IDENTIFICATION OF PBT AND vPvB SUBSTANCE

RESULTS OF EVALUATION OF PBT / vPvB PROPERTIES

This dossier covers the substance manufactured and supplied as detailed below.

Substance name: Decamethylcyclopentasiloxane

EINECS number: 208-764-9

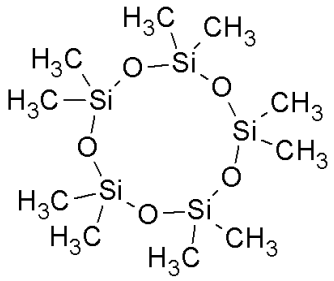
EINECS name: Decamethylcyclopentasiloxane

CAS number: 541-02-6

Registration number(s): Link to ECHA dissemination site for D5

Molecular formula: $C_{10}H_{30}O_5Si_5$

Structural formula:



Composition: The purity of decamethylcyclopentasiloxane (D5) is generally greater than 90 per cent (and often higher than this; for example, a minimum purity of 96-99 per cent is quoted for one major user of D5). The main impurities[1] are small amounts of hexamethylcyclotrisiloxane (D3: CAS no.: 541-05-9), octamethylcyclotetrasiloxane (D4; CAS no.: 556-67-2) and dodecamethylcyclohexasiloxane (D6; CAS no.: 540-97-6) (EA, 2009a).

[1] The actual amounts of each of these impurities present has not been reported but the combined amount could be up to 10 per cent.

Summary of how the substance meets the CMR (Cat 1 or 2), PBT or vPvB criteria, or is considered to be a substance of an equivalent level of concern

Decamethylcyclopentasiloxane (D5) was discussed by former EU PBT Working Group on a number of occasions. As a result of these discussions the substance was included in Regulation (EC) No. 465/2008 of 28th May 2008, which required industry to conduct an environmental monitoring programme and submit the results by November 2009. In addition, Industry has voluntarily carried out a large number of other studies relevant to the PBT and vPvB assessment for this substance. Following review of this information, the Rapporteur submitted an evaluation report to the European Chemicals Agency (ECHA) in October 2010. Since then, several more studies have been carried out in Japan and submitted to the Rapporteur by the registrants, and some further academic studies have been published. In addition, a report from a Board of Review in Canada has become available. For completeness a literature search was carried out by the Rapporteur on 26th January 2012 (some *ad hoc* papers were also included after that date). A draft of the evaluation was circulated to Industry for comment during summer 2012 and further information submitted in their response was incorporated into the final document. This evaluation is therefore an update of the 2010 report, summarising all the relevant new data available and considering their significance in relation to the PBT and vPvB criteria.

Based on the available information, D5 meets the Annex XIII criteria for a 'very persistent and very bioaccumulative' (vPvB) substance in the environment due to its persistence in sediment and a high bioconcentration factor in fish. This conclusion was endorsed by the ECHA PBT Expert Group in November 2012. The available evidence with respect to biomagnification is inconclusive: two field studies (Lake Pepin and Olsofjord) suggest that trophic dilution occurs in benthic and benthipelagic food chains, but for pelagic food chains one study (Tokyo Bay) suggests that trophic dilution was occurring whilst another study (Lake Mjøsa) suggests that trophic magnification may have been occurring. A similar finding concerning possible trophic magnification in pelagic food chains is suggested in a fifth study that is of uncertain reliability (Lake Opeongo). Taken together, the weight of evidence from the field studies is that trophic dilution is occurring although it has to be noted that there is still uncertainty around this for pelagic food chains in particular. Although the T criteria are not met, there are some uncertainties relating to the limited available data on mammalian, avian and fish reproductive effects, and toxicity has been observed in sediment and soil organisms.

The conclusion that D4 should be considered to be both a vPvB and PBT substance is a relevant consideration for D5, given that it may be present as an impurity above 0.1 per cent w/w.

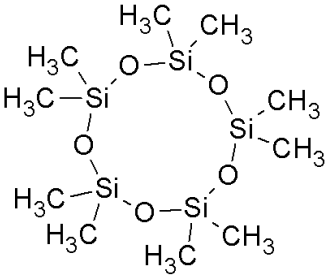
Contents

JUSTIFICATION

Note: A detailed review of existing information on the properties of D5 was published by EA (2009a). In the following sections, the information from this previous review has been described only briefly under the heading *Summary of information from existing evaluation*. It is understood that these data have been included as robust study summaries in the Chemical Safety Reports submitted by the registrants under the REACH Regulation, although a comparison has not been done for the purposes of this report. New information that has become available since the EA (2009a) report was completed is reported under the heading *New information*.

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifier of the substance

Name:	Decamethylcyclopentasiloxane
EC Number:	208-764-9
CAS Number:	541-02-6
IUPAC Name:	Decamethylcyclopentasiloxane
Molecular Formula:	$C_{10}H_{30}O_5Si_5$
Structural Formula:	
Molecular Weight:	370.8 g/mole
Synonyms (and registered trade names):	AEC Cyclopentasiloxane, Baysilone D5, Botanisil CP-33, Cyclic dimethylsiloxane pentamer, Cyclo-decamethylpentasiloxane, Cyclopentasiloxane, Cyclopentasiloxane, decamethyl-, Cyclosiloxane D5, D5, DC 245, DC 345, Decamethylpentacyclosiloxane, Dimethylsiloxane pentamer, Dow Corning 245, Dow Corning 345, Dow Corning 345EU, KF 995, Mirasil CM 5, NUC Silicone VS 7158, Oel Z040, Pentacyclomethicone, Pentamer D5, SB 32, SF 1202, Silbione V5, Silicone SF 1202, TSF 405, VS 7158, Wacker Belsil Z020, Wacker Belsil CM 040.

The abbreviation D5 will be used for the substance throughout this dossier.

1.2 Composition of the substance

The purity of D5 is generally at least 90 per cent (often higher than this figure). The main impurities are hexamethylcyclotrisiloxane (D3; CAS no. 541-05-9), octamethylcyclotetrasiloxane (D4; CAS no. 556-67-2) and dodecamethylcyclohexasiloxane (D6; CAS no. 540-97-6) (EA, 2009a). The actual amount of each of these substances present has not been reported, but based on the stated purity of D5 the combined amount of these impurities could be up to around 10 per cent.

1.3 Physico-chemical properties

The physico-chemical property data are summarised in Table 1. The data are taken from the recent environmental evaluation report by EA (2009a).

Table 1 Summary of relevant physico-chemical properties

REACH ref Annex, §	Property	Value	Comments
V, 5.1	Physical state at 20°C and 101.3 kPa	Liquid	
V, 5.2	Melting / freezing point	-38°C	Experimental value taken from EA (2009a).
V, 5.3	Boiling point	211°C at 1,013 hPa	Experimental value taken from EA (2009a).
V, 5.5	Vapour pressure at 25°C	33.2 Pa	Derived from a temperature-vapour pressure correlation using critically evaluated data. Taken from EA (2009a).
V, 5.7	Water solubility at 20°C	0.017 mg/l (at 23ºC)	Experimental value taken from EA (2009a).
V, 5.8	Partition coefficient n-octanol/water (K_{ow}, log value) at 25°C	8.03	Experimental value (slow stirring method) taken from EA (2009a).
VII, 5.19	Dissociation constant (pKa)	Not relevant	EA (2009a).

2 MANUFACTURE AND USES

Four companies produce or supply D5 in the EU (EA, 2009a). The actual quantity produced or supplied by each company is confidential information. The main uses of D5 can be divided into five areas:

- Use as a site-limited chemical intermediate at the site of production.
- Use as an off-site chemical intermediate.

- Use in personal care products (e.g. cosmetic, skin- and hair-care products).
- Use in household products (e.g. cleaning products).
- Use in industrial/institutional cleaning (e.g. dry cleaning).

The total amount of D5 used in the EU is confidential. EA (2009a) reports that in 2004, around 2,283 tonnes were used as an off-site intermediate for the production of silicone polymers and 17,300 tonnes were used in personal care products in the EU. The amounts used in the other applications are confidential.

3 CLASSIFICATION AND LABELLING

D5 is not classified in either Annex I of Directive 67/548/EEC or Annex VI of Regulation (EC) No. 1272/2008.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 Degradation

4.1.1 Abiotic degradation

4.1.1.1 Summary of information from existing evaluation

Atmospheric degradation

Degradation of D5 will occur in the atmosphere by reaction with atmospheric hydroxyl radicals. The half-life for this reaction is estimated to be 10.4 days (EA, 2009a) based on a hydroxyl radical reaction rate constant of 1.55×10^{-12} cm^3/molecule/s determined by Atkinson (1991) at 24°C and an average atmospheric hydroxyl radical concentration of 5×10^5 molecule/cm^3. The products of the reaction are expected to be silanols, which are removed from the atmosphere by wet deposition (either adsorbed onto particulates or dissolved).

Hydrolysis

D5 undergoes hydrolysis. The rate of hydrolysis is dependent on the pH and temperature. The rate is relatively slow at near neutral pH (half-life ~ 71 days at pH 7 and 25°C) but is more rapid at higher and lower pHs (for example half-life ~ 9 days at pH 8 and 25°C). The rate of the reaction also decreases with decreasing temperature and the following half-lives were recommended in the environmental evaluation by EA (2009a).

- Hydrolysis half-life at pH 7 and 12°C (freshwater) = 315 days.
- Hydrolysis half-life at pH 8 and 9°C (marine water) = 64 days.

The main degradation product formed during the abiotic degradation of D5 is expected to be dimethylsilanediol and this is expected to undergo further degradation processes in the environment to ultimately form carbon dioxide and silicic acid and/or silica.

4.1.1.2 New information

Atmospheric degradation

Xu and Kim (no year) estimated the atmospheric half-life of D5 in various locations taking into account the yearly average hydroxyl radical concentration measured in that location. The data are summarised in Table 2 (for comparison, the default hydroxyl radical concentration normally assumed in the EUSES model/REACH Guidance is lower, at 5×10^5 molecules/cm^3). The atmospheric half-lives estimated (based on the reaction rate constant (k_{OH}) determined by Atkinson (1991)) ranged between 0.6 and 2.6 days for three urban areas, 5.2 days for a semi-rural area, 6.5 and 9.8 days for two rural areas and 6.5 days for a marine area. The authors pointed out that D5 is released mostly to urban and suburban atmospheres.

Table 2 Locations and yearly hydroxyl radical concentrations used in the Xu and Kim (no year) study

Area	Location	Measured yearly average hydroxyl radical concentration (molecule/cm^3)	Reference used for hydroxyl radical concentration data	Estimated atmospheric half-life of D5 (days)
Marine	Finokalia, Greece	0.8×10^6	Mandalakis *et al.* (2003)	6.5
Rural	Kanto, Japan	0.53×10^6	Suzuki *et al.* (1984)	9.8
	Spring/Rock Spring, PA, USA	1.2×10^6	Ren *et al.* (2005)	6.5
Semi-rural	Italy	1×10^6	Hjorth *et al.* (1984)	5.2
Urban	Nashville, TN, USA[1]	9×10^6	Nunnermacker *et al.* (1998)	0.6
	Four Corners, USA[1]	7.1×10^6	Davis (1977)	0.7
	Schauinsland, Germany[1]	2×10^6	Kramp and Volz-Thomas (1997)	2.6

Note: 1) For these locations, measured data on the yearly average hydroxyl radical concentration were not available. The yearly average was estimated by Xu and Kim from the maximum concentration assuming the yearly average concentration = 0.75 × the summer daily average concentration, and the summer daily average concentration = summer maximum concentration/4.

A series of studies by Navea *et al.* (2009a and 2009b), Xu (no year), Kim *et al.* (2008) and Kim & Xu (2009a and 2009b) have investigated further the adsorption of D4 and, in some cases D5 (although some of the studies only investigated D4 the results are thought to also be applicable to D5), onto atmospheric aerosol components and the subsequent degradation on the aerosol. The results of these studies suggest that reaction of D5 with a number of mineral aerosols such as kaolinite, illite, mica and hematite can significantly contribute to the overall removal of D5 from the gas phase of the atmosphere, especially under dry conditions, and this removal can be promoted by ozone and sunlight.

Overall the studies suggest that reaction of D5 with mineral aerosols is important to the atmospheric degradation of D5 and will contribute to its removal from the atmosphere. Navea *et al.* (2009a) estimated that the atmospheric lifetime[2] of D5, taking into account reaction with aerosols, could be around 4.9 days.

Hydrolysis

No new information is available.

4.1.2 Biotic degradation

4.1.2.1 Summary of information from existing evaluation

The available standard biodegradation experiments show little evidence that D5 is biodegradable. However, D5 is highly volatile and will partition readily into the air from water, which makes it unavailable to the micoorganisms in the test systems used (EA, 2009a). Therefore although the available data appear to indicate that D5 is not readily biodegradable, they do not provide absolute proof of this.

Degradation of D5 has been demonstrated in dry soils (e.g. Xu (1999) and Xu and Chandra (1999)), most probably by an abiotic process. Half-lives for the reaction were estimated in EA (2009a) to be around 9.7-12.5 days for dry temperate soils in equilibrium with air of relative humidity of 50 to 90 per cent and 0.1 to 0.19 days for tropical soils in equilibrium with air of 50 to 90 per cent relative humidity. However, the presence of moisture significantly reduced the rate of degradation and EA (2009a) concluded that although it is possible that such degradation in soils could occur in the environment (for example under low relative humidity or drought conditions and degradation in some soils could still be rapid in dry soils equilibrated with air of 100 per cent relative humidity) this was unlikely to be the typical case (particularly for agricultural soil where watering of crops during dry conditions may be expected)[3].

[2] The atmospheric lifetime is the time for the concentration to fall to 1/e (around 1/2.7 or approximately 37 per cent) of its original value. The equivalent half-life would be approximately 3.4 days.

[3] A recent study by Sánchez-Brunete (2010) has shown that D5 is detectable in agricultural soils, sludge amended soils and industrial soils from Spain. However it is not possible to deduce a likely rate of degradation in soil from these data.

4.1.2.2 New information

Xu (2010a) investigated the degradation of ^{14}C-labelled D5 in aquatic sediment under both aerobic and anaerobic conditions (incubation under a nitrogen atmosphere). The method used was based on the OECD Test Guideline 308 but with modifications to minimise the headspace volume (to limit loss from volatilisation) and to add the test substance (as a solution in ethylene glycol monomethyl ether) directly to the sediment phase rather than the water phase. The sediment used was natural freshwater sediment collected from Lake Pepin, Minnesota, USA (this lake is known to receive inputs of D5 from urban sources upstream (for more details, see Section 4.3.3.2) and so the sediment was likely to have been pre-exposed to D5). The tests were carried out at 24°C. The sediment had a pH of 7.9 and an organic carbon content of 3.7 per cent.

The incubations were carried out using 250 ml flasks containing 25 g dry weight sediment (approximate depth 2.5 cm) and overlying water. The overlying water was lake water, and this was added to fill the flask leaving only a small headspace of 40 ml. The initial D5 concentration used was ~130-200 µg/kg dry weight. Sterile controls were prepared in a similar way but with the addition of sodium azide.

At occasions during the test, aeration was carried out for the aerobic sediments and nitrogen gas exchange was carried out for the anaerobic experiments. The exchanged gases were collected and analysed for $^{14}CO_2$ and $^{14}CH_4$ and any ^{14}C-containing volatile compounds in the exchanged gases were collected in a cooled (-68 to -74°C) glass coil, transferred to an air tight syringe and reintroduced into the headspace of the test vessels. In addition at various time points duplicate sediment samples were sacrificed for analysis of the parent compound and ^{14}C present in the sediment and water phases and the headspace.

The experiments were carried out for up to 245 days under aerobic conditions and up to 201 days under anaerobic conditions. The total number of sampling periods during this time was seven for the aerobic and anaerobic controls, seven for the biotic anaerobic samples and nine for the biotic aerobic samples. Two test vessels were sacrificed for analysis at each time point.

The recovery of radioactivity in the experiment was generally >80 per cent (average 83.0 per cent excluding two samples with a lower recovery) under aerobic conditions, but lower (average 68.3 per cent) under anaerobic conditions. As the recovery rates were generally constant over the entire experimental period this indicated that the low recovery was most likely related to loss during the spiking process or in the early incubation period. Therefore, the kinetics for degradation were determined based on the total amount of radiolabel recovered rather than the total amount of radiolabel added as this would be less sensitive to the low recovery.

The majority of the ^{14}C-D5 in the system (>96 per cent) was found to be associated with the sediment phase. Degradation of D5 was evident under both aerobic and anaerobic conditions (a slow decrease in the amount of D5 occurred while the amounts of the major degradation products (dimethylsilanediol and non-extractable substances (presumed by the authors to most likely be other silanols)) increased), but the degradation rate was found to be slow. In addition a slow degradation was also evident in the sterile controls indicating that at least part of the degradation is abiotic in nature. The half-lives at 24°C were estimated to be around 1,200 days under the biotic, aerobic conditions, 2,700 days under sterile aerobic conditions, 3,100 days under biotic, anaerobic conditions and 800 days under sterile anaerobic

conditions. Minimal amounts of mineralisation products ($^{14}CO_2$ and $^{14}CH_4$) were found to be formed.

It should be noted that the sediment used in these studies was collected on the 22nd May 2008 but the degradation studies themselves were not initiated until 13th January 2009. Therefore the sediment was stored for over seven months (the sediment was stored at 4°C in sealed containers and the containers were opened on three occasions to allow air exchange to occur and the sediment for the aerobic experiment was very well mixed at test initiation in order to provide further aeration). The OECD Test Guideline 308 recommends that the sediment is stored at 4°C for a maximum of four weeks and that the sediment used for the aerobic studies should be stored with free access to air. The effect of the prolonged storage used in the current study on the biological viability of the sediment is unknown.

In addition, only one sediment was tested here whereas the OECD 308 Test Guideline recommends that two different sediments are used (one with a high organic carbon content (2.5-7.5 per cent) and fine texture and one with a low organic carbon content (0.5-2.5 per cent) and coarse texture). The organic carbon content of the of the Lake Pepin sediment was 3.7 per cent (it is not clear if this was determined at the time of collection of the sediment or the time of the test initiation) and the effect of the prolonged storage on the organic carbon content of the sediment (or indeed changes in the organic carbon content over the timescale of the actual degradation experiment) is unknown.

Although these deviations from the OECD Test Guideline are not ideal, the results of the study suggest strongly that degradation of D5 in sediment is predominantly an abiotic process and so the prolonged storage of the sediment prior to test initiation may not be so important in this case. The effect of organic carbon content of the sediment on the degradation rate is currently unknown.

Evidence that D5 may have the potential to biodegrade (mineralise) following adaptation of the microorganisms has been reported in a recent poster presentation by van Egmond and Finnegan (2010). Only brief details of the study are currently available. In order to maintain relatively high concentrations of D5 (99.5 per cent purity) in the aqueous phase the study was carried out using pieces of polydimethylsiloxane (PDMS) tubing (approximately 8 ×12 mm) that had been soaked in D5 for 48 hours prior to use (3 replicates were used). The biodegradation of the D5 adsorbed to the tube was carried out using a respirometric test system using homogenised activated sludge (settled supernate; source of the inoculum was not given) as the inoculum and 300 ml of mineral medium. The tests were carried out at 20°C and biodegradation was monitored by oxygen consumption.

Degradation was found to occur after a lag time of around 35 days (this was indicated to be 10 per cent above control theoretical oxygen demand; the controls used were not given but were presumably PDMS tubing) and a continual increase in biological oxygen demand was evident from this point onward until the experiment was stopped on day 60. The formation of a biofilm on the tubing was also evident.

A second series of experiments was carried out using fresh mineral media inoculated with the original tubing (now containing the biofilm) from the first series of experiments and fresh tubing containing D5. Here biodegradation was evident around 4 days after addition of the tubing and the biological oxygen demand of the system was increased over that seen in the first series of experiments. This suggested that the biofilm was responsible for the degradation seen (a separate experiment using the mineral media from the first series of

experiments as inoculum with fresh tubing containing D5 showed little or no biodegradation indicating that the biofilm on the tubing rather than microorganisms in the bulk medium was responsible for the degradation seen).

In order to confirm that D5 was being degraded in the test system, a final series of experiments was carried out in a batch study using ^{14}C-labelled D5. In this study the D5 was administered to the test system adsorbed onto PDMS discs (approximately 27.9 µg ^{14}C-D5 per disc) and mineralisation was determined by measuring the $^{14}CO_2$ evolved. The inoculum used in this study was the adapted inoculum (containing a biofilm). No significant differences were observed in the $^{14}CO_2$ evolved from the test system compared with controls (<1 per cent of the total radioactivity in both case). At the end of the experiment, over 95 per cent of the ^{14}C-D5 was found to remain on the PDMS discs and minimal amounts were present in the aqueous phase. Van Egmond and Finnegan (2010) suggested that transfer of D5 to the active biofilm may have been too limited in this test system to allow measurable biodegradation to be seen.

Overall, these results are suggestive that biodegradation (mineralisation) of D5 could occur, particularly with adapted microorganisms, where availability of the substance to the microorganisms is enhanced. However, the extent or time-frame for biodegradation in the environment is difficult to estimate from the results of this study. In addition, the experiments with ^{14}C-labelled substance did not confirm that mineralisation of D5 was occurring and van Egmond and Finnegan (2010) indicated that further work would be needed to confirm which components of the test system had been degraded.

4.1.3 Summary and discussion of persistence

The main degradation process for D5 in water is hydrolysis, with a half-life dependent on the pH and temperature of the water. The extrapolated hydrolysis half-lives are 315 days at pH 7 and 12°C, and 64 days at pH 8 and 9°C (as considered in the REACH TGD for freshwater and marine environments respectively).

The new data available on the degradation of D5 in sediment show that it has a long degradation half-life in sediment (of the order of 800-3,100 days at 24°C, expected to be longer at lower temperatures).

The situation is less clear for soil. Although rapid degradation of D5 is evident in dry soils in equilibrium with air of relative humidity up to around 90 per cent, the rate of reaction reduces markedly with increasing moisture content. Therefore it is probable that under some situations rapid degradation of D5 may occur, but in other situations the degradation will be much slower.

When considering the persistence of D5 in the environment it is also important to note that D5 is volatile and will be lost from surface water and soil by volatilisation (see Section 4.2). The degradation half-life of D5 in the atmosphere is estimated to be around 10.4 days (although the half-life may be shorter in urban and suburban areas). Thus volatilisation followed by subsequent degradation in the atmosphere is an important process in the overall persistence of D5 in the environment.

4.2 Environmental distribution

4.2.1 Adsorption

4.2.1.1 Summary of information from existing evaluation

An organic carbon-water partition coefficient (K_{oc}) of 1.5×10^5 l/kg (log K_{oc} = 5.17) was recommended for D5 by EA (2009a). This value was obtained from a high-quality experimental study using the OECD Test Guideline 106 batch equilibrium method carried out by Durham (2007).

4.2.1.2 New information

Whelan *et al.* (2009) have determined the adsorption coefficients for D5 with a natural humic acid derived from coal. The experiments were carried out by investigating the effect of humic acid (at concentrations between 0.5 and 10 mg C/l) on the volatilisation of ^{14}C-labelled D5 from stirred solution at 25°C. The data were fitted to a kinetic model that took into account all loss processes including sorption to glass surfaces (measurements showed that this was negligible, accounting for only around 0.5-1 per cent of the total radioactivity added), formation of hydrolysis products (based on the known hydrolysis rate at the temperature and pH of the experiment (half-life of 9 days at pH 8 and 25°C)) and formation of irreversibly-bound residues (this was a theoretical assumption used to improve the fit of the model to the available experimental data). Using this system the mean dissolved humic acid-water partition coefficient (K_{DOC}) for D5 was estimated to be 190,550 l/kg (mean log K_{DOC} = 5.28, range log K_{DOC} 5.04-5.40).

A further study by Whelan *et al.* (2010) has estimated the value of K_{oc} for D5 using filtered river water samples. The method used was similar to the above study. The total organic carbon content of the samples was 1.3 mg C/l (samples filtered to 0.45 µm) and 5.1 mg/l (samples filtered to 125 µm). The mean K_{oc} determined was 1,445,440 l/kg (mean log K_{oc} = 6.16; range log K_{oc} 5.8-6.33).

The effect of ageing on the bioavailability of D5 in natural and artificial sediments has been investigated by van Egmond and Sanders (2010). The study is currently available as a poster presentation and only brief details are given. A diffusive sampling technique based on a polymer resin was used to determine the freely dissolved concentration of D5 in various sediments including a natural lake sediment, a clay soil and an artificial sediment (based on OECD Test Guideline 218 and aged for 4 months at 4°C prior to use). The sediments were spiked with ^{14}C-labelled D5 at a concentration of 0.3-0.5 mg/kg dry weight and allowed to age for 2, 16 or 30 days at 4°C. After this ageing period, accurately weighed aliquots of the sediment were added to vials coated with the polymer resin and incubated at 15°C on a roller mixer for up to 8 days. The concentrations of D5 present in the water phase and the sediment phase were then determined and the K_{oc} value estimated. The estimated log K_{oc} value was found to be 5.6-5.7 for the natural soil, 5.2-5.4 for the natural sediment and 5.4-5.5 for the

artificial sediment, which is in good agreement with previous studies. No effect of ageing on the D5 adsorption was evident.

The partitioning of D5 to organic carbon from different sources has been reported in a poster presentation by van Egmond *et al.* (2010a). The sources of organic carbon included river sediment, activated sludge, digester sludge and waste water treatment plant influent and effluent, peat and humic acid. The experiments were carried out by equilibrating the organic carbon source with pure water for 24 hours and then determining the concentration of D5 in the water phase (via a headspace technique) and the total sediment phase. For some samples (river sediment, activated sludge, digester sludge, influent and effluent) the samples contained sufficient native D5 to carry out the investigation (i.e. no further D5 was added to the samples) but for the experiments with peat and humic acid the samples were spiked with D5 at around 300 ng/l prior to incubation. The mean log K_{oc} values determined were 5.24 and 5.09 for settled sewage sludge (influent), 4.77 and 4.84 for river sediment, 4.90 for activated sludge, 5.16-5.33 for digester sludge, 4.91 for effluent, 4.08 for peat and 4.16 for humic acid.

4.2.2 Distribution modelling

4.2.2.1 Summary of information from existing evaluation

The high Henry's law constant for D5 (around 3.34×10^6 Pa m^3/mole at 25°C (taken from EA, 2009a)) means that it will volatilise rapidly from water and soil. EA (2009a) estimated that the rate constant for volatilisation from soil would be around 0.71 day^{-1} for agricultural soil and 1.4 day^{-1} for grassland, corresponding to volatilisation half-lives of 1 and 0.5 days respectively.

EA (2009a) estimated the volatilisation half-life would be around 2 hours in a river (assumed to have a depth of 1 m, a current velocity of 1 m/s and a wind velocity of 5 m/s) and 183 hours in a shallow lake (assumed to have a depth of 1 m, a current velocity of 0.05 m/s and a wind velocity of 0.5 m/s). These estimates were carried out using the USEPA EPI estimation program.

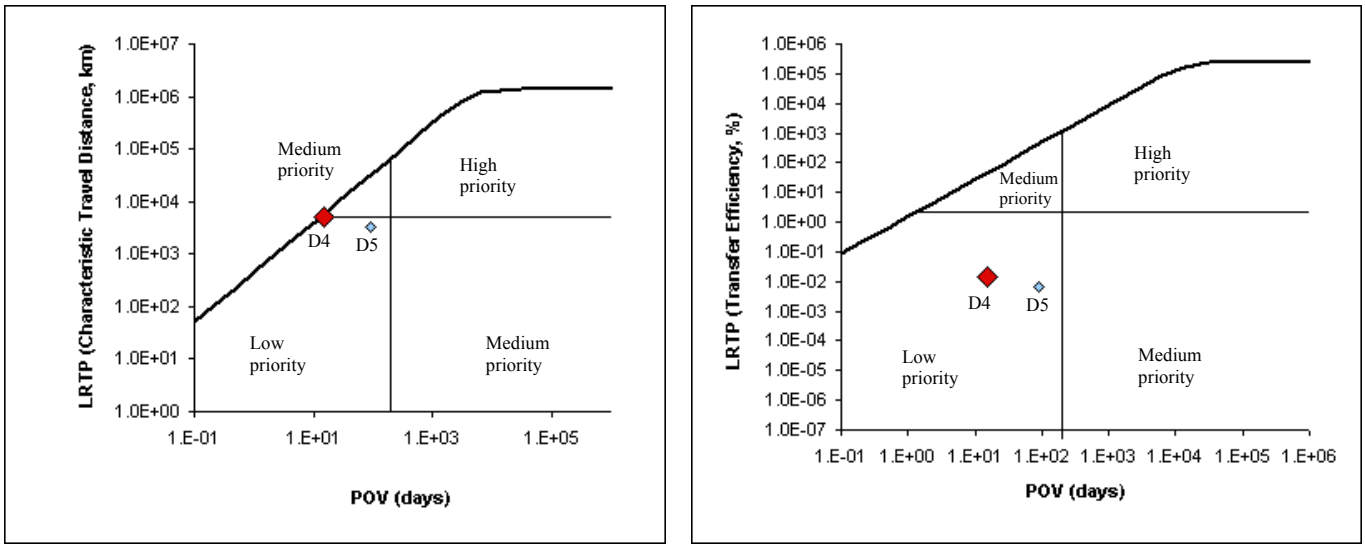
A number of regional and global modelling studies were also reported in EA (2009a). These studies generally investigated the predicted environmental distribution, long-range transport potential and overall environmental persistence[4] or half-life of D5. In general terms, the studies showed that D5 would be expected to transfer readily from the aquatic compartment to the atmosphere where it degrades. This process is expected to be attenuated to some extent by adsorption onto sediments, and the modelling predictions suggested that a substantial fraction[5] of D5 could be in the sediment phase at steady-state (particularly if released to the water phase) and that D5 may have a relatively high persistence in sediments. The predictions also suggested that although D5 has the potential to be transported long distances in the atmosphere, the very high Henry's law constant means that it has a very low potential for re-

[4] Environmental persistence is usually determined in terms of the time taken for a concentration to fall to 1/e of its starting value, i.e. the environmental half-life ≈ 0.69×persistence.

[5] The actual fraction depends on a large number of assumptions, including the fraction released to water, sedimentation rate, etc.

deposition to surface media in remote regions. The long-range transport potential using the OECD Screening Tool is summarised in Figure 1 (based on a study by Xu (2007b) reported in EA (2009a)).

Figure 1 Summary of long-range transport potential using the OECD Screening Tool



4.2.2.2 New information

Whelan *et al.* (2009) investigated the effect of adsorption of D5 to dissolved humic acid (in the range 1 to 10 mg C/l) on the predicted rate of volatilisation from hypothetical water bodies of different depths. The calculations assumed a hydrolysis half-life of 64 days (representing pH 8 and a temperature of 9°C). A series of calculations was also carried out assuming no hydrolysis occurred. The estimated half-life (combined half-life for volatilisation and hydrolysis) was found to depend on the depth of water assumed. The results are summarised in Table 3. As can be seen, association of D5 with dissolved organic carbon/humic acids leads to a progressive increase in the predicted volatilisation half-life.

Table 3 Estimated half-lives for D5 in water bodies of different depths

Water depth (m)	Hydrolysis assumed	Predicted volatilisation half-life (days)			
		DOC = 0 mg/l	DOC = 1 mg/l	DOC = 5 mg/l	DOC = 10 mg/l
1	None	0.58	0.69	1.15	1.74
	Half-life 64 days	0.60	0.68	1.1	1.7
10	None	5.8	6.9	11.5	17.4
	Half-life 64 days	5.3	6.3	10.5	15.7
100	None	58	69	115	174
	Half-life 64 days	31	36	60	89

Note: DOC = Dissolved organic carbon.

A series of modelling studies has been carried out looking at the behaviour of D5 in various aquatic systems using local and regional modelling approaches. The studies are summarised in Table 4. They were carried out using the best available measured data for the physico-chemical properties of D5 taking into account their known (or predicted) temperature dependence (for log K_{ow}, the air-water partition coefficient and the octanol-air partition coefficient). The variation of the predicted behaviour with temperature/season was investigated in some of the studies. The models were parameterised to reflect as closely as possible the particular environment being modelled, though the resulting predictions are subject to uncertainties resulting from the underlying assumptions and simplifications in the models.

The release rate of D5 into the water compartment of the model was generally based on a per capita release rate to waste water (taken from EA, 2009a; this essentially assumed that 10 per cent of the use in personal care products is released to waste water and 90 per cent of the use is released to air) and took into account the size of the population releasing into the environment being modelled, and the removal during waste water treatment.

With one exception no sensitivity analysis was carried out in the studies other than investigating the effect of temperature, and no predictions were made for known substances of concern. For the Whelan (2009d) study, a limited sensitivity analysis was carried out in relation to the predictions. This found that several key model outputs (for example the concentrations and persistence in sediment) were very sensitive to the organic carbon-water partition coefficient and the sedimentation velocity assumed in the model in particular.

Table 4 Predicted persistence of D5 in water in various aquatic systems

System	Model used	Main assumptions[1]	Main findings	Reference
Lake Pepin	Quantitative Water Air Sediment Interaction (QWASI Model). This is a steady-state non-equilibrium Level III fugacity model. The model was parameterised to reflect the properties of Lake Pepin.	Total D5 flux to lake 357-536 kg/year via waste water after waste water treatment (removal during waste water treatment assumed to be between 97 per cent and 98 per cent). The estimate was based on a population of 4,200,000 discharging into the river feeding the lake. Concentration of D5 in air was assumed to be constant at 10 ng/m^3. Degradation in water takes place by hydrolysis at pH 8 and 14°C (the mean annual water temperature in the lake) in the dissolved phase only. This results in a degradation half-life in water 35 days and a degradation half-life in sediment of 96 years (the sediment half-lives were estimated at a temperature of 8°C which was considered to be more appropriate for sediment than the mean annual water temperature). log K_{oc} = 5.17 (at 25°C). log K_{ow} = 8.05 (at 25°C) or 7.86 (at 14°C). log K_{aw} = 2.47 (at 14°C). log K_{oa} = 5.39 (at 14°C).	The predicted total concentration in water and sediment are 10-15 ng/l and 121-181 µg/kg dry weight respectively (for comparison the levels of D5 in sediments from Lake Pepin are of the order of 27 µg/kg wet weight; see Powell *et al.* (2009a) in Section 4.3.3.2. Assuming the default water content of sediment from the REACH Guidance this concentration corresponds to around 124 µg/kg dry weight which is in excellent agreement with the modelled data). The fraction of the total steady state mass in the lake is estimated to be distributed 20 per cent in the water phase and 80 per cent in the sediment phase. The persistence[2] in the model system was estimated by investigating the effect of the cessation of emissions after a certain time period. The persistence in sediment was estimated to be 126 days (approximate half-life of 87 days). The main driving force in this persistence estimate was sediment burial and re-suspension (a sediment burial flux of 14 g/m^2/day was assumed in the model to reflect the very high sediment accumulation rates in Lake Pepin). However, it should be noted that the recent sediment core data from Lake Pepin suggest a much longer half-life for D5 in sediment; see Section 4.2.3. The persistence in the water column was found to be 7.06 days (approximate half-life 4.9 days) reflecting loss via advective outflow and volatilisation, along with hydrolysis to a lesser extent, and the overall persistence was estimated to be 28.7 days (approximate half-life 19.8 days).	Whelan (2009a)

System	Model used	Main assumptions[1]	Main findings	Reference
Inner Oslofjord	Coastal Zone Model for Persistent Organic Pollutants (CoZMo-POP) and the Oslofjord POP model. Both models are multimedia fate and transport models The models were parameterised to reflect the properties of Oslofjord.	Total D5 flux via waste water 136 kg/year after waste water treatment (removal during waste water treatment was assumed to be 98 per cent for D5). This estimate was based on a population of 1,600,000 discharging into the catchment. Degradation in water takes place by hydrolysis in the dissolved phase only. The resulting degradation half-lives in water at 25°C were assumed to be 71 days at pH 7 and 8.6 days at pH 8. The equivalent values for sediment (at 25°C) were 522 years at pH 7 and 63 years at pH 8. log K_{oc} = 5.17 (at 25°C). log K_{ow} = 8.05 (at 25°C). Vapour pressure 30.4 Pa at 25°C. Although the above properties refer to 25°C the actual modelling was carried out using the known seasonal temperature variation in the water of Oslofjord. Three water compartments were assumed, freshwater/estuarine (temperature varied between ~0°C and ~16°C), open/coastal seawater (temperature varied between ~3°C and ~17°C) and deep seawater (at a constant temperature of approximately 7°C) (all temperatures are approximate here as they are read from a graph in the report).	The concentrations predicted were found to vary seasonally with water temperature reflecting the temperature dependence of hydrolysis and volatilisation (concentrations generally highest in the winter time and lowest in the late summer). The total concentrations in the water column were estimated to be below the levels that would be detectable analytically with current methods (<10 ng/l). The predicted concentrations of D5 in sediment were between 20 and 350 µg/kg dry weight with the Oslofjord POP model and a maximum of 8 µg/kg dry weight with the CoZMo-POP model. These results are generally consistent with the monitoring study of Schlabach *et al.* (2007) (see EA (2009a) which found D5 was present in the range 93-920 µg/kg dry weight in Inner Oslofjord and the recent study by Powell *et al.* (2009c and 2010; reported in Section 4.3.3.2) which found mean D5 concentrations around 137-149 µg/kg wet weight (equivalent to around 630-685 µg/kg dry weight using the default water content for sediment from the REACH Guidance). The persistence of D5 was also investigated by modelling the decline in concentrations following cessation of emissions. The concentrations were found to decline rapidly in all compartments using the Oslofjord POP model. The CoZMo-POP model also predicted a rapid decline in the concentrations in water and estimated the dissipation half-life in sediment to be around 396 days, mainly as a result of sediment burial. Volatilisation was found to be the most important loss process from the water column, accounting for >50 per cent of the emissions.	Whelan (2009b)

System	Model used	Main assumptions[1]	Main findings	Reference
Lake Ontario	QWASI Model adapted to Lake Ontario.	Total D5 flux to lake 1,000 kg/year via waste water after waste water treatment (removal during waste water treatment was assumed to be 97 per cent for D5). This estimate was based on a population of 7,135,800 discharging into the catchment. Concentration of D5 in air was assumed to be constant at 10 ng/m^3. Degradation in water takes place by hydrolysis at pH 8 and 9°C in the dissolved phase only. This results in a degradation half-life in water of 66 days and a degradation half-life in sediment of 96 years. log K_{oc} = 5.2 (at 25°C). log K_{ow} = 8.05 (at 25°C). Temperature correction was applied to partition coefficients assuming the following energies of phase transfer (ΔU) = 29 kJ/mole for octanol-water, -51.4 kJ/mole for octanol-air and 80.4 kJ/mole for air-water. These are the recommended values from the Whelan (2009d) study below[3].	The predicted concentrations in water and sediment were 0.12 ng/l and 1.1 µg/kg dry weight respectively. The fraction of the total steady state mass in the lake is estimated to be distributed 83.7 per cent in the water phase and 16.3 per cent in the sediment phase. These data refer to 9°C. When the simulation was run at 2°C the predicted concentrations in water and sediment were 0.23 ng/l and 1.3 µg/kg dry weight respectively, and the percentage steady state mass was distributed 89.1 per cent in the water phase and 10.3 per cent in the sediment phase. At 20°C the predicted concentrations were 0.036 ng/l in water and 0.65 µg/kg dry weight in the sediment, with 72.5 per cent of the steady state mass in the water phase and 27.5 per cent in the sediment. The persistence in the model system was estimated by investigating the effect of the cessation of emissions after a certain time period. The persistence in sediment was estimated to be 2,985 days (equivalent to a half-life of around 2,060 days) at all three temperatures. The main driving force in this persistence estimate was sediment burial and re-suspension. The persistence in the water column was found to range between 22 days at 20°C (summer) to 139 days at 2°C (winter) (equivalent to half-lives of 15 days (summer) and 96 days (winter)). The overall persistence ranged between 30 days (summer) and 155 days (winter), equivalent to half-lives of 21 days (summer) and 107 days (winter).	Whelan (2009c)

System	Model used	Main assumptions[1]	Main findings	Reference
Regional scale model system representing a freshwater – estuarine – coastal – open marine continuum	CoZMo-POP. The model was set up with environmental parameters consistent with the Baltic Proper.	Emissions to the environment were estimated on a per capita basis taking into account the population surrounding the Baltic Proper. For this simulation it was estimated that the total emission of D5 was 1,991.7 tonnes/year to air and 7 tonnes/year to water after waste water treatment (assuming 97 per cent is removed during waste water treatment). Emissions to soil were not considered. Degradation in water takes place by hydrolysis in the dissolved phase only. This results in degradation half-lives in water (at 25°C) of 71 days for freshwater (at pH 7), 9 days for coastal and open water (at pH 8) and 40 days estuarine waters (the mean of the freshwater and open marine water half-life). A temperature correction was applied to the half-lives in the models. The half-lives in sediment were estimated to be 96.4 years for freshwater and estuarine water and 122 years for marine water. log K_{oc} = 5.17 (at 25°C). log K_{ow} = 8.05 (at 25°C). log K_{aw} = 3.01 (at 25°C). log K_{oa} = 5.04 (at 25°C). Temperature correction was applied to partition coefficients assuming the following energies of phase transfer (ΔU) = 29 kJ/mole for octanol-water, -51.4 kJ/mole for octanol-air and 80.4 kJ/mole for air-water[3]. The modelling was carried out using seasonal temperature profiles appropriate to the Baltic Proper.	For air, the simulation found that the concentrations rapidly reached a cyclic steady state (within 2 years). The predicted concentrations were between around 100 and 500 ng/m^3, with the lowest concentrations occurring in July-August and the highest concentrations occurring in March. On cessation of emissions in the model the concentrations in air were predicted to decline rapidly. For freshwater and estuarine water, the simulation predicted that a cyclic steady state would be rapidly reached (within 1 year). The maximum predicted concentrations were around 0.45 ng/l for freshwater and 0.15 ng/l for estuarine water, with the maximum concentrations predicted to occur in the summer. The concentrations predicted in marine water were very low (<0.014 ng/l), with the concentrations in deep water being more than an order of magnitude lower than in surface water. For sediment, the maximum predicted concentrations were around 30 µg/kg in freshwater sediment and 5 µg/kg in estuarine sediment. The model predicted some seasonality in the concentrations but Whelan (2009d) cautioned that this may be the result of a 'modelling artefact'. The concentrations in marine sediments were estimated to be <0.2 µg/kg in coastal sediments and <0.004 µg/kg in deep water sediments and little seasonal variation was predicted in the deep water sediment concentration. The time to reach steady state in the deep water sediment was estimated to be around 9 years. On cessation of emissions in the model, the effective half-lives of D5 were estimated to be around 7 months in coastal sediment and 18 months in deep water sediments. A net deposition of D5 from air to the open sea was predicted between September and April dependent on the assumed emission distribution to air, water and soil. However, the total predicted net deposition was very low (of the order of 4×10^{-3} per cent of the total emission). A limited sensitivity analysis indicated that the predicted behaviour of D5 was very sensitive to the K_{oc} value assumed, the particulate organic carbon deposition velocity, burial velocity and inter basin transfer rate.	Whelan (2009d)

Note: 1) K_{oc} = organic carbon-water partition coefficient.
K_{ow} = octanol-water partition coefficient.
K_{aw} = air-water partition coefficient.
K_{oa} = octanol-air partition coefficient.

2) Persistence is defined as the time taken for the concentration to fall to 1/e of its starting value, i.e. the environmental half-life ≈ 0.69×persistence.

3) These values were taken from a study by Xu (2007a) and are based on an estimate of the ΔU for octanol-air using a linear free energy relationship. A more recent study by Xu (2009) has determined the ΔU values for D5 to be -40.0 kJ/mole for octanol-water partition, 47.9 kJ/mole for octanol-air partition and -92.7 kJ/mole for air-water partition. These values were determined based on measurements of octanol/air/water three-phase equilibrium over the temperature range 6°C to 35°C. It should be noted that the values measured by Xu (2009) are different from those used in the modelling. In particular, the sign (whether the energy change is positive or negative), as well as the actual values, are different in Xu (2009) from those used in the modelling studies. CES (2010b) indicates that these differences in the sign result from different conventions for defining the terms in different studies and have no effect on the modelling results because these differences were taken into account in the model parameterisation. Furthermore, both CES (2010b) and Xu (2009) consider that the impact of the small differences in the actual values (ignoring the sign) on the predicted fate, transport and distribution should be small.

Gouin (2010) investigated the overall environmental persistence, characteristic travel distance (CTD) and transfer efficiency (TE) for a range of substances, including D5, using the OECD Tool[6] for estimating overall persistence (P_{OV}) and long-range transport potential (LRTP) (Wegmann *et al.*, 2009). In addition, the Arctic Contamination Potential ($eACP_{10}$)[7] was also investigated using the GloboPOP model. For D5, the modelling was carried out assuming a half-life of 240 hours (10 days) in air, 1,704 hours (71 days) in water and 5,500 hours (229 days) in both soil and sediment. The resulting parameters estimated for D5 were an overall environmental persistence of 92 days, a CTD of around 5,000 km, a TE of 0.01 per cent and an $eACP_{10}$ of 6.3×10^{-6} per cent[8]. The lag-time (defined in the study as the time taken for 95 per cent of the substance to be removed from the global environment following cessation of emissions; the calculations were carried out using GloboPOP) was estimated to be <1 year when D5 is emitted to air, and between 1 and 3 years when D5 is emitted to water or soil.

Further distribution modelling for D5 has been carried out using the Equilibrium Criterion (EQC) multimedia fugacity model (Kim *et al.*, 2011). The model was implemented as a spreadsheet version that allowed Monte Carlo simulations to be carried out to investigate the sensitivity of the model results to various inputs. All simulations were carried out assuming a temperature of 25°C using the EQC level III (steady state dynamic) model. The physico-chemical properties assumed for D5 were a vapour pressure of 33.2 Pa, a Henry's law constant of 33.0 atm m^3/mol, a log K_{ow} of 5.17, a K_{oc} of 1.48×10^5 l/kg and a BCF of 13,300 l/kg. The degradation half-lives were assumed to be 166 hours in air, 1,691 hours in water, 302 hours in soil and 74,400 hours in sediment. Seven different emission scenarios were investigated using the model assuming a standard release rate of 1,000 kg/hour to a) air only, b) to water only, c) to soil only, d) to air and water equally, e) to air and soil equally, f) to water and soil equally and g) to air, water and soil equally. In addition, a more realistic emission scenario was also carried out assuming a release rate of 950 kg/hour to air, 5 kg/hour to water and 45 kg/hour to soil.

When the substance was assumed to be released to water only, removal by reaction (10.3 per cent) and advection (25.2 per cent) in the water phase was predicted along with transport to the air (51.1 per cent) and sediment (13.3 per cent). Removal from the sediment phase was predicted be very slow and this resulted in a high proportion of the steady state mass being predicted to occur in the sediment (94 per cent of the steady state amount) and a long overall persistence time of around 202 days. The most important parameters governing the predicted distribution were found to be the K_{oc} and the half-life in sediment.

When released to soil only, 93.9 per cent of the emission was predicted to be volatilised to air, with 6.13 per cent being removed by degradation. The distribution of the steady state mass within the system was predicted to be 71.2 per cent to air and 28.7 per cent to soil and a short overall persistence time of 3.9 days was predicted. A similarly short overall persistence time was predicted when the release was to air alone.

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[6] See: http://www.oecd.org/document/17/0,3343,en_2649_34373_40754961_1_1_1_1,00.html.

[7] The ratio of the amount estimated to be present in Arctic surface media to the cumulative amount emitted following 10 years of steady-state emission. Three different emission scenarios were considered (emission into the lower air, water and soil compartment) with the majority of the emission being to the northern hemisphere (with 34.15 per cent being emitted in the north-subtropic zone).

[8] The values given are the highest values based on results obtained from three different emission scenarios (i.e. emission to air, water and soil where appropriate).

For the more realistic scenario most of the total mass of D5 in the system was distributed between air (73.5 per cent of the total steady state mass) and sediment (23.9 per cent of the total steady state mass) and the overall persistence time was estimated to be 4.0 days. The sensitivity analysis indicated that the K_{oc} was the dominant factor controlling the total variability associated with the mass distribution and advection time, and half-life in air was the dominant factor controlling the total variability associated with reaction loss and overall persistence times. The emission rate to water was also identified as an important parameter affecting the predicted fate, distribution and transport of D5.

Very similar results as above for D5 using the EQC model were reported by Hughes *et al.* (2012) and Kim *et al.* (2012).

Brief details of a study modelling the atmospheric concentrations of D5 in the Northern Hemisphere are available (Hansen *et al.*, 2010). The study used the Danish Eulerian Hemispheric Model (DEHM) to simulate the atmospheric concentrations in the first half of 2009. The D5 partitioning properties used in the model were taken from EA (2009a) and the heats of phase change for D5 were taken from Xu (2009). The results showed that D5 is predicted to distribute to all parts of the Northern Hemisphere. The average concentrations predicted for January were up to around 120 ng/m^3 in parts of the model. In summer elevated levels of D5 are predicted to be limited to areas close to emission sources as a result of efficient removal from the atmosphere by reaction with hydroxyl radicals. The results of the model were compared with measurements from a site in central Sweden made between January and June 2009 (Kierkegaard *et al.*, 2010a and McLachlan *et al.*, 2010b). The agreement between the modeled results and measurements was generally very good with the best agreement seen in late spring/summer but with the model predicting higher concentrations than found in winter/early spring. A sensitivity analysis found that this discrepancy between predicted and measured concentrations could not be explained by uncertainties in the partitioning properties or the emission estimates used for D5.

The atmospheric concentrations of D5 have been modeled using the BETR global V2.0 model which is a global-scale multi-media mass-balance model (MacLeod *et al.*, 2011). The properties of D5 used in the model were taken from Gouin (2010) and the emissions of D5 to air used in the model were estimated to be 20 million kg/year globally (no emissions to water appear to have been assumed in the model). The model results predicted that at steady state over 75 per cent of the global inventory of D5 is in the atmosphere with most of the remainder in soils. Removal from the global environment is dominated by reaction with hydroxyl radicals in the atmosphere and the overall residence time of D5 in the global environment was estimated to be 31.6 days. The modeled concentrations were in good agreement with the measurements of McLachlan *et al.* (2010b).

The possibility of deposition of D5 from the atmosphere has been considered at an expert panel workshop held by the Global Silicones Counsel (Global Silicones Counsel, 2009). In general, it was thought that four main processes can contribute to atmospheric deposition:

- Vapour condensation.
- Gas absorption.

- Wet deposition.
- Dry particle deposition.

Vapour condensation was considered to be not relevant to D5 as this can occur only when the concentration in air exceeds the concentration corresponding to the saturated vapour pressure at any given temperature, and the concentrations of D5 predicted in Arctic air are many orders of magnitude lower that the saturated vapour pressure.

Similarly, wet gaseous deposition at temperatures above freezing point was not considered to be a significant process for D5 owing to the high K_{AW} (air-water partition coefficient) for D5. Wet and dry deposition via organic and mineral aerosols was also not thought to be significant as, although D5 may be expected to partition to such aerosols, the aerosol/air partition coefficients for D5 are not sufficiently large to offset the low concentrations of such aerosols in the atmosphere (i.e. a significant flux of D5 to surface media would not be expected).

Global Silicones Counsel (2009) also considered the potential for deposition of D4 and D5 at or below freezing point adsorbed onto the surface of snow crystals (the calculations were given for D4 only but the discussion and conclusions are also relevant for D5). It was concluded that deposition of D4 is potentially possible if the snow-air partition coefficient is very high. However, the snow-air partition coefficient for D4 is relatively small (predicted to be around 0.01 m^3/m^2) and based on this value, and assuming an air concentration of 5 ng/m^3, the maximum concentration of D4 adsorbed by snow was estimated to be around 300 ng/m^3 or a maximum of about 1 per cent of the amount of D4 in the air compartment (assuming an atmosphere height of 6 km and a very high snow area index[9] of 6,000 m^2/m^2; for more compacted snow (snow area index 1,000-3,000 m^2/m^2) the maximum concentration of D4 adsorbed was predicted to fall to 50-150 ng/m^3). Global Silicones Counsel (2009) reported that similar results would also be expected for D5 but that the amounts of D5 predicted in the snow may be slightly higher than for D4.

It is important to note that the D5 deposited in snow is only temporarily stored in the deposited snow. As the snow melts, the majority of D5 will volatilise from the water.

Overall, the expert panel workshop concluded that the ultimate deposition of D5 from the atmosphere to surface media is unlikely to be significant.

The results of a modelling assessment of the contribution from surface/air exchange to the deposition potential for D5 were presented and discussed at the EU Member States Siloxanes Workshop in June 2010 (Xu, 2010b; Dow Corning, 2010). The study considered the partitioning of D5 from air to soil, plant biomass (rye grass and deciduous tree leaves) and aquatic suspended particulates using an equilibrium modelling approach. For the study, plant-air partition coefficients (K_{BA}) were estimated from the known octanol-air partition coefficient using the method developed by Kömp and McLachlan (1997) and the soil-air and suspended particulate-air partition coefficients (K_{SA} and K_{SPA}, respectively) were estimated from the known organic carbon-water partition coefficient (K_{OC}) and air-water partition coefficient (K_{AW}).

[9] Snow area index is the vertically integrated surface area of snow crystals.

The log K_{BA} value for D5 was estimated to be 2.16 at 25°C (values ranged between 3.66 at -20°C and 2.03 at 30°C) which is around two log units or more lower than values estimated by Kömp and McLachlan (1997) for polychlorinated biphenyls. The log K_{SA} values estimated for D5 were between 0.67 and 1.19 (estimates for temperatures between 20°C and 25°C and organic carbon contents of 1-2.6 per cent) and 2.66 and 0.87 (estimated for temperatures between -20°C and 30°C and an organic carbon content of 3 per cent) which are around 4 to 5 log units lower than estimated for more known persistent organic pollutants such as hexachlorobenzene and 2,4,4'-trichlorobiphenyl (PCB-28). The log K_{SPA} was estimated to be between 3.58 at -20°C and 1.78 at 30°C (both assuming an organic carbon content of 50 per cent). Based on these partition coefficients, Xu (2010b) and Dow Corning (2010) estimated that surface/air exchange processes would make only a negligibly small contribution (<1 per cent of the total mass in air) to the deposition potential of D5 in remote regions even at low temperature (~0°C).

4.2.3 Other new information

A survey of the levels of D5 in eleven sediment samples from the Barents Sea (part of the Arctic Ocean located north of Norway and Russia) has been undertaken by Bakke *et al.* (2008). The samples were collected in 2006/2007 and included two samples from the Kola Transect (latitude 71,3683 and 72,1833) one sample from the Shtokman structure (latitude 72,8667), three samples from the Pechora Sea (latitude 68,6633, 70,3817 and 70,5983), three samples from Tromsøflaket (latitude 71,1580, 71,3138 and 71,3193), one sample from Sternøysundet (latitude 70,2302) and one sample from Troms II (latitude 70,1357). D5 was detectable in two of the eleven samples (one from the Kola Transect and one from the Pechora Sea) at a concentration of 11 and 13 µg/kg dry weight respectively. The source is unknown. Little information on the quality control methods employed in this study was given and so the significance of the findings is unclear.

Another recent study has investigated the levels of D5 in sediments in remote regions (Campbell, 2010). The main focus of the study was on the levels of D5 in biota (these results are reported in Section 4.3.3.4) but a number of sediment samples were also collected. The samples were collected in 2009 from Adventfjorden (approximately 78°13'N 15°40'E) and Kongsfjorden (approximately 78°55'N 11°54'E) in Svalbard. Although these are considered to be remote regions it should be noted that there are potential local sources of emission of D5 in the area. Kongsfjorden is located on the west coast of Svalbard and has a permanent research station in the area (at Ny Alesund) with up to 150 personnel in the summer. Cruise ships also make periodic stops at Ny Alesund during spring and summer. Adventfjorden was considered to be the least remote of the sampling sites as Longyearbyen (the capital of Svalbard with around 2,500 inhabitants) is located in the area.

The sediment samples were collected in a linear transect away from the waste water effluent pipe from the communities of Longyearbyen (surface sediment samples collected from Adventfjorden in front of the effluent pipe and 50, 100, 200 and 400 metres away from the pipe) and Ny Alesund (surface sediment samples collected from Kongsfjorden at distances of 90, 155, 220, 300 and 420 metres away from the pipe). The samples were subdivided into three subsamples and sent to three laboratories for analysis (giving a total number of 15

samples for each of Adventfjorden and Kongsfjorden). Precautions were taken during the sample collection, processing and analysis to avoid inadvertent contamination with D5.

The method detection limit was in the range 1.16 to 5.87 µg/kg dry weight. For Adventfjorden, D5 was detectable in five of the fifteen samples at concentrations of 4.13 to 9.82 µg/kg dry weight, with the concentration found being marginally higher near to the waste water outfalls than in those taken at distance. D5 was not detectable in any of the samples from Kongsfjorden. This indicates that the local population is likely to be the main source of D5 in these samples rather than D5 resulting from long-range transport. Similar (or the same) results are given in a poster presentation by Warner *et al.* (2010a) and a publication by Warner *et al.* (2010b). In this latter paper the sediment concentrations are shown graphically and appear to range from ~2 µg/kg dry weight to ~0.7 µg/kg dry weight, which is lower than reported in the Campbell (2010b) paper.

Powell (2009 and 2010a) reports the interim results from an evaluation of D5 in sediment cores from the depositional areas of Lake Pepin. The cores were taken from three locations (towards the upstream end, intermediate and towards the downstream end of the lake) in the lake in July 2006. The cores were dated based on correlation of the magnetic susceptibility of the core with that from reference cores that had previously been dated directly using ^{210}Pb measurements. The 80 cm-depth layer in the cores corresponded to deposition around 1972 in the upstream sample, 1975 in the intermediate sample and 1960 in the downstream sample. D5 was found to be detectable at all depths in the core down to 80 cm. The concentration of D5 was generally greatest at a depth of around 15 cm, and the concentrations in the downstream core were generally greater than in the intermediate and upstream core (the concentrations in these two cores were generally similar). The peak concentrations of D5 corresponded to around 2002 and were in the range 136 to 165 µg/kg dry weight[10]. The rates of accumulation were found to be similar in all three sediment cores, with D5 showing an increasing rate of accumulation from near background levels in 1975 to a peak rate of accumulation in 2003. However the increase was not continuous, for example an increasing rate of accumulation between 1985 and 1993 was observed followed by a decreasing rate of accumulation until around 1997 with an increasing rate of accumulation again occurring from 1997 until around 2003 followed by continued decrease in the rate of accumulation. The pattern of accumulation appeared to track the known population growth of the Twin Cities metropolitan area, and the subsequent implementation of improved waste water treatment practices at the metropolitan waste water treatment plant in the area.

Powell (2010a) concluded that the occurrence of D5 in sediments deposited in the early 1970s corresponded with the introduction of cyclic volatile methyl siloxane products into personal care products. Furthermore, Powell (2010a) argued that as D5 was still detectable in these layers, and the levels found in subsequent layers appeared to track the increased use of D5 and the known implementation of improved waste water treatment in the area, the implication is that degradation of D5 in the sediment core was slow. Although no degradation half-life can be estimated from the data, this does provide further direct evidence that D5 is persistent in sediment.

[10] The concentration of D5 is given as 131 to 212 µg/g dry weight (i.e. 131 to 212 mg/kg dry weight) in one part of the Powell (2009) paper, but the graphs in the paper indicate the concentrations are 131 to 212 ng/g dry weight (i.e. 131 to 212 µg/kg dry weight). It is assumed that the µg/g unit is an error as all other measurements are in ng in the paper. The values quoted here are from the Powell (2010) paper.

A study by Genualdi *et al.* (2011) has investigated the global distribution of D5 in air samples collected at 20 sites worldwide, including five locations in the Arctic. The samples were collected between April and June 2009. Field blanks were also collected at each sampling location and on average the concentrations in the field blanks were around 4 per cent of those in the samples. All the D5 concentrations reported were individually blank corrected. At one location (Sable Island) the concentration of D5 in the blank was higher than the sample and so this point was excluded from the data set. The concentration of D5 was detectable in eighteen of the remaining nineteen samples at a concentration between 0.14 ng/m^3 and 280 ng/m^3 (the highest concentration was measured in Paris, France). For the five more northerly (Arctic) locations, the D5 concentrations were 0.58 ng/m^3 at Alert, Canada (82.45°N, 63.50°W), 4.0 ng/m^3 at Ny Alesund, Norway (78.90°N, 11.89°W), 0.3 ng/m^3 at Barrow, United States (71.32°N, 156.6°W), 0.14 ng/m^3 at Storhofdi, Iceland (63.40°N, 20.28°W) and 3.3 ng/m^3 at Little Fox Lake, Canada (61.35°N, 135.6°W).

Krogseth *et al*. (2012 & 2013) report measured atmospheric concentrations of D5 from samples collected at the Zeppelin observatory, Svalbard, Norway (79°N, 12°E) in late August through to early December 2011. A solid phase extraction active air sampling method was used, and concentrations were measured using GC/MS. It was thought that some losses may have occurred during sampling and storage, but average concentrations of D5 were found to be four times higher in early winter (2.94 ± 0.46 ng/m^3) than in late summer (0.73 ± 0.31 ng/m^3). The results were broadly in line with modelling predictions, with variation in levels explained by seasonality of hydroxyl radical concentration.

4.2.4 Summary of environmental distribution

The properties of D5 mean that it is volatile and also adsorbs strongly onto soil and sediment. Therefore it is important that these properties are considered in relation to the environmental persistence of D5. A number of new modelling studies are available and the results of these studies are generally comparable. Although they generally predict a relatively short persistence in the water column (owing to loss from volatilisation and to a lesser extent hydrolysis) the models also predict that a significant proportion of D5 will distribute to the sediment phase and that the persistence of D5 in sediment may be much longer than found in the water column. Furthermore, in many simulations, the persistence in sediment is related to the rate of sediment burial and re-suspension assumed in the model. This does not necessarily result in an overall loss of D5 from the environment but rather, in the case of sediment burial, results in transfer of D5 to deeper sediment layers where it may persist. The actual fraction of D5 distributed to sediment and the persistence of D5 in sediment in any one system will depend on a number of site-specific factors including the pH, the water depth, the temperature, the sediment deposition rate, the concentration of particulate and dissolved organic carbon, etc. For the recently investigated models the half-life of D5 in sediment was estimated to be around 87 days for Lake Pepin, ~396 days for Inner Oslofjord, ~2,060 days for Lake Ontario, ~7 months for coastal sediment in the Baltic Proper and ~18 months for deep water sediment in the Baltic Proper. In addition, actual sediment core data from Lake Pepin suggest strongly that D5 has a half-life much longer than predicted in the modelling exercise for that lake.

Transport to remote regions via air is likely to occur but the substance has a low potential for subsequent deposition to surface media in such regions.

4.3 Bioaccumulation

When considering the available information on bioaccumulation it is important to recognise that current bioaccumulation theories suggest accumulation in an organism will depend on several factors, including the lipid content of the organism. Therefore in order to compare data from different studies it is usual to lipid normalise the data (or in the case of sediment to normalise the data to the organic carbon content) in order to try to factor out differences between studies resulting solely from differences in lipid contents between the species used[11]. Such normalisation is particularly important when considering field studies investigating biomagnification processes where comparisons are made between concentrations with species from different trophic levels. In the following Sections lipid normalisation has been carried out where possible and appropriate. However it should be noted that such lipid normalisation assumes that D5 partitions primarily to the lipid compartment in an organism. Whilst it is thought that this is a good approximation for lipophilic chemicals in general, and so also highly likely to be the case for D5, this has not yet been unequivocally demonstrated for D5.

4.3.1 Screening data

D5 has a log K_{ow} of 8.03.

4.3.2 Measured bioaccumulation data

4.3.2.1 Summary of information from existing evaluation

A number of bioaccumulation studies using D5 were reviewed in detail in EA (2009a). A summary of the available studies is given in Table 5.

Overall the available experimental data show that D5 bioconcentrates in fish and is taken up from food. The most reliable value for the steady-state BCF is 7,060 l/kg based on total ^{14}C measurements. Although this value may contain a contribution from metabolites as well as parent D5, parent compound analysis indicated that a large proportion of the body burden (83 per cent) was parent compound and so this value is considered to be appropriate for consideration in the PBT and vPvB assessment (the BCF based on parent compound alone would be around 5,860 l/kg based on this percentage).

[11] Lipid- and organic carbon normalization of accumulation factors such as biomagnification factors (BMFs) and biota-sediment accumulation factors (BSAF) effectively results in the factor being expressed as a fugacity ratio (Woodburn, 2010).

Table 5 Summary of available bioaccumulation data for D5 (taken from EA, 2009a)

Species	Exposure concentration	Value	Validity/comment	Reference
Chironomus riparius (midge)	13-180 mg/kg dry weight in sediment	Biota sediment accumulation factors (BSAF) in the range 0.46 to 1.2	Use with care – no information was given as to whether steady state was reached – based on total ^{14}C	IUCLID (2005)
Oncorhynchus mykiss (rainbow trout)	5.8 µg/l	BCF = 3,362 l/kg	Use with care – no information was given as to whether steady state was reached – based on parent compound	Annelin and Frye (1989)
	2.4 µg/l	BCF > 2,000 l/kg	Use with care – only a limited number of measurements carried out – no information on the basis (parent compound or total ^{14}C) of the measurement	IUCLID (2005)
	500 mg/kg food	BMF = 0.22	Valid – wet weight fish/wet weight food steady-state value based on total ^{14}C (the value based on parent compound is expected to be similar)	Dow Corning (2006)
		BMF = 0.63	Valid – lipid normalised steady-state value based on total ^{14}C (similar value expected for parent compound)	
		BMF = 1.39	Valid – wet weight fish/wet weight food kinetic, growth corrected value based on total ^{14}C (the value based on parent compound is expected to be similar)	
		BMF = 3.9	Valid – lipid normalised kinetic, growth corrected value based on total ^{14}C (similar value expected for parent compound)	
Carassius auratus (goldfish)	306-425 mg/kg food (mixture of oligomers)	Value not given but reported to be similar to that for *Poecilia reticulata*	Invalid – exposure concentration not well defined – based on parent compound	Opperhuizen *et al.* (1987)
	Saturated solution	Value not given but reported to be similar to that for *Poecilia reticulata*		
Poecilia reticulata (guppy)	1,008-1,044 mg/kg food (mixture of oligomers)	BMF = 0.05	Invalid – exposure concentration not well defined – based on parent compound	Opperhuizen *et al.* (1987)
		BCF = 1,010		
	Dietary study	No result obtained	Invalid – exposure concentration could not be maintained	Bruggeman *et al.* (1984)

Species	Exposure concentration	Value	Validity/comment	Reference
Pimephales promelas (Fathead minnow)	1.1 µg/l	BCF = 7,060 l/kg	Valid – steady-state value based on total ^{14}C (the value based on parent compound is estimated to be ≥5,860 l/kg)	Drottar (2005) and IUCLID (2005)
		BCF = 13,300 l/kg	Use with care – kinetic value – a large amount of scatter evident amongst some of the depuration data – based on total ^{14}C (the value based on parent compound is estimated to be ≥11,039 l/kg)	
	15 µg/l	BCF = 1,950 l/kg	Use with care – steady-state value – exposure concentration was close to the water solubility limit – based on total ^{14}C (the value based on parent compound is estimated to be ≥1,619 l/kg)	
		BCF = 5,260 l/kg	Use with care – kinetic value – exposure concentration close to water solubility limit and a large amount of scatter evident amongst some of the depuration data – based on total ^{14}C (the value based on parent compound is estimated to be ≥4,358 l/kg)	
Unspecified	Not given	BCF ~3,200 l/kg	Use with care – few details given but may be related to the Annelin and Frye (1989) study with *O. mykiss*	Chandra (1997)

Note: DOC = Dissolved organic carbon.

4.3.2.2 New information

Fish bioconcentration studies

i) Further experimental information on the uptake of D5 by rainbow trout (*Oncorhynchus mykiss*) is reported as part of a study developing a physiologically based pharmacokinetic model for accumulation of D5 (Domoradzki, 2009). Only limited details are given, as follows. Drottar and Miller (2003) exposed rainbow trout of weight 3.5 g to D5 via water (concentration 16 µg/l) for 9 days followed by a 9-day depuration period in clean water. The concentration in the fish determined after 9 days' uptake appears to be around 35,159 µg/kg. No BCF for this study was reported in Domoradzki (2009) but it is clear from the data reported that steady state had not been reached over the 9-day time period. No information was given as to whether or not the exposure concentration remained constant over this time period (the concentration used is slightly above the water solubility of D5). The ratio of the concentration in fish to the concentration in water at day 9 would suggest a BCF of at least 2,200 l/kg.

ii) A new bioconcentration study with common carp (*Cyprinus carpio*) (CERI, 2010) has been reviewed for the purposes of this evaluation but has not been summarised because it is not yet publicly available. It appears to be well carried out, and shows that the mean steady state BCF is 12,049 – 12,617 l/kg (based on parent compound analysis) or 10,550 – 11,048 l/kg when normalised to a 5% lipid content. The depuration half-life was estimated to be between 19 and 22 days. It can therefore be

concluded that the BCF in this species appears to be the same order of magnitude as in fathead minnow (see Table 5), i.e. well above 5,000 l/kg.

iii) Bioconcentration factors have been determined as part of a flow-through fish early life-stage toxicity test with D5, and these are summarised here (further details of the toxicity study are given in Section 7.1.1.1). Parrott *et al*. (2010) exposed fathead minnow (*Pimephales promelas*) to five concentrations of D5 from the egg to juvenile stages (a total of 65 days, 5 days in the egg stage and 60 days post hatch in the larval to juvenile stages). A solvent (dimethyl sulphoxide) was used to prepare the stock solutions. The concentration of solvent in the exposure tank was 20 µl/l (experiment 3). A control and solvent control were run in each case. The concentrations of D5 measured were found to be consistent over the entire exposure period, and the mean concentrations measured were 0.253, 0.815, 1.68, 3.63 and 8.22 µg/l at the five treatment levels. Traces of D5 were also found to be present in both the control (mean concentration 0.00925 µg/l) and solvent control (mean concentration 0.0117 mg/l) tanks. No adverse effects on the organisms were noted at these exposure levels (further details of the toxicity study are given in Section 7.1.1.1).

The concentrations of D5 present in the exposed fish were determined at day 28, day 47-48 and day 60 post hatch (composite fish samples were analysed). In addition, fish from an additional experiment at day 18-19 post hatch were also analysed (the mean D5 exposure concentrations in this experiment were: control 0.00387 µg/l, solvent control 0.00755 µg/l and five treatment levels of 0.711, 1.59, 6.01, 14.2 and 41.7 µg/l; the solvent concentration in this study was 40 µl/l). A total of four replicate measurements were taken at each sampling point for each treatment level in each experiment.

The BCF values determined in this study are summarised in Table 6. Measurable concentrations of D5 were found in the control and solvent control fish and so it was also possible to derive BCFs for the control populations as well as the treatment groups.

The lipid contents of the fish increased with age of the fish and were around 0.61-0.73 per cent at day 18 post hatch, 1.1-1.6 per cent at day 28 post hatch, 1.9-2.4 per cent at day 48 post hatch and 3.0-3.9 per cent at day 60 post hatch.

It should also be noted that the growth of the fish in this experiment was significant. Although not given in the test report, it is possible to estimate the growth rate constant from the data reported for day 28, day 48 and day 60 post hatch as around 0.077 day^{-1}. However, it is not possible to estimate the overall depuration kinetics in this experiment and so the significance of growth dilution cannot be examined quantitatively.

Overall, although there are limitations with the Parrott *et al.* (2010) study, the results do provide evidence for a BCF for D5 of between around 2,000 and 5,000 l/kg and above. These values were obtained in rapidly growing fish (larval and juvenile stages) and the BCF appeared to increase with the time post hatch, probably following the increase in lipid seen in the fish. The values at day 60 post hatch were obtained in fish with lipid contents of 3.0-3.9 per cent. Normalising the values to a "standard" lipid content of 5 per cent would increase the reported BCFs by a factor of around 1.3-1.7 times.

Table 6 Summary of bioconcentration factors determined in fathead minnows

Exposure group	Average BCF (l/kg) at time point (days post hatch (dph))[a]			
	18-19 dph[b]	28 dph	47-48 dph	60 dph
Control (0.00925 µg/l)		2,064±1,771	1,325±1,098	14,683±1,389
Solvent control (0.0117 µg/l)		1,966±1,211	1,860±1,180	11,694±1,164
0.253 µg/l		4,047±1,870	5,493±2,898	8,187±4,132
0.815 µg/l		5,014±1,645	5,175±2,603	3,216±692
1.68 µg/l		3,643±573	4,985±806	2,914±545
3.63 µg/l		5,973±2,293	4,766±1,659	10,419±5,216
8.22 µg/l		2,329±892	2,061±488	15,502±11,608
Control (0.00387 µg/l)	2,524±1,076			
Solvent control (0.00755 µg/l)	2,184±3,266			
0.711 µg/l	631±251			
1.59 µg/l	472±347			
6.01 µg/l	255±104			
14.2 µg/l	241±248			
41.7 µg/l[c]	97.7±39			

Note: a) The values represent the average (± standard deviation) of four determinations. For the calculation of BCF for the earlier sampling points, Parrott *et al.* (2010) used the average concentration in water up to the time of sampling rather than the overall average over the entire experimental period. The concentrations in water were consistent across all sampling points.
b) Determined in a separate experiment
c) Measured concentration exceeds the water solubility of D5.

Fish dietary studies

Further experimental information on the uptake of D5 by rainbow trout (*Oncorhynchus mykiss*) is reported as part of a study developing a physiologically based pharmacokinetic model for accumulation of D5 (Domoradzki, 2009). Only limited details are given, as follows:

i) Durham *et al.* (2009a) fed D5 to one fish (weight 499 g) at a concentration of 238 mg/kg feed for five days. The fish was fed 1 g of food per day and so the dietary concentration of 238 mg/kg is roughly equivalent to a daily dose of 0.5 mg/kg bw/day. The fish was sacrificed on day 6 and the concentration of radioactivity and parent compound in the fish whole body was determined. At this time point around 69 per cent of the radioactivity in the fish was as parent D5 and 31 per cent was as metabolites. The concentration in the fish was estimated to be around 1,516 µg/kg. No accumulation factor was reported in Domaradzki (2009) for this study, and it is unknown if steady state had been reached. After 5 days' feeding the ratio of the concentration in the fish to the concentration in the diet was around 0.16.

A study has been performed for the Japanese regulatory authorities, and is summarised below.

ii) A GLP dietary accumulation test using D5 has been carried out in carp (*Cyprinus carpio*) using the draft version of the OECD TG 305 dietary exposure test (draft version 10 of August 31st 2010). The full study report (CERI, 2011) is currently available only in Japanese but the raw data presented allow for all of the reported bioaccumulation parameters to be verified. In the test carp were exposed to a diet containing[12] D4 (mean concentration 219 μg/g), D5 (mean concentration 221 μg/g) and/or a reference substance (hexachlorobenzene at a mean concentration of 97.2 μg/g), for thirteen days (at a feeding rate of 3 per cent of body weight per day) followed by a 28-day depuration period. The food used had a lipid content of 16.1 per cent and the concentration of D5 in the food was found to be stable over the duration of the uptake phase. The fish were 6.6-7.2 cm in length at the start of the test. The test was carried out at a temperature of 24.6-25°C at a pH of 8.0-81. At various times during the uptake phase (day 4, 7 and 13) and depuration phase (days 1, 4, 7, 14 and 28) groups of four fish were sampled and individually analysed for the presence of D5 (the gut contents appear to have been removed prior to analysis). The weights of the fish were also determined at these timepoints to allow the growth rate constant to be determined. The mean lipid content of the test fish was found to be 5.77 per cent. The lipid contents were found to increase as the test progressed (from 4.16 per cent prior to the test to 7.98 per cent at the end of the depuration phase).

   The mean concentration of D5 determined in the fish at the end of the uptake phase was 21.4 μg/g (standard deviation 5.2 μg/g). The analytical method used was a GC-MS method and so presumably determined the concentration of parent compound. The key bioaccumulation parameters derived from the study are summarised in Table 7 (these parameters have all been verified for this evaluation report from the raw data presented in CERI (2011)).

   The growth-corrected and lipid-normalised BMF from this study is 0.956 [reported as 0.957 in CERI (2011); the small difference probably results from rounding] using the calculation method in the draft OECD 305 test guideline. As explained in the footnotes to Table 7, the available data suggest that this calculation method may have underestimated the concentration in fish at the end of the uptake phase and that the actual growth-corrected and lipid-normalised BMF for D5 may have been around 1.19-1.21 in this study. The equivalent value of the lipid-normalised and growth-corrected BMF for the hexachlorobenzene reference substance was 1.16. The CERI (2011) report also estimated the growth-corrected and lipid-normalised BMF by fitting the data directly using the Berkeley Madonna Software (version 8.3.18) and this gave a value of 0.918 for D5 and 1.24 for hexachlorobenzene [these values have not been re-verified for the purposes of this evaluation].

   Overall the study appears to be well conducted and reliable and the results suggest that the lipid-normalised and growth-corrected BMF for D5 is close to one.

[12] It is not entirely clear from the Japanese report whether the exposure was to all three substances simultaneously or whether three separate experiments were carried out.

Table 7 Summary of bioaccumulation parameters from the CERI (2011) dietary accumulation test

Parameter	Value	Comment
Overall depuration rate constant (k_2)	0.0449 day^{-1} [depuration half-life 15.4 days]	Obtained from the slope of a plot of ln [$Conc_{fish}$] against time.
Growth rate constant (k_g)	0.0224 day^{-1}	Obtained from the slope of a plot of ln [fish weight] against time for the test fish during the depuration phase [see note a].
Growth-corrected depuration rate constant ($k_{growth\text{-}corrected}$)	0.0225 day^{-1} [depuration half-life 30.8 days]	$k_{growth\text{-}corrected} = k_2 - k_g$ (rate constant subtraction method)
Growth-corrected depuration rate constant ($k_{growth\text{-}corrected}$), alternative method	0.0234 day^{-1} [depuration half-life 29.6 days]	Obtained from the slope of a plot of ln [amount fish] against time for the test fish during the depuration phase [see note b].
Assimilation efficiency	0.257 [0.320-0.326][c]	Determined from the intercept of the ln [$Conc_{fish}$] against time plot [see note c].
BMF	0.172	Using the overall depuration rate constant and assimilation efficiency of 0.257
Growth-corrected BMF	0.343	Using the growth-corrected depuration rate constant of 0.0225 day^{-1} and assimilation efficiency of 0.257
Growth-corrected and lipid-normalised BMF	0.956 [1.191-1.214]	Lipid normalised using the ratio of the lipid content in food and the mean lipid content in the test fish [see note c].

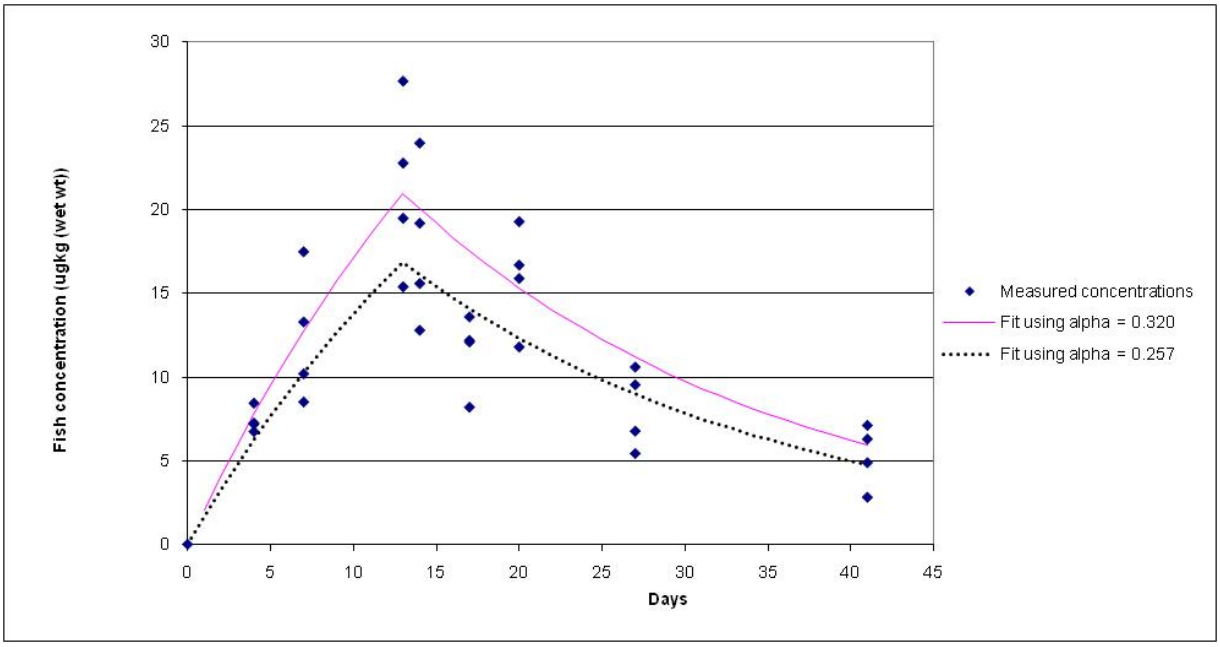
Note: a) The growth rate constant obtained during the depuration phase for the test population was used as there was a statistically significant difference between the growth rate constants during the uptake phase and depuration phase for both the control group and test group, and between the growth rate constant during the depuration phase for the test population and the control group (significance tested using the t-test with α=0.05). This means that the control group should not be combined with the test group and the data for the uptake phase should not be combined with the data for the depuration phase. Thus the most appropriate growth rate constant is from the test population during the depuration phase. These differences, although statistically significant, were relatively small in magnitude, and did not necessarily indicate a toxic effect in the treatment group as, although the growth rate constant for the treatment group during uptake phase was lower than for the control group (0.0272 day^{-1} for the treatment group compared with 0.0338 day^{-1} for the control group) the opposite was true for the depuration phase (0.0224 day^{-1} for the treatment group compared with 0.0209 for the control group).

b) As differences were evident in the growth rate constant obtained during the uptake and depuration phases of the experiment, an alternative method (based on the amount of substance present in fish during the depuration phase (Brooke and Crookes, 2012)) was used to estimate the growth-corrected depuration rate constant. This value is similar to that obtained using the rate constant subtraction method and provides further reassurance in the growth-corrected depuration rate constant.

c) Using this method the concentration in fish estimated at the start of the uptake phase was 16.9 µg/g. This is markedly lower than the concentration in fish measured on day 13 of uptake (mean concentration 21.4 µg/g). If the mean measured concentration on day 13 is used, the assimilation efficiency can be estimated to be higher at 0.326. The equivalent lipid and growth

corrected BMF is then 1.214. The assimilation efficiency can also be obtained by fitting (least squares) the relevant equation from the draft OECD 305 test guideline to the concentrations measured at each timepoint during the uptake phase. When this is done the assimilation efficiency is estimated to be 0.320 (similar to the value estimated from the day 13 concentration) and the equivalent lipid and growth corrected BMF is then 1.191. The fit to the measured data using this approach is shown in **Figure 2**.

Figure 2 **Plot showing fit to the experimental data for the CERI (2011) dietary study**



The REACH Guidance (and also the revised OECD 305 test guideline) indicates that it is possible to estimate a BCF from the results of a feeding study if a rate constant for the uptake from water (k_1) can be estimated. This k_1 value can be used in combination with the depuration rate constant measured in the feeding study to estimate a kinetic BCF. The method suggested in the REACH Guidance for estimating the k_1 value is based on Sijm *et al.* (1995) which estimates the k_1 value from the fish weight but other methods have also been evaluated (Environment Agency, 2011). The resulting BCFs estimated using these methods are shown below in Table 8. Estimates are based on the initial fish weight at the start of the test and the fish weight at the end of the uptake phase (day 13); a lipid content of 5.77 per cent was assumed where necessary. The method reference refers to the methods reviewed in Environment Agency (2011); only the recommended methods from that report have been used (see Environment Agency (2011) for further details).

The predicted growth-corrected BCF values using these methods are in the range 4,244 to 24,620 l/kg which is in broad agreement with the experimental BCF values. However, it should be recognized that these are estimates and it is not known if the assumptions inherent in the calculations are appropriate for D5 (the calculations assume that the k_1 value can be reliably predicted for D5 and that the growth-corrected depuration rate constant obtained by dietary exposure is the same as the growth-corrected depuration rate constant following aqueous exposure).

Table 8 Estimates for BCF from the results of the CERI (2011) feeding study

Reference	Estimated non-growth corrected BCF (l/kg)		Estimated growth-corrected BCF (l/kg)	
	Day 0	Day 13	Day 0	Day 13
Sijm *et al.* (1995)	7,235	6,372	14,438	12,715
Hendriks *et al.* (2001)	6,252	5,661	12,476	11,297
Thomann (1989)	12,337	11,172	24,620	22,294
Barber (2001)	12,181	11,427	24,308	22,802
Barber *et al.* (1991)	11,600	10,791	23,148	21,535
Erickson and McKim (1990a)	11,891	11,172	23,728	22,294
Erickson and McKim (1990b)	9,074	8,288	18,107	16,540
Hayton and Barron (1990)	8,410	7,780	16,782	15,526
Streit and Sire (1993)	7,201	6,764	14,371	13,497
Barber (2003) (observed)	7,418	6,860	14,803	13,690
Barber (2003) (calibrated)	8,202	6,970	16,367	13,908
Spacie and Hamelink (1982)	2,127	2,127	4,244	4,244
Tolls and Sijm (1995)	3,465	3,465	6,915	6,915
Maximum	12,337	11,427	24,620	22,802
Minimum	2,127	2,127	4,244	4,244
Mean	8,261	7,604	16,485	15,174

Invertebrate studies

The uptake and accumulation of D5 from sediment by the oligochaete *Lumbriculus variegatus* has been determined (Krueger *et al.*, 2008). The test was carried out using a 28-day exposure period followed by a 22-day depuration period. The substance used in the test had a purity of 99.19 per cent.

The sediment used in the study was based on the recommendations of OECD Test Guideline 218 and was composed of 10 per cent peat moss, 70 per cent sand and 20 per cent silt and clay. The organic carbon content of the sediment was determined to be 3.2 per cent during the uptake phase and 2.7 per cent during the depuration phase. The dilution water used was well water (dissolve oxygen concentration ≥75 per cent saturation, pH 8.0 to 8.1 and temperature 23±1°C).

The test chambers consisted of 9 litre aquaria containing 1 litre of sediment and 5 litres of water. The system used was a flow-through system where the water flow rate provided two volume additions per day. Two nominal test concentrations were used, 100 and 1,000 mg/kg dry weight, along with a control group. In order to spike the sediment, neat test substance was firstly mixed with the peat component of the sediment for around 16 hours. After this time, the remaining components of the sediment were added to the peat, and the sediment was mixed for a further 40 minutes before being added to the test chambers. Sufficient food for 28 days was also added to the sediment prior to the addition of the water. The sediment/water system was conditioned for 48 hours prior to introduction of the test organisms. Similar test chambers, but without the addition of D5, were prepared for the depuration phase.

The test was initiated by adding approximately one gram (wet weight) of oligochaetes to each test chamber. Three replicate chambers in each treatment group and two replicates in the control were sacrificed for analysis on day 0, day 14 and day 28 of the uptake phase. At the end of the uptake phase, the organisms from three replicates of each treatment group and two replicates from the control group were sieved from the sediment, counted and transferred to replicate chambers containing clean sediment and water for the depuration phase. Three replicates of each treatment group and two replicates of the control group was sacrificed for analysis on day 14 of the depuration phase, and a further replicate from each treatment group was sacrificed on day 22 of the depuration phase for determination of the lipid content of the organisms. The mean lipid content of the organisms was found to be 1.86 per cent.

For the nominal 100 mg/kg dry weight treatment group the measured concentration of D5 in the sediment was found to be 14.2 mg/kg dry weight on day 0 of the study, 30.6 mg/kg dry weight on day 14 of the study, and 17.7 mg/kg dry weight on day 28 of the study. The overall mean concentration over the entire 28-day period was 20.8 mg/kg dry weight, which corresponds to around 21 per cent of the nominal concentration. For the nominal 1,000 mg/kg dry weight treatment group, the measured concentration of D5 in the sediment was 376 mg/kg dry weight at day 0, 355 mg/kg dry weight at day 14 and 278 mg/kg dry weight on day 28. The mean concentration over the 28-day period was 336 mg/kg, which corresponds to 34 per cent of the nominal. There are a number of factors that should be considered here.

- No special measures were taken to avoid loss from volatilisation during the spiking of the sediment. This probably explains why the measured concentrations are only 21 to 34 per cent of the nominal values.

- No specific measures were taken to avoid loss from volatilisation during the uptake phase. In addition, the test was carried out using a flow-through system. Under the conditions used, any D5 present (partitioning into) the water phase would be continually lost from the system. This may explain the apparent declining concentrations in the sediment that were seen during the study, particularly at the higher dosing level (however, as noted above, the variability in the measured concentration data is unknown).

The concentrations found in the oligochaetes during the study are summarised in Table 9.

Based on these data, Krueger *et al.* (2008) estimated the BAF to be 4.27 for the 100 mg/kg dry weight (nominal) treatment group and 0.46 for the 1,000 mg/kg dry weight (nominal) treatment group. These values appear to be derived based on the mean measured exposure concentration over the 28 day uptake period and the measured concentration in the organisms measured on day 28. However, the appropriateness of this approach, particularly at the higher concentration group can be questioned for the following reasons.

- The concentration of D5 in the sediment appeared to decrease during the test.

- The concentration of D5 in the organisms in the 1,000 mg/kg dry weight (nominal) treatment group was slightly higher on day 14 of the uptake than found on day 28 of the uptake.

Table 9 Uptake and depuration of D5 by *Lumbriculus variegatus*

Time point (days)	Nominal sediment level (mg/kg dry weight)	Measured sediment level (mg/kg dry weight)[1]	Measured concentration in *Lumbriculus variegatus* (mg/kg)[1]	Bioaccumulation factor[2]
0	100	14.2		
14	100	30.6	95	3.1
28	100	17.7	89	5.0
42 (depuration day 14)	0	0	5.93	
0	1,000	376		
14	1,000	355	177	0.50
28	1,000	278	155	0.56
42 (depuration day 14)	0	0	9.21	

Note: 1) Concentrations based on measurements in on replicate.
2) Bioaccumulation factor is estimated here as the ratio of the concentration in whole organisms (mg/kg) at the given time point divided by the concentration in sediment (mg/kg dry weight) measured at the same time point.

To try to investigate these uncertainties further, the Environment Agency has performed a re-analysis using the data obtained at each time point separately. The results are summarised in Table 9. Using this approach the mean bioaccumulation factors obtained are 4.1 for the 100 mg/kg (nominal) treatment group and 0.53 for the 1,000 mg/kg (nominal) treatment group. These values are similar to those derived in the original test report, which suggests that these uncertainties are not significant in terms of the overall bioaccumulation factor obtained. The difference in the bioaccumulation factor obtained at the two different exposure concentrations is considered further below.

Krueger *et al.* (2008) also determined the kinetics of the uptake and depuration. The uptake (k_1) and depuration (k_2) rate constants were determined to be 0.830 day^{-1} and 0.193[13] day^{-1} for the 100 mg/kg dry weight (nominal) treatment group (giving a kinetic bioaccumulation factor of 4.29) and 0.092 day^{-1} and 0.201 day^{-1} for the 1,000 mg/kg dry weight (nominal) treatment group (giving a kinetic bioaccumulation factor of 0.46 mg/kg). Similar to the steady state bioaccumulation factors determined by Krueger *et al.* (2008) these values are determined assuming the mean measured concentration over the entire 28-day exposure period, and the uptake rate constant is determined from the measured concentration in the organisms on day 28 of the uptake. The depuration rate constants obtained correspond to depuration half-lives of 3.4 to 3.6 days.

CES (2010a) have recently re-analysed the kinetic data from this study. In this re-analysis the rate constants have been estimated from all of the available data for exposure days 14 and 28 along with clearance day 14. In this analysis the kinetic bioaccumulation factor was 4.5 for the low dose group and 2.0 for the high dose group.

[13] In the Krueger *et al.* (2008) test report the value of k_2 is reported as 0.092 day^{-1} for the low dose group. However this appears to be an error. The correct value for k_2, based on the reported concentrations in the oligochaetes at the end of the uptake phase and day 14 of the depuration phase is 0.193 day^{-1}. Similarly the k_1 value for the high dose group was reported as 0.193 day^{-1} but should be 0.092 day^{-1}. This has subsequently been confirmed (CES, 2010).

A further possible source of uncertainty in this study is the fact that the organisms reproduced during the study. Therefore the offspring would have been exposed for a shorter period than the parents (and reproduction itself could provide an additional parental depuration mechanism). However, as it is not possible to analyse parent and offspring separately such complications are unavoidable in such a study. As steady state appears to have been reach quickly (within 14 days) and the study was carried out over 28 days, this uncertainty is probably of little overall consequence in interpreting the data.

Overall the study is considered to be a "use with care" study, owing to the limited amount of analysis that was carried out, and the possibility that the exposure concentrations declined during the test. Nevertheless the results are considered relevant and usable for use in the PBT and vPvB assessment, as the substance has been shown to be persistent in sediment (see Section 4.1).

In order to consider these data in relation to the PBT and vPvB criteria it is necessary to consider how the bioaccumulation factors determined relate to the bioconcentration factors used in the criteria. One way to do this is to assume that the main route of exposure of the organisms during the test was via the sediment pore water. If this is the case then the concentration in the pore water can be related to the concentration in the sediment using the following equation.

$$Conc_{water} = \frac{Conc_{sed,orgC}}{K_{OC}}$$

Where $Conc_{water}$ = concentration in (pore) water (mg/l)

$Conc_{sed,\ orgC}$ = concentration in sediment on a mg/kg organic carbon basis. The sediment organic carbon content was 3.2 per cent.

K_{oc} = organic carbon-water partition coefficient. This is 1.5×10^5 l/kg for D5 (EA, 2009a).

This equation assumes that the pore water concentration is in equilibrium with the sediment and it is possible that this was not the case in the experiment (for example the D5 was initially added to the solid phase of the sediment and the time taken for the D5 to equilibrate with the water phase is not known). This therefore introduces some uncertainty in the derived pore water concentration.

Using this approach to obtain the concentration in pore water at each time point in Table 9, the equivalent BCF value can be estimated (the concentration in the organism at the time point (mg/kg) divided by the concentration in pore water at the same time point (mg/l)) to be in the approximate range 15,000 to 24,000 l/kg for the 100 mg/kg (nominal) treatment group and 2,400 to 2,700 l/kg for the 1,000 mg/kg (nominal) treatment group. It is interesting to note that for the 1,000 mg/kg (nominal) treatment group the estimated concentration of D5 in the pore water is above the actual water solubility of the substance (the estimated pore water concentrations are in the range 0.058 to 0.074 mg/l compared to the water solubility of 0.017 mg/l) and this may explain why the bioaccumulation factor and apparent BCF obtained for this treatment group is much lower than found for the 100 mg/kg (nominal) treatment group i.e. the pore water may have been saturated at the higher treatment group. If it is assumed that the concentration in pore water at the 1,000 mg/kg (nominal) treatment level was limited to the water solubility (i.e. 0.017 mg/l), the equivalent BCFs that would then be estimated are around 9,000 to 10,000 l/kg which are in reasonable agreement with those obtained from the 100 mg/kg (nominal) treatment group. Therefore this appears to be a

plausible explanation for the differences seen between the two treatment groups, although it is recognised that there are a number of assumptions, and hence uncertainties, inherent in these estimates (in particular the assumption that the pore water concentration is in equilibrium with the sediment concentration).

The bioaccumulation in sediment organisms has also been investigated in a toxicity study for D5 with the benthic invertebrate *Hyalella azteca* (Norwood *et al.*, 2010). In the test the organisms were exposed to six concentrations of D5 in two natural sediments for 28 days. The two sediments used were from Lake Erie (which consisted of 0.5 per cent organic carbon, 19 per cent clay, 75 per cent silt and 6 per cent sand) and Lake Restoule (which consisted of 11 per cent organic carbon, 6 per cent clay, 70 per cent silt and 24 per cent sand). The nominal D5 concentrations used in the sediment were between 28 and 889 mg/kg dry weight for the Lake Erie sediment and between 21.5 and 1,664 mg/kg dry weight for the Lake Restoule sediment. The actual concentrations present in the sediment were measured at the start and end of the test and samples of the overlying water were also collected at the start, midpoint and end of the test. For the main toxicity test, the organisms were present in the sediment. However, to investigate bioaccumulation via the water phase, caged animals were placed in the water columns for seven days (starting at week 2 of the experiment). The concentrations present in the animals were measured after allowing the guts to clear for 24 hours. Both biota-sediment accumulation factors (BSAFs; estimated as the concentration in organism (mg/kg lipid weight)/concentration in sediment (mg/kg organic carbon)) and bioaccumulation factors (BAFs; estimated as at concentration in organism (mg/kg wet weight)/concentration in overlying water (mg/l)) were estimated in the study for both the sediment-exposed and caged animals.

The actual measured concentrations in the Lake Erie sediment were close to nominal at the lower concentrations but were only around 30 per cent of the nominal at the high concentrations. The concentrations measured at day 28 were similar to those measured at day 0, showing that the concentrations were stable over the exposure period and that most of the loss at the higher concentration occurred during spiking of the sediment. For the Lake Restoule sediments, the mean measured concentrations were around eight times higher than nominal at the lower levels and around 92 per cent of nominal at the highest concentration. The concentration measured at day 28 was generally slightly higher than at day 0, showing that there was no measurable decline in concentration over the test. Norwood *et al*. (2010) concluded that the concentration in both sediments was approaching the maximum (or saturation) concentration at the highest concentration tested (estimated to be around 300 mg/kg dry weight or 65,000 mg/kg organic carbon for Lake Erie sediment and 1,300 mg/kg dry weight or 10,000 mg/kg organic carbon for Lake Restoule sediment).

The concentration in overlying water was found to be more variable and ranged from not detectable to 25 µg/l (above the water solubility of D5). The solubility limit was exceeded in only four of the forty samples analysed and may have been a result of the presence of particulates or colloidal matter in the samples.

The mean values (range given in brackets) determined for the BSAFs were 0.0525 (0.015-0.189) for the sediment-exposed organisms in Lake Erie sediment, 0.815 (0.072-1.97) for the sediment-exposed organisms in Lake Restoule sediment, 0.0014 (0.0001-0.0061) for the caged organisms in the Lake Erie experiment and 0.068 (0.003-0.212) for the caged organisms in the Lake Restoule experiment. The equivalent BAFs were 16,000 l/kg (2,180-56,000 l/kg) for the sediment-exposed organisms in Lake Erie sediment, 56,000 l/kg (507-

294,000 l/kg) for the sediment-exposed organisms in Lake Restoule sediment, 435 l/kg (18-1,440 l/kg) for the cage organisms in the Lake Erie experiment and 2,890 l/kg (98-16,300 l/kg) in the caged animals in the Lake Restoule sediment.

Norwood *et al.* (2010) considered that the BAFs were not reliable owing to the variability in the measured water concentrations but noted that, for the sediment-exposed organisms, most of the BAFs derived were >1,000 l/kg with many values >10,000 l/kg. The BAFs derived for the caged organisms were significantly lower, suggesting that either the organisms accumulated most of the D5 directly from sediment or that a 7-day exposure was not of sufficient duration to allow steady state to be reached.

The BSAF values were found to be more consistent than the BAF values for the sediment-exposed organism over 28 days. Furthermore, the BSAF was generally <1 indicating that the organisms accumulated D5 at lipid normalised concentrations lower than the organic carbon normalised concentration in sediment, implying that significant bioaccumulation was not occurring.

4.3.3 Other supporting information

4.3.3.1 Metabolism studies

Summary of information from existing evaluation

EA (2009a) summarised the available toxico-kinetic studies in mammals. These show that D5 is rapidly eliminated from mammalian systems (by exhalation and metabolism) and so it has a low potential for accumulation in mammals. However it was also noted that the pharmacokinetic behaviour after oral exposure is complex and does not appear to be as well understood as the inhalation and dermal routes of exposure (although rapid metabolism following oral exposure was thought to occur it is possible that some of the administered D5 is available for storage in lipid compartments of the animal).

Distribution and metabolism in fish following oral exposure has also been investigated and this showed that around 14 per cent of the recovered dose was present as metabolites within 96 hours of dosing and the half-life for elimination from blood was estimated to be around 70 hours (EA, 2009a).

There is no information on the behaviour in birds.

New information

No new information has been located.

4.3.3.2 Field bioaccumulation data

Summary of information from existing evaluation

No field bioaccumulation studies were reported in EA (2009a).

New information

Field studies investigating the bioaccumulation of D5 have now been carried out. It should be noted that there is a lack of agreed guidelines and methodologies for carrying out and interpreting such studies[14], for example relating to the number of species and number of samples (of different life cycle stages) for each species that should be considered, how the feeding relationships and trophic levels within the food chain are best assigned, and how the statistical significance of the findings should be assessed. This therefore introduces some uncertainties when interpreting the results from such studies and assessing the significance of the findings in relation to the overall PBT or vPvB assessment. It should also be noted that although the REACH Guidance document indicates that the results from such field studies should be considered as part of the overall evaluation of the data, Chapter R.11.1.3.2 of the REACH Guidance[15] indicates that the absence of a biomagnification potential cannot be used on its own to conclude that the B or vB criteria are not fulfilled. The new data are summarised below.

Trophic magnification

Five food chains have been investigated in some detail.

1. The bioaccumulation of D5 has been studied in a natural freshwater aquatic food chain in Lake Pepin, Upper Mississippi River, Minnesota, USA (44°29'N 92°18'W) (Powell *et al.*, 2009a). The lake has a surface area of 102.7 km^2, a length of 33.5 km and a mean depth of 5.4 m. The hydraulic residence time of the lake ranges from around 6 days (high flow) to 47 days (low flow). The lake is around 80 km downstream of the cities of Minneapolis and Saint Paul (estimated population of 3.2 million in 2006). The lake acts as a sink for sediment-associated contaminants from the inflowing river and sediment accumulation rates range from 20-30 kg/m^2/year in the upstream end of the lake to 3-5 kg/m^2/year in the downstream end of the lake.

   The food chain considered included surface sediment, benthic macroinvertebrates (two genera, two families) and 15 fish species (14 genera, 9 families). The fish were collected on the 4th and 5th September 2007 and the surface sediments and benthic macroinvertebrates were collected between the 20th and 22nd May 2008 (the influence of temporal differences in exposure conditions is unknown). The fish were collected in near-

[14] In order to try to address some of these issues, an Expert Workshop on "Lab to Field Bioaccumulation" sponsored by the Health and Environmental Sciences Institute (HESI), the Society of Environmental Toxicology and Chemistry (SETAC) and the United States Environmental Protection Agency (USEPA) was held on 18-19 November 2009 to identify and discuss impacts of ecosystem and ecological variables on trophic magnification factors. The findings of this workshop have been recently published (e.g. Borgå *et al.* (2011) and Conder *et al.* (2011).

[15] Page 25-26 of the Guidance on information requirements and chemical safety assessment. Chapter R.11: PBT Assessment.

shore areas of the lake (apparently over most of the length of the lake; since fish move the sampling location does not necessarily reflect where they are exposed), and sediment and benthic macroinvertebrates were collected from 25 locations along five shore-to-shore transects positioned perpendicular to the flow axis of the lake. Small fish and macroinvertebrates were pooled into composite samples for each species whereas large fish were analysed as individuals. A rigorous quality control procedure was implemented during the sampling and analysis to minimise contamination of the samples. This included field blanks and field spiked samples for sediment and laboratory blanks for sediment and fish. The measured concentrations were corrected for background levels found in laboratory blanks.

Trophic level (TL) of the organisms was determined by means of $\delta^{15}N$ measurements[16] and ranged from TL ~2.0 (benthic detrivores such as *Chironomus* sp. and *Hexagenia* sp.) to TL ~3.7 (pelagic piscivores such as largemouth bass and walleye). The trophic levels, and concentrations found, are summarised in Table 10. The following point should be noted in relation to the concentrations found and the limit of detection (LOD), method detection limit (MDL) and limit of quantification (LOQ)[17]. The concentrations of D5 in the sediment were all greater than the MDL but were less than the LOQ in 18 out of 25 samples.

A plot of the natural logarithm (ln) of the mean measured concentrations (on a lipid weight basis) against the trophic level is shown in Figure 3. The antilog of the slope[18] of the regression line gives the Trophic Magnification Factor (TMF). The TMF for D5 in this food web can therefore be estimated to be around 0.20 based on the mean measured lipid normalised concentrations. The TMF value quoted in Powell *et al.* (2009a) is slightly smaller than this value (TMF 0.18) and this value was derived based on a regression using all 52 individual observations rather than the mean values per species. As the value derived by Powell *et al.* (2009a) is based on each individual data point it is preferred over the TMF derived from the mean concentration for each species in Figure 3 as it minimises errors associated with unbalanced sampling (for example different numbers of organisms were collected for each species)[19]. Powell *et al.* (2009a) estimate a further TMF of 0.11 using trophic guilds (here the data were assigned to one of six

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[16] $\delta^{15}N = \left[\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right] \times 1000$ where R_{sample} is the $^{15}N/^{14}N$ abundance (in parts per thousand) in the sample and $R_{standard}$ is the $^{15}N/^{14}N$ abundance in a standard (atmospheric nitrogen gas). The trophic level of a consumer is defined as follows, assuming the trophic level of midge larvae is 2: $TL = 2 + \frac{\left(\delta^{15}N_{consumer} - \delta^{15}N_{midge}\right)}{3.4}$.

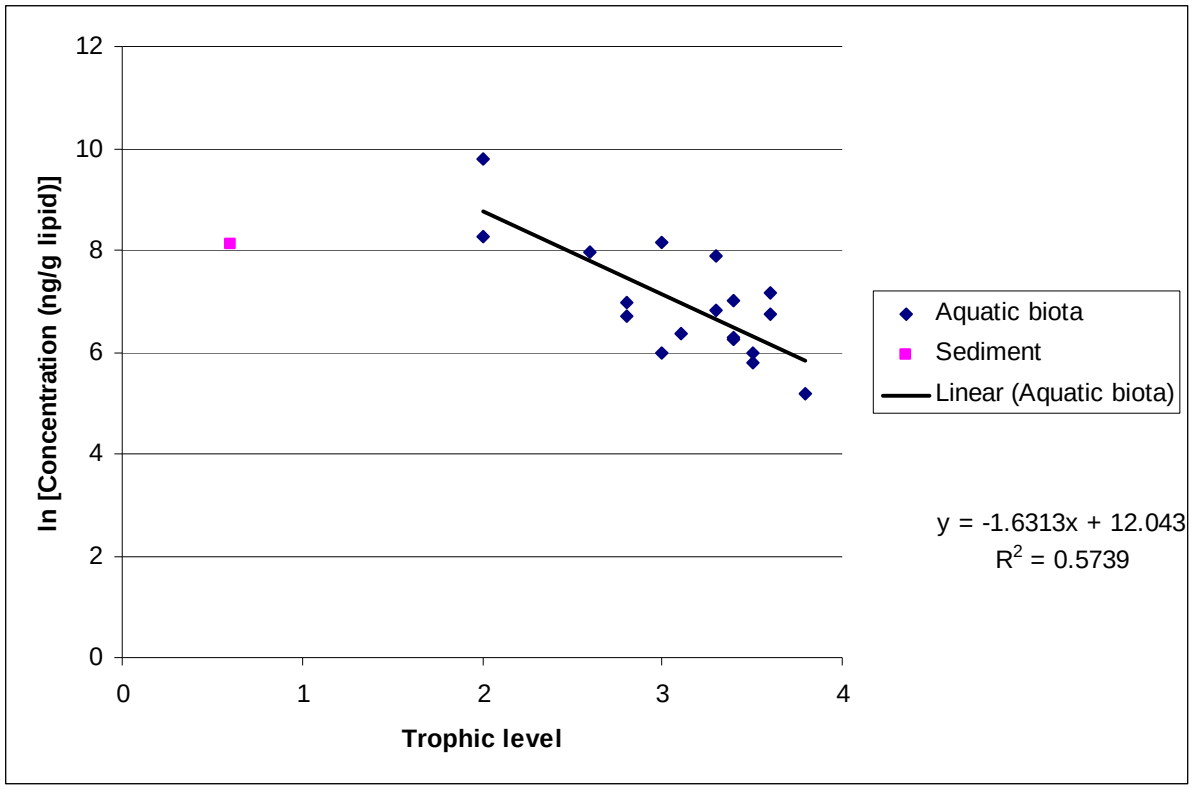
[17] Limit of detection (LOD) is based on the ability of the analytical method to distinguish between signal and noise. The method detection limit (MDL) is a measure of the analytical method's ability to quantify an analyte in a sample matrix. The limit of quantification (LOQ) is the minimum level of a substance in a sample that can be detected and accurately quantified (this was defined as three times the MDL in the current study).

[18] The slope of the plot is statistically significant ($p<0.05$) and the regression line had an R^2 of 0.5739. The slope of the plot was -1.631 with a standard error of 0.351. The lower and upper 95th percentile values of the slope were -2.376 and -0.886 respectively (equivalent to a TMF range of 0.093 to 0.41).

[19] The test report does not give the individual concentrations for each data point (rather they are shown graphically). Therefore the mean data reported by Powell *et al.* (2009a) have had to be used here to construct Figure 3 in order to illustrate the findings. Given the different numbers of samples for each species it would have been preferable to reconstruct Figure 3 here using the individual data points for this evaluation report but this was not possible.

trophic guilds[20] and the mean value per trophic guild used in the regression). Based on these analyses, the TMF for D5 is clearly less than 1 in this food web, and lies in the approximate range 0.1-0.2.

Figure 3 Plot of ln [mean concentration] (on a lipid weight basis[21]) against trophic level for the Lake Pepin food chain



Note: In the actual paper the plots are given with the error bars shown. For several of the species the error bars do not overlap with the regression line.

[20] The six trophic guilds considered were detrivores, planktivores, omnivores, invertivores, carnivores and piscivores.

[21] The sediment concentration is on a ng/g organic carbon basis.

Table 10 Accumulation of D5 in the Lake Pepin food chain

Sample	Number of samples analysed	Trophic level	Mean measured D5 concentration (±standard deviation)	
			µg/kg wet weight	µg/kg lipid
Surface sediment - samples taken from whole lake	25	0.7	26.7±6.4	3,289±522[1]
Surface sediments - samples taken from where benthic macroinvertebrates were collected	5	0.6	28.2±6.7	3,433±566[1]
Midge (*Chironomous sp.*)	5 composites	2.0	154±73	18,114±8,860
Burrowing mayfly (*Hexagenia sp.*)	2 composites	2.0	98.7±0.9	3,895±341
White sucker (*Catostomus commersoni*)	1	2.6	58.5	2,865
Common carp (*Cyprinus carpio*)	3	2.8	137±65	1,050±467
Gizzard shad (*Dorosoma cepedianum*)	4	2.8	69.2±25.4	816±222
Gizzard shad (young of year) (*Dorosoma cepedianum*)	3 composites	3.0	15.1±2.5	402±40
Silver redhorse (*Moxostoma anisurum*)	3	3.0	250±105	3,412±804
Bluegill sunfish (*Lepomis macrochirus*)	3	3.1	27.4±5.2	580±132
River carpsucker (*Carpiodes carpio*)	1	3.3	447	2,654
Shorthead redhorse (*Moxostoma macrolepidotum*)	3	3.3	58.4±5.5	927±124
Freshwater drum (*Aplodinotus grunniens*)	3	3.4	24.2±18.8	513±399
Emerald shiner (*Nitropis atherinoides*)	4 composites	3.4	34.9±9.6	1,087±467
Black crappie (*Pomoxis nigromaculatus*)	3	3.4	36.9±3.2	531±49
White bass (*Morone chrysops*)	3	3.5	21.8±4.1	332±77
Smallmouth bass (*Micropterus dolomieu*)	3	3.5	22.9±4.1	398±43
Quillback carpsucker (*Carpiodes cyrinus*)	2	3.6	159±27	1,283±35
Walleye (*Stizistedion vitruem*)	3	3.6	58.3±10.1	848±92
Largemouth bass (*Micropterus salmoides*)	3	3.8	7.5±3.0	175±38

Note: 1) Sediment concentrations are expressed on a total organic carbon basis rather than a lipid basis.

The paper also estimated the biomagnification factor (BMF) for various organisms, taking into account the composition of the diet of each organism[22], and biota-sediment accumulation factors (BSAF). A correction was also applied to the BMF to take account of the trophic level increase (this was designated BMF_{TL}) in the Powell *et al.* (2009a) report. However it was later found out that the correction originally applied was incorrect, and an alternative method was used to correct for the trophic level (CES, 2010a). The equation used is shown below. This method effectively converts the BMF (that is defined for a specific predator-prey interaction) into a TMF (which is usually obtained from the antilog of the slope of a plot of ln [concentration] against trophic level).

$$\ln[BMF_{TL}] = \frac{\ln[BMF]}{TL_{Pred} - TL_{Prey}}$$

Where BMF_{TL} = corrected BMF. This is equivalent to the TMF.

BMF = the observed BMF for a given predator-prey interaction.

TL_{Pred} = the trophic level of the predator.

TL_{Prey} = the trophic level of the prey.

The resulting BMF, BMF_{TL} (using the method proposed in CES (2010a)) and BSAF values are summarised in Table 11.

As can be seen from Table 11, the BMF is only above 1 for the two benthic macroinvertebrates species at the bottom of the food chain and there is a general progressive reduction in the BMF with increasing trophic level. This confirms the results of the TMF analysis that trophic dilution of D5 appears to be occurring in this food chain.

The BMF_{TL} follows the same general trend as the BMF with values above 1 being obtained for midge and burrowing mayfly only.

The BSAFs obtained are generally less than 1 (with the exception of silver redhorse) for the fish species and above 1 for midge larvae and mayfly nymphs (the sediment and invertebrates appear to have been collected together, unlike the fish).

Overall, despite the small sample sizes and large variation in tissue concentrations for some individual species, the results of this study suggest that the concentrations of D5 were generally highest in the benthic microinvertebrates and decreased with increasing trophic level within the food chain. Powell *et al.* (2009a) considered that the fact that the concentrations and various accumulation factors were highest in the organisms having a close association with the sediment compartment indicated that the main source of D5 in the food chain was sediment rather than water, and that most uptake in the food chain occurred from dietary exposure rather than water-phase exposure. Based on this Powell *et al.* (2009a) concluded that bioconcentration was not an important process in this food chain but the uptake was rather controlled by dietary uptake and associated mitigation

[22] The BMF was calculated by dividing the mean lipid normalised concentration in the predator by the mean lipid normalised concentration in the diet of the predatory. The concentrations in diet were calculated as the mean diet-weighted concentration taking into account the fraction of each prey item that constituted the diet. The assumed feeding relationships were complex and took into account the known (or assumed) composition of the diet for each species – it was not a simple single predator- single prey relationship.

processes such as metabolism, growth dilution and low uptake and assimilation efficiencies.

Table 11 BMF, BMF_{TL} and BSAF values derived for D5 for the Lake Pepin food chain

Sample	Trophic level	BSAF	BMF[2]	BMF_{TL}
Midge	2.0	5.3	5.3[1]	3.5
Burrowing mayfly	2.0	1.1	1.1[1]	1.1
White sucker	2.6	0.8	0.5	0.3
Common carp	2.8	0.3	0.2	0.2
Gizzard shad	2.8	0.2	0.2	0.4
Gizzard shad (young of year)	3.0	0.1	0.1	0.3
Silver redhorse	3.0	1.0	0.6	0.6
Bluegill sunfish	3.1	0.2	0.1	0.1
River carpsucker	3.3	0.8	0.4	0.5
Shorthead redhorse	3.3	0.3	0.1	0.3
Freshwater drum	3.4	0.1	<0.1	0.1
Emerald shiner	3.4	0.3	0.3	0.5
Black crappie	3.4	0.2	0.1	0.1
White bass	3.5	0.1	0.1	0.1
Smallmouth bass	3.5	0.1	0.1	0.1
Quillback carpsucker	3.6	0.4	0.2	0.4
Walleye	3.6	0.2	0.2	0.2
Largemouth bass	3.8	0.1	<0.1	0.1

Note: 1) For the benthic macroinvertebrates the diet was considered to consist mainly of sediment detritus (75-80 per cent) and plankton (20-25 per cent). No concentration data were available for sediment detritus or plankton and so it was assumed that the concentrations were the same as the organic carbon normalised concentration in sediment. Therefore the BMF is numerically equivalent to the BSAF.

2) In order to carry out these estimates the diets of the species were simplified and in many cases included a component from sediment detritus, plankton, fish eggs and terrestrial insects along with the other species included in the study. As no concentrations were measured for some of these assumed dietary components, the concentrations were estimated and this introduces some uncertainty into the resulting BMF values.

Although the data show that D5 does not biomagnify in this food chain (as demonstrated by the low TMF and declining BMFs with increasing trophic level), the results are not so conclusive as to whether or not uptake via bioconcentration was significant or not compared with dietary exposure. The reason for this is that the contribution from the water phase cannot be fully assessed due to the lack of data on the levels of D5 in water. Although the concentrations are clearly higher in the organisms associated with the sediment, and so accumulation through sediment and diet appears to be the most likely explanation, it cannot totally be ruled out that the concentration found in these organisms is contributed to by exposure via sediment pore water or overlying water (i.e.

bioconcentration processes). This is considered further in Section 4.3.3.3. It should also be noted that many of the same mitigation processes suggested by Powell *et al.* (2009a) in relation to dietary exposure would also be relevant if significant uptake also occurred via the water phase, for example increasing metabolic capacity (or other elimination mechanisms) with increasing trophic level would equally explain the decreasing concentrations with increasing trophic level if the exposure was mainly via the water phase or via diet. In practical terms, it is not so important to determine the exact route of exposure as the BMF, TMF and BSAF will reflect the combined exposure via both water and food in this food chain.

When considering these data one final point is important. The sediment and benthic macroinvertebrates were collected at a different point in time than the fish (May 2008 versus September 2008). This introduces some uncertainties when comparing the concentrations found in fish to those found in sediment and benthic macroinvertebrates as the concentration of D5 in the sediment (and overlying water) may have been different on the two sampling occasions (for example the hydraulic residence time of the lake has been shown to vary between around 6 days (high flow) and 47 days (low flow)), and the modelling work carried out by Whelan (2009b), admittedly on a different aquatic system, indicates some seasonality in the concentration in water may occur owing to the temperature dependence of hydrolysis and volatilisation (resulting in higher concentrations in winter time and lower concentrations in late summer). However, as the fish were all sampled at the same time this finding would not affect the conclusions that can be drawn regarding the trends in concentration with trophic level in the fish samples. Indeed, when the TMF is calculated omitting the macroinvertebrates (plot not shown) the TMF is still below 1 (around 0.28 when estimated using the mean measured concentration for each species; although in this case the correlation coefficient for the plot of ln [concentration] against trophic level[23] is low (r^2 = 0.27), the slope is still statistically significant ($p<0.05$)). A 'leave one out' analysis was not performed, so the influence of any individual data point (i.e. individual species' trophic position or measured concentration) on the analysis is unknown. The placing of different species at particular trophic levels might not always reflect known ecological relationships, especially if diets differ slightly in different locations (e.g. there is some difference for the Oslofjord species depending whether they were sampled from the inner or outer estuary – see study 3 below).

As a follow-on to the Lake Pepin field study a number of mink (*Mustela vison*) from the same area have been analysed for the presence of D5 (Woodburn and Durham, 2009; Woodburn et al., 2011). The samples (three males and one female) were collected from the tributaries of Lake Pepin between the 5th and 12th November 2008. Samples of fat, liver and muscle from each individual were analysed. The stomach contents of the mink indicated that the dietary composition of the mink ranged from predominantly aquatic organisms (one of the mink) to virtually exclusively terrestrial species (two of the mink). The concentrations of D5 found in the mink ranged between 18 and 92 µg/kg lipid (mean 44 µg/kg lipid) in muscle, 6 and 88 µg/kg lipid (mean 44 µg/kg lipid) in fat and 6 and 25 µg/kg lipid (mean 15 µg/kg lipid) in liver. Comparing these concentrations with the concentrations measured in fish in Lake Pepin (Table 10) it can be seen that the lipid normalised concentrations in mink are much lower than found in the fish, providing

[23] The slope of the plot was -1.258 with a standard error of 0.553. The lower and upper 95th percentile values of the slope were -2.445 and -0.0715 respectively (equivalent to a TMF range of 0.087 to 0.93)

further evidence that although D5 can accumulate through this food chain all the way up to top predators, biomagnification does not appear to be occurring (at least for the aquatic food web; it should also be recognised that only a limited number of samples was included that may not be fully representative of all possible top predatory diets and species).

A further follow-up to the Lake Pepin study has been carried out by Powell and Seston (2011). This investigated the bioaccumulation behaviour of polychlorinated biphenyls (PCBs) in the same food chain. These substances are known to biomagnify in the environment and so it was thought that the results for these reference chemicals could be used to benchmark the information available for D4 in the same food chain. Study samples of surface sediment, zooplankton, macroinvertebrates and fish (15 species) were collected and analysed for PCBs (the study included PCB-5+8, -18, -28, -44, -52, -66, -77, -101, -105, -118, -126, -128, -138, -153, -170, -180, -187, -195, -206 and -209). The sediment and benthic macroinvertebrates were collected from four locations along a shore-to-shore transect of the lake on the 20th May 2010. The zooplankton were collected on the 4th June 2010 by horizontal tow during an obvious *Daphnia* sp. bloom and the fish were collected on 19th July 2010 by electrofishing in near-shore areas on the Minnesota and Wisconsin borders of the lake. For most fish species, only one to three animals were collected (summarised in Table 12).

The trophic level of biota was estimated based on measurements of stable isotopes of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$). In the previous study for Lake Pepin (described above) trophic levels were assigned using a trophic enrichment factor ($\Delta^{15}N$) of 3.4‰. However, when this value was used in the current study it resulted in walleye occupying a very high trophic level of 5.7, which was considered unlikely. Therefore, in addition to this value, trophic levels were also estimated using an enrichment factor of 4.642‰ (estimated assuming the trophic level separation between walleye and their diet was 1.0), 5.344‰ (estimated from the slope of a plot of $\delta^{15}N$ against relative trophic position assuming trophic levels of 2.0 for zooplankton, 3.0 for young-of-year gizzard shad, 4.1 for sauger and 4.3 for walleye) and 6.067‰ (estimated assuming the TMF for a reference material PCB was 4.65, as the mean value from the published literature).

Biota-sediment accumulation factors (BSAFs) for the PCB congeners were found to generally increase with increasing trophic level and were generally smallest in the benthic detritivores. The BSAF was also found to generally increase with the degree of chlorination in the PCB, being lowest for the least chlorinated PCBs (e.g. BSAFs were between around 0.7 to 1.1 for PCB-5+8 and PCB-18) and reaching around 11.3-15.8 for PCB-128, -138, -153, -180 and -187, before declining to around 1.1 to 3.8 for the most highly chlorinated congeners (e.g. PCB-195, -206 and -209).

The trophic level-corrected biomagnification factors were generally greatest in the species occupying the highest trophic level and followed a similar pattern to the BSAFs.

Table 12 Samples collected in the Lake Pepin PCB study

Sample	Number of samples	Trophic level			
		$\Delta^{15}N$=3.4	$\Delta^{15}N$=4.642	$\Delta^{15}N$=5.344	$\Delta^{15}N$=6.067
Surface sediment	4				
Zooplankton	4 composites	2.0	2.0	2.0	2.0
Burrowing mayfly (*Hexagenia sp.*)	4 composites	3.3	3.0	2.8	2.7
Midge (*Chironomous sp.*)	3 composites	3.4	3.0	2.9	2.8
Gizzard shad (young of year) (*Dorosoma cepedianum*)	1 composite	3.8	3.3	3.2	3.0
Bluegill sunfish (*Lepomis macrochirus*)	3	4.1	3.5	3.3	3.2
Emerald shiner (*Nitropis atherinoides*)	1	4.3	3.7	3.4	3.3
Common carp (*Cyprinus carpio*)	3	4.3	3.7	3.5	3.3
Gizzard shad (*Dorosoma cepedianum*)	1	4.6	3.9	3.6	3.5
Shorthead redhorse (*Moxostoma macrolepidotum*)	3	4.7	4.0	3.7	3.5
Quillback carpsucker (*Carpiodes cyrinus*)	2	4.7	4.1	3.8	3.6
Freshwater drum (*Aplodinotus grunniens*)	3	4.8	4.1	3.8	3.6
River carpsucker (*Carpiodes carpio*)	3	4.9	4.1	3.8	3.6
Black crappie (*Pomoxis nigromaculatus*)	4	5.0	4.2	3.9	3.7
White bass (*Morone chrysops*)	3	5.1	4.3	4.0	3.7
Silver redhorse (*Moxostoma anisurum*)	3	5.1	4.3	4.0	3.8
Smallmouth bass (*Micropterus dolomieu*)	3	5.2	4.3	4.0	3.8
Largemouth bass (*Micropterus salmoides*)	3	5.3	4.4	4.1	3.7
Sauger (*Sander Canadensis*)	3	5.4	4.5	4.2	3.9
Walleye (*Sander vitreus*)	2	5.7	4.7	4.4	4.1

TMF values were generally above one (range 1.5 to 5.1), but a few congeners did show TMF values below one including PCB-5+8, -18, -77, -126, -195 and -209. These were estimated using a $\Delta^{15}N$ of 6.067‰ as this was thought to be most appropriate to this food chain (it was estimated by calibrating the food chain to the known value for the reference chemical). However, it was noted that the value of $\Delta^{15}N$ chosen has a large impact on the estimated trophic level position and subsequent TMF calculation. Although this is the case, the $\Delta^{15}N$ effectively defines the "length" of the food chain in terms of the trophic

levels covered and it does not affect whether the TMF derived is above one (concentrations increasing with trophic level) or less than one (concentrations decreasing with trophic level) and so similar results were obtained when the other $\Delta^{15}N$ were considered. The study showed that, for the majority of PCBs considered, the TMF was greater than one in the Lake Pepin food chain, which contrasts with the situation for D5.

Powell (2012b) reports that when the TMF for D5 for Lake Pepin is calculated using a $\Delta^{15}N$ value of 6.067‰ to define the trophic levels for the species, the TMF value obtained is 0.2. Other estimates for the TMF of D5 for this food chain, benchmarked against PCB-180, are 0.1 (Powell *et al*., 2012) and 0.07 (Powell *et al*., 2011). These analyses are currently available as platform presentations and few details are given so the reasons for the different estimates are not clear. However, they all suggest that the TMF for D5 in this food chain is below one.

2. A second field study investigating the bioaccumulation of D5 has been carried out in Lake Opeongo, Algonquin Park, Canada (Powell *et al.*, 2009b and 2010a). Lake Opeongo is around 250 km north of Toronto (45°42'N 78°24'W) and is considered to be relatively remote from major population centres. The lake is oligotrophic and has a surface area of 58.6 km^2, a maximum depth of 49.4 m and a mean depth of 14.6 m. The lake is free from potential sources of D5 resulting from sewage and runoff, although there is recreational camping and canoeing in the area. Samples of surface sediment, sediment cores and zooplankton were collected on the 2nd and 3rd October 2007 and samples of yellow perch (*Perca flavescens*), cisco (*Coreogonus artedi*) and lake trout (*Salvelinus namaycush*) were collected on the 26th to 31st October 2007. The sediment and zooplankton were collected at representative locations throughout the lake, whereas the fish were sampled from the southern arm of the lake only (the exact locations were not given). Zooplankton were known to represent a significant fraction of the diet for the forage fish (e.g. small yellow perch and cisco) and these fish were thought to be a significant fraction of the diet for lake trout (Martin and Fry (1972), Vander Zanden and Rasmussen (1996) and Vander Zanden *et al.* (1999 and 2000)).

   With the exception of the fish, the sampling procedure included field quality control samples which enabled contamination during collection, handling and subsequent analysis to be assessed. However it was not possible to include field quality control samples for the fish samples and, although precautions were taken to avoid contamination (for example the personnel carrying out the sampling were instructed to refrain from using personal care products), it was not possible to assess the extent of contamination of the fish samples that may have occurred in the field and subsequent handling. In particular, CES (2010a) notes that the predatory species (lake trout) and the forage species (yellow perch and cisco) were collected on two separate days by two separate field crews. Furthermore the lake trout were subject to greater handling in the field (as they were measured for length and weight) compared with the forage species.

   The concentrations of D5 measured in the samples are summarised in Table 13. A variable instrumental blank response was seen (presumably originating from the laboratory reagents used in the analytical procedure) in all analyses which made detection and accurate quantification in the samples difficult. All of the concentrations reported were corrected for this background contamination but the variability in the background contamination introduced some uncertainty into the data. The method detection limit in all samples ranged from 1.8 to 3.1 µg/kg wet weight. The following points should be

noted in relation to the concentrations found and the limit of detection (LOD), method detection limit (MDL) and limit of quantification (LOQ):

- For sediment and zooplankton the levels of D5 were all less than the LOD. The concentration present was assumed to be equal to the LOD divided by the sample mass that was analysed.
- For yellow perch, the concentration of D5 was less than the LOD in one out of seven fish and above the LOD but below the MDL in the remaining six fish.

Table 13 Accumulation of D5 in the Lake Opeongo food chain

Sample	Number of samples analysed	Trophic level	Mean measured D5 concentration (±standard error)	
			µg/kg wet weight	µg/kg lipid
Surface sediment	9 (2 sediment cores and 7 surface sediments)		[1.35±0.04][3]	[124±7.8][1, 3]
Zooplankton	3 pooled samples	2.0[2]	[2.02±0.19][3]	[50.6±4.9][3]
Cisco	7 composite samples and individuals	3.0	3.40±0.22	70.3±4.5
Yellow perch	7 composite samples and individuals	3.1	(1.38±0.29)[4]	(3.3±7.1)[4]
Lake trout	5 individuals	3.7	12.7±2.37	166±35

Note: 1) Sediment concentrations are expressed on a total organic carbon basis rather than a lipid basis.
2) No $\delta^{15}N$ data were available. Zooplankton was assumed to be in trophic level 2.
3) Values in square brackets are where the measured concentrations were below the limit of detection (LOD). Here the concentration was estimated to be equal to the limit of detection divided by the sample mass that was analysed.
4) Values in round brackets are concentrations that were above the limit of detection (LOD) but below the method detection limit (MDL) and are reported as the actual concentration found.

The trophic level of each species was determined using $\delta^{15}N$ values. In this case the trophic level was determined relative to the $\delta^{15}N$ value for cisco, which was assumed to be in trophic level 3. The trophic level data are summarised in Table 13.

Based on the lipid normalised data, Powell *et al.* (2010a) estimated predator-prey BMF values[24] for lake trout-perch and lake trout-cisco by bootstrap analysis using Monte-Carlo simulation. The mean BMFs estimated were 5.2 (95 per cent confidence interval 3.0 to 8.6) for the lake trout-perch relationship and 2.3 (95 per cent confidence interval 1.5 to 3.5) for the lake trout-cisco relationship. The bootstrap analysis indicated that there was a high probability that the BMF values were above 1.

[24] These were defined as the concentration in predator (on a lipid normalised basis)/concentration in prey (on a lipid normalised basis) and assume that the diet of predator (in this case lake trout) consisted solely of the single prey species.

The source of D5 in Lake Opeongo is unknown. Powell *et al.* (2010a) considered it likely that the main source was from personal care products of people using the lake for recreational purposes, although atmospheric transport could not be ruled out. Powell *et al.* (2010a) considered that such recreational use would lead to D5 entering the water column and that accumulation in the food chain would be driven by bioconcentration processes combined with dietary exposures. Thus the pattern of accumulation seen in Lake Opeongo appears to differ from that seen in Lake Pepin, with uptake in the latter appearing to be driven by accumulation from sediment and the food chain according to the authors.

Overall the data for Lake Opeongo suggest that uptake via water exposure is important in this food chain, and that the BMFs for a top predator are greater than 1, implying biomagnification is occurring. However it should be recognised that there are some significant uncertainties with the Lake Opeongo study. These are summarised below.

- The levels found in some parts of the food chain were less than the analytical detection limit.
- There was a relatively high (and variable) analytical background contamination.
- The quality control program for the fish sampling did not allow the extent of contamination during sampling and handling to be assessed. As noted earlier, lake trout were subject to greater handling in the field than both yellow perch and cisco, so there is a possibility that the statistically significantly higher ($p<0.01$) concentrations in this species were caused to some extent by contamination.

To address these uncertainties, Powell *et al.* (2010a) indicated that it was intended that further fish would be sampled (using an appropriate quality control program) and analysed under laboratory conditions that have recently been optimized to minimise and better control the laboratory background contamination. However CES (2010b) indicates that this is now not possible owing to analytical sensitivity issues associated with samples from this system coupled with the increased difficulty in transporting samples from Canada into the United States. As a result of this, CES (2010b) reported that other lakes were being evaluated as a substitute for Lake Opeongo. The criteria being used for selection of a suitable lake include that the lake must receive some waste water effluent and the food web in the lake must be comparable to that in Lake Opeongo (i.e. a pelagic food chain consisting of zooplankton, cisco and lake trout). However, no further studies have been performed yet.

3. A further field study investigating the bioaccumulation potential of D5 has been carried out for the aquatic marine food chain of inner and outer Oslofjord, Norway (Powell *et al.*, 2009c and 2010b). The samples analysed included surface sediment, zooplankton, benthic macroinvertebrates (three species, three genera, three families), shellfish (four species, three genera, two families) and finfish (14 species, 13 genera, seven families). The samples were all collected between the 12th and 14th November 2008 and the trophic level of each species was determined based on $\delta^{15}N$ measurements relative to that of zooplankton (assuming that the trophic level of zooplankton was 2).

The study included a quality control program that investigated the possible contamination of the samples during sampling and analysis. This included field quality control samples for fish (but not sediments, zooplankton and macroinvertebrates) and a rigorous laboratory quality control program. The field crew refrained from using any personal care products during the collection of the samples.

Atlantic cod (*Gadus morhua*) were found to occupy the highest trophic level (TL ~4) and investigation of the gut contents indicated that they were feeding exclusively on shrimp at the time of collection (the gut contents of the other fish species were not evaluated). Analysis of carbon flows (based on ^{13}C-measurements) in the food chain suggested that the trophic dynamics in Oslofjord were best described as representing a compressed food web that was dominated by a benthipelagic food chain. The dominant species in this food chain were identified and the analysis of the data concentrated on these dominant species.

The lipid-normalised concentrations of D5 were found to be highly variable across species and the levels found were generally higher in samples from the inner Oslofjord than the outer Oslofjord. Fish can presumably move between the two locations, although the extent to which this occurs in the sampled species' populations is unknown. The concentrations found are summarised in Table 14.

It was found that the concentrations of total cyclic volatile methyl siloxanes (cVMS, i.e. D4, D5 and D6) were typically greatest in the lowest trophic levels species (such as benthic macroinvertebrates and zooplankton) and decreased with increasing trophic level, with the lowest concentrations being found in the highest trophic level (e.g. Atlantic cod).

^{13}C-measurements in the various organisms were used to determine the food web dynamics operating in both the inner and outer Oslofjord. Based on similarities in the ^{13}C-signatures the various species were assigned to one of four food chains[25]. The dominant food chain[26] was found to include 14 of the 22 species in the study and the trophic magnification factors (TMFs) for this dominant food chain were derived using the lipid normalised concentration data. The TMFs derived for D5 are summarised in Table 15.

The TMF was below 1 for both the inner and outer Oslofjord. Powell *et al.* (2010b) indicated that future work will include better identification and characterisation of the Oslofjord food web so that TMFs can be calculated for all appropriate food chains. CES (2010b) reports some preliminary results from this further work. A pelagic-dominated food chain has been identified for the Inner Oslofjord based on ^{13}C-signatures (a similar food chain could not be identified for the Outer Oslofjord owing to an insufficient number of species). Atlantic cod were again found to occupy the highest trophic level in this pelagic food chain. The mean TMF for D5 in this pelagic food chain was 0.4 with a

[25] Based on a significant difference in the signature compared with that for Atlantic cod, northern shrimp and Atlantic herring.

[26] The dominant food chain consisted of worms, sea urchin, mussel (species A and B), jellyfish, northern shrimp, European whiting, haddock, European plaice, long rough dab, common sole, Vahl's eelpout, poor cod and Atlantic cod.

probability of 1 per cent that the TMF was greater than 1 (estimated using Monte-Carlo simulation with bootstrap analysis). This is comparable with the TMF of 0.3 (with a probability of 0 per cent that the TMF was greater than 1) estimated in Table 15 for the benthic dominated food chain. No further details of this analysis are currently available.

Table 14 Concentrations of D5 measured in Oslofjord

Species	Inner Oslofjord				Outer Oslofjord			
	Number of samples	Trophic level	Concentration (±standard error)		Number of samples	Trophic level	Concentration (±standard error)	
			µg/kg wet weight	µg/kg lipd[1]			µg/kg wet weight	µg/kg lipd[1]
Sediment (0-1 cm depth)	7		149±27	16,930±2,390	5		3.7±1.1	425±130
Sediment (1-2 cm depth)	8		137±21	14,510±2,300	6		2.9±0.4	394±62
Blue mussel (*Mytilus edulis*)	5	1.5	69.8±33.2	5,333±1,303				
Sea urchin (*Brissopsis lyrifera*)					3	2.1	13.3±2.4	4,159±761
Worms	1	1.7	553	172,777	1	2.1	4.0	1,254
Jellyfish	1	2.0	6.7	1,195	1	2.2	0.4	65
Plankton	1	2.0	368	49,594	1	2.2	10.1	928
Mussels (species A)	2	2.6	39.3±11.5	4,468±277	3	3.1	14.1±0.2	1,029±55
Mussels (species B)	2	2.8	208.1±43.7	34,137±18,322	3	3.0	4.3±0.1	537±50
Atlantic herring (*Clupea harengus*)	6	3.0	1,407±347	18,379±3,113				
Northern shrimp (*Pandalus borealis*)	6	3.0	107±11	3,723±319	6	3.0	17.7±5.6	495±105
European plaice (*Pleuronectes platessa*)	6	3.1	1,435±27	28,136±2,936	5	3.4	49.0±14.5	1,884±402
Coalfish (*Pollachius virens*)	6	3.3	115±32	4,799±1,208	6	3.6	9.7±3.2	156±15
Common sole (*Solea vulgaris*)					3	3.4	28.8±7.4	531±84
Norway pout (*Trisopterus esmarkii*)	6	3.3	710±141	8,951±996	10	3.5	22.3±3.4	308±32

Species	Inner Oslofjord				Outer Oslofjord			
	Number of samples	Trophic level	Concentration (±standard error)		Number of samples	Trophic level	Concentration (±standard error)	
			µg/kg wet weight	µg/kg lipd[1]			µg/kg wet weight	µg/kg lipd[1]
European hake (*Merluccius merluccius*)	4	3.4	784±387	25,832±10,098				
Starry skate (*Amblyraja radiate*)					3	3.5	27.6±11.1	1,020±366
Haddock (*Melanogrammus aeglefinus*)	4	3.8	214±51	4,429±882	12	3.7	5.3±1.3	159±30
European whiting (*Merlangius merlangus*)	6	3.8	87.5±16	7,105±839				
Long rough dab (*Hippoglossoides platessoides*)	6	3.8	386±82	19,806±4,664	6	3.6	7.8±1.0	304±28
Vahl's eelpout (*Lycodes vahlii*)	6	3.8	31.7±8.7	3,121±612				
North Atlantic Pollock (*Pollachius pollachius*)	6	3.8	1,159±487	26,106±9,645				
Poor cod (*Trisopterus minutus*)	6	3.8	43.4±14.1	1,455±176				
Atlantic cod (*Gadus morhua*)	6	4.0	61.7±19.5	2,026±265	6	4.1	11.5±5.4	223±62

Note: 1) The concentrations in sediment are µg/kg organic carbon.

In addition to the TMFs, Powell *et al.* (2010b) also determined biomagnification factors (BMFs) for various predator-prey interactions. The BMF values determined for D5 were 0.7-0.9 for Atlantic cod-shrimp (probability of a BMF >1 was 13-30 per cent) and 0.2 for Atlantic cod-herring (probability of a BMF >1 was 0 per cent). The data are also summarised in Table 15.

It should be noted that the BMFs were not corrected for differences in trophic level in this case as both predator-prey relationships were separated by a single trophic level step.

Powell *et al.* (2010b) concluded that the data show that biomagnification of D5 was not occurring in this food chain. It is noted that the number of samples was small.

Table 15 Trophic magnification factors (TMF) and biomagnification factors (BMFs) for D5 in Oslofjord

Food web grouping	Location	Derived accumulation factor[3]
Dominant food chain[2] trophic magnification factor	Inner Oslofjord	Mean TMF = 0.3[1] (95% confidence interval 0.1 to 0.4; probability TMF >1 0.0%; mean fit of regression model (r^2) 45%)
	Outer Oslofjord	Mean TMF = 0.4 (95% confidence interval 0.2 to 0.7; probability TMF >1 0.0%: mean fit of regression model (r^2) 41%)
Atlantic cod-shrimp biomagnification factor	Inner Oslofjord	Mean BMF = 0.7 (95% confidence interval 0.3 to 1.5; probability BMF>1 13%)
	Outer Oslofjord	Mean BMF = 0.9 (95% confidence interval 0.2 to 2.8; probability BMF>1 30%)
Atlantic cod-herring biomagnification factor	Inner Oslofjord	Mean BMF = 0.2 (95% confidence interval 0.1 to 0.4; probability BMF>1 0%)
	Outer Oslofjord	No estimate possible

Note: 1) The TMF were calculated based on regression analysis of the long transformed lipid normalised concentration against trophic level.

2) The dominant species present in the food chain were identified based on ^{13}C flows.

3) Variability associated with the TMF and BMF was evaluated by bootstrap analysis using Monte Carlo simulation.

4. Borgå (2012) reports the results of a further study investigating the TMF for D5. This study was carried out on a pelagic food web in Lake Mjøsa in Norway (60°53'N, 10°41E). The lake is 117 km long, 14 km wide with an average and maximum depth of 153 m and 453 m, respectively. The lake is situated in an agricultural area and there is also some industrial activity. The top predator in the food chain is brown trout (*Salmo trutta*) and the food chain has been studied previously for other contaminants.

   The samples included in the study were zooplankton from the epilimnion (predominantly *Daphnia galeata*) and hypolimnion (predominantly copepods *Limnocalanus macrurus*), *Mysis relicta* from the hypolimnion and the following fish species, vendace (*Corogonus albula*) smelt (*Osmerus eperlanus*) and brown trout (*Salmo trutta*). The zooplankton

samples along with *Mysis relicta* samples were collected mid-lake near to Skreia on either the 22nd September 2010 or 27th September 2010 and the fish samples were collected either in the northern part of the lake (smelt) or near to Skreia (vendace and trout) between 11th September and 19th October 2010. As all three fish species are pelagic, Borgå (2012) assumed that the influence of sampling location on contaminant exposure would be negligible.

Precautions were taken during the sampling and subsequent analysis of the samples to avoid inadvertent contamination of the samples. The measures taken included avoidance of use of personal care products for 24 hours prior to sampling, collection of field blanks during sampling and analysis of procedural blanks, field blanks and an internal matrix control sample (herring homogenate) with each set of eight samples along with duplicate analysis of three brown trout and two vendace samples. The limit of quantification was set to the mean plus ten times the standard deviation of the procedural blanks. The results were not blank corrected (samples that contained less than five times the corresponding field blank were considered to be below the limit of quantification). The trophic level of the samples was assigned based on $\delta^{15}N$ measurements and $\delta^{13}C$ measurements were used to identify whether the carbon source to the food web was predominantly from the same source for all organisms studied. A number of chlorinated and brominated compounds[27] were also analysed in the samples as benchmark substances.

The concentration of D5 was found to be above the limit of quantification in all samples except for the four samples of zooplankton from the epilimnion. The amount of D5 in field blanks was generally low compared with the concentrations in the samples. The results are summarised in Table 16.

Table 16 Accumulation of D5 in the Lake Mjøsa food chain

Sample	Number of samples analysed	Trophic level	Concentration range (µg/kg wet weight)	Mean lipid normalised D5 concentration (µg/kg lipid) (±standard deviation)[a]
Zooplankton (predominantly *Daphnia galeata*) - epilimnion	4 pooled samples[b]	2.0	<2.8-<4.2	<1,210
Zooplankton (predominantly *Limnocalanus macrurus*) - hypolimnion	4 pooled samples[b]	2.7	30.6-49.4	3,600
Mysis relicta - hypolimnion	4 pooled samples[b]	2.6	10.8-14.6	630
Vendace	5 muscle samples[b]	3.6	45.5-214	3,200 (±650)
Smelt	5 muscle samples	4.1	123-199	18,700 (±2,700)
Brown trout	5 muscle samples[b]	4.2	8.7-194.5	4,000 (±1,480)

Note: a) Standard deviations were not reported for the zooplankton or *Mysis relicta* samples.
b) Two samples were analysed in duplicate for vendace and three samples were analysed in triplicate for brown trout. The zooplankton and *Mysis* samples were considered as pseudoreplicates. To

[27] PCB-153 (2,2',4,4'5,5'-hexachlorobiphenyl); PCB-180 (2,2',3,4,4',5,5'-heptachlorobiphenyl); p,p'-DDE (p,p'-dichlorodiphenyldichloroethylene); BDE-47 (2,2',4,4'-tetrabromodiphenyl ether); BDE-99 (2,2',4,4',5-pentabromodiphenyl ether).

maintain the statistical power of the analysis, each sample was weighted by √n (where n is the number of replicates) as the precision of the estimates increases with the square root of the group size.

The $\delta^{13}C$ measurements demonstrated that the organisms in the food web were predominantly feeding on a carbon source from a similar origin (the authors considered that they were indicative of a predominantly pelagic food chain) and the trophic level assignments were consistent with known feeding relationships in the food web. Borgå *et al.* (2012) considered that trout feed predominantly on smelt and some vendace. Smelt were thought to feed predominantly on *Mysis* and zooplankton with an increasing degree of cannibalism when the fish are larger than 10 cm (the fish sampled in this study were 20.5-23.7 cm in length). Vendace were thought to feed mainly on zooplankton. For the invertebrates, *L. macrurus* is omnivorous and feeds on algae and zooplankton, *D. galeata* feeds predominantly on algae and *Mysis relicta* feeds predominantly on water fleas.

The TMF was estimated from a regression of the lipid normalised concentrations[28] against trophic level (the zooplankton from the epilimnion were included in this regression). This gave a TMF of 2.28 for D5 (95 per cent confidence interval 1.22-4.29, p=0.013, R^2=0.33). The TMF for D5 was found to be sensitive to which of the higher trophic level species were included in the regression. When smelt were excluded, the TMF was estimated to be 1.62 (95 per cent confidence interval 0.96-2.72, p=0.066, R^2=0.28) and the regression was no longer statistically significant (p >0.05). When brown trout were excluded, the TMF was estimated to be 3.58 (95 per cent confidence interval 1.82-7.03, p=0.0016, R^2=0.61). It is relevant to note that the smelt were collected from a different area of the lake than the other fish (four specimens from one location and a fifth from another) and so could potentially have been exposed to different concentrations of D5 than the other species. However, as noted above, Borgå *et al*. (2012) assumed that as these fish species are pelagic and cover large areas in search of food, the influence of sampling location on contaminant exposure would be negligible. If the smelt are excluded from the analysis, the TMF is still estimated to be above one (although not at 95% certainty that it is above one).

The TMFs for the benchmark substances for the whole food web were 4.9 for PCB-153, 6.01 for PCB-180, 3.90 for p,p'-DDE, 5.82 for BDE-47 and 2.43 for BDE-99.

It is important to note that the number of samples analysed in this study was relatively small (four to five per species). Furthermore, the fish concentrations were determined from muscle samples rather than whole fish, and the relationship between the two is unknown. However, in another study from Japan (SIAJ, 2011; see below) the wet weight concentration in whole fish samples (pale chub, common carp, yellowfin goby, flathead mullet and Japanese seabass) tended to be higher than in the edible part of the same fish. These factors introduce some further uncertainty into the results from this study.

Overall the Borgå *et al*. (2012) study provides evidence that the TMF for D5 in this pelagic food chain could be above 1, and the results are reasonably consistent with the data from Lake Opeongo reported above. This suggests that the bioaccumulation pattern

[28] For the fish samples analysed in duplicate and the samples of zooplankton and *Mysis* (which were considered as pseudoreplicates) the calculation of TMF was based on the mean concentration of D5. In the statistical analysis the influence of each species was weighted by the square root of the number of samples as the precision of the estimates increases with the square root of their group size. This was considered by Borgå *et al*. (2012) to be a conservative approach to maintain statistical power of the analysis.

may differ between food chains driven mainly by bioconcentration processes (where exposure may be mainly via the water column) and those driven mainly by dietary transfer from sediment (as appears to be the case for the Lake Pepin and Oslofjord field studies).

5. A preliminary study into the bioaccumulation of D5 in a pelagic marine food web in Tokyo Bay is reported by Powell (2012). The study incorporated two PCB congeners as a reference chemical (PCB-153) and a benchmark chemical (PCB-180). The samples used in the study were collected between October and November 2011. The aim was to generate information to guide the experimental design of a subsequent five-year monitoring program to be conducted in Tokyo Bay. The samples consisted of sediments and the following fish species: adult Japanese sea bass (*Lateolabrax japonicus*), adult red barracuda (*Sphyraena pinguis*), adult chub mackerel (*Scomber japonicus*), adult and juvenile dotted gizzard shad (*Konosirus punctatus*), juvenile Japanese anchovy (*Engraulis japonicus*), juvenile Japanese scaled sardine (*Sardinella zunasi*) and juvenile white croaker (*Pennahia argentata*).

   Surface sediment samples (top 1 cm) were collected from 20 locations within the study area (approximately 500 km^2, sampled across the bay and about 30 km seaward) using a stratified random sampling design. Samples of fish were collected by commercial fishermen from the same study area. Powell (2012) indicates that a rigorous quality control program was followed which included reference samples, control samples and blank samples to verify that the samples were not contaminated by sample storage and processing procedures (although it is not entirely clear if this extended to the sampling by the commercial fishermen themselves).

   The fish sampled were pelagic with the exception of white croaker (benthopelagic) and Japanese sea bass (demersal). The carbon isotopic signature ($\delta^{13}C$) indicated that all of the fish were feeding on the same or a similar carbon source but that this was different from that of the sediment. Therefore it was considered that the biota samples were representative of a pelagic food chain. Trophic levels for the biota were assigned based on $\delta^{15}N$ measurements assuming a trophic enrichment factor ($\Delta^{15}N$) of 3.2 (this value was estimated by defining the TMF of the benchmark chemical PCB-180 as 4.0 and using this to calibrate the food web, i.e. the $\Delta^{15}N$ value chosen is that which results in a TMF of 4 for PCB-180).

   The sediment measurements showed a concentration gradient for D5 (no data were presented on the levels of PCB-153 and PCB-180 and so it is not clear whether the reference substance and benchmark substance were also subject to a concentration gradient in the study area), indicating that exposure of the organisms may vary within the study area. Powell (2012) considered that as most of the fish sampled were pelagic these would actively move throughout the study area and so the impact of variable exposure would be minimal for these species. However, Powell (2012) noted that the Japanese sea bass was a demersal species that does not migrate as actively as other species and so it could be exposed to higher concentrations compared with other organisms in the sampled foodchain. To correct for this, the BSAF was used to correct the BMF and TMF for variable exposure based on the relationship that $TMF_{LIPID}=TMF_{BSAF}$ and $BMF_{LIPID}=BMF_{BSAF}$. The exact method used to carry out these corrections was not given in the paper. Furthermore, these corrections appear to have been applied only to the siloxane and not the reference and benchmark chemicals. (Powell (2012) noted that

concentration gradients resulting from point source emissions are generally not a significant concern for chemicals with diffuse emissions such as PCBs; however, as noted above there were no data reported for these two substances for sediment to check that this was the case).

The sediment measurements showed a concentration gradient for D5 (no data were presented on the levels of PCB-153 and PCB-180 and so it is not clear whether the reference substance and benchmark substance were also subject to a concentration gradient in the study area) indicating that exposure of the organisms may vary within the study area. Powell (2012a) considered that as most of the fish sampled were pelagic these would actively migrate throughout the study area and so the impact of variable exposure would be minimal for thse species. However, Powell (2012a) noted that the Japanese sea bass was a demersal species that does not migrate as actively as other species and so it could be exposed to higher concentrations compared with other organisms in the sampled foodchain. In order to correct for this, the BSAF was used to correct the BMF and TMF for variable exposure based on the relationship that $TMF_{LIPID} = TMF_{BSAF}$ and $BMF_{LIPID}=BMF_{BSAF}$. The exact method used to carry out these corrections was not given in the paper. Further, these corrections appear to have been applied only to D5 and not the reference and benchmark chemicals (Powell (2012a) noted that concentration gradients resulting from point source emissions are generally not a significant concern for chemicals with diffuse emissions such as PCBs; however as noted above there were no data reported for these two substances for sediment in order to check that this was the case).

The sediment sampling design allowed mean concentrations (and hence BSAF values) to be calculated for each section of the study area (the study area was divided into four sections based on the gradient of D5 concentrations observed).

The concentrations reported in the sediment and biota samples are summarised in Table 17. The sediment concentrations are reported as µg/kg wet weight values but no units are given in the Powell (2012a) paper for the biota samples. For Table 17 it has been assumed that they are also µg/kg wet weight values. The corresponding concentrations on a lipid weight or organic carbon weight basis have been estimated from the information on organic carbon and lipid contents given in the paper.

The BSAF, BMF and TMF values derived by Powell from the data are summarized in Table 18. In all cases mean values, 95% confidence intervals and the probability that the value was greater than one were estimated by bootstrap analysis using Monte Carlo simulation.

For the BSAF, values above one were obtained for D5 only for the juvenile Japanese scaled sardine (mean BSAF 1.4 g organic carbon/g lipid; probability of value being above one was 71%). No BSAF values were calculated for the two PCB reference substances.

For the BMF, values of one were obtained for D5 for both the red barracuda – white croaker and red baraccuda – juvenile dotted gizzard shad feeding relationships (the probability that the value was greater than one was 35 and 37 per cent, respectively). The remaining BMF values for the predator – prey interactions considered were all below one. For comparison, the BMF values obtained for PCB-153 and PCB-180 were in the range 3.5-8.9 and 3.9-10, respectively, for the four sea bass – prey interactions (BMFs were not calculated for other predator – prey interactions).

Table 17 Concentrations of D5 in the Tokyo Bay food chain

Sample	Number of samples analysed	Lipid/ organic carbon content (%)	Trophic level	Mean measured D5 concentration (±standard deviation)	
				µg/kg wet weight	µg/kg lipid or µg/kg organic carbon
Surface sediment – Sector 1	2	0.86± 0.021		100±9.2	11,628
Surface sediments – Sector 2	6	0.93± 0.052		66±5.7	7,097
Surface sediments – Sector 3	6	0.78 ±0.36		34±19	4,359
Surface sediments – Sector 4	6	0.55 ±0.34		14±11	2,545
Dotted gizzard shad juvenile (*Konosirus punctatus*)	3 composites (each of 11 individuals)	7.9±0.76	3.0	250±16	3,165
White croaker juvenile (*Pennahia argentata*)	3 composites (each of 13 individuals)	5.9±1.0	3.1	190±13	3,220
Japanese scaled sardine juvenile (*Sardinella zunasi*)	3 composites (each of 48 individuals)	4.5±0.45	3.2	280±13	6,222
Japanese anchovy juvenile (*Engraulis japonicas*)	3 composites (each of 55 individuals)	3.9±0.42	3.5	140±7.7	3,590
Dotted gizzard shad adult (*Konosirus punctatus*)	1 composite (of 5 individuals)	17(±6.8)[a]	3.9	140(±84)[a]	823
Chub mackerel adult (*Scomber japonicas*)	1 composite (of 4 individuals)	20(±8.0)[a]	4.2	210(±120)[a]	1,050
Red barracuda adult (*Sphyraena pinguis*)	1 composite (of 5 individuals)	11(±4.4)[a]	4.2	330(±200)[a]	3,000
Japanese sea bass adult (*Lateolabrax japonicas*)	6 individuals	6.4±2.7	4.4	230±78	3,594

Note: a) The standard deviations for these samples were estimated from the 90th percentile coefficient of variation of replicate analyses of three or more samples from previous studies.

b) Estimated from the mean wet weight concentration and mean organic carbon contents given in Powell (2012a).

Table 18 Bioaccumulation parameters derived for of D5 in the Tokyo Bay food chain by Powell (2012a)

Parameter	Mean value[a]	95% confidence interval[a]	Probability the value is >1[a]	Comment
BSAF for Japanese sea bass (adult)	0.5	0.2-0.8	<1%	Units are g-total organic carbon/g-lipid
BSAF for red barracuda (adult)	0.7	0.2-1.7	15%	Units are g-total organic carbon/g-lipid
BSAF for chub mackerel	0.2	0.1-0.6	<1%	Units are g-total organic carbon/g-lipid
BSAF for dotted gizzard shad	0.2	0.1-0.5	<1%	Units are g-total organic carbon/g-lipid
BSAF for Japanese anchovy (juvenile)	0.8	0.6-1.1	5.7%	Units are g-total organic carbon/g-lipid
BSAF for Japanese scaled sardine	**1.4**	1.1-1.7	71%	Units are g-total organic carbon/g-lipid
BSAF for white croaker (juvenile)	0.7	0.5-1.1	5.5%	Units are g-total organic carbon/g-lipid
BSAF for dotted gizzard shad (juvenile)	0.7	0.6-0.8	<1%	Units are g-total organic carbon/g-lipid
BMF for Japanese sea bass – Japanese anchovy	0.6	0.1-1.1	4%	Lipid normalised[b].
BMF for Japanese sea bass – Japanese scaled sardine	0.4	0.1-0.7	<1%	Lipid normalised[b].
BMF for Japanese sea bass – white croaker	0.7	0.3-1.2	11%	Lipid normalised[b].
BMF for Japanese sea bass – dotted gizzard shad (juvenile)	0.7	0.4-1.1	9%	Lipid normalised[b].
BMF for red barracuda – Japanese anchovy	0.9	0.1-3.5	28%	Lipid normalised[b].
BMF for red barracuda – Japanese scaled sardine	0.5	0.0-1.2	6%	Lipid normalised[b].
BMF for red barracuda – white croaker	**1.0**	0.2-2.8	35%	Lipid normalised[b].

Parameter	Mean value[a]	95% confidence interval[a]	Probability the value is >1[a]	Comment
BMF for red barracuda – dotted gizzard shad (juvenile)	**1.0**	0.2-2.5	37%	Lipid normalised[b].
BMF for chub mackerel – Japanese anchovy	0.2	0.0-0.7	<1%	Lipid normalised[b].
BMF for chub mackerel – Japanese scaled sardine	0.2	0.0-0.5	<1%	Lipid normalised[b].
BMF for chub mackerel – white croaker	0.4	0.0-0.9	1%	Lipid normalised[b].
BMF for chub mackerel – dotted gizzard shad (juvenile)	0.4	0.0-0.9	1%	Lipid normalised[b].
BMF for dotted gizzard shad (adult) – Japanese scaled sardine	0.1	0.0-0.4	<1%	Lipid normalised[b].
BMF for dotted gizzard shad (adult) – white croaker	0.2	0.0-0.7	<1%	Lipid normalised[b].
BMF for dotted gizzard shad (adult) – dotted gizzard shad (juvenile)	0.2	0.0-0.7	<1%	Lipid normalised[b].
TMF – food web including Japanese sea bass	0.5	0.3-1.0	2.5%	Obtained from the slope of a plot of ln [Concentration in fish (lipid weight basis)] against trophic level.
TMF – food web without Japanese sea bass	0.5	0.2-1.1	3.5%	Obtained from the slope of a plot of ln [Concentration in fish (lipid weight basis)] against trophic level.

Note: a) Mean values, 95% confidence intervals and probabilities that the values were greater than 1 were estimated by bootstrap analysis using Monte Carlo simulation.

b) The BMF values were calculated for possible predator-prey relationships where the difference in trophic level between the two species was greater than 0.7. The values were then adjusted for this difference to effectively normalise the BMF to a trophic level difference of 1.

The TMF for D5 was calculated to be 0.5 and was independent of whether or not the data for Japanese sea bass were included or excluded from the analysis. The probability that the TMF was above one was low, at between 2.5 and 3.5 per cent. In contrast, the TMF for PCB-153 was 3.7 and the TMF for PCB-180 was 4.0 when the Japanese sea bass data

were included (no analysis was done excluding the Japanese sea bass) and the probability of the TMF being above 1 was approaching 100 per cent in both cases.

On the face of it, these data suggest that the bioaccumulation potential of D5 is much lower than PCB-153 and -180 with a TMF of 0.5, although some BSAF and BMF values are above one. However, there are a number of potential uncertainties with the way the analysis of the data was carried out that warrant further consideration. These are outlined below.

- The trophic level assignments were based on the assumption that the TMF for PCB-180 was 4.0, so the system was effectively calibrated to the benchmark chemical. This affects the magnitude of the slope of the ln [concentration] versus trophic level plot, but not whether the gradient is positive or negative. If the trophic level assignments were different, a different TMF would have been derived, but it would still be below one.

- The calculation of the the mean, 95% confidence intervals and probability of values being above one were all carried out by bootstrap analysis using Monte Carlo simulation. One of the inputs into such analysis is the standard deviation in the measured concentrations in the various species in the food web. For D5, these standard deviations were known for five of the eight species included in the food web. For the remaining three species, the standard deviations were estimated based on previous studies conducted on Lake Pepin. The standard deviations assigned are summarized in Table 17. It is evident from these data that the standard deviations for the samples where they could be measured are much smaller (typically 6-34%) than in the samples where the standard deviations were estimated (typically 57-61%). Therefore, the calculations of the statistics in the study may have been influenced more by the samples for which the standard deviation was estimated than those for which the standard deviation was known.

- The sediment levels show that there was a concentration gradient in the study area for D5. The Powell (2012a) analysis corrects for this in the BMF and TMF calculations by using the information on the BSAF values. It is not clear from the test report how this correction was carried out. In addition, and more importantly, it is not clear whether such a correction is actually appropriate. Powell (2012a) states in the report that "most of the sampled food web organisms were pelagic species that actively migrate throughout the study area feeding on nekton (free-swimming organisms), zooplankton, and phytoplankton" and it was assumed that the impact of variable exposure would be minimal for such species. The one species identified as potentially not migrating widely in the study area was Japanese sea bass. Correction for variable exposure was therefore probably not necessary for seven of the eight species in the study.

- The study assumes that there is no concentration gradient for the two PCB reference substances and so the TMF values were not corrected for this gradient in the same way as the TMF values for D5. There is no information provided to show whether or not this is appropriate.

To investigate the possible significance of some of the assumptions made by Powell (2012a) in correcting the TMF for D5, the TMF has been recalculated for the purposes of this evaluation using the concentration data and trophic level data as reported in the study but without correcting for the concentration gradient in the sediment. The results of this

analysis are shown in Figure 4 (including the data for Japanese sea bass) and Figure 5 (excluding the Japanese sea bass data). When the data are analysed in this way, a similar picture emerges in that the TMF value obtained from the slope of the regression is still below one in both cases. However, several of the BMFs for individual predator-prey interactions involving Japanese sea bass as the predator are now close to or above one. The relevant data are summarized in Table 19 and Table 20. The significance of the BMFs above one for Japanese sea bass is unclear as this species is the one most likely to be influenced by concentration gradients within the sampled area and so the values presented in Powell (2012a) would be preferred over these values. Overall, the re-analysis carried out here generally confirms that the TMF for D5 in this food chain is below one.

Figure 4 Plot of ln (concentration in fish) against trophic level for the Tokyo Bay food chain including the data for Japanese sea bass (not corrected for concentration gradient).

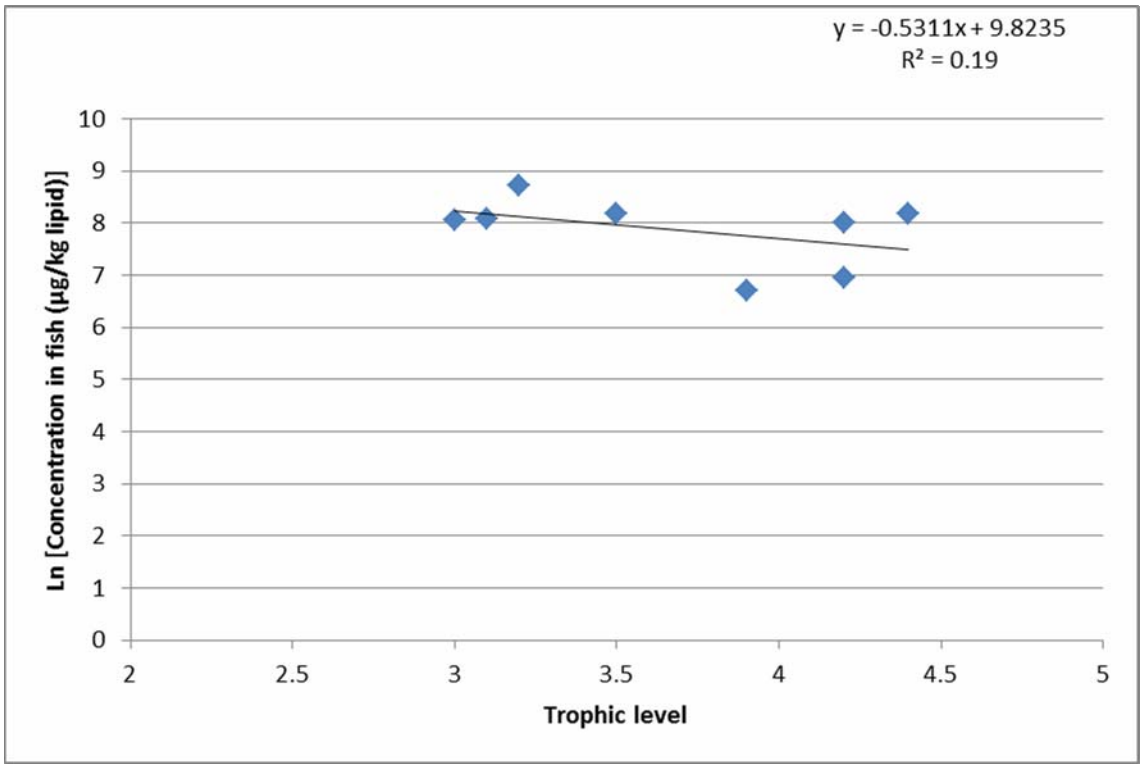


Figure 5 Plot of ln (concentration in fish) against trophic level for the Tokyo Bay food chain excluding the data for Japanese sea bass (not corrected for concentration gradient).

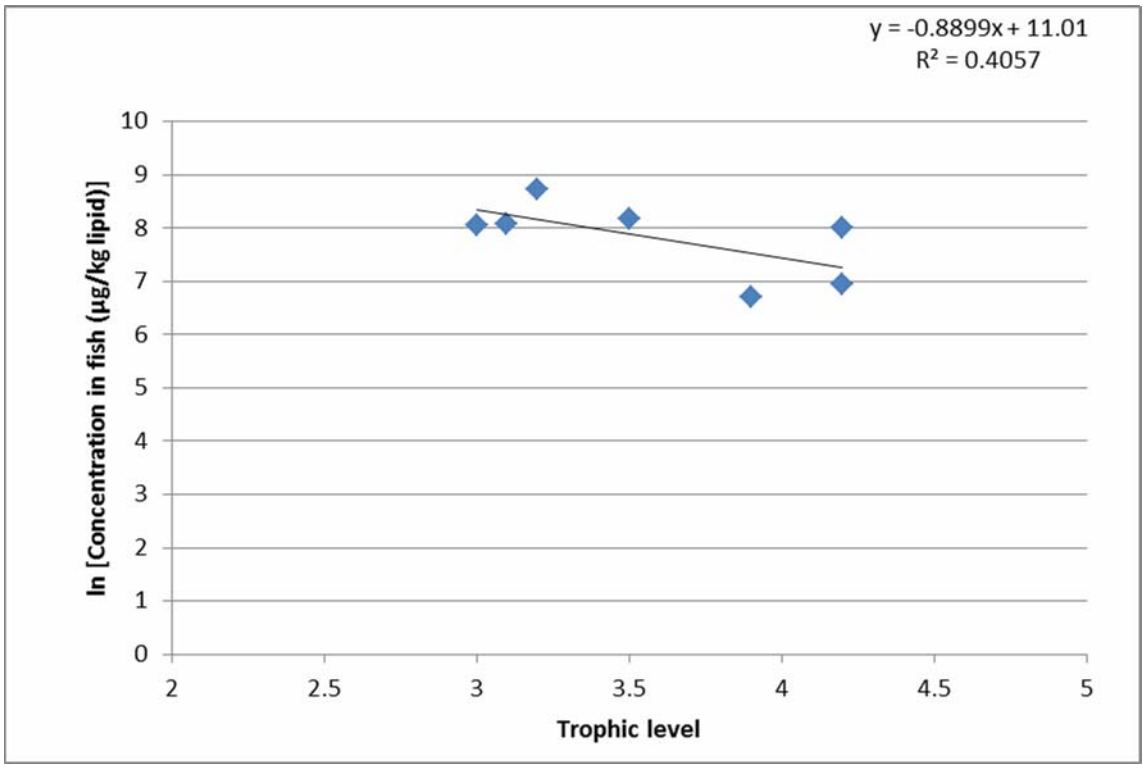


Table 19 Bioaccumulation parameters derived for of D5 in the Tokyo Bay food – BMF values reanalysed for this evaluation

Parameter	Value based on the ratio lipid normalised concentrations	Value corrected for differences in trophic levela
BMF for Japanese sea bass – Japanese anchovy	**1.00**	1.00
BMF for Japanese sea bass – Japanese scaled sardine	0.58	0.66
BMF for Japanese sea bass – white croaker	**1.12**	1.08
BMF for Japanese sea bass – dotted gizzard shad (juvenile)	**1.14**	1.10
BMF for red barracuda – Japanese anchovy	0.84	0.77
BMF for red barracuda – Japanese scaled sardine	0.48	0.52
BMF for red barracuda – white croaker	0.93	0.94
BMF for red barracuda – dotted gizzard shad (juvenile)	0.95	0.96
BMF for chub mackerel – Japanese anchovy	0.29	0.17
BMF for chub mackerel – Japanese scaled sardine	0.17	0.17
BMF for chub mackerel – white croaker	0.33	0.36
BMF for chub mackerel – dotted gizzard shad (juvenile)	0.33	0.40
BMF for dotted gizzard shad (adult) – Japanese scaled sardine	0.13	0.06
BMF for dotted gizzard shad (adult) – white croaker	0.26	0.18
BMF for dotted gizzard shad (adult) – dotted gizzard shad (juvenile)	0.26	0.22

Note: a) The values were corrected for the difference in trophic level using the equation outlined in CES, (2010a) and discussed earlier in this section. The actual method used by Powell (2012a) was not given.

Table 20 Bioaccumulation parameters derived for of D5 in the Tokyo Bay food – BMF values reanalysed for this evaluation

Food web	Parameter[a]	Value
All fish species including Japanese sea bass	Slope of plot	-0.531
	TMF	0.59
	95% Confidence interval of the slope	-1.626 to 0.564
	95% Confidence interval of the TMF	0.20 to 1.76
	p-value of slope[b]	0.28
	R2 of regression	0.19
All fish species excluding Japanese sea bass	Slope of plot	-0.890
	TMF	0.41
	95% Confidence interval of the slope	-2.128 to 0.348
	95% Confidence interval of the TMF	0.12 to 1.42
	p-value of slope[b]	0.12
	R^2 of regression	0.41

Note: a) The TMF value was estimated from the slope of a plot of ln [Concentration] against trophic level. The statistical values are derived by linear regression analysis.

b) The p-value indicates that the slope is not statistically different from zero.

In addition to the above five field studies summarised above, some preliminary results have been provided on the levels of D5 in pike (*Esox lucius*) and roach (*Rutilus rutilus*) obtained from the River Cam in the UK (van Egmond, 2012). The fish were obtained from a section of the river that receives effluent from the city of Cambridge. Two individual pike (one 30 cm in length and one 50 cm in length) and a composite sample of eight roach were analysed. The lipid content of the two pike was 0.44 per cent and 0.49 per cent and the lipid content of the roach sample was 0.62 per cent. The concentration of D5 in the roach sample was 44.7 mg/kg lipid (mean of duplicate analyses of the sample). The concentration of D5 in the pike was lower at 2.8 mg/kg lipid in one sample (mean of duplicate analyses of the sample) and 3.4 mg/kg lipid (single analysis). Thus these results show a decrease in concentration between roach and pike. The significance of this finding is unclear given the very small sample size, and questionable lipid contents (they appear to be rather low). It is therefore not considered further in this report.

When considering the available field studies that have investigated trophic magnification, the limitations of the studies should be taken into account. As noted earlier, no agreed methodology currently exists for carrying out such studies, or interpretation of the results of such studies, although it is recognised that work is now underway to address this. For the available studies for D5 (Lake Pepin, Oslofjord, Lake Opeongo, Lake Mjøsa and Tokyo Bay) it should be noted that there are limitations in terms of the sampling (in general only a small

number of samples were obtained for each species; in some cases just single samples) which introduces some uncertainty over how representative the data are for each species in the areas sampled, particularly when samples are taken at different time points or locations within the water body.

CES (2010b) and Powell (2010b) summarises the developing thinking in terms of analysis of data from such studies based on the HESI/SETAC/USEPA Expert Workshop on 'Lab to Field Bioaccumulation' that was held on the 18-19th November 2009 (now published in two publications (Borgå *et al.* (2011) and Conder *et al.* (2011)). CES (2010b) recommends that the level of uncertainty associated with the TMF value is best investigated using Monte-Carlo simulation with bootstrapping (as was done with the Oslofjord data) as this allows the probability of a TMF>1 to be estimated. In addition it was recommended that the TMF should be derived based on regression analysis across all individual samples, rather than by using the mean concentration per species as this reduces bias introduced by unequal sample sizes for each species. It is understood that in some of the available studies, although only the mean concentrations per species were generally reported in the study report, the TMF values generated in the report were derived using the individual data points rather than the species means (for example in Lake Pepin). For the Lake Mjøsa study, the influence of each species was weighted depending on the number of replicate/pseudoreplicate samples analysed (with no replicate samples appearing to be used individually). CES (2010b) and Powell (2010b) also suggest that the use of Monte-Carlo simulation with bootstrap analysis can be used to reduce the uncertainty associated with seasonal variability. However, this would imply that the distribution of concentrations is known (or could be estimated) for all species at different times of the year. This may not necessarily be the case with Lake Pepin for example, as the macroinvertebrates were sampled in May and the fish were sampled in September and so the distribution of concentrations found for each species will not contain a seasonal element.

CES (2010c) and Powell (2010b) outline a number of other possible areas of uncertainty where further work may be needed in order to better understand the derivation and interpretation of TMF values. These are briefly summarised below.

- Improved knowledge of the ecology of food webs, including guidance on the use of $\delta^{15}N$ and $\delta^{14}C$ in trophic level assignment.
- Uncertainty in field measurements resulting from potential spatial and temporal inhomogeneity in exposure and sample collection, including:
  - Unbalanced test designs (over/under representation of certain species).
  - Sample collection bias.
  - Lack of statistical power.
  - Seasonal variability of short-lived species.
  - Age variation of long-lived species.
- Different food chains (benthic versus pelagic)[29], which may give rise to:

[29] These may be relevant considerations when comparing the data from Lake Mjøsa (and Lake Opeongo) with those from Lake Pepin and Oslofjord.

  - Differences in chemical accumulation dynamics between benthic and pelagic food webs.
  - Disproportionate/different exposure levels for contaminants across benthic versus pelagic food chains.
- Multiple sources of contamination in food webs (exposure via food, water and sediment).
- Use of reference materials with known bioaccumulation properties.

The available TMF data for D5 up to 2009 (i.e. minus the Lake Mjøsa and Tokyo Bay data) were been considered at an expert panel workshop organized by the Global Silicones Counsel (Global Silicones Counsel, 2009). This workshop identified the following as sources of uncertainty and challenges associated with the interpretation of TMF values.

- Different energy requirements and biotransformation abilities between poikilotherms and homeotherms.
- Opportunistic feeders rather than specialist feeders may confound the results.
- Variations with size of a given species, particularly invertebrates.

The workshop agreed that the TMF is the "gold standard" for evaluating bioaccumulation. However it was also noted that the available data for D5 do not allow a definitive assessment of the bioaccumulation potential to be made.

A more recent evaluation of the bioaccumulation potential for D5 was carried out by a Canadian Board of Review (BOR, 2012; Gobas *et al*., 2011). This considered the data available up to around 2011 (i.e. again minus the Lake Mjøsa and Tokyo Bay data). The expert review (Gobas *et al.*, 2011) concluded that the weight of evidence was that D5 is not a bioaccumulative substance within the meaning of the Canadian Bioaccumulation and Persistence Regulations (Government of Canada, 2000). The overall conclusions of the Board of Review were that although D5 can accumulate in organisms, it does not biomagnify through the food chain.

Other measures of accumulation

A number of field studies comparing the uptake of D5 with certain benchmark chemicals have also been carried out. The results from some of these studies are currently available as poster presentations only. The available details are summarised below.

- The accumulation of D5 in the Humber Estuary, UK, has been studied by van Egmond *et al.* (2010b) and Kierkegaard (2011) (the sediment data are also reported in Hastie *et al.* (2010b) and Sparham *et al.* (2011)). Six intertidal sites in the lower estuary were sampled between 24th September and 15th October 2009. The samples of surface sediment (1-2 cm depth; 9 samples per site, three samples collected within 1 m of each of the three ragworm sampling locations at the site), ragworm (50 individuals from each of three locations at each site) and flounder (1-3 samples per location, although no flounder were obtained at one of the sites) were collected from the six locations in the estuary and were analysed for both D5 and the benchmarking chemical, 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB-180). All personnel involved in the sampling and analysis

avoided use of personal care products in order to minimise the potential for inadvertent contamination of the samples. The ragworm samples were depurated for 24 hours prior to analysis and pooled samples of 5-10 individuals were analysed. For the flounder skin-free dorsal fillets from individuals were analysed. Field blanks were incorporated into the sampling scheme in order to check for possible inadvertent contamination of the samples during collection and processing and procedural blanks and control samples were routinely analysed along with the samples. The D5 concentrations found ranged between 60 and 260 µg/kg dry weight (2,600-8,700 µg/kg organic carbon) in sediment, 51 and 760 µg/kg fresh weight in ragworm and 12 and 300 µg/kg fresh weight in flounder fillet. The highest concentrations were generally found at the sampling site in the inner estuary and the concentrations were found to decrease down the estuary. The lipid levels in biota could not be measured in many of the samples and so a "benchmarking" ratio approach, based on the ratio of the multi-media bioaccumulation factor (mmBAFs) for D5 to that of PCB-180, was used to investigate the bioaccumulation potential of D5. The mmBAF represents the fraction of the chemical present in an environment that has accumulated in an organism and is estimated as the ratio of the amount of chemical in an organism to the amount of chemical in the environment. For the current study the mmBAF ratio of D5:PCB-180 approximates to the ratio of the sediment-biota bioaccumulation factors (BSAF) for D5 to that for PCB-180 in the same sample. A total of 19 ratios for ragworms and 13 ratios for flounder were calculated from the measured data. The mean $\log_{10}$ ratio was above 0 (i.e. the bioaccumulation ratio for D5:PCB-180 was >1; the mean mmBAF for D5 was around twice that for PCB-180) indicating that D5 was bioaccumulating to a greater extent than PCB-180 in these organisms.

It should be noted that the concentration in flounder samples relates to fillet (i.e. muscle) rather than whole body, and the relationship between the two are unknown. In addition, it is not known if this relationship is the same for both D5 and PCB-180. In another study from Japan (SIAJ, 2011; see below) the wet weight concentration in whole fish samples (pale chub, common carp, yellowfin goby, flathead mullet and Japanese seabass) tended to be higher than in the edible part of the same fish. This may introduce some uncertainty into the flounder results from this study.

van Egmond (2010) has carried out a further analysis of these data. Where possible the BSAF for D5 in polychaetes was estimated on a lipid/organic carbon normalised basis. The BSAF values determined were in the range 0.6 to 4.3. Assuming a log K_{oc} of 5.2 for D5, the estimated BCF (assuming exposure was via pore water only) was in the range 2,826 to 4,656 for the polychaetes on a whole body weight basis. These BCFs estimated from the field data are around 3-8 times lower than estimated in Section 4.3.2.2 for *Lumbriculus variegatus*, suggesting that the accumulation in sediment organisms in the environment may be lower than suggested from laboratory experiments using high sediment loadings. However, it should be noted that this analysis is dependent on the K_{oc} assumed in the calculations (there may be some variation of this between different types of sediment) and the assumption that uptake is mainly via pore water.

- A similar benchmarking study has been carried out using samples from lakes in Sweden (Kierkegaard and McLachlan, 2010; Kierkegaard *et al*.,2012b). Samples of perch *Perca fluviatilis* muscle (three to five fish per lake) and surface sediments (top 5 cm, four sites per lake, 20 m apart) were collected in November to December 2009 from six lakes that

received waste water treatment plant effluent. The levels of D5 and the benchmarking chemical (PCB-180) were determined in samples and BSAFs for D5 and PCB-180 estimated. In this case the BSAFs were normalised to the lipid content of the fish and the organic carbon content of the sediment. The D5 concentrations in perch and sediment were correlated. The BSAFs for D5 ranged between 0.06 and 4.8 over the six lakes, with four values between 0.3 and 0.7. Kierkegaard and McLachlan (2010) concluded that the proximity of the normalised BSAF to one suggested that the levels of D5 in perch and sediment were close to partitioning equilibrium and indicated that extensive metabolism of D5 in perch was not occurring. The use of BSAF in this context might not be helpful, because it is not known whether the residues of D5 found in perch tissue are the result of exposure to sediment, food, water, or a combination of these.

The ratio of the normalised BSAF for D5 to that for PCB-180 was used to assess the bioaccumulation potential of D5. Kierkegaard *et al*. (2012b) presented this ratio as the multimedia bioaccumulation factor (mmBAF) for D5 (representing the fraction of the contaminant present in 1 m^2 of the whole aquatic environment that is transferred to the fish) divided by the mmBAF for PCB-180. This ratio varied between 0.2 and 3 for five of the lakes, and was just above 0.1 for the remaining lake (it was suggested that this may have been due to the fish living mainly upstream of the sewage discharge). Kierkegaard and McLachlan (2010) and Kierkegaard *et al*. (2012b) concluded that the proximity of these ratios to one indicates that the bioaccumulation of D5 in perch is similar to that of PCB-180. One reason for the variability in the ratios was thought to be a result of the variability of the D5 concentration in the sediment (concentration gradient from the point of discharge) within a given area.

- A final benchmarking study using PCB-180 has been carried out in fish from the Baltic Sea (Kierkegaard *et al.*, 2010b). The samples analysed were taken from the sample bank of the Swedish Museum of Natural History and included herring (*Clupea harengus*) (collected in 2007) and blue mussel, European flounder, perch, smelt, white fish, eelpout, turbot, cod, cod liver and grey seal (*Halichoerus grypus*) (all collected in 2008). D5 was found to be present in all ten species. The levels on a lipid weight basis were found to be lowest in the top predator (grey seal) but no clear relationship between the D5 concentration and trophic function was evident in the other species sampled. The ratio of the concentration of D5 to the concentration of PCB-180 was used to assess the biomagnification potential of D5. This ratio showed no consistent trend with trophic function among the water-breathing organisms indicating that biomagnification of D5 followed a similar trend to that of PCB-180 (the ratio was between approximately 1 and 8 across all species). However, this ratio decreased by a factor of around 80 in the grey seal compared to the median level in fish muscle, indicating that the biomagnification of D5 in seal was much lower than for PCB-180.

  Further details are provided by Kierkegaard *et al*. (2012a). Samples of seal blubber were obtained from three animals that had drowned in nets north of Västervik, Sweden in the autumn of 2008. The sub-samples were taken from parts of the tissue that had not been exposed to air or packaging material. Three herring from a nearby monitoring station that had been sampled in the same year (as part of the Swedish Marine Monitoring Program) were also analyzed. Although no special precautions had been followed during the collection and storage of the fish, dorsal muscle samples were excised without skin and measures were taken to reduce contamination during sample preparation and instrumental

analysis. Extraction of the biological samples was performed with a purge and trap method, followed by immediate GC/MS analysis. A procedural blank and a control sample were analyzed with every extraction round of eight samples. D5 was quantifiable in each of the three seal blubber samples, at a mean concentration of 18 ng/g ww (range 9–24 ng/g ww), which was similar to levels measured in seals from Danish waters (17–24 ng/g ww) by Kaj et al. (2005). Although the lipid content of the blubber samples was not available, blubber is known to consist primarily of lipid, so the wet weight and lipid normalized concentrations were considered to be the same. The lipid normalized concentrations in the herring (234 to >1,150 ng/g lw) were significantly higher than the concentration in seal blubber. The fish concentrations were similar to those measured from a larger sample collected in 2007 (mean 137 ng/g lw). Despite lack of blank correction, the small sample size and the fact that the concentrations are not based on whole body homogenates, these results suggest that D5 is a contaminant throughout the food chain, but does not biomagnify in Grey Seals (herring accounts for ~80% of the diet of Grey Seals in the Baltic food web).

Kierkegaard *et al*. (2012a) also present more detail on the levels in herring. Three fish were analysed from each of ten sites along the Swedish coast from the Baltic to the North Sea. D5 was present in every dorsal muscle sample, at a mean concentration of 137 ng/g lw (range 15 – 718 ng/g lw) (specially collected field blank samples contained quantities of D5 corresponding to 0.5–2% of the analyte quantities in the fish collected from the same site). There was considerable variation between the three individual fish from each site. The herring samples allowed the spatial trend in the concentration of D5 to be investigated. The highest levels were found in samples from the Baltic Proper (consistent with a wastewater source) with markedly lower levels in samples collected from the Swedish west coast.

When considering these data comparing the apparent accumulation of D5 with that of a reference compound, it is important to note that a similarity between the pattern seen for D5 and the reference compound does not necessarily mean that D5 accumulates by the same processes as the reference compound. This is discussed further below.

For the comparison using the biota-sediment accumulation factors (BSAF; e.g. van Egmond *et al.*, 2010b; and Kierkegaard and McLachlan, 2010) it is important to consider the underlying properties and behaviour of the substances in the environment. In this respect there are a number of important differences between D5 and the reference compound PCB-180 (as discussed in Fisk and Wilmot, 2010). These are summarised below.

- The releases of PCB-180 to the environment should have decreased (or more or less ceased) over recent years and so any substance detected probably has been in the environment for many years. This contrasts with D5 where the presence in the samples reflects current (and on-going) emissions. Furthermore, PCBs in general are known to bind to two broad types of site on sediment particles (reversible and almost irreversible), and therefore a high degree of irreversible adsorption may be expected for PCB-180, particularly in aged sediments (see Fisk and Wilmot (2010) for further discussion). In contrast to this, the adsorption of D5 is thought to be reversible with little or no effect of ageing. This results in an important distinction between PCB-180 and D5 as it would be expected that PCB-180 may be associated with deeper sediments but can be found in surface sediments as a result of disturbance, etc.,

whereas D5 would be expected to occur in newly deposited sediments and interstitial water.

- The consequence of this is that the exposure of organisms through sediment is likely to be predominantly via ingestion for PCB-180 as little or no substance would be expected to be present in interstitial water, whereas the exposure to D5 would be expected to be via both ingestion and interstitial water.

- As the actual BSAF value is a combination of all routes of exposure it is not possible to infer from the data that the accumulation potential of D5 through any one route (e.g. diet) is similar to that for PBC-180. However, it can be inferred that the net result of all routes of exposure would lead to similar concentrations in the organism for D5 and PCB-180 for a given concentration in sediment.

- A similar situation arises when considering the Kierkegaard *et al.* (2010b) results. Here the concentration in any one organism depends again on the combined exposure via all routes (food, water and possibly direct ingestion of sediment) and these are likely to be very different for D5 compared with PCB-180. Furthermore, in this case, as only the relative concentrations in the fish are used for the comparison (with no indication of the relative exposure), it is not possible to infer anything about the overall magnitude of accumulation of D5 compared with PCB-180. The constancy of the ratio of the concentration of D5 to PCB-180 in the fish that were sampled does indicate that the net result of all possible processes for D5 results in a similar pattern of accumulation as PCB-180 across the fish species (and indeed shows a marked difference in accumulation between D5 and PCB-180 in the seals). However, it is not possible to infer the actual magnitude of the overall accumulation factors (e.g. BMF, TMF, etc.) for D5, nor the routes of exposure (bioconcentration versus uptake from food, etc.) from this comparison.

  A preliminary further analysis of the data from the Kierkegaard *et al.* (2010b) study has been carried out by Woodburn *et al.* (2010). The approximate D5/PCB-180 concentration ratios were interpolated from the plots in the original poster presentation, and trophic levels were assigned to the various species based on the FishBase database (http://wwww.fishbase.use/search.php). Using this approach a decrease in the D5/PCB-180 concentration ratio was found with increasing trophic level across the fish species (with and without the seal data), indicating that the TMF for D5 was lower than for PCB-180 in this food chain. This analysis does not allow the actual magnitude for the TMF of D5 to be estimated.

  As both the concentration of D5 and the D5/PCB-180 concentration ratios are given graphically in the Kierkegaard *et al.* (2010b) paper it is possible to also estimate/extrapolate the concentrations of PCB-180 in the organisms, allowing, in conjunction with the assumptions used in Woodburn *et al.* (2010), the actual TMF for PCB-180 and D5 to be estimated. If this is done, it is evident that the PCB-180 concentrations were relatively constant in the various fish, implying a TMF close to one in fish (although the concentrations in seals were higher than in the fish). In contrast to this, D5 appears to show a slight decrease in concentration with increasing

trophic level (and the concentrations in seals are markedly lower than in fish), implying a TMF below one[30].

Overall, although the available "benchmarking" studies appear, at first sight, to show some similarity between the accumulation behaviour of D5 and PCB-180, particularly in benthic species, there are considerable uncertainties in interpreting these data. In addition, the relatively limited sample sizes and inherent variability in the measured concentrations mean that relatively small, but important, differences between the behaviour of D5 and PCB-180 may not be apparent (for example slightly increasing or decreasing concentrations across the food chain).

A field study from Japan has recently investigated the sediment biota accumulation factor (BSAF) for D5 in fish (SIAJ, 2011). The samples of sediment and biota were collected from the Tama River, Arakaw River and Tone River, which are representative of the rivers in the Kanto Region. Both the Tama River and Arakawa River flow into Tokyo Bay. The samples were collected at various locations along the river lengths during 2010 (some sampling on the Tama River was also carried out in 2009). The sediment samples consisted of the surface layer (top 3 cm) from areas on the river where sediment was likely to accumulate. Fish were caught by net or rod in the same area (fish were generally collected within a two to three week period for each species at a site, but a month or so apart for different species at some sites). The samples collected were analysed for the presence of D5 (both whole fish and edible parts were analysed).

It should be noted that the method used for extraction of D5 from sediment involved solvent extraction in hexane and then concentrating the hexane extracts to a total volume of 1 ml by evaporation at 25°C under a stream of nitrogen. It is not clear whether this step in the extraction process would have resulted in loss of D5 and hence underestimation of the concentration present in sediment (no similar evaporation step was included in the extraction of biota). However, the quality control procedures used included recovery tests (carried out in 2009) and these showed a recovery of 101 per cent with a standard deviation of 3.3 per cent (total of seven recovery samples) for D5 indicating that loss of D5 during sample extraction was limited (no recovery tests appear to have been carried out for the 2010 sampling).

It should also be noted that no information is given in the report on measures that were taken to avoid inadvertent contamination of the samples during collection (e.g. avoidance of the use of personal care products containing D5).

The results are summarised in Table 21.

[30] For PCB-180 the estimated TMF using this approach is ~1 in fish alone or ~1.2 if the seal data are included. For D5 the estimated TMF is ~0.6 across the fish species or ~0.5 including the seal data. Given the uncertainties in this analysis (reading the concentrations from graphs, differences in sampling locations, assignment of trophic levels, etc.), little certainty can be assigned to the TMF values for D5 or PCB-180 derived using this approach.

Table 21 Summary of BSAFs derived from rivers in Japan

River	Location[1]	Sample[6]	N[5]	Concentration[2]		Derived biota-sediment accumulation factor[3]
				µg/kg wet wt.	µg/kg organic carbon or µg/kg lipid	
Tama River	Mid-stream	Sediment	3	40±4.5	26,000±3,000	
		Pale chub	3	320±4.2	7,200±93	0.3
		Common carp	3	660±25	16,000±640	0.6
	Down-stream	Sediment	6	197±124	63,000±3,100	
		Yellowfin goby	3	170±7.9	6,200±280	0.1
		Flathead mullet	3	5,200±400	100,000±7,800	1.6
		Japanese seabass	3	260±20	11,000±850	0.2
Arakawa River	Mid-stream	Sediment	6	46±33	18,000±16,000	
		Pale chub	3	160±4.1	2,300±61	0.1
		Common carp	3	160±22	6,200±870	0.3
	Down-stream	Sediment	6	1,167±82	96,000±11,000	
		Yellowfin goby	3	280±30	13,000±1,400	0.1
		Flathead mullet	3	3,900±55	73,000±1,000	0.8
		Japanese seabass	3	510±53	18,000±1,800	0.2
Tone River	Mid-stream	Sediment	6	145±31	13,000±1,600	
		Pale chub	3	260±8.8	3,500±120	0.3
		Common carp	3	170±16	7,200±670	0.6
	Down-stream	Sediment	6	115±5.5	15,000±2,100	
		Yellowfin goby	3	[36±1.8][4]	[1,800±92][4]	[0.1][4]
		Flathead mullet	3	1,500±64	25,000±1,100	1.7
		Japanese seabass	3	140±13	1,600±150	0.1

Note: 1) These terms are used in the SIAJ (2011) report. The terms relate to the distance downstream from the origin of the river. Midstream relates to sampling at approximately mid-length of the river. Downstream relates to sampling at the river mouth.

2) Mean ± standard deviation. The concentrations in fish represent whole fish concentrations. The concentrations in the edible portions were determined separately.

3) The BSAFs were calculated using the lipid-normalised concentration in biota/organic carbon-normalised concentration in sediment.

4) The concentration was above the method detection limit but below the limit of quantification. The method detection limit was determined by repetitive analysis of samples. The limit of quantification was defined as three times the method detection limit.
5) Number of samples: with the exception of the midstream sample from Tama River, the sediment samples were collected from each of two locations.
6) Latin names: Pale chub – *Zacco platypus*, common carp – *Cyprinus carpio*, yellowfin goby – *Acanthogobius flavimanus*, flathead mullet – *Mugil cephalus* and Japanese seabass – *Lateolabrax japonicas*.

The sampling sites were generally influenced by local sources (e.g. waste water treatment plants (WWTP) and densely populated urban areas; WWTP discharge contributes up to about 50-70% of the river flow in some locations). The BSAF values derived (based on the lipid-normalised concentration in fish/organic carbon-normalised concentration in sediment) were below 1 for pale chub, common carp, yellowfin goby and Japanese seabass. However, two of the three values derived for flathead mullet were above 1. Flathead mullet was reported to feed on sediment, ingesting detritus, algae and polychaetes present in the sediment and this was thought to result in a higher intake of D5 than the other species analysed. It should be noted that the number of samples was very small so their representivity is unknown. The fish samples were generally collected in October or November, so seasonal variation is also unknown.

It is relevant to note from this study that relatively high levels of D5 were detectable in some of the samples from the area, particularly sediment (up to 96,000 µg/kg organic carbon) and flathead mullet (up to 100,000 µg/kg lipid). As noted above, the relatively high concentrations most likely relate to local sources of release. $\delta^{13}C$-analysis was carried out on both the sediment and biota samples in this study in order to determine the likely origin of the carbon in the food chain (land origin or marine origin). The sediment from midstream and downstream locations generally showed the sediment to be of land origin (the midstream sample from the Arakawa River gave a $\delta^{13}C$ value midway between land and marine origin). The carp samples from midstream had $\delta^{13}C$ values typical of land origin but the pale chub from midstream showed a wider range of $\delta^{13}C$ values, with the pale chub from the Arakawa River having a value more consistent with marine origin (possibly reflecting the findings for sediment) than land origin. The $\delta^{13}C$ values from the downstream biota samples reflected differences in habitat and food web between the species. Yellowfin goby is a demersal fish that lives over sediments of land origin. Flathead mullet feeds mainly on detritus accumulated on the river bottom (and attached algae) but also takes up sand and mud along with these items. Therefore the food of flathead mullet is likely to be highly influenced by the local concentrations of D5 in the sediment. Both the yellowfin goby and flathead mullet had $\delta^{13}C$ values close to those expected for a food chain of land origin. In contrast, Japanese seabass are thought to travel long distances between the river mouth area and the ocean and the $\delta^{13}C$ values for this species were found to be intermediate between land and marine origin. The probable movement of Japanese seabass in and out of the sampling area means that the actual exposure of this species via sediment is uncertain.

In addition to these data, samples of fish were also collected from Tokyo Bay. These showed generally lower concentrations of D5 (≤1,300 µg/kg lipid). SIAJ (2011) used the carbon and nitrogen stable isotope ratio determined in the various samples to try to assign each species to a trophic level. However, clear predator-prey relationships were not established and so tropic levels could not be calculated.

Fugacity

It has been argued that although some of the available BCF and BSAF values are suggestive of a high bioaccumulation potential for D5, when considered on a fugacity basis, the bioaccumulation potential is much lower than, for example, certain chlorinated biphenyls that are known to bioaccumulate. For example, Gobas *et al*. (2011) in their submission to the Canadian Board of Review of D5 concluded that the biota/water fugacity ratios for the bioconcentration and biota-sediment studies available at that time were all less than 0.0033, and the biota/sediment fugacity ratios were less than 0.0064. Similar findings are reported by Woodburn (2010 and 2011).

Although at face value these fugacity ratios suggest that D5 has a low bioaccumulation potential, it is important to note that the calculation of the fugacity ratio is itself an approximation and, importantly for the analysis, it effectively assumes that the D5 solubility in (or affinity for) octanol is a good surrogate for the solubility in (or affinity for) lipids, i.e. the equilibrium constant between lipid and water approximates to the K_{ow}. Recent work by Kozerski (2011) suggests this may not be the case, and that the actual equilibrium constant between lipid and water for D5 is at least one to two orders of magnitude lower than suggested by its K_{ow}. If this is the case then the calculated fugacity ratios would be at least one to two orders of magnitude higher than estimated above[31]. Therefore the low fugacity ratios calculated by Gobas *et al.* (2011) and Woodburn (2010 and 2011) should be treated with caution until more is understood about the lipid-water partitioning of D5.

It is also relevant to note that this uncertainty over the relationship between the lipid-water partitioning and octanol-water partitioning for D5 may also be relevant to bioaccumulation models that are based on a fugacity approach (depending how the model is formulated).

4.3.3.3 Modelling studies

Summary of information from existing evaluation

EA (2009a) reports the results of physiologically based pharmacokinetic modelling studies considering both inhalation and dermal exposure of D5 in mammalian systems (but not oral exposure). The models were developed by Anderson (2005) and Reddy *et al.* (2004 and 2005) and were based on a comprehensive data set developed using both single and repeated inhalation studies in rats, a single inhalation exposure study in humans and both *in vitro* and *in vivo* percutaneous absorption studies. The model included a sequestered pool of D5 (presumed to be in lipoproteins) released from the liver, distributed by the blood, and cleared from the blood into fat. The inhalation model showed that metabolism and exhalation are important mechanisms for elimination of D5 and that the rapid clearance by these two routes means that D5 does not accumulate, despite a high predicted blood-to-fat partitioning behaviour.

Using the dermal absorption model, absorption of D5 was thought to be very limited with only around 0.05 per cent being systemically adsorbed. Furthermore, the dermally absorbed

[31] The exact values estimated for the lipid-water partition coefficient (K_{LW}) are not given in the paper but are shown graphically. The calculated log K_{LW} from the plot looks to be around 5.5 for D5 – this value would increase the quoted calculated fugacity ratios for biota-water and biota-sediment by around a factor of 340.

dose is predicted to enter the venous circulation and move directly to the lungs, from which >90 per cent of this is eliminated via exhalation prior to it being available systemically.

New information

Domoradzki (2009) developed a physiologically-based pharmacokinetic model for exposure of rainbow trout (*Oncorhynchus mykiss*) to D5 by both dietary and water exposure routes. The model was parameterized using data from a 96-hour metabolism study (Springer, 2007; study discussed in detail in EA, 2009a). The model was able to predict the accumulation seen in other laboratory accumulation experiments reasonably well (results are only expressed graphically), for example the studies of Durham *et al.* (2009a) and Drottar and Miller (2003) described in Section 4.3.2.2 and the feeding study of Drottar *et al.* (2006) discussed in detail in EA (2009a)[32]. The model was then used to simulate a bioconcentration study where rainbow trout (initial weight 2 g) were exposed to D5 at a concentration of 1.1 µg/l for 35 days followed by a 70 day depuration period. The simulation indicated that the body concentration would reach 5,178 µg/kg after 35 days, which is equivalent to a BCF of 4,707 l/kg. However it should be noted that the concentration-time plots in the paper indicate that although steady state was being approached, it had not yet been reached in the simulation. The model appears to have considered that no growth of the fish was occurring and so no growth dilution would be included in the simulation. The inclusion of growth dilution into the model would be expected to reduce the BCF predicted.

A modelling study for D5 has been carried out to compare the predicted bioaccumulation with the bioaccumulation observed in both laboratory experiments and in the field situation (HydroQual Inc., 2009). The bioaccumulation model used was the Thomann-Farley food chain model (Thomann *et al.*, 1992) and takes into account accumulation from both dietary and aqueous exposure. The aim of the study was to try to reconcile the aqueous and dietary accumulation measured for D5 in the laboratory (Domoradzki *et al.*, 2006) with the field measurements found in the Lake Pepin study summarised in Section 4.3.3.2 (Powell *et al.*, 2009a).

The model was firstly applied to the laboratory data. The laboratory data were used to calibrate the key parameters in the model (such as gill and dietary chemical assimilation efficiencies). The model was found to describe the observed laboratory data reasonably well. The laboratory-calibrated model was then used to predict the field data generated in the Lake Pepin study. In order to simplify the modelling the fish species were grouped into two general feeding classes: forage fish (which were assumed to consume a diet consisting 100 per cent of benthic invertebrates) and piscivorous fish (which were assumed to consume a diet consisting of 25 per cent small fish and 75 per cent benthic invertebrates). The model was run by specifying the concentrations in the diet species (benthic invertebrates and young-of-year fish) to be the mean concentration in these species from the field data.

Under these conditions the model was found to predict the general trends of the D5 concentrations in fish reasonably well, with the forage fish generally showing higher concentrations than piscivorous fish, consistent with trophic dilution. In addition the model predicted that the concentrations within fish would decrease with the size of the fish as a result of growth and elimination rates that are faster than the rates of accumulation from diet and water exposures. The model calculations also suggested that the primary route of

[32] In EA (2009) the study is referenced as Dow Corning (2006b).

exposure was through the diet (>90 per cent for D5). A key uncertainty in the modelling data is the assumption of a single elimination rate to take account of metabolism and the various excretion mechanisms within the fish. As noted by HydroQual Inc. (2009) such elimination rates can vary substantially between different fish species.

It is possible that the findings in the HydroQual Inc. (2009) over the percentage contribution from diet may be influenced by some of the initial parameters assumed in the model. In particular, the concentration in benthic macroinvertebrates (~120 µg/kg wet weight) and the young-of-year fish (21 µg/kg wet weight) were based on the actual data from the Lake Pepin field study (and not predicted within the model) whereas the freely dissolved concentration for each cyclic siloxane was set at 0.1 ng/l. As the actual concentration of freely dissolved D5 was not known in the Lake Pepin study this may have influenced the predictions towards accumulation from diet over accumulation from water.

This issue has been considered further in CES (2010a). The modelling carried out by Whelan (2009a) (reported in Table 4) estimated that the total concentration of D5 in Lake Pepin would be of the order of 10-15 ng/l. Further modelling work using the CoZMO-POP 2 model indicated a total concentration of D5 in water in the Lake to be of the order of 1 ng/l, and a similar estimate of a maximum of 2 ng/l was also obtained using pharmacokinetic modelling based on the measured prey concentrations for a piscivorous fish species in Lake Pepin (CES, 2010a). Taking into account adsorption onto suspended matter and dissolved organic carbon in the lake, CES (2010a) estimate that the equivalent freely dissolved concentration of D5 would be around 0.1-0.5 ng/l, and most probably ≤0.1 ng/l, which is consistent with the findings from the HydroQual Inc. (2009) study. CES (2010a) also carried out further pharmacokinetic modelling of the levels found in a piscivorous fish species (largemouth bass) using the Lake Pepin data. This analysis investigated the estimated water uptake versus dietary uptake in this species for a series of D5 water concentrations. The estimates obtained ranged from 61 per cent from water and 39 per cent from diet assuming a freely dissolved concentration of 10 ng/l to 0.1 per cent for water and 99.9 per cent from diet assuming a freely dissolved concentration of 0.001 ng/l. However the best fit to the available bioaccumulation kinetics for fish was found assuming a dissolved water concentration of 0.05 ng/l or lower and here the percentage uptake from water was ≤6 per cent and the percentage uptake from diet was ≥94 per cent.

Overall the modelling carried out on the Lake Pepin data set provides strong evidence that uptake in this food chain was dominated by dietary exposure with bioconcentration processes making only a small contribution to the uptake seen. It should however be noted that sediment concentrations measured in the lake (3,289 µg/kg organic carbon (standard deviation ±522 µg/kg organic carbon)) are much higher than would be expected from a freely dissolved concentration of 0.1 ng/l (e.g. assuming the K_{oc} of 1.5×10^5 l/kg reflects the partitioning between the dissolved water phase and the sediment phase, a sediment concentration of around 15 µg/kg organic carbon would be expected). Therefore the sediments in Lake Pepin appear to be more highly contaminated with D5 than might be expected from the predicted concentration in the water phase and this may partly explain the pattern of uptake seen in this food chain.

McLachlan *et al.* (submitted (a)) and McLachlan and Kierkegaard (2009) have used the CoZMoMAN model[33] to assess the persistence and bioaccumulation potential of D5. As the paper has not yet been formally published, only very brief details of the study are given here. The behaviour of D5 was found to be dependent upon whether the substance was released to air or released to water (the effect of release to soil via sewage sludge was not considered). When released to air, the model predicted that D5 would be rapidly eliminated by photodegradation reactions with only a very small percentage of the substance transferring to the water compartment. As a consequence the very low concentrations in water would mean that the concentrations in aquatic organisms would also be very low. In contrast to this, when D5 was assumed to be released to surface water, significant concentrations in aquatic organisms were predicted. The persistence of D5 in the aquatic compartment was investigated by modelling the decline in concentrations within the system following a cessation of emissions into the system. The persistence was found to be dependent on the K_{oc} value assumed. When a log K_{oc} value of 7.64 was used, the overall elimination half-life from the aquatic biota system was around 3.5 years but this was reduced to around 0.28 years (~100 days) when a log K_{oc} of 5.17 was assumed. The reason for this was that the lower log K_{oc} results in a higher loss rate from the aquatic compartment from volatilisation.

Gobas *et al.* (2011) investigated the bioaccumulation potential of D5 using an adaptation of the Gobas (1993) model. The log K_{ow} and log K_{oc} assumed for D5 in the model were 8.03 and 5.17, respectively, and four sizes of fish were included (10g 5 per cent lipid, 100g 10 per cent lipid, 1,000 g 15 per cent lipid and 10,000 g 20 per cent lipid). The dietary absorption efficiency for D5 was set to 40 per cent. Using a rate constant of 0.027 day^{-1} resulted in a predicted BCF of 13,800 l/kg for the smallest fish and a BMF of 0.79 kg/kg. The predicted BCFs and BMFs were found to progressively decrease with increasing size of the fish suggesting that the concentrations in the fish would decrease with increasing size of the fish. A TMF of around 0.28 was estimated from these data by Gobas *et al.* (2011). Increasing the metabolic rate constant to 0.25 day^{-1} resulted in lower predicted BCFs, BAFs and TMFs (in this case the BCF for the 10 g fish was around 2,100 l/kg).

A modelling study using the AQUAWEB model is briefly reported in a poster presentation by Woodburn *et al.* (2009). A foodweb consisting of three benthic invertebrates (caddisfly larvae, midge and mayfly) and fourteen fish species was constructed and the TMF for D5 was estimated from the results of the modelling. The TMF for D5 was predicted to be below one in the food chain. Few other details of this study (including the assumptions made and data used) are currently available.

Whelan and Breivik (2013) also investigated pelagic food chain transfer of D5 in the Inner Oslofjord using two dynamic models (the Oslofjord POP Model and the aquatic component of ACC-HUMAN). Predicted concentrations in herring (*Culpea harengus*) and cod (*Gadus morhua*) agreed well with measured data from the inner fjord when measured concentrations in zooplankton were used to set the initial dissolved-phase aqueous concentrations. Trophic dilution was predicted, principally due to a combination of *in vivo* metabolism and reduced gut absorption efficiency (as a consequence of the high K_{ow}).

[33] This model was developed by linking the environmental fate model CoZMoPOP with the bioaccumulation model ACC-HUMAN.

As noted in Section 4.3.3.2, the uncertainty over the relationship between the lipid-water partitioning and octanol-water partitioning for D5 may also be relevant to bioaccumulation models that are based on a fugacity approach (depending on how the model is formulated).

4.3.3.4 Measured concentrations in biota

Summary of information from existing evaluation

The available monitoring data for D5 in general are summarised in EA (2009a). Of most relevance to the PBT and vPvB assessment are data on the occurrence of D5 in biota from marine areas and from remote regions. The available relevant data are briefly summarised below.

- D5 was not detectable (<5 µg/kg wet weight) in 19 samples of fish muscle from various locations (including background sites and sites near to potential point sources) in an around Sweden. The fish species included Baltic herring, herring, eelpout, salmon, flounder and perch (Kaj *et al.*, 2005).

- EVONIK Industries (2007) carried out a survey of the levels of D5 in freshwater and marine fish from Europe. The analytical detection limit was 10 µg/kg wet weight. For the marine samples D5 was not detected in samples of 11 species from the North East Atlantic, six species from the Baltic Sea close to the mouth of the Odra Rive, and one species from the Baltic Sea. For the freshwater fish, D5 was not detected in three species from Lake Nipgård, Denmark, and two out of three species from Lake Constance (D5 was detectable in an eel sample but the level was below the limit of quantification (<30 µg/kg wet weight) of the analytical method). In contrast to these data, D5 was present at much higher concentrations (between 150 and 2,600 µg/kg) wet weight in fish from the River Rhine, Germany (close to the Dutch Border) showing that relatively high concentrations of D5 can occur in biota in some environments, presumably close to sources of release.

- TemaNord (2005) reports levels of D5 of <5 to 2,200 µg/kg fresh weight in biota from Nordic countries. The concentrations were generally elevated in urban areas and in areas close to sewage treatment plants, and only few background samples showed detectable levels. The samples included marine and freshwater fish, marine mammals and seabird eggs. The highest level found was 2,200 µg/kg fresh weight for cod liver from the Inner Oslofjord in Norway but detectable levels of D5 were also found in samples of seal blubber from Denmark and pilot whale blubber from the Faroe Islands.

- Schlabach *et al.* (2007) investigated the levels of D5 in biota from the Inner Oslofjord. The samples included common mussels, flounder fillet, flounder liver, cod liver and cod stomach contents (mainly krill, shrimp and small crabs). D5 was detectable in all of the samples. The highest levels found were in cod liver (~1,500-2,000 µg/kg wet weight).

- A preliminary screening study of the levels of D5 in mussels from the Southern North Sea was carried out by Boehmer *et al.* (2007). Around 30-50 blue mussels were collected from the intertidal areas from sites at Rømø and Hu Bugt (Denmark), Norderney (Germany), Ameland (the Netherlands), and Ambleteuse and Cap Gris

Nez (France). In all a total of 23 composite samples (each of two to six individuals) were analysed. The levels of D5 found were below the method detection limit (<6.6 µg/kg) in ten samples, between the method detection limit and the method limit of quantification in nine samples (the estimated concentrations were in the range 8.8 to 19.3 µg/kg) and above the method limit of quantification in four samples (the concentrations found were in the range 24.7 to 33.1 µg/kg).

- A survey of the levels of D5 in livers of seabirds from Bjørnøya (Svalbard: 74°30'N, 19°01'E) has been undertaken by Knudsen *et al.* (2007). The samples collected included 21 glaucous gulls (*Larus hyperboreus*) and two great black-backed gulls (*L. marinus*) found dead or dying in 2003, 2004 and 2005. Of the 23 birds collected, ten were completely or severely emaciated, seven were emaciated (but the emaciation was probably not so severe as to be the cause of death) and six were in normal or slightly below normal condition. Ten liver samples from the glaucous gulls were randomly selected for the analysis of D5. D5 was found to be present in all of the ten samples at a concentration between 32.2 and 68.8 µg/kg wet weight. The influence of reduced fat levels on the amounts of D5 that were detectable is unknown.

New information

The available new information on the levels of D5 in biota, including biota samples from remote regions are summarised in Table 22. The sampling and analysis protocols in the majority of these studies have generally attempted to minimise the potential problems from inadvertent/background contamination of the samples[34]. Where this is not necessarily the case this is noted in the table. In addition to the data in Table 22, other monitoring data for biota have been generated in investigations of food chain accumulation (see Section 4.3.3.2).

Of most relevance to the PBT and vPvB assessment are the studies by Campbell (2010; very brief details of this study are given in an interim report by Campbell (2009) and some of the results appear to be given in a poster presentation by Warner *et al.* (2010a) and a paper by Warner *et al.* (2010b))) and by Evenset *et al.* (2009) of the levels of D5 in biota from remote regions (around Svalbard).

For the Campbell (2010) study, the samples were collected on two expeditions, one carried out in July and August 2008 and one in July and August 2009. Three laboratories were involved in analysing the 2009 samples in order to allow inter-laboratory comparisons of the results to be made (these laboratories also analysed the 2008 samples but in some cases the analysis for a particular species was carried out by one laboratory only). Precautions were taken during sampling and analysis to avoid contamination and the samples were collected by appropriately trained experts/personnel. The sampling locations and samples collected are summarised below.

- Kongsfjorden in 2008. Benthic organisms, zooplankton, kittiwakes and black guillemot.
- Liefdefjorden in 2008. Benthic organisms.

[34] Recent studies (e.g. Hastie *et al.* (2010a)) have shown the importance of controlling such inadvertent contamination for D5.

- Bjørnøya in 2008. Glaucous gull.
- Sweden in 2008. Herring, sprat and herring gull.
- Adventfjorden in 2009. Sediment, juvenile Atlantic cod and sculpin.
- Kongsfjorden in 2009. Sediment, bearded seals, Atlantic cod and zooplankton.
- Liefdefjorden in 2009. Sculpin and zooplankton.
- Nordkappsundet in 2009. Zooplankton

The 2008 sampling was carried out in Kongsfjorden (~78°55'N 11°54'E) and Liefdefjorden (~79°34'N 12°44'E) within the Svalbard archipelago, Bjørnøya (Svalbard) and off the west coast of Sweden. The 2009 samples were collected mainly from Adventfjorden (~78°13'N 15°40'E), Kongsfjorden and Liefdefjorden within the Svalbard archipelago, with some additional zooplankton samples collected from Nordkappsundet (~81°N, 21°E). Liefdefjorden is accessible only from the north and has no settlements on its shores but has frequent visits from cruise ships during the summer months. Liefdefjorden was considered by Cambell (2010) to be the most remote of the locations sampled on Svalbard in 2009. Kongsfjorden is located on the west coast of Svalbard and has a permanent research station in the area (at Ny Alesund) with up to 150 personnel in the summer. Cruise ships also make periodic stops at Ny Alesund during spring and summer. Adventfjorden was considered to be the least remote of the 2009 sampling sites as Longyearbyen (the capital of Svalbard with around 2,500 inhabitants) is located in the area.

The results are summarised in Table 22 (where D5 was not detected in one or more samples the method detection limit is given; the limit of quantification was generally set as three times the method detection limit[35]). In addition to biota, as indicated above, sediment samples were also collected from some locations. These results are reported in Section 4.2.3 (and appear to confirm a local emission source to Adventfjorden).

D5 was detectable in some samples of Atlantic cod (*Gadus morhua*) liver, bivalves (*Astarte borealis* and *Chlamys islandies*), glaucous gull (*Larus hyperboreus*) liver and muscle, herring gull (*Larus argentatus*) muscle and liver, sculpin liver[36] and whole body, sea urchin, seal blubber, shrimp, sprat and zooplankton.

Where detectable, the concentration of D5 was generally close to the method detection limit. However, it is noteworthy that levels up to 110 µg/kg wet weight (Atlantic cod liver) and 345 µg/kg wet weight (sculpin liver) were found in samples from Adventfjorden (which may reflect a local source). D5 was also still detectable in some of the samples from the more remote locations.

The glaucous gull samples from the Campbell (2010) study are also of particular interest as these were collected from Bjørnøya. As mentioned above, a previous study by Knudsen *et al.* (2007) had found relatively high levels (between 32.2 and 68.8 µg/kg wet weight) of D5 in samples of glaucous gull liver from this area. In contrast, Campbell (2010) found that the D5

[35] In many of the samples, although D5 was detectable, the concentration present was below the limit of quantification. Here the actual concentration reported has been given regardless of whether it is above or below the limit of quantification. There is therefore some uncertainty in the accurate quantification of concentrations close to the limit of detection.

[36] Species name not given.

levels were much lower (detectable in 3 out of 8 liver samples at a concentration of 0.93-2.5 µg/kg wet weight). This suggests that the previous concentrations reported by Knudsen *et al.* (2007) may have been affected by inadvertent contamination of the samples with D5 during collection and/or subsequent analysis (although the nutritional status and health of the birds might also play a role, since this could influence the lipid content of the liver).

It is interesting to note that in this study some of the higher concentrations are found in fish such as Atlantic cod and sculpin rather than invertebrates (in contrast with some of the field bioaccumulation studies reported in Section 4.3.3.2). The lack of information on predatory-prey relationships and lipid contents, and the limited numbers of samples, etc., precludes a detailed evaluation of the bioaccumulation potential for D5 in this food chain. However, Warner (2010b) calculated biota-sediment accumulation factors (BSAF) for both cod and sculpin (based on the ratio of the concentration in fish (µg/kg lipid) to the concentration in sediment (µg/kg organic carbon)) for both cod and sculpin from Adventfjorden. The mean BSAF for cod was estimated to be 2.4 (range 0.6 to 4.9) and the mean BSAF for sculpin was 7.3 (range 0.7 to 30). The sediment samples collected immediately downstream of the effluent outflow into Aventfjorden were not included in these estimates as the samples were not considered representative of the exposure levels to fish in this area. It is not clear from the paper whether these BSAFs were calculated using liver concentrations or whole fish concentrations.

The Evenset *et al.* (2009) study showed that D5 was detected frequently in samples of Atlantic cod (*Gadus morhua*) and polar cod (*Boreogadus saida*). However, D5 was detectable in only one sample of seabird liver (kittiwake (*Rissa tridactyla*)), and this positive finding is questionable as D5 was also present in the field blank from this area (and so contamination of the sample during handling, transport and processing cannot be ruled out). D5 was not detectable in sediment samples collected on the west coast of Spitsbergen. When considering these findings with the earlier findings of Knudsen *et al.* (2007) in glaucous gulls (see above), Evenset *et al.* (2009) noted that kittiwake and glaucous gulls have different diets (glaucous gull is omnivorous whereas kittiwake feed mainly in the pelagic zone on crustaceans and small fish) and glaucous gulls generally have much higher levels of persistent organic contaminants than kittiwakes. The source of D5 exposure is not known.

Overall the Campbell (2010) and Evenset *et al.* (2009) studies confirm that D5 is present in some biota samples from remote regions, generally at very low concentrations (close to the limit of detection). However, the results also indicate that local sources of D5 exist even in remote locations (and may lead to locally elevated concentrations). Although it is not clear if local sources can explain all such findings, the possibility of local sources even in remote locations means that the interpretation of the data in terms of long-range transport potential for D5 is difficult.

Table 22 Measured concentrations of D5 in biota

Species	Location	Measured concentration	Comment	Reference
Arctic char (*Salvelinus alpinus*)	Samples from urban and remote lakes in Sweden	Not detectable (<1 µg/kg[1] wet weight) (9 samples from remote locations) 12 µg/kg wet weight (mean of 4 samples from Lake Vättern)	Samples analysed were dorsal muscle tissue samples. Results given in a poster presentation.	Kierkegaard *et al.* (2008)
	Samples from urban and remote lakes in Sweden	Below the limit of quantification (<0.79 µg/kg wet weight) (10 samples from remote locations (Lake Abiskojaure, Lake Tjulträsk and Lake Stor-Björjön) 9.1-20 µg/kg wet weight (4 samples from Lake Vättern in 2007) 4.3-9.3 µg/kg wet weight (3 samples from Lake Vättern in 2008)	Samples analysed were skin-free dorsal muscle samples.	Kierkegaard *et al.* (2010c)
Atlantic cod (*Gadus morhua*) – liver	Samples from remote region around Svalbard (Kongsfjorden)[2]	2.7-4.6 µg/kg wet weight or 6.7-15.3 µg/kg lipid (detected in 5 out of 5 samples)	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Evenset *et al.* (2009)
	Samples from remote region around Svalbard (Kongsfjorden)[4]	1.9-8.8 µg/kg wet weight (detectable in 18 out of 19 samples[5] in 2009; method detection limit was 0.68 to 1.77 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
	Samples from remote region around Svalbard (Adventfjorden)[4]	13-110 µg/kg wet weight (detectable in 11 out of 11 samples[5] in 2009).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)

Species	Location	Measured concentration	Comment	Reference
	Samples from remote region (the exact location is unclear but was probably either Kongsfjorden or Liefdefjorden)	6.22-7.99 µg/kg wet weight (detected in 3 out of 3 samples from 2008).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
	Seventeen samples from inner Oslofjord.	36-3,137 µg/kg wet weight (detected in all seventeen samples)	Part of an interlaboratory comparison study (see text)	Durham *et al.* (2009b)
Herring (*Clupea harengus*)	Samples from urban areas in Sweden	0.8-4.2 µg/kg wet weight (3 samples from the inner Stockholm archipelago).	Samples analysed were dorsal muscle tissue samples. Results given in a poster presentation.	Kierkegaard *et al.* (2008)
	Lagnö, Baltic Sea	<0.5 to 4.3 µg/kg wet weight (detected in 6 out of 9 samples)	Samples analysed were skin-free dorsal muscle samples.	Kierkegaard *et al*. (2010c)
Bivalve (*Astarte borealis*)	Samples from remote region (the exact location is unclear but was either Kongsfjorden or Liefdefjorden)	0.80 µg/kg wet weight (single sample from 2008).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Bivalve (*Chlamys islandies*)	Samples from remote region (the exact location is unclear but was either Kongsfjorden or Liefdefjorden)	0.63-1.26 µg/kg wet weight (detectable in 3 out of 3 samples from 2008).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
	Samples from remote region around Svalbard (Kongsfjorden)	Not detectable in 3 samples in 2008 (method detection limit 1.83-2.36 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)

Species	Location	Measured concentration	Comment	Reference
	Samples from remote region around Svalbard (Liefdefjorden)	Not detectable in 4 samples in 2008 (method detection limit 1.83-2.36 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Bivalve (*Mya truncate*)	Samples from remote region around Svalbard (Kongsfjorden)	Not detectable in 4 samples in 2008 (method detection limit 1.8-2.6 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
	Samples from remote region around Svalbard (Liefdefjorden)	Not detectable in 2 samples in 2008 (method detection limit 2.18-2.46 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Bivalve (*Serripes groenlandica*)	Samples from remote region around Svalbard (Kongsfjorden)	Not detectable in 2 samples in 2008 (method detection limit 1.85-2.75 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
	Samples from remote region around Svalbard (Liefdefjorden)	Not detectable in 2 samples in 2008 (method detection limit 1.98-2.12 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Black guillemot (*Cepphus grille*) - liver	Samples from remote region around Svalbard (Kongsfjorden)	Not detectable in 2 samples in 2008 (method detection limit 1.9 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)

Species	Location	Measured concentration	Comment	Reference
Black guillemot (*Cepphus grille*) - muscle	Samples from remote region around Svalbard (Kongsfjorden)	Not detectable in 2 samples in 2008 (method detection limit 1.9 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Black guillemot (*Cepphus grille*) - plasma	Samples from remote region around Svalbard (Kongsfjorden)	Not detectable in 10 samples in 2008 (method detection limit 6.54-6.73 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Black guillemot (*Cepphus grille*) – blood cells	Samples from remote region around Svalbard (Kongsfjorden)	Not detectable in 10 samples in 2008 (method detection limit 4.96-14.0 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Common eider (*Somateria mollissima*) - liver	Samples from remote region around Svalbard (Kongsfjorden)[2]	Not detectable (<2.8 µg/kg wet weight or <168 µg/kg lipid) (5 samples)	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Evenset *et al.* (2009)
Freshwater mussels[3]	Samples from the River Nene, UK (influenced by urban sources)	Up to around 500-600 µg/kg wet weight (values given graphically only).	Results given in a poster presentation. Few details are available.	Kierkegaard *et al.* (2008)
Glaucous gull (*Larus hyperboreus*) - liver	Samples from remote region - Bjørnøya	0.93-2.5 µg/kg wet weight (detectable in 3 out of 8 samples[5] in 2008; method detection limit was between 0.58 and 1.9 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Glaucous gull (*Larus hyperboreus*) - muscle	Samples from remote region - Bjørnøya	2.59-3.42 µg/kg wet weight (detectable in 3 out of 5 samples in 2008; method detection limit 1.9 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)

Species	Location	Measured concentration	Comment	Reference
Herring[3]	Samples from west coast of Sweden (Skagerrak)	Not detectable in 6 samples from 2008 (method detection limit 0.48-0.76 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Herring (*Clupea harengus*) – dorsal muscle	Samples from ten sites along the Swedish coast from the Baltic to the North Sea (three individuals per site)	Detected in all samples from archived specimens collected in 2007, at a mean concentration of 137 ng/g lw (range 15 – 718 ng/g lw).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Kierkegaard *et al.* (2010b & 2012a)
Grey seal (*Halichoerus grypus*) - blubber	Three individuals that drowned in fishing nets north of Västervik, Sweden in the autumn of 2008	Detected in all samples of blubber, at a mean concentration of 18 ng/g ww (range 9–24 ng/g ww).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Kierkegaard et al. (2012a)
Herring gull (*Larus argentatus*) - liver	Samples from remote region around the west coast of Sweden	1.27-2.65 µg/kg wet weight (detectable in 3 out of 12 samples[5] in 2008; method detection limit was between 0.64 and 1.9 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Herring gull (*Larus argentatus*) - muscle	Samples from remote region around the west coast of Sweden	0.92-5.08 µg/kg wet weight (detectable in 6 out of 9 samples[5] in 2008; method detection limit was between 0.84 and 1.9 µg/kg wet weight where reported).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Kittiwake (*Rissa tridactyla*) – liver	Samples from remote regions around Svalbard (Kongsfjorden and Liefdefjorden)[2]	Not detectable – 1.5 µg/kg wet weight or not detectable to 60 µg/kg lipid (detected in 1 out of 9 samples; the detection limit for the non-detectable samples range between <1.7 and <2.6 µg/kg wet weight or <36 to <101 µg/kg lipid).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes. However, D5 was detected in the field blank from this site and so contamination of the sample during processing cannot be excluded.	Evenset *et al.* (2009)

Species	Location	Measured concentration	Comment	Reference
Kittiwake (*Rissa tridactyla*) - blood	Samples from remote region around Svalbard (Kongsfjorden)	Not detectable in 13 samples in 2008 (method detection limit in the range 2.53-7.77 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Perch (*Perca fluviatilis*)	Samples from rural and remote lakes in Sweden	Not detectable (<1 µg/kg[1] wet weight) (21 samples from both rural and remote locations).	Dorsal muscle tissue samples. Results given in a poster presentation.	Kierkegaard *et al.* (2008)
Perch[3]	Samples collected in November to December 2009 from six Swedish lakes that received sewage effluent (3-5 fish/lake)	Detected above the limit of quantitation in all fish but five. Mean concentrations for each lake were 0.8 – 14.4 ng/g ww, with levels in fish from the same lake varying by a factor of between 2 and 9.	Dorsal muscle tissue samples. Lipid content of perch muscle tissue varied little between individuals and lakes (~0.6%).	Kierkegaard *et al*. (2012b)
	Samples collected in September 2007 from six Swedish lakes that did not receive sewage effluent (3 fish/ lake)	Detected in all samples between the limits of quantitation and detection (reported range: 0.12 – 0.60 ng/g ww). True levels could have been higher, as the extraction time of 24 hours was shown to be insufficient for complete extraction.		
Polar cod (*Boreogadus saida*) – liver and whole fish	Samples from remote regions around Svalbard (Liefdefjorden, Billefjorden and close to Moffen)[2]	6.9-19.1 µg/kg wet weight or 18-55 µg/kg lipid (detected in 6 out of 6 liver samples). <2.5-5.1 µg/kg wet weight or <74-128 µg/kg lipid (detected in 4 out of 5 whole fish samples).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Evenset *et al.* (2009)
Sculpin[3] - liver	Samples from remote region around Svalbard (Liefdefjorden)	0.72-2.9 µg/kg wet weight (detectable in 8 out 18 samples[5] in 2009; method detection limit was 0.68 to 1.77 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
	Samples from remote region around Svalbard (Adventfjorden)[4]	6.9-345 µg/kg wet weight (detectable in 16 out of 16 samples[5] in 2009).		
	Samples from remote region (the exact location is unclear but was either Kongsfjorden or Liefdefjorden)	1.50-3.03 µg/kg wet weight (detected in 3 out of 5 samples in 2008; method detection limit 1.09-2.21 µg/kg wet weight).		

Species	Location	Measured concentration	Comment	Reference
Sculpin[3] – whole body	Samples from remote region (the exact location is unclear but was either Kongsfjorden or Liefdefjorden)	Not detectable in 5 samples from 2008 (method detection limit 1.9 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Sculpin[3] – whole body minus liver	Samples from remote region (the exact location is unclear but was either Kongsfjorden or Liefdefjorden)	1.66-5.97 µg/kg wet weight (detected in 5 out of 5 samples in 2008).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Sea urchin[3]	Samples from remote region (the exact location is unclear but was either Kongsfjorden or Liefdefjorden)	0.30-0.87 µg/kg wet weight (detected in 3 out of 3 samples in 2008).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Seal[3] blubber	Samples from remote region around Svalbard (Kongsfjorden)[4]	2.6 to 2.85 µg/kg wet weight (detected in 4 out of 10 samples[5] in 2009; method detection limit 1.59 to 1.77 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Shrimp (*Pandulus borealis*)	Samples from remote region around Svalbard (Kongsfjorden)	Not detectable in 3 samples (method detection limit 1.78-2.52 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Shrimp[3]	Samples from remote region around Svalbard (Liefdefjorden)	3.26 µg/kg wet weight (detected in one out of two samples[5] from 2008; method detection limit 1.9 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)

Species	Location	Measured concentration	Comment	Reference
Shrimp[3] – composite samples	Samples from remote region around Svalbard (the exact location is unclear but was either Kongsfjorden or Liefdefjorden)	1.44-1.77 µg/kg wet weight (detected in 2 out of 2 composite samples from 2008).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Sprat[3]	Samples from west coast of Sweden (Skagerrak)	0.99-4.13 µg/kg wet weight (detected in 3 out of 4 samples from 2008; method detection limit 0.63 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
Zooplankton	Samples from remote region around Svalbard (Liefdefjorden)	Not detectable in 9 samples[5] in 2009 (method detection limit was in the range 0.68 to 1.77 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
	Samples from remote region around Svalbard (Kongsfjorden)[4]	Not detectable in 9 samples[5] in 2009 (method detection limit was in the range 0.68 to 1.77 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
	Samples from remote region around Svalbard (Kongsfjorden)	0.73-0.93 µg/kg wet weight (detected in 3 out of 3 samples in 2008).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)
	Samples from remote region (Nordkappsundet)	Detected in one out of samples[5] at 2.06 µg/kg wet weight in 2009 (method detection limit was in the range 0.68 to 1.77 µg/kg wet weight).	Precautions were taken during sampling and analysis to avoid contamination with cyclic siloxanes.	Campbell (2010)

Note: 1) Below the limit of quantification.
2) Marine sediment samples were also collected in Kongsfjorden and Liefdefjorden. D5 was not detected in any of the sediment samples (concentration typically <5 µg/kg dry weight).
3) The species scientific name was not given in the paper.

4) Marine sediment samples were also collected in Kongsfjorden and Adventfjorden in 2009. D5 was not detected in 15 sediment samples from Kongsfjorden (method detection limit 0.47 to 2.36 µg/kg wet weight) but was detectable in 9 out of 15 samples from Adventfjorden at a concentration of 0.57 to 3.91 µg/kg wet weight (method detection limit 0.47 to 2.36 µg/kg wet weight).
5) The total number of samples here refers to the total number of sample analysed across each laboratory. As three laboratories were involved, and generally two or three of the laboratories each analysed a sub-sample from each organism, the total number of organisms collected would be smaller than indicated by the sampling numbers.

An interlaboratory comparison of the levels of D5 in cod liver from the inner Oslofjord has been carried out by Durham *et al.* (2009b). Seventeen fish were collected in December 2007 and were sent to three laboratories for dissection (each laboratory received five or six fish) and the liver samples were then analysed by all three laboratories. Overall agreement between the three laboratories was generally good and D5 was found in all samples at concentrations between around 36 and 3,137 µg/kg wet weight. The levels found were in agreement with those of previous studies in the area (e.g. TemaNord (2005) and Schlabach *et al.* (2007)) and confirm that relatively high levels of D5 occur in biota taken from areas close to sources of release.

4.3.4 Summary and discussion of bioaccumulation

A large amount of data is available on the bioaccumulation potential for D5. These are summarised below.

- A fish BCF of 7,060 l/kg was measured for fathead minnow (BCFs in the range 2,000-5,000 l/kg and above were also measured as part of a fish early life stage test with this species; the fish were growing rapidly and normalisation to a "standard" lipid content of 5 per cent would increase the reported BCFs by a factor of around 1.3-1.7 times). The BCF also appears to be above 10,000 l/kg for common carp, with a reported steady state BCF in the range 12,049 – 12,617 l/kg (based on parent compound analysis) or 10,550 – 11,048 l/kg when normalised to a 5% lipid content (the kinetic lipid-normalised BCF is higher). The depuration half-life was estimated to be between 19 and 22 days.

- The measured dietary BMF is 0.63 (steady state lipid normalised value) or 1.39 (growth corrected kinetic value; not lipid normalised) in rainbow trout. A dietary BMF of around 1 or above (growth corrected and lipid normalised BMF of 0.96-1.21) has been measured in carp.

- Laboratory accumulation studies with invertebrates (*Lumbriculus variegatus*) imply bioaccumulation factors of the order of 0.5 to 5 (based on the concentration in whole organisms (mg/kg) divided by the concentration in sediment (mg/kg dry weight). If it is assumed that exposure is mainly via pore water the equivalent BCF for D5 is in the range 1,000-24,000 l/kg; however there is considerable uncertainty in these estimates.

- Similarly, a laboratory accumulation study with *Hyalella azteca* gave mean biota-sediment accumulation factors (based on the concentration in whole organism (mg/kg lipid) divided by the concentration in sediment (mg/kg organic carbon)) of 0.053 and 0.82 in two sediments. Although high bioaccumulation factors could also be derived in this study (>1,000 l/kg) these were considered to be not reliable owing to the variability in the measured water concentrations.

- BSAF values (based on the lipid normalised concentration in biota/organic carbon normalised concentration in sediment) above one have been determined in some samples of flathead mullet from rivers in Japan. In addition, a benchmarking study suggests that the BSAF for D5 is higher than that for PCB-180 in ragworm and flounder in a UK estuary.

- A mixed picture is presented by field monitoring studies:

- The Lake Pepin field study shows that the trophic magnification factor (TMF) of D5 is less than one in this food web. The levels of D5 are highest in benthic invertebrates (and BSAF values above one are derived for the benthic invertebrates) and the results suggest that uptake from food rather than bioconcentration is the dominant uptake route in the food chain.
- The Lake Opeongo field study suggests that biomagnification may be occurring in a 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. Further work is needed to clarify this issue. Powell *et al.* (2010a) indicated that it was originally intended that further fish from Lake Opeongo would be sampled (using an appropriate quality control program) and analysed under laboratory conditions that have recently been optimized to minimise and better control the laboratory background contamination. However, CES (2010b) indicates that this is now not possible for logistical reasons. A repeat study has not been performed.
- The Oslofjord field study shows that the overall TMF for D5 is below one in this food web.
- The Lake Mjøsa field study provides indications that the TMF could be above one for D5. The actual value depends on which species are included in the analysis (2.28 for the whole food chain, 1.62 when smelt were omitted and 3.58 when trout were omitted), and the species at the highest trophic position (brown trout) had lower concentrations than smelt. Nevertheless, the TMF is still above one even when the smelt data are omitted. The smelt were sampled from a different area of the lake than the other species included in the study and so their inclusion in the regression could be questioned. However, as a pelagic species that ranges widely in the lake, this might not be important. This was a pelagic food chain (like Lake Opeongo) and contrasts with the benthic/benthipelagic food chains studied in Lake Pepin and Oslofjord and the pelagic food chain studied in Tokyo Bay.
- The Tokyo Bay field study shows that the overall TMF for D5 is below one in this food web. However, one individual BSAF was above one in this study (and two BMFs were equal to one).

In an evaluation relating to D4, RIVM (2012) suggested that the apparent differences between studies could possibly be the result of a deviation from thermodynamic equilibrium between sediment and water for those systems that receive the substance adhered to suspended particles from a sewage treatment plant (rather than from atmospheric deposition or direct emission). In food chains that originate from the pelagic environment, a different picture is obtained, as suggested for the pelagic part of the food chain in Lake Mjøsa (and to some extent Lake Opeongo), but not Tokyo Bay.

- Three new studies are available on the levels of D5 present in biota in remote regions. These studies are important as precautions were taken to avoid possible contamination of the samples with D5 during sampling, processing and analysis (such inadvertent contamination could have adversely affected the findings from earlier studies). In one study (Evenset *et al.*, 2009), although the overall sample numbers are

low, the results show that D5 has been detected in samples of Atlantic cod and polar cod and Kittiwake liver. The levels are generally low (often close to the limit of detection, and frequently not detectable) but higher levels (up to 60 µg/kg lipid in Kittiwake liver and 128 µg/kg lipid in samples of polar cod) have also been reported.

The second study (Campbell, 2010) found that D5 was detectable in some samples of Atlantic cod liver, bivalves, glaucous gull (*Larus hyperboreus*) liver and muscle, herring gull muscle and liver, sculpin liver and whole body, sea urchin, seal blubber, shrimp, sprat and zooplankton. Where detectable, the concentration of D5 was generally low, close to the method detection limit. However, it is noteworthy that levels of D5 up to 110 µg/kg wet weight (Atlantic cod liver) and 345 µg/kg wet weight (sculpin liver) were found in samples from Adventfjorden (which may reflect a local source) but D5 was still detectable in some of the samples from other more locations.

The third study is by Kierkegaard *et al.* (2010c). This found that D5 was not quantifiable in ten samples of Arctic char from remote lakes in Sweden (limit of quantification was <0.79 µg/kg wet weight). However , the substance was found in Arctic char and Baltic herring from more urban areas (Lake Vättern and Lagnö, Baltic Sea).

- The levels of D5 in biota are generally highest in samples collected from close to sources of emission. For example levels up to 3,137 µg/kg wet weight (i.e. 3 mg/kg or 3 ppm) have been measured in fish liver samples from Inner Oslofjord and up to 2,600 up to 2,600 µg/kg wet weight (i.e. 2.6 mg/kg or 2.6 ppm) in whole fish from the River Rhine. Although the data generally show that overall trophic dilution is occurring it is important to note that D5 is detectable in a wide range of species and trophic levels in food chains the food chains that have been sampled (for example Lake Pepin and Oslofjord; see Section 4.3.3.2) where sources of D5 exist.

- D5 can accumulate through the food chain all the way up to top predatory mammals (for example three mink in the Lake Pepin study; detectable levels of D5 have previously been found in samples of seal blubber from Denmark and pilot whale blubber from the Faroe Islands). However, biomagnification does not appear to be occurring (at least for the aquatic food web). No information is available for birds from similar food chains.

Overall the available field data show that D5 is detectable in biota in the environment, particularly in areas close to sources of release, but in some cases in samples from more remote regions (albeit at low concentrations typically close to the analytical detection limit. The available information on biomagnification in aquatic ecosystems is contradictory. There is evidence from predominantly benthic food chains and a pelagic marine food chain that trophic dilution is occurring. However, the available evidence from predominantly pelagic freshwater food chains suggests that trophic magnification may be occurring in those food chains. Biomagnification in top predatory mammals is not expected to occur, although D5 has been found throughout aquatic food webs, including in mink.

4.4 Secondary poisoning

Not relevant for this dossier.

5 HUMAN HEALTH HAZARD ASSESSMENT

A review of information related to human health is included in EA (2009a) and a more recent review by the Scientific Committee on Consumer Safety (SCCS, 2010) is also available. D5 is not classified on the basis of carcinogenicity, mutagenicity or reproductive toxicity. The carcinogenic potential of D5 was assessed in a single inhalation study using F344 rats (details of the study are summarised in EA, 2009a). No neoplastic changes were reported in the respiratory tract or in the liver in the study (these sites were identified as target tissues in repeated exposure studies), but there was an increased incidence of uterine endometrial adenomas and adenocarcinomas and a NOAEL of 40 ppm was identified. Mechanistic studies indicated that the uterine tumours arise because D5 acts as a dopamine agonist. Differences in the reproductive ageing process between humans and rodents mean that this mechanism is not relevant to humans, but it could be relevant to other mammal and bird species. EA (2009a) suggested that because the carcinogenic effect occurs late in life, it is not an effect that influences the sustainability of a population in a general sense, and therefore it was not necessary to take the carcinogenicity of D5 into account in a risk assessment for secondary poisoning of wildlife exposed via the food chain.

The main mammalian toxicological effect of concern identified for the secondary poisoning assessment was enlargement of the liver. This is thought to occur by a mechanism (a phenobarbital-type enzyme induction response) that is not relevant to humans, but the effects are considered relevant to wildlife (see EA (2009a) for a detailed discussion). The NOAEL for these effects is thought to be around 19 mg/kg bw/day. No functional or histopathological changes to the liver accompany the liver weight changes.

It is also important to note that adverse effects on reproduction have been reported for the related substance D4. For example, in inhalation reproductive studies D4 causes a reduction in the numbers of corpora lutea that manifest as reduced litter sizes at concentrations of 500 ppm and above (Environment Agency, 2009b). This is believed to involve interference with luteinising hormone pathways, and D4 has been classified in Annex VI of Regulation (EC) No. 1272/2008 as follows:

Hazard class and category: Repr. 2.

Hazard statement: H361f: Suspected of damaging fertility.

The potential reproductive toxicity of D5 has been examined in a one-generation inhalation range finding study and a two-generation inhalation reproductive study (Environment Agency, 2009a). However, the highest concentrations tested were 132 ppm (one-generation study) and 160 ppm (two-generation study) (the maximum concentrations achievable), which are both below the NOAEL identified for D4. Given the structural similarities between D5 and D4, Environment Agency (2009a) considered that it is possible that positive findings might be obtained for D5 if higher systemic doses were achieved, for example after oral dosing. This raises a concern that D5 may have the potential to cause adverse effects on reproduction (due to interference with a hormonal pathway), which is a remaining uncertainty. However, it should be noted that administration of D5 by the oral route results in a different kinetic profile than administration by inhalation, with more D5 being bound and not available for interaction with tissues by the oral route.

Environment Agency (2009a) considered that liver enlargement was the most sensitive effect resulting from exposure to D5 (i.e. the NOAEL for liver enlargement would likely be protective for effects on reproduction).

6 HUMAN HEALTH HAZARD ASSESSMENT OF PHYSICOCHEMICAL PROPERTIES

Not relevant for this dossier.

7 ENVIRONMENTAL HAZARD ASSESSMENT

7.1 Aquatic compartment (including sediment)

7.1.1 Toxicity test results

7.1.1.1 Fish

Summary of information from existing evaluation

The short- and long-term toxicity studies for D5 were reviewed in detail in EA (2009a). This evaluation concluded that D5 was not toxic to fish at concentrations up to its water solubility limit (0.017 mg/l at 23ºC). However, it was noted that the available long-term fish toxicity data were derived from bioaccumulation studies rather than standard ecotoxicity tests, and did not consider possible sensitive life stages or all toxicological end points (the tests are not comparable with a fish early lifestage test for example, and the studies generally focussed on mortality and visual inspection for overt signs of toxicity). It was noted that depuration of accumulated D5 from fish liver is slow, and that the long-term impact of such accumulation is not known.

New information

As part of a GLP bioconcentration study, a limit test was carried out to investigate the toxicity of D5 (purity 97.3% by GC) to Japanese medaka (*Oryzias latipes*) over 96 hours (CERI (2010); details of the bioconcentration study are reported in Section 4.3.2.2). Very few details of this test were provided. The nominal concentration was 45 mg/l which significantly exceeds the reported water solubility; the test solution was prepared with a solvent/dispersant. The experiment was carried out using a semi-static test method with renewal of test water every 8 to 16 hours, and a control was also used. This resulted in a 96-h LC_{50} >45 mg/l. The full study report is currently available only in Japanese. This result is consistent with the previous data on the short-term toxicity of D5 to fish, where no adverse effects have been seen at concentrations up to the water solubility limit.

An OECD Test Guideline 210 Fish Early Lifestage toxicity test has been carried out using D5 (Lee, 2009). The species used in the test was rainbow trout (*Oncorhynchus mykiss*) and the overall duration of the study was 90 days (30 days to hatch and 60 days post-hatch). The D5 used had a purity of 99.16 per cent and stock solutions of the substance for use in the test were prepared in dimethylformamide. The test was carried out using a flow-through system. The flow rate was such as to provide 7.7 aquarium volumes per day (90 per cent replacement time) up to day 75. On day 75 it was found that the exposure concentrations were lower than expected (possibly owing to the increased biomass present in the aquarium by this time point) and so the flow rate was increased to proved around 15 aquarium volumes per day (90 per cent replacement time of 4 hours) for the remainder of the study. The dilution water used was well water with hardness in the range 38 to 60 mg/l as $CaCO_3$ and a pH in the range 6.3 to 7.3. The test was carried out at a temperature of 12°C±2°C and the dissolved oxygen concentration was found to be in the range 6.6 to 11 mg/l throughout the test.

A total of five test concentrations (nominally 17 µg/l, 8.5 µg/l, 4.3 µg/l, 2.1 µg/l and 1.1 µg/l) were tested along with a control and solvent control (containing 0.034 ml/l of dimethylformamide). Four replicates were used for each treatment and control group. At the start of the test, each replicate consisted of 30 fertilized eggs (the eggs were approximately 1.25 hours old (post-fertilization) at the start of the test). The fertility of the exposed eggs was assessed on day 19 of the study and the percentage hatch was determined on day 30 of the study (at this time no more than 10 per cent unhatched viable embryos remained in any replicate). The post-hatch phase of the study was carried out using 15 embryos/larvae (these were selected on day 19 of the study in order to assure unbiased thinning of the larvae at the completion of hatch). The larvae were fed three times daily from day 9 post-hatch. The test was terminated at 60 days post-hatch. At this time point the percentage larval survival was determined, along with mean larval weight and length.

During the course of the test, samples of water were collected and analysed for the concentration of D5 present. The mean (±standard deviation) concentrations of D5 determined in the five exposure groups were 14±2.3 µg/l, 7.8±1.3 µg/l, 4.0±0.67 µg/l, 2.0±0.35 µg/l and 0.92±0.16 µg/l, which represented 82 to 95 per cent of the nominal concentrations.

No statistically significant difference (95 per cent level of certainty) was found between the control response and solvent control response for any endpoint considered, and so the responses from the treatment groups were compared with the pooled control group.

The mean embryo viability determined on day 19 of the test was in the range 68 to 81 per cent, which was consistent with the laboratory's expectation and historical performance. The mean per cent hatch determined on day 30 of the study was found to be 82 per cent in the control and 89 per cent in the solvent control (pooled control was 86 per cent). The mean per cent hatch in the D5 treatment groups was in the range 83 per cent to 94 per cent and these values were not statistically significantly different from the pooled control. Therefore no treatment-related effects on hatching success were evident in this study.

The mean per cent normal larvae in the control and solvent control at the end of the hatching period (day 30) were both 98 per cent. The mean per cent normal larvae in the D5 treatment groups was in the range 93 per cent to 99 per cent. No statistically significant differences were evident between the treatment groups and the pooled control groups. Therefore no treatment-related effects on the per cent normal larvae were evident.

At the end of the test (60 days post-hatch), the mean larval survival in the control group and solvent control group was 92 per cent and 90 per cent respectively (the pooled control was 91 per cent). The mean larval survival in the treatment groups was in the range 90 per cent to 92 per cent, which were not statistically significantly different from the pooled control group. Therefore no treatment-related effects on larval survival were evident.

The mean total length of larvae on day 60 post-hatch was 52.5 mm in the control group and 52.1 mm in the solvent control group (the pooled control group was reported to be 52.1 mm[37]). The mean total lengths of larvae in the treatment groups were in the range 51.2 mm to 52.0 mm, which were not statistically significantly different from the pooled control group. Similarly no statistically significant differences were found in the mean dried weight at day 60 post hatch of the treatment groups compared with the pooled control group. The mean dried weight of the larvae was 0.239 g in the control group and 0.238 g in the solvent control group (pooled control 0.239 g). The mean dried in the treatment groups was in the range 0.236 g to 0.246 g.

Overall, this study is a good quality (valid without restrictions) study. The overall NOEC from the study is determined to be ≥14 µg/l, the highest concentration tested.

A second fish early life stage test has been carried out with D5 (Parrott *et al.*, 2010). This test was with the egg to embryo-larval stages of fathead minnow (*Pimephales promelas*) and the total exposure period was 65 days (approximately five days in the egg stage and 60 days in the larval to juvenile stages). As well as toxicity, the study also investigated the bioaccumulation potential of D5 (reported separately in Section 4.3.2.2). A total of five D5 concentrations were used in the test (1.25, 2.64, 5.59, 11.8 and 25.0 µg/l for experiment 3). The test system was a flow-through system and a solvent (dimethyl sulphoxide) was used to prepare the stock solutions. The concentration of solvent in the exposure tank was either 40 µl/l (experiments 1 and 2) or 20 µl/l (experiment 3). A control and solvent control were run in each case.

Four replicates were used for each exposure level, with thirty eggs in each replicate at the start of the test. In all, three experiments were run. Experiment 1 was carried out using nominal concentrations between 2.5 and 50 µg/l but was terminated at days 18 and 19 post hatch owing to poor control survival (thought to result largely from the use of some inferior eggs in the experiment). Experiment 2 used the same nominal exposure concentrations but was again terminated early (on days 11 and 13 post hatch) when a malfunction in the water filtration system resulted in a large number of larval deaths. Experiment 3 was carried out using a nominal concentration range of 1.25 to 25 µg/l and was carried out until 60 days post hatch. No significant problems with the controls were seen on this occasion. The key time points during the study were at day 28 post hatch, where the fish were thinned to 18 per replicate, and day 48 post hatch, where the fish were thinned to 12 per tank.

The concentration of D5 in the water was determined analytically at intervals during the study. The concentrations measured were found to be consistent over the entire exposure period, and the mean concentrations measured were 0.253, 0.815, 1.68, 3.63 and 8.66 µg/l at the five treatment levels.

[37] This value appears to be an error. Based on the raw data given in the test report, the mean larval length in the pooled control group should be 52.3 mm; this does not affect the conclusions of the study. This has subsequently been confirmed by CES (2010).

No significant adverse effects were found between any of the treatment groups and the control groups for any of the endpoints monitored in the study (egg survival, percentage hatch, and survival, length weight and condition factor of the fish at days 28, 48 and 60 post hatch). There was a statistically significant increase in the condition factor in the two highest exposure groups compared to the control groups by day 60 post hatch but this was not considered to be an adverse effect.

Overall the study is considered to be of good quality (valid without restriction) and the NOEC is ≥8.66 µg/l.

The results from an unpublished 45-day toxicity study with rainbow trout (*Oncorhynchus mykiss*) are reported in Environment Canada (2011). The test report has not been provided to the rapporteur and so a brief summary of the results as reported in Environment Canada (2011) is provided below.

The test was carried out by Drottar and Woodburn (2009) using the OECD 204 Test Guideline but the exposure period was increased from 14 days to 45 days based on the estimated time to reach approximately 80 per cent of the steady state concentration in the fish following a previous bioconcentration study. Groups of ten juvenile fish were exposed to five concentrations of D5 (two replicates per concentration), along with replicate controls and solvent control (100 µl/l dimethylformamide). The nominal D5 concentrations used were 1.1, 2.1, 4.3, 8.5 and 17 µg/l but the concentrations were not verified analytically.

At the end of the 45 day exposure period all surviving fish appeared to be normal and healthy. The mortality seen in the negative control, solvent control and 1.1., 2.1, 4.3, 8.5 and 17 µg/l treatment groups was 5, 5, 0, 5, 25, 20 and 5 per cent respectively. The mortality seen in the 4.3 µg/l treatment group was statistically significantly ($p \leq 0.05$) higher than in the pooled control group. However, as there was no significant mortality at the higher test concentrations this mortality was not considered to be treatment-related. The 45-day LC_{50} was therefore determined to be >17 µg/l. The reliability of the results from this test is, however, questionable owing to a lack of analytical verification of the actual test concentration.

7.1.1.2 Aquatic invertebrates

Summary of information from existing evaluation

The short- and long-term toxicity studies for D5 were reviewed in detail in EA (2009a). This evaluation concluded that D5 was not toxic at concentrations up to its water solubility limit (0.017 mg/l at 23ºC) in both short-term studies and a 21-day reproduction study with *Daphnia magna*.

New information

No new information is available.

7.1.1.3 Algae and aquatic plants

Summary of information from existing evaluation

The available algal toxicity studies for D5 were reviewed in detail in EA (2009a). This evaluation concluded that D5 was not toxic at concentrations up to its water solubility limit (0.017 mg/l at 23ºC).

New information

No new information is available.

7.1.1.4 Quantitative structure-activity relationships (QSARs)

QSAR estimates for the toxicity of D5 are given in EA (2009a). However, these estimates are not relevant for this dossier as actual experimental data are now available for all relevant aquatic toxicity endpoints.

The available information suggests that D5 is not toxic to aquatic organisms at concentrations up to its solubility limit in water (17 µg/l). The REACH guidance document indicates that for substances with a narcotic mode of action, a toxic effect (lethality) is unlikely at body burdens below around 2 mmole/kg body weight (critical body burden) (the critical body burden values given in the REACH guidance are in the general range 2-8 mmol/kg body weight for acute effects).

For D5, 2 mmole/kg is equivalent to a concentration of 742 mg/kg body weight. Based on the water solubility of 17 µg/l and a fish BCF of 5,860-14,000 l/kg, the "maximum" concentration in fish that would result from prolonged exposure to the substance at its solubility in water would be 99-238 mg/kg body weight which is below this critical body burden for acutely toxic effects. This provides theoretical support for the observation that no acute toxicity is seen in toxicity tests involving exposure via the water phase only[38].

However, it should be noted that the critical body burden is only reasonably well defined for lethality. No critical body burdens are generally available for sub-lethal effects. One way to consider this is to base the critical body burden for D5 on the available long-term toxicity data for the related substance D4. These data are reviewed in EA (2009b) and a summary is presented below.

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. Following longer-term exposure, toxicity to fish is apparent, and the long-term NOEC for *Oncorhynchus mykiss* was determined to be 4.4 µg/l in a 14-day study and ≥4.4 µg/l (the highest concentration tested; no adverse effects

[38] It does not necessarily follow that this body burden can never be achieved in theory in the environment, since exposure via food could contribute to the total body burden as well as bioconcentration. For example, BAFs up to 56,000 l/kg have been determined for some sediment-dwelling organisms (see Section 7.1.1.5) and, if the concentration of D5 in the sediment pore water reached 17 µg/l then the concentration in the organism could reach 952 mg/kg body weight. This is consistent with effects seen at high D5 concentrations in some laboratory tests with sediment organisms.

were seen at this concentration) in a 93-day study. For invertebrates the 21-day NOEC with *Daphnia magna* was 7.9 µg/l (EA, 2009b).

Taking the long-term NOEC for fish to be 4.4 µg/l and the fish BCF to be 12,400 l/kg (EA, 2009b) then the critical body burden of D4 corresponding to the NOEC would be 54.6 mg/kg or 0.18 mmol/kg. Assuming that D5 acts by the same mechanism as D4, the equivalent body burden for D5 would be 68 mg/kg body weight. As noted above, it is theoretically possible for this body burden to be exceeded on long-term exposure of fish to concentrations of D5 close to its solubility limit if the BCF is above 5,000 l/kg.

Taking this into account, although no toxicity has been demonstrated in any long-term toxicity study using water-only exposures, effects cannot be excluded, and the true NOEC for D5 is probably close to the water solubility limit of the substance.

7.1.1.5 Sediment organisms

Summary of information from existing evaluation

EA (2009) summarises the available sediment toxicity data. Long-term sediment toxicity studies were available for two species (*Chironomus riparius* and *Lumbriculus variegatus*). The lowest NOEC from these studies was 70 mg/kg dry weight, obtained in a 28-day study with *Chironomus riparius*. The sediment used in this study had an organic carbon content of 3.2 per cent. Normalising this value to a standard organic carbon content gives a $NOEC_{standard}$ of 109 mg/kg dry weight.

New information

A sediment toxicity test has been carried out with D5 on the amphipod *Hyalella azteca* (Picard, 2009). The test method was based on the OPPTS Draft Guideline 850.1735. The D5 used had a purity of 99.16 per cent. The sediment was a natural sediment consisting of 83 per cent sand, 12 per cent silt and 5 per cent clay. The sediment had a pH of 6.0 and an organic carbon content of 4.8 per cent. The overlying water used was well water with a hardness of 54 mg/l as $CaCO_3$ and a pH of 7.1.

D5 was added to the sediment as a solution in dimethylformamide. The nominal concentrations tested were 16, 31, 63, 125, 250 and 500 mg/kg dry weight. Controls and solvent controls (containing 8.25 ml dimethylformamide in 0.82 kg dry sediment) were also prepared. Each test chamber consisted of 100 ml (approximately 4 cm depth) of sediment and 175 ml of overlying water.

The tests were carried out at 23±1°C over 28 days. An intermittent-flow system was used, whereby the overlying water was renewed at intervals (50 ml was renewed on seven occasions each day giving two volume additions per 24 hours). Eight replicates per treatment group were used to evaluate the biological response. Each replicate consisted of ten, 8-day-old amphipods at the start of the test. A further four replicates per treatment were used for analytical purposes. The amphipods were fed daily with a combination of yeast, cereal leaves and flaked fish food suspension throughout the test. The diet used was not spiked with D5.

The mean measured concentration in sediment over the 28-day period was determined to be 18, 28, 62, 130, 230 and 460 mg/kg dry weight in the nominal 16, 31, 63, 125, 250 and 500 mg/kg dry weight treatments respectively. The mean measured concentrations correspond to around 90-113 per cent of the nominal values.

The biological response seen in the control group for all endpoints was not statistically significantly different (at the 95 per cent confidence level) from the solvent control group and so the two control groups were pooled for comparison with the treatment groups.

For the survival endpoint, the mean survival in the control group and solvent control group was 98 per cent and 84 per cent respectively. The survival in the treatment groups was 94 per cent at 18 mg/kg dry weight, 83 per cent at 28 mg/kg dry weight, 98 per cent at 62 mg/kg dry weight, 93 per cent at 130 mg/kg dry weight, 64 per cent at 230 mg/kg dry weight and 19 per cent at 460 mg/kg dry weight. The survival was statistically significantly reduced compared with the pooled control group at 230 mg/kg dry weight and 460 mg/kg dry weight. Therefore the NOEC for survival was 130 mg/kg dry weight.

The other endpoint investigated was growth, determined as the mean dry weight per amphipod. This was found to be 0.49 mg in the control group and 0.54 mg in the solvent control group. For the treatment group, this parameter was only investigated for the 130 mg/kg dry weight treatment group and below as reduced survival was seen at higher concentrations. The average dry weight per amphipod was found to be 0.51 mg in the 18 mg/kg dry weight treatment, 0.36 mg in the 28 mg/kg dry weight treatment, 0.42 mg in the 62 mg/kg dry weight treatment and 0.46 mg in the 130 mg/kg treatment. These values were not statistically significantly different from the pooled control except for the 28 mg/kg dry weight treatment group. However, it is apparent that for this treatment group survival in one of the eight replicates was reduced (survival was 0 per cent in one replicate and 70 to 100 per cent in the remaining seven) and it was thought that this may have been due to human error during addition of the organisms to the test vessel or recovery from the test vessel, or other non-substance related factors. Given that no statistically significant effects on growth were evident at the two higher test concentrations it was considered that the effects seen at 28 mg/kg dry weight were not treatment-related.

Overall the NOEC from this study was 130 mg/kg dry weight (the equivalent $NOEC_{standard}$ would be 135 mg/kg dry weight, normalised to for a sediment with 5 per cent organic carbon content). The EC_{50} for survival was estimated to be 310 mg/kg dry weight (95 per cent confidence intervals 210 to 360 mg/kg dry weight). The study is considered to be of good quality (valid without restriction).

A second toxicity study with *Hyalella azteca* has been carried out by Norwood *et al.* (2010). The test was carried out using two natural sediments, one from Lake Erie (composition 0.5 per cent organic carbon, 19 per cent clay, 75 per cent silt and 6 per cent sand) and one from Lake Restoule (composition 11 per cent organic carbon, 6 per cent clay, 70 per cent silt and 24 per cent sand). A total of five concentrations of D5 were used for each sediment. The nominal concentrations were 28, 62, 130, 230, 460 and 889 mg/kg dry weight for the Lake Erie sediment and 21.5, 51.3, 122, 292, 697 and 1,664 mg/kg dry weight for the Lake Restoule sediment. The D5 was added to the sediment as a solution in dimethyl formamide and a control and solvent control were also run. Four replicates, each of fifteen organisms were run for each exposure level. Each replicate contained around 15 ml of wet sediment and dechlorinated tap water was added to give a total volume of 1 litre. The exposure vessels

were incubated at 25°C and the animals were fed fish food flakes (not spiked with D5) during the test.

The concentrations present in the sediment were analytically determined at the start and end of the test. The concentrations were found to be relatively stable over the course of the test but in some cases differed from the nominal concentrations (see also Section 4.3.2.2 where the bioaccumulation part of this study is discussed), and the toxicity results were expressed in terms of the mean concentration measured in sediment over the 28-day period. The mean measured concentrations in the Lake Erie sediment were 21.7, 62, 154, 197, 260 and 283 mg/kg dry weight for the five exposure levels and the mean measured concentrations in the Lake Restoule sediment were 67.4, 303, 641, 558, 1,081 and 1,181 mg/kg dry weight for the five exposure levels. Traces of D5 could be detected in the control and solvent control sediment but these were close to the detection limits and were significantly lower than the spiked concentrations.

At the end of the 28-day exposure period the total survival and growth (based on weight of the organisms) of the organisms was determined. A dose-related increase in mortality was seen in both sediments at day 28 with the mean per cent survival declining to 17 per cent at 283 mg/kg dry weight in the Lake Erie sediment and 18 per cent at 1,181 mg/kg dry weight in the Lake Restole sediment. The mean survival in the control and solvent control was 90 per cent and 87 per cent respectively for the Lake Erie sediment and 75 per cent and 85 per cent respectively for the Lake Restole sediment. The LC_{50}s derived from the study for survival were 194 mg/kg dry weight for the Lake Erie sediment and 785 mg/kg dry weight for the Lake Restoule sediment. The NOECs for survival were 62 mg/kg dry weight for the Lake Erie sediment and 641 mg/kg dry weight for the Lake Restoule sediment (note: the LOEC value for Lake Restoule, 558 mg/kg dry weight, is actually below the NOEC, owing to the fact that the concentrations actually measured at these two exposure levels are the opposite way around to what would be expected based on the nominal concentrations).

There were no significant differences in the growth of the organisms in any of the treatment groups compared with the control groups in the Lake Erie sediments and so the NOEC for growth in this sediment is ≥283 mg/kg dry weight. A 34 per cent reduction in growth compared with the growth in controls was evident at the highest exposure concentration in the Lake Restoule sediment and an EC_{25} for growth of 821 mg/kg dry weight was calculated for this endpoint.

The study is considered to be of good quality (valid without restriction). Overall the growth endpoint was considered to be less sensitive to D5 than the survival endpoint and the overall NOECs from the study are 62 mg/kg dry weight for the Lake Erie sediment and around 641 mg/kg dry weight for the Lake Restoule sediment. Normalising these NOECS to a standard organic carbon content of 5 per cent results in a $NOEC_{standard}$ of 620 mg/kg dry weight for the Lake Erie sediment and 290 mg/kg dry weight for the Lake Restoule sediment.

A further chronic toxicity study has been carried out for D5 with the bacterivorous nematode *Caenorhabditis elegans* (Vaughan and Roberts, 2009). The study method used was based on the draft ISO/TC 147/SC 5 N method[39]). In the test juvenile *C. elegans* were exposed to D5 (nominal concentrations of 0.1, 1.0 and 10 mg/kg dry weight) in artificial sediment under

[39] ISO/TC 147/SC 5 N, ISO/WD Nemotoda.2. Water Quality – Determination of the toxic effect of sediment and soil samples on growth, fertility and reproduction of *Caenorhabditis elegans* (Nematoda), Draft 2006.

static conditions for 96 hours at 20°C (96 hours is sufficient for the control test organisms to complete a whole life cycle). The substance was added to the sediment as a solution in acetone and was allowed to equilibrate with the sediment for seven days before the start of the test. A total of four replicates per treatment group were used in the study, with ten first-stage juveniles being used for each replicate at the start of the test. A control and solvent control were also run. The endpoints determined in the study were inhibition of growth (mean measured increase in body length), fertility (percentage gravid test organisms) and reproduction (mean number of offspring per female).

The D5 concentrations in the sediment were measured at the start of the test (day 0) and after 96 hours. The mean concentrations measured at day 0 were 0.054, 0.51 and 4.3 mg/kg dry weight for the 0.1, 1.0 and 10 mg/kg dry weight treatments. The respective concentrations measured after 96 hours were 0.052, 0.43 and 2.1 mg/kg dry weight, indicating that the concentrations declined slightly during the test (more than 50 per cent in the top dose).

No treatment related effects were apparent in any of the treatment groups when compared with the control groups for the growth, fertility and reproduction endpoints. However, it was noted that the mean reproduction in the control and solvent control was 1.9 and 5.7 offspring per female respectively, which was well below the validity criteria of at least 30 offspring per female given in the test guideline. Therefore, although no effects were seen in this study, the results of the study should be treated with caution as the test is of questionable validity in relation to the reproduction endpoint in particular.

7.1.1.6 Other aquatic organisms

No data are available.

7.1.1.7 Summary of aquatic toxicity data

The available aquatic toxicity data for fish, invertebrates and algae show that D5 does not cause toxic effects in either short- or long-term studies at concentrations up to its water solubility limit (~0.017 mg/l).

Long-term sediment data are also available, covering four species (although the test for one of the species is of questionable validity). The lowest valid NOECs from these studies were 70 mg/kg dry weight, obtained in a 28-day study with *Chironomus riparius*, and 62 mg/kg dry weight in a 28-day study with *Hyalella azteca*. The lowest NOEC when normalised to a standard organic carbon content of 5 per cent is a $NOEC_{standard}$ of 109 mg/kg dry weight for *Chironomus riparius* (for comparison with the pelagic organisms, the equivalent pore water concentration, assuming that the effects seen occur via exposure to pore water, is estimated to be around 0.014 mg/l using the methods outlined in the REACH Guidance; this is close to the solubility limit for D5 in pure water).

7.2 Terrestrial compartment

7.2.1 Toxicity test results

7.2.1.1 Summary of information from existing evaluation

No toxicity data were available for soil organisms in the existing evaluation.

7.2.1.2 New information

The toxicity of D5 to soil organisms has been studied by Soil Toxicology Laboratory (2010). The results are also published in a paper by Velicogna *et al.* (2012). The methods used followed Environment Canada's standardized biological test methods (Environment Canada, 2004, 2005 and 2007 which are broadly similar to the corresponding ISO and/or OECD Test Guideline). In these tests D5 was applied to soil by firstly spiking the D5 into organic cow manure and then adding the spiked cow manure to a natural sandy loam soil at a rate corresponding to 5 g dry biosolids/kg dry soil. This rate of application is equivalent to a biosolids spreading rate of 8 tonnes/ha, which is a common application rate for biosolids on agricultural soils. The moisture content of the amended soil was around 38 per cent and the pH was 7.55. Two controls were used for the test, one prepared using unspiked cow manure and the second (negative control) consisting of an artificial soil (10 per cent air-dried peat, 20 per cent kaolin clay and 70 per cent silica sand). The organic carbon contents of the test soils were not given, but the organic carbon content of the cow manure used was 31.8 per cent (not clear if this is on a dry weight or wet weight basis).

Range-finding tests were firstly carried out using four plant species (barley (*Hordeum vulgare L.,* monocot), durum wheat (*Triticum durum*, monocot), red clover (*Trifolium pretense*, dicot) and radish (*Raphanus sativus*, dicot)), a springtail (*Folsomia candida*) and earthworm (*Eisenia andrei*). During these trials, the concentration of D5 in soil was measured at the start of the test and at weekly intervals thereafter (the length of the range-finding tests was between 7 and 28 days depending on the species). Loss of D5 from the test system was evident; the average percentage loss was 56 per cent on day 14 and 78 per cent on day 28. The results of the range finding tests were used to determine the dosages and species to be tested in the definitive test. For the plants, effects were seen with barley and, to a lesser extent with durum wheat. No significant effects were noted with either of the two dicot species tested. Barley was selected for the definitive test, along with red clover (as an example of a dicot, primarily chosen owing to the availability of seeds at the time of the test).

The definitive tests were carried out using nine D5 concentrations. The duration of the tests was 14 days for plants, 28 days for springtails and 56 days for earthworms. The concentration of D5 in the soil was measured analytically only on day 0 of the definitive test and so the results are presented in terms of the initial concentration (significant loss of D5 over the test period would be expected based on the range-finding test results).

For the plants, the emergence of both species was not affected at the highest concentrations tested (3,127 mg/kg dry weight for barley and 4,054 mg/kg dry weight for red clover). No effects were seen with red clover for the other endpoints determined (shoot and root length and individual dry mass). For barley, the shoot and root length and individual dry mass declined with increasing exposure concentration, and the most sensitive endpoint was the

individual dry mass of barley roots for which an 14-d IC_{50} of 209 mg/kg dry weight was determined.

For the springtail test, treatment related effects on both adult survival and juvenile production were seen. The 28-d LC_{50} for adult survival was 813 mg/kg dry weight and the 28d-IC_{50} for juvenile production was 767 mg/kg dry weight.

For the earthworm test, no treatment related effects on adult survival were seen at day 28. A concentration-related decrease in juvenile production was seen, but the 28-d IC_{50} for the effect was above the highest concentration tested (>4,074 mg/kg dry weight). The decrease in juvenile production was statistically significant ($p<0.05$) compared with the controls at concentrations of 507 mg/kg dry weight and above. The mean individual dry mass was found to increase at concentrations of 1,093 mg/kg dry weight and above (possibly as a result of less competition for food).

Overall, the most sensitive species tested was barley with a 14-d IC_{50} of 209 mg/kg dry weight. No NOECs were reported in the study.

The organic carbon content of the soil used in the test was not given and so it is not possible to normalise the reported effect concentrations to a standard organic carbon content of 2%, nor is it possible to estimate the equivalent pore water concentration at these exposure levels. It is also important to note that the results were reported based on the concentration of D5 measured on day 0 of the study only. It is likely that significant loss by volatilisation would have occurred during the test. Therefore these results should be used with care.

7.2.1.3 Summary of terrestrial toxicity data

D5 has been shown to cause effects on plants, springtails and earthworms. The lowest reported IC_{50} was 209 mg/kg dry weight for barley. It is important to note, however, that the results available are based on the initial concentration of D5 in soil. Significant loss through volatilisation would be expected in the test system used and so the actual exposure concentrations (and hence effect concentrations) may be significantly lower than those based on the initial concentration.

7.3 Atmospheric compartment

No relevant information available.

7.4 Microbiological activity in sewage treatment systems

Not relevant for this assessment.

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

7.5.1 Toxicity to birds

A range-finding test as a preliminary to a reproductive toxicity study has been carried out with Japanese quail (*Coturnix coturnix japonica*) (Stafford, 2012). Pairs of birds were

exposed to D5 via their diet at nominal concentrations of 250, 500 and 1,000 mg/kg feed (the total numbers of pairs were 7 in the control group and 6, 5 and 5 in the treatment groups respectively). The birds were 14 days of age at the start of the test and were fed under reduced light hours (7 hours light, 17 hours dark) for the first four weeks. The light hours were then increased (14 hours light, 10 hours dark) to stimulate egg production (egg production was at an adequate level within 3 weeks of photostimulation). After this time five sets of eggs were collected (a set was the weekly production of eggs) over a period of approximately 8 weeks. The egg sets were incubated, candled for embryo viability and survival and hatch. The study was ended once the five egg set had hatched.

All of the pairs produced eggs. However, one pair in the 500 mg/kg feed group produced only a small number of normal eggs (six normal, one soft-shell) and none of these were fertile. The data for this pair were omitted from the subsequent evaluation of the egg production data (i.e. effectively only four pairs were used from the 500 mg/kg feed group). Based on the good reproductive performance of the other pairs in this treatment group, Stafford (2012) considered that the poor performance of this one pair was not treatment-related.

Owing to the unequal number of replicates in the control and each treatment group, the egg production and hatching data were presented as proportional data. The following endpoints were monitored in the study: average total food consumption per bird, total eggs laid, total eggs cracked, total eggs set, egg set of laid, total eggs viable, eggs viable of set, total surviving embryos, surviving embryos of viable eggs, total hatchlings, total hatchlings of surviving embryos, average hatchling weight, male body weights, female body weights, total male weight gain and total female weight gain. No treatment-related effects on egg production or hatching were evident. In addition no treatment-related effects on adult mortality, body weight gain or behavioural abnormalities were seen.

The results of this test suggest that D5 did not cause treatment-related effects at concentrations up to 1,000 mg/kg feed. However, it should be noted that the proportion of viable eggs of those incubated for the control was relatively low (0.65 as a proportional average) compared with the treatment groups (0.82 for the 250 mg/kg group, 0.73 for the 500 mg/kg group and 0.83 for the 1,000 mg/kg group). The OECD 206 Test Guideline suggests that the normal value for viability (expressed as the per cent viable embryos of eggs set) is in the region of 80-92 per cent. Although expressed on a different basis it is possible that the control response here could have been lower than would normally be expected. In addition, it should also be noted that the test was designed as a range finding test and not all endpoints were investigated (e.g. egg shell thickness). Therefore the results should be used with care.

8 PBT AND vPvB

8.1 Comparison with criteria from Annex XIII

Persistence

A substance is considered to be persistent (P) if it has a 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.

D5 is considered to be not readily biodegradable but it does degrade in water by hydrolysis. The half-life for hydrolysis is dependent on the pH and temperature. EA (2009) reviewed the available data and recommended the following half-life values.

- Hydrolysis half-life at pH 7 and 12°C (freshwater) = 365 days.
- Hydrolysis half-life at pH 8 and 9°C (marine water) = 64 days.

Furthermore, EA (2009) reports the approximate pH ranges between which the hydrolysis half-life of D5 would be 60 days or longer. These are given below:

- pH ~6.3 to ~7.1 at 25°C.
- pH ~5.7 to ~7.9 at 12°C.
- pH ~5.6 to ~8.0 at 9°C.

Outside of these ranges the hydrolysis half-life would be below 60 days. It is important to note that the standard generic environmental conditions normally assumed in the REACH Guidance are a pH of 7 and a temperature of 12°C for freshwater environments and a pH of 8 and a temperature of 9°C for the marine environment. Under both sets of conditions, the hydrolysis half-life would be above 60 days. Therefore it is concluded that D5 meets the Annex XIII criteria for a very persistent (vP) substance in water under some circumstances (although there will be water bodies where the half-life is below 60 days).

However, D5 is highly adsorptive to organic matter in suspended solids, sediment and soils, so the relevance of hydrolysis for such a hydrophobic substance is low. D5 has a long degradation half-life in sediment (of the order of 800-3,100 days at 24°C and would be expected to be longer at lower temperatures). This is again above the Annex XIII criteria for a persistent (P) and very persistent (vP) substance. Persistence in sediment is supported by the sediment core data from Lake Pepin.

For soil, the situation is less clear: although rapid degradation of D5 is evident in dry soils in equilibrium with air of relative humidity up to around 90 per cent, the rate of reaction reduces markedly with increasing moisture content. Therefore it is probable that under some situations rapid degradation of D5 may occur, but in other situations the degradation in soil will be slower.

When considering the persistence of D5 in any one medium it is important to recognise that it is highly volatile and so can be lost from water bodies (and soil) by this mechanism (and this

is likely to be the major removal mechanism in some water bodies and soil). Therefore to account for these factors it is necessary to consider the persistence of the substance in the whole environment rather than just the water or sediment compartment alone.

Various modelling approaches have been used to estimate the expected environmental distribution and overall persistence of D5. Although these generally predict a relatively short persistence in the water column (owing to loss from volatilisation and to a lesser extent hydrolysis) the models also generally predict that a significant proportion of D5 will distribute to the sediment phase and that the persistence of D5 in sediment may be much longer than found in the water column. Furthermore, in many simulations, the persistence in sediment is related to the rate of sediment burial and re-suspension assumed in the model. This itself does not necessarily result in an overall loss of D5 from the environment but rather, in the case of sediment burial, results in transfer of D5 to deeper sediment layers where it may persist. The actual fraction of D5 distributed to sediment and the persistence of D5 in sediment in any one system will depend on a number of site-specific factors including the pH, the water depth, the temperature, the sediment deposition rate, the concentration of particulate and dissolved organic carbon, etc. For the systems recently investigated the effective half-life of D5 in sediment was estimated to be around 87 days (Lake Pepin), 396 days (Inner Oslofjord), 2,060 days (Lake Ontario), 7 months (coastal sediment, Baltic Proper) and 18 months (deep water sediment; Baltic Proper). In addition, actual sediment core data from Lake Pepin strongly suggest that D5 has a half-life in sediment much longer than predicted in the modelling exercise for that lake.

The available modelling studies on long-range transport potential of D5 (both reported in this evaluation and the EA (2009) report) suggest that although D5 can be transported to remote regions to some extent via the atmosphere, significant deposition in remote regions is unlikely. Transport through the marine environment is also unlikely given D5's overall volatility and hydrolytic instability at normal pHs of the marine environment.

It should be noted that although the models generally predict an overall relatively short persistence in water and air (and the environment as a whole[40]), D5 has been found in samples from remote regions (for example air samples from the Arctic, sediment from the Barents Sea and biota from Svalbard). The interpretation of the monitoring data in remote regions is complicated by two main issues: firstly, the possibility of inadvertent contamination of the samples with D5 during collection and analysis unless adequate controls are taken to limit this and secondly, the likelihood of local sources of emission in some remote areas. Thus, although the actual transport process is not clear (local sources, sediment transport, food chain transfer and/or aerial deposition) these data do suggest that D5 is sufficiently persistent to allow occurrence in biota in remote regions.

An expert panel workshop hosted by the Global Silicones Counsel has considered the relative importance of overall persistence compared with compartment-specific persistence for D5 (Global Silicones Counsel, 2009). The workshop participants agreed that "it is not appropriate to imply that overall persistence is more important than compartment-specific persistence because the overall persistence is derived by adding the persistence from each of

[40] The overall persistence estimated in global-type models can be considered as effectively the weighted average of the persistence in the various compartments. Since, at steady-state, a high proportion of D5 in the model is expected to be in the atmosphere, the overall persistence is governed mainly by the persistence in air, and to a lesser extent by the persistence in water. Thus an overall relatively short environmental persistence does not preclude a high persistence of D5 in sediment.

the relevant environmental compartments" and that "persistence should be based on a compartment of concern, not persistence in each compartment".

Overall the available data suggest that D5 can be considered to meet the Annex XIII criteria for a persistent (P) and very persistent (vP) substance based on the measured and predicted half-lives in water and sediment.

Bioaccumulation

According to Annex XIII of REACH, 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. However, the REACH Annex XIII criteria are currently being discussed in terms of using a weight of evidence approach in the assessment of B and vB. Given the large amount of data available for D5 a weight of evidence approach is considered appropriate in this case. In order to facilitate this, the available evidence has been categorised in terms of providing unequivocal/strong support, equivocal support or no support in relation to a number of important issues.

i) Information providing **unequivocal** support for B or vB under the current Annex XIII criteria:

- The measured fish BCF for D5 is 5,860 l/kg in fathead minnow and so it clearly meets the Annex XIII B and vB criteria. This is supported by additional BCF data for common carp, which significantly exceed the vB criterion (BCF > 10,000 l/kg).

ii) Information providing **unequivocal** support that D5 is bioaccumulative or very bioaccumulative in the broader sense:

- No unequivocal information to support this.

iii) Information providing **equivocal** support that D5 is bioaccumulative or very bioaccumulative in the broader sense:

- Laboratory accumulation studies with invertebrates (*Lumbriculus variegatus*) imply bioaccumulation factors of the order of 0.5 to 5, based on the concentration in whole organisms (mg/kg) divided by the concentration in sediment (mg/kg dry weight). If it is assumed that exposure is mainly via pore water the equivalent BCF for D5 is in the range 1,000-24,000 l/kg. A similar analysis of data for polychaetes from the Humber Estuary results in lower estimates of the BCF of between around 2,800 and 4,600. However there is considerable uncertainty in these estimates. In addition, BSAF values of >1 are derived for benthic invertebrates in the Lake Pepin field study and polychaetes in the Humber Estuary.

- A fish feeding accumulation study is available for D5 with rainbow trout (reviewed in detail in EA (2009) and summarised in Section 4.3.2.1 of this report) showing that uptake of D5 from food can occur. Although the steady-state BMF is below 1, much of the depuration seen in the fish in this study appears to result from growth dilution. Therefore the BMF for D5 could be above one in fish that are not growing rapidly (as shown by the growth-corrected values in Section 4.3.2.1). In addition to this, the study found that, although there is evidence of metabolism of D5 in the fish, the growth

corrected depuration half-life is relatively long (estimated to be around 74 days), and a significant amount of D5 is still present in the fish liver 42 days after exposure had ceased. A further fish feeding study is available with carp which suggests that the growth corrected and lipid normalised BMF in this species is around 1 or above. These data therefore provide supporting evidence that D5 may be bioaccumulative, particularly in slow-growing fish.

- Field studies provide a somewhat mixed picture of the bioaccumulation behaviour of D5, which could be linked to different sources of the substance that in turn might lead in some cases to deviation from thermodynamic equilibria. For example, there is some evidence from pelagic based food chains (Lakes Mjøsa and Opeongo, but not Tokyo Bay) that biomagnification may be occurring (with TMFs in the range 1.62 – 3.58 for Lake Mjøsa, depending which species are included). In contrast, food chains dominated by benthic exposure (related to the introduction of the substance adsorbed to suspended matter from sewage treatment works) show TMFs below one (Lake Pepin, Oslofjord and Tokyo Bay). BSAFs and BMFs for some individual feeding relationships are also greater than or equal to one, particularly towards the base of the food web. For example, a field study from Japan found that whilst most BSAFs (expressed on a lipid normalised concentration in biota/organic carbon normalised concentration in sediment) for fish were below one, the BSAFs for flathead mullet were above one in two locations.

- Three "benchmarking" studies using PCB-180 as the reference chemical are available. These studies appear to show that the overall behaviour of D5 in various food chains is similar to that of PCB-180 when benthic invertebrates and fish are considered but indicate a much lower accumulation of D5 relative to PCB-180 in aquatic mammals. However, there are considerable uncertainties in interpreting these data (for example related to potentially different routes of exposure of D5 versus PCB-180) and the relatively limited sample sizes and inherent variability in the measured concentrations mean that relatively small, but important, differences between the behaviour of D5 and PCB-180 may not be apparent (for example slightly increasing or decreasing concentrations across the food chain).

- D5 has been found to be present in a wide range of organisms (particularly fish and aquatic invertebrates but also birds and mammals). Levels of D5 in livers of wild fish have been detected at levels above 3 mg/kg wet weight in polluted areas. D5 is also found in biota in regions with low background levels in abiotic media (e.g. Svalbard) (generally at very low concentrations close to the analytical detection limit, but up to 60 µg/kg lipid in Kittiwake liver and 128 µg/kg lipid in samples of polar cod in one study and levels of up to 110 µg/kg wet weight (Atlantic cod liver) and 345 µg/kg wet weight (sculpin liver) in a second study), and has been reported in marine mammal blubber and marine bird livers. It should be noted that in these studies in remote regions D5 was not detected in a significant number of samples and it is possible that these elevated concentrations reflect local sources in remote regions rather then long-range transport of D5 to remote regions (although it is not clear if local sources can explain all such findings).

iv) Studies providing contrary/non-supporting information that D5 is bioaccumulative or very bioaccumulative in the broader sense:

- Two benthic/benthipelagic food web studies (Lake Pepin and Oslofjord) suggest that TMFs and BMFs are below one in the food chains that were investigated. A study of a pelagic food chain in Tokyo Bay also indicates that the TMF for D5 is below one (with only a very small probability of the value being above 1 (2.5-3.5%). In addition, BMFs for specific predator-prey relationships were one or below. Nevertheless, these studies demonstrate that D5 is present in a variety of species throughout the food web, including top predatory mammals in one case. Therefore although the data suggests that biomagnification of D5 is not occurring, D5 is detectable in biota in the environment, particularly near to sources of release.

- Laboratory studies using natural sediments with *Hyalella azteca* have found BSAF (expressed on a lipid normalised concentration in biota/organic carbon normalised concentration in sediment) generally below 1 for this species. Although high bioaccumulation factors could also be derived in this study (>1,000 l/kg) these were considered to be not reliable owing to the variability in the measured water concentrations.

- The bioaccumulation potential for D5 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 (reviewed in detail in EA (2009)). This relates to the more rapid elimination kinetics (via respired air) and more rapid metabolism in rodents compared with fish. The toxicokinetics of D5 in mammals exposed via oral routes appear to be less clear than for inhalation and, although it is likely that rapid metabolism and/or excretion does occur, it is possible that some of the D5 is available for storage in the lipid compartments of the animal. EA (2009) notes that there are some uncertainties over whether this behaviour after oral exposure is a consequence of the high concentrations and method of administration (e.g. gavage) in oral studies, and also over whether the D5 associated with the lipid fractions in the body is actually biologically active (although the influence of fat metabolism on D5 bioavailability at different stages of the life cycle is unknown). Although accumulation in mammals appears to be lower than in other aquatic organisms, the top predator in some food chains may not be air breathing, and no information is available for birds.

One of the principal concerns around bioaccumulative substances is the likelihood that they will increase in concentration up the food chain. Whilst trophic magnification factors might be considered to be the ultimate measure of a substance's ability to bioaccumulate significantly (e.g. Weisbrod *et al*. (2009) and Gobas *et al.* (2009))[41], field studies must be

[41] It should be noted that in relation to biomagnification potential the current REACH Guidance states that "However, because food chain transfer and secondary poisoning are basic concerns in relation to PBT and vPvB substances, an indication of a 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". Taken from Section R.11.1.3.2 of the Guidance on information requirements and chemical safety assessment, Chapter R.11: PBT Assessment.

treated with caution due to the limitations of sampling, uncertainties in food chain relationships and analytical variation.

There is unequivocal evidence that D5 can be found throughout aquatic food chains, including top predators such as mink. There is equivocal evidence to suggest that although D5 is frequently found in biota in the environment, the highest concentrations are associated with local sources of release (including in many cases its presence in biota in remote regions). Accumulation from sediment has been demonstrated. The available evidence with respect to biomagnification is inconclusive: two field studies (Lake Pepin and OsloFjord) suggest that trophic dilution occurs in benthic and benthipelagic food chains and one field study (Tokyo Bay) suggests trophic dilution is occurring in a pelagic food chain, but a fourth study (Lake Mjøsa) suggests that trophic magnification may have been occurring in a pelagic food chain. A similar finding of trophic magnification in pelagic food chains in a fifth study (Lake Opeongo) is of uncertain reliability. The potential for biomagnification in mammals appears to be low.

In conclusion, D5 meets the Annex XIII criteria for vB based on the fish BCF. Although trophic dilution has been observed in several food chains, this is not sufficient to overrule this conclusion given the other evidence that is available.

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; or
- the substance is classified as carcinogenic (category 1 or 2), mutagenic (category 1 or 2) or toxic for reproduction (category 1, 2 or 3)[42]; or
- there is other evidence of chronic toxicity, as identified by the classifications T, R48, or Xn, R48, according to Directive 67/548/EEC[43].

The available aquatic toxicity data for fish, invertebrates and algae show that D5 does not cause toxic effects in either short- or long-term studies at concentrations up to its water solubility limit. Therefore it can be concluded that D5 does not meet the Annex XIII criteria for a toxic substance based on its aquatic toxicity. Theoretical considerations based on body burden approaches suggest that effects on fish following long-term exposure cannot be excluded, and the true NOEC for D5 in aquatic organisms is probably close to its water solubility limit (17 µg/l). It is noted that the related substance D4 has effects on mammalian reproduction (see below), and no data are available to determine whether D5 (or D4) affects fish reproduction.

Toxicity of D5 has been observed in sediment and soil organisms. The calculated likely pore water concentration in these tests corresponding to the lowest NOEC seen is around 0.014 mg/l (close to the water solubility limit of the substance) in sediment organisms (it is

[42] The CLP Regulation (EC) No 1272/2008 has amended this to be substances classified as carcinogenic (category 1A or 1B), germ cell mutagenic (category 1A or 1B), or toxic for reproduction (category 1A, 1B or 2).
[43] The CLP Regulation (EC) No 1272/2008 has amended this to be "there is 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".

not possible to carry out the calculation for the available soil toxicity data). Thus the sediment data are consistent with the substance not meeting the Annex XIII criteria for a toxic substance.

D5 is not classified on the basis of carcinogenicity, mutagenicity, or reproductive toxicity, so it does not meet the Annex XIII T criteria based on its human health classification. Nevertheless, there are some concerns that must be taken into account:

- Liver enlargement in rats, thought to occur by a mechanism that is not relevant to humans (a phenobarbital-type enzyme induction response), but could be relevant to other wildlife. The NOAEL for these effects is 5 mg/kg bw/day, which is low enough to be considered a similar level of concern to wildlife as a substance with an R48 classification. No functional or histopathological changes to the liver accompany the liver weight changes, so it is unclear whether these changes alone are sufficiently adverse to be considered within the PBT assessment.

- An increased incidence of uterine endometrial adenomas and adenocarcinomas in rats following inhalation exposure (NOAEL of 40 ppm). Although these tumours occur by a mechanism that is not relevant to humans, they might be relevant to other mammal and bird species. The carcinogenic effect occurs late in life, so appears not to be an effect that influences the sustainability of a population at a general level. It is also relevant to note that Category 3 carcinogens do not trigger the T criterion, so the cancer end point alone is not a sufficient cause for concern in this context.

- The related substance D4 has been shown to cause effects on reproduction in mammals via inhalation (and is classified for such effects). This is believed to be due to interference with luteinising hormone pathways. Although no adverse effects were seen in reproductive toxicity tests carried out with D5 via inhalation exposure, the maximum concentrations achievable were below those at which D4 caused effects. Therefore, it cannot currently be ruled out that D5 could cause similar effects on reproduction if higher systemic doses were achieved (e.g. following oral dosing). However, it should be noted that administration of D5 by the oral route results in a different kinetic profile than administration by inhalation, with more D5 being bound and not available for interaction with tissues by the oral route.

- A range-finding test as a preliminary to an avian reproductive toxicity study has been carried out with D5 with Japanese quail. The results of this test suggest that D5 did not cause treatment-related effects at concentrations up to 1,000 mg/kg feed. However, owing to the nature of this test, the results should be used with care.

Overall, the available data suggest that D5 does not meet the T criteria, but there are uncertainties in the interpretation of the available database for mammals (and only limited data are available for fish and birds).

8.2 Assessment of substances of an equivalent level of concern

Not relevant for this dossier.

8.3 Emission characterisation

Since this dossier relates to evaluation of the data in the context of whether the PBT criteria are met, emission characterisation is not relevant. A detailed assessment of the emissions of D5 throughout the lifecycle is included in EA (2009).

8.4 Conclusion of PBT and vPvB or equivalent level of concern assessment

Based on the available data, D5 clearly meets the REACH Annex XIII criteria for a vPvB substance due to its persistence in sediment and a high fish bioconcentration factor from laboratory studies. The available evidence with respect to biomagnification is inconclusive: two field studies (Lake Pepin and Oslofjord) suggest that trophic dilution occurs in benthic and benthipelagic food chains and one field study (Tokyo Bay) suggests that trophic dilution is occurring in a pelagic food chain, but a fourth study (Lake Mjøsa) suggests that trophic magnification may have been occurring in a further pelagic food chain. A similar finding concerning biomagnification in a pelagic food chains in a fifth study (Lake Opeongo) is of uncertain reliability. The balance of evidence suggests it does not meet the T criteria, so it is not a PBT substance (although there are some uncertainties relating to the limited availability of data on mammalian, avian and fish reproductive effects, and toxicity has been observed in sediment and soil organisms).

The conclusion that D4 should be considered to be both a vPvB and PBT substance is a relevant consideration for D5, given that it may be present as an impurity above 0.1 per cent w/w.

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

Information on the uses, exposure and environmental risks of D5 throughout its lifecycle are included in EA (2009). No information has been sought on alternatives.

OTHER INFORMATION

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APPENDIX 1 – OTHER NEW DATA AND ON-GOING/PLANNED STUDIES

This appendix outlines other data that have become available since EA (2009a) was published. These studies are considered to be more relevant to the quantitative risk assessment aspects (i.e. PEC/PNEC-type assessment) than the PBT and vPvB evaluation and so they have not been reviewed in detail. In some cases, they provide similar information to that already considered in EA (2009a) (e.g. journal publications of industry test reports). In addition, information has been received from Industry on a number of on-going or planned research initiatives. Brief details of these studies are also given.

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