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EXTRACT OF PBT INFORMATION FOR D4

Introductory remarks

Information on the environmental fate and effects of D4 is extensive. As well as robust study summaries available in the REACH registration dossiers, the available data have been reviewed in great depth by regulators in Europe in a UK national assessment (EA, 2009), a Dutch national assessment (RIVM, 2012) and a PBT Fact Sheet that was discussed and agreed by the ECHA PBT Expert Group in November 2012 (followed by submission of the document by the UK to ECHA as a formal dossier under the REACH transitional measures; EA, 2013; provided as Appendix 1), as well as Canada (Government of Canada, 2008). This report covers the available scientific literature published up to the end of 2013, using the PUBMED database and a search strategy that focussed on papers relevant to PBT assessment (particularly bioaccumulation). Further studies have been provided by the REACH registrants' representatives and some EU regulatory authorities.

Given the large amount of data available, and in the interests of conciseness, Sections B.1.3, B.4 and B.7 of this report only summarise the most important findings relevant to the PBT assessment. Key studies are referenced and (unless otherwise stated) original study reports have been reviewed by the dossier submitter (DS) and are considered to be relevant for inclusion in this assessment (i.e. reliable with or without restrictions). Full details and all other study references can be found in the other documents mentioned above (particularly Appendix 1, with new information in Appendix 2). Given the amount of detail presented in the appendices, robust study summaries have not been produced for the purposes of this report.
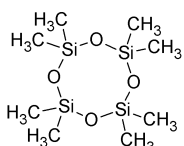
B. Information on hazard and risk

B.1 Identity of the substance and physical and chemical properties

B.1.1 Name and other identifiers of the substances

Name:	Octamethylcyclotetrasiloxane
EC Number:	209-136-7
CAS Number:	556-67-2
IUPAC Name:	2,2,4,4,6,6,8,8-octamethyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane
Molecular Formula:	$C_8H_{24}O_4Si_4$
Structural Formula:	
Molecular Weight:	296.62 g/mole
Synonyms (and registered trade names):	Cyclic dimethylsiloxane tetramer, Cyclen D4/OMCTS, Cyclen D4/OMCTS WN, Cyclomethicone, Cyclotetrasiloxane, octamethyl-, Cyclotetrasiloxane, D4, Dow Corning 244, KF 994, DC 344, DC 244, Dow Corning 344, NUC silicone VS 7207, Oel Z020, OMCTS, SF 1173,

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Tetramere D4/OMCTS, Tetramere D4/OMCTS Silbione,
TSF 404, Volasil 244 and VS 7207.

The abbreviation D4 will be used for the substance throughout this report.

B.1.2 Composition of the substance

D4 is a monoconstituent substance. Octamethylcyclotetrasiloxane is typically present in the substance at a concentration of $\geq$80% w/w.

Table 1.2.1 Constituents

Constituent	Typical concentration	Concentration range	Remarks
Octamethylcyclotetrasiloxane EC no.: 209-136-7	$\geq$80%	80-100%	Main constituent

D4 may contain the analogue substance D5 (decamethylcyclopentasiloxane, EC no.: 208-764-9) as an impurity at concentrations of ≤5% w/w.

B.1.3 Physicochemical properties

Data in Table 1 were obtained from the public registration information on the ECHA website (http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances; date of access 9 September 2014).

Table 1   Summary of physicochemical properties

Property	Value	Comments
Physical state at 20°C and 101.3 kPa	Liquid	-
Vapour pressure	132 Pa at 25 °C	Derived from a temperature-vapour pressure correlation using critically evaluated data (see EA (2009) for further discussion).
Water solubility	0.056 mg/L at 23 °C	Varaprath *et al*. (1996) (slow-stirring method)
n-Octanol/water partition coefficient (K_{OW})	6.49 ($\log_{10}$ value) at 25 °C	OECD Test Guideline 123 (slow-stirring method) Original report not reviewed by DS; considered 'reliable without restriction' by the registrants. EA (2009) discussed the preliminary findings from this study and found them to be consistent with other data.
Henry's Law constant	12 atm.m^3/mol at 21.7°C [1.21×10^6 Pa.m^3/ mol]	Non-standard syringe method for simultaneous measurement of K_{OW}, K_{OA} and K_{AW}. Original report not reviewed by DS; considered 'reliable with restrictions' by the registrants as it was not conducted to GLP. EA (2009) discussed the preliminary findings from this study and found them to be consistent with other data.
n-Octanol/air partition coefficient (K_{OA})	4.22 ($\log_{10}$ value) at 24 °C cited in CSRs (no data on public website) [4.34 ($\log_{10}$ value) at 25 °C cited in EA (2009)]	
Air/water partition coefficient (K_{AW})	2.69 ± 0.13 ($\log_{10}$ value) at 21.7 °C	

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Although log K_{OW} is an important surrogate property for environmental fate assessment, measured data for key end points (e.g. bioaccumulation) are available and therefore preferred.

B.4 Environmental fate properties

B.4.1 Degradation

Air

D4 is highly volatile (with a vapour pressure of 132 Pa at 25 °C; see Section B.1.3) and its degradation half-life in the atmosphere is estimated to be around 12.7 to 15.8 days (mean value ~14 days) due to reaction with atmospheric hydroxyl radicals (assuming an average atmospheric hydroxyl radical concentration of 5×10^5 molecule/cm^3 and a measured rate constant of 1.01×10^{-12} to 1.26×10^{-12} cm^3/molecule/s – the half-life is probably shorter in urban and suburban areas). Reaction with other atmospheric photo-oxidants is likely to be negligible in comparison. The degradation products are expected to be silanols, which are removed from the atmosphere by wet deposition (either adsorbed onto particulates or dissolved).

Water

Despite its low water solubility (0.056 mg/L at 23°C), D4 hydrolyses in water. A standard test modified to prevent volatile losses gives a hydrolysis half-life of ~1.8 hours at pH 4, ~69-144 hours at pH 7 and ~0.9-1 hour at pH 9 (at 25°C) or 4.8 hours at pH 4, 54 hours at pH 7 and ~6 hours at pH 9 (at 10°C) (Dow Corning, 2004 & 2005). Hydrolysis half-lives estimated from these data in EA (2009) are 16.7 days at pH 7 and 12°C, and 2.9 days at pH 8 and 9°C (considered to represent typical freshwater and marine environments, respectively)[1].

Standard tests suggest that D4 is not readily biodegradable (3.7% mineralisation after 29 days) (Springborn Smithers Laboratories, 2005). Interpretation is complicated by the high volatility of the substance meaning that it was present in the headspace of the test vessels. Additional studies suggest that D4 might be susceptible to biodegradation, particularly with adapted microorganisms. However, mineralisation has not been confirmed, and the results cannot be used to predict the extent or time-frame for biodegradation in the environment.

Sediment

Based on OECD TG 308 sediment simulation studies, D4 has an estimated degradation half-life of 365 days in anaerobic sediment and 242 days in aerobic sediment at 24°C (expected to be longer at lower temperatures) (Xu, 2009a & 2009b; full details are provided in Appendix 1). The sediment half-life appears to depend on the sediment characteristics (e.g. pH and organic carbon content); for example, a half-life of 47 days at 24°C (equivalent to a half-life of 123 days at 12°C) was measured in sediment collected from a different location that had a lower pH for the overlying water (pH 6.95 versus pH 7.9) and a lower organic carbon content (2.9 per cent versus 3.7 per cent) (Xu and Miller, 2008).

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[1] According to comments submitted during public consultation (PC), slightly different values have been estimated by Environment Canada (17.1 days at pH 7 and 12 °C, and 3.0 days at pH 8 and 9°C).

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D4 was also detected in sediment cores collected in 2006 from Lake Pepin, USA down to depths that correlated with the 1960s/70s (based on magnetic susceptibility measurements with reference cores that had previously been dated directly using ^{210}Pb measurements) (Powell, 2009 & 2010). As D4 was still detectable in these layers at least thirty years following deposition, and the levels found in subsequent layers appeared to track the known use of D4 and the known implementation of improved waste water treatment in the area, the implication is that degradation of D4 in the sediment was slow (the study authors estimated a half-life of up to 2.5 years).

Soil

D4 degrades rapidly in dry soils (e.g. the soil half-life was estimated to be around 4.1 – 5.3 days for temperate soils at a relative humidity of 50 to 90 per cent), but the rate of reaction reduces markedly with increasing soil moisture content (essentially no degradation was seen in soil at 100 per cent relative humidity) (Xu, 1999; Xu and Chandra, 1999). This is believed to involve an abiotic mechanism. It is probable that under some situations rapid degradation of D4 may occur, but in other situations the degradation will be much slower. The data do not allow a half-life to be derived that can be compared with the Annex XIII criteria (e.g. representative of conditions in a standard OECD TG 307 study).

The main degradation product is likely to be dimethylsilanediol. This is expected to undergo further degradation processes in the environment to ultimately form carbon dioxide and silicic acid and/or silica.

Other considerations

D4's high volatility and relatively long atmospheric half-life indicate that a significant portion of emissions will reside in the air. It therefore has the potential to undergo long-range transport to remote regions via the atmosphere. Monitoring data in locations truly remote from human activity are very sparse. However, Krogseth *et al.* (2013) report D4 concentrations in Arctic air samples of up to 0.95 ng/m^3 in late summer and up to 2.13 ng/m^3 in early winter, at Svalbard[2] (although the reliability of these findings is uncertain as they were similar to levels found in storage control samples).

(The potential for re-deposition to surface water and land will be considered in the planned restriction dossier.)

D4 is poorly soluble in water, volatile and also adsorbs strongly to soil and sediment (see Sections B.1.3 & B.4.2). These are important for assessing its overall environmental persistence, and various modelling approaches have been used to investigate this. The modelling is limited by a lack of sensitivity analysis, but in general terms, it predicts a relatively short persistence in the water column (due to volatilisation and hydrolysis) but significant distribution to sediment where persistence may be much higher (depending on a number of site-specific factors including pH, water depth, temperature, sediment deposition rate, concentration of particulate and dissolved organic carbon, rate of sediment burial and re-suspension, etc.). The modelled effective half-life of D4 in sediment is around 72 days (Lake Pepin, USA), 285 days (Inner Oslofjord, Norway) and 342 days (Lake Ontario, Canada/USA). Compared to the actual half-life from sediment core data from Lake Pepin (see above), these may be underestimates.

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[2] The site's altitude means that most of the time it is above the local inversion layer, limiting the influence of local sources (such as from nearby Ny-Ålesund).

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B.4.2 Environmental distribution

Adsorption potential

A reliable experimental study over a range of conditions for three different soils gave a mean log K_{oc} (organic carbon-water partition coefficient) of 4.22 from the adsorption isotherm experiments (Miller, 2007). This is equivalent to a K_{oc} of 1.7×10^4 L/kg. A lower log K_{oc} value (mean: 3.86) was measured using activated sludge samples.

It is therefore likely that D4 will adsorb strongly to organic matter in sediment and soil. The very low water solubility and high volatility also indicate that leaching from soil is not expected to be a significant process in the environment.

B 4.3 Bioaccumulation

Several studies have been performed that allow the derivation of a fish bioconcentration factor (BCF), three of which are considered reliable and relevant in the context of this report:

- A steady-state BCF of 12,400 L/kg based on total ^{14}C measurements was measured for Fathead Minnow *Pimephales promelas* (Fackler *et al*., 1995; full details of this study are provided in EA, 2009). Chemical analysis indicated that a large proportion of the body burden (~93 per cent) was parent compound – the BCF based on parent compound alone would be ≥11,495 L/kg. A further review of this study by RIVM (2012) queried whether steady state had actually been reached, and could not reproduce the average water concentration of 0.23 µg/L cited in the study report. The data were therefore reanalysed with a kinetic model, accounting for the variable water concentrations in the uptake phase. This resulted in a BCF of 19,000 L/kg, or 14,900 L/kg when normalised to a fish containing 5% lipid (it is not indicated whether this value was corrected to take account of the contribution of metabolites).

- The steady state BCF for Common Carp *Cyprinus carpio* was reported to be in the range 3,000 – 4,000 L/kg (based on parent compound analysis) in two studies (CERI, 2007 and 2010; full details are provided in Appendix 2)[3]. The fish lipid content was close to the 5 per cent value considered in the REACH guidance document, so the data do not require lipid normalisation. The depuration half-life was estimated to be between 6.5 and 8.8 days. The kinetic BCF in one of the studies was in the range 4,100 - 5,500 L/kg (without growth correction; it is higher if growth is taken into account).

  It is understood that two further bioconcentration tests with D4 in this species have been performed in Japan (CES, personal communication), but the data have not been made available to the DS (these are "older" data from "CERI/MSI").

Two reliable fish dietary bioaccumulation studies are available that permit the derivation of a biomagnification factor (BMF):

- A dietary BMF of 0.47 (steady state lipid-normalised value), 1.8 (growth-corrected kinetic value; not lipid normalised) or 4.6 (growth corrected kinetic

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[3] These Japanese-government funded studies are not included in the CSRs.

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value; lipid normalised[4]) was measured in Rainbow Trout *Oncorhynchus mykiss* (Dow Corning, 2007; full details of this study are provided in EA, 2009).

The mean measured concentration of D4 in fish (<u>minus</u> liver and digestive tract) was 100 mg/kg wet weight (ww) at day 1 of depuration (following 35 days of uptake). Fish growth was significant, and the growth-corrected depuration rate constant was 0.00659 day^{-1}. The growth-corrected depuration half-life can be estimated as 105 days from this study, and whole-body autoradiography showed that a significant amount of radioactivity remained in the gall bladder, with moderate amounts remaining in the gastrointestinal tract, liver, and gastrointestinal tract, 42 days after exposure ceased.

- A growth-corrected and lipid-normalised BMF of 0.51 has been measured in *C. carpio* (CERI, 2011; full details are provided in Appendix 1); a higher value of ~0.7 is obtained if the measured concentrations in fish during the uptake phase are used.

  The mean measured concentration of D4 in fish was 27.4 mg/kg ww after 13 days of uptake. Fish growth was significant, and the growth-corrected depuration rate constant was ~0.058 day^{-1}. Consequently, the growth-corrected depuration half-life was ~30 days. (Steady-state does not appear to have been reached during the 13-day uptake phase.)

A method for estimating BCF values from the growth-corrected depuration rate constant derived from dietary studies is given in the REACH Guidance Document and further methods are given in EA (2011) and Brooke *et al*. (2012). Most of these methods are based on the weight of the fish, and the validity of such estimates is unknown. Since reliable measured BCF data are already available, an extrapolation from BMF data has not been carried out for the purposes of this report. Although there is currently no guidance for the interpretation of dietary studies against the B/vB criteria, the DS notes the following:

- EA (2012) reports the results of an analysis of depuration rate constants (k_2) and found that a value ≤ 0.065 day^{-1} (or a lipid-normalised k_2 ≤0.085 day^{-1}) was consistent with a BCF of ≥5,000 L/kg (normalised to a 5% lipid content)[5]. Thus the low rate of depuration seen in the feeding studies with *O. mykiss* and *C. carpio* is consistent with the BCF for D4 being >5,000 L/kg[6].

- Inoue *et al.* (2012) investigated the correlation of dietary BMF with BCF in *C. carpio* for eight aromatic compounds with log K_{OW} values in the range 4.3-9.0. This indicated that a BMF (growth-corrected and lipid-normalised) above 0.31 corresponds to a BCF (lipid normalised) over 5,000 L/kg. D4's BMF of 0.51 in *C. carpio* therefore appears to correlate with a BCF >5,000 L/kg when compared with other highly bioaccumulative substances, although the general applicability of this correlation is unknown.

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[4] Fish lipid content was 3.44% at the start, 6.74% at the end of uptake and 7.85% at the end of the study; the mean lipid content was 5.83%. RIVM (2012) presents further analysis of the kinetic data, and suggests that the lipid normalized BMF is 1.8.

[5] Goss *et al*. (2013) propose that a substance is not expected to bioaccumulate if the rate constant for elimination is higher than 0.01 d^{-1}. This is based on a first principles approach without considering actual data. In contrast, EA (2012) is based on an analysis of laboratory feeding studies.

[6] D4 was one of over 100 substances included in the BCF data set that formed the basis for the analysis; however, D4 data from dietary studies were not considered.

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Further studies are available that provide additional insight into the bioaccumulative behaviour of this substance:

- A laboratory accumulation study with the sediment worm *Lumbriculus variegatus* gave bioaccumulation factors (BAF) in the range of 13 – 20 depending on dose (based on the concentrations measured in sediment and the organisms at the end of the 28-day uptake period) (Krueger *et al.*, 2008). Taking the sediment organic carbon content and mean lipid content of the worms into account allows biota-sediment accumulation factors (BSAF) of 19 – 28 to be derived (see EA, 2013)[7]. The study has limitations because no special measures were taken to avoid loss from volatilisation during the spiking of the sediment or the uptake phase, and the actual number of measurements was low.

  If it is assumed that exposure was mainly via pore water, the equivalent BCF for D4 is in the approximate range 7,000 to 11,000 L/kg, although there is considerable uncertainty in these estimates.

- A laboratory study with the insect *Chironomus tentans* gave BSAF values of 0.6-2.6 (Kent *et al.,* 1994). These values should be interpreted with caution because no information was given as to whether steady state was reached, and it is possible that the results were based on total ^{14}C measurements (i.e. may include metabolites).

- BSAF values above one have been determined for fourteen of fifteen fish species sampled from rivers in Japan (SIAJ, 2011). Concentrations in sediment were generally very low, but for three samples in which the concentrations in both fish and sediment were above the limit of quantification, BSAFs were 1.5 (Yellowfin Goby *Acanthogobius flavimanus*), 1.9 (Flathead Mullet *Mugil cephalus*) and 2.1 (Japanese Seabass *Lateolabrax japonicas*). The number of samples was very small so their representivity is unknown.

- BSAF values were investigated in the ragworm *Hediste diversicolor* and Flounder (*Pleuronectes flesus*) in a UK estuary (both species are benthic feeders) (Kierkegaard *et al*., 2011). Concentrations were below 1-2 µg/kg dry weight in sediment, and varied between not detectable and 20 µg/kg ww in ragworm and between not detectable and 10 µg/kg ww in Flounder fillet. Lipid levels were not measurable in many of the samples and so a "benchmarking" ratio approach was used, based on the ratio of the multi-media bioaccumulation factor (mmBAFs) for D4 to that of PCB-180 (a known bioaccumulative substance). This approximates to the ratio of the BSAF for D4 to that for PCB-180 in the same sample. The ratio was between 6 and 14, indicating that D4 was bioaccumulating to a greater extent than PCB-180 in these organisms. Kierkegaard *et al.* (2011) considered

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[7] The REACH registrations cite slightly different values (6.7 to 19.7) that were derived in the original test report from the mean measured exposure concentration over the 28-day uptake period and the measured concentration in the organisms measured on day 28. The validity of this approach (particularly at the higher concentration group) can be questioned for the following reasons:
  - The concentration of D4 in the sediment appeared to decrease during the test (particularly in the higher exposure group).
  - The concentration of D4 in the organisms in the 20 mg/kg dry weight (nominal) treatment group was much higher on day 14 of the uptake than found on day 28 of the uptake. The reason for this is not clear (there is no discussion of this in the test report) and, as only one replicate was analysed at each time point, it is not clear whether the 14-day or 28-day value is an outlier.
To try to investigate these uncertainties further, the DS performed a re-analysis using the data obtained at each time point separately. The results are summarised in EA (2013), which found that a) the bioaccumulation factors obtained at the two concentration levels are broadly similar, and b) the bioaccumulation factor obtained at the two time points in the 20 mg/kg dry weight (nominal) group are reasonably consistent. This is the basis for the values cited in this report.

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that these were minimum values as the concentrations of D4 in the sediment were generally below the limit of quantification (the limit of quantification was used in the calculation of these ratios).

- The bioaccumulation potential for D4 in mammals appears to be much lower than may be expected based on the fish BCF or log K_{OW} alone, particularly in relation to inhalation exposure (as discussed in EA, 2009 and Appendix 1). This relates to the more rapid elimination kinetics (via respired air given the high K_{AW} value) and more rapid metabolism in rodents compared with fish. The pharmacokinetic behaviour of D4 in mammals exposed via oral routes is complex and does not appear to be as well understood as the inhalation and dermal routes.

- Several field studies are available[8]. The interpretation of such studies is evolving and it is clear that they can be complicated by a range of factors such as migratory behaviour of the species sampled, difficulties in establishing trophic position and feeding relationships, concentration gradients in water and/or sediment, and measurement limitations (e.g. in terms of temporal and spatial coverage, sample numbers (especially for larger species), specific tissue versus whole body, contamination during sampling, processing and analysis, etc.). The DS therefore considers that the findings should be treated with caution:

  o Lake Pepin, USA (Powell *et al.*, 2009a): the trophic magnification factor (TMF) of D4 is less than one (~0.24-0.36) in this predominantly benthic food chain. Interpretation is complicated by the low concentrations that were found (e.g. fish concentrations were all above the method detection limit but below the limit of quantification for 8 out of 16 species). The levels of D4 were generally highest in benthic invertebrates.

    BMFs in the range of 1–20 were estimated for the two benthic macroinvertebrate species at the bottom of the food chain and two fish species, although the food source in each case included plankton and/or sediment detritus; plankton was not sampled and so concentrations were estimated, which introduces some uncertainty.

    The highest BSAF (~20) was obtained for midge larvae, and BSAFs were also above 1 for mayfly nymphs and 14 out of the 16 fish species. These values may be sensitive to the uncertainties over the actual concentration of D4 present in the sediment.

  o Oslofjord, Norway (Powell *et al.*, 2009c & 2010b): the overall TMF for D4 is below one (0.5-0.7) in this benthi-pelagic food web. At the time of sampling, Atlantic Cod were feeding mainly on shrimp, and the BMF for this feeding relationship was 1.0 for the inner Oslofjord and 1.4 for the

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[8] A further field study has been carried out at Lake Champlain, USA, highlighted during PC (Powell, 2014), but this has not been reviewed by the DS. The median TMF was calculated as 1.3 – 1.4, and the probability that the TMF exceeded 1.0 was in the region of 80%. However, the variability was high, and the median r^2 value was in the range 3-4%. Attempts were made to adjust the fish concentrations for likely exposure, and this gave a median TMF of 0.6 – 2.9. The report's conclusion was that a reliable TMF could not be obtained for D4.

The DS is also aware of a further relevant study which has been published since the close of the PC in December 2014 (Jia *et al.*, 2015). This has not been evaluated, but the abstract indicates that whilst a statistically significant positive correlation was not found between lipid normalized D4 concentrations and trophic level in marine organisms, the estimated TMF was 1.16 (95% confidence interval: 0.94 – 1.44, 94.7% probability of observing a TMF > 1). This re-emphasises the problems in assessing the actual level of trophic magnification.

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outer Oslofjord. The number of samples was small, so the robustness of this estimate is unclear.

Further analysis of the data by RIVM (2012) (ranking species on the basis of average stable carbon isotope ratios) gave TMFs of 0.60 for the benthic food chain, 3.27 for the pelagic food chain, and 1.66 for the whole ecosystem of the inner Oslofjord. None of the slopes was significantly different from zero (the slope for the pelagic based food web is close to significant (p=0.07; 95% CI: -0.1371 to 2.504), leaving the 90% confidence interval of the TMF to vary from 0.87 to 12.2). For the outer Oslofjord, the estimated TMFs were 0.83 for the benthic food chain, 2.21 for the pelagic food chain, and 1.37 for the whole ecosystem (although again, none of the slopes is statistically significant).

o Lake Erie, Canada (McGoldrick *et al.*, 2014; this study is summarised in Appendix 2): TMFs were below 1 in this predominantly benthic food chain, although a TMF above 1 was suggested from one of the food web configurations (with a 49% probability that the TMF is above 1 when both zooplankton and the top predator (Walleye) were excluded). PCB-180 was also found to have a TMF below 1 for some food web configurations.

o Tokyo Bay, Japan (Powell, 2012): the overall TMF is below one in this marine pelagic food web (0.3-0.6, depending on the calculation method). BSAF values above one were obtained for several species (including species towards the top of the food chain such as Japanese Sea Bass (mean BSAF 1.4)) and BMFs were above one (up to 1.7) for three out of the four predator–prey interactions involving Japanese Sea Bass (the probability that the value was greater than one was between 57 and 79 per cent for these three interactions). The remaining BMF values for the predator – prey interactions considered were all below one.

A second study at the same location indicated that the TMF for D4 was ≤1, although the BSAF was above one for some species at the bottom of the food chain (Powell *et al.*, 2014; this study is summarised in Appendix 2).

o Lake Opeongo, Canada (Powell *et al.*, 2009c & 2010a): mean BMFs were estimated to be 2.4 (95 per cent confidence interval 1.6 to 3.3) for the Lake Trout-Perch relationship and 1.9 (95 per cent confidence interval 1.3 to 2.7) for the Lake Trout-Cisco relationship, with bootstrap analysis indicating that there was a high probability that the BMF values were above 1. The levels found in the lowest parts of the food chain were less than the analytical detection limit. Biomagnification may therefore be occurring in this pelagic food web, although the analytical background concentrations were relatively high and variable, and it is also possible that contamination might have occurred during sampling, which causes significant uncertainties in this finding.

o Lake Mjøsa and Lake Randsfjorden, Norway (Borgå *et al.*, 2012; Borgå *et al.*, 2013a & 2013b; the latter two studies are summarised in Appendix 2): the TMF determined in both lakes was similar and the overall combined TMF was 0.70 with a 95% confidence interval of 0.56-0.88. In addition, the levels of D4 did not correlate in the pelagic food

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chain with the reference substances that are known to biomagnify (PCB-153 and p,p'-DDE).

- o Lake Ontario, Canada (CES, 2014; this study is summarised in Appendix 2): D4 was detected in all species sampled (including mysids and a top predatory fish). Individual feeding relationships could indicate BMFs above 1 (e.g. BMF = 1.5 for the Lake Trout-Alewife feeding relationship on a lipid weight basis), but there is significant overlap in concentration between species. A TMF was not derived, but a supplementary study by the same research group suggests that the TMF for D4 in this freshwater benthipelagic food web was ≤1.

It is apparent that different conclusions can be drawn from some studies depending on the food chain configuration that is assumed. The information on trophic magnification in aquatic food webs is therefore equivocal. The majority of studies show that trophic magnification does not occur. However, there is a possibility that D4 may be subject to biomagnification (BMFs above one) in some food webs or feeding relationships[9]. Overall, the field studies provide some additional evidence that the substance is significantly bioaccumulative.

- Regardless of whether D4 undergoes trophic magnification or not, the field studies show that it can be found in aquatic food webs at many locations, including top predatory fish and Grey Seal (*Halichoerus grypus*) (in addition to the references cited above, also Evenset *et al.*, 2009; Kierkegaard *et al*., 2010 & 2013[10]; CES, 2014).

Biota levels are generally highest in samples collected from close to sources of emission. Compared to the analogue D5, concentrations are generally relatively low with many non-detects (which may be a consequence of its relatively minor use in emissive applications), but some samples contain up to a few tens of microgram per kilogram wet weight (ww), and concentrations in the range 0.1 – 0.9 mg/kg ww have been reported in tissues of some fish species (e.g. Roach *Rutilus rutilus*, Ide (or Orfe) *Leuciscus idus* and European Eel *Aguilla aguilla* in the River Rhine, Germany (EVONIK Industries, 2007; summarised in EA, 2009 – a full report is not available[11]) and also Cod liver from several localities (TemaNord, 2005; Schlabach *et al.*, 2007; Durham *et al.*, 2009)).

Comparisons of wet weight biota concentration data between substances are complicated by differences in the scale and route of exposure, lipid content of individual organisms, and sampling/analytical methodology. Nevertheless, the highest levels of D4 found in fish are within an order of magnitude of measured freshwater fish concentrations of up to 9.4 mg/kg ww for hexabromocyclododecane (HBCDD, CAS no. 25637-99-4) (EC, 2008a; ECHA, 2008a) and up to 1.4 mg/kg ww for pentabromodiphenyl ether (pentaBDE, CAS

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[9] For example, a BMF of 1.4 was found for shrimp-Atlantic Cod in the outer Oslofjord (Powell et al., 2009c & 2010b), with estimated TMFs >1 for the pelagic food chain and the whole ecosystem (RIVM, 2012); a TMF above 1 was found for one food web configuration in Lake Erie (McGoldrick et al., 2014); BMFs were above one (up to 1.7) for three out of the four predator–prey interactions involving Japanese Sea Bass in Tokyo Bay, Japan (Powell, 2012); mean BMFs > 1 were found for the Lake Trout-Perch and the Lake Trout-Cisco relationship in Lake Opeongo, Canada (Powell et al., 2009c & 2010a); and the BMF was 1.5 for the Lake Trout-Alewife feeding relationship in Lake Ontario, Canada (CES, 2014).

[10] This study is cited in EA (2013) [Appendix 1] as Kierkegaard *et al*. (2012) as it was in press at the time.

[11] Full details of this study have not been made available to the DS by the company involved. It is important because it suggests high tissue concentrations in fish close to point sources. In contrast, the majority of biota monitoring studies have been carried in out in large lakes or marine environments where concentrations are expected to be lower. This may introduce bias to the available monitoring information.

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no. 32534-81-9) (Appendix 1 of ECHA, 2012a). Molar concentration is inversely proportional to the molecular weight (MW). The MW of D4 (296.6 g/mole) is around 46-52 per cent of the MW for these two substances (MWs in the range 565-642 g/mole), so there will be about twice as many D4 molecules present in the fish than both HBCDD and pentaBDE when the concentrations are the same.

- Appendix 2 of this report extends this idea further by comparing D4 concentrations in laboratory fish bioconcentration tests with other substances that have already been agreed to meet the vB criterion by the Member State Committee. Whole body concentrations achieved during laboratory bioconcentration studies were up to around 2.6 mg/kg ww for Fathead Minnow *P. promelas* (Fackler *et al*., 1995) and 10 mg/kg ww for Common Carp *C. carpio* (CERI, 2007). Higher concentrations have been observed in feeding studies, i.e. 100 mg/kg ww (not including liver) immediately after 35 days of uptake in *P. promelas* (Dow Corning, 2007) and 27.4 mg/kg ww after 13 days of uptake in *C. carpio* (CERI, 2011).

  The analysis shows that D4 can achieve whole fish concentrations similar to a range of substances that are widely accepted as being very bioaccumulative (e.g. UV-328 and UV-320, long chain perfluorocarboxylic acids, musk xylene, hexaBDE and HBCDD).

- D4 is also present in biota in remote regions, including fish (e.g. Atlantic Cod *Gadus morhua* and Polar Cod *Boreogadus saida*) and birds (e.g. Black-legged Kittiwake *Rissa tridactyla* and Glaucous Gull *Larus hyperboreus*) in the European Arctic (Campbell, 2010). The levels are generally low (often close to the limit of detection, and frequently not detectable) but higher levels (up to 9.2 μg/kg wet weight in cod liver and 6.5 μg/kg wet weight in Glaucous Gull liver) have also been reported. Although some of the high levels might be linked to local sources (i.e. WWTP discharge points), D4 is still detectable in some of the samples from more remote locations.

B.7 Environmental hazard assessment

B 7.1 Aquatic compartment (including sediments)

The solubility of D4 in pure water is 0.056 mg/L (56 μg/L) at 23 °C (see Section B.1.3).

D4 is not toxic to fish when they are exposed for short durations (e.g. up to 96 hours) at concentrations up to the water solubility limit. However, it causes toxicity in fish over longer exposure durations. Sousa *et al*. (1995) performed several experiments with Rainbow Trout (*O. mykiss*):

- In a prolonged acute toxicity test, 20 per cent mortality was observed at an exposure concentration of 6.9 μg/L, and the 14-day NOEC was 4.4 μg/L. Additional studies indicated that smaller fish appear to be more sensitive to D4 than larger fish.

- In contrast, a NOEC of ≥4.4 μg/L was obtained from a long-term (93-day) fish early life stage toxicity study with the same species (this was the highest concentration tested and no adverse effects were observed). It cannot be ruled out that effects might have been observed at higher concentrations (as suggested by the prolonged acute test).

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Generally, a longer-term test with early life stages is preferable to a prolonged acute test for the purposes of chronic toxicity assessment. However, the two studies did not overlap in test concentration, so the true level of toxicity to fish over the long-term is unclear. Overall, the NOEC for fish is assumed to be around 4 – 6 µg/L, although there is some uncertainty in the actual value and the reasons for the differences between the two studies. It is noted that this substance has effects on mammalian reproduction, possibly involving an endocrine pathway (see Section B 7.5), and no data are available to determine whether it affects fish reproduction.

D4 is not toxic to aquatic invertebrates when they are exposed for short durations at concentrations up to the water solubility limit. Following longer exposure, D4 does cause toxicity, with a 21-day $NOEC_{survival}$ for *Daphnia magna* of 7.9 µg/L (Sousa *et al*., 1995).

No reliable laboratory data are available on the toxicity of D4 to algae but consideration of QSAR data in EA (2009) suggests that algae should not be more sensitive to D4 than fish or invertebrates.

Long-term sediment toxicity studies are available for three species (*Chironomus riparius, Ch. tentans* and *Lumbriculus variegatus*). The lowest NOEC is <0.73 mg/kg dry weight, obtained in a 28-day study with *Lumbriculus variegatus* (Krueger *et al*., 2009) (although a higher NOEC of 13 mg/kg dry weight was found for this species in a second study (Picard, 2009))[12]*.* If the results are normalised to a standard organic carbon content of 5 per cent, the $NOEC_{standard}$ is <1.5 mg/kg dry weight. For comparison with pelagic organisms (assuming that the effects occur due to exposure via pore water), the equivalent pore water concentration is estimated to be around <2 µg/L using the methods outlined in the REACH Guidance. This value is well below the solubility limit of the substance in pure water.

B 7.2 Terrestrial compartment

No test data are available for D4. The registrants use a category approach to fill the data gaps but this has not been reviewed for the purposes of this report.

B 7.5 Non compartment specific effects relevant for the food chain (secondary poisoning)

No relevant data are available for birds.

In relation to mammals, D4 has a harmonised human health classification under Regulation (EC) No. 1272/2008, as follows:

- Hazard class and category: Repr. 2.

- Hazard statement: H361f: Suspected of damaging fertility.

The classification arises from a mammalian study using inhalation exposure, and the effects are believed to be due to interference with luteinising hormone pathways.

B.8 PBT and vPvB assessment

B 8.1 Assessment of PBT/vPvB Properties – Comparison with the Criteria of Annex XIII

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[12] Original test reports have been reviewed by Environment Canada but not the DS.

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Persistence

A substance is considered to be persistent (P) if it has a degradation half-life >60 days in marine water or >40 days in fresh or estuarine water, or >180 days in marine sediment or >120 days in freshwater or estuarine sediment or soil. A substance is considered to be very persistent (vP) if it has a half-life >60 days in marine, fresh or estuarine water, or >180 days in marine, freshwater or estuarine sediment, or soil.

D4 is not readily biodegradable. Although it can hydrolyse in pure water with a relatively short half-life (e.g. 16.7 days at pH 7 and 12°C), it is highly adsorptive to organic matter in suspended solids, sediment and soils, and this adsorption may limit the rate of hydrolysis in natural waters. A conclusion about overall persistence in natural waters cannot be drawn in the absence of definitive data.

In freshwater sediment, D4 has a degradation half-life of the order of 242 – 365 days at 24°C, expected to be longer at lower temperatures. Persistence in sediment is also supported by the sediment core data from Lake Pepin, USA.

The available data do not allow a reliable soil degradation half-life to be derived.

It is therefore concluded that D4 meets the Annex XIII criteria for a very persistent (vP) substance in sediment (a decision cannot be made for water or soil).

> Note: The registrants conclude that the substance meets the P and vP criteria for sediment (updated submission of 14 October 2014).

Bioaccumulation

A substance is considered to be bioaccumulative (B) if it has a bioconcentration factor (BCF) >2,000 L/kg or very bioaccumulative (vB) if it has a BCF >5,000 L/kg. REACH Annex XIII also allows a weight of evidence approach.

The key data for D4 are a measured steady state fish BCF >10,000 L/kg in Fathead Minnow (*P. promelas*) and >2,000 L/kg in Common Carp (*C. carpio*). The result for *P. promelas* clearly meets the Annex XIII criteria for vB.

In addition, a BMF above one (1.8-4.6) has been reported for Rainbow Trout (*O. mykiss*) in a fish dietary study. The low depuration rate constants are consistent with the BCF for D4 being >5,000 L/kg in both this species and *C. carpio*. The depuration half-life in fish is long at around 105 days in *O. mykiss* and ~30 days for *C. carpio*, with a significant amount of D4 still present in the gall bladder 42 days after exposure had ceased in one study. Both studies lead to significant whole body concentrations (e.g. 100 mg/kg ww without liver in one study).

Field studies typically show that trophic magnification is not occurring in many aquatic food webs. However, BSAF values above one have been measured for benthic invertebrates and fish in both laboratory and field studies, and BMFs above one have been measured for some fish feeding relationships in field studies.

There is also unequivocal evidence that D4 can be found in a wide range of organisms (particularly fish and aquatic invertebrates but also birds and mammals) throughout aquatic food chains, including top predatory fish such as Lake Trout and Cod, as well as Grey Seal *Halichoerus grypus*. Concentrations are generally relatively low, but have been reported to be up to 900 µg/kg wet weight for some wild fish species at locations with significant local sources. This is within an order of magnitude of contamination levels of other substances (HBCDD and pentaBDE) that are considered to meet the vB criteria (and maximum concentrations achieved in fish bioconcentration tests are similar to a range of substances that are considered to meet the vB criterion). Although accumulation in air-breathing mammals is expected to be lower than in other aquatic

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organisms, the top predator in some food chains may not be air breathing (e.g. sharks, which have not been sampled).

D4 is also found in fish, birds and marine mammals sampled from remote regions with low background levels in abiotic media (e.g. Svalbard in the European Arctic). Levels are generally very low (often close to the analytical detection limit, and frequently not detectable). Nevertheless, higher levels (up to 9.2 µg/kg wet weight in cod liver and 6.5 µg/kg wet weight in Glaucous Gull liver) have also been reported. It is possible that these elevated concentrations reflect local sources (i.e. WWTP discharge points), although it is not clear if this can explain all such findings.

Overall, D4 meets the Annex XIII criteria for vB based on the fish BCF, supported by the other available data.

> Note: The registrants (updated submission of 14 October 2014) accept that the substance meets the B and vB criteria based on laboratory fish bioconcentration data. However, they consider that the weight of evidence from laboratory and field biomagnification data (supported by fugacity modelling, which is not considered in this report since actual measured data are preferred) indicates that D4 is unlikely to biomagnify in the food chain and therefore should not be considered as B/vB. Nevertheless, this contradicts the view of the ECHA PBT Expert Group as well as the ECHA Guidance for PBT assessment (Chapter R11), which states that "an indication of biomagnification potential can on its own right be considered to conclude that a substance meets the B or vB criteria but ***absence of such a biomagnification potential cannot be used to conclude that these criteria are not fulfilled***" (emphasis added). The DS considers that a lack of biomagnification potential, although clearly important for a complete overview of the ways a substance may accumulate in organisms, is not sufficient to outweigh the fact that it meets the B or vB criteria based on BCF alone (since accumulation in any part of the food chain might be a significant concern). In any case, there *is* evidence of biomagnification in some food chains for D4 (as recognised by the registrants).

Toxicity

A substance fulfils the toxicity criterion (T) when:

- *the long term no observed effect concentration (NOEC) for marine or freshwater organisms is less than 0.01 mg/L (10 µg/L); or*

- *the substance is classified as carcinogenic (category 1A or 1B), mutagenic (category 1A or 1B) or toxic for reproduction (category 1A, 1B or 2); or*

- *there is other evidence of chronic toxicity, as defined by the classifications STOT (repeated exposure), category 1 (oral, dermal, inhalation of gases/vapours, inhalation of dust/mist/fume) or category 2 (oral, dermal, inhalation of gases/vapours, inhalation of dust/mist/fume, according to Regulation (EC) No 1272/2008.*

D4 has a long-term fish NOEC of around 4 – 6 µg/L (although there is some uncertainty in this value) and a long-term $NOEC_{survival}$ of 7.9 µg/L for *Daphnia magna*. Significant toxicity to invertebrates is also apparent in sediment organism studies. 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.

> Note: The registrants accept that the substance meets the T criterion (updated submission of 14 October 2014).

Conclusion

D4 meets the REACH Annex XIII criteria for both a PBT and vPvB substance.

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Note: In the summary of PBT properties in the CSRs (updated submission of 14 October 2014), the registrants accept that D4 meets the current REACH Annex XIII criteria for PBT and vPvB properties on the basis of available laboratory data. However, they consider that REACH guidance on the use of weight-of-evidence for PBT/vPvB assessment is limited; this is an area of science still changing, and areas of development and uncertainty are still being discussed amongst technical leaders in the field. The registrants' assessment of the weight-of-evidence is that D4 meets neither the vPvB nor PBT criteria. **The DS disagrees with this conclusion.**

D4 is also a vPvB containing substance, as D5 may be present as an impurity above 0.1 per cent w/w.

None of the REACH registrants identifies D4 as a vPvB-containing substance, because they take a similar view about the bioaccumulative properties of the impurity D5 as they do for D4.

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