams;
- silicone greases for gear and bearing lubrications;
- silicone pastes for valve lubricants, mould-release agents, and electrical and electronic protection;
- pressure-sensitive adhesives;
- textile manufacturing additives (waterproofing and softness & wetting agent); and
- paper sizing and paper coating additives.

Modified PDMS are used as intermediates and as waterproofing agents for textiles and wall boards, high-temperature oil baths, greases, diffusion pump fluids, paint additives, gasket materials, release agents for plastics and urethane parts, for cutting oils, personal care products, household care products, automotive care products, and in plastic modification.

Organosiloxane (silicone) elastomers are used for coatings, gels, sealants, and rubbers (for the manufacture of tubes, rods, wire and cable insulation, and continuous profile); coated textiles and glass cloth (used to form tubes and hoses of complex shapes); electrical connectors, O-ring seals, valves, electrical components, health care products, and sports equipment (goggles and scuba masks); silicone foam for building and construction fire-stop systems and as pipe insulation in power plants. It is also used in the production of sealants, encapsulants, foams, coatings, caulking, and mould making. Applications of heat-cured rubber include tubing, hoses, wire and cable insulation, penetration seals, laminates, release coatings, foams, and other moulded and extruded articles, such as gaskets, key pads, ignition cables, belting, and catheters. Gel applications include electronic encapsulates and wound-dressing patches. One component cold-cured rubbers are used as caulks and sealants for expansion joints and windows, for seals, gaskets, and shock-absorbing fixing in vehicles and domestic appliances, and in heat-resistant adhesives. Two component cold-cured (addition cured) rubbers are used as dielectric gels, for electronic and electrical encapsulation, in fire-resistant cable coatings, in foamed sealants, and in resin-casting moulds. Two-component cold-cured (condensation cured) rubbers are used as moulding compounds for furniture and construction, in paper anti-adhesion coatings, as electrical component sealants, as roofing membranes, and as window and curtain walling sealants. Heat-cured silicone rubbers are used in chemical resistant and medical tubing and mouldings, flexible and rigid foams, press-foamed automobile seals, and wire and cable jacketing. Also in paper release coatings used in label systems.

The breakdown of the total use between the various main applications in Western Europe for 2002 was:

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- sealants, 210,000 tonnes (~32 per cent)
- elastomers, 139,000 tonnes (~21 per cent)
- fluids, 139,000 tonnes (~21 per cent)
- specialities, 92,000 tonnes (~14 per cent)
- silanes, 60,000 tonnes (~9 per cent)
- resins, 20,000 tonnes (~3 per cent).

Another, more detailed, breakdown was given for the Western European use of elastomers and silicone fluids. For elastomers, 20 per cent were used in automotive applications, 15 per cent in electrical fittings, 14 per cent in medical and healthcare applications, 9 per cent in appliances, 9 per cent in consumer goods, 7 per cent in textile coatings, 7 per cent in paints and coatings, 7 per cent in mould making, 5 per cent in business machines, and 7 per cent in other applications.

For the silicone fluids, 26 per cent were used as processing aids, 18 per cent in personal care products, 15 per cent in paper coatings, 10 per cent in paints and coatings, 7 per cent as mechanical fluids, 5 per cent in textile applications, and 24 per cent in other applications. Further information has been included in the annex on the use of silicone polymers in the oil/gas, paper/pulp and detergent industries.

### **Alternatives**

Due to the equilibrium nature of the reaction that leads to the formation of silicone polymers from cVMS, it is generally not possible to reduce D4 and D5 to below 0.1% w/w in polymers at the manufacturing stage. It is possible that other polymer systems might be suitable for some applications, but the high demand for silicone polymers suggests that they are the material of choice for many. In this context, the polymers can also be made using linear siloxane monomers. However, this is currently a minor technology in Europe. A major silicone manufacturing company has indicated that they could make the switch to this technology over a number of years (the situation for other companies and investment required is not known).

In addition, the linear siloxanes may also have similar environmental issues as the cVMS in terms of their PBT profiles. For example, some have been reviewed by the OECD, and the following conclusions presented in Table 2 were drawn:

**Table 2 Summary of reviewed data for linear siloxanes**

<b>Chemical</b>	<b>Hazard profile</b>	<b>Area of Use</b>
<b>Octamethyltrisiloxane (L3)</b>	Due to hydrolysis L3 possesses properties indicating a low aquatic hazard profile (at the limit of the water solubility), although it has potential to bioaccumulate and is not readily biodegradable. L3 possesses properties indicating a hazard for human health (repeated-dose toxicity).  L3 therefore meets the screening P criterion, is vB, and T on the basis of mammalian data.	L3 is used in personal care (25-40%) and consumer products, as a chemical intermediate (0.1-100%) and as an intermediate for silicone oligomers and polymers.
<b>Trisiloxane, 1,1,1,5,5,5-hexamethyl-3,3-</b>	M4Q possesses properties indicating a hazard for the	M4Q is an organic substance that occurs as a reaction by-product or

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<b>bis[(trimethylsilyl)oxy] M4Q</b>	environment. It is not readily biodegradable and is expected to bioaccumulate.	impurity in a wide range of silicon-based products, including those found in adhesives, sealants, processing intermediates, lubricants, antifoaming agents, paints and coatings. This is therefore not an alternative to D4 or D5 but may be present in substitutes.
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Environment Canada is reviewing the linear siloxanes. They have completed screening assessments for linear siloxanes L3 (octamethyltrisiloxane (MDM), CAS No. 107-51-7) and M4Q that concluded that it did not meet the criteria for CEPA 1999 and also include data for L4 (decamethyltetrasiloxane, CAS No. 141-62-8) and L5 PTS, (dodecamethylpentasiloxane, CAS No. 141-63-9), as analogues.<sup>8</sup> In addition, the UK has added L2, L3, L4 and L5 to the Community Rolling Action Plan to evaluate their hazards and risks. Conclusions are unlikely to be available until 2018 at the earliest.

A more detailed assessment of alternatives will be undertaken for the Annex XV dossier.

### **3.2.2 Use in personal care products**

D4 is used directly in the manufacture of cosmetic, skin- and hair-care formulations. The Cosmetic Toiletry and Perfumery Association (CTPA) indicate that the functions of the cVMS used in cosmetics in the UK are, in general, in the following three main areas (EA, 2009a):

- as hair-conditioning agents,
- as skin-conditioning agents (emollient),
- as solvents.

The types of products in which they are reported to be used include aftershave lotions, colognes, toilet waters, perfumery products, baby lotions, oils, powders and creams, baby shampoos, bath oils and bath salts, etc., make-up products, make-up removers and skin cleaning products, deodorants and antiperspirants, eye creams and eye make-up products (such as powders, mascaras, pencils, etc.), general make-up (such as foundations, blushers, face powders, and lipsticks), shampoos, conditioners, and hair dyes and colours, hair sprays, shaving products, skin-care preparations (such as creams, lotions, cleansers, and toners), sun creams and after-sun products, and hair-grooming aids.

SCCS (2010) adds that cVMS are used in various cosmetic products as an antistatic/ emollient/humectant/solvent/viscosity controlling/hair conditioning ingredient and for the good spreadability of the products. One company initially said that D4 is used in all cosmetic products at an average concentration of 1 %. However, published data in the scientific literature indicated that cyclomethicone may be present in some cosmetic products, for instance in antiperspirants, at concentrations >40 %. COLIPA provided limited information on typical use patterns and concentrations, which has been supplemented by information

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<sup>8</sup> Additional substances that might be relevant as substitutes in some or all uses of D4 include hexamethyldisiloxane (HMDS, CAS no. 107-46-0), previously reviewed by OSPAR and included on the draft CoRAP; and 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS, CAS no. 1873-88-7), which is due to be reviewed by the OECD later in 2011.

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provided by the Norwegian authorities (Talberg, 2006 – see Table 3) and the Danish EPA (2005) on use concentrations and relevant subgroups of cosmetic products. This and recent surveys on organosilicone compounds in personal-care and household products (Horii & Kannan, 2008; Wang et al., 2009; CIR, 2009) indicate the presence of both D4 and D5 in many cosmetic products.

**Table 3 Concentration of D4 and D5 in different types of cosmetic products according to Talberg (2006)<sup>9</sup>**

Type of product	Number of product within group	Average concentration (%)	Range (%)
Sun protection products (SPP)	25	7.2	0.5 - 24
Skin care products (SCP)	17	5.7	1 – 16.5
<i>SPP and SCP combined</i>	42	6.6	-
Hair styling products	4	2.0	1 - 5
Hair care (not colours)	4	14.2	3 - 28
<i>Hair care combined</i>	8	8.1	-
Rouge, powder	8	9.9	2 – 33.6
Deodorants and antiperspirants	4	23	8 - 45
All products	62	8.3	-

It is worth noting that cyclomethicone (D4 and/or D5) is not present in all cosmetic products: the Danish EPA<sup>10</sup> has a database in which 766 cosmetic products are registered with respect to their chemical content: 61 products (8%) contain D4 or cyclomethicone (D4 and/or D5). These are hair styling products, shampoos, conditioners and stick deodorants (Lassen et al., 2005). Another database (Skin Deep), established by the American environmental organisation the Environmental Working group, lists 14,900 cosmetic products and their ingredients. According to this database, 719 products contain cyclomethicone, and 964 products contain D5, i.e. about 11% of all cosmetic products (cited from Talberg, 2006). Data published in the final report of the Cosmetic Ingredient Review Expert Panel (CIR, 2009) support similar conclusions on use patterns in various product categories. For example, D5 is reportedly used in 60 out of 499 mascara products, suggesting that about 12% of mascara products on the market contain cyclomethicone (SCCS, 2010).

For the environmental emission estimates in EA (2009a), it was assumed that the cVMS is lost rapidly to air via volatilisation after application of products to the skin (antiperspirants, skin care products, etc.); i.e. it is assumed that the skin is not washed immediately after application of the product. However, for hair care products (shampoos, conditioners) it was assumed that the cVMS is lost to water during use (since the hair is wetted/washed during or immediately after application of the product). It is understood that industry has since performed additional studies to investigate skin retention and wash-off for several product types. These data will be reviewed as part of a larger review of technical data during Annexe XV dossier production.

## **Alternatives**

<sup>9</sup> The information on D4 and D5 concentrations was actually taken from the American branch periodical Cosmetic & Toiletries Magazine (C&TM), which regularly provides formulations for many different types of cosmetics.

<sup>10</sup> (<http://www.mst.dk/NR/rdonlyres/13C1D483-54CE-48BCB281-5F51EBCF7460/0/engudgavelayout.pdf>)

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As noted above, a significant proportion of personal care products do not contain cVMS. It is therefore clear that the overall function of the product (e.g. perspiration prevention, hair conditioning, etc.) can be delivered without their use. However, it is recognised that cVMS have particular technical properties that make them useful for specific product formulations. Direct substitution with alternative substances to deliver those same properties is currently considered difficult. (Industry, personal communication). Low molecular weight silicone materials may be able to deliver similar volatility/drying properties. As they are produced in lower volumes, they are more expensive.

The trend in these applications is for D4 to be replaced by D5. In addition, it is noted that D6 is also used in personal care products. D6 is considered a possible direct substitute for D4 and D5, in some if not all product types, imparting all of the desired properties. However industry does not currently have the capacity to produce sufficient D6 to satisfy the requirements of the personal care industry (personal communication).

Personal care product formulators can, if needed, replace cVMS where they are used as solvents and carriers because alternatives do exist for these functions. Organofunctional silicones used with natural esters can act as a substitute for cVMS in antiperspirants imparting the same characteristics<sup>11</sup>. Other alternatives are emollients such as esterified vegetable oils, and whilst not considered a drop-in replacement they can be formulated to make face, body, sun, and hair care products with the same feel as siloxane-containing products. Micronized wax dispersions are also possible alternatives with hair conditioning, shine, and strengthening properties. 'Silk Conditioning Polymers' can also be used: the polymer minimises hair breakage allowing a comb to glide through. It is also claimed that these polymers have a small environmental footprint.

An entirely different approach to cVMS is already on the market in the form of a cationic polymer. Used as a conditioner and rheology stabiliser, it enhances deposition of silicone on hair and skin, meaning less silicone is required in a formulation and ultimately less goes down the drain.

### ***3.2.3 Use in household products***

D4 is used directly in the manufacture of cleaning products, which may include polishes, waxes etc., it is also used in car care products such as tyre refinishers and polishes and waxes ([www.silicones-europe.com](http://www.silicones-europe.com)). The UK risk evaluation report (EA, 2009b) made an assumption of the volumes and uses of household products. The Chemical Safety Report (CSR) for this use indicates that the aquatic emissions from this use are insignificant in comparison to the personal care sector. The use in household products is considered a minor use in terms of tonnage and product market. The UK Cleaning Products Industry Association (UKCPI) believes that D4 is not currently used in their products and therefore any EU-wide risk management measures will not impact their industry.

### ***Alternatives***

The trend in this application is for D4 to be replaced by D5. Other alternatives are also available, and a more detailed assessment of alternatives will be undertaken

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<sup>11</sup> <http://pubs.acs.org/cen/coverstory/89/8918cover.html> Chemical and Engineering News

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for the Annex XV dossier. Contacts have been made with the trade associations who represent the industry who manufacture possible alternatives.

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**Table 4: Summary of available information on D4: major uses and availability of alternative substances**

Use	Alternatives		
	Available substances	Identified environmental hazard	Technical and economic feasibility
Sun protection products (SPP)	D5	vPvB	Substitution already occurring.
	D6	Contains a vPvB substance as an impurity	
	Esterified vegetable oils		
	Cationic polymer		
Skin care products (SCP)	D5	vPvB	Substitution already occurring.
	D6	Contains a vPvB substance as an impurity	
	Esterified vegetable oils		
	Cationic polymer		
Hair styling products	D5	vPvB	Substitution already occurring.
	D6	Contains a vPvB substance as an impurity	
	Esterified vegetable oils		
	Micronized wax dispersions		
	Cationic polymer		
Hair care (not colours)	D5	vPvB	Substitution already occurring.
	D6	Contains a vPvB substance as an impurity	
	Esterified vegetable oils		
	Micronized wax dispersions		
	Cationic polymer		
Deodorants and antiperspirants	D5	vPvB	Substitution already occurring.
	D6	Contains a vPvB substance as an impurity	
	Organofunctional silicones/ natural esters		
	Esterified vegetable oils		
	Cationic polymer		
Fabric Conditioner	D5	vPvB	Substitution already occurring.
Wax Polish	D5	vPvB	Substitution already occurring.
Shoe Polish	D5	vPvB	Substitution already occurring.

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### **3.3 Sources of uncertainty**

The following sources of uncertainty have been identified and could influence decisions on the most appropriate regulatory action to take:

#### ***Identity and composition:***

- A number of related commercial substances contain D4 as an impurity, sometimes above 0.1% w/w. Impurity profiles vary between manufacturers.
- D4 is also present above 0.1% w/w in most silicone polymers.

#### ***PBT properties:***

- The UK CA considers that there is no uncertainty about whether D4 meets the Annex XIII criteria, but registrants have not identified D4 as a PBT substance, because they believe that the evidence for biomagnification is weak. However, the EU has since agreed that it clearly meets the vPvB criteria, and on that basis, the UK CA considers that D5 should be managed accordingly. Its unusual fate and behaviour properties mean that releases to air are assumed to be of low concern. This assumption affects the extent to which risk management is necessary.
- Its unusual fate and behaviour properties mean that releases to air are assumed to be of low concern, based on the available experimental data and modelling studies. This assumption affects the extent to which risk management is necessary.

#### ***Use pattern:***

- In EA (2009a), assumptions were made about the extent of loss to waste water from various consumer products. This could be refined with better information on wash off rates, market splits and product composition data.

#### ***Use and availability of alternatives***

- It is not clear if it is possible to reformulate products to remove or reduce the levels of D4 without affecting the technical performance of the product.
- The extent to which D4 could be substituted with less hazardous alternatives is not clear. This is partly due to a lack of information on which substances may be suitable and partly due to a lack of information on the hazardous properties of the alternatives that have been identified.

## **4. Justification for further intervention at the European level**

Given the high tonnage, large number of potential users and widespread use pattern, European-wide measures to minimise emissions would be appropriate, since the substance is considered to meet the Annex XIII PBT/vPvB criteria. There is the potential for release during the manufacture of products formulated with D4 and during the use and disposal of such products. Products manufactured with D4 in one Member State may be transported to and used in other Member States. In addition, countries within the EU may be exposed to D4 emissions caused by other member states, regardless of action to reduce D4 use within their own borders. This means that it is appropriate to consider EU-wide measures for risk reduction. This offers the most effective way to implement controls efficiently and uniformly within the EU.

D4 can be transported long distances in the atmosphere. The European Commission may decide to examine its potential listing as a Persistent Organic Pollutant under international conventions at a later stage. This aspect has not been considered as the focus of this RMO paper is on EU controls. However, it is

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worth noting that D4 is not expected to redeposit to any significant extent in remote environments

Another reason for proposing EU-wide measures to control the manufacture/use of D4 stems from the need to avoid trade and competition distortions, which could occur within the EU under measures imposed at a national level. Proposing measures to control the manufacture/use of D4 at a community level ensures a "level playing field" such that the burden on enterprises from any legislative requirements does not result in them becoming less competitive in the EU market, as compared to the case if national level measures are taken.

## **5. Identification of risk management options**

The following legislative instruments and other initiatives have the potential to influence emissions to the environment:

- REACH: The following elements of REACH have the potential to control emissions to the environment.
  - Registration
  - Evaluation
  - Authorisation (including candidate listing)
  - Restriction
- Water Framework Directive (2000/60/EC)
- The Solvents Emissions Directive (1999/13/EC) (as amended by Directive 2004/42/EC)
- Integrated Pollution Prevention and Control (IPPC) Directive (2008/1/EC)
- Waste Framework Directive (2008/98/EC)
- Sewage Sludge Directive (86/278/EEC)
- Voluntary Product Stewardship

The primary goal for regulatory action on D4 is to reduce the level of risk (i.e. emission) that the use of this substance poses to the aquatic environment. This RMO paper therefore looks at the potential for different tools to provide the additional information that is required and considers the way in which legislation could be used to take additional regulatory action.

## **6. Assessment of the identified risk management options**

### **6.1 REACH**

The supply of D4 onto the European market is within the scope of REACH. The following elements of REACH have the potential to address the issues with D4:

- Registration
- Substance Evaluation
- Authorisation (including candidate listing)
- Restriction

The baseline against which other risk management options will be assessed is the registration of D4 under REACH.

#### **Registration**

The ECHA website confirms registration of D4 has taken place. Eight registrations have been submitted, and eighteen exposure scenarios and corresponding recommended risk management measures (RMMs) are identified.

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None of the CSRs identifies D4 as a PBT substance, and so the recommended RMMs do not specifically seek to minimise emissions. The only environmental RMMs mentioned in the CSRs are effluent treatment in a wastewater treatment plant (WWTP), and/or use of air emission abatement equipment, depending on the exposure scenario. These are related to the control of PEC/PNEC risks. Although a detailed review has not been performed, it is understood that the lead registrant's risk assessment is based on a number of assumptions that are not included in the REACH Technical Guidance (e.g. a change in the default connection rate to WWTP, implying less untreated wastewater is discharged direct to rivers, which is relevant for the regional background concentration). It is therefore unclear whether the recommended RMMs are indeed adequate to control the PEC/PNEC risks, or set an acceptable baseline for current emissions.

Modelling in the lead registrant's CSR (Section 10.19) suggests that a reduction in D4 concentrations in water and sediment can be achieved by reducing emissions to water but would not be affected significantly by reduction in emissions to air (it is not clear if this relates to this registrant's tonnage only, but presumably this is the case). On this basis, the CSRs do not provide evidence that emissions of this SVHC have been minimised to a sufficient extent.

### ***Substance Evaluation***

An EU Member State evaluation under the transitional arrangements (EA, 2010a) has already established that the substance meets the Annex XIII criteria. There is no formal mechanism for agreement of evaluation dossiers in this context, although an informal PBT workshop of interested Member States accepted the conclusions in November 2010. Additional information relevant to risk management is being generated for the Canadian authorities, so substance evaluation would not seem to be a suitable route. Authorisation and restriction should therefore be considered. In particular, REACH would appear to be the primary mechanism that could be used to apply controls on imported goods.

### ***Authorisation (including candidate listing)***

D4 is supplied in high tonnages. Its use as an additive in a variety of consumer products creates a potential for significant, diffuse releases to the environment. D4 meets the criteria of a PBT/vPvB substance. D4 could therefore be considered to meet Article 57(d) and (e) for the identification of a SVHC. On this basis, it is considered that D4 fulfils all the relevant criteria for inclusion on Annex XIV. This would create pressure on industry to find substitutes in the long-term. Nevertheless, there are some additional considerations to bear in mind:

- i) Authorisation does not apply to the principal use of the substance as a chemical intermediate, and so is not able to address any issues arising from the presence of D4 as a significant impurity in polymeric products.
- ii) Candidate listing could lead to commercial pressure to move away from the use of D4 for polymeric uses (which are generally expected to be low risk, yet high volume), with unknown consequences (e.g. replacement with equally or more harmful substances).
- iii) Environmental concentrations are expected to respond to reductions in waste water emissions rather than air emissions. Annex XIV listing would capture any use, regardless of the level of risk it poses, and therefore provides a somewhat blunt tool to address the risks. This might be dealt with by specifying

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product exclusions, but these would need to be carefully described. The work to do this might be equivalent to that needed to develop a restriction proposal.

iv) D4 can be a significant impurity in other substances (such as D6), which would therefore be a source of environmental exposure. Authorisation would not be able to address this source, unless the higher homologues were also added to Annex XIV. Since some suppliers might be able to produce the higher homologues with D4 levels below 0.1% w/w, this would be unfair.

### ***Restriction***

Restrictions can be introduced when there is an unacceptable risk to human health or the environment arising from the manufacture, placing on the market and use of a substance and the risk needs to be addressed on a Community-wide basis. A restriction can also address article imports (if relevant) and production and use of chemical intermediates, which authorisation is unable to address.

D4 is of concern due to its PBT/vPvB properties. This concern applies to any use where there is the potential for environmental release. However, environmental concentrations can only be reduced significantly by controlling aquatic emissions. D4 has a wide range of uses. The greatest aquatic emissions (in a regional context), are from use in personal care products. Restriction could provide a targeted risk management approach, as it can specifically address those uses with significant releases which pose the greatest risk to wastewater. The scope of the restriction is therefore important and it is suggested that in the first instance a restriction could be targeted at personal care products. However, if new evidence shows that other uses create unacceptable risks further regulatory action may need to be considered at a later date.

Introduction of a restriction on the use of D4 would require the identification of a suitable alternative for all uses that fall within the scope of the restriction. Personal care products are available that do not contain cVMS to provide the desired function, so this should be possible. The introduction of a restriction will mean that the same legislative requirements apply to imported articles as those manufactured within the EU.

## ***6.2 Other Legislative measures***<sup>12</sup>

### ***Water Framework Directive (WFD) (2000/60/EC):***

This provides a framework for the protection of inland surface waters, transitional waters, coastal water and groundwater. It places duties on Member States to regulate the release of discharges into the aquatic environment. The Directive itself does not provide any mechanisms to gather information about a substance/product or to regulate emissions directly. Local emissions to the environment would be controlled by national measures including environmental permits. D4 is not a current Priority Substance (PS) or Priority Hazardous Substance (PHS). There would therefore be a delay before the relevant Commission committees could consider it, in line with the planning cycle for inclusion of new substances.

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<sup>12</sup> Although one of the main uses of concern is in personal care products, the Cosmetics Directive 76/768/EEC (and its draft revision) only considers risks to human health, and does not address environmental concerns. It is therefore not relevant for this RMO paper.

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Identification of D4 as a Priority (Hazardous) Substance would require the Commission to establish an Environmental Quality Standard (EQS) at the European level. Member States would then be obliged to carry out measures to achieve the EQS, where it is technically feasible and not disproportionately costly to do so. If D4 were to be designated as a Priority Hazardous Substance then Member States would also have to carry out measures for the cessation, or phasing out of discharges, emissions and losses to the aquatic environment.

The Water Framework Directive is potentially an important risk management tool in this case because the primary concern relates to aquatic discharges. However, there is an issue of timing and consistency. The current PS/PHS prioritisation round is being finalised at the moment, and the next round will not be complete until 2015. Even if the substance were to be considered during the next round there is no guarantee that it would be identified as a PS/PHS as this may depend on information on environmental levels, etc. If it was accepted as a PS/PHS, the Directive still does not provide an effective way to reduce emissions, and measures may vary across the EU due to differences in national priorities. Supply controls are likely to be much more cost effective than improvements at wastewater treatment plants. Nevertheless, it might provide a useful monitoring tool to assess whether aquatic emissions are declining following the introduction of relevant risk management under REACH.

***The Solvents Emissions Directive 1999/13/EC (as amended by Directive 2004/42/EC):***

This legislation is not especially relevant to emissions to wastewater, but is listed here because D4 is a volatile organic compound (VOC) within the meaning of the legislation.

The purpose of the Solvent Emissions Directive is to prevent or reduce the direct and indirect effects of emissions of VOCs into the environment, mainly via air, by providing measures and procedures to be implemented for certain activities. These activities are listed in Annex I of the Directive, and are within scope of the Directive provided they are operated above the emission thresholds listed in Annex IIA. It appears that none of the uses of D4 fall within scope, and so this risk management option is not considered further.

It should be noted that in contrast to other organic compounds of similar reactivity, the breakdown of cVMS in the atmosphere does not lead to the formation of ground-level ozone.

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### ***Integrated Pollution Prevention and Control (IPPC) Directive (2008/1/EC):***

The aim of the IPPC directive is to regulate emissions to the environment from installations conducting specified operations. The IPPC Directive will apply to some sites that use D4, because of the nature and size of the installations. Parts of the life cycle affected include<sup>13</sup>:

- Production of D4;
- Polymer production (mainly larger installations; does not apply to processing alone); and
- Production of amorphous silica.

All installations covered by Annex I of the Directive must obtain a permit from the national authorities to continue operating. Permits place a requirement for the use of Best Available Techniques (BAT) to reduce emissions and the impact on the environment as a whole, and must include emission limit values for pollutants, in particular those listed in Annex III<sup>14</sup> to the Directive, likely to be emitted from the installation concerned in significant quantities. In addition, the Directive provides for emission limit values to be established at the Community level. Such emission limits would apply to the categories of installations listed in Annex I to the Directive.

A recommendation could therefore be made to IPPC authorities to strengthen Best Available Techniques Reference (BREF) Documents. However, since the uses that lead to significant wastewater emissions are not covered by the Directive (other than D4 production), this measure would only be partially useful in the context of risk management for this substance.

### ***Waste Framework Directive (2008/98/EC):***

This sets out basic requirements for the management of defined wastes (including waste oils<sup>15</sup>) using a hierarchy approach to ensure recovery or disposal without risk to water, air, soil, plants or animals. Costs are borne by the waste producer or waste holder. The harmonised classification for D4 under the CLP Regulation is Aquatic Chronic 4 (H413), based on a water solubility below 1 mg/l and a lack of ready biodegradation and log Kow >3. There is no M-factor. The 2nd ATP to the CLP Regulation will result in a more stringent environmental classification since the lowest reliable aquatic NOEC is around 4.4 µg/l (equivalent to Aquatic Chronic 1 (H410)). The M-factor would be 10, implying that any waste mixture containing D4 at a concentration above 2.5% w/w would be considered to be hazardous waste. In addition, waste oils must be collected separately (where technically feasible) and Member States may, according to national conditions, apply

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<sup>13</sup> It follows that the IPPC Directive does not apply to the following parts of the life cycle (unless one of the other activities in Annex I to the Directive takes place and where the D4 application is directly associated with the main activity):

- polymers - small installations where synthesis takes place, and all sites that only compound or convert (unless certain substances, e.g. lead, are used
- Formulation of personal care products,

<sup>14</sup> Annex III of the Directive provides an indicative list of the main polluting substances to be taken into account for fixing emission limit values. For air, this includes volatile organic compounds, and for water, substances and preparations which have been proved to possess properties which may affect reproduction in or via the aquatic environment, or persistent and bioaccumulable organic toxic substances.

<sup>15</sup> This could apply to silicone oils made from D4. Waste waters are excluded from the scope of this Directive to the extent that they are covered by other Community legislation.

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additional measures such as technical requirements, producer responsibility, economic instruments or voluntary agreements. Waste treatment facilities must obtain permits from the relevant competent authority, which specify technical and other requirements for each type of operation permitted, as well as the safety and precautionary measures to be taken (with monitoring conditions where necessary). Waste management plans must be produced by Member States, which may include economic and other instruments in tackling various waste problems, and awareness campaigns directed at specific sets of consumers.

Waste legislation has limited applicability to the uses of D4 with the greatest aquatic emissions (i.e. consumer products and waste water emissions from specific industrial applications), and so it is not considered further in this RMO paper.

***The Sewage Sludge Directive (86/278/EEC):***

This Directive regulates the use of sewage sludge in agriculture in such a way as to prevent harmful effects on soil, vegetation, animals and humans, with a focus on certain heavy metals. A stakeholder consultation on possible revision has taken place, but major changes to include specific organic substances are not currently envisaged. Since there are no specific requirements at present, this risk management measure is not considered further.

**6.3 Non-legislative measures**

Industry has set up a voluntary product stewardship arrangement. The industry's objective is to assess emissions to the aquatic environment by targeting the most significant sources directly (e.g. manufacturing sites, personal care formulation sites, etc.) and to demonstrate that they do not pose a risk to the environment.

The D4 REACH consortium has a range of activities under assessment, ongoing or planned, including a proposed environmental monitoring programme, investigation of mass loadings in wastewater treatment plant (WWTP), studies of personal care product wash-off, emission surveys and site audits. The plan is to identify sites with the highest emissions and audit them to find ways of improving waste management practice. This work will run over the next five years, as the data are collated and recommendations made.

As far as we are aware the exact nature and scope of this activity has not been established yet and its starting date is unclear. As a voluntary initiative, the take up rate by downstream users may vary between sectors as well as suppliers, and it is not clear what overall level of emission reduction will be achieved or when the results of the initiative will be available.

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**Table 5: Summary assessment of general risk management options with respect to effectiveness, proportionality and practicality criteria**

	<b>DO NOTHING (REGISTRATION, VOLUNTARY PRODUCT STEWARDSHIP)</b>	<b>NON-REACH RMOs</b>	<b>RESTRICTION</b>	<b>AUTHORISATION</b>
<b>Effectiveness</b>	<p>Eight registrations have been submitted, but none of them identify D4 as a PBT substance, and so the recommended risk management measures do not specifically seek to minimise emissions. An EU Member State evaluation (EA, 2010a) has established that the substance meets the Annex XIII criteria, so authorisation and restriction should be considered. In particular, REACH would appear to be the primary mechanism that could be used to apply controls on imported goods.</p> <p>Industry has set up a voluntary product stewardship arrangement. The industry's objective is to assess emissions to the aquatic environment by targeting the most significant sources directly (e.g. manufacturing sites, personal care formulation sites, etc.) and to demonstrate that they do not pose a risk to the environment. The exact nature and scope of this activity has not been finalised. The REACH consortium has a range of activities under assessment, ongoing or planned. This work will run over the next five years.</p> <p>As a voluntary initiative, the take</p>	<p>Under WFD D4 is not a current Priority Substance or Priority Hazardous Substance. There would therefore be a delay before the relevant Commission committees could consider it, in line with the planning cycle for inclusion of new substances. Identification of D4 as a Priority (Hazardous) Substance would require the Commission to establish an Environmental Quality Standard (EQS) at the European level.</p> <p>This instrument does not address emissions to air or land and relies on national measures, including environmental permits, to control release to water. This creates the potential for inconsistency between MS and seems unlikely to be able to deliver a consistent and harmonised level of emission reduction across Europe within a reasonable period.</p> <p>IPPC covers some but not all user sites, and does not address diffuse exposures such as those arising from use and wash off of a product. Only larger installations may be affected by intervention leaving the potential for the aggregated releases from smaller installations to continue</p>	<p>Measures to minimise release could be introduced within 3-4 years.</p> <p>Restrictions can be applied to all life cycle stages and to imported articles, and can be targeted to aquatic emissions. They can also be flexible depending on the applications considered within scope.</p> <p>Given D4's widespread application, it may be challenging to develop proposals that tackle easy-to-substitute uses while taking into account essential (but potentially overlapping) uses where substitution may be problematic in the short and medium term. The process is likely to require considerable resource from the proposing Member State and from industry because of technical discussions and consultations.</p> <p>Given that the introduction of restrictions is reliant on MS demonstrating an unacceptable risk there is the potential for debate about the strength of evidence presented.</p>	<p>Authorisation has the potential to remove all non-essential uses while allowing essential uses to continue and creating pressure to move to alternatives in the long run.</p> <p>D4 users would be obliged to provide information on alternatives and related research and development.</p> <p>All (potential) D4 users face the same responsibility regardless of current emissions.</p> <p>Might result in a large number of authorisation applications, due to the diversity of current uses.</p> <p>Where authorisations are granted, these uses could result in the continuation of emissions to the environment. Given that derogations to restrictions may be needed for these uses, it is not clear that authorisation will present a greater environmental burden in the short and medium term than restrictions.</p> <p>It is noted that Art 60(10) places a duty on holders of an authorisation to ensure exposure is reduced to as low a level as is technically and practically</p>

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	<b>DO NOTHING (REGISTRATION, VOLUNTARY PRODUCT STEWARDSHIP)</b>	<b>NON-REACH RMOs</b>	<b>RESTRICTION</b>	<b>AUTHORISATION</b>
	<p>up rate by downstream users may vary between sectors, and it is not clear what overall level of emission reduction will be achieved.</p> <p>Cleaning products have not been considered as part of this initiative due to the much smaller use volume.</p>	<p>at an unacceptable level.</p> <p>A recommendation could be made to IPPC authorities to strengthen Best Available Techniques Reference (BREF) Documents. However, since the uses that lead to significant wastewater emissions are not covered by the Directive (other than D4 production), this would only be partially useful in the context of risk management for this substance.</p> <p>A disadvantage of both IPPC and WFD is that these focus on reducing emissions that are already occurring. This requires the regulation of each site that emits the substance. In contrast, measures under REACH are targeted upstream and are therefore more efficient since many fewer actors need to be regulated to reduce emissions.</p>		<p>possible in addition to any conditions that are set when the authorisation is granted. This should help to minimise the environmental burden for any authorisations that are granted.</p>
<b>Proportionality (Cost-effectiveness)</b>	<p>No additional costs other than those already accounted for by the industry in implementing this project will arise from this option. However, in terms of cost-effectiveness, the extent of emission reduction is likely to be relatively low.</p>	<p>It is likely that the costs to develop and implement measures under the Water Framework Directive will be disproportionate to the reductions in emissions that could be achieved (e.g. national legislation, modifications to WWTP, monitoring commitments, etc.). For IPPC sites, an update to BREF guidance might be cost-effective.</p>	<p>The complexity of the use profile and the alternatives assessment will place considerable resource burdens on a Member State wishing to develop a restriction proposal for D4. There may also be costs to industry as a result of the numerous technical discussions and consultations that are likely to be required to ensure the proposals are workable and enforceable.</p> <p>A more detailed analysis is</p>	<p>Administrative costs for applicants might be disproportionate, depending on the commercial importance of the use being applied for.</p> <p>Allows the risks and benefits for each use to be assessed on a case-by-case basis.</p> <p>Possible economic disadvantages to EU manufacturers of articles if comparable measures to restrict the use of D4 in imported</p>

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			<p>required to determine if the costs to implement and comply with targeted restrictions will be proportionate to emission reduction.</p> <p>Possible advantages to suppliers of alternatives if they are based within the EU.</p>	<p>products are not introduced or if there are delays.</p>
<b>Practicality (Clarity to duty holders)</b>	<p>Industry is unlikely to conclude that the substance is PBT/vPvB, so a clear message to reduce emissions is unlikely to be developed and communicated to all downstream users.</p> <p>There is the potential for DUs to implement differing standards of emissions control depending on whether or not they have access to and chose to implement the advice that is disseminated from the voluntary stewardship programme.</p>	<p>Legislative frameworks already exist but in some cases (e.g. IPPC) do not apply to all downstream users. This creates imbalances in the duties placed on downstream users.</p> <p>In order to implement certain non REACH measures it will be necessary to ensure that a suitable environmental analytical monitoring method is developed and agreed upon.</p>	<p>Enforceability and monitoring of restrictions could be incorporated within current legislation, e.g. via IPPC/Water Framework Directive, although since these do not address all parts of the life cycle or release routes, other mechanisms would also be needed.</p> <p>It will be necessary to ensure that suitable analytical monitoring methods are in place.</p> <p>A restriction is very clear to duty holders.</p>	<p>By judging each use on its own merits, authorisation enables provisions to be tailored to specific use situations. It might be necessary to ensure that suitable analytical monitoring methods are in place.</p>
<b>Regulatory consistency</b>	<p>REACH applies across all EU Member States thus there will be no inconsistency in implementation between Member States.</p>	<p>The level of emission reduction achieved will depend on the approaches taken by individual Member States and their mechanisms for enforcement creating a potential for different requirements in different Member States.</p>	<p>Good.</p>	<p>Good.</p>
<b>Uncertainties</b>	<p>As a voluntary initiative, the take up rate by downstream users may vary between sectors, and it</p>	<p>Source apportionment would need to be carried out for the purposes of the Water</p>	<p>The levels of emission associated with certain uses are unclear. It is therefore difficult to make an</p>	<p>Uncertainties around environmental and human health impacts of alternatives. Further</p>

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	<p>is not clear what overall level of emission reduction will be achieved. Cleaning products have not been considered as part of this initiative. It is not clear how effective measures that are targeted at downstream users will be at minimising emissions during service life and disposal, particularly for consumer goods.</p>	<p>Framework Directive to establish which uses are important at an individual catchment level. Monitoring might also be necessary to establish the relative priority of action.</p>	<p>accurate estimate of the risk without more data. Alternatives need to be identified and evidence sought regarding their human health and environmental classification.</p>	<p>information regarding possible alternatives is being sourced from the industry</p>



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## **7. Conclusions on the most appropriate (combination of) risk management option(s)**

D4 is a high tonnage substance. It is present in a very wide variety of consumer products and therefore has significant potential for environmental release. In terms of achieving the highest level of emission reduction for least cost, and given the nature of the risk (i.e. that aquatic concentrations can be reduced by controls on waste water emissions rather than air emissions), we propose to prioritise risk management based on the magnitude of aquatic emissions.

At this stage, the UK considers a targeted restriction for the manufacture and use of personal care products will be the most appropriate route to reduce environmental concentrations.

Of the measures available under the REACH Regulation, restriction is preferred to authorisation because:

- It provides a more flexible approach to achieve the aims of emission reduction as it can be targeted to those applications that pose the greatest risk (i.e. waste water discharges from relatively minor uses of the substance).
- It is likely to achieve a significant reduction in environmental concentrations more quickly.
- It can cover all relevant parts of the life cycle, including the presence of D4 as an impurity in polymeric products (where relevant) and higher molecular weight homologues like D6<sup>16</sup>.
- It would avoid the creation of an unnecessary burden on companies whose products do not lead to significant waste water discharges.
- It will prevent the substitution of D5 with D4.

The exact nature and scope of the restriction will depend on the detailed analysis that will be performed as the Annex XV dossier is developed, but we anticipate that it would most likely relate to concentration limits for personal care (and possibly sub-categories thereof), and possibly waste water emission limits at non-IPPC sites. Alternative products already exist, and the fact that manufacturers of personal care products are already substituting this substance indicates that they have (or are developing) effective substitutes. It has been proposed in the restriction text that the Commission could review the emissions from other sources after a period of 10 years of entry into force of the restriction. This would give relevant industry sectors time to consider the importance of other relevant sources, and could include a review of monitoring data to see if the proposed restriction has effectively removed inputs to wastewater treatment plants.

For IPPC sites, the emission limit developed in the Annex XV dossier could be proposed for inclusion in the relevant BREF documents. The Commission should

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<sup>16</sup> Industry (personal communication) has confirmed that an impurity level of 0.1% w/w or below is practically achievable in D5 using suitable distillation apparatus. It may also be possible to remove it from silicone polymers by stripping techniques. The necessary equipment is not currently in place at all manufacturing sites, and requires an investment of several million euros. Improved distillation efficiency also entails an energy cost, and therefore increased carbon dioxide emission (D4 is easier to remove than D5 due to its higher vapour pressure).

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also consider whether D4 should be identified as a Water Framework Directive Priority (Hazardous) Substance as part of the next round of negotiations.

#### **References**

Chemical & Engineering News, ISSN 0009-2347, Copyright © 2011 American Chemical Society. Available from <http://pubs.acs.org/cen/coverstory/89/8918cover.html>.

Cosmetic Ingredient Review (2009) Amended Final Report of the Cosmetic Ingredient: Review Expert Panel of the Safety Assessment of Cyclomethicone, Cyclotetrasiloxane, Cyclopentasiloxane, Cyclohexasiloxane, and Cycloheptasiloxane. December 8, 2009

Dow Corning Volatile Cyclic Siloxanes: Status update: April 2011. [http://www.univarusa.com/vwr-inc/tools.nsf/0/7951B6CDCEDE97798825787F005B1807/\\$file/DC%20Volatile-Cyclic-Siloxanes-Fact-Sheet-April-2011.pdf](http://www.univarusa.com/vwr-inc/tools.nsf/0/7951B6CDCEDE97798825787F005B1807/$file/DC%20Volatile-Cyclic-Siloxanes-Fact-Sheet-April-2011.pdf)

EA, 2009a. Environmental Risk Assessment Report: Octamethylcyclotetrasiloxane. ISBN: 978-1-84911-031-0. Environment Agency April 2009. Available from <http://publications.environment-agency.gov.uk/pdf/SCHO0309BPOZ-E-E.pdf>.

EA, 2009b. Environmental Risk Assessment Report: Decamethylcyclopentasiloxane. ISBN: 978-1-84911-029-7. Environment Agency April 2009. Available from <http://publications.environment-agency.gov.uk/pdf/SCHO0309BPOX-E-E.pdf>.

EA, 2009c. Environmental Risk Assessment Report: Dodecamethylcyclohexasiloxane. ISBN: 978-1-84911-030-3. Environment Agency April 2009. Available from <http://publications.environment-agency.gov.uk/pdf/SCHO0309BPOY-E-E.pdf>.

EA, 2010a. D4 PBT Evaluation Factsheet. Final version of September 2010.

EA, 2010b. D5 PBT Evaluation Factsheet. Final version of September 2010.

EA, 2010c. Guidance on gas treatment technologies for landfill gas engines. Report LFTGN06. Second Edition. Environment Agency, Bristol. Available from <http://publications.environment-agency.gov.uk/PDF/GEHO0311BTON-E-E.pdf>.

SCCS, 2010. Opinion on Cyclomethicone: Octamethylcyclotetrasiloxane (Cyclotetrasiloxane, D4) and Decamethylcyclopentasiloxane (Cyclopentasiloxane, D5). Scientific Committee on Consumer Safety, Directorate-General for Health & Consumers. Available from [http://ec.europa.eu/health/scientific\\_committees/consumer\\_safety/index\\_en.htm](http://ec.europa.eu/health/scientific_committees/consumer_safety/index_en.htm)

Talberg H.J., Cyclic siloxanes D4 and D5 – in which concentration and with what frequency are they used in cosmetic products? Norwegian Food Safety Authority. Note 2006-11-19

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## **RMO Appendix – Potential releases of D4 to the aquatic environment during the use of silicone polymer-based antifoaming agents**

A review of potential sources of D4 by a contractor for the UK CA (wca, 2013) suggested that emissions from silicone polymer-based antifoaming agents could be a significant contributor to overall releases to the aquatic environment. The UK CA was not aware of these uses at the time the original RMO analysis was drafted, and so has subsequently performed more detailed investigations. Our findings are summarised below.

### **Detergents**

The 2010, 2012 and 2014 CSRs do not include any descriptive or quantitative information about this application, which appeared for the first time in an industry socio economic analysis (SEA) in 2013 (AMEC, 2013a&b; PFA, 2012).

It appears that the use in detergents is relatively small compared to other sources (just over 3 tonnes/year of D4 is expected to be present in the polymers as impurities):

- Two-thirds of the silicone polymer antifoaming agents are used in domestic laundry detergents (in which D4 is present at levels “a lot” less than 0.1% w/w) with 100% release to domestic wastewater (Peter Fisk, pers comm.).
- The other third is used in the textile industry (with D4 levels <0.01% w/w in the polymer), with the assumption that there is 100% release to wastewater, and treatment equivalent to a municipal WWTP at 90% of sites (i.e. 10% is discharged direct to surface water). This treatment is undertaken to meet local regulation of the activities carried out at the sites. Using the information from industry’s SEA, total continental releases of D4 to wastewater are expected to be 2 tonnes/year for domestic laundry detergents and 1 tonne/year from industrial (textile) detergents.

The resulting contribution to the overall emissions of these substances to surface waters is ca. 15% for D4, which is <1 tonne/year. We therefore currently consider these two scenarios to be of low relevance for further risk management.

### **Paper and pulp industry**

The CSRs assume that 15,000 tonnes/year of silicone polymer are used as antifoaming agents in pulp processing and paper manufacture. The average concentration of D4 in these polymers is 0.15% w/w, i.e. there is approximately 22.5 tonnes/year of D4 (PFA, 2012).

Information provided to the dossier submitter by both the manufacturers of antifoam agents and the operators of pulp mills within the EU indicates that silicone-based antifoams are used in the pulp washing phase of chemical pulp production. The antifoam removes entrained air from within the pulp and surface foam generated during its production.

Chemical pulp is used to produce a high quality product, but with a much lower yield. Over 90% of chemical pulp production is via the Kraft process. Antifoam agents are necessary in this process as excessive foam reduces washing efficiency and can cause overflow from the washing vat, which in extreme circumstances can halt production. According to anecdotal evidence from the industry given via personal communication silicone-based antifoam agents are

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preferred in most cases to other antifoam agents due to high efficiency, efficacy and better antifoam removal from the pulp.

Addition rates of antifoam products vary between users depending on the process and technical and quality issues. However, due to issues with final product quality, the use of any antifoam is kept to a minimum.

The Emission Scenario Document (ESD) for the pulp, paper and board industry (OECD, 2009) indicates that all materials used for antifoaming should be assumed to be emitted via wastewater. The document indicates that effluents from these processes will at least undergo primary treatment before being discharged either to wastewater or surface water. The primary treated effluents are likely to undergo further biological treatment either on-site or off-site at a municipal WWTP<sup>17</sup>.

The BAT Reference Document (BREF) for the pulp and paper industry (EC, 2015) indicates that use of antifoaming agents (“defoamers”) occurs both within the paper making process and also during on-site wastewater treatment (see “Other applications” below). The antifoaming agents are considered to be predominantly discharged in the effluent. D4 however is much more volatile than the silicone polymers in which it is an impurity. Following information on the operating conditions in the Kraft process provided by the Finnish Safety and Chemicals Agency (responsible for regulating paper mills in Finland) (pers. comm.), it seems unlikely that residual D4 would be discharged to surface waters because:

- The chemical pulp washing process runs at a temperature of 80-95 °C. Some volatile components, including D4, are likely to be driven off at this stage. After the washing phase the separated weak black liquor is evaporated into dry matter. The temperature during evaporation rises up to ca. 135 °C. At this stage other volatile components, such as methanol and turpentine are recovered for further processing. Given the relatively high volatility of D4 it seems likely that it will also be volatilized at this stage and either released to air (with appropriate abatement measures) or present in the distillate as an impurity.
- The concentrated liquor from the evaporation stage is then incinerated at around 1000-1100 °C to generate electricity and heat. Any residual silicone polymers/siloxanes would be broken down in this process due to the very high incineration temperature.
- The air emissions containing the volatile components of the process are often controlled by steam stripping and then incineration. This process efficiently mineralizes all organic substances present. Another way to treat the air emissions is to discharge the condensates to the biological WWTP. Once discharged to waste water treatment the removal rate for D4 is over 95%.

The relatively low concentration of residual D4 in silicone antifoams used in the pulp and paper industry suggests a maximum theoretical emission of between 1.5 and 22.5 tonnes/year for each substance, The practice of minimizing the amount

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<sup>17</sup> JS Seaman, Environment Agency (Regulated Industry - Site Based Regulation) (pers. comm.) suggested that 90% of UK paper mill sites would either discharge their wastewater for treatment at a municipal WWTP, or treat it on-site to an equivalent standard. The remaining 10% of sites discharge direct to surface water after onsite treatment.

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used to ensure final product quality, the high temperatures of the pulp washing and evaporation stages causing volatilization of D4, the incineration of liquors and steam-stripped air emissions, and/or the use of on-site and off-site waste water treatment for air emission condensates (leading to over 95% removal), implies that final releases of D4 to surface water from the paper and pulp industry will be *significantly* lower than 1 tonne/year for each substance across the whole EU. The actual amount cannot be estimated with certainty due to the lack of confirmatory analytical data for pulp mill effluents.

## **Oil and gas industry**

### **Silicone antifoams for the oil/gas industry**

Silicone polymer-based antifoam agents are used to eliminate foam in oil and gas production, refining and processing. In the CSRs, a total potential emission of four tonnes per year of D4 was predicted due to their presence as a residual impurity in the polymers at an average concentration of 0.4% w/w in 1,000 tonnes/year of polymer (PFA, 2012). This application was assumed to result in a direct emission of 100% to surface (marine) waters.

- **Use in drilling muds:** The presence of foams slows production and triggers maintenance operations, which is a particular problem on offshore rigs because of the limited space and weight restrictions (AMEC, 2013c). Antifoam agents are added to drilling muds to prevent foaming during separation of the cuttings from the fluid by centrifugation. One major oil producer (Statoil Norway, pers. comm.) has indicated to the dossier submitter that silicone-based antifoam agents were not used for this purpose in their operations in the EU in 2013. Due to the practice of recycling drilling muds following separation of the cuttings back into the well, some residual antifoam may be present in the muds.
- **Use in well cementing:** Silicone-based antifoams are added to low viscosity cements used in well consolidation to remove bubbles from the cement and increase its strength. As the antifoam is added to the cement prior to use in the well, the application is considered by the operators to be well controlled. A small amount may be lost during application of the cement but this is considered minimal and infrequent so this application has not been considered further (Reconsile Consortium and Statoil Norway, pers comm.).
- **Gas-oil separation:** Silicone-based antifoams are mainly used in gas-oil separation to prevent foam occurring during depressurisation (Reconsile consortium). Two main types of silicone polymer – i.e. PDMS (polydimethylsiloxane) and FS (fluorosiloxanes) – are used depending on process conditions and the nature of the gas/oil/water mix. The antifoam products typically contain 5-10% w/w silicone polymer, and the typical dosage of the antifoam products into the crude oil for separation is 5-20 ppm. Given the typical concentration for D4 as an impurity in the silicone polymers (0.15% according to PFA, 2012), the range of residual D4 present in the crude oil is estimated to be 3 to 38 ppb. (Statoil Norway, pers comm.)

The high octanol-water partition coefficients of D4 (6.49 as  $\log_{10}$  values) mean that it will partition predominantly to the oil phase (i.e. the concentration in oil will be at least around 1000000 times higher than in water). This oil ends up at refineries, and it has been reported that residual D4 causes problems in crude oil refining (Reconsile Consortium and Statoil Norway, pers comm.), which is one reason why dosing of antifoams in separation is kept to a minimum.

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It is possible that a small amount of D4 may remain in the waste water produced during separation. Assuming that 4 tonnes/year is a reasonably accurate estimate of the total amount available for release, partitioning with oil should mean that there will be much less than 1 kg/year of each substance in the waste water. This wastewater is cleaned via flotation cells, hydrocyclones or different kinds of centrifuges, if necessary, prior to disposal. Disposal methods for the waste water depend on whether production is on- or offshore, but can include discharge back to the sea (provided the water meets local limits for oil content) or injection into the ground to provide pressure to extract further oil from the well, hundreds or thousands of metres below the ground/sea bed (Statoil Norway, pers. comm.).

In summary, the main source of D4 emissions from oil and gas operations is likely to be in waste water from gas-oil separation activities, which may undergo further treatment prior to discharge. Given the low dosage rates and the high partitioning of D4 into the oil phase, the use of silicone polymers in antifoams in the oil and gas industry is not considered to be a significant source of aquatic emissions.

### **Other applications**

From an Internet search, various silicone polymers can be used in antifoaming agents in several sectors that were not mentioned in either the CSRs or the industry socio-economic analysis (SEA) from 2013.

- According to Blackburn Chemicals<sup>18</sup> (pers. comm.) silicone antifoams are generally not used in the food sector, where vegetable oil-, hydrocarbon- and alkoxane-based defoamers are preferred. However, the UK CA notes that this company offers a dimethyl polysiloxane product (Dispelair® SE 81A) that is said to be an effective foam control agent suitable for use in fermentation systems.
- Blackburn Chemicals offers one silicone-based product (Dispelair® SE 81A) as an effective control for surfactant type foam in WWTP, which is suitable for aeration lagoons. However, a representative of water supply companies in the UK has stated that silicone-based antifoams are not routinely used in final effluent treatment to treat foaming incidents at wastewater treatment plant (WWTP) (B. Ellor, UKWIR<sup>19</sup>, pers. comm.). It is possible that they are used more at industrial WWTP.
- Blackburn Chemicals supplies several modified polysiloxane antifoaming agents for use in metal working fluids. These are used with soluble oils, fully- and semi-synthetic cutting fluids and metal cleaners. The UK CA notes that controls are in place to minimise the release of oils from operations that involve metal working fluids. Disposal of metal working fluids should be done in line with the Waste Framework Directive (2008/98/EC). As long as this is followed the releases of D4 associated with use in metal working fluids will be minimal.
- Blackburn Chemicals offers several silicone-based antifoaming agents (e.g. Dispelair® CF 328, 737 and 890/895) for use in aqueous surface coatings to prevent air entrainment during the production of paints, adhesives and varnishes. They also prevent air bubbles from causing defects in the coating film upon application. The products containing silicones are specifically sold for use in

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<sup>18</sup> <http://www.bbchem.co.uk/home.htm>

<sup>19</sup> <https://www.ukwir.org/site/web/content/home>

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medium to high PVC paints and a broad range of aqueous systems including gloss, elastomeric coatings, polymer latex systems and inks.

No information has been sought about these uses or their relevance as a source of D4 emissions to the aquatic environment in the EU. Further information would be welcome.

## **OVERALL CONCLUSION**

Although silicone polymer-based antifoaming agents are an additional source of D4 emissions to the environment, the available evidence suggests that it makes a very small contribution to the overall releases of these substances. There currently appears to be no reason to seek further risk management of these uses, although further information on use in the textile, food, WWTP, metal working and surface coating industries would be useful.

## **References**

AMEC 2013a. Socio-Economic Analysis for Cyclic Siloxanes: Report on octamethylcyclotetrasiloxane (D4). Confidential Final Report, January 2013. AMEC Environment and Infrastructure UK Ltd

AMEC 2013b. Socio-Economic Analysis for Cyclic Siloxanes: Annex – Case Study for Use in Antifoaming Agents in Detergents (Silicone Polymers Containing Residues of D4 and D5). Confidential Final Report, January 2013. AMEC Environment and Infrastructure UK Ltd

AMEC 2013c. Socio-Economic Analysis for Cyclic Siloxanes: Annex – Case Study for Use in Antifoaming Agents in Oil Drilling (Silicone Polymers Containing Residues of D4 and D5). Confidential Final Report, January 2013. AMEC Environment and Infrastructure UK Ltd

EC, 2001. Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Pulp and Paper Industry December 2001, European Commission

OECD 2009. OECD SERIES ON EMISSION SCENARIO DOCUMENTS Number 23 EMISSION SCENARIO DOCUMENTS ON PULIP, PAPER AND BOARD INDUSTRY, Organisation for Economic Co-operation and Development

PFA 2012. Interim reports: technical support for D4 and D5 SEA. Confidential report to the Silicones Industry by Peter Fisk Associates

wca 2013. Siloxanes restrictions options – Confidential final report to the Environment Agency, November 2013. WCA Environment Limited.