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Environmental Risk Assessment Report: Decamethylcyclopentasiloxane

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Steve Killeen

Head of Science

Executive Summary

The Environment Agency's environmental risk assessment for decamethylcyclopentasiloxane (D5) is based on the methods outlined in the European Union (EU) Technical Guidance Document for the risk assessment of new and existing chemicals. The persistence, bioaccumulative, and toxic (PBT) status is assessed, and a 'quantitative' risk assessment made by comparison of exposure with effects.

Persistence, bioaccumulative, and toxic status

D5 meets the screening criteria for a very persistent (vP) and very bioaccumulative (vB) substance. It is unlikely to meet the screening criteria for persistent organic pollutants in long-range transport.

Laboratory studies indicate that D5 is not readily biodegradable in aquatic systems. However, it is difficult to interpret some of the results because of the rapid loss of D5 through volatilisation. A standard test modified to prevent such loss gives a hydrolysis pH-dependent half-life of 71 days at pH 7 and nine days at pH 8 (both at 25°C). The equivalent half-life at pH 7 and12°C is estimated to be around 315 days, and those at higher pHs (e.g. around 8, as can occur in the marine environment) and 9°C are estimated as 64 days. The final products of the hydrolysis of D5 are not thought to have PBT properties.

The lack of biodegradation in laboratory tests and the relatively slow rate of hydrolysis at pHs around 7 mean D5 meets the persistent and vP criteria for water. Although, the volatility of D5 affects its residence time in water–sediment systems, and is probably the predominant removal mechanism for D5 from water, adsorption onto sediments also occurs. D5 lost to air because of its high volatility undergoes subsequent degradation in the air.

The bioconcentration factor (BCF) for BCF of D5 in fish is 7060 l/kg (determined experimentally). In addition, D5 is accumulated by fish from diet, and a growth-corrected and lipid-normalised biomagnification factor (BMF) of 3.9 is derived from the available experimental data. Thus, D5 meets the vB criterion.

D5 shows essentially no acute toxicity to aquatic organisms when tested at concentrations up to its water solubility limit, as do the limited long-term toxicity data available. In addition, D5 is not classified as a carcinogenic, mutagenic, or reprotoxic compound. Based on these data D5 does not meet the toxic criterion. However, the available long-term fish toxicity data may not cover all of the relevant toxicological endpoints, so it is not fully established whether or not D5 has the potential to cause effects in fish over long-term exposure. For example, a recent accumulation study with fish shows only slow depuration of accumulated D5 from the liver, and the long-term impact of the accumulation in liver of fish is not known. In addition, effects on liver weight occur in rats at relatively low doses of D5. However, it is not clear if these effects alone are sufficient to warrant D5 as toxic.

The overall conclusions of the PBT assessment are:

- D5 meets the screening criteria for vPvB substances but some mitigating factors need to be considered further, in particular that D5 is lost from water by volatilisation to the air, where subsequent degradation occurs.

- The current criteria for persistence are related to degradation half-lives in each individual compartment (aquatic, sediment, etc.). These may not be the most appropriate for a substance such as D5 as it is likely to be removed from the aquatic compartment more rapidly by physical process than by degradation. Thus, the overall persistence of the substance, including the potential for transport over distances and the effects at remote locations, needs to be assessed. Currently there are no criteria for this, so both further scientific discussion and consideration at a policy level are required.
- Uncertainties exist over the long-term toxicity of D5 to fish. Available data suggest that it shows no adverse effects at concentrations up to its water solubility, but these data may not cover all the relevant toxicological endpoints. Further long-term toxicity testing with fish will reduce these uncertainties, but the actual need for such tests is unclear.

Quantitative risk assessment

The risks from the normal use of D5 to water, sediments, soil, and predators are assessed using standard models and the information available. The property data set is reasonably complete, but in some areas further information will be valuable. This assessment therefore makes recommendations about the significance of gaps and or uncertainties in the data, and suggests where further research should be focussed.

The main uses of D5 are as an intermediate for the production of other chemicals (silicone polymers), in personal care products (e.g. cosmetic products and skin- and hair-care products), in household products, and in industrial/institutional cleaning. Use as an intermediate in the formation of silicone polymers effectively consumes the D5, although trace amounts in the final products can be subsequently released to the environment. Use of D5 in personal care and household products results in widespread exposure to the environment.

Estimates of the potential emissions to the environment from D5's key life-cycle stages are based on industry research and Emission Scenario Documents, or, in the absence of any other information, worst-case default assumptions. Monitoring data available for some life-cycle stages are taken into account where relevant. Risk characterisation ratios above one indicate an unacceptable risk for the environment and are identified for some life-cycle stages relevant to the UK.

Some information provided by industry is treated as confidential and not given in this report, although the data are used to develop appropriate emission scenarios. These data are included in a confidential annex that supports the assessment, which is available via the Project Manager where appropriate.

The overall conclusions of the quantitative risk assessment are:

- No risks are identified to the air, water, and the terrestrial compartments, nor to humans exposed via the environment from the production and all uses of D5.
- No risks are identified to predators from the production and all uses of D5 in the UK. (Scenarios at two sites outside the EU and not relevant to the UK lead to risk characterisation ratios >1 for freshwater predators.)

- Uncertainties are associated with the assessment for predators because of the BMFs and predicted no effect concentrations used. Little guidance is currently available on the best ways to interpret the specific data used in this assessment. In addition, it is not currently possible to assess fully the risks to predators through the consumption of earthworms, although the available evidence suggests that exposure via this route does not lead to a risk.
- Risks are identified to freshwater sediments from the life-cycle stages of the production of D5 and its on-site use as an intermediate, from some personal care formulation sites, from the use of personal care products by the general public, and from regional sources of D5. These life-cycle stages are relevant to the UK and are based on the best information available. Where data gaps occur estimates are made, which inevitably increases the uncertainty in any risk identified and conclusion drawn.
- The risks identified for sediment require further exposure information for production sites in the UK, and in relation to the formulation and use of personal care products. This could take the form of statistically analysed site-specific data on emissions (e.g. further effluent monitoring or monitoring of the receiving water).

Subject to any revised predicted environmental concentrations for sediment that may result from the provision of the information outlined above, further testing may be required, such as a long-term toxicity test with *Hyalella azteca* (or similar) using spiked sediment.

Industry is undertaking a voluntary test programme to address some of these issues, the results of which will be useful to refine the assessments. It is understood that the studies of D5 currently being considered, or underway, are:

- evaluation of additional atmospheric degradation pathways;
- degradation in a wastewater treatment plant and sludge;
- degradation in sediment under aerobic and anaerobic conditions;
- further modelling of the environmental distribution and overall fate;
- sediment bioaccumulation study with *Lumbriculus* spp;
- sediment toxicity study with *Hyalella azteca*;
- bioaccumulation using physiologically based pharmacokinetic (PBPK) models of fish;
- bioaccumulation using extensions of the PBPK model for fish and mammals to other species;
- environmental monitoring (including air, sewage effluent, river water, sediment, and biota), such as a mussel-screening study, a river distribution and die-away study downstream from a known point source with site-specific monitoring, and a long-term monitoring programme to investigate the persistence and bioaccumulation potential in the field, which is likely to involve:
  - time trends using freshwater and marine sediment cores from local, regional, and remote locations and archived biota samples;

  - spatial distributions using sediment and biota samples along transects of freshwaters from local, regional, and remote locations;
  - marine samples (sediment and biota) from regional and remote locations;
  - air samples from local, regional, and remote locations;
- development of analytical methodology to support the above studies.

Contents

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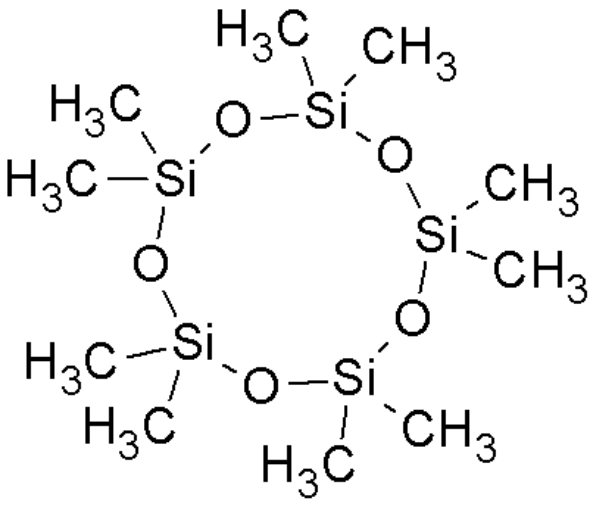
1 General decamethylcyclopentasiloxane information

1.1 Identification of decamethylcyclopentasiloxane

- CAS No: 541-02-6
- EINECS No: 208-764-9
- EINECS Name: Decamethylcyclopentasiloxane
- Molecular formula: $C_{10}H_{30}O_5Si_5$
- Molecular weight: 370.8 g/mol
- Smiles notation: C[Si]1(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O[Si](C)(C)O1
- Structural formula:



Other names, abbreviations, trade names, and registered trademarks for decamethylcyclopentasiloxane (D5) in current use include (CES, 2005b):

- AEC Cyclopentasiloxane
- Baysilone D5
- Botanisil CP-33
- Cyclic dimethylsiloxane pentamer
- Cyclo-decamethylpenasiloxane

- Cyclopentasiloxane[1]
- Cyclopentasiloxane, decamethyl-
- Cyclosiloxane D5
- D5
- DC 245
- DC 345
- Decamethylpentacyclosiloxane
- Dimethylsiloxane pentamer
- Dow Corning 245
- Dow Corning 345[2]
- Dow Corning 345EU[2]
- KF 995
- Mirasil CM 5
- NUC Silicone VS 7158
- Oel Z040
- Pentacyclomethicone
- Pentamer D5
- SB 32[3]
- SF 1202
- Silbione V5
- Silicone SF 1202
- TSF 405[3]
- VS 7158
- Wacker Belsil Z020
- Wacker Belsil CM 040.

Names, abbreviations, trade names, and registered trademarks no longer in current use (or their current use could not be confirmed) are given below. Although these names are no longer used, it is useful to include them here as they may be referred to in some of the older literature:

- DC 2-5252C
- Dow Corning 2-5252C

[1] Cyclopentasiloxane is the International Nomenclature Cosmetic Ingredient (INCI) used to identify D5 in personal care products.
[2] This substance is a mixture that contains D5.
[3] Name used only in the Pacific area.

- Execol D 5
- LS 9000
- SH 245
- Silbione 70045V5
- TSF 465
- Union Carbide 7158 Silicone Fluid
- Volasil 245.

In Europe, decamethylcyclopentasiloxane is commonly referred to as D5, and this abbreviation is used in this assessment.

Also relevant to this assessment is the CAS Number 69430-24-6. This relates to a mixture of dimethyl-substituted cyclosiloxanes with less than eight (typically between three and seven) dimethylsiloxane groups in the ring (Environment Canada, 2008). The name commonly associated with this CAS Number is cyclomethicone, but other names include cyclopolydimethylsiloxane, cyclopolydimethylsiloxane (DX), cyclosiloxanes di-Me, dimethylcyclopolysiloxane, polydimethyl siloxy cyclics, polydimethylcyclosiloxane, and mixed cyclosiloxane. The D5 in cyclomethicone is accounted for in this assessment.

1.2 Purity, impurity, and additives

1.2.1 Purity and impurities

The purity of D5 is generally >90 per cent (often higher than this). The main impurities are small amounts of hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4) and dodecamethylcyclohexasiloxane (D6).

1.2.2 Additives

No additives are present in commercial D5.

1.3 Physicochemical properties

1.3.1 Physical state (at normal temperature and pressure)

D5 is an oily liquid at room temperature and atmospheric pressure (Merck, 1996).

1.3.2 Melting point

The melting point of D5 is –38°C (Merck, 1996; IUCLID, 2005). A similar melting point of –44°C is also reported in IUCLID (2005).

A melting point of –38°C is used in this assessment.

1.3.3 Boiling point

Merck (1996) gives the boiling point as 210°C at atmospheric pressure and 101°C at a reduced pressure of 20 mmHg. Chandra (1997) reviews the available measured data and estimation methods for D5 and reports that the measured boiling point was 211°C and the best estimate for the boiling point was 218°C. IUCLID (2005) also gives the recommended boiling point as 211°C at atmospheric pressure and, in addition, gives values of 209.9 and 210°C.

A boiling point of 211°C is used in this assessment.

1.3.4 Density

The relative density of D5 is 0.9593 (Merck, 1996). Chandra (1997) reviews the measured data and estimation methods available for D5 and reports that the measured density at 20°C was 0.955 g/cm^3 and the best estimate for the density at 20°C was 0.959 g/cm^3. IUCLID (2005) gives the density as 0.954 g/cm^3 at 25°C based on interpolation from a temperature–density correlation. Where a density is needed, this IUCLID value is used in this assessment.

1.3.5 Vapour pressure

The vapour pressure of D5 was measured using an ebulliometer (Flaningam, 1986). The substance tested was distilled prior to use and had a purity of 99.70 per cent. The vapour pressure of D5 was determined over a temperature range of 383–496 K (110-223°C). The corresponding pressure range was 4.0–133 kPa at these temperatures. The data were fitted to the Antoine equation as follows:

$$\ln P_v = A - B/(T + C)$$

where P_v is the vapour pressure in Pa, T is the temperature in Kelvin, A is a constant (= 20.3178 for D5), B is a constant (= 3292.00 for D5) and, C is a constant (= –109.657 for D5).

The standard deviation in the experimental vapour pressure for this equation was given as 0.012 kPa. Using this equation, the vapour pressure of D5 can be estimated as 11 Pa at 20°C and 17 Pa at 25°C.

The vapour pressure data were also fitted to the AIChE DIPPR[4] equation. The root mean square percentage error in this method was given as 1.32 per cent over the temperature range 274–619 K.

$$\ln P_v = A + B/T + C \times \ln(T) + D \times T^E$$

where P_v is the vapour pressure in Pa, T is the temperature in Kelvin, A is a constant (= 94.421 for D5), B is a constant (= –10,153 for D5), C = constant (= –10.031 for D5), D = constant (= 7.47649×10^{-18} for D5), E = constant (= 6 for D5).

Using this equation, the vapour pressure of D5 can be estimated as 16 Pa at 20°C and 25 Pa at 25°C. The agreement between the vapour pressures obtained using the DIPPR method and the Antoine method is good. Although the paper indicates that, within the range of the experimental data generated, the Antoine equation is more accurate, the temperature range for which the DIPPR equation is valid covers ambient environmental temperatures and so these values are considered more reliable for use in this risk assessment.

[4] American Institute of Chemical Engineers – Design Institute for Physical Properties.

IUCLID (2000) gives the vapour pressure as 16 Pa, but gives no indication of the temperature to which this value refers, and an original source for the data is not given. This is presumably the value from Flaningam (1986) derived above.

Another value for the vapour pressure for D5 of 33.2 Pa at 25°C is given in IUCLID (2005). This value is an interpolated value derived from a temperature–vapour pressure correlation (the AIChE DIPPR method) using critically evaluated data obtained over the temperature range –38 to 346°C. The actual data used in the correlation and the resulting fitted parameters were not reported. However, as the temperature range covered appears to be larger than that in the Flaningam (1986) paper, this value will be taken as the more reliable value (although there is very good agreement between the two studies).

A vapour pressure for D5 of 0.174 mmHg (~23 Pa) at 25°C is given in IUCLID (2005). Few other details of how this value was determined are available.

The vapour pressure of D5 at 25°C can be estimated as 29 Pa (0.218 mmHg) using the US Environmental Protection Agency (USEPA) Estimation Program Interface (EPI) (v3.12) estimation software. The value represents the mean of estimates using the Antoine method and the modified grain method, and is based on an experimental boiling point of 210°C.

The database within the EPI software also contains an experimental value for the vapour pressure of D5. This is 0.20 mmHg (~27 Pa) at 25°C and is an extrapolated value referenced to Flaningam (1986). The estimated value above is in good agreement with this value.

Chandra (1997) reviews the measured data and estimation methods available for D5 and reports that the measured vapour pressure at 25°C was 0.174 mmHg (~23 Pa) and the best estimate for the vapour pressure at 25°C was 0.23 mmHg (~31 Pa). The measured value appears to be based on data from the Flaningam (1986) study.

A vapour pressure of 33.2 Pa at 25°C as given in IUCLID (2005) is used in this assessment. This value is derived from a temperature–vapour pressure correlation using critically evaluated data.

1.3.6 Water solubility

Varaprath *et al*. (1996) determined the water solubility of D5 using a slow-stirring method to avoid the formation of colloidal suspensions. The method involved adding D5 to the surface of the water (1500 ml of water in a 2 l flask; sufficient D5 was added to cover the water) and gently stirring the water phase (avoiding cavitation and turbulence). The test was carried out at 23°C. At various time points, samples were run off from the bottom of the flask via a tap and analysed for D5. The water solubility was given as 17.03 ± 0.72 µg/l (mean ± standard deviation) at 23°C based on six determinations.

IUCLID (2005) reports a water solubility value for D5 of <5 µg/l at 25°C. However, no other details of this study are available.

Using the USEPA EPI (v3.12) estimation software a water solubility of 0.046 mg/l at 25°C can be estimated for D5 using a log *n*-octanol–water partition coefficient (log K_{ow}) of 5.20 (the method applies a correction for cyclic siloxanes).

A second estimate for the water solubility of D5 of 0.019 mg/l at 25°C is also obtained from the USEPA EPI program. This value is estimated by a fragment approach.

Chandra (1997) reviews the available measured data and estimation methods for D5 and reports that the measured water solubility at room temperature was 17 µg/l and the best estimate for the water solubility at 25°C was 17 µg/l.

A water solubility of 17 µg/l at 23–25°C is used in this assessment. This is based on the Varaprath *et al*. (1996) study and the review by Chandra (1997).

1.3.7 *n*-Octanol–water partition coefficient

Bruggeman *et al.* (1984) determined the log K_{ow} of D5 to be 5.2 using a high performance liquid chromatography (HPLC) retention time method. A homologous series of *n*-alkylbenzenes were used as reference compounds.

The log K_{ow} for D5 was recently determined using the slow-stirring method according to the Organisation for Economic Co-operation and Development (OECD) draft guideline (2002 version). The full test report is not yet available but details of the test are reported in IUCLID (2005). The tests were carried out at 22°C using ^{14}C-labelled D5 (the radiochemical purity was 99.45 per cent) using around 800 ml of octanol-saturated water, and 50 ml of water-saturated octanol. A known mass of the radiolabelled D5 was added to the octanol phase, and then another 50 ml of water-saturated octanol was added. The test vessels were tightly stoppered and slowly stirred (such that the vortex at the interface between the water and octanol was 0.5–2.5 cm). Samples of octanol and water were collected after 24 hours (and at a minimum of five hour periods thereafter) until the system had reached equilibrium (as shown by four consecutive time points). Equilibrium was obtained within 11 days and the log K_{ow} value was determined to be 4.76 at 22.4°C.

Noted that D5 undergoes hydrolysis, particularly at pH values above and below pH 7 (see Section 3.2.2.10). It is not clear from the information reported if the possibility of hydrolysis was taken into account in this study, particularly as the results may be based on total ^{14}C-measurements rather than on parent-compound analysis (this is especially important as the products of hydrolysis of D5 are more water soluble and less hydrophobic than D5 itself). Therefore there are currently some doubts over this value.

The log K_{ow} is given as 5.7 in IUCLID (2000). No other details of the test conditions used, or the original source of the data, were given. It is possible that this is an estimated value (see below).

A log K_{ow} of 5.71 can be estimated for D5 using the USEPA EPI (v3.12) estimation software. This program estimates the log K_{ow} from the chemical structure using a fragment method.

Further work to investigate the log K_{ow} for D5 is being undertaken on a voluntary basis by the industry. Preliminary results from some of this work were made available in a poster presentation (Xu and Kozerski, 2007). The log K_{ow} values reported for D5 are 8.03 using a slow-stirring method and 8.07 using a syringe method. For comparison, Xu and Kozerski (2007) also calculated a value for the log K_{ow} using linear solvation energy relationships. The value for D5 predicted using this method was 7.61. It is understood that the analytical methodology used in the slow-stirring method was based on parent-compound analysis to avoid complications from hydrolysis of D5 or the presence of more soluble impurities (which may be a problem in studies based on ^{14}C analysis; Plotzke, 2007). No other details of these studies are currently available.

Xu *et al*. (2007) reports the same log K_{ow} for D5 of 8.03 from a slow-stirring method based on a study by Kozerski *et al*. (2007). Again, no other details of this study are currently available.

Several measured values and estimates for log K_{ow} are available for D5. There is reasonable agreement between the two measured values reported in the open literature (5.2 and 4.76). However, few experimental details are available on how one of these studies was carried out and the other study was based on ^{14}C analysis and so could have been affected by hydrolysis of D5. More recent work by Xu and Kozerski (2007) indicates that the log K_{ow} value may be substantially higher than those in the studies carried out so far and, although it is not currently possible to validate these studies fully, a higher value of 8.03 is used in the

assessment (it is understood that this value was obtained using a slow-stirring method designed to avoid problems from hydrolysis of D5). This value is also self-consistent with some of the other partition coefficients used for D5.[5] However, to recognise the uncertainty in the log K_{ow} value for D5, an analysis was carried out to assess the sensitivity of the assessment to a lower log K_{ow} value of 5.2. The results of this analysis are given in Appendix A.

As experimental values are available for some of the key partition coefficients that can be derived from log K_{ow} in the risk assessment process, notably fish bioconcentration factor (BCF) and organic carbon–water partition coefficient (K_{oc}), the actual value chosen for log K_{ow} will not affect these parameters.

1.3.8 Hazardous physicochemical properties

1.3.8.1 Flash point

The flash point of D5 is reported (IUCLID, 2005) to be 70°C (DIN 51755 method), 77°C and 82.7°C (closed cup method), and 85°C (open cup method).

1.3.8.2 Auto ignition

The auto ignition temperature of D5 is 372°C (IUCLID, 2005).

1.3.8.3 Explosivity

No information is available.

1.3.8.4 Oxidising properties

No information is available. D5 is not expected to have oxidising properties.

1.3.9 Other relevant physicochemical properties

1.3.9.1 Granulometry

Not relevant – D5 is a liquid.

1.3.9.2 Surface tension

The surface tension of D5 is 18.9 mN/m at 20°C and 18.5 mN/m at 25°C (Dow Corning internal data; CES, 2005b).

[5] For example, using the log K_{oa} of 5.07 at 25°C (see Section 1.3.9, subsection Octanol-air partition coefficient) and the log K_{aw} of 3.13 (see Section 1.3.9, subsection Henry's law constant) a value for log K_{ow} of 8.2 can be estimated. This shows that a log K_{ow} of around 8 is consistent with the log K_{oa} and log K_{aw} values.

1.3.9.3 Henry's law constant

Kochetkov *et al*. (2001) determined the Henry's law constant of D5 using two different methods. The first was a static method in which a saturated solution of D5 in water was equilibrated with air in the headspace of a sealed container for 48 hours and the equilibrium concentration of D5 in each phase determined. To avoid the formation of colloidal suspensions of D5 in the water phase, the saturated solution was initially prepared by gentle shaking for two days, followed by a four day settling period; it was finally filtered (0.45 µm) to remove any microemulsions prior to use. The second method was a vapour entry loop method specifically designed to avoid having to add the D5 directly to water (and hence avoid any colloidal emulsion formation). In this method the vapour phase was essentially saturated with D5 by bubbling air though pure D5 and then a portion of this saturated vapour was continuously circulated through water in a sealed system for 48 hours. At the end of this period the concentrations of D5 in both the water and air phases were determined. All experiments were carried out at 26°C.

The values (mean ± standard deviation) for the dimensionless Henry's law constant (or air–water partition coefficient, K_{aw}) determined for D5 were 13 ± 1 (equivalent to a Henry's law constant of 32,317 Pa m^3/mol) in the static method and 12 ± 2 (equivalent to a Henry's law constant of 29,831 Pa m^3/mol) in the vapour entry loop method. Very good agreement was therefore obtained using the two methods. A reference substance (benzene) was also tested using the same methods; this gave dimensionless Henry's law constants of 0.25 and 0.19 using the two methods, respectively, which agree well with literature values (0.19–0.23).

Kochetkov *et al.* (2001) also summarised the values for the dimensionless Henry's law constant for D5 at around room temperature obtained in earlier studies published in the literature. These included values of 5.5 and 10. These literature values are in good agreement with the values determined by Kochetkov *et al*. (2001).

David *et al*. (2000) determined the Henry's law constant for D5 in simulated and actual wastewaters. The tests were carried out using an 'equilibrium partitioning in closed systems' (EPICS) method. This system used essentially closed bottles with two different air-to water ratios. Tests were conducted using pure water and also actual and simulated wastewater with variable concentrations of humic acids (2–150 mg/l), wastewater solids (100–2500 mg/l), and KCl (0.001–0.02 M) to represent dissolved solids. The dimensionless Henry's law constant was 5.46 in pure water, 0.781 in actual wastewater, and 3.11 in simulated wastewater (extrapolated to zero organic carbon content). The tests with synthetic wastewaters showed that the Henry's law constant decreases slightly with increasing concentrations of humic acid and dissolved solids, but that this decrease was less than an order of magnitude over the concentration range tested.

The Henry's law constant for D5 can be estimated as 0.12 atm m^3/mol (12,159 Pa m^3/mol) using the USEPA EPI (v3.12) estimation software. The value is estimated from the chemical structure using the bond contribution method.

The database within the EPI software also contains an experimental value for the Henry's law constant of D5. This is 0.40 atm m^3/mol (40,530 Pa m^3/mol) at 25°C, but no reference to the data is given [it is possible it was estimated from an experimental vapour pressure of 0.20 mmHg (see Section 1.3.51.3.5) and an experimental water solubility of 0.24 mg/l (it is not clear where this latter value comes from)].

Chandra (1997) calculated the dimensionless Henry's law constant for D5 to be 268 at 25°C (equivalent to a non-dimensionless value of 663,989 Pa m^3/mol) based on its vapour pressure and water solubility. The same author reports an experimental value for the dimensionless Henry's law constant of 5.5 at 25°C (equivalent to a value of 13,627 Pa m^3/mol at 25°C).

Further work to investigate the Henry's law constant for D5 is being undertaken on a voluntary basis by the industry. Preliminary results from some of this work were made available in a poster presentation (Xu and Kozerski, 2007). This reports values for the dimensionless Henry's law constant of 1175 (reported as log K_{aw} = 3.07) using a syringe method and of 427 (reported as a log value of 2.63) calculated using a linear solvation energy relationship. The temperature of the determinations is not stated (but was most likely at room temperature) and no other details of these studies are currently available. These values are significantly higher than those in other studies (assuming a temperature of around 25°C they are equivalent to Henry's law constants of 2,910,000 Pa m^3/mol and 1,060,000 Pa m^3/mol, respectively).

Another report by Xu *et al*. (2007) recommends a value for the dimensionless Henry's law constant for D5 as 1350 (reported as log K_{aw} = 3.13) at 25°C. This is based on an as yet unavailable study by Xu and Kropscott [2007, reported in Xu *et al*. (2007)] and is presumably related to the above results of Xu and Kozerski (2007). This value is equivalent to a Henry's law constant of 3,342,000 Pa m^3/mol.

The available data on Henry's law constant for D5 shows that many of the measured values are significantly lower than would be predicted based on the water solubility and vapour pressure alone, although the new determinations by Xu and Kozerski (2007) and Xu and Kropscott (2007) are higher than would be predicted. This implies that there is some inconsistency in these measured parameters and suggests that there is some uncertainty in one or more of these parameters. However, the prediction of Henry's law constant from water solubility and vapour pressure is dependent on the substance showing ideal behaviour in solution; from the available data it is possible that this is not the case for D5. Therefore, the Henry's law constants determined directly by experiment are considered in the assessment.

Although few details of the recent determinations of the Henry's law constant by Xu and Kozerski (2007) and Xu and Kropscott (2007) are currently available, this study was carried out by industry on a voluntary basis to address some of the uncertainties in this risk assessment. It is understood that the methodologies used were designed to avoid the potential problems of testing D5. Therefore, although currently it is not possible to validate these results fully, the value for the Henry's law constant for D5 will be taken to be 3,342,000 Pa m^3/mol at 25°C (dimensionless Henry's law constant of 1350) based on the results of the study by Xu and Kropscott (2007). This value is self-consistent with the other partition coefficients used for D5.[6]

To assess the sensitivity of the assessment to the Henry's law constant, and to reflect the uncertainty in the determination of this parameter, the effect of using a lower value of 32,317 Pa m^3/mol at 26°C (dimensionless Henry's law constant of 13) on the conclusions of the risk assessment were also considered, based on the work of Kochetkov *et al*. (2001). The results of this analysis are given in Appendix A.

1.3.9.4 Octanol–air partition coefficient

Very recently, the results of a study that investigated the octanol–air partition coefficient (K_{oa}) of D5 have become available (Xu, 2006). The study was carried out using a mixture of ^{14}C-labelled D4, D5, and D6. The purity of the D5 used was 99.0 per cent. The tests were carried out using gas syringes. Mixtures of the test substances in *n*-octanol were prepared [D5 concentrations between 1.5 and 99 ppm (mg/l) were tested; two concentrations per temperature were used] and around 1-5 ml of this solution was added to 100 ml gas

[6] For example, using the log K_{oa} of 5.07 at 25°C (see Section 1.3.9, subsection Octanol–air partition coefficient) and the log K_{ow} of 8.03 (see Section 1.3.7) a value for log K_{aw} of 2.96 can be estimated. This shows that a log K_{aw} of around 3 is consistent with the log K_{oa} and log K_{ow} values.

syringes. The syringes were incubated at temperatures of –4°C, 5°C, 24°C, and 40°C. After equilibration for one hour, both the gas phases and the octanol phases were analysed for the presence of D5. The mean log octanol–air coefficients (log K_{oa}) determined for D5 were 5.93 at –4°C, 5.63 at 5°C, 4.96 at 24°C and 4.58 at 40°C. The temperature dependence of the log K_{oa} value was fitted to the equation:

$$\log K_{oa} = A + B/T$$

where A and B are constants (B is related to the internal energy change for D5 when it evaporates from the octanol to the air), and T is the absolute temperature (K).

The heat of evaporation (ΔU) was calculated from the B value to be 51.4 kJ/mol for D5.

Other values for K_{oa} are reported in a poster presentation by Xu and Kozerski (2007). This reports measured log K_{oa} values of 5.06 using dry octanol and 5.00 using wet octanol. The temperature of the determinations was not stated and no other experimental details are available. It is likely that these values relate to the above study by Xu (2006) in which a similar log K_{oa} of 4.96 was determined at 24°C. Xu and Kozerski (2007) also calculated values for the log K_{oa} using linear solvation energy relationships. The values for D5 predicted using this method are 5.36 for dry octanol and 5.16 for wet octanol. Few other details of these calculations are currently available.

Xu *et al*. (2007) recommend a log K_{oa} value for D5 of 5.07 at 25°C. This is presumably based on the above study and calculated to 25°C. This value is considered in this risk assessment when appropriate.

1.3.10 Summary of physicochemical properties

The physicochemical properties of D5 are summarised in Table 1.1.

Table 1.1 Summary of physicochemical properties

Property	Value used in risk assessment	Alternative value used in sensitivity analysis[1]
Melting point	–38°C	
Boiling point	211°C	
Density	0.954 g/cm^3 at 25°C	
Vapour pressure	33.2 Pa at 25°C	
Water solubility	17 µg/l at 23–25°C	
Log K_{ow}	8.03	5.2
Henry's law constant	3,342,000 Pa m^3/mol at 25°C	32,317 Pa m^3/mole at 26°C
Log K_{oa}	5.07 at 25°C	
Conversion factor for air	1 ppm = 15.2 mg/m^3 at 25°C	

Note: [1]The effects of these values on the conclusions of the risk assessment are considered in Appendix A.

Some of the new data on the physicochemical properties of D5, notably the log K_{ow}, the Henry's law constant, and log K_{oa}, have become available only very recently. These data were not generally available when some of the modelling work described in Section 5.5.2.1 was carried out. The implications of this are discussed in Section 5.2.2.

2 General information on exposure

2.1 General introduction to the silicone industry

Although this report is concerned only with the non-polymeric cyclic organosiloxanes, in particular D5, to evaluate the potential for release to the environment it is necessary to understand the full life-cycle of products made from the substance of interest. This is particularly important in this instance, as a major use of D5 is as a monomer in the manufacture of polymeric materials. Such polymers could contain residual amounts of D5 (and, in some cases, could possibly break down to form small amounts of D5) and so the uses of the polymeric materials could, in some cases, act as sources of release to the environment of D5.

Therefore in this section we provide a general overview of the silicone industry relevant to the cyclic organosiloxanes. The specific uses of D5 itself are considered in more detail in Section 2.30.

A review of the commercially significant organosilicon materials produced worldwide is published (Chandra, 1997). The review is based to a large extent on information from the USA, but it indicates that the industry in the United States of America (USA) is broadly similar to that in the European Union (EU) and Japan. The review provides useful background information for this project, and the main findings are summarised below. The information in the Chandra (1997) review is supplemented with information from other relevant sources.

Chandra (1997) considered five basic groups of organosiloxanes (also known as silicones) and these are outlined in the sections below.

2.1.1 Oligomeric organosiloxanes

This group covers both cyclic and linear substances. The general formulae for oligomeric organosiloxanes are (Chandra, 1997):

- $(R_2SiO)_x$ – cyclic substances, in which R is usually a methyl group, but can also be hydrogen, a vinyl group, a phenyl group or a trifluoropropyl ($CF_3CH_2CH_2$–) group, and x = 3, 4, 5, 6, etc. D5 falls into this group.
- $R_3SiO(SiR_2O)_nSiR_3$ – linear substances in which R is usually a methyl group, but can also be a phenyl group, and n = 0, 1, 2, 3, 4, etc.

The linear products are manufactured by the stoichiometric co-hydrolysis of two chlorosilanes (Chandra, 1997). An example reaction scheme is:

$$2(CH_3)_3SiCl + (CH_3)_2SiCl_2 + 2H_2O \rightarrow (CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_3 + 4HCl$$

Hydrogen chloride is recovered and the products are purified by distillation.

The cyclic products are formed by the hydrolysis of dimethyldichlorosilane. Oligomeric siloxanols are formed as a by-product (the mixture of cyclic products and oligomeric siloxanols is often called hydrolysate):

$$(CH_3)_2SiCl_2 + 2H_2O \rightarrow (CH_3)_2Si(OH)_2 + 2HCl$$

$$[(CH_3)_2Si(OH)_2]_{x+y} \rightarrow [(CH_3)_2SiO]_x + HO[Si(CH_3)_2O]_yH$$

where one product is a cyclic siloxane (x = 3, 4, 5, 6, etc.) and the other an oligomeric siloxanol (y = 2, 3, 4, etc.).

The value of x and y, and the ratio of linear to cyclic products, depends on the hydrolysis conditions used, for example the amount of water, the acidity, and the use of solvents (Chandra, 1997).

The hydrolysis of dimethyldichlorosilane is carried out commercially using either a batch or a continuous process (Rich *et al.*, 1997). In a typical process, the dimethyldichlorosilane is mixed with 22 per cent aqueous hydrochloric acid in a continuous reactor. The hydrolysate and concentrated hydrochloric acid are then separated in a decanter and the hydrogen chloride is converted into methyl chloride (a starting material in the production of dimethyldichlorosilane). The hydrolysate is then washed to remove residual acid, neutralised, dried, and filtered. The water from the washing and neutralisation procedure is treated in an on-site wastewater treatment plant or reused in the hydrolysis process. The typical yield of cyclic oligomers is between 35 and 50 per cent, and consists mainly of D4 and D5.

The complete conversion of dimethyldichlorosilane into linear silanols is possible using a continuous hydrolysis process, in which the cyclic products are separated from the linear oligomers by a stripping process and re-introduced into the process with the dimethyldichlorosilane starting material (Rich *et al*., 1997). Linear silanols can also be produced by methanolysis of dimethyldichlorosilane.

The cyclic products may be separated and purified by distillation (Chandra, 1997).

Very pure (>99.99 per cent) dimethyldichlorosilane starting material is needed if the linear fraction of siloxane oligomers is to be used directly in the manufacture of silicone polymers (Rich *et al.*, 1997). The presence of methyltrichlorosilane impurity in the starting material can produce significant amounts of trifunctional units in the resulting oligomers, which then may adversely affect the properties of the final polymeric products. If high-purity dimethyldichlorosilane is not used, an additional cracking step must be included in the overall production process. In the cracking step, the hydrolysate is depolymerised in the presence of strong bases or acids to give cyclic monomers, such as D4 and D5, which are removed by distillation. The trifunctional by-products remain in the reaction medium and are periodically removed.

As a group, the oligomeric organosiloxanes are also known as volatile methylsiloxanes (VMSs).

Around 87 per cent of the VMSs produced in the USA in 1993 were used as site-limited intermediates for the production of polymeric siloxanes (Chandra, 1997). The remaining 13 per cent (around 20,000 tonnes) were used in personal care products (particularly the D4 and D5 cyclic products). The primary uses in personal care products were as carriers in antiperspirants, deodorants, and skin-care products, and as conditioners for hair-care products.

The Cosmetic Toiletry and Perfumery Association (CTPA) have indicated that the functions of the cyclic siloxanes used in cosmetics in the UK are, in general, in three main areas – as hair-conditioning agents, as skin-conditioning agents (emollient), and as solvents (CTPA, personal communication). The types of products in which they are reported to be used include aftershave lotions, colognes, toilet waters, perfumery products, baby lotions, oils, powders and creams, baby shampoos, bath oils and bath salts, etc., make-up products, make-up removers and skin-cleaning products, deodorants and antiperspirants, eye creams and eye make-up products (such as powders, mascaras, pencils, etc.), general make-up (such as foundations, blushers, face powders, and lipsticks), shampoos, conditioners, hair

dyes and/or colours, hair sprays, shaving products, skin-care preparations (such as creams, lotions, cleansers, and toners), sun creams and after-sun products, and hair-grooming aids.

2.1.2 Polymeric dimethylsiloxanes

More that 80 per cent of commercial organosilicon products are based on polydimethylsiloxane (PDMS; Chandra, 1997). The general structures are:

$$(CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$$

or

$$HO[Si(CH_3)_2O]_nH$$

where n = 5 to 6000, or more.

The starting material for the manufacture of PDMS is dimethyldichlorosilane. The first step in the process is hydrolysis to form cyclic siloxanes and/or linear siloxanols according to the reactions outlined in Section 2.1.10. PDMS itself is then formed by either the ring-opening polymerisation of cyclic siloxanes or the polycondensation of linear siloxanols in the presence of an endblocker, such as $[(CH_3)_3Si]_2O$, and heat under acid or alkaline conditions (Chandra, 1997). Example reactions are summarised as:

$$n/4[(CH_3)_2SiO]_4 + [(CH_3)_3Si]_2O \rightarrow (CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$$

$$HO[Si(CH_3)_2O]_nH + [(CH_3)_3Si]_2O \rightarrow (CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$$

The ratio of the endblocker to $–Si(CH_3)_2O–$ units in the starting material effectively determines the degree of polymerisation (n). The absence of any branching or cross-linking units (that arise from the processing conditions and/or impurities in the starting materials) is important when manufacturing PDMS with a high degree of polymerisation (i.e. with a long chain length; Chandra, 1997).

For the ring-opening polymerisation process, the commercially most important cyclic monomer used is D4 (Rich *et al.*, 1997), but other cyclic monomers, such as D5 and D6, are also used. The process can be carried out under anionic (basic) or cationic (acidic) conditions or in aqueous emulsions. The anionic polymerisation can be conducted in a batch reactor or in a continuously stirred reactor. The viscosity of the polymer and the type of end group can be easily controlled by the amounts of water and triorganosilyl chain-terminating groups added. A plasma polymerisation process was also developed for applications in which a well-defined, thin polymer film is needed, such as in optics, electronics, or biomedicine.

Both the polycondensation and, in particular, the ring-opening polymerisation process can result in the formation of a mixture of high molecular weight polymer and low molecular weight cyclic oligomers as the reactions are effectively equilibrium reactions (Rich *et al.*, 1997). For the ring-opening polymerisation process, the position of the equilibrium depends on the nature of the substituents on silicon and on the concentration of the siloxane units, but it is independent of the starting siloxane composition and the polymerisation conditions. The equilibrium concentration of cyclosiloxanes is thought to be around 18 per cent by weight and is thought to consist of a continuous population to at least D400, but with D4, D5, and D6 making up >95 per cent of the total cyclic fraction.

Low viscosity ($<10^5$ mm^2/s) PDMS-based fluids are usually prepared by an acid-catalysed process, using either a continuous process or glass-lined batch reactors, at temperatures up to 180°C (Rich *et al.*, 1997). After reaction the fluids are filtered and the residual low molecular weight cyclic and linear siloxanes are removed by stripping under vacuum at elevated temperature.

High viscosity (>10^6 mm^2/s; high molecular weight) PDMS-based fluids (oils and gums) are usually prepared by base-catalysed, ring-opening polymerisation of D3 or D4, or by condensation polymerisation of silanol-terminated PDMS. Potassium silanoate or transient catalysts, such as tetramethylammonium hydroxide or tetrabutylphosphonium hydroxide, are used in the ring-opening process. The transient catalysts are destroyed at temperatures >150°C.

Around 138,000 tonnes of PDMS was produced in or imported into the USA in 1993 (Chandra, 1997). Around 62 per cent of this was used as site-limited intermediates in the production of elastomers, pressure-sensitive adhesives, and modified PDMS fluids (see below).

The non-intermediate industrial uses of PDMS are numerous (Chandra, 1997). Industrial uses in the USA include antifoams, softness and wetting agents in textile manufacturing, components of polishes and other surface treatment formulations, lubricants and mould release agents, paper coatings, and as dielectric fluids and heat transfer liquids. PDMS is also used in consumer applications such as personal, household, and automotive care products.

Ashford (1994) also indicates numerous uses for PDMS, such as a foaming agent in oil processing; a flow and/or gloss improver in alkyd paints and varnishes; a lubricant in polishes and maintenance products; and that it is used in anti-adhesion coatings; in hydraulic, dielectric, and heat-transfer fluids and diffusion pump oils; in barrier creams, lipstick, and pharmaceuticals; in lubricants for motors, instruments, and precision bearings; in silicone emulsions used as antifoams; in anti-adherence coatings; in mould-release agents; in textile waterproofing; in silicone greases for gear and bearing lubrications; in silicone pastes for valve lubricants, mould release agents, and electrical and electronic protection; and as an additive in textile and paper sizing.

Silicone oils are stable over a wide temperature range (Rich *et al.*, 1997). The inclusion of diphenyl or phenylmethylsiloxy groups into the polymer (see modified PDMS; Section 2.1.30) reduces the pour point of the fluid and increases the temperature stability. Methylsilicone oils are stable in air at 150°C for long periods of time, and undergo only slow degradation at temperatures up to 200°C. Increasing the amounts of phenyl-containing substituents increases the heat resistance and, for example, high molecular weight methylphenylsilicones can be used in air at up to 250°C for several hours. Stabilisers such as *p*-aminophenol, naphthols, metal acetonylacetonates, and iron octoate can be used to improve the thermal stability.

When heated, PDMS fluids decompose by two main mechanisms (Rich *et al.*, 1997). At temperatures above 140°C retrocyclisation into volatile cyclic siloxanes, such as D3 and D4, can occur. The decomposition is catalysed by acids and bases. At temperatures of 200–250°C thermal oxidation can occur and lead to the formation of formaldehyde, CO_2, water, and alkylsilicones.

PDMS is approved for food use in the UK (known as E900).[7]

Based on the above discussion it appears that PDMS products may contain a range of cyclic siloxanes which may be present in small amounts as impurities (particularly D4, D5, and D6; see Section 3.1.7.10). Furthermore, under certain conditions (elevated temperatures in the presence of acid and basic catalysts) PDMS products may decompose to form small amounts of cyclic siloxanes. Therefore the uses of PDMS are potentially relevant to the life cycle of D5.

[7] See http://www.food.gov.uk/safereating/additivesbranch/enumberlist.

2.1.3 Modified polymeric dimethylsiloxanes

A range of modified PDMSs is also available, in which some of the methyl groups are replaced by other groups (Chandra, 1997). These have the general formulae.

$$(CH_3)_3SiO(SiX(CH_3)O)_m[Si(CH_3)_2O]_nSi(CH_3)_3$$

or

$$X(CH_3)_2SiO(Si(CH_3)_2O)_nSi(CH_3)_2X$$

where X = H, alkyl, vinyl, phenyl, $CF_3CH_2CH_2$–, aminoalkyl, or epoxyalkyl.

Modified PDMS is commonly manufactured by the catalysed ring-opening copolymerisation of an appropriate functional monomer (either cyclic or linear) with a cyclic oligomeric siloxane and an endblocker such as $[(CH_3)_3Si]_2O$. Example reaction schemes are:

$$[(CH_3)_2SiO]_x + [X(CH_3)SiO]_y + [(CH_3)_3Si]_2O \rightarrow (CH_3)_3SiO[Si(CH_3)_2O]_x[SiX(CH_3)O]_ySi(CH_3)_3$$

cyclic cyclic linear

or

$$[(CH_3)_2SiO]_x + [X(CH_3)_2Si]_2O + \rightarrow X(CH_3)_2SiO[Si(CH_3)_2O]_xSi(CH_3)_2X$$

cyclic linear

where X = H, alkyl, vinyl, phenyl, $CF_3CH_2CH_2$–, aminoalkyl, or epoxyalkyl.

The cyclic and linear functional monomers are made (sometimes *in-situ*) from the corresponding alkoxysilanes according to the processes.

$$Y[X(CH_3)Si(OR)_2] + yH_2O \rightarrow [X(CH_3)SiO]_y + 2yROH$$

cyclic

or

$$2X(CH_3)_2SiOR + H_2O \rightarrow [X(CH_3)_2Si]_2O + 2ROH$$

linear

Other methods for synthesis of modified PDMS are by the hydrosilylation reaction or by nucleophilic substitution reactions.

The most significant modified PDMS fluids, on a commercial basis, include the methyl(hydrido)siloxanes, methyl(vinyl)siloxanes, methyl(alkyl)siloxanes, methyl(phenyl)siloxanes, methyl(trifluoropropyl)siloxanes and methyl(aminoalkyl)siloxanes (Chandra, 1997).

The methyl(hydrido)- and methyl(vinyl)siloxanes contain reactive sites for cross-linking in the production of silicone elastomers (see Section 2.1.5). The methyl(hydrido)siloxanes are also used as intermediates and as waterproofing agents for textiles and wall boards.

The methyl(phenyl)siloxanes are used as high-temperature oil baths, greases, diffusion pump fluids, and paint additives.

The trifluoropropyl group gives greater solvent and fuel resistance to the silicone rubber used in, for example, gasket materials.

The methyl(alkyl)siloxanes are used as release agents for plastics and urethane parts, for cutting oils, and as paint additives.

The methyl(aminoalkyl)siloxanes are used in a wide range of applications, such as textiles, personal care products, household care products, automotive care products, and in plastic modification (the aminoalkyl group acts as a reactive site to give a permanent point of attachment).

Similar to the case with PDMS, modified PDMS polymer products may contain small amounts of cyclic siloxanes as impurities (the levels are currently unclear). Therefore the uses of modified PDMS are potentially relevant to the life cycle of D5.

2.1.4 Organosiloxane resins

These resins are made from starting materials not covered by this assessment (i.e. trichlorosilanes and other silanes) and so they are not considered further.

2.1.5 Organosiloxane elastomers

Organosiloxane (silicone) elastomers (rubbers) are used for coatings, gels, sealants, and rubbers (Chandra, 1997). They are cross-linked PDMS and some have trifluoropropyl or phenyl groups replacing some of the methyl groups in the PDMS.

Many systems have been developed for cross-linking PDMS (curing and vulcanising). The curing systems can be broadly divided into three main types: peroxide cure, hydrosilylation, or addition cure and condensation cure (Rich *et al*., 1997). Other curing systems that can be used include high-energy radiation cure and photo-initiated radiation cure.

Peroxide curing systems work at elevated temperatures and use peroxides such as dibenzoyl peroxide, bis-*p*-chlorobenzoyl peroxide, bis-2,4-dichlorobenzoyl peroxide, dicumyl peroxide, di-*t*-butyl peroxide and 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane (Rich *et al.*, 1997). The amount and type of peroxide used determines the cure temperature and overall properties of the final rubber. Vinyl-containing polymers are often used to control the cross-linking reaction.

The addition cure (hydrosilylation) system involves the reaction between a silicon hydride group and a vinyl group to form an ethylenic linkage (Rich *et al*., 1997). The reaction is catalysed by certain metals such as platinum. Inhibitors can also be incorporated into the products to increase the storage life and cure temperature to allow the product to be more easily handled during use.

The condensation cure system involves the condensation of silanol groups to form siloxanes (Rich *et al.*, 1997). Curing agents include alkoxysilanes, acyloxysilanes, silicon hydrides, or methylethyloximesilanes. Catalysts for the reactions include acids, bases, and organometallic compounds [e.g. carboxylic acid complexes of tin(II) and tin(IV)].

Some formulations are supplied as one-part systems whereas others are supplied as two-part systems. Some products cure at room temperature [room temperature vulcanising (RTV)] while others are heat-cured [heat-activated vulcanising (HAV)].

A typical example of a one-part cold-cured system would be based on hydroxyl-terminated PDMS with methyl triacetoxysilane as the curing agent. Curing occurs by a condensation reaction in the presence of moisture which releases acetic acid. Cold-cured two-part systems can be cured either by condensation reaction or by addition reaction. An example of a condensation cured two-part system would be based on hydroxyl-terminated PDMS and ethyl silicate. An example of an addition cured two-part system would be based on vinylated-PDMS, PDMS, and a cross-linking agent. An example of a heat-cured system would be based on vinylated-PDMS and fumed silica (Ashford, 1994).

Rich *et al.* (1997) indicate that most silicone rubbers contain additives such as filler. Reinforcing fillers are used at concentrations of 10–25 per cent by weight to increase the tensile strength, tear strength, and abrasion resistance, and include finely divided silicas prepared by vapour-phase hydrolysis or oxidation of chlorosilanes, dehydrated silica gels, precipitated silicas, diatomaceous silicas, and finely ground high-assay natural silicas. Non-reinforcing fillers are used to reduce the cost of the product and to improve heat stability, impart colour, and increase electrical conductivity. Non-reinforcing fillers include calcium carbonate, clays, silicates, aluminates, pigment-grade oxides (e.g. ferric oxide), fumed oxides of titanium, aluminium and zirconium, and carbon black. Plasticity and process aids are also often added to aid subsequent processing. Rich *et al.* (1997) indicate that, in some situations, the silica particles used as fillers may be reacted with hot vapours of low molecular weight cyclic siloxanes and hexamethyldisiloxane prior to incorporation in the rubber, as an alternative to aid subsequent processing.

RTV silicones cure on exposure to atmospheric oxygen, the rate of cure depending on the temperature and humidity (Rich *et al*., 1997). Uncured products are reported to have a shelf-life of six months to several years. Two main curing systems are used based on either acetoxy silicone compounds or alkoxy silicone compounds. Both work in essentially the same way, by reaction with the silanol group in silanol-terminated PDMS, which results in the formation of hydrolytically unstable acetoxy- or alkoxy-groups. These groups hydrolyse on exposure to moisture (releasing either acetic acid or alcohols) resulting in the formation of diol groups at the end of the PDMS, which can then undergo condensation reactions (catalysts may be used to increase the rate of cure) and lead to formation of cured silicone rubber. The commercial uses of the acetoxy-based products are limited by the odour and corrosive nature of the acetic acid formed. One-part RTV silicone products find applications in household consumer products, construction products, and industrial adhesives.

Heat-cured silicone rubbers are processed using similar methods used for natural rubber (Rich *et al.*, 1997). For example, the high molecular weight PDMS polymer (often termed gum) and fillers are firstly compounded using a dough or Banbury-type mixer. Catalysts (curing agents) are then added and the rubber is further compounded on water-cooled roll mills. For small batches the entire process can be carried out on a two-roll mill.

Heat-cured silicone rubber is commercially available in a variety of compounded, semi-compounded, or uncompounded forms; for example gum stock, reinforced gum stock, partially filled gum, uncatalysed compounds, dispersions, and catalysed compounds (Rich *et al.,* 1997). The rubber is frequently re-worked on a rubber mill prior to use (i.e. worked until it is a smooth continuous sheet).

The most common processing method for heat-cured silicone rubber is compression moulding at 100–180°C under pressure (5.5–10.3 MPa) using mould-release compounds (Rich *et al*., 1997). Under these conditions the rubber usually cures in a few minutes. Other processes that can be used include extrusion (for the manufacture of tubes, rods, wire, and cable insulation, and continuous profile). Following extrusion the products are initially cured in hot air or steam tunnels at 300–450°C under reduced pressure (276–690 kPa) for several minutes. The products are then further cured (post-cured) in air or steam for another 30–90 minutes.

Coated textiles and glass cloth are made by dissolving the gum stock in solvent and applying the rubber by dip coating (Rich *et al*., 1997). After drying the coating is cured in heated towers. The treated textiles can be used to form tubes and hoses of complex shapes.

Silicone rubber made from a low viscosity starting material can be processed by liquid-injection moulding (Rich *et al*., 1997). In this process the rubber is injected into moulds similar to those used for plastic-injection moulding and cured within the mould. This process allows complex shapes to be moulded. In the system the rubber is rapidly cured (in 10–40 seconds) using a low moulding pressure (2–20 MPa) at temperatures of 150–260°C. The

process is used for applications such as electrical connectors, O-ring seals, valves, electrical components, healthcare products, and sports equipment (goggles and scuba masks).

The rubber used for liquid-injection moulding is usually a two-part system (Rich *et al*., 1997). One part of the system (Part A) contains a linear dimethylsiloxane polymer with terminal and pendent vinyl groups, fillers, a hydrosilylation (addition) catalyst (e.g. platinum), and a catalyst inhibitor. The second part (Part B) contains a linear dimethylsiloxane polymer with pendent Si–H groups, fillers, pigments, and stabilisers. One-part systems, in which the hydrosilylation catalyst is deactivated at room temperature (it reactivates when heated to >100°C), have also been developed.

Foamed or sponge silicone rubber products can also be manufactured by incorporating suitable blowing agents into the rubber stock (Rich *et al.*, 1997). The polymer systems used are generally similar to the two-part systems used in liquid-injection moulding, but one part also contains water, alcohol, and an emulsifying agent. The two parts are mixed at room temperature which initiates the cross-linking reaction and also results in the formation of hydrogen gas (from the platinum-catalysed reaction of the hydroxyl groups from the water and/or alcohol with the Si–H groups) which acts as the blowing agent. The typical time for foam formation is around 20 minutes. Silicone foam, particularly when quartz is used as a filler, has good flammability characteristics and so is used in building and construction fire-stop systems and as pipe insulation in power plants.

Primers (such as silicate or titanate esters from the hydrolysis of tetra-ethylorthosilicate or tetra-ethyltitanate) are used when silicone rubber is to be bonded onto surfaces such as those of metals, plastics, or ceramics (Rich *et al*., 1997).

Organic solvent can diffuse into silicone rubber and significantly decrease the physical properties of the rubber (Rich *et al.*, 1997). For applications where the material may be exposed to solvents, for example fuel tank sealants, solvent-resistant rubber based on trifluoropropylmethylsiloxane (or β-cyanoethylmethylsiloxane, although these are of much less importance commercially) polymers are available.

Pure water is reported to have little effect on the properties of silicone rubber, but prolonged exposure to aqueous acids or bases can cause degradation of the rubber to a sticky gum (Rich *et al.*, 1997).

Around 89,000 tonnes of silicone elastomers were produced or imported in the USA in 1993 (Chandra, 1997). Applications of RTV products include sealants, encapsulants, foams, coatings, caulking, and mould making. Applications of heat-cured rubber include tubing, hoses, wire and cable insulation, penetration seals, laminates, release coatings, foams, and other moulded and extruded articles such as gaskets, key pads, ignition cables, belting, and catheters. Gel applications include electronic encapsulates and wound-dressing patches.

Ashford (1994) lists many possible uses for silicone rubbers (elastomers). One-component cold-cured rubbers are used as caulks and/or sealants for expansion joints and windows, for seals, gaskets, and shock-absorbing fixing in vehicles and domestic appliances, and in heat-resistant adhesives. Two-component cold-cured (addition cured) rubbers are used as dielectric gels, for electronic and/or electrical encapsulation, in fire-resistant cable coatings, in foamed sealants, and in resin casting moulds. Two-component cold-cured (condensation cured) rubbers are used as moulding compounds for furniture and construction, in paper anti-adhesion coatings, as electrical component sealants, as roofing membranes, and as window and curtain walling sealants. Heat-cured silicone rubbers are used in chemical-resistant and medical tubing and mouldings, flexible and rigid foams, press-foamed automobile seals, and wire and cable jacketing.

Rich *et al.* (1997) indicate that a growing area of use of thermally cured silicones is in paper-release coatings which are used in label systems. The silicone coating forms part of the

disposable liner and is applied to substrates such as supercalendered kraft paper, glassines, and thermally sensitive films, such as polyethylene and polypropylene. The coatings are usually based on solvent-free mixtures of PDMS with terminal vinyl groups, a cross-linking agent that contains Si–H groups, a hydrosilylation catalyst (typically platinum), and a cure inhibitor. MQ resins [clusters of quadrafunctional silicate groups (Q) end-capped with monofunctional trimethylsiloxy groups (M)] may also be incorporated as control-release additives. Curing is carried out at 150°C or lower and line speeds of up to 460 m/minute can be achieved. It is also indicated that the industry is evolving towards using ultraviolet (UV) curable products.

Similar to the case with PDMS, silicone elastomers may contain small residual quantities of cyclic siloxanes and so the uses of silicone elastomers are relevant to the life cycle of D5.

2.1.6 Consumption of silicones

The Centre Européen des Silicones (CES) have published figures on the total worldwide consumption of silicones in 2002.[8] The total worldwide production in 2002 was 2,000,000 tonnes, with 33 per cent (~660,000 tonnes) used in Western Europe, 34 per cent (680,000 tonnes) used in North America, 28 per cent (560,000 tonnes) used in Asia, and 5 per cent (100,000 tonnes) used in the rest of the world. Lassen *et al.* (2005) report a smaller consumption of silicones in 2002 in Western Europe of 296,000 tonnes/year.

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

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

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

For the silicone fluids, 26 per cent were used as processing aids, 18 per cent in personal care products, 15 per cent in paper coatings, 10 per cent in paints and coatings, 7 per cent as mechanical fluids, 5 per cent in textile applications, and 24 per cent in other applications.

2.2 Production of cyclic siloxanes in the EU

Four companies produce or supply D5 in the EU, and a manufacturing site exists in the UK. The actual quantities produced at the various sites are confidential. The information available is summarised in a confidential annex to this report.

[8] See http://www.silicones-europe.com/ab_facts.html.

2.3 Uses

The uses of D5 can broadly be defined in five main areas:

- as a site-limited chemical intermediate at the site of production;
- as an off-site chemical intermediate;
- in personal care products (e.g. cosmetic products and skin- and hair-care products);
- in household products (e.g. cleaning products);
- in industrial/institutional cleaning (e.g. dry cleaning).

Information on the amounts of D5 supplied in the EU and the UK is provided by CES. Some of these figures are confidential and are summarised in the confidential annex to this report. The non-confidential figures for D5 are summarised in Table 2.1.

Table 2.1 Uses of D5 in the UK and Europe

Life-cycle step	**Amount used in Europe (tonnes/year)**		**Amount used in the UK (tonnes/year)**	
	2003	**2004**	**2003**	**2004**
Chemical intermediate – internal	Confidential	Confidential	Confidential	Confidential
Chemical intermediate – external	1594 [1]	2283 [1]	4 [1]	0 [1]
Personal care	16,329	17,300	4389	4387
Household products	Confidential	Confidential	Confidential	Confidential
Industrial/institutional cleaning	Confidential	Confidential	Confidential	Confidential
Other/unspecified	Confidential	Confidential	Confidential	Confidential
Total	**Confidential**	**Confidential**	**Confidential**	**Confidential**

Note: [1]The figures for the chemical intermediate – external use were provided in a subsequent survey of CES members and downstream users (CES, 2005b).

In a recent study in Denmark Lassen *et al.* (2005) report that D5 was released to air from two out of the ten car polishes investigated. The Danish Product Register contains 33 products registered in the area of polishes and waxes that contain cyclic dimethylsiloxanes, but the actual chemicals included in the products are not clear. The total registered amount of such products is relatively low (~2 tonnes/year). Other uses of D5 reported in the Substances in Products in the Nordic Countries (SPIN) database include fuel additives, surface treatments, fillers, impregnation material, adhesives, binding agents, paints, lacquers and varnishes, reprographic agents, softeners, surface active agents, and process regulators (TemaNord, 2005). Environment Canada (2008) indicates that in Canada, there may be some use of D5 in surfactants and defoamers (D5 content between 1 per cent and 80 per cent). These uses have not been confirmed for the UK in the CES survey and so are not considered again here. It is possible that these may refer to uses of PDMs made from D5 rather than direct use of D5 (e.g. the D5 emitted from the car polishes could have resulted from unreacted monomer in PDMs in the polish).

2.4 Life cycle

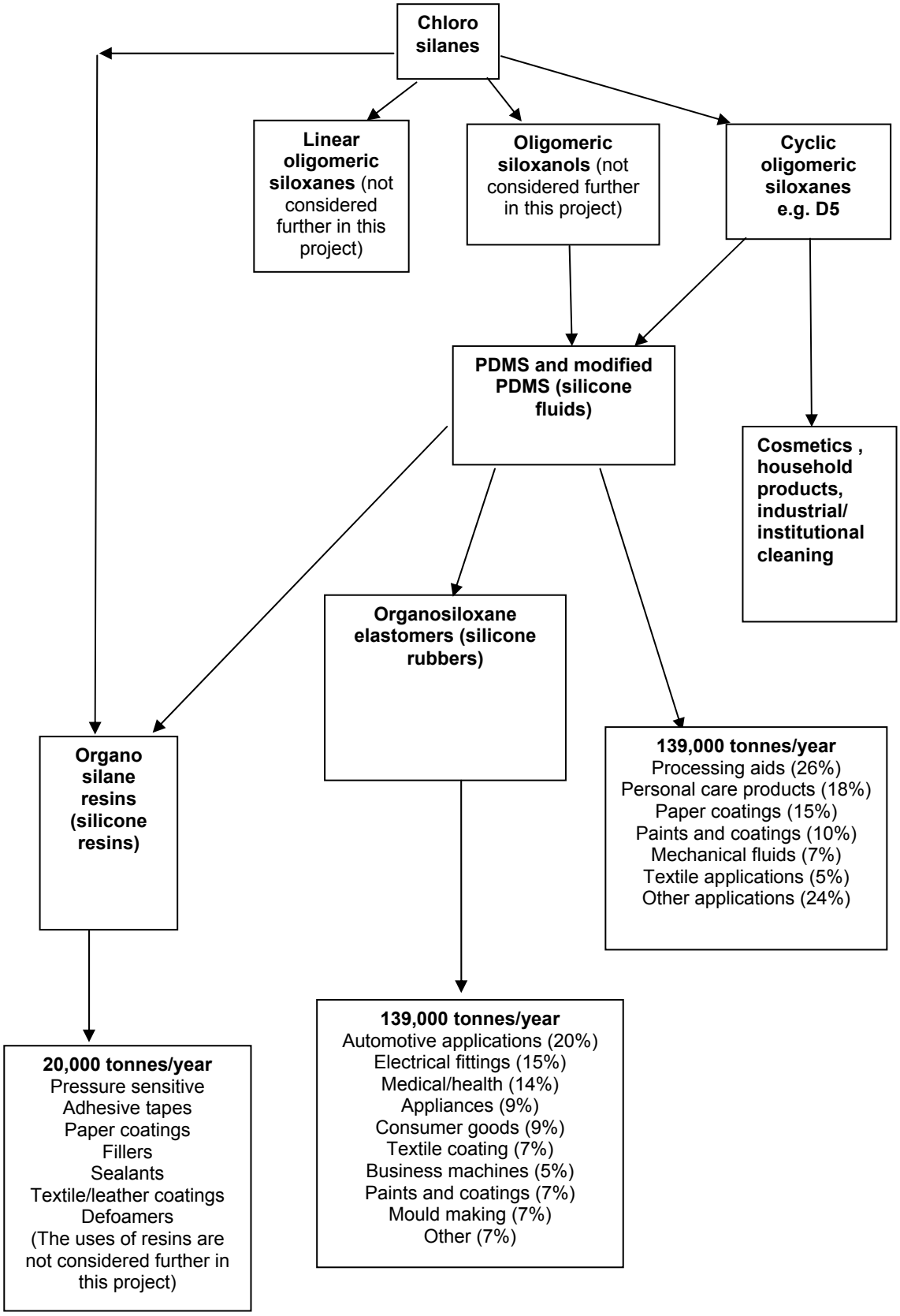
The overall life cycle of the various silicone products relevant to this project is summarised in Figure 2.1. Other (possibly experimental) uses of D5 include use as solvent for ozone during the treatment of wastewater (Ward *et al*., 2004). It is not thought that any of these uses are currently carried out on a large scale in the EU.

2.5 Trends

Based on the confidential information provided for this assessment, the production of D5 in the UK has shown an increasing trend over recent years. The off-site uses (off-site use as a chemical intermediate, use in personal care products, use in household products, use in industrial/institutional cleaning, and as solvent) show a generally increasing trend in both the UK and the EU. Note that this analysis is based on relatively few data points (in some cases only two years).

The use of D5 in personal care products is showing an increasing trend.

Figure 2.1 Western European usage of silicones


Chloro silanes
Linear oligomeric siloxanes (not considered further in this project)
Oligomeric siloxanols (not considered further in this project)
Cyclic oligomeric siloxanes e.g. D5
PDMS and modified PDMS (silicone fluids)
Cosmetics , household products, industrial/ institutional cleaning
Organosiloxane elastomers (silicone rubbers)
Organo silane resins (silicone resins)
139,000 tonnes/year
Processing aids (26%)
Personal care products (18%)
Paper coatings (15%)
Paints and coatings (10%)
Mechanical fluids (7%)
Textile applications (5%)
Other applications (24%)
139,000 tonnes/year
Automotive applications (20%)
Electrical fittings (15%)
Medical/health (14%)
Appliances (9%)
Consumer goods (9%)
Textile coating (7%)
Business machines (5%)
Paints and coatings (7%)
Mould making (7%)
Other (7%)
20,000 tonnes/year
Pressure sensitive Adhesive tapes
Paper coatings
Fillers
Sealants
Textile/leather coatings
Defoamers
(The uses of resins are not considered further in this project)

2.6 Legislative controls

Some uses of D5 fall under Council Directive 1999/13/EC of 11th March 1999 on the limitation of emissions of volatile organic compounds (VOCs) caused by the use of organic solvents in certain activities and installations. Under this directive a VOC is defined as an organic compound that has a vapour pressure of 10 Pa or more at 20°C. The vapour pressure of D5 is 33.2 Pa at 25°C and around 16 Pa at 20°C (see Section 1.3.51.3.5) and so would be classified as a VOC under this Directive. The Directive outlines a series of values for emission limits for air that apply to installations that carry out a number of processes involving solvents. The appropriate emission-limit values related to VOCs from dry cleaning are summarised as: total emission limit value of 20 g solvent/kg of product cleaned and dried (certain exemptions also apply).

The requirements of the Directive apply to both new installations and existing installations (existing installations had to comply with the Directive by 31 October 2007).

In the USA, VMSs, including D5, are exempt from VOC legislation because laboratory experiments at the University of California demonstrated that, in contrast to other organic compounds of similar reactivity, the breakdown of VMSs in the atmosphere does not lead to the formation of ground-level ozone (CES, 2005b). This work was also substantiated by Harwell Laboratory in the UK. Using computer modelling, the photochemical ozone creation potentials (POCPs) for a number of VMSs were calculated under European atmospheric conditions. It was concluded that the POCP value for D5 was close to zero.

In Germany, D5 is considered as a general organic substance in relation to limiting air emissions. The emission limit according to TA Luft (based on total carbon) is 0.5 kg carbon/hour, which equates to an emission limit for D5 of 1.55 kg D5/hour or a maximum of 50 mg carbon/m^3 (= 155 mg D5/m^3). For indoor air, no specific Niedrigste Interessierende Konzentration (NIK) exists for D5. D5 is therefore included under the general category of other substances for which no NIK standard has been derived, the sum of which must be <0.1 mg/m^3.

3 Environmental exposure

3.1 Environmental releases

In this assessment, releases to the environment are considered in various scenarios. The background to these is explained more fully in the Technical Guidance Document (TGD). The local environment is considered to be the environment near to a site of release (e.g. a production, formulation or processing site). The regional environment is taken to represent a highly industrialised area. The continental environment is the size of the EU and is generally used to obtain ‘background' concentrations of the substance.

A preliminary worst-case estimate of the emissions was carried out using the A and B Tables from Appendix I of the TGD. According to the TGD the B Tables, which are used to define the size of the local site, should be applied to the total EU volume of the substance used unless there are indications that it is used at numerous sites, in which case the regional volume (10 per cent of the total EU volume) should be used. This is known as the 10 per cent rule. For D5 we have information on both the total EU volume and the volume used in the UK, and so the B Tables are used on the UK volume to estimate the representative sizes for the sites in the UK where appropriate.

The regional releases are taken as 10 per cent of the total EU release, unless the release from a single site accounts for >10 per cent of the total EU release.

The emission estimates are based on the 2004 production and use data where available.

The Predicted Environmental Concentrations (PECs) are calculated using the European Union System for the Evaluation of Substances (EUSES) 2.0.3 program, which implements the methods given in the TGD.

3.1.1 Production and use as a chemical intermediate on-site

3.1.1.1 Default release estimate

- The emissions from the UK production site can be estimated using the A and B Tables from the TGD. The relevant emission factors (taken from Table A1.1 or Table A2.2) for main category {(MC) = 1c – (isolated intermediates stored off-site)} D5 are:0.0001 (0.01 per cent) to air
- 0.003 (0.3 per cent) to wastewater.

The emissions estimated using these figures are confidential. The number of days of operation is estimated (Table B1.6) as 300 days.

3.1.1.2 Other emission data

Information is available on the amounts of D5 in various effluent streams at the production sites in the EU. This information is summarised in Section 3.3.1.2. The data represent the emissions from the whole site and so will include any on-site use of D5 as an intermediate.

Based on these figures, for D5 the emissions to water after waste treatment at the actual UK plant can be estimated using the appropriate effluent flows as of the order 0.0024–0.0084 kg/day. These data are based on measurements taken around 2001. Using the 2001 production data for this site (confidential), an appropriate emission factor for D5 was derived

and applied to the 2004 consumption data (details of the calculation are given in the confidential annex). This was used to estimate the current emission of D5 from the UK production site (after wastewater treatment) as 3.1 kg/year or 0.010 kg/day.

3.1.1.3 Summary of emissions used in preliminary assessment

For the preliminary assessment, the emissions to water estimated in Section 3.1.1.20 will be used, along with the default emissions estimated for air (see Section 3.1.1.10). Note that the emissions to water are based on relatively few measurements and so are themselves uncertain, but even so it is clear from the limited data available that the actual emissions to water from the site are much lower than would be predicted from the default values.

The emission estimates for local D5 to air used in this assessment are:

- confidential to air
- 3.1 kg/year or 0.010 kg/day to surface water.

The number of days of emission is 300.

In addition, the PEC calculation also takes into account the information available on the size of the wastewater treatment plant [average flow 321 m^3/hour (0.089 m^3/s); 95th percentile high flow 499 m^3/hour (0.14 m^3/s)] and the flow of the receiving water (mean flow 0.225 m^3/s; 95th percentile low flow 0.039 m^3/s). Based on the mean flow rates, the average dilution factor at this site is 0.225/0.089 = 2.5. No dilution would be expected based on the 95th percentile low flow of the river and the 95th percentile high flow of the effluent treatment plant.

3.1.2 Use as a chemical intermediate off-site

The relevant industry category (IC) for this use is IC = 3: Chemical Industry: Chemicals used in synthesis. The relevant use category (UC) is UC = 33 (Intermediates). The default emission factors for off-site use as an intermediate are given in Table A3.3 of the TGD. The appropriate emission factors for D5 are (assuming MC = 3 as a default):

- 0.001 (0.1 per cent) to air
- 0.007 (0.7 per cent) to wastewater (wet process)
- 0 to wastewater (dry process).

More information has been provided on the UK use in this area. CES (2005b) recently completed the analysis of a questionnaire that requested more details on D5 emissions to water from UK and EU sites at which D5 is used as an intermediate for off-site polymer synthesis. The information is summarised in the confidential annex. In the survey, a ‘dry process’ was defined as a process that does not involve aqueous processing of D5 and therefore does not result in release of D5 to the aqueous effluent stream from the site.

The CES (2005b) survey found that >99 per cent of the total volume of D5 used as an off-site intermediate in the EU to manufacture polymers does not result in emissions to the water compartment.

In the UK, no D5 was sold for this purpose in 2004 (a small amount was used in 2003, but this was all used in a dry process). For continental Europe, the CES (2005b) survey identified one site that used D5 in a wet process. More information was obtained from this site and used to derive D5 emission estimates:

- Intermediate in polymer synthesis, wet process:

- local (UK) – no use
- local (EU) – 0.16 kg/day to air and 1.7 × 10–5 kg/day to wastewater
- total UK 0 kg/year to air and 0 kg/year to wastewater
- regional – confidential
- total EU – confidential
- the number of days of emission for the local site is confidential.

- Intermediate in polymer synthesis, dry process:
  - local (UK) – no use
  - local (EU) – 685 kg/year or 5 kg/day to air and0 kg/year to wastewater
  - total UK – 0 kg/year to air and 0 kg/year to wastewater
  - regional – confidential
  - total EU – confidential
  - the number of days of emission for the local site is 137 days.

For the emissions to wastewater from the local site, the known size of the wastewater treatment plant is taken into account herein.

3.1.3 Use in personal care products

For this use the relevant IC is 5: Personal/Domestic. The relevant UC is 15 (Cosmetics).

3.1.3.1 Formulation

The default emissions from formulation of personal care products can be estimated using Table A2.#[9] of the TGD. The relevant emission factors are summarised as:

- formulation of liquid products – 0.00002 (0.002 per cent) to air and 0.0009 (0.09 per cent) to wastewater
- Others and unknown – 0.0002 (0.02 per cent) to air and 0.0009 (0.09 per cent) to wastewater.

As D5 is used to make a range of products, both solids and liquids, the higher emission factor to air is used in the calculations as a worst case.

The worst-case amount formulated on a site and the number of days of formulation can be estimated using Table B2.3 of the TGD. This table applies to the total volume of cosmetics that contain the substance in a region.

The cyclic siloxane contents of cosmetic and skin-care products can vary widely, from a few percent to 90 per cent or more. Therefore, to carry out a preliminary analysis here, a figure of around 30 per cent is taken. Using this figure and the amount of D5 supplied to the personal care industry in the UK, the total amounts of cosmetics and personal care products that are formulated in the UK and contain D5 can be estimated as ca. 14,000 tonnes/year.

[9] This is how the Table is numbered in the Technical Guidance Document. The actual number is not clear.

Using these figures in Table B2.3 gives the amount of cosmetics that contain D5 and the amount of D5 formulated, on a worst-case local site over 300days, as ca. 10,000 tonnes/year and ca. 3000 tonnes/year, respectively.

A survey of 39 cosmetic formulation sites in the UK was undertaken by the CTPA. The amounts of D4, D5, and cyclomethicone (a general term used for mixtures of D4, D5, and D6) used at the sites were determined. No use of any of these substances was reported at 21 of the sites. The amounts used at the other sites are confidential, but it was clear from the results of the survey that only one or two sites are of the size represented by the upper end of the consumption range for D5, with many sites using much smaller volumes than this upper limit. Based on these data the appropriate size for a representative generic site was estimated to be around 255 tonnes/year of D5 over 300 days (although larger sites than this exist, most sites would be at or below this level of consumption; site-specific information of the larger sites is used in the assessment, see below).

Using this value and the above default emission factors, the emissions of D5 from formulation can be estimated as

- local, generic site – 51 kg/year or 0.17 kg/day to air and 230 kg/year or 0.77 kg/day to wastewater
- total UK emission – 798 kg/year to air and 3948 kg/year to wastewater
- regional – 315 kg/year to air and 1557 kg/year to wastewater
- total EU emission – 3,149 kg/year to air and 15,570 kg/year to wastewater.

In addition the CTPA survey allowed us to make estimates for the release of D5 from sites that used D5 itself or cyclomethicone. These calculations are confidential but the local releases per site in the UK were in the range 5×10^{-5} to ca. 1 kg/day to air and 2.4×10^{-4} to ca. 5 kg/day to wastewater. The number of days of emission from the local site is taken as 300 in all cases.

The estimates for UK sites that use D5 are considered in this assessment. Similarly, a survey of the major EU formulation sites outside the UK that use D5 was undertaken (CES, 2006). These data are confidential, but are considered in Appendix B.

3.1.3.2 Use by general public

The emissions to the environment from use by the general public are assumed to be 90 per cent to air and 10 per cent to wastewater. This is based on the assumption that 100 per cent emission to air will occur for products applied to the skin (e.g. skin creams, antiperspirants, etc.) and 100 per cent emission to wastewater will occur for hair-care products (which may be washed out immediately after application), along with an analysis of the relative proportion of these two types of products that contain cyclic siloxanes in the UK.

The amounts of D5 used to formulate personal care products in the EU and the UK are summarised in Section 2.30. However, CTPA indicate that companies in the UK export a large amount of the products formulated in the UK to other parts of the EU and the world. The actual amounts of personal care products that contain D5 used in the UK are unknown, but as a first approximation the CTPA suggest that the UK market should be taken as 14.7 per cent of the old EU15 plus Norway and Switzerland.

Based on the UK market being 14.7 per cent of the total EU, the amounts of cosmetics that contain D5 (assuming a content of 30 per cent as before) and of D5 itself used in the UK can therefore be estimated as ca. 8500 tonnes/year and ca. 2500 tonnes/year, respectively.

For the local assessment it is assumed that this tonnage is equally distributed about the UK. Using a UK population of 60 million, the average usage for D5 in personal care products can be 0.042 kg/person/year.

Assuming a local site (in this case a wastewater treatment plant) serves 10,000 inhabitants, and that 10 per cent of the products used are released to water and 90 per cent are released to air, the local release to such a plant can be estimated (release is assumed to occur over 365 days/year). The regional release is based on a population of 2×10^7 inhabitants, as recommended in the TGD. It is only relevant to consider the direct release to air from use of personal care products at the regional and continental levels. The estimates for D5 are:

- local – 42 kg/year or 0.12 kg/day to wastewater
- total UK – 2,288,700 kg/year to air and 254,300 kg/year to wastewater
- regional – 756,000 kg/year to air and84,000 kg/year to wastewater
- total EU – 15,570,000 kg/year to air and 1,730,000 kg/year to wastewater.

The number of days of emission from the local scenario is 365 days in all cases.

3.1.4 Household products

The relevant IC for this use is IC = 5: Personal/Domestic. The relevant UC is 9 (Cleaning/washing agents).

3.1.4.1 Formulation

Site-specific information was used to estimate the release from formulation of household products that contain D5. Details of the calculations are confidential (the calculations are summarised in the confidential annex).

3.1.4.2 Use by general public

Confidential information was used to estimate the release of D5 from household products. The local release to wastewater was estimated at around 6.0×10^{-3} kg/day for this scenario. Emissions to air will also occur (only considered at a regional level for this application). Other details of the calculations are considered confidential.

3.1.5 Industrial/institutional cleaning

This use represents use in dry cleaning. The relevant IC for this use is 6: Public domain. The relevant UC is 9 (Cleaning/washing agents).

3.1.5.1 Formulation

No formulation step is used for this application and so no emissions are estimated.

3.1.5.2 Use in industrial/institutional cleaning

Confidential information was used to estimate the release of D5 from industrial/institutional cleaning products. The calculation method assumes that emissions to wastewater of D5 are limited by its low solubility in water and the small amounts of wastewater generated by the

process. The local emission to wastewater is estimated at around 8.5×10^{-8} kg/day (i.e. negligible). Emissions to air can also occur (estimated to be around 0.33 kg/day as a worst case at a local site). Other details of the calculations are considered confidential.

Council Directive 1999/13/EC will limit the total emissions of solvent from dry cleaning to 20 g solvent/kg at all sites once fully implemented (see Section 2.60). This would limit the emissions to air from dry cleaning to a maximum of around 0.2 kg/day for the scenario considered here.

3.1.6 Other and/or unspecified uses

According to the figures given in Section 2.3 a very small amount of D5 is currently unaccounted for (given as other and/or unspecified uses). It is not clear if these small tonnages represent actual new uses that are not already covered in the assessment or rather result merely from the different ways companies report their data. However, as the tonnages involved are generally small, they are not considered again in this assessment.

3.1.7 Other sources of emission

3.1.7.1 Impurities in PDMS polymers

PDMS-based polymers may contain residual amounts of D5 which may subsequently be lost via volatilisation during the lifetime of these polymers. Figures for the amounts of residual monomer in PDMS-based products were provided by CES and are summarised in Table 3.1 (Europe) and

Table 3.2 (UK).

Table 3.1 D5 impurities contained in silicone products (total EU)

Application	**2004 EU sales (tonnes)**	**Residual monomer content (D5) (%)**	**Amounts of residual monomer (D5) (tonnes)**
Sealants	210,000	0.057	119.9
Elastomers	139,000	0.086	119.7
Fluids and specialities	204,000	0.311	634.3
Silanes	60,000	0	0
Resins	20,000	0	0
Total			**873.9**

Table 3.2 D5 impurities contained in silicone products (UK)

Application	2004 UK sales (tonnes)[1]	Residual monomer content (D5) (%)	Amounts of residual monomer (D5) (tonnes)
Sealants	[31,500]	0.057	16.9
Elastomers	[20,850]	0.086	16.5
Fluids and specialities	[30,600]	0.311	55.1
Silanes	[9,000]	0	0
Resins	[3,000]	0	0
Total			**88.5**

Note: [1]Full figures were not available. Where data were missing these were estimated from total EU sales assuming that the UK accounts for 15 per cent of the total sales.

With the exception of elastomers, the figures relate to the amount of the monomer in the PDMS polymers as sold. For elastomers the figures refer to the amount of monomer released to air during the post-curing of silicone rubbers.

The factors that affect the levels of volatile products in fabricated silicone elastomers are considered by Toub (2002). The total level of volatile silicone products (including both linear and cyclic siloxanes) varies according to the particular formulation, manufacturing process, shape of the manufactured article, and the storage conditions, but is generally in the range 0.05–3 per cent by weight in the cured silicone rubber product. Example contents of various cured high-consistency rubber sheet products were in the range <0.01–0.61 per cent by weight for D4, <0.01–0.42 per cent by weight for D5, and <0.01–0.37 per cent by weight for D6. The level depended on the actual rubber formulation and the thickness of the article. The sheet exposure time was an important factor in relation to the residual levels. For example, after storage for one week the residual level of D4 in the cured rubber was below the detection limit, independent of the thickness of the article. Post backing for two hours at 200°C also reduced significantly the residual amounts of D4 in the product. Similar reductions in residual levels would be expected for D5.

As a first approximation it is assumed that all of the residual monomer is lost from the PDMS product by volatilisation during the first year of use. On this basis the UK, regional (taken as 10 per cent of the total EU), and total EU emissions of D5 from this source can be estimated as:

- total UK – 88,500 kg/year to air
- regional – 87,390 kg/year to air
- total EU – 873,900 kg/year to air.

3.1.7.2 Breakdown of PDMS polymers

A number of literature sources indicate that D5 (and other cyclic oligomeric siloxanes) can be formed during the breakdown of PDMS. In this section we focus on the most relevant studies that have investigated this breakdown process rather than provide an in-depth review of the overall degradation of PDMS and other silicone polymers (this is beyond the scope of the current risk assessment).

In many of the studies the PDMS used is specified in terms of the viscosity, as this is usually used to classify the various types of PDMS fluids (Chandra, 1997):

- low viscosity – kinematic viscosity in the range 0.65–20 centistokes (cst)
- medium viscosity – kinematic viscosity in the range 50–1000 cst
- high viscosity – kinematic viscosity in the range 5000 to 250,000 cst
- gums – kinematic viscosity >500,000 cst.

The relevant information on the identity of the substance (i.e. viscosity and any other data) is given for each study wherever available.

Weschler (1988) showed that five main cyclic siloxanes were formed when samples of PDMS (viscosities between 20 and 30,000 cst) were pyrolysed at temperatures of between 700 and 980°C for one second (the atmosphere used in this study was not totally clear, but appears to have been helium). The relative abundances of the products formed were relatively constant over the range of PDMS products studied, with the products being in the approximate ratio of 100:36:13:8:6 for D3, D4, D5, D6, and tetradecamethylcycloheptasiloxane (D7). No information was given on the yields of volatile products formed under these conditions. The author noted that this product distribution was similar to that in earlier work by Thomas and Kendrick (1969) in experiments using a vacuum at 420°C for five hours.

Camino *et al.* (2002) report that earlier work had shown that the thermal degradation of PDMS end-blocked with $(CH_3)Si–$ groups in inert atmospheres (e.g. N_2) and under vacuum resulted in depolymerisation and the formation of cyclic oligomers. The most abundant cyclic oligomer is D3, but irregularly decreasing amounts of D4, D5, D6, and higher oligomers can also be formed. In air the decomposition is accompanied by the formation of some silica powder. It is also reported that cationic reactions on glass surfaces can contribute to the thermal degradation of PDMS polymers.

Camino *et al.* (2002) carried out other experiments to investigate the mechanism of thermal degradation of PDMS [end-blocked with $(CH_3)Si–$ groups and containing a vinylmethylsiloxane unit every 1400th $–(CH_3)_2–Si–O–$ unit, with a viscosity of 8×10^6 mPa[10]]. Experiments were carried out in either a helium or air atmosphere in a glass container. Two types of heating regime were used. The first involved a programmed temperature increase of 10°C/minute up to 80°C, equilibration for one minute, 10°C/minute from 80°C to 400°C, then held at this temperature for one hour. The second involved flash pyrolysis in which the sample was heated rapidly at 80°C/minute up to 800°C and then held at this temperature for ten minutes. The products evolved during the heating were collected and analysed. In the programmed temperature-increase experiments the relative amounts of the cyclic degradation products formed were 100:74:25:43:16 for D3, D4, D5, D6, and D7, respectively, under a helium atmosphere and 100:67:32:44:18 for the same products under an air atmosphere. Higher cyclic siloxane oligomers were also formed in smaller amounts. The actual absolute yields of the products were not given, but it is indicated in the paper that the major volatile products from the experiments in air are water and CO_2 (and also SiO_2), which result from the gas-phase oxidation of the volatile cyclic oligomers formed.

The flash pyrolysis experiments showed that linear siloxane oligomers and rearranged siloxane compounds were formed, along with the cyclic siloxane oligomers. Under these conditions D4 became the dominant cyclic oligomer (the relative abundance was

[10] The viscosity is given in the paper as mPa. However this unit is not normally associated with viscosity. It may be that the actual unit should be millipoise (mP) or mPa s (both are units of dynamic viscosity, 1 mPa s = 10 mP). To convert from dynamic viscosity into kinematic viscosity, the specific gravity of the fluid is needed (i.e. 1 centistoke = 1 centipoise/specific gravity).

85:100:37:27:17 in a helium atmosphere and 56:100:31:23:18 in an air atmosphere for the products D3, D4, D5, D6, and D7, respectively). Oxidation of the volatile products to CO_2, water, and SiO_2 was more limited under these conditions in the air atmosphere than in the slow-heating experiments. Again, no information was given on the absolute yields of volatile products formed under these conditions.

Overall, Camino *et al.* (2002) concluded that thermal degradation of PDMS occurs through two competing mechanisms. The first mechanism is a molecular mechanism to form cyclic oligomers. This involves scission of the Si–O bond and the reaction is favoured in flexible chains at lower temperatures. The second mechanism, which prevails at higher temperatures, is a radical mechanism that involves homolytic scission of the $Si–CH_3$ bond. This results in the formation of cross-links within the molecule, which in turn decreases the flexibility of the PDMS and hinders the splitting of the cyclic oligomers.

Similar products were also found in thermal degradation studies by Lomakin *et al*. (2003). In these experiments, samples of PDMS (molecular weight 10^7 g/mol with terminal methyl groups, the viscosity was not given) were pyrolysed at temperatures between 300 and 800°C in glass cells with flowing air. D5 accounted for 17.9 per cent at 300°C, 22.9 per cent at 400°C, 23.0 per cent at 500°C, 10.9 per cent at 600°C, 14.4 per cent at 700°C, and 16.2 per cent at 800°C of the total volatile products formed. D5 was also formed in similar experiments using a blend of polystyrene and PDMS (80:20 ratio). The actual yields of volatile products at the different temperatures were not given in the paper. The results of thermogravimetric analysis were given graphically and generally showed little weight loss from the PDMS polymer alone in air at temperatures up to around 300°C, with around 50 per cent weight loss by 500°C (no further weight loss appeared to occur at higher temperatures).

Nielsen (1979) reports that significant degradation of PDMS occurs in the absence of air and catalysts at temperatures above 350°C. Experiments carried out at 370°C with different PDMS products (PDMS fluids with viscosities 50, 100, 1,000, or 10,000 cst) under a nitrogen atmosphere showed the formation of both cyclic and linear volatile polysiloxanes (including D5). The actual yields of volatile products at the different temperatures were not given in the paper. The results of thermogravimetric analysis were given graphically and these generally showed little weight loss from the PDMS polymer alone in air at temperatures up to around 300°C, with around 50 per cent weight loss by 500°C (no further weight loss appeared to occur at higher temperatures). The composition of the volatile products formed depended on the composition of the PDMS, and also changed with time in the experiment as the composition of the residual PDMS fluid changed. For example, the 10,000 cst PDMS product gave only cyclic volatiles until much of the fluid had been volatilised, whereas the 50 to 1,000 cst PDMS substances evolved significant amounts of linear volatile products throughout the degradation.

Patel and Skinner (2001, 2003) found that cyclic polymethylsiloxane species from D4 to D18 could be extracted from samples of room-temperature vulcanised polysiloxane rubbers (prepared by adding tin octoate catalyst to RTV5370 gum) that had been thermally aged in inert gas atmospheres (argon), sometimes in the presence of moisture, at temperatures up to 190°C for 48 hours [longer term experiments were also carried out at lower temperatures (e.g. 80°C for six months) but few details of the results of these experiments were given]. The extraction was carried out by immersing the polymer in toluene at 70°C for 96 hours. Under these conditions (aging at 190°C for 48 hours) the amount of extractable matter was around 5.5 per cent of the initial weight of the polymer when the polymer was aged at 190°C in sealed containers and 2.7 per cent of the initial weight when aged at 190°C in the open air (for comparison the amount of extractable matter from the virgin sample was 3 per cent of the initial weight of the polymer). The cyclic siloxanes contributed around 50 per cent of the weight of the extractable material from the aged samples (the contribution to the extractable material from the virgin sample was not clear). These substances were thought to form as a result of thermally activated degradation processes that involve depolymerisation reactions of

the polymer chains. However, in practice, room-temperature vulcanised rubber is not designed to be used at high temperatures for extended periods of time. The emissions to air during post-curing of elastomers are already considered in 3.1.6, subsection Impurities in PDMS polymers0.

When the results of the thermal degradation studies are considered, although these show that D5 can be formed under certain high temperature conditions, it also needs to be remembered that, under the usual conditions of use, PDMS polymers are known to possess a high degree of thermal stability. According to CES (2005b), PDMS polymers are not recommended for use at temperatures greater than 150°C in contact with air. The Silicone Industry's guidance is also that under sealed conditions (exclusion of air) the average use-temperature should not exceed 250°C and the maximum temperature should not exceed 300°C. Also, the available pyrolysis studies were carried out mainly at 300°C or higher and only limited information is available on formation of potential breakdown products at lower temperatures. Although it is expected that PDMS and other silicone polymers would become increasingly stable at lower temperatures. For example, although the above data show that D5 appears to make up a similar fraction of the total volatiles products formed at each temperature, the amount of total volatile products formed will vary with temperature and is likely to decrease with decreasing temperature below 300°C. This means that the actual thermal breakdown of PDMS polymers during normal use will be minimal.

As well as thermal breakdown, PDMS polymers can also undergo degradation in soils. The products of this degradation depend to a large extent on the conditions used. Similar to the case with cyclic siloxanes (see Section 3.2.3) the degradation is an abiotic process related to the acid sites on minerals in the soil and is sensitive to the water content of the soil. The relevant information on this for PDMS is summarised below.

The degradation of PDMS was studied using a USEPA standard soil (Carpenter *et al*., 1995). The substance tested was ^{14}C-PDMS with a viscosity of 350 cst. The soil used had a moisture content of 2 per cent and was a sieved blend that consisted of 20 per cent soil, 20 per cent sand, 25 per cent silt, 5 per cent gravel, 22.5 per cent kaolinite, and 7.5 per cent montmorillonite. In three spiking methods used the soil was slurried with:

- a solution of PDMS in hexane and the hexane was evaporated under a stream of dry nitrogen;
- a solution of PDMS in hexane followed by filtration;
- an aqueous emulsion of PDMS, filtered and air dried to a 2 per cent moisture content.

The initial concentration was around 350–400 mg/kg. The spiked soils were then incubated (the temperature was not given) in covered glass jars. Degradation of PDMS was apparent in all systems after just a few hours (as seen by a change in the molecular weight distribution of the components of the polymer). Over longer periods (six months to one year) significant formation of low molecular weight siloxanols was apparent. In the aqueous extract of the soil after one year of incubation dimethylsilanediol was the major water-soluble degradation product, with smaller amounts of the dimer and trimer diols also present.

An experiment was also carried out to investigate the formation of volatile products during the degradation (Carpenter *et al*., 1995). In this experiment the spiked soil was incubated for one week in a vessel swept with nitrogen. Volatile degradation products were collected using a charcoal trap. No cyclic siloxanes were formed under these conditions. In extracts from the soil a series of linear silanol-terminated oligomers (with seven siloxane units or less) were identified as the principal products.

The mass balance obtained in this study was reported to be relatively low for soils incubated for long periods. This was taken to indicate that some of the low molecular weight breakdown

products may be tightly bound to soil. This is consistent with the findings of Lehmann *et al.* (1994, 1995), Lehmann and Miller (1996), Xu (1998), and Xu *et al.* (1998) which show that as the soil dries the binding of dimethylsilanediol to soil increases (i.e. the dimethylsilanediol can no longer be easily extracted with organic solvents, such as tetrahydrofuran, but can readily be extracted by dilute aqueous acid solution).

Lehmann *et al.* (1994) showed that ^{14}C-labelled PDMS (200 cst viscosity, number average molecular weight 6642 g/mol) degraded slowly when incubated in a Londo sandy clay loam soil with a water content of 12 per cent. The radiolabel in the substance tested was randomly distributed on the methyl groups. The soil was collected from an agricultural field in Michigan (top 5 cm) and was sieved (2 mm) and stored at 4°C prior to use. It had an organic matter content of 2.4 per cent, a pH of 7, and a sand:silt:clay ratio of 50:28:22.

The test system used consisted of 50 g of soil in biometer flasks to which 0.5 ml of a solution of PDMS in tetrahydrofuran was added to give an initial PDMS concentration of 100 mg/kg. The soil was left uncovered for three hours to allow the solvent to evaporate, and then CO_2 and volatiles traps were added. Next, the flasks were attached to an oxygen manifold and incubated at a constant moisture content at 25°C for up to 25 weeks. A second set of experiments investigated the effect of soil drying on the degradation rate. These samples were prepared in a similar way as above, except that 5 g of soil in centrifuge tubes was used, a foam plug moistened with PDMS (350 cst viscosity) was inserted into the neck of the tube (to trap volatiles), and the tubes were set open to dry at 25°C for up to 14 days.

In the experiments using moist soil (12.2–13.2 per cent moisture) the amount of water-extractable ^{14}C in the soil increased with time, which suggests that the polymer degraded to smaller, water-soluble compounds. After 25 weeks incubation the yield of low molecular weight water-soluble products was around 2.9 per cent of the radioactivity initially applied. The soil-extractable degradation products were identified as low molecular weight linear siloxanols of general formula $HO–[Si(CH_3)_2O]_n–H$.

A small number of volatile ^{14}C-compounds were also evident (collected in the trap). These compounds were not identified, but accounted for around only 0.5 per cent of the applied radioactivity after 25 weeks. In addition, a small amount of $^{14}CO_2$ was found (around 0.19 per cent of the total ^{14}C applied). The overall mass balance from these experiments was generally very good (in the range 92.8–107.2 per cent), which indicates that all the major degradation products were accounted for. When the soil was allowed to dry (from a moisture content of 12 per cent to around 3 per cent over the period of a week), degradation was much more rapid.

For the soil drying experiments, the soil was found to dry steadily from an initial water content of around 12 per cent to a water content of around 2–3 per cent by day four. After this time the water content remained relatively constant throughout the experiment. No degradation of PDMS was evident over the first three days of the experiment. On day four a decrease in the molecular weight distribution and a slight formation of water-soluble degradation products was evident. However, by day seven a significant breakdown of the PDMS to low molecular weight products was found and by day 14 the water-extractable and acid-extractable (0.1 M HCl) products accounted for around 18.2 per cent and 11.5 per cent, respectively, of the total radioactivity applied. No significant amounts of volatile products were formed (<0.11 per cent of the amount of radioactivity applied). The mass balance from this experiment was again very good (99.0–107.4 per cent).

Additional experiments on the microbial degradation of the low molecular weight products found in this study showed that dimethylsilanediol would be the major ultimate degradation product.

Lehmann *et al.* (1994) concluded that the degradation of PDMS was probably not biological in origin as it was more rapid at lower soil-moisture contents, conditions that are less favourable to microbial populations.

A follow-on study using seven soils from the USA of differing pH, percentage per cent organic matter, texture, mineralogy, and geographic origin demonstrated the general applicability of this degradation route (Lehmann *et al.*, 1995). Moist soils (initial moisture between 8 and 31 per cent, depending on the soil) were amended with ^{14}C-PDMS (viscosity 350 cst and number average molecular weight 9440 g/mol) and maintained at 23°C for up to 14 days (during which the soils were allowed to dry naturally). In all soils, PDMS degraded to low molecular weight, water-soluble products over the 14 days of the experiment (for one soil the experiment was extended to 28 days). The main degradation product found was dimethylsilanediol. Other small silanols or cyclic siloxanes were either not detected or were formed in only trace amounts. Additional experiments were carried out to investigate the effects of the loading rate on the degradation products seen with one soil (Londo soil). At loadings of around 100 mg/kg – the dominant degradation product seen was dimethylsilanediol, using both moist and oven-dried soil. However, at very high PDMS loadings (1 per cent or 10,000 mg/kg), a higher proportion of cyclic products (in this case mainly D4) was formed. Taking these results, along with the earlier findings of Buch and Ingebrigtson (1979), it was concluded that formation of cyclic products would be significant only at very high PDMS loadings, especially if they are rapidly volatilised from the soil by a stream of air.

Another study by Lehmann *et al.* (2000) investigated the degradation of PDMS in field soils under natural conditions. The substance tested was a commercially available PDMS emulsion. The PDMS had a viscosity of 350 cst. Aqueous emulsions of PDMS were sprayed onto four soil plots (each 2.44 m by 2.44 m) in Michigan in May 1997 to give concentrations of 0 (control), 215 mg/kg (low treatment), 430 mg/kg (medium treatment), and 860 mg/kg (high treatment). Soil cores (0–5 and 5–10 cm) were collected every two weeks over the following summer and analysed for total soil PDMS and decreases in molecular weight of the PDMS remaining. The concentration of PDMS had decreased by 50 per cent within 4.5, 5.3, and 9.6 weeks for the low, medium, and high treatments, respectively. Dimethylsilanediol was the main degradation product identified in the soil columns (this was found in most samples at <5 per cent of the original PDMS concentration). Another application of the medium-treatment level was carried out in late August. This showed a slow degradation of PDMS occurred during the cool, wet autumn months followed by around 40 per cent degradation over the winter months, with further, extensive degradation occurring over the summer of 1998. These findings are consistent with the results of the laboratory studies. Substances that volatilised from the soil were not collected in this study.

A summary paper of the degradative behaviour of PDMS in soils is given by Stevens (1998). This paper concludes that the dimethylsilanediol is likely to be the major ultimate degradation product from PDMS in the environment. Dimethylsilanediol is very soluble in water (245 g per 100 g) and slow biodegradation into $^{14}CO_2$ and silicic acid [$Si(OH)_4$] in soil was demonstrated – a route for the ultimate mineralisation of PDMS.

Stevens (1998) also reports work by Carpenter (1996) that showed relatively slow degradation of ^{14}C-labelled PDMS (viscosity 350 cst) in freshwater sediments. After one year around 5–10 per cent of the PDMS had been degraded to dimethylsilanediol, and approximately 0.25 per cent of the applied radioactivity was found as $^{14}CO_2$.

Xu *et al*. (1998) showed that a range of different clay minerals (including kaolinite, montmorillonite, nontronite, beidellite, illite, chlorite, allophone, gibbsite, and goethite) commonly found in soils all catalysed the degradation of ^{14}C-labelled PDMS (viscosity 350 cst) when exposed at a relative humidity of 32 per cent. The more effective minerals were

those with higher proportions of Al–OH functional groups on the surface, and the rate of degradation was also related to the specific surface area of the mineral.

Xu (1998) investigated further the effect of moisture levels and exchangeable cations on the degradation of PDMS fluid by clay minerals. The PDMS tested was ^{14}C-labelled, but no information on the viscosity was given (by comparison with other studies carried out by this author it is likely that the substance had a low viscosity, probably around 350 cst). The minerals used included kaolinite, talc, and Arizona montmorillonite saturated with Na^+, Ca^{2+}, or Al^{3+}. In the tests, freeze-dried clay mineral was weighed into 35 ml glass tubes (0.1 g mineral per tube), placed in desiccators at either 32 per cent or 100 per cent relative humidity, and equilibrated for five days at 22°C. Around 100 µl of ^{14}C-labelled PDMS solution was then added to each tube and the tubes were flushed with air at the correct relative humidity for 15 minutes, sealed and then replaced in the desiccator for up to 30 days. The initial PDMS concentration was ~2 g/kg. At various times during the study, tubes were sequentially extracted (the headspace was not analysed directly) and analysed for degradation products. A shift in the molecular weight distribution of the polymers indicates that degradation to lower molecular weight products was occurring.

The main final degradation product found in this study was dimethylsilanediol, although some volatile cyclic products were evident in the experiments with Al-saturated montmorillonite at high humidity. This latter finding was based on the low mass balance of total ^{14}C from this clay and subsequent direct measurement of volatile products [identified as D4 (major product), D3, and D5) in a follow-up study (the mass balance obtained for the other clays was close to 100 per cent, which indicates that little or no volatile products had formed].

Degradation (hydrolysis) occurred predominantly through random scission of the Si–O–Si backbone of the polymer (the degradation pathway was similar for all clay types, exchangeable cations, and humidities studied). The degradation proceeded in two stages (both zero order on the PDMS concentration; these kinetics may be a consequence of the very high PDMS loading used). The rate of the first stage increased with the increase in polarising power of the exchangeable cation (i.e. $Al^{3+} >> Ca^{2+} > Na^+$) and decreased humidity.

Xu (1998) concluded that reaction proceeded via the hydrolysis of the PDMS to form linear silanols with three to five $Si(CH_3)_2O$ units. These intermediate products could degrade further to form dimethylsilanediol or could cyclise to form D4, D3, or D5, etc. The actual products formed under any given conditions were to result from the relative rates of the formation of the linear silanols from PDMS and these two competing reactions. Conditions that best favour formation of volatile cyclic products would be a combination of high soil moisture and a rapid PDMS degradation rate. However, this combination is unlikely to exist in reality as the PDMS degradation rate decreases with increasing soil moisture content. Therefore the potential for volatile cyclic products to form from PDMS in soils under field conditions was considered to be low.

Similarly, Xu (1999) reports that formation of cyclic siloxane oligomers could occur in soils as a result of rearrangement and/or hydrolysis reactions (ring-chain equilibrium) of PDMS polymers. The cyclic products formed can be lost from the soil by volatilisation, or can themselves undergo degradation (see Section 3.2.30) and so the ultimate degradation product of PDMS in soil was again thought to be dimethylsilanediol. The hydrolysis was thought to be catalysed by soil clays, with clay minerals of low pH such as kaolinite and montmorillonite being the most effective.

The degradation of PDMS in soil (a silt loam) was also investigated under field conditions using test plots (5 m by 5 m) amended with anaerobically digested municipal biosolids (Traina *et al*., 2002). The study was carried out over a four year period following a single application of 0, 15, or 100 tonne/ha of municipal biosolids (containing around 1272 mg/kg PDMS; the types of PDMS in the biosolids was not given). The plots were used to grow corn

and soy bean during the test and were tilled to a depth of 10 cm each spring. The soil water level was found to be >100 g/kg (10 per cent) over most of the test period. The half-life of PDMS was found to be in the region of 876–1443 days in the top 10 cm of the plot under these conditions. When amended soils were brought into laboratory conditions and allowed to dry [the water content fell to <50 g/kg (<5 per cent) within two weeks], much more rapid degradation was evident (>80 per cent of the PDMS was transformed to low molecular weight products within 20 days). This study did not investigate the formation of volatile degradation products.

In summary, PDMS-based polymers appear to be able to break down to form D4, D5, and D6 under certain conditions. This occurs in the laboratory when PDMS is heated to relatively high temperatures and also in soil at ambient temperatures using high loading rates (e.g. >2000 mg/kg). The resulting emission to the environment from such processes is very difficult, if not impossible, to estimate as the yield depends on the specific conditions to which the polymers are exposed.

In terms of a possible source of emission to the environment, the degradation of PDMS polymers in soil is probably the more important to consider. Thermal degradation requires exposure to high temperatures for extended periods and, although this could theoretically occur in some uses, the fraction of the total PDMS polymers produced that would be exposed to such conditions is likely to be small. Also, the extent of degradation is likely to be minimal because the generally high thermal stability of the PDMS polymers (the emissions of residual levels of D4, D5, and D6 in PDMS polymers under normal conditions of use is considered in Section 3.1.7.10). For soil a significant amount of PDMS is used in ‘down the drain’ products, such as personal care products, etc. The properties of PDMS polymers are such that removal during wastewater treatment is likely to be mainly by adsorption onto sewage sludge and so spreading of such sludge onto soil is likely to provide a significant route of exposure. For example, Fendinger *et al*. (1997) measured PDMS levels of 290-5155 mg/kg in sewage sludge from eight wastewater treatment plants in North America, and found PDMS at <0.41–10.4 mg/kg in soil from locations where sludge was applied. [However, these conditions represent excessive loadings normally found under field conditions, even where there are very high rates of sewage sludge application (CES, 2005b).] The available information (above) indicates that, although cyclic siloxanes can be formed from degradation of PDMS under some situations, they are generally not the major products found under field conditions.

A reliable quantification of the amounts of cyclic siloxanes that may be formed from PDMS degradation in soil and from incineration of PDMS requires an in-depth assessment of the use pattern, sources, and fate of PDMS in the environment. This is beyond the scope of this risk assessment. However, an attempt is made below to provide an initial estimate of the possible magnitude of these emissions, but the estimates obtained are highly uncertain, as a large number of assumptions and simplifications are made.

The approach is based on data presented in Chandra (1997). This report contains the results of a survey carried out in 1993 by the manufacturers of silicone products in the USA. The survey provided estimates of the amounts of silicone products that would be emitted to wastewater or disposed of as waste to landfill or incineration over the life cycle of the product. The survey included the possible emissions from both use and disposal of the substances, but excluded the emissions from use of the substances as site-limited intermediates for the production of other substances. The results of the survey are summarised in Table 3.3.

Table 3.3 Estimated emissions of PDMS-based products in the USA in 1993 (taken from Chandra, 1997)

Substance or application	1993 consumption (tonnes/year)[2]	Emission (tonnes/year)			Estimated emission factor (fraction of total consumption)		
		Wastewater	Landfill and/or incineration	Other and/or soil	Wastewater	Landfill and/or incineration	Other and/or soil
PDMS	138,000	13,590	24,810	13,380	0.0985	0.180	0.0970
Modified PDMS	15,300	742	3,330	294	0.0485	0.218	0.0192
PEMS[1]	18,240	2,690	7,210	340	0.148	0.395	0.0186
Resins	7,230	0	2,420	310	0	0.335	0.0429
Elastomers	89,210	0	89,130	0	0	0.999	0
Total	**267,980**	**17,022**	**126,900**	**14,324**			

Notes: [1]PEMS is polyethermethylsiloxane.
[2]The consumption figures include the amounts used as site-limited intermediates. Emissions from site-limited intermediate use are not considered in the emission figures.

For PDMS, Chandra (1997) indicated that the primary uses other than site-limited intermediate ones were in industrial applications (e.g. as antifoams, softeners, and wetting agents in textile manufacturing, transformer dielectric fluids, and heat-transfer liquids) and in consumer applications (such as personal care, and household and automotive care products, such as polishes). Chandra (1997) estimated that the main source of release to wastewater was use in personal care products and various processing aids. At the end of the product life-cycle, the estimate was that around 24,810 tonnes/year of PDMS is landfilled, incinerated, or recycled (largely as textile or paper coatings, but also in the form of electrical and mechanical fluids). In addition, around 13,380 tonnes/year was estimated to be dispersed to the environment from use in household products (such as polishes) and some industrial applications (such as lubricants and mould-release agents).

Several types of modified PDMS were considered in the Chandra (1997) survey. Uses other than site-limited intermediate ones considered in the survey are summarised as:

- methyl(phenyl)siloxanes – high-temperature oil baths, greases, diffusion pump fluids, and paint additives;
- methyl(hydrido)siloxanes – waterproofers for textiles and wall boards;
- methyl(alkyl)siloxanes – release agents for plastic and urethane parts, cutting oils, and paint additives;
- methyl(aminoalkyl)siloxanes – many applications including textiles, personal care products, household care products, automotive care products, and plastic modification.

The estimated emissions to wastewater were thought to come primarily from the use of methyl(aminoalkyl)- or methyl(alkyl)siloxanes. The main sources to landfill and incineration were thought to be from uses such as textile coatings, high-temperature oil baths, wall-board coatings, rubber compounds, and powder treatment.

The main uses other than site-limited intermediate ones of polyethermethylsiloxanes thought to lead to emissions to wastewater were from textile and personal care products. The main source to landfill and incineration was from use in urethane foam. In addition, a direct emission to soil of around 340 tonnes/year was estimated from use as an agricultural adjuvant.

The main uses of cured resins identified in the Chandra (1997) survey were as electrical varnishes, moulding compounds, components of decorative and high-temperature paints, abrasion-resistant coatings, laminating and/or adhesive materials, masonry water repellents, adhesive promoters, and components of silicone pressure-sensitive adhesives. Virtually all of the resin entering the environment was thought to be disposed of by either landfill or incineration. However, it was also considered that some resins used as components of coatings and paints, for example, may be subjected to weathering and wear over time and so may result in diffuse emission to the environment over time. It was estimated that this may amount to around 310 tonnes/year.

The main uses of RTV elastomers considered in the Chandra (1997) survey were as sealants, encapsulants, foam coatings, caulking, and mould making. Heat-cured rubber applications (included tubing, hoses) wire and cable insulation, penetration seals, laminates, release coatings, foams, and other moulded and extruded articles. Gel applications included electrical encapsulants and wound-dressing patches. It was estimated that virtually all of the elastomers would be either landfilled or incinerated at the end of their life cycle.

From the data presented in Chandra (1997) it is possible to estimate emission factors based on the total consumption in the USA in 1993 (Table 3.3). These emission factors were used to estimate the possible emissions in the EU, using the EU consumption data for PDMS-based products and the known consumption rates for 2004. The resulting emissions are summarised in

Table 3.4. The assumptions made in these estimates are:

- the overall use pattern for PDMS-based products in the USA in 1993 is also applicable to the EU in 2004;
- the emission factor for PDMS derived from Chandra (1997) is applicable to the use of PDMS fluids in the EU [the main uses of PDMS considered in the Chandra (1997) survey that lead to emissions to the environment were fluid uses];

The emission factor for elastomers from the Chandra (1997) survey is applicable to both elastomers and sealants. The Chandra (1997) survey effectively provides a mass-balance approach for the ultimate fate of the total consumption in the USA in 1993. It is assumed here that the data can be used to estimate a yearly emission from the yearly consumption figure. However, the emissions identified in the Chandra (1997) survey do not necessarily occur within the same year. For example, disposal to landfill occurs at the end of the article's lifetime, which may be many years after the article was produced. Implicit in the assumption to estimate the yearly emissions from the yearly consumption figure is that for any emission for substances with long lifetimes a 'steady-state' situation exists at some point in time assuming a constant consumption rate. For example, if a product has a ten-year lifetime and is then disposed of to landfill, there will be no disposal over the first nine years, but from the tenth year onwards the amount disposed will correspond to the amount produced in that year. A similar argument can be applied to substances and/or products that are continuously emitted during use but where the product is used over more than one year.

Table 3.4 Estimated emissions of PDMS-based products in the EU

Application	2004 EU sales (tonnes/year)	Assumed emission factor (fraction of total consumption)			Emission (tonnes/year)		
		Wastewater	Landfill and/or incineration	Other and/or soil	Wastewater	Landfill and/or incineration	Other and/or soil
Sealants	210,000	0	0.999	0		209,790	
Elastomers	139,000	0	0.999	0		138,861	
Fluids and specialities	204,000	0.0985	0.180	0.0970	20,094	36,720	19,788
Silanes[1]	60,000	N/A[1]	N/A[1]	N/A[1]	N/A[1]	N/A[1]	N/A[1]
Resins	20,000	0	0.335	0	0	6,700	0
Total	**633,000**				**20,094**	**392,071**	**19,788**

Note: [1]Silanes are non-polymeric products used mainly as intermediates in the production of other products. They are not relevant to the discussions here.

The next stage is to estimate the amount of D5 that may be emitted from the PDMS-based products emitted to the environment.

Some products have structural differences to PDMS, which means that it may not be possible to estimate the amount of D5 that could be emitted from them using the available data for PDMS. For example, the polyethermethylsiloxanes generally have a high polyether content (30–80 per cent) and so the environmental fate of these products may be different than that for PDMS (Chandra, 1997). The amounts of polyethermethylsiloxanes used in the EU are not given separately in the consumption figures (they are probably included in the fluids and specialities uses).

In particular, it can be questioned whether the degradation of resins and elastomers in the environment will be similar to that of PDMS. Both resins and elastomers are cross-linked, intractable solids. Chandra (1997) reports that silicone elastomers do not appear to be degraded in landfills, possibly as a result of their limited bioavailability in the environment. Therefore both resins and elastomers are not considered to be a source of D5 in the environment through biodegradation. The same considerations could also apply to sealants, which again have a degree of cross-linking in their cured state.

Therefore, in terms of the potential to form D5 from biodegradation, the emissions of PDMS fluids and specialities are likely to be the dominant source. As shown in

Table 3.4, it is estimated that in the EU around 20,100 tonnes/year are emitted to wastewater, 36,800 tonnes/year are disposed of via landfill and/or incineration, and 19,800 tonnes/year are estimated to be released from diffuse sources, probably mainly to soil.

To provide a rough estimate of the amount of cyclic siloxanes that could be emitted from this source, the assumptions made are:

- The amount of cyclic siloxanes and other volatile products emitted during the degradation in soil is around 0.5 per cent of the PDMS added to the soil (based on Lehmann *et al.*, 1994). This was obtained in experiments with a 200 cst viscosity fluid. It is assumed here that these data are also applicable to medium and high viscosity PDMS fluids.

- The typical wastewater treatment plant connection rate in the EU is 80 per cent (the default value from the TGD) and the majority of PDMS fluids that enter a wastewater treatment plant will be adsorbed onto the sludge and subsequently applied to agricultural land. This then amounts to ~16,080 tonnes of PDMS fluids.
- Of the amount disposed, it is assumed that 72 per cent is landfilled and 7 per cent is incinerated (with the remainder treated by other methods). This is based on the known pattern of waste treatment in England and Wales in 2004–2005 at waste-management facilities licensed or permitted by the Environment Agency.[11] Thus, the estimated amount of PDMS fluids landfilled in the EU is ~26,500 tonnes/year, with ~2600 tonnes/year incinerated.
- The amount of D5 formed during the degradation is assumed to be around 25 per cent of the total cyclic siloxanes and other volatile products. The actual identity of the volatile products formed in the Lehmann *et al.* (1994) study was not determined. This is a significant source of uncertainty in the estimates.

The amount of PDMS fluids thought to reach soil (either from diffuse emissions or application of sewage sludge) is therefore estimated as ~35,900 tonnes/year. Assuming that 0.5 per cent of this is degraded to cyclic siloxanes and other volatile products, the total amount of such products formed is estimated to be around 179,500 kg/year. Thus the amount of this that could be D5 is estimated to be around 44,875 kg/year. As this represents a volatile loss from the soil it should be considered as an emission to air.

It is estimated that around 26,500 tonnes/year of PDMS fluids could be disposed to landfills in the EU. The conditions in landfills are typically anaerobic in nature and there is little information available on the degradation of PDMS under such conditions. If it was assumed again that the yield of cyclic siloxanes and other volatile products during degradation in landfills was around 0.5 per cent, with 25 per cent of this comprising D5, then the amount of D5 emitted could be around 33,125 kg/year. However, this figure is highly speculative as the actual behaviour of PDMS under anaerobic conditions is unclear.

To determine the significance of this source in comparison to releases from direct uses of D5, these estimated emissions of 44,875–78,000 kg/year should be compared with the total estimated EU emissions of D5 to air. However, the total EU emission to air is confidential, but the estimated emission from PDMS breakdown is <0.3 per cent of this. Therefore, although there are large uncertainties in the approach used here to estimate the emissions from degradation of PDMS polymers, it not appear to be a major source of D5 in the environment when compared with the emissions from direct uses of D5, and so this source is not considered again in the assessment.

It is not currently possible to estimate the amount of D5 that may be present in the soil from the degradation of PDMS polymers. This is considered in relation to the PECs calculated for soil in Section 3.3.2.1.

It is also estimated that a substantial amount of other polymeric siloxane products (such as sealants, elastomers, and resins) may be emitted to the environment and, in particular, may be disposed of into landfill. It is assumed here that because these substances have a substantial amount of cross-linking in the polymer, they are less degradable than PDMS fluids and so their potential to emit cyclic siloxanes from degradation is much lower. However, there appears to be little actual information available as to how cyclic siloxanes form from such products under conditions found in landfills. Therefore it is difficult to evaluate fully this possible source here. This is considered in Section 3.1.73.

[11] See http://www.environment-agency.gov.uk/subjects/waste/?version=1&lang=_e.

As well as landfill, PDMS liquids, and other polymeric siloxane products will also be disposed of by incineration. It is not possible to estimate the amounts of cyclic siloxane products formed during the high temperature incineration process. However, it is considered that the conditions will effectively destroy any cyclic products formed, and so the emissions of D5 from incineration are expected to be small compared with other sources of D5 emission. This is considered in Section 3.1.7.3).

3.1.7.3 Other sources

Some data reported in the literature suggest sources of emission of D5 other than those considered elsewhere in this report. These data are summarised here. However, information is lacking on the quality-control methods used in the analyses. While this in itself does not mean the data are unreliable, there are potential problems of contamination in the analysis of D5 (see Section 3.30 for more details). It is therefore possible that some of the reported occurrences of D5 from these sources may result from analytical artefacts and so do not themselves represent significant sources of emission of D5 to the environment.

D5 was detected at a concentration of 0.06 μg/m^3 in the flue gas from a municipal waste incineration plant (Jay and Stieglitz, 1995).

The emissions from waste-incineration processes are expected to be low as small-scale pool-burning tests indicate that cyclic siloxanes with boiling points of around 250°C and lower (i.e. D4, D5, and D6) burn rapidly and completely (indeed, more rapidly than hydrocarbons of similar volatility) to form CO_2, water, and amorphous silica without ash formation [Lipowitz and Ziemelis (1976), Stevens (1996)]. Siloxane products with higher boiling points (such as PDMS fluids and polymers) burn less readily and must firstly undergo thermal rearrangement to form more volatile cyclic siloxanes (this process is slow at temperatures <350°C), which are then readily combusted. Therefore it is concluded that the emissions of D5 from waste incineration are likely to be low and so this potential source is not considered again here. Although D5 has been reported in the flue gas from a municipal waste incinerator (see above), the concentration measured was relatively low and it is also possible that, owing to the difficulties in analysing low concentrations of D5, this could be an analytical artefact rather than an actual emission in the flue gas.

Salthammer (1997) investigated, using 1 m^3 glass chambers, the emissions of VOCs from 44 samples of wood coated with various furniture coatings. The sample loading rate used was 1.0 m^2/m^3 and the experiments were carried out at 23°C, at a relative humidity of 45 per cent and using an air exchange rate of 1/hour. D5 was found in the chamber air from one of the samples, but no other details are given on the emission rates or concentrations. As there is currently no reported use of D5 in coatings it is thought that these data either reflect a historic use of D5, represent the emissions from unreacted D5 in PDMS polymers used in coatings (and so the emissions are already accounted for in Section 3.1.7.1), or the D5 found was an analytical artefact (see Section 3.3).

In chamber experiments several oligomeric siloxanes (including D5) were detected in the volatiles emitted from various samples of flexible foam mattresses (Hillier *et al*., 2003). However, the same siloxanes were also emitted from various raw materials used to make the foams (e.g. polyols). This was thought to be an analytical artefact from the breakdown of the PDMS layer on the needles used for sampling and sample injection. The paper indicates that, as these needles were not used in the experiments with the foam samples themselves, it was unlikely that this source of contamination occurred in those experiments. However, given the findings with the polyol experiments, the results from the flexible foam experiments must be considered uncertain. Therefore this is not considered to be a significant source of emission of D5 to the environment.

A number of occurrences of D5 emitted from landfill sites are reported. For example, IUCLID (2005) indicates that D5 was detected in biogas from landfill sites in the USA [concentration 1–5 mg/m^3 biogas, total for D5 and D4 (Niemann, 1997)] and Germany [concentration <12 mg/m^3 biogas, with the majority <5 mg/m^3 biogas (Hagmann *et al*., 1999) and concentration 0.4-1.1 mg/m^3 (Schweigkofler and Niessner, 1999)]. In addition, Schwarzbauer *et al.* (2002) found D5 in landfill leachate at a sanitary landfill in Germany. The concentration was not given, but the detection limit of the analytical method used was around 50 ng/l. The origin of D5 in the landfills is not totally clear, but could result from a number of sources, including disposal of products that contain D5 (such as personal care products, etc.) or disposal of products that contain PDMS polymers with subsequent emission of unreacted D5 (see Section 3.1.7.1.) or subsequent breakdown of the PDMS polymer to form D5 (see Section 3.1.7.1). It is not possible to quantify the actual amounts of D5 that may be emitted to air and to leachate from landfill sites in the UK and in the EU; however, these emissions are likely to be at least partly covered by the worst-case approach used to estimate the regional and continental emissions elsewhere in this report.

A recent report by Schripp *et al*. (2007) indicates that D5 may be emitted from polyurethane foams. The study used a microchamber to evaluate the VOCs emitted from foam samples at a temperature of 65°C. The samples used were taken from each side of a cube of polyurethane foam using a stamping tool (diameter 5 cm) to a depth of 5 cm. Two 1 cm slices were then cut from either end of the core for use in the chamber. The substances emitted from the samples were analysed using a gas chromatography–mass spectrometry (GC–MS) method and D5 was identified as one of the predominant substances emitted from the samples. More tests using samples of a second foam carried out at temperatures between 20 and 100°C again showed that D5 was emitted from the foam, but the emission rate increased only slowly with increasing temperature. Schripp *et al*. (2007) indicate that the D5 in these samples may have resulted from siloxanes used to control the foaming process during manufacture of the foam. No use of D5 in polyurethane foams is reported in the CES survey of uses (see Section 2.3) and so it is not considered specifically in this risk assessment. It is known, for example, that certain PDMS products may be used in polyurethane foam (e.g. Zhang *et al*., 1999) and it is possible that the D5 in these samples results from D5 impurities in the PDMS used. If so, then the emissions from this use would already be accounted for at a regional and continental scale (see Section 3.1.7.1).

Cao *et al*. (2007a, 2007b) report that D5 was present in essential oil extracted from Marchantiaceae plants (*Marchantia convoluta*) from China. Few details are given on the quality-control measures used in the analysis and so it is possible that these findings represent analytical artefacts rather than a true occurrence of D5 in the samples.

Rosati *et al.* (2007) found that D5 was released during the cooking of some types of microwave popcorn. The quality-control procedures used in this study included the analysis of blanks daily, and it appears that D5 was not detectable in these blanks. The source of D5 in these experiments is unclear.

Jann and Wilke (2006) report that D5 was emitted from some hardcopy devices such as printers, copiers, and multifunctional devices. It is not clear if the emissions are related to use of D5 itself or to a D5 impurity in PDMS-based polymers used within the device. In addition, few details are given on the quality-control measures used in the analysis.

Traces of D5 were tentatively detected in the volatile and semi-volatile gases formed in pyrolysis and combustion studies using waste lubricant oil from a diesel vehicle. The experiments were carried out in a tubular reactor at 500 and 850°C (Fuentes *et al*., 2007). D5 was tentatively detected only in the pyrolysis experiment at 500°C. No D5 was detected in either the pyrolysis study at 850°C or the combustion studies at 500 and 850°C.

3.1.8 Summary of preliminary worst-case emission estimates

The preliminary worst-case emission estimates for D5 are summarised in Table 3.5. The continental emissions represent the total EU emissions minus the regional emissions. For the environmental modelling at the regional and continental level an 80 per cent connection rate to the wastewater treatment plant is assumed.

Table 3.5 Summary of emission estimates for D5

Scenario	Local emission		Regional emission (kg/year)	Continental emission (kg/year)
	Amount (kg/day)	Number of days		
Production and on-site use as an intermediate	Confidential to air 0.010 to surface water	300	Confidential to air 3.1 to surface water	Not quantified
Chemical intermediate – off-site – wet process (non-UK)	0.16 to air 1.7×10^{-5} to wastewater		Confidential to air Confidential to wastewater	Confidential to air Confidential to wastewater
Chemical intermediate – off-site – dry process (non-UK)	5 to air 0 to wastewater	137	Confidential to air 0 to wastewater	Confidential to air 0 to wastewater
Personal care products – formulation – UK sites	4×10^{-4} to ca. 1 to air 7.3×10^{-4} to ca. 5.1 to wastewater	300	315 to air 1557 to wastewater	2834 to air 14,013 to wastewater
Personal care products formulation – non-UK sites	See Appendix B			
Personal care products – formulation – generic site (non-UK)	0.17 to air 0.77 to wastewater	300		
Personal care products – use	0.12 to wastewater	365	756,000 to air 84,000 to wastewater	14,814,000 to air 1,646,000 to wastewater
Household products – formulation	Confidential to air Confidential to wastewater		Confidential to air Confidential to wastewater	Confidential to air Confidential to wastewater
Household products – use	ca. 6×10^{-3} to wastewater		Confidential to air Confidential to wastewater	Confidential to air Confidential to wastewater
Industrial/institutional cleaning – formulation	Not relevant		Not relevant	Not relevant
Industrial/institutional cleaning – use	<0.33l to air ca. 8.5×10^{-8} to wastewater		Confidential to air Confidential to wastewater	Confidential to air Confidential to wastewater

Residual monomer in PDMS		87,390 to air	786,510 to air
Breakdown of PDMS		Not quantified	Not quantified
Total[1]		**Confidential**	**Confidential**

Note: [1]The totals take into account the 80 per cent connection rate to the wastewater treatment plant.

A further emission of 44,875–78,000 kg/year of D5 to air is estimated from the possible degradation of PDMS polymers in soil and landfills in the EU. However, the estimation is subject to a large uncertainty and so is not taken into account in the total emissions estimated in Table 3.5. This is not thought to impact significantly on the resulting PECs.

3.2 Environmental fate and distribution

3.2.1 Atmospheric degradation

3.2.1.1 Photo-oxidation

Atkinson (1991) determined the rate constant for reaction of D5 with atmospheric hydroxyl radicals (k_{OH}) to be 1.55×10^{-12} cm^3/mol/s at 24°C using a relative-rate method. Atkinson (1991) also determined experimental values for the rate constants for reaction with atmospheric ozone and NO_3 as $<3 \times 10^{-20}$ cm^3/molecule/s and $<3 \times 10^{-16}$ cm^3/molecule/s, respectively. The values again refer to a temperature of 24°C.

The rate constant for D5 reaction with atmospheric hydroxyl radicals can be estimated as 1.50×10^{-12} cm^3/molecule/s using the AOP(v1.91) program that is part of the USEPA EPI (v3.12) estimation software.

Chandramouli and Kamens (2001) studied the degradation of D5 in an outdoor smog chamber that contained fine road-dust particles. The chamber used had a volume of 190 m^3 and was located in Pittsboro, USA. The road-dust sample was from Arizona and particle size distribution measurements showed that 95 per cent of the particles had diameters <2.6 µm. The experiments were carried out in either February 1997 or October 1998. In the experiments 25 µl of D5 and a linear siloxane oligomer (decamethyltetrasiloxane) were injected into the chamber (to give an initial concentration of 0.008 ppm in the chamber). To generate hydroxyl radicals in the chamber, the atmosphere also contained 0.35 ppm of NO and NO_2 and 2 ppm of propylene. For the experiment carried out in February the chamber had a temperature of 6–15°C, a relative humidity of 58–70 per cent, and a total suspended particulate concentration of 660 µg/m^3. Similarly, for the October experiment the chamber had a temperature of 24–27°C, a relative humidity of 70–98 per cent, and a total suspended particulate concentration of 894 µg/m^3. At various times during the experiment the gas and particulate phases were analysed for D5 and degradation products.

Loss by reaction with hydroxyl radicals was the only significant removal mechanism determined in this study. No measurable amount of D5 was found in the particulate phase. The main degradation product identified from the reaction of D5 under these conditions was the monohydroxy derivative of D5. Previous studies by Latimer *et al*. (1998) showed that this product adsorbs onto particulates in the atmosphere. The work by Chandramouli and Kamens (2001) confirmed that the degradation product was adsorbed to the particulate phase in this study (>99.5 per cent of that formed was thought to be associated with the particulate phase), and also showed that once adsorbed D5 appeared to be relatively stable.

Latimer *et al.* (1998) investigated the partitioning behaviour of D5 onto atmospheric particulates in order to determine whether such partitioning was a significant factor in the overall atmospheric fate (including degradation and potential for deposition) of D5. The study was carried out using several different aerosols [carbonaceous aerosols formed from wood, diesel, or coal combustion and an inorganic aerosol consisting of crustal dust (with a metals content of 45.9 per cent Si, 17.3 per cent Ca, 14.6 per cent Mg, 12.4 per cent Al, 5.9 per cent Fe, and 3.8 per cent K; the dust aerosol used had a particle size $\leq$2.5 µm)]. The aerosols used were chosen to be representative of the aerosol types that are significant contributors to both urban and rural atmospheric aerosols. The experiments were carried out using smog chambers at a range of temperatures, aerosol concentrations, and relative humidities. The concentration of D5 initially added to the chambers was in the range 50–500 µg/m^3. The resulting concentrations determined in the vapour and particulate phase after equilibration are summarised in Table 3.6. These results show that, under all conditions studied, the vast majority of the D5 was associated with the gaseous phase, even at low temperatures. This indicates that the atmospheric fate (and transport) of D5 is governed mainly by its gas-phase reactions.

Table 3.6 Partitioning of D5 to atmospheric particulates

Aerosol concentration (total suspended particulates)	**Temperature (°C)**	**Relative humidity (%)**	**Particulate phase concentration (ng/m^3)/gas phase concentration (ng/m^3)**			
			Coal aerosol	**Diesel aerosol**	**Wood aerosol**	**Crustal dust aerosol**
10 µg/m^3	0	50	4.6×10^{-5}	7.4×10^{-5}	2.7×10^{-6}	1.2×10^{-3}
		90	3.3×10^{-5}	7.4×10^{-5}	8.0×10^{-6}	5.1×10^{-4}
	25	50	6.9×10^{-6}	6.6×10^{-6}	1.3×10^{-7}	9.1×10^{-7}
		90	4.9×10^{-6}	6.6×10^{-6}	3.7×10^{-7}	3.8×10^{-7}
50 µg/m^3	0	50	2.3×10^{-4}	3.7×10^{-4}	1.4×10^{-5}	6.1×10^{-3}
		90	1.6×10^{-4}	3.7×10^{-4}	4.0×10^{-5}	2.5×10^{-3}
	25	50	3.5×10^{-5}	3.3×10^{-5}	6.3×10^{-6}	4.6×10^{-6}
		90	2.5×10^{-5}	3.3×10^{-5}	1.9×10^{-6}	1.9×10^{-6}
100 µg/m^3	0	50	4.6×10^{-4}	7.4×10^{-4}	2.7×10^{-5}	0.012
		90	3.3×10^{-4}	7.4×10^{-4}	8.0×10^{-5}	5.1×10^{-3}
	25	50	6.9×10^{-5}	6.6×10^{-5}	1.3×10^{-6}	9.1×10^{-6}
		90	4.9×10^{-5}	6.6×10^{-5}	3.7×10^{-6}	3.8×10^{-6}
500 µg/m^3	0	50	2.3×10^{-3}	3.7×10^{-3}	1.4×10^{-4}	0.061
		90	1.6×10^{-3}	3.7×10^{-3}	4.0×10^{-4}	2.5×10^{-3}
	25	50	3.5×10^{-4}	3.3×10^{-4}	6.3×10^{-6}	4.6×10^{-5}
		90	2.5×10^{-4}	3.3×10^{-4}	1.9×10^{-5}	1.9×10^{-5}

An assessment of the atmospheric fate of VMSs and their degradation products was made by Whelan *et al.* (2004). The assessment used a simple equilibrium partitioning model to

investigate the relative rates of removal of two representative VMSs (the linear decamethyltetrasiloxane and D4) and their siloxanol degradation products by reaction and atmospheric deposition. Although the calculations were carried out for only one cyclic VMS, the findings of the paper are equally applicable to other cyclic VMSs such as D5. The modelling is based on the work of Atkinson (1991) and Sommerlade *et al.* (1993), which demonstrate that siloxanes break down in the atmosphere to form hydroxyl-substituted silanols by reaction with atmospheric hydroxyl radicals. As substitution proceeds the silanols become increasingly water-soluble and less volatile, and so tend to be washed out of the atmosphere by wet deposition. Silanols are also assumed to be subject to hydrolysis reactions when dissolved in liquid water droplets. Removal by dry deposition is also accounted for in the approach, but scavenging of particulates from the air by wet deposition is not. The findings from the model indicate that the parent siloxanes and the monohydroxy degradation products occurred mainly in the vapour phase, with relatively small amounts associated with the water phase and particulate phase (although the small size of the water- and particulate-phase compartments in the atmosphere means that the concentrations in these phases can approach or exceed those in the vapour phase). The degradation products as the hydroxyl substitution proceeded are predicted to be associated mainly with the dissolved phase and the particulate phase. However, the decreasing concentration of precursor molecules (resulting from the removal processes considered) means that the maximum dissolved- and particulate-phase concentrations occur for degradation products with two hydroxyl substituents. The concentrations of degradation products with higher levels of hydroxyl substitution are predicted to decrease markedly with increasing substitution. The siloxane diols present in precipitation are also predicted to undergo further reaction via hydrolysis, and so result in a mixture of siloxanes products (depending on the atmospheric residence time and the pH). Overall, it is concluded that >99 per cent of the VMSs are removed from the atmosphere as silanols in wet deposition and <1 per cent as silanols in dry deposition.

Assuming an average atmospheric hydroxyl radical concentration of 5×10^5 molecule/cm^3 and a rate constant of 1.55×10^{-12} cm^3/molecule/s, the atmospheric half-life for D5 can be estimated as 10.4 days. Degradation by reaction with other atmospheric photo-oxidants is likely to be negligible compared with that by the hydroxyl radical reaction. The products from the reaction are expected to be silanols, which are removed from the atmosphere by wet deposition (either adsorbed onto particulates or dissolved). Buch *et al.* (1984) demonstrated that dimethylsilanediol and other water-soluble dimethylsiloxanols can be degraded further by aqueous photolytic oxidative demethylation reactions. The final products of the degradation of dimethylsiloxanols are expected to be silicic acid and/or silica and CO_2 (Chandra, 1997; Buch *et al.*, 1984).

It is understood that further work to investigate the atmospheric degradation of D5 by other degradation mechanisms is currently underway. Preliminary results of some of these studies are briefly reported in a presentation by Plotzke (2007). The studies are to investigate the degradation of D5 catalysed by aerosols in the presence of ozone, hydroxyl radicals, and UV among other mechanisms. The preliminary results so far indicate that a rapid and significant removal of D5 from air occurs in the presence of mineral aerosols (e.g. kaolinite and haematite aerosols) and that ozone can increase the rate of removal. However, few details of these studies are currently available.

3.2.1.2 Photolysis

No information is available on the direct photolysis of D5 in the atmosphere.

3.2.2 Aquatic degradation

3.2.2.1 Hydrolysis

A preliminary hydrolysis study with D5 was carried out recently (Dow Corning, 2005a). The test method was based on the OECD 111 test guideline, but was modified to take account of the volatility of D5. The substance tested was ^{14}C-labelled D5 (the purity is not stated). Stock solutions of the test substance were prepared in acetonitrile and 50 ml of the appropriate aqueous buffer were added to aliquots (500 µl, to give a nominal D5 concentration in the buffer of 5.8 µg/l) of this stock solution, and the spiked buffer immediately transferred to between nine and 11 tubes. The tubes used had an internal diameter of 4.2 mm, were 200 mm in length, and contained around 2.2 ml of test solution. They were heat sealed (the headspace of the sealed tubes was estimated to be around 6 per cent of the total volume) and then incubated in the dark at 25°C prior to analysis. Experiments were carried out at pHs of 3.97 (formic acid–tetramethylammonium hydroxide buffer; two experiments were carried out at this pH), 8.4 [hydrochloric acid–tris(hydroxymethyl)aminomethane buffer], and 9.0 and 9.7 (both using boric acid–tetramethylammonium hydroxide buffer). The buffer solutions used had a concentration of 1–2 mM (no attempt was made to maintain a constant ionic strength between the various experiments).

At various time points during the experiments single tubes were opened and analysed for D5. The entire contents of the tube (approximately 2.2 ml) were transferred to a gas-tight syringe and 1 g of this solution weighed into a vial that contained scintillation cocktail (for analysis by liquid-scintillation counting) and the remaining 1 ml was injected into a HPLC system. The emptied tube was rinsed twice with tetrahydrofuran and the rinses were also analysed by liquid-scintillation counting (to determine the overall mass balance of the experiment). The mass balance for the two experiments at pH 3.97 and the experiment at pH 9.7 were generally in the range 80-90 per cent. For the other pHs the recovery was slightly lower, but generally >70 per cent. In all cases the difference between the maximum and minimum recovery within any one kinetic run was within 7–11 per cent. The solvent rinses consistently contained between 2 and 4 per cent of the total radioactivity, which indicates that little or no physical adsorption of the reactant or degradation products occurred. These results suggest that any loss of D5 from the system occurred during the filling and flame sealing of the tubes.

The hydrolysis half-lives obtained at 25°C were 14.1 and 14.2 hours at pH 3.97 (two experiments), 125 hours at pH 8.38, 28.9 hours at pH 9.01, and 5.59 hours at pH 9.68. Using these data the second-order rate constant for the acid-catalysed hydrolysis (k_H) and hydroxyl-catalysed hydrolysis (k_{OH}) were determined to be 458 l/mol/hour and 2630 l/mol/hour, respectively (this analysis assumes that the rate of the uncatalysed hydrolysis reaction is negligible compared with the acid- and base-catalysed reactions).

Using these kinetic constants it is possible to estimate the hydrolysis half-life at any pH. Dow Corning (2005a) estimates the hydrolysis half-life at 25°C to be 17 days at pH 7.8 and 95 days at pH 7.

The products from the hydrolysis reaction were thought to be dimethylsiloxane-α,ω-diols [i.e. $HO(Me_2SiO)_nH$, with n = 1 to 5), with the ultimate product being dimethylsilanediol.

A second, definitive hydrolysis study has since been carried out to confirm these results (Dow Corning, 2006a). This study investigated the degradation kinetics at pH 4, 7, and 9 at temperatures of 10°C, 25°C, and 35°C. Additional pH evaluations (pH 5.5 and 8 at 25°C) were also included to allow the comparison of a kinetic approach to determine the rate with the actual data. The method used was based on the OECD 111 test guideline, and flame-sealed tubes (the tubes again had an internal diameter of 4.2 mm, a length of 200 mm, and contained around 2.2 ml of test solution) were used to minimise loss through volatilisation. The substance tested was ^{14}C-labelled and had a purity of 98.9 per cent. The tests were

carried out in 0.002 M aqueous buffer solutions. The buffer systems used were formic or acetic acid–tetramethylammonium hydroxide (pH 4 and 5.5, respectively), hydrochloric acid–imidazole or tris(hydroxymethyl)aminomethane (pH 7 and pH 8, respectively) and boric acid–tetramethylammonium hydroxide (pH 9). The test substance was added to the buffer as a solution in acetonitrile. The target nominal concentration of D5 was 6 µg/l and the amount of acetonitrile present in the final test solution was 1 per cent volume/volume (the limit suggested in the test guideline). The test vials were flame-sealed immediately after addition of ^{14}C-labelled D5.

At various times during the test, the contents of the vials were analysed for D5 and degradation products. The total recovery of radioactivity in the experiment ranged between 76 and 90 per cent (based on the initial amount of radiolabel added to the vial) for the experiments at pH 4 and pH 9, but was lower in some cases (around 65 per cent) in the experiments at pH 8 and 5.5. In all cases, the amount of radioactivity adsorbed onto the glass walls was negligibly small compared with that in solution. Although the recovery was below that suggested in the test guideline (the test guideline suggests a recovery of 90–110 per cent is preferable), the actual variation in the recovery within a series of experiments was generally low (i.e. the difference between the minimum and maximum recovery was <16 per cent, and the standard deviation for within-experiment recovery typically ranged from 2 to 6 per cent). Therefore it was concluded that reliable kinetics could be derived from the data (i.e. the concentration data for D5 were normalised to the total amount of radiolabel measured in the solution).

In contrast to the experiments carried out under acid or alkaline conditions, the mean recoveries in the experiments at pH 7 were generally in the range 33–56 per cent and much larger variability was seen between the maximum and minimum recovery within any one given experiment. In particular, although the initial recovery (within one hour of the start of the experiment) was generally in line with the experiments at other pHs, a systematic decrease in the recovery with time was evident in the pH 7 experiments.

Overall, it was hypothesised that at all pHs, a systematic losses of ^{14}C-label occurred during the solution preparation, particularly in filling and sealing of the vials, to the (small) headspace present in the sealed vials, and during sampling. This then explains the, in some cases, somewhat low, but relatively consistent recoveries found in the experiments at pH 4, 5.5, 8, and 9, and the initial recoveries found at pH 7. It was also suggested that the decreasing recovery with time in the experiments at pH 7 were probably the result of a slow diffusion of D5 from aqueous solution to the vapour phase. The impact of this effect on the overall kinetics would depend on the relative rate of hydrolysis of D5 to the rate of exchange across the air–water interface. This was most likely to be important at pH 7 when the hydrolysis rate is slow, but was not significant in the experiments at pH 4, 5.5, 8, and 9 (i.e. the data at pH 4, 5.5, 8, and 9 were consistent with a simple first-order degradation process). Therefore to analyse the data from the pH 7 experiments, a linear two-box model was used that accounted for the slow diffusive exchange of the volatile D5 across the air–water interface, as well as the hydrolysis in aqueous solution. This model fits the experimental data reasonably well, and is used to derive estimates for the first-order rate constant for hydrolysis at pH 7.

The decreasing recovery with time in the experiments at pH 7 could also be explained by a leak from the headspace of the vials. Using the dimensionless Henry's law constant (K_{aw}) of D5 of 13 (see Section 1.3.9.3) and assuming that the headspace present was around 6 per cent of the total volume of the tube [based on the Dow Corning (2005a) study that used a similar method to that in Dow Corning (2006a)] it can be estimated that, if equilibrium was reached between the water and air phases in the experiment, around 45 per cent of the D5 would be present in the headspace. Therefore, a small leak from the headspace could also have caused the decreasing recovery with time.

Given the relatively high dimensionless Henry's law constant for D5, it might be expected that it would transfer reasonably rapidly from the water phase to the air phase, which would not tend to favour the slow diffusion explanation given in Dow Corning (2006a). However, the glass bottles used had a small liquid surface area to volume ratio of 0.06/cm (internal surface area of 0.14 cm^2 to a liquid volume of 2.2 cm^3) and the tubes were not shaken or disturbed during the incubation. Thus it cannot be ruled out that relatively slow diffusion from the liquid phase to the headspace caused the observed kinetics.

The alternative explanation (reasonably rapid establishment of an equilibrium concentration of D5 in the headspace with a slow leak of the headspace from the vial) implies a loss of total radioactivity from the system with time. This could be distinguished from the above possibility by mass balance if the headspace was sampled as well as the water phase. The sampling method used involved opening the tube after scoring with a glass cutter above the solution level and then transferring the entire contents (around 2.2 ml of liquid) of the tube to a 2.5 ml gas-tight syringe, and so it is likely that only a very small fraction of the headspace was sampled. Therefore it is not possible to distinguish unambiguously between the two possible explanations in the study.

The rate of hydrolysis was found to be dependent upon both the pH and temperature. Based on the results at pH 4 (at which acid-catalysed hydrolysis predominates) and pH 9 (at which base-catalysed hydrolysis predominates), rate constants were determined for the:

- hydronium ion (acid) catalysed reaction, k_{H3O}:
  - 210 l/mol/hour at 10°C
  - 742 l/mol/hour at 25°C
  - 1600 l/mol/hour at 35°C
- hydroxide ion (base) catalysed reaction, k_{OH}:
  - 484 l/mol/hour at 10°C
  - 3200 l/mol/hour at 25°C
  - 10,700 l/mol/hour at 35°C

The temperature dependence of these reaction-rate constants was investigated using an Arrhenius plot. The activation energies derived from this plot were determined as 59.4 kJ/mol for the acid-catalysed reaction and 87.2 kJ/mol for the base-catalysed reaction. The Arrhenius constant (A; or pre-exponential factor) was determined as 1.94×10^9/h for the acid-catalysed reaction and 6.41×10^{13}/h for the base-catalysed reaction.

The reproducibility of kinetic data was tested by conducting four experiments at pH 9 and 25°C. The four half-lives obtained were in the range 19–32 hours, which suggests relatively poor reproducibility. It was thought that this may be associated with the age of the spiking solution used in some of these replicates. When freshly prepared spiking solutions were used, more consistent results were to be obtained. No explanation for this effect could be found as there was no evidence of a chemical change in the D5 in the aged spiking solution compared with the freshly prepared solution.

The intermediate products of the hydrolysis reaction were dimethylsiloxane-α,ω-diol oligomers [$HO(Me_2SiO)_nH$ (n = 2–5), with the final product of hydrolysis being monomeric dimethylsilanediol [$Me_2Si(OH)_2$].

The general kinetic equation for the overall rate constant for hydrolysis of D5 was considered in Dow Corning (2006a) to.

$$k_{obs} = k_O + k_{H3O}[H_3O]^+ + k_{OH}[OH^-] + k_a[\text{acid}] + k_b[\text{base}]$$

where

- k_{obs} is the observed or actual first-order rate constant for hydrolysis at any given pH (per hour);
- k_O is the first-order rate constant for the uncatalysed hydrolysis reaction (per hour);
- k_{H30} is the rate constant for the hydronium ion-catalysed reaction (l/mol/hour);
- k_{OH} is the rate constant for the hydroxide ion-catalysed reaction (l/mol/hour);
- k_a is the rate constant for general acid-catalysed reaction (l/mol/hour);
- k_b is the rate constant for general base-catalysed reaction (l/mol/hour).

It was assumed that at pH 4 and pH 9 the hydronium ion-catalysed and hydroxide ion-catalysed reactions, respectively, dominated and so the values of k_{H30} and k_{OH} could be derived. In this analysis it was assumed that the contribution of the uncatalysed reaction (and general acid- and base-catalysed reactions) to the overall rate of hydrolysis is low (this was confirmed by the experiments at pH 7; see below).

Using the above kinetic data and ignoring any possible contribution from the uncatalysed hydrolysis (and general acid- and/or base-catalysed hydrolysis), half-lives can be estimated at 9°C and 12°C (the two temperatures most relevant to the TGD methodology) and 25°C (Table 3.7).

Table 3.7 Variation of half-life of for hydrolysis of D5 with temperature and pH

Temperature (°C)	pH	Half-life (days)
0	5	15
	6	147
	7	449
	8	64
	9	6
12	5	12
	6	112
	7	315
	8	43
	9	4
25	5	4
	5.5	12
	6	37
	7	71
	8	9
	9	1

For comparison with these estimates, the hydrolysis half-lives determined in the Dow Corning (2006a) study at pH 5.5 and pH 8 at 25°C were 14.6 days and 8.9 days. As can be seen, the estimates in Table 3.7 are in excellent agreement with the available experimental data at these two pHs.

As explained above, the experimental data at pH 7 could not be explained by a simple first-order hydrolysis reaction, and so the data were fitted to a two-box model. The first-order rate constants for the hydrolysis reaction obtained with this model are 5.30×10^{-5} per hour at 10°C, 4.36×10^{-4} per hour at 25°C, and 1.38×10^{-3} per hour at 35°C. These rate constants are equivalent to hydrolysis half-lives of 555 hours at 10°C, 66 hours at 25°C, and 21 hours at 35°C. As can be seen, given the uncertainties in the methods used to measure these data, the estimates summarised above at 25°C and 9°C appear to be in generally good agreement with the available experimental data at pH 7.

Therefore, it can be concluded that the kinetics of hydrolysis appear to be adequately described in terms of an acid (hydronium ion) catalysed component and a base (hydroxonium ion) catalysed component. The contribution to the total rate of reaction from the uncatalysed component appears to be negligibly small. The estimated half-lives obtained using the values of k_{H30} and k_{OH} (and the known variation with temperature of these rate constants) outlined above are therefore considered reliable enough to use in the risk assessment.

For a related substance (D4) the kinetics of hydrolysis indicate a degree of reversibility in the reaction towards the end of the decay curve, although it is not clear whether this is caused by reversibility or by other factors such as D4 in the headspace (see Environment Agency, 2008). There is no indication from the available data for D5 that such reversibility also occurs in the latter stages of the D5 hydrolysis. The possible reversibility for D4 was thought to result from the initial step of the reaction (the formation of linear octamethyltetrasiloxane-α,ω-diol), which could reform D4 by cyclisation. For D5 the initial step of the reaction would likely form decamethyltetrasiloxane-α,ω-diol. If it is assumed that the reaction is reversible, it can be postulated that the reformation rate of the linear α,ω-diols to form the respective cyclised products will be dependent on molecular properties (e.g. chain flexibility, distance between recombination sites, etc.) and so would most likely be less favourable for D5 than for D4 (as the intermediate from D5 has a longer carbon chain than that from D4). Therefore, although it is possible that the hydrolysis reaction of D5 could also have a degree of reversibility in the first step (as has been suggested for D4), this is probably not significant in terms of the actual hydrolysis of D5 in the environment and so is not considered again here.

3.2.1.2 Photolysis

No information is available on the direct photolysis of D5 in water.

3.2.1.3 Biodegradation

The details of two unpublished biodegradation studies with D5 are given in IUCLID (2005).

The first study was an OECD 310 ready biodegradability – CO_2 in sealed vessels test. The activated sludge and sewage used as the inoculum in this test was collected from a wastewater treatment plant that treated primarily domestic waste. The concentration of organic carbon (C) of D5 used in the test was 20 mg C/l and the inoculum concentration was 10 mg solids/l. The test was carried out at a temperature of 20.0–23.3°C. The vessels used in the test were 160 ml serum bottles that contained 107 ml of mineral medium. At various times during the test, samples of headspace gas were analysed for total inorganic carbon

(mainly CO_2; as only the headspace was analysed a correction was applied to take account of CO_2 that would be present in the solution phase). Little or no degradation of D5 was seen over 28 days under these conditions (<1.1 per cent of the theoretical CO_2 formation was seen).

Sodium benzoate was used as a positive control substance in the test. This showed 96.8 per cent degradation at 14 days and 100 per cent degradation at 28 days. A toxicity control (which contained both D5 and sodium benzoate) showed around 57 per cent degradation after 28 days.

Although this test was carried out using a sealed system, a headspace was present in the test vessels (as the total volume of the vessels was 160 ml, the headspace volume would be around 53 ml for a liquid volume of 107 ml). Thus, even though D5 would not be lost from the system by volatilisation, a significant amount of D5 would be in the headspace and so not available for biodegradation. The dimensionless Henry's law constant effectively represents the equilibrium partition coefficient between water and air. Taking the dimensionless Henry's law constant to be around 13 to 1350 (see Section 1.3.9.3), at equilibrium a concentration in air of around 13 to 1350 times that in water is expected. As the volume of water:air in this experiment was approximately 2:1, the mass of D5 in air at equilibrium is expected to be around 7 to 700 times that in water (i.e. the majority of D5 would be n the headspace).

The second test reported in IUCLID (2005) was a Modified Sturm (CO_2 evolution) Test. The inoculum used was derived from domestic sewage and D5 was tested at a concentration of 46.6 mg/l (equivalent to a 15 mg C/l) and the test was carried out at 20.3–22°C. Sodium benzoate was used as a positive control substance. Again, little or no biodegradation of D5 was seen over 28 days in this system (0 per cent after 14 days and –2 per cent after 28 days). Around 75 per cent degradation of the positive control substance was seen after 14 days (reaching 79 per cent after 29 days). No details are given of any measures to prevent loss from volatilisation in this test (the standard OECD 301B CO_2 evolution test is not ideal for volatile substances).

Another study recently investigated the biodegradation of D5 by activated sludge microorganisms (Itrich and Federle, 2007). The D5 used in the study was ^{14}C-labelled on the methyl groups (no information was given on the purity of the D5 used). The activated sludge sample used in the experiment was taken from a waste-water treatment plant in Ohio, USA. The plant received primarily domestic wastewater and the solids content of the activated sludge samples was 2228 mg/l.

The test method used had previously been optimised to account for the volatile and adsorptive behaviour of D5. Briefly, a stock solution of the test substance was prepared in tetrahydrofuran. This stock solution was then mixed with a concentrated solution of surfactant (a C_{45} alkyl sulfate) prior to dispersion in water. This dosing system was chosen to simulate domestic 'grey water'.

The test vessels consisted of sealed 4 l flasks that contained 2 l of activated sludge and 11 ml of the D5 dosing solution. The final concentrations of D5 and the surfactant in the test vessel were 7.2 µg/l and 3 mg/l, respectively, and the pH of the solution was 7.1 [a small amount of tetrahydrofuran was also present in the test system (~0.016 ml/l)]. An abiotic control was prepared in the same manner, except that the activated sludge was sterilised using mercuric chloride followed by autoclaving for 90 minutes. The pH of the abiotic control was adjusted to a pH of 7.1 to match that of the biotic vessel. The test vessels were incubated at 22°C for 28 days. During the test the headspace was continuously purged with CO_2- free air, and the sludge was continuously mixed using a stirrer. Traps were used to collect volatiles continuously and CO_2 evolved during the test. The CO_2 traps were analysed periodically over the entire period of the test and the volatile traps were analysed on day 21. In addition, samples of the sludge solids were collected at intervals and analysed for both ^{14}C and the parent compound [both the extractable (using tetrahydrofuran) and non-extractable

substance were determined]. The distribution of ^{14}C-label among the media sampled in the biotic experiment is summarised in

Figure 3.1.

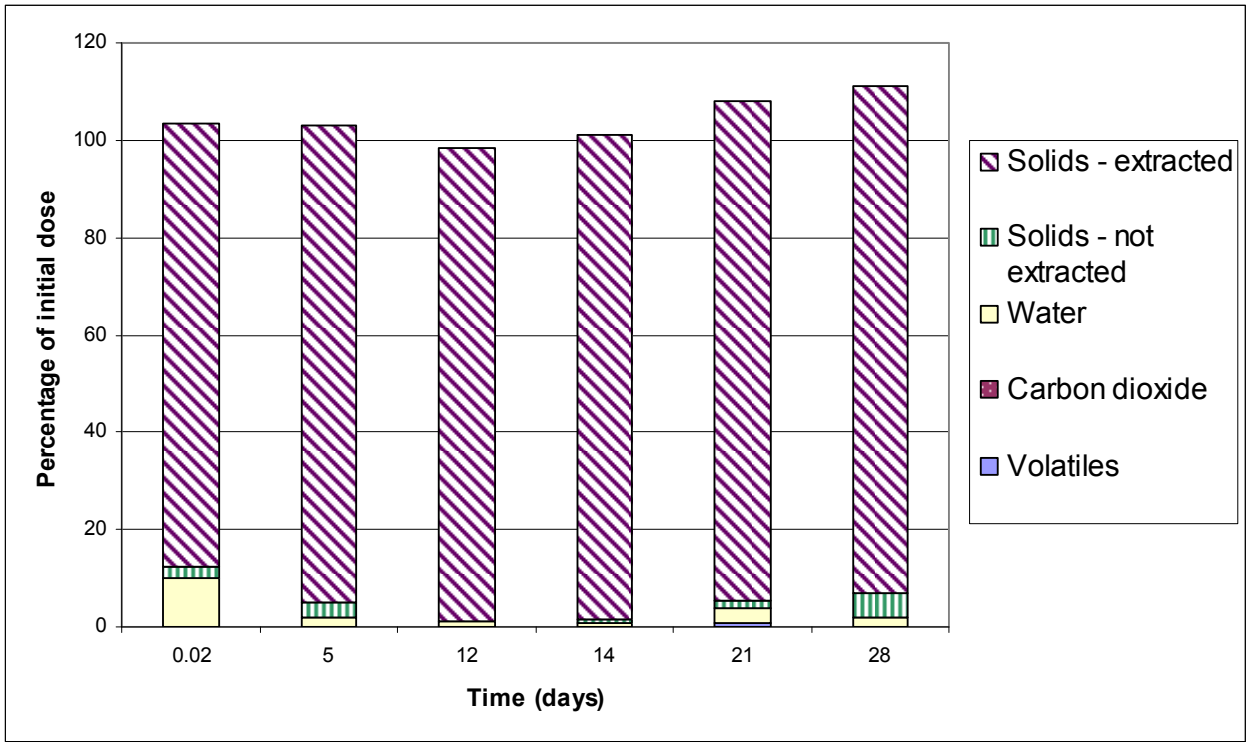
Overall recovery of ^{14}C from the test chambers was good, with an average of 102.1 per cent in the biotic vessels and 99.2 per cent in the abiotic vessels over the 28 day period of the study. The distribution of radioactivity between the various phases in the abiotic control was relatively constant at all sampling times, with the vast majority (~85 per cent of the initial dose) associated with the extracts from the sludge solids and smaller amounts associated with the aqueous phase (~10 per cent of the initial dose), the non-extractable sludge solids (<4 per cent of the initial dose), and the volatiles (~2.5 per cent of the initial dose after 21 days). No $^{14}CO_2$ was evident in the abiotic control.

The distribution of ^{14}C-label in the biotic vessel was very similar to that found in the abiotic control at the first sampling point (after 0.02 days), but after this time there was a decrease in the amount of ^{14}C-label in the aqueous phase (<3 per cent of the initial dose from day five onwards) with a concurrent increase in the extracts from the sludge solids (>97 per cent of the initial dose from day five onwards). This discrepancy between the biotic treatments and the abiotic controls was thought to result from biodegradation of the surfactant present in the biotic treatments as the experiment progressed. This affected the partitioning behaviour of D5 in the biotic treatment compared with that of the abiotic control. The amounts of ^{14}C-label in the biotic treatments associated with the other phases studied were very small (<5 per cent of the initial dose associated with non-extractable solids and <1 per cent of the initial dose associated with the volatile fraction). No significant formation of $^{14}CO_2$ was observed during the study.

Some of the tetrahydrofuran extracts from the sludge solids were also analysed for the parent compound. These showed that the majority (88-99 per cent) of the radioactivity in these extracts from both the biotic treatment and the abiotic controls was parent compound. No evidence for metabolites was apparent in these analyses.

Overall the results of this study show that no significant biodegradation or other transformation (e.g. hydrolysis) or loss process (e.g. volatilisation) occurred under the conditions of the study.

Figure 3.1 Distribution of ^{14}C-label in activated sludge (Itrich and Federle, 2007)



3.2.3 Degradation in soil

The degradation of D5 in soil was investigated by Xu (1999). The study was designed to analyse the significance of all possible degradation pathways, including ring-opening polymerisation reactions (essentially to form PDMS), demethylation reactions, and hydrolysis reactions.

The soil used in the study was the Wahiawa Series from the Kunia area, Hawaii. The soil was air dried before use. The tests were carried out using ^{14}C-labelled D5 (radiochemical purity >99 per cent) and the chemical was dissolved in pentane prior to spiking the soil. The tests were carried out in Teflon tubes that contained either 1 g or 5 g of soil, 0.25 ml of the pentane solution of D5 was then added to the soil, and the tube was flushed with air for two minutes. The initial target D5 concentrations were in the range 40–200 mg/kg dry weight. The spiked soil was then incubated in the closed tubes for between ten minutes and seven days in the dark at room temperature. At the end of the incubation period the soils were solvent extracted and both the D5 that remained and the degradation products were determined. The overall recovery of total ^{14}C in the study was around 99 per cent [Xu personal communication, as reported in CES (2005b)].

D5 was found to hydrolyse rapidly in the experiments, to form more polar products. For example, around 38 per cent of the D5 disappeared and seven hydrolysis products were evident after 0.5 hours incubation, and by 24 hours only two main hydrolysis products remained. The reaction was thought to proceed via ring-opening hydrolysis to form the linear decamethylpentasiloxane diol (pentamer diol), with subsequent loss of dimethylsilane diol to form the octamethyltetrasiloxane diol (tetramer diol), hexamethyltrisiloxane diol (trimer diol), and tetramethyldisiloxane diol (dimer diol) and eventually dimethylsilane diol. One other unidentified product was found after 0.5 hours incubation, but this had totally disappeared by 24 hours.

According to Xu (1999) earlier studies show that dimethylsilanediol (the final degradation product of D5) is lost from soil by volatilisation and biodegradation. The ultimate biodegradation products of dimethylsilanediol are likely to be CO_2 and silica (Chandra, 1997). In addition, any dimethylsilanediol lost from the soil by volatilisation may be subject to degradation to CO_2 and silicic acid and/or silica in the atmosphere. This therefore provides a complete degradation pathway for D5 in soil.

Xu and Chandra (1999) carried out more experiments on two soils to better establish the rate of degradation and volatilisation from soil. One was a typical temperate soil (coarse-textured alfisol), with a pH of 7.6 and organic matter content of 2.4 per cent, and consisted of 50 per cent sand, 28 per cent silt, and 22 per cent clay. The predominant clay minerals present in this soil were illite and chlorite. The other soil was an example of a highly weathered soil (a clay oxisol), with a pH of 4.9 and an organic matter content of 2.2 per cent, and consisted of 21.2 per cent sand, 24.0 per cent silt, and 54.8 per cent clay. The predominant clay minerals present in this soil were kaolinite, gibbsite, and goethite.

Most of the tests were carried out with D4, but some were also carried out with D5 and D6. The general conclusions found with the experiments with D4 are also relevant to the other cyclic siloxanes. The substances tested were ^{14}C-labelled (radiochemical purity >99 per cent). The degradation experiments were carried out using sealed systems under different relative humidities (32 per cent, 92 per cent, and 100 per cent). The soils were prepared by pre-equilibrating samples of 5 g of air-dried soil in 30 ml Teflon tubes to the required relative humidity atmosphere in a desiccator. After a seven day pre-equilibration period the soil was spiked with the ^{14}C-labelled substance as a solution in pentane (the amount of substance added was equivalent to an initial soil concentration of ~40 mg/kg dry weight) and the tube was immediately capped. After two minutes the cap was removed and the tube flushed with air of the correct humidity for 90–120 seconds to evaporate the solvent. After this the tubes were recapped and incubated at 22°C for between 0 and 21 days. The experiments to investigate the volatilisation loss were prepared in a similar way, but were incubated without capping.

At various times the amount of ^{14}C-substance in the soil was determined. D4 degraded in the test system, with the rate increasing with decreasing relative humidity. The rate of degradation was also generally faster in the weathered soil than in the temperate soil. The degradation half-lives determined were around 0.89 days (21 hours), 0.08 days (1.9 hours), and 0.04 days (58 minutes) in the weathered soil at relative humidities of 100 per cent, 92 per cent, and 32 per cent, respectively, and 5.25 and 3.54 days in the temperate soil at relative humidities of 92 per cent and 32 per cent, respectively (little or no degradation of D4 was seen in the temperate soil at 100 per cent relative humidity). Results for D5 and D6 were only given for the weathered soil at a relative humidity of 32 per cent. Under these conditions, the half-lives for D5 and D6 were 0.08 days (1.9 hours) and 1.38 days, respectively, compared with 58 minutes for D4 under the same conditions. Overall it was concluded that the rate of degradation was D4 > D5 >> D6 in these test systems.

The degradation seen was thought to result from hydrolysis reactions catalysed by the surface activity of soil clays. The increase in moisture of the soil was thought to decrease the surface acidity and thus the hydrolysis rate. The differences in the degradation rates obtained in the weathered soil compared with those in the temperate soil occurred because the weathered soil had a higher clay content, and the clay minerals in this soil were kaolinite (around 50 per cent of the clay minerals) and gibbsite (around 10 per cent of the clay minerals), both of which are highly effective catalysts of PDMS. In contrast, as well as having a lower clay content, the clay minerals in the temperate soil were illite and chlorite (the former is one of the least-effective catalysts for hydrolysis of Si–O–Si linkages).

The volatilisation experiments were only carried out with D4 in temperate soils. These showed that loss by volatilisation from soil was a significant competing process for D4 in soils

in open systems. At a relative humidity of around 50 per cent, volatilisation was found to account for about 40 per cent of the total loss of D4, but loss by volatilisation was negligible compared to loss from degradation in dry soils (relative humidity 32 per cent). In soils at high relative humidity (~100 per cent) loss by volatilisation was the dominant removal process for D4 (e.g. 80 per cent loss by volatilisation was seen over the incubation period, compared with 5 per cent by degradation). These results are relevant for D5 but, given the higher log K_{ow}, and lower vapour pressure and Henry's law constant for D5 (log K_{ow} 8.03, vapour pressure 33.2 Pa at 25°C, and Henry's law constant 3.34×10^6 Pa m^3/mol at 25°C) compared with D4 (log K_{ow} 6.49, vapour pressure 132 Pa at 25°C, and Henry's law constant 1.21×10^6 Pa m^3/mol at 25°C; see Environment Agency, 2008) the loss of D5 by volatilisation is expected to be lower than that for D4.

3.2.4 Evaluation of environmental degradation data

3.2.4.1 Abiotic degradation

Degradation of D5 will occur in the atmosphere by reaction with atmospheric hydroxyl radicals. Hydrolysis of D5 can also occur. This reaction is thought to be relatively slow at near neutral pH (half-life ~71 days at pH 7 and 25°C), but is expected to be more rapid at higher (and lower) pHs (half-life ~nine days at pH 8 and 25°C).

In terms of the environmental risk assessment, the TGD recommends that a pH of 7 and a temperature of 12°C are used for the freshwater environment. For the marine environment a higher pH (around 8), but lower temperature (around 9°C) are considered. The relevant hydrolysis half-lives for D5 under these conditions are summarised in Table 3.8.

Table 3.8 D5 half-lives for freshwater (pH 7) and the marine environment (pH 8)

Temperature (°C)	Hydrolysis half-life (days)	
	pH 7	**pH 8**
25	71	9
12	315	43
	449	64

In terms of the risk assessment, a half-life of >60 days has important consequences for the persistent, bioaccumulative, and toxic (PBT) assessment in particular (see Section 5.5.2). The available hydrolysis data allow the half-life to be estimated for any pH. The predicted variation of hydrolysis half-life with pH is shown in Figure 3.2. Based on this analysis the critical pH range over which the estimated hydrolysis half-life for D5 is 60 days or more can be determined as:

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

An analysis of the pH of water in the major water courses in the EU has been provided (R. Gerhards, personal communication). The information used in the analysis was obtained from the European Environment Agency website. The average pH values for 261 European rivers were classified into 0.1 pH steps and plotted in the frequency diagram shown in Figure 3.3. This shows that a number of the rivers are in the critical pH range (i.e. pH ~5.6 to ~7.9) at

12°C, and a smaller fraction are also in the critical pH range (i.e. pH ~6.3 to ~7.1) at 25°C (to obtain the actual volume of water in the EU in this range requires knowledge of the flow-weighted pH in the various rivers).

Another analysis of the pH of surface water in the EU was carried out by Gerhards (2005). This analysis focussed on the major European catchment areas (rather than on individual rivers) which transport the (treated) wastewater from approximately 285 million people (i.e. over half of the total EU population of 450 million people). The pH of all rivers included in the survey was in the range 7.57–8.36, with most having a pH close to 8.0. When the discharge volume was used as a weighting factor, the average pH of the waters was calculated as 7.9. The relatively high overall pH is thought to result from the widespread installation of equipment to remove sulfur dioxide from electric power generation plants, which in turn has reduced 'acid rain' and lead to a slow increase in the overall pH of surface water. For marine waters, the pH of the North Sea varies between 7.9 and 8.4, with an average value of 8.2.

Another analysis of the pH of surface waters in the EU was carried out for the EU risk assessment on nickel (ECB, 2005). In this analysis, a slightly different approach was taken in that the 10th, 50th, and 90th percentiles of the pH in surface waters in the EU were estimated using data in the Surface Water Database and the GEMS/Water database, and appears to include data for lakes as well as rivers. The values for these pH percentiles were 6.5, 7.4, and 8.0, respectively, for European freshwaters. A similar analysis carried out for UK freshwaters gave the 10th, 50th and 90th pH percentiles as 7.0 or 7.3, 7.7 and 7.9, and 8.2 and 8.4, respectively, depending on the database used for the pH data. Again, this analysis indicates that a number of surface waters have pHs in the critical ranges for the hydrolysis of D5 (the actual volume of water in the EU in these ranges is not known). There are apparent differences in the pH ranges obtained in this analysis and those obtained by Gerhards (2005) above. Some of these differences probably occurred because the analysis carried out in ECB (2005) considered data from selected rivers and lakes in Austria, Belgium, Denmark, Finland, France, Germany, The Netherlands, Sweden, and the UK, whereas the analysis by Gerhards (2005) considered the major catchment areas in Europe. In addition, in the analysis by Gerhards (2005) the pH was flow-weighted, which was not done in the analysis in ECB (2005).

Based on the above data, it has to be concluded that a number of water bodies in the EU have properties such that the hydrolysis half-life is 60 days or greater in the body. However, when the persistence in a region is considered, the water bodies likely to be of varying pH and so it is difficult to define a representative half-life for D5 in such an area. As indicated above, the TGD recommends a pH of 7 when hydrolysis data that varies as a function of pH are considered, and so the relevant half-life for this pH (and a temperature of 12°C) is used for the regional risk assessment as a worst case. The frequency distribution shown in Figure 3.3 indicates that a large proportion of rivers within the EU have pHs higher than 7 (and so will have a correspondingly lower hydrolysis half-life for D5), but to counterbalance this, the maximum hydrolysis half-life for D5 occurs around pH 6.5–6.7 (see Figure 3.2) and so a number of river bodies in the EU have half-lives longer than 315 days.

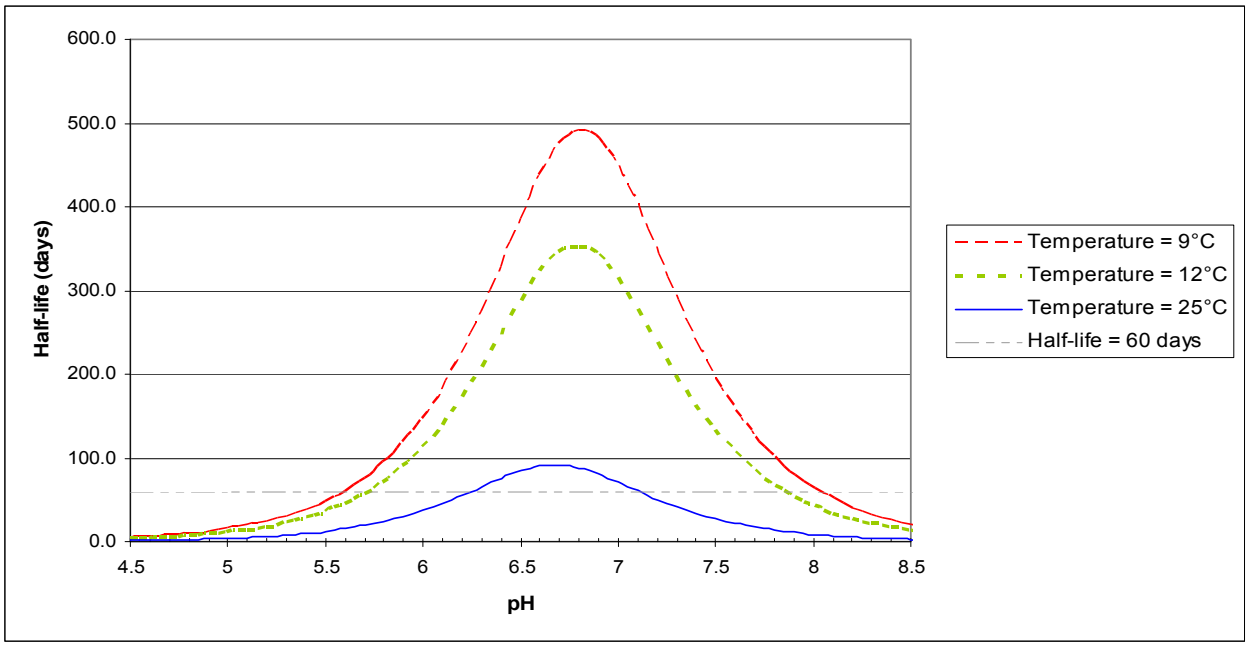


Figure 3.2 Variation of hydrolysis half-life with pH and temperature

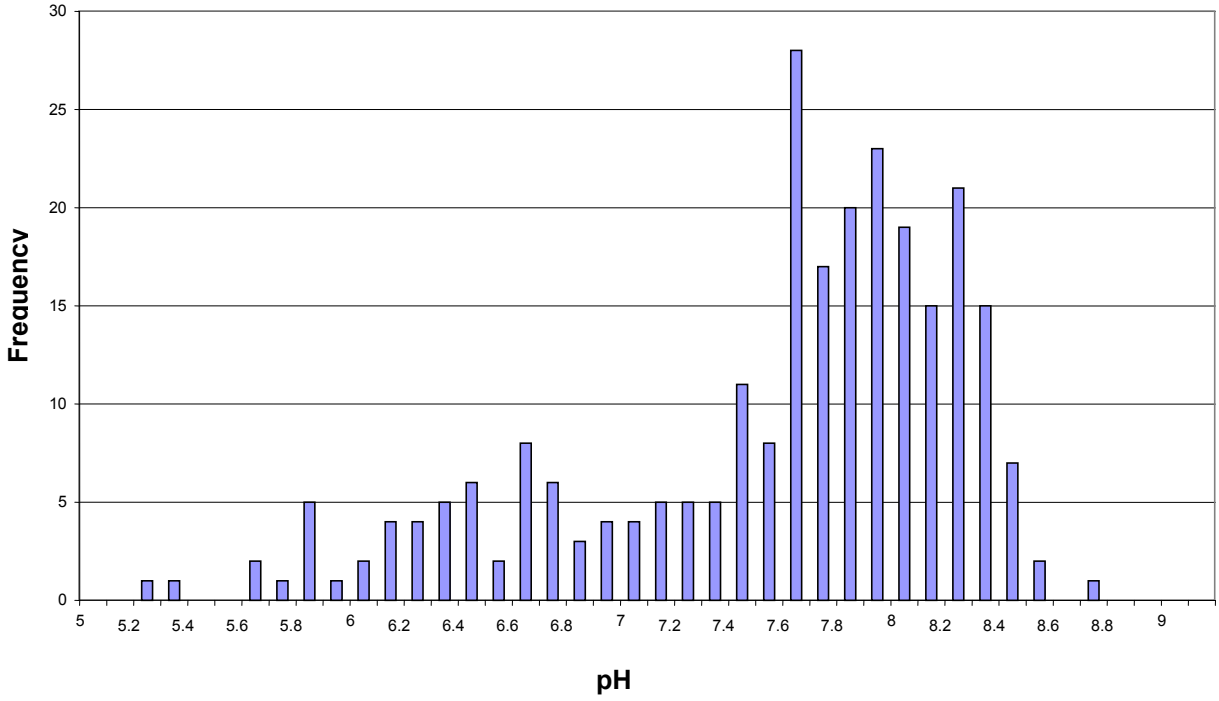


Figure 3.3 Frequency distribution of pH values in 261 European rivers

More information on the hydrolysis of D5 at pHs around 7 is currently being generated. This information would be useful to confirm the expected hydrolysis half-life at pHs around 7 in the environment. The results of this hydrolysis study are important to the risk assessment,

particularly the PBT assessment (see Section 5.5.2) and so this area should be revisited once the full results of the study are available.

In summary, the abiotic half-lives assumed in the assessment are:

- atmospheric photo-oxidation, 10.4 days
- photodegradation in air, infinite
- photodegradation in water, infinite
- hydrolysis (pH 7, 12°C), 315 days
- hydrolysis (pH 8, 9°C, marine), 64 days (used for PBT assessment only).

The main degradation product formed during the abiotic degradation of D5 is likely to be dimethylsilanediol. D5 is expected to undergo further degradation processes in the environment to ultimately form CO_2 and silicic acid and/or silica.

3.2.4.2 Biodegradation

Overall, 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 thus makes it unavailable to the microorganisms in the test systems used. Therefore, to test for biodegradation of D5 is very difficult. For example, even in the standard biodegradation test that uses effectively sealed systems, it is likely that the major proportion of D5 would be in the headspace in the test rather than in the water phase. Thus, 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 (most probably by an abiotic process). However, the presence of moisture significantly reduced the rate of degradation such that when the dried soil was equilibrated with a 100 per cent relative humidity atmosphere essentially no degradation was seen. In terms of the environment, although dry soils may exist in some situations (e.g. drought), most soils contain moisture, and even dry soils are exposed to moisture in the air [as was simulated in the studies by Xu (1999) and Xu and Chandra (1999)]. Thus, although it is possible that such degradation in soils could occur under some circumstances in the environment (low relative humidity, drought conditions), this is unlikely to be the typical case. Furthermore, one of the main soil compartments relevant to the risk assessment is agricultural soil. Here crops are likely to be watered during dry conditions and so the degradation under such conditions is likely to be limited.

Another analysis of the soil degradation data for D5 has been carried out [Xu, personal communication, as reported in CES (2005b), Xu (2007a)]. The analysis is based on the data of Xu and Chandra (1999) and uses the assumptions:

- the ratio of degradation rates of the various cyclic VMSs relative to D5 is the same at any given moisture level in different soils;
- the rates of degradation of any given cyclic VMS is linearly related to water the potential [which is, in turn, linearly related to log (relative humidity) as measured with Londo soil].

The estimated half-lives of D5 in a temperate soil and a tropical soil using this approach are summarised in Table 3.9 [the Xu and Chandra (1999) study was carried out at 22°C].

Table 3.9 D5 half-lives for temperate and tropical soils

Relative humidity (%)	Half-lives (days)	
	Temperate soil	Tropical soil
50	9.7	0.11
70	11.1	0.14
90	12.5	0.19

The half-lives in Table 3.9 relate to a dry soil exposed in air of the stated relative humidity. CES (2005b) indicates that, for comparison, the water content of Londo soil (as used by Xu and Chandra, 1999) in the 32.5 per cent relative humidity experiment is 2.1 per cent.

Using similar assumptions to the above, a half-life of 5.7 days was estimated for a typical soil in the dry season in France [Xu, personal communication, as reported in CES (2005b)]. In France the soil moisture content may regularly decline to between 5 and 10 per cent during the summer months.

The degradation seen in the soil studies with cyclic siloxanes parallels that seen with PDMS (see Section 3.1.7.2). The degradation of PDMS was also dependent on the soil moisture content (among other factors) and, although degradation was generally slow with increasing water content of the soil, it still occurred. Using representative soils, significant degradation of PDMS occurred over periods of several months to a year under field conditions (with half-lives of the order of 1000 days estimated in one set of experiments). The similarity for the mechanisms of degradation of PDMS and D5 implies that degradation would still occur for D5 in wet soils. The available studies on cyclic siloxanes are not able to provide any direct evidence of this, as volatilisation becomes the most dominant removal mechanism from moist soil in the experiments carried out (i.e. all the D5 is lost from the soil before degradation can occur).

The main degradation product of D5 in soils is eventually likely to be dimethylsilanediol, which is expected to undergo further degradation processes in the environment and to ultimately form CO_2 and silica and/or silicic acid. This, therefore, provides a complete mineralisation pathway for D5 in soils in which such degradation occurs.

In terms of this assessment, it is assumed that D5 is not biodegradable as a worst case. However, in the environment it is likely to be removed from aquatic systems and terrestrial systems by volatilisation into the atmosphere. Removal by volatilisation is built into the PEC calculations for both water (at a regional level only) and soil (at a local and regional level). To reflect the evidence that D5 can also be removed from soil by degradation, the effect of including example degradation rates (e.g. assuming half-lives of six months, one year, and ten years at 12°C, as well as 5.7 days at 22°C, as estimated above for a typical soil in the dry season in France) on the resulting PEC calculations is investigated (see Section 3.3.2.1). Also, under some conditions (e.g. particularly dry spells) the degradation of D5 in soil could become more rapid (and become the dominant removal process from the soil). However, this would not represent a realistic worst-case situation as explained above.

3.2.5 Environmental partitioning

3.2.5.1 Adsorption coefficients

Calculated values

A value for K_{oc} of 1.45×10^5 l/kg can be estimated for D5 from its chemical structure using the USEPA EPI (v3.12) estimation software.

Chandra (1997) estimated K_{oc} for D5 using four different correlation equations (which related the K_{oc} to water solubility or log K_{ow}). The mean value for the estimated K_{oc} was 39,810 l/kg.

A K_{oc} of 24,000 l/kg was estimated for D5 from the results of experiments that investigated the effect of humic acids and wastewater solids on the measured Henry's law constant of D5 in synthetic wastewaters (David *et al.*, 2000).

Using a log K_{ow} value of 8.03 the partition coefficients in Table 3.10 can estimated using the methods outlined in the TGD. The equivalent values obtained using a log K_{ow} of 5.2 are also shown.

Table 3.10 Partition coefficients for D5 using K_{ow} values of 8.03 and 5.2

	Log K_{ow} 8.03	**log K_{ow} 5.2**
Organic carbon–water partition coefficient (K_{oc})	4.0×10^6 l/kg	2.1×10^4 l/kg
Solids–water partition coefficient in soil (K_{soil})	8.1×10^4 l/kg	410 l/kg
Solids–water partition coefficient in sediment (K_{sed})	2.0×10^5 l/kg	1.0×10^3 l/kg
Solids–water partition coefficient in suspended matter (K_{susp})	4.0×10^5 l/kg	2.1×10^3 l/kg
Soil–water partition coefficient ($K_{soil–water}$)	1.2×10^5 m^3/m^3	900 m^3/m^3
Suspended matter–water partition coefficient ($K_{susp–water}$)	1.0×10^5 m^3/m^3	510 m^3/m^3
Sediment–water partition coefficient ($K_{sed–water}$)	1.0×10^5 m^3/m^3	510 m^3/m^3

Experimental values

A recent, high-quality study was undertaken by industry on a voluntary basis to investigate the actual K_{oc} value for D5. The study was carried out in accordance with good laboratory practice (GLP) using the OECD 106 batch equilibrium method (Durham, 2007). Earlier draft versions of this risk assessment had shown the importance of K_{oc} to the assessment of the affects of D5 in the sediment compartment in particular, and the study was undertaken to address the uncertainties in this endpoint.

The test substance used was ^{13}C-labelled D5 with a purity of 98.8 per cent. ^{13}C-D5 was chosen to facilitate the analysis of low levels of D5 in the water phase (enriched ^{13}C-D5 has an inherently lower analytical background than unlabelled D5).

Three soils were used in the study. These were collected from the UK and covered a range of organic carbon contents (2.0–5.5 per cent) and pH values (pH 5.5–8.3). The properties of each soil used are summarised in Table 3.11.

A number of experiments were carried out to investigate the effect of the soil:water ratio and equilibration time on the K_{oc} value determined. These were used to calculate the optimum conditions for the definitive adsorption isotherm studies.

Table 3.11 Properties of soils used in the K_{oc} determination for D5 (Durham, 2007)

Property		**Soil**		
		Silty loam	**Sandy loam**	**Sandy–clay loam**
Soil pH		6.6	5.5	8.3
Organic carbon content (per cent weight by weight)		3.4	2.0	5.5
Cation exchange capacity [milliequivalent (meq)/100g]		18.0	9.9	20.4
Water-holding capacity (per cent weight by weight)		41.1	16.4	31.4
Composition (per cent by weight)	Sand	22	72	61
	Silt	56	13	19
	Clay	22	15	20

The methodology used was similar in all cases. Each experiment was carried out in duplicate. Briefly, the required amount of test soil (see below) and approximately 25 g of 0.01 M $CaCl_2$ solution were added to the test vessel (a glass tube fitted with a screw cap). The soil–water mixtures were mixed overnight on a rotational mixer. The experiments were initiated by the addition of 25 µl of a solution of ^{13}C-D5 in N,N-dimethylformamide.[12] The solution was added to the soil–water mixture via a valve in the screw cap. The test vessel was then returned to the mixer and incubated at constant temperature for the required time. The average temperature during the experiments was 25.6°C (standard deviation ±0.4°C). At the end of the incubation period, the levels of ^{13}C-D5 in both the aqueous and solid phases were determined. The analytical methodology used was subject to an extensive quality assurance and quality control procedure to minimise the influence of analytical artefacts in the concentrations measured. Checks were also made to ensure that the test substance was stable during the determinations and that adsorption onto the surface of the test vessel was not significant.

The first set of studies was designed to determine the optimal soil:solution ratio. These were carried out using the sandy–clay loam at two different soil:solution ratios, 1:50 and 1:100 weight by weight. The test vessels were spiked with 200 ng ^{13}C-D5 per tube and equilibrated for one, three, eight, 16, 24, or 30 hours. Equilibrium was reached by 24 hours, and the log K_{oc} values determined after 24 hours were similar at the two soil:solution ratios (mean log K_{oc} = 5.21 at the 1:50 ratio and 5.17 at the 1:100 ratio). As the impact of the soil:solution ratio on the K_{oc} was minimal, a soil:solution ratio of 1:50 was used in all subsequent experiments because this facilitated the analysis of the water phase.

[12] The amount of N,N-dimethylformamide in the test vessel was 0.1 per cent volume/volume of the aqueous phase, which is consistent with the limit stated in the test guideline.

The next series of experiments investigated the time to equilibrium in the two remaining soils (sandy loam and silty loam) using a soil:solution ratio of 1:50 spiked with 200 ng ^{13}C-D5 per tube. Equilibrium was again found to be reached within 24 hours and the mean log K_{oc} values determined after 24 hours were 5.31 for the sandy loam and 5.27 for the silty loam.

Desorption experiments were also carried out using all three soils by placing the solid phase in fresh $CaCl_2$ after equilibrium had been reached and monitoring the re-attainment of equilibrium. The desorption equilibrium was rapidly attained (within one hour) and the mean log K_{oc} was determined as 5.37 for the sandy loam, 5.33 for the silty loam, and 5.25 for the sandy–clay loam.

The definitive experiments determined the adsorption isotherms in each soil. These experiments used a soil:solution ratio of 1:50 and a range of ^{13}C-D5 concentrations (the nominal spiked amounts were 10, 25, 63, 160, 400, and 800 ng/tube). The K_{oc} value was determined after 24 hours of incubation. The K_{oc} data were evaluated using the Freundlich equation. The adsorption isotherms were linear over the concentration range studied and the mean log K_{oc} values determined (± standard deviation) were 5.29 ± 0.03 for the sandy loam, 5.25 ± 0.01 for the silty loam, and 4.98 ± 0.04 for the sandy–clay loam. The overall average log K_{oc} value from these experiments was 5.17 ± 0.14.

The final series of experiments determined the desorption isotherms using the same six nominal concentrations of ^{13}C-D5. In these experiments, the test vessels were spiked with the ^{13}C-D5 and equilibrated for 24 hours. After which the aqueous phase was removed, fresh $CaCl_2$ added, and the vessel was incubated for another 24 hours. The K_{oc} values were then determined and evaluated using the Freundlich equation.

The desorption isotherms were linear over the concentration range studied and the mean log K_{oc} values determined (± standard deviation) were 5.40 ± 0.03 for the sandy loam, 5.38 ± 0.01 for the silty loam, and 5.25 ± 0.04 for the sandy–clay loam. The overall average log K_{oc} value from these experiments was 5.34 ± 0.08. When compared with the values obtained in the adsorption isotherm experiments, there is a small, but systematic, increase in the log K_{oc} obtained, which suggests only a minor apparent irreversibility in the adsorption–desorption of D5 for short contact times. However, adsorption to natural particles is a complex process, and the short contact times used in this study may favour faster sorption processes over other processes that could occur in the environment over longer timescales.

Overall this is a high-quality study that gives reproducible results over a range of experimental conditions for three different soils. The mean log K_{oc} of 5.17 from the adsorption isotherm experiments is used in the risk assessment. This is equivalent to a K_{oc} of 1.5×10^5 l/kg.[13]

Summary of adsorption coefficients used in the risk assessment

The K_{oc} value is taken to be 1.5×10^5 l/kg. The other adsorption coefficients used in this assessment are summarised below. These are estimated from the K_{oc} value using the methods outlined in the TGD.

- K_{oc}, 1.5×10^5 l/kg
- K_{soil}, 3.0×10^3 l/kg
- K_{sed}, 7.5×10^3 l/kg
- K_{susp}, 1.5×10^4 l/kg

[13] In the original test report the K_{oc} values were given as dimensionless values as the concentration in the aqueous phase was determined in terms of the mass (rather than volume) of solution. As the density of 0.01 M $CaCl_2$ solution is close to 1 kg/l, the dimensionless K_{oc} is numerically equivalent to a value with units of l/kg (this is the form used in the methodology in the TGD).

- $K_{soil-water}$, 4.8×10^3 m^3/m^3
- $K_{susp-water}$, 3.8×10^3 m^3/m^3
- $K_{sed-water}$, 3.8×10^3 m^3/m^3.

3.2.5.2 Behaviour in wastewater treatment plants

The behaviour of D5 during wastewater treatment was investigated using a pilot-scale municipal activated sludge wastewater treatment plant (Parker *et al*., 1999). The overall removal of D5 in the system was 95.8 per cent, but it is reported that the overall mass balance for the chemical in the experiment was generally low. Modelling experiments indicate that the low mass balance is probably caused by an underestimation of the removal by primary sludge that resulted from the sampling method used (grab samples were taken which may not accurately reflect the high variability found in the primary influent suspended solids concentration). When this underestimation is taken into account it appears that loss via volatilisation and loss by adsorption onto sludge solids contributed approximately equally to the total removal seen.

Kazuyuki *et al*. (2007) determined that the total removal efficiency for D5 in a municipal wastewater treatment plant in Japan was about 97 per cent – removal occurred mainly by adsorption to sludge and volatilisation. It is also reported that the concentration of D5 in excess sludge was around twice that in primary sludge and that about 20-50 per cent of the D5 that entered the anaerobic digestion process partitioned to the biogas formed during the process. The original paper is in Japanese and the information is taken from the abstract only.

The expected behaviour of D5 during wastewater treatment is estimated using the Simpletreat model within EUSES 2.0.3. The resulting distribution is:

- percentage to air, 22.1 per cent
- percentage to sludge, 73.2 per cent
- percentage degraded, 0 per cent
- percentage to water, 4.7 per cent.

Therefore the overall removal predicted is around 95.3 per cent. This value is in very good agreement with the results from Parker *et al*. (1999) and is used in the subsequent PEC calculations herein.

3.2.6 Adsorption

The K_{oc} for D5 is determined as 1.5×10^5 l/kg. This means that D5 will adsorb strongly to sediment and soil. Given that it is also of very low water solubility and highly volatile, leaching from soil is not expected to be a significant process in the environment.

3.2.7 Volatilisation

The high Henry's law constant for D5 (3.34×10^6 Pa m^3/mol at 25°C) means that it is likely to volatilise rapidly from water and soil. The rate constant for volatilisation from soil is estimated as 0.71/day for agricultural soil and 1.4/day for grassland using the methods outlined in the TGD. These rate constants correspond to volatilisation half-lives of one day and 0.5 day, respectively. These volatilisation half-lives are taken into account in the subsequent PEC calculations.

An estimate for the volatilisation rate from water can be obtained using the USEPA EPI estimation program. With the Henry's law constant above the volatilisation half-life for D5 can be estimated as two hours in a river (the estimate assumes the river has a depth of 1 m, a current velocity of 1 m/s, and a wind velocity of 5 m/s) and as 183 hours in a shallow lake (the estimate assumes that the lake has a depth of 1 m, a current velocity of 0.05 m/s, and a wind velocity of 0.5 m/s).

Within the TGD method (and EUSES) the volatilisation from surface water is not considered at a local level (but it is included in the regional and continental models).

3.2.8 Precipitation

Although D5 has a high volatility, it also has a high log K_{ow}. Therefore the substance may adsorb onto atmospheric aerosols. However, the available experimental and modelling data indicate that, in the atmosphere, D5 is present almost entirely in the vapour phase (see Section 3.2.1.1). This, coupled with the very low water solubility of D5, suggests that removal from the atmosphere by wet and dry deposition is likely to be minimal.

3.2.9 Bioaccumulation and metabolism

Reports of several studies that investigated the accumulation and metabolism of D5 are available. Radiolabelled (i.e. ^{14}C-labelled) D5 was used in some of the accumulation studies. In these experiments, measurements of body burdens (and hence accumulation factors) based on total ^{14}C measurements may overestimate the actual accumulation of D5 (as such measurements may include contributions from metabolites) when compared with measurements based on parent-compound analysis. In Section 3.2.9.1, care is taken to clearly distinguish the actual basis for the measurements.

3.2.9.1 Experimental data

The uptake of D5 from water by fish was studied by Annelin and Frye (1989). The substance used in the test was not radiolabelled D5 from a commercial source (no other information was available on the purity of the substance used). The study used a resaturation method (whereby the exposure solution was continuously passed through a column that contained sand coated with D5) to maintain a reasonably constant exposure concentration. The bioconcentration experiments were carried out with rainbow trout (*Oncorhynchus mykiss)* of approximately 0.9–1.7 g in size. The water used in the test had a hardness of 104 mg/l as $CaCO_3$, pH of 7.6, and a dissolved oxygen concentration of 8.0 mg/l. The exposure tank had a total volume of 120 l and the recirculation rate through the resaturation column was 10 l/hour. Exposure was for 28 days at 12°C. Both the water phase and the fish were analysed for D5 using a gas–liquid chromatographic method. After 28 days exposure, the concentration of D5 in the fish had reached a mean level of 19.5 mg/kg. The concentration of D5 in the water phase averaged 5.8 µg/l over the exposure period. Based on these data it is possible to estimate a BCF for D5 of 3362 l/kg based on parent-compound analysis.

A second experiment was carried out using a surfactant (at a concentration of 10 mg/l) to aid the solubility of D5 in the dilution water (Annelin and Frye, 1989). Here the concentration of D5 in the water increased to around 125 µg/l, but the overall level of D5 in the exposed fish reached approximated the same level (~20 mg/kg) as in the experiment without the surfactant.

Chandra (1997) reports a value for log BCF of 3.5 (BCF ~3200 l/kg) for D5. This is an experimentally determined value from an unpublished study. No other details appear to be

available, but it is likely that it is derived from the Annelin and Frye (1989) study outlined above.

The bioconcentration of D5 was investigated in a recent unpublished OECD 305 study (Drottar, 2005; IUCLID, 2005). The test was carried out with fathead minnows (*Pimephales promelas*) at 22°C using a flow-through system with a 35 day exposure period and a 70 day depuration period. The substance tested was ^{14}C-labelled D5 with a radiochemical purity of 98.48per cent. Two concentrations of D5 were tested [mean measured concentrations (± standard deviation) of 1.1 ± 0.11 µg/l and 15 ± 0.6 µg/l over the 35 day exposure period], and no treatment-related signs of toxicity were seen throughout the test. Stock solutions of the test substance were prepared in dimethylformamide and these were delivered to sealed mixing chambers (at a flow rate of 0.060 ml/minute), in which they were mixed with dilution water [dechlorinated tap water (hardness ~120 mg/l as $CaCO_3$, pH 6.3–7.6) at a flow rate of 600 ml/minute] before entering the test tanks. The concentration of dimethylformamide in the test vessel was 0.1 ml/l and a solvent control was run at this concentration. Two replicates were carried out for each treatment level. At various times during the test, four fish per treatment group (or two for the control group) were analysed for D5 by total radioactivity measurements. The tissue concentrations of D5 (measured as total radioactivity) reached steady state after 14 days of exposure [no statistically significant difference ($p > 0.05$[14]) was found in the tissue concentrations measured on days 14, 21, 28, and 35 of the experiment; the mean tissue concentrations[15] (± standard deviation) at these time points were 6228 ± 2, 424 µg/kg, 6844 ± 2490 µg/kg, 8657 ± 1969 µg/kg, and 9329 ± 2, 860 µg/kg, respectively, in the 1.1 µg/l treatments, and 22,823 ± 5, 197 µg/kg, 34,972 ± 14,275 µg/kg, 28,468 ± 7, 171 µg/kg, and 30,576 ± 11,329 µg/kg, respectively, for the 15 µg/l treatment group]. The steady-state BCF was 7060 l/kg for the 1.1 µg/l treatment and 1950 l/kg for the 15 µg/l treatment based on the mean tissue concentrations according to the total ^{14}C measured between day 14 and day 35.

Around 83 per cent of the body burden was found to be the parent compound, which implies that the BCF based on parent compound may be lower than that based on total ^{14}C measurements. However, the concentration in water was also based on total ^{14}C measurements, which in turn may overestimate the concentration of the parent compound in the water phase if excreted metabolites were present in the water (no information was available on the fraction of the radioactivity present in the water phase that was parent compound). Thus, taking into account that 83 per cent of the radioactivity in the fish was parent compound, it can be estimated that the BCF based on parent compound alone would be ≥860 l/kg for the 1.1 µg/l treatment and ≥1619 l/kg for the 15 µg/l treatment.

Depuration of the accumulated radioactivity was found to be slow (the first-order rate constants for depuration ranged from 0.0179/day (15 µg/l treatment group) to 0.0294/day (for the 1.1 µg/l treatment group)). These are equivalent to depuration half-lives of 24–39 days. The corresponding first-order rate constants for the uptake phase of the study were 93.8/day (for the 15 µg/l treatment) and 390.9/day (for the 1.1 µg/l treatment). Based on the kinetic data, a BCF (based on total ^{14}C) of 13,300 l/kg for the 1.1 µg/l treatment group and 5250 l/kg for the 15 µg/l treatment group was estimated (the equivalent BCFs corrected for the fraction of the total radioactivity in the fish that was parent compound would be ≥11,039 l/kg and ≥4358 l/kg, respectively). The fish used in this test had a mean lipid content [based on the

[14] In Drottar (2005) the significant differences were tested using analysis of variance at $p > 0.05$ after checking for normality and homogeneity of variance using Shapiro–Wilk's test and Bartlett's test. It is assumed here that this implies a >95 per cent probability that the data were randomly sampled from the same population, although this is more usually expressed as $p < 0.05$. The alternative interpretation is that there was a >5 per cent probability that the data were randomly sampled from the same population, which implies that steady state may not have been reached.

[15] The mean and standard deviations of the concentrations at individual timepoints were not given in the test report (Drottar, 2005). They have been estimated here using the raw data from the report for each timepoint.

analysis of a subset of six individuals (two each from the controls, and low and high treatment group)] of 2.9 per cent (range 1.62–5.0 per cent) at day zero, 4.1 per cent (range 1.71–8.36 per cent) at the end of the uptake phase (day 35), and 5.2 per cent (range 2.68–7.24 per cent) at the end of the depuration phase (day 105).

There appears to be a large amount of scatter among the depuration data at some time points [these are displayed graphically in Drottar (2005)] and so the kinetic BCFs may be less certain than the steady-state BCFs derived directly from the measured tissue levels. Thus these kinetic data are supportive of the steady-state BCFs given above.

Also, the highest concentration tested in this study (15 µg/l) is very close to the water solubility of the test substance (17 µg/l). Although the test concentration appears to have been adequately maintained at this level throughout the test, the analytical method used involved collection of the water samples from mid-depth using a pipette and analysing the water samples directly by scintillation counting. Thus the measured levels represent total levels of D5 and not necessarily the dissolved concentrations. It is therefore possible that, at the highest concentration tested, some of the D5 may not have been present in the dissolved phase (which may explain why a generally lower level of accumulation was found at the highest test concentration compared with the lowest test concentration). For this reason, the result obtained at steady state for the 1.1 µg/l treatment (i.e. a BCF of 7060 l/kg based on total ^{14}C measurements) is considered to be the most representative value for the BCF of D5 from this study.

IUCLID (2005) also gives details of the uptake of D5 reported in an unpublished 14 day prolonged acute-toxicity test with rainbow trout (*O. mykiss*). In this study fish were exposed to a single concentration of 2.4 µg/l for 14 days. At the end of the study the exposed fish were found to have a mean body concentration of D5 of 5550 mg/kg (this number appears to be a mistake; as the BCF is reported to be at least 2000 l/kg the actual mean body concentration was most probably 5.5 mg/kg). IUCLID (2005) indicates that the limited number of measurements carried out in this test means it cannot be used to derive a true BCF, but it does indicate that the actual BCF is at least 2000 l/kg. No indication was given in IUCLID (2005) as to whether these data are based on parent compound or total ^{14}C analysis.

The uptake and elimination of D5 was studied in guppies (*Poecilia reticulata*) and goldfish (*Carassius auratus*) through exposure via water or food (Opperhuizen *et al.*, 1987). The exposures were to a mixture of cyclic siloxane oligomers (ranging from D3 to D9) and linear oligomers (ranging from hexamethyldisiloxane to hexadecylmethylheptasiloxane). The substances tested were not radiolabelled from commercial sources (no other information was available on the purity of the substances used). The analytical method used involved analysis of the parent compound by gas chromatography equipped with a flame ionisation detector or mass spectrometer. The spiked food was prepared by adding a solution of the test compounds in pentane to the food and evaporation of the solvent. The resulting concentrations in food were stated to be in the range 306–425 mg/kg for the cyclic oligomers in the goldfish experiments and 1008–1044 mg/kg in the guppy experiments. [However, when displayed graphically in Opperhuizen *et al.* (1987) these concentrations appear to be around 1 mg/kg.] No information is given on whether freshly spiked food was prepared at regular intervals during the experiment or how stable the concentrations were on storage of the food.

For the water-exposure experiments a saturated solution of the test substances was prepared using a continuous-flow saturation system. However, a film of test substance was always present on the surface of the water when solutions were prepared in this manner. The saturated solution was continuously circulated through the exposure vessels during the experiment. The actual concentrations present in the test vessels are not reported. The water-exposure experiments were only carried out with guppies.

The fish used in the test had an average weight and lipid content of 0.17 g and 6.5 per cent (guppies) or 1.8 g and 2.3 per cent (goldfish). The tests were carried out at a temperature of 22°C using a mixture of 50 per cent tap water and 50 per cent demineralised water. The water was continuously aerated during the dietary exposure experiments and in the water-exposure experiments was aerated with pure oxygen added via a capillary tube. In the feeding experiments the feeding rate used was 25 mg/g each day and the exposure period was for up to 12 weeks. In the water-exposure experiments the fish were exposed for 20 days. In all cases the exposed fish were placed on a clean diet and/or in clean water after the exposure period to monitor the depuration of the accumulated chemicals.

Uptake of the cyclic oligomers occurred in both the water-exposure experiments and the dietary exposure experiments. For D5 the steady-state BCF was 1010 l/kg based on parent compound, and the steady-state biomagnification factor (BMF) from the food experiment was 0.05 for guppies, again based on parent compound (similar results were said to be obtained with goldfish). The depuration half-life was around 3.9 days. Given the uncertainties over the exposure concentrations discussed above, these values should be treated with caution.

Opperhuizen *et al*. (1987) also carried out a similar experiment in which fish were exposed to either a single linear oligomer (hexadecylmethylheptasiloxane) or a single cyclic oligomer (D7). Evidence was presented for the formation of cyclic siloxane products (ranging from D5 to D9) in fish in some of these experiments, but it could not be established whether this was the result of impurities present in the materials, whether such materials were formed by transformation in the water phase followed by subsequent uptake, or whether they were formed by metabolic processes in the fish.

Bruggeman *et al.* (1984) attempted to determine the dietary uptake of D5 by guppies (*Po. reticulata*). However, the experimental method used (the food was spiked by adding the D5 as a solution in toluene followed by evaporation of the solvent) meant that all of the D5 was lost from the food during sample preparation and so it was not possible to carry out the study for D5.

Another dietary accumulation study using D5 was completed recently (Dow Corning, 2006b). The test substance was ^{14}C-labelled and had a radiochemical purity of 98.7 per cent. The fish used in this test were rainbow trout (*O. mykiss*), with an average length of 54 mm (range 49–64 mm) and an average weight of 1.2 g (range 0.98–2.2 g) at the start of the test. The lipid content of the fish increased with time during the study, ranging from 2.81 per cent before the start of the study to 6.96 per cent at the end of the depuration phase. The mean lipid content throughout the study was 5.23 per cent.

The food (trout chow, lipid content 14.8 per cent) was dosed with a nominal D5 concentration of 500 mg/kg and a constant feeding rate of 3 per cent wet body weight (bw) per day was used. The mean measured D5 concentration in the food was 458 mg/kg (92 per cent of the nominal) based on parent-compound measurements at days zero, 14, 23, 30, and 37 of the test, and was stable throughout the duration of the test. A control group (receiving diet without D5) was also run. The study consisted of a 35 day uptake period followed by a 42 day depuration phase.

The water used in the test was dechlorinated municipal water and had an average hardness of 113 mg/l as $CaCO_3$. A flow-through test system was used to maintain the water quality throughout the test. Two replicate test chambers, each containing 70 fish at the start of the test, were used for each treatment group. The volume of water in each test chamber was 42 litres and the flow rates were adjusted to provide approximately ten volume additions per day. The temperature was maintained at 12°C ± 2°C throughout the test (the temperature fell to 8.6°C on one day during the study) and the pH of the water was in the range 6.8–8.4.

One trout died during the study. This was not thought to be treatment related and all other fish appeared normal and healthy during the study. The dissolved oxygen concentration was

generally >60 per cent of saturation, but was below this level on a few sampling occasions (the lowest dissolved oxygen concentration was 5.9 mg/l or 56 per cent of saturation).

Fish tissues (three fish per sampling event) were analysed for both total radioactivity and parent compound on days one, three, seven, ten, 14, 21, 28, and 35 of the uptake phase and days one, two, four, seven, 14, 28, and 42 of the depuration phase. Prior to analysis, the digestive tracts of the fish were removed and analysed separately. In addition, fish were also subject to whole body autoradiography on days one and ten of the uptake phase and days two, 14, and 42 of the depuration phase. Water samples were also collected daily from day two to day 36 of the experiment and analysed for radioactivity.

The concentrations in fish determined by parent-compound analysis were generally similar to those determined by total radioactivity analysis (the concentrations generally agreed to within 10 per cent), but the concentrations determined by parent-compound analysis were generally slightly higher than those determined by total radioactivity measurements at most time points. This implies that most of the radioactivity present in the fish is as parent compound. Therefore it is expected that the results would be similar regardless of whether they are determined on a parent-compound analysis or total ^{14}C analysis.

The levels of D5 found in the fish tissues during the study are summarised in Table 3.12.

The level of D5 in the fish tissue appeared to reach steady state by day 21 of the uptake phase (the concentrations of the parent compound were not statistically significantly different ($p>0.05$[14]) on days 21, 28, and 35) and the mean tissue concentration of parent compound over this period was 102 mg/kg wet weight based on total ^{14}C. Therefore the BMF based on total ^{14}C can be estimated as 0.22 on a wet weight fish/wet weight food basis. Taking into account the lipid content of the fish and food, the lipid normalised BMF can be estimated as 0.63 based on total ^{14}C.

Table 3.12 Uptake of ^{14}C-D5 by *O. mykiss* from food

Day	Mean concentration in fish minus digestive tract (mg/kg wet weight)[1]		Percentage of total radioactivity in digestive tract[2]	Concentration in fish including digestive tract based on total radiolabel (mg/kg wet weight)[1]
	Parent compound	Total radiolabel		
Uptake phase				
1	4.23 ± 1.36	3.25 ± 0.79	65.6	8.05 ± 1.00
3	14.0 ± 1.3	13.8 ± 1.2	51.7	24.7 ± 2.0
7	31.9 ± 2.2	29.5 ± 1.5	31.3	38.3 ± 1.7
10	41.9 ± 3.1	37.3 ± 2.5	36.1	51.6 ± 4.1
14	56.6 ± 1.1	52.3 ± 1.0	30.9	66.7 ± 2.0
21	92.0 ± 1.9	80.9 ± 1.7	20.7	90.9 ± 1.8
28	102 ± 7	89.9 ± 4.8	27.7	110 ± 7
35	111 ± 7	101 ± 6	27.0	121 ± 6
Depuration phase				
1	83.5 ± 3.8	89.8 ± 4.2	25.6	107 ± 3
2	104 ± 2	101 ± 3	22.1	113 ± 2
4	94.5 ± 7.0	101 ± 6	16.6	108 ± 6

7	76.0 ± 7.4	72.2 ± 5.8	19.7	79.3 ± 5.0
14	62.5 ± 3.7	59.3 ± 3.8	21.8	67.4 ± 4.2
28	36.5 ± 1.1	36.2 ± 1.5	22.3	41.5 ± 1.5
42	25.0 ± 2.0	25.8 ± 1.6	18.0	28.2 ± 1.8

Notes: [1]±, standard error.

[2]Figures are the percentage of the total amount of radiolabel present in the fish (as mg/fish) associated with the digestive tract.

The uptake and depuration kinetics were also determined in the study. The rate constants for fish-growth dilution were determined during both the uptake phase (0.0356/day) and depuration phase (0.0267/day). The growth corrected uptake and depuration rate constants were determined to be 0.0131/day and 0.00939/day. The kinetic BMF based on total ^{14}C was estimated as 1.39 on a wet weight fish/wet weight food basis, using the growth-corrected uptake and depuration rate constants. The growth-corrected depuration half-life can be estimated as 74 days.[16]

Domoradzki (2008) indicates that the above rate constants for fish growth may be in error. These growth-rate constants were estimated by linear regression using a natural log transformation of fish weight versus time (the exact method used is not totally clear). However, Domoradzki (2008) suggests that it is more appropriate to estimate the fish-growth constant using the fish growth model:

$$\text{fish weight} = \text{initial fish weight} \times (1 + G \times \text{time})$$

where G is the fish growth rate constant (with units per time).

Using this method to determine the growth rate constant, Domoradzki (2008) estimated a lower kinetic BMF of 0.61 on a wet weight fish/wet weight food basis for D5.

However, this approach to estimate the growth-corrected uptake and depuration appears to be in error as it is not the fish growth-rate constant itself that is important, rather the rate constant for growth dilution, and these are not necessarily the same parameter. One way to estimate the growth dilution rate constant is to visualise a hypothetical fish in which the only process that reduces the concentration is growth dilution. For such a fish and assuming growth dilution is a first-order kinetic process (a fundamental assumption in the whole growth-correction procedure) the model is:

$$\frac{d[concentration]}{dt} = -k_{growth\_diltuuion}[concentration]$$

This can be solved to give ln[concentration] = $-k_{growth\_dilution} \times t$ + constant.

Assuming that the initial amount of chemical in the fish is 1 mg (the amount assumed is not important for this analysis), the concentration in the fish at any time (t) can be estimated as [concentration] = 1/fish weight. Substituting this in the above equation, a plot of ln(1/fish weight) against time should give a straight line with a slope equal to $-k_{growth\_dilution}$. Such plots were constructed using the raw fish weight data given in the Dow Corning (2006b) report and these gave good straight lines. Furthermore, the values for $k_{growth\_dilution}$ were almost identical to those used for the growth-rate constants in the original Dow Corning (2006b) report. Therefore the correction proposed by Domoradzki (2008) does not appear to be appropriate and so is not considered again here.

[16] The depuration half-life not corrected for growth is around 19 days. This shows the importance of fish growth as a depuration mechanism in this study.

The kinetic BMF on a lipid-normalised basis is not reported in Dow Corning (2006b). Using the known lipid contents of the fish (mean 5.23 per cent) and food (14.8 per cent), the lipid-normalised kinetic BMF can be estimated as around 3.9 based on total ^{14}C.

Whole-body autoradiography showed that a significant amount of radioactivity remained in the liver and in the intestinal content in the lower portion of the intestine on day 42 of the depuration phase. Smaller amounts of radioactivity remained in the pyloric caeca, kidney, and adipose tissue.

The concentration of total radioactivity in the water samples varied, but was ≤1.94 µg/l throughout the course of the study. No parent-compound analysis was carried out on the water samples and so it is not clear if these concentrations relate to metabolites or D5 itself. If the levels do represent D5 it is possible that accumulation of D5 from the water phase could also have occurred during this study. However, it is likely that if D5 was in the water phase, it would be associated with faecal pellets or other particulate matter and hence may not necessarily be available for bioconcentration in the fish.

The above-quoted concentrations, kinetics, and BMFs are based on the concentration of parent compound in fish tissues minus the contribution from the digestive tract. The amount of radioactivity present in the digestive tract was determined separately in the study, and these results (expressed as the percentage of the total radioactivity present per fish) are summarised in Table 3.12. The actual concentrations of radioactivity in the fish, including the contribution from the digestive tract, were not given in Dow Corning (2006b), but are estimated here from data on the total amount of radioactivity per fish and the wet weight of the fish.

As Table 3.12 shows, the amount of radioactivity in the digestive tract makes a significant contribution to the total amount of radioactivity in the fish, particularly during the uptake phase, but also during the depuration phase, during which it contributes around 20 per cent of the total amount present. Dow Corning (2006b) indicates that 'the observation that the concentration of radioactivity remained high in the digestive tract even after dosing was discontinued is suggestive of metabolism with metabolite(s) entering the digestive tract through enterohepatic circulation'. However, as only ^{14}C-measurements appear to have been carried out on the digestive tract it is not clear if the radioactivity present in the digestive tract represents parent compound or metabolites.

The results of other work to investigate the elimination and metabolism of orally administered ^{14}C-labelled D_5 in rainbow trout (*O. mykiss*) were made available for this assessment. The work consists of a preliminary study to develop the necessary methodology, to be followed by a definitive study.

In the preliminary study (Springer, 2007a), four female fish (weight 872–1138 g) were held under laboratory conditions for two weeks prior to the start of the test, and they were fed daily until two days before the test began. This fasting period was used to ensure that the gastrointestinal tract would be empty. The ^{14}C-labelled D5 used had a radiochemical purity of 99.01 per cent and was mixed with unlabelled D5 (purity 99.19 per cent) prior to use. The test substance was dissolved in corn oil and administered by gavage to three of the four fish (approximately 1 ml/kg of the oil solution was administered to each fish to give a single nominal dose of 15 mg/kg bw). The actual doses received were between 78.6 per cent and 85.7 per cent of the nominal target dose. Blood samples were collected via an aortic cannula and urinary output was collected via a urinary catheter at intervals over a 96 hour period. After 96 hours, samples of bile, liver, digestive tract, fat, egg sacs, and carcass were collected. The various samples were analysed for the parent compound and total radioactivity.

It was thought that during the test two of the exposed fish regurgitated some of the administered dose (traces of oil were present on the water surface of the tanks and around

13 per cent of the dose was found in the tank of one of the fish; a second fish had consistently lower concentrations in the various samples than the other fish) and so analysis of the results focussed mainly on those for one of the exposed fish only. Recovery of total ^{14}C from this fish was around 69 per cent of the administered dose.

The results show that metabolism of D5 did occur and that 96 hours after administration of the dose, the highest concentration of the radioactivity was found in the bile, but only around 4 per cent of this was the parent compound. For the liver, around 46 per cent of the radioactivity was parent compound, and around 50 per cent of the radioactivity in the digestive tract was identified as parent compound. Fewer metabolites appeared to be present in the egg sacs (~81 per cent of the radioactivity was identified as parent compound) and fat (~98 per cent of the radioactivity was identified as parent compound).

In terms of the total amount of radioactivity present (expressed as the total burden in each tissue) the digestive tract contained the highest burden (of both total radioactivity and parent compound), followed by bile (mainly metabolites).

For the blood samples, the radioactivity found was mainly parent compound. In urine, the highest concentrations of radioactivity occurred between 72 and 96 hours. No D5 was detectable in the urine – the radioactivity consisted of metabolites more polar than D5.

The definitive study (Springer, 2007b) was carried out in a similar way to the preliminary study, but with some modifications. The main modifications included dosing each fish with only 0.5 ml/kg of the corn oil solution of D5 and to continue feeding up to 24 hours before dosing (these measures were taken to reduce regurgitation of the applied dose). In addition, samples of faeces and released eggs were also collected to try to improve the mass balance. The ^{14}C-labelled D5 substance tested in this study had a radiochemical purity of 97.6 per cent and the nominal dose was again 15 mg/kg. The actual doses received were between 78.6 per cent and 85.7 per cent of the nominal target dose.

Traces of oil were again seen on the surface of the water in the tanks after administration of the dose, but the amount of ^{14}C-label in the oil was only around 0.005–0.2 per cent of the administered dose. The average recovery of ^{14}C in this experiment was 78 per cent. The majority of the recovered dose was found to be eliminated in faeces (75 per cent of the recovered dose), with smaller amounts being recovered in the carcass (17 per cent of the recovered dose), and tissues and blood (8 per cent of the recovered dose).

Metabolism of D5 was again evident in some tissues. The highest concentration of radioactivity was found in the bile, mainly as metabolites (<1 per cent of the recovered dose was as parent compound). For the radioactivity present in the liver, digestive tract, and egg sacs, around 60 per cent, 70 per cent, and 56 per cent, respectively, of the total radiolabel present was as parent material, and almost all of the radioactivity in fat was parent material. The radioactivity found in blood represented mainly parent compound and the half-life for elimination from blood was around 70 hours. The highest levels in urine occurred 72–96 hours after dosing, and the radiolabel present consisted entirely of metabolites more polar than D5.

In terms of total burden, the digestive tract contained the highest burden of both radioactivity and parent compound, with eggs containing the next highest burden.

Extracts of bile, digestive tract, and liver were analysed further order to obtain a profile of possible metabolites. Bile was found to contain several metabolites more polar than D5, and one metabolite more polar than D5 was indicated in the digestive tract. It was not possible to obtain any further data on the metabolites in the liver because of analytical limitations.

Overall, the calculated percentage of metabolites that occurred within 96 hours of dosing was around 14 per cent of the recovered dose.

The accumulation of D5 by midge (*Chironomus riparius*) larvae was investigated as part of an unpublished toxicity study (Putt, 2003; IUCLID, 2005). The substance tested was a commercial sample of D5 (purity 99.35 per cent) mixed with ^{14}C-labelled D5. The study was carried out using artificial sediment with an organic carbon content of 2 per cent. Further information on the experimental conditions used and the results of the toxicity study are given in Section 4.1.8. The midge larvae were analysed for the presence of total ^{14}C-residues after a ten day exposure period. The results of this analysis are summarised in Table 3.13. Levels in the midge were generally very similar to the levels found in the sediment.

Table 3.13 Uptake of ^{14}C-D5 by *Chironomus riparius* from sediment

Mean sediment concentration (mg/kg dry weight)	Mean concentration of ^{14}C-D5 in midge (mg/kg wet weight)	Sediment accumulation factor (based on total ^{14}C)
13	15	1.2
30	35	1.1
73	60	0.83
180	80	0.46

The available accumulation data for D5 are summarised in Table 3.14. Overall, the steady-state BCF of D5 for fish is 7060 l/kg based on total ^{14}C measurements. Other (less reliable) studies are available that support this value. Uptake of D5 by fish from food was also investigated, but the feeding studies are not sufficiently consistent to allow a reliable accumulation factor to be determined. D5 can also be taken up by invertebrates from sediment. The sediment accumulation factors found were in the range 0.46–1.2 (based on total ^{14}C measurements and on a dry weight in sediment concentration).

Table 3.14 Summary of available bioaccumulation data for D5

Species	Exposure concentration	Value	Validity	Reference
C. auratus	306–425 mg/kg food (mixture of oligomers)	Value not given, but reported to be similar to that for *Po. reticulata* (BMF ~0.05)	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 *Po. reticulata* (BCF ~1010 l/kg)		
Ch. riparius	13–180 mg/kg dry weight in sediment	Sediment accumulation factors 0.46–1.2	Use with care – no information was given as to whether steady state was reached – based on total ^{14}C	IUCLID (2005)

Species	Exposure concentration	Value	Validity	Reference
O. mykiss	5.8 µg/l	BCF = 3362	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 >2000 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 – steady-state value on a wet weight fish/wet weight food basis – based on total ^{14}C (the value based on parent compound is expected to be similar)	Dow Corning (2006b)
		BMF = 0.63	Valid – steady-state value on a lipid-normalised basis – based on total ^{14}C (the value based on parent compound is expected to be similar)	
		BMF = 1.39	Valid – kinetic, growth-corrected value on a wet weight fish/wet weight food basis – based on total ^{14}C (the value based on parent compound is expected to be similar)	
		BMF = 3.9	Valid – kinetic, growth-corrected value on a lipid normalised basis – based on total ^{14}C (the value based on parent compound is expected to be similar)	
P. promelas	1.1 µg/l	BCF = 7060 l/kg	Valid – steady-state value based on total ^{14}C (the value based on parent compound is estimated to be ≥5860 l/kg)	Drottar (2005) 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)	

Species	Exposure concentration	Value	Validity	Reference
	15 µg/l	BCF = 1950 l/kg	Use with care – steady-state value – exposure concentration was close to water-solubility limit – based on total ^{14}C (the value based on parent compound is estimated to be ≥1619 l/kg)	Drottar (2005) IUCLID (2005)
		BCF = 5260 l/kg	Use with care – kinetic value – exposure concentration close to water-solubility limit and a large amount of scatter evident among some of the depuration data – based on total ^{14}C (the value based on parent compound is estimated to be ≥4358 l/kg)	
Po. reticulata	1008–1044 mg/kg food (mixture of oligomers)	BMF = 0.05	Invalid – exposure concentration not well defined – based on parent compound	Opperhuizen *et al.* (1987)
	Saturated solution	BCF = 1010 l/kg		
	Dietary study		Invalid – exposure concentration not well defined – based on parent compound	Bruggeman *et al.* (1984)
Unspecified	Not given	BCF ~3200 l/kg	Use with care – few details given	Chandra (1997)

D5's uptake and metabolism in mammalian systems is also relevant, particularly in relation to the PBT assessment (see Section 5.5.2). The available mammalian uptake and metabolism data for D5 [including a number of unpublished studies and published work by Varaprath *et al*. (1999, 2003), Plotzke *et al*. (2000), Andersen *et al*. (2001), Sarangapani *et al.* (2003) on both D4 and D5] are summarised in CES (2005a). Most of the available mammalian toxicokinetic and toxicity data were obtained using inhalation exposure (as this is one of the primary routes of exposure of humans and, given the volatility of D5, it is significantly easier to test the substance by this route of exposure than by dermal and oral routes), but dermal and oral exposures were also considered. The behaviours of both D4 and D5 were found to be broadly similar. It was concluded that the kinetics of D5 in rats after oral exposure are different from those found after inhalation and dermal exposure. The kinetics of ^{14}C-D5 after inhalation and dermal exposure are thought to be very similar. Inhalation studies showed that retention of D5 after single and multiple exposure was relatively low (~4–5 per cent of the inhaled dose for single exposures and ~8–10 per cent of the inhaled dose for multiple exposures). Approximately 50_80 per cent of this retained dose was attributed to deposition on the fur in males (the equivalent value for females was ~60–70 per cent). Radioactivity was widely distributed to tissue of both males and females, with the maximum concentrations observed in the majority of tissues within three hours post-exposure. Elimination of radioactivity from the rats after inhalation was also investigated. A similar elimination via urine (~12 per cent) and faeces (~16 per cent) occurred in both males and females after both single and multiple exposures. Elimination via exhalation was generally higher (~45 per cent in males and females after multiple exposure or females after single exposure, and ~72 per

cent in males after single exposure). The majority of the radioactivity in plasma, liver, and lung immediately after exposure was attributed to the parent compound, but only a very small fraction of the remaining radioactivity was parent compound from 24–168 hours post-exposure. Urine contained several metabolites (none of which corresponded to the parent compound), but in contrast the major substance found in faeces was thought to be the parent compound.

Physiologically based pharmacokinetic modelling was also carried out for both inhalation and dermal exposures of D5 (Anderson, 2005, Reddy *et al*., 2004, 2005). These models are 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 includes 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 shows that metabolism and exhalation are important mechanisms for elimination of D5, and that the rapid clearance by these two routes of elimination means that D5 does not accumulate, despite a high predicted blood-to-fat partitioning behaviour.

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

After oral exposure, D5 is thought to enter the blood via the lymphatics within the core of chylomicrons and other lipoproteins [and so is in a different form to that for inhalation or dermal routes of exposure (CES, 2005a)]. Therefore an assumption of rapid elimination via the lungs from an oral dose cannot be made. However, it is likely that the substance is rapidly metabolised in mammals after oral exposure (in a similar way to the absorbed dose following inhalation exposure). Indeed, CES (2005a) reports the results of an unpublished study that investigated the metabolic profile of ^{14}C-D5 after oral exposure. Analysis of the urine identified two major metabolites (dimethylsilanediol and methylsilanetriol) and seven minor metabolites (mainly linear siloxane oligomers). No parent D5 was found in the urine. This demonstrates that metabolism of D5 occurred after oral administration.

Another (unpublished) review of the pharmacokinetics of cyclic siloxanes was made available (Andersen, 2005; CES, 2005b). Around 20 per cent of a dose of D5 administered orally by gavage in corn oil was found to be systemically absorbed. The remainder of the radioactivity (around 80 per cent of the administered dose) was excreted unchanged in the faeces. Of the 20 per cent that was absorbed, 50–60 per cent was eliminated as unchanged D5 in exhaled air and around 20 per cent was eliminated as water-soluble metabolites in urine. This demonstrates that elimination by these two routes is significant after oral administration, similar to that after inhalation exposure. The review concludes that oral dosing leads to more complex pharmacokinetics than inhalation or dermal dosing as the oral uptake appears to be associated with siloxanes as microemulsions. These microemulsions are thought not to dissolve readily in plasma and blood, and would be removed from the circulation initially by actions of cells of the reticuloendothelium system in liver (where the D5 would be readily metabolised) and spleen. It also concludes that uptake after oral dosing may be associated with lipid transport, such as chylomicron formation, and so may not be available for metabolism or excretion via exhalation. Overall, the differences seen between oral dosing and inhalation and/or dermal dosing suggest a much higher persistence of D5 in blood after oral dosing, but that it is likely that this persistence results from D5 being present in a pool within the body that is less available. Thus the results from oral studies using relatively high doses in an oil vehicle should be used with caution when drawing conclusions for more normal routes of exposure at lower doses.

Based on the above, there is clearly some uncertainty in extrapolating the results from laboratory oral gavage studies, in which relatively high doses of D5 dissolved in a vehicle are

used, to the situation in the environment where D5 is distributed in the body (probably associated with the lipid fraction) of the food organism (e.g. a fish). These different modes of administration could possibly lead to D5 being present in a different form within the gut for gavage studies compared with feeding in the wild.

Overall, it can be concluded that D5 is likely to be rapidly eliminated from mammalian systems and so appears to have a low potential to accumulate in mammals. However, the pharmacokinetic behaviour after oral administration is complex, and does not appear to be as well understood as other routes of exposure. The bioaccumulation behaviour in mammals in relation to the PBT criteria is considered in Section 5.5.2.

3.2.9.2 Calculated BCFs and BMFs

BCF values for fish and earthworms can be estimated from log K_{ow} values using the methods outlined in the TGD:

- for log K_{ow} 8.03 the BCF for fish is 24,300 l/kg and it is not possible to estimate[17] that for earthworms;
- for log K_{ow} 5.2 the BCF for fish is 5250 l/kg that for earthworms is1900 l/kg.

The predicted value for fish using a log K_{ow} of 8.03 is a factor of 3.4 higher than that found experimentally, and so the experimentally determined values are used in the assessment. For earthworms no experimental value is available to compare with the predicted BCF.

Using the experimentally determined BCF for fish of 7060 l/kg based on total ^{14}C measurements, the default BMFs from the TGD appropriate for the secondary poisoning assessment are:

- a BMF_1 for predators of 10,
- a BMF_2 for top predators of 10.

Feeding studies carried out with fish exposed to D5 via the diet generally show a much lower level of uptake, which implies that a BMF lower than the default value of 10 would be appropriate for D5.

A recent feeding study (Dow Corning, 2006b) with fish exposed to D5 lead to BMFs for D5 of:

- 0.22, steady-state value on a wet weight fish/wet weight food basis;
- 0.63, steady-state value on a lipid-normalised basis;
- 1.39, kinetic, growth-corrected value on a wet weight fish/wet weight food basis;
- 3.9, kinetic, growth-corrected value on a lipid-normalised basis.

(The values are based on total ^{14}C measurements; the values based on parent compound analysis are expected to be similar to these.)

These values are all considered to be reliable, and it is preferable to consider these in place of the TGD default values. The key question for the assessment is, therefore, which of these values is most appropriate to use in the PEC calculations.

The TGD recommends that the BMF value used should, where possible, be lipid normalised and so the lipid-normalised values from above appear to be the most appropriate to use in the risk assessment. The TGD does not give any guidance as to whether growth-corrected

[17] The Technical Guidance Document advises that the methodology should only be applied to substances with log K_{ow} values in the range 1 to 8.

BMFs should be used in preference to BMFs that are not growth corrected. For D5 this is an important consideration, as the depuration seen in the study is dominated by growth dilution, which has implications for the accumulation likely to occur in slow-growing adult fish compared with those in fast-growing juvenile fish. Thus, although the steady-state, lipid-corrected BMF was 0.63 in this study, it is possible that much higher levels of accumulation could be seen in adult fish and so it is considered relevant to use the growth-corrected and lipid-normalised BMF of 3.9 in this assessment. This value is therefore used for the BMF of both predators and top predators in the assessment. Although this value is corrected for both lipid content and growth of the fish, there are further difficulties in extrapolating the results of laboratory feeding studies to the field situation, as one of the key determinants is the assimilation or absorption efficiency of the chemical in the gut. This depends on, among other things, the digestibility of the food consumed and it is possible that the digestibility of the food used in laboratory studies (trout chow in this case) may not be representative of the digestibility of prey in the natural aquatic environment.

D5 has shown a much lower level of accumulation in mammals than in fish. Therefore, although exposure to mammals is predicted to occur via consumption of fish (this is considered in the secondary poisoning scenario in Section 3.3.4), D5 is not itself expected to accumulate significantly in the exposed mammals. Mammals that consume other mammals are therefore likely to be at much lower risk from secondary poisoning than are mammals that consume fish.

3.2.9.3 Summary of bioaccumulation

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 7060 l/kg based on total ^{14}C measurements, and this value is used in the assessment. Although this value may contain a contribution from metabolites as well as parent D5, parent-compound analysis indicates that a large proportion of the body burden (83 per cent) was parent compound and so this value is considered appropriate to use in the risk assessment as a realistic worst-case approach. A growth- and lipid-corrected BMF of 3.9 based on total ^{14}C measurements was determined in a fish feeding study and this is also used in the assessment as a realistic worst case.

In summary, the accumulation factors used in the assessment are:

- BCF for fish, 7060 l/kg
- BMF_1 for predators,
- BMF_2 for top predators, 3.9
- BCF for earthworms, 1900 l/kg.

3.3 Environmental concentrations

In this section we outline the predicted concentrations and the available measured concentrations in various environmental compartments.

The predicted concentrations were estimated using EUSES 2.0.3, which implements the methods outlined in the TGD.

The wide uses of silicone compounds in general (some of which may contain trace amounts of the substances of interest) and the use of D5 itself in personal care products mean the environmental samples could have been contaminated during storage and handling in the laboratory and so the measured concentrations may not reflect the actual environmental conditions. For example, Helmig *et al.* (1989) found D5 (and other cyclic oligomeric

siloxanes) in laboratory blank samples from various adsorption tubes used to collect air samples. Pedersen *et al*. (2003) found D5 in blank samples when analysing run-off samples from irrigated fields; this possibly originated from column bleed of vial septa. Similarly, Gasking (1988) reports that breakdown of septa used in gas chromatography could be a source of silicone oligomers and that evaporation apparatus could also be a source of D5 in the laboratory. The compounds were thought to originate from the column coating or the sealing material in the gas chromatographic system used. The analytical problems which may be encountered when analysing silicones were highlighted in a recent poster presentation by Varaprath *et al.* (2005). Therefore, to validate the measured data for use in this risk assessment, it is vital that the responses seen in the laboratory blank samples (and other relevant quality-assurance details) are reported in the original paper to avoid 'false positive' results.

Also relevant is that D5 is a highly volatile substance, particularly from water, and therefore to avoid potential loss from volatilisation care is required during the sample collection, storage, and, in particular, the extraction procedure. The results from recovery experiments are a useful insurance in this respect.

3.3.1 Aquatic compartment (surface water, sediment, and wastewater treatment plant)

3.3.1.1 Predicted environmental concentrations

The predicted concentrations in surface water, sediment, and wastewater are summarised in Table 3.15.

The predicted concentration in water from use of D5 in personal care products by the general public is being investigated using the Geography-referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER)[18] model (Whelan, 2006b). The study is 'work in progress', but the initial findings were made available for this report. Removal of D5 from the water column in the model is assumed to occur via two mechanisms, volatilisation (volatilisation half-life of 6.9 hours was assumed) and deposition of sorbed material to bed sediments (a sedimentation rate constant of 0.0001/h was assumed). Degradation by hydrolysis is not considered. The estimated amount of D5 transferred into the aquatic waste stream is assumed to be around 13.7 mg/person/day, which gives a typical sewage treatment plant influent concentration of around 68 µg/l (in line with available measurements). The model was run for the Aire–Calder catchment and the concentrations estimated immediately downstream of each point source ($PEC_{initial}$) and the average concentration for the catchment downstream of wastewater treatment plants ($PEC_{catchment}$) were estimated (Table 3.16).The estimates in Table 3.16 are in reasonably good agreement with those obtained using EUSES (the estimated influent concentration to the wastewater treatment plant in the EUSES calculation was 60 µg/l). The results also demonstrate the importance of volatilisation in reducing the initial concentration of D5 in the water (the calculations in Table 3.15 assume no volatilisation in the receiving water at the local level and so are analogous to the $PEC_{initial}$ above).

Table 3.15 Predicted concentrations in surface water, sediment, and wastewater treatment plants

Scenario	PEC

[18] Further details are available from http://www.great-er.org/pages/home.cfm. Theseestimates were carried out using the alternative values for the physicochemical properties outlined in Table 1.1.

	Surface water (µg/l)	Sediment (mg/kg wet weight)	Wastewater treatment plant (mg/l)
Production and on-site use as an intermediate	0.52	1.7	1.3×10^{-3}
Off-site use as an intermediate – wet process (non-UK)	0.10	0.33	4.6×10^{-10}
Off-site use as an intermediate – dry process (non-UK)	0.10	0.33	0
Personal care products – formulation – UK sites	0.12	0.39	2.6×10^{-4}
	0.19	0.63	8.2×10^{-4}
	0.10	0.33	2.3×10^{-5}
	0.16	0.53	7.5×10^{-4}
	0.52	1.7	5.2×10^{-3}
	0.16	0.53	7.7×10^{-4}
	0.15	0.48	5.9×10^{-4}
	0.19	0.62	1.1×10^{-3}
	0.11	0.35	8.7×10^{-5}
	0.58	1.9	5.9×10^{-3}
	0.46	1.5	4.4×10^{-3}
	0.28	0.92	2.3×10^{-3}
	0.13	0.44	4.2×10^{-4}
	0.11	0.34	6.6×10^{-5}
	0.10	0.33	1.4×10^{-7}
	0.11	0.37	1.6×10^{-4}
	0.12	0.38	1.9×10^{-4}
	0.48	1.6	4.7×10^{-3}
Personal care products – formulation – generic site (non-UK)[1]	1.6	5.1	0.018
Personal care products – use by general public	0.33	1.1	2.8×10^{-3}
Household products – formulation	0.10	0.33	0
Household products – use	0.11	0.36	1.4×10^{-4}
Industrial/institutional cleaning – use	0.10	0.33	2.0×10^{-9}

Regional	0.10	0.65	

Note: [1]See Appendix B for site-specific calculations for non-UK formulation sites.

Table 3.16 Estimates for D5 concentrations in the Aire–Calder catchment

	$PEC_{initial}$ (µg/l	$PEC_{catchment}$ (µg/l)
Assuming no in-stream removal	0.79	0.35
Assuming sedimentation only	0.75	0.34
Assuming volatilisation only	0.64	0.094
Assuming both sedimentation and volatilisation	0.63	0.093

3.3.1.2 Measured environmental concentrations

Levels of D5 in various water systems in Europe have been studied. Precautions were taken during the sample collection (i.e. by avoiding aeration and/or bubbling of the sample and through the use of sealed containers with no headspace for storage) and analysis to avoid loss through volatilisation (Boehmer and Gerhards, 2003). The analytical method used had a detection limit of 0.02 µg/l. Laboratory blank samples were run at regular intervals. On occasions, traces of D5 were found in the blank samples. In these cases the average blank value was subtracted from the field values, and the detection limit then set as twice the average blank samples. The recovery of the method was in the range 90–140 per cent for D5 concentrations in the range 1–2 µg/l, which was considered acceptable given the low concentrations.

The levels of D5 found in industrial waste-water treatment plants at silicone production sites and municipal wastewater treatment plants are summarised in Tables 3.17 and 3.18, respectively. The concentrations in influent refer to total concentrations (i.e. adsorbed plus dissolved).

Table 3.17 Levels of D5 in silicone industry wastewater treatment plants in Europe (Boehmer and Gerhards, 2003)

Location of silicone producer	**Sampling data**	**D5 concentration (µg/l)**			**Estimated removal in treatment plant (%)**
		Influent	**Effluent**	**Downstream**	
Germany I	January 2001	3120 and 2,900	26.7 and 25.8	<0.02	99

Germany II	7th Feb 2001		6.0	<0.02	
	8th Feb 2001		0.22	<0.02	
	9th Feb 2001		0.32	<0.02	
France	March 2001	3694, 1706, and 365	<0.02[1]	<0.02[1]	>99.9[1]
UK			0.2 and 0.7	0.4 and 0.4	

Note: [1]Effluent and downstream samples may have been taken at different times to the influent samples.

Table 3.18 Levels of D5 in municipal wastewater treatment plants in Europe (Boehmer and Gerhards, 2003)

Wastewater treatment plant	Sampling data	D5 concentration			Estimated removal in treatment plant (%)
		Influent (µg/l)	Effluent (µg/l)	Sewage sludge (mg/kg dry weight)	
Meltenham – UK	September 2000	50.1	0.62	No data	99
Crofton – UK	September 2000	11.2	1.0	No data	91
WWTP 1 – Germany	Spring 2000	8.9	0.5	2.3	94
WWTP 2 – Germany	Spring 2000	4.6	0.1	0.37	98
WWTP 3 – Germany	Summer 2000	1.3, 1.3, and 2.7	No data	0.10	

An unpublished survey of influent, effluent, and removal efficiency of D5 was carried out in four wastewater treatment plants in the USA. A summary of the results is given in IUCLID (2005). The mean influent concentrations at the plants were in the range 1.35–5.91 µg/l and the mean effluent concentrations at the plants were 0.05–0.5 µg/l. The overall removal efficiency at the three treatment plants using activated sludge was around 90 per cent. The overall removal efficiency at the other treatment plant (which used oxidation ditch treatment) was lower, at 60 per cent.

Aramendía *et al*. (1998) detected D5 at concentrations of 0.39 µg/l and 0.098 µg/l in two samples of effluent from a wastewater treatment plant in Córdoba, Spain. The first sample was collected at a time when the plant was working poorly (as a result of a failure in the biological treatment system) and the second sample was collected when the plant was operating correctly. No quality-assurance details are reported.

The levels of D5 in marine-water samples taken from the mouth of the River Mersey (six samples collected in January 2001) and Cardiff Bay (six samples collected in February 2001) were all below the limit of detection (0.02 µg/l for the River Mersey samples and 0.04 µg/l for the Cardiff Bay samples; Boehmer and Gerhards, 2003).

Boehmer and Gerhards (2003) also determined the levels of D5 in river sediments and marine sediments from Europe. The results of these analyses are summarised in Table 3.19.

Table 3.19 Levels of D5 in sediments in Europe (Boehmer and Gerhards, 2003)

Location	Measured level (µg/kg dry weight)[1]	Comment
Freshwater		
River Rhine	12	Sampled at Karlsruhe
	<3	Sampled at Wiesbaden
	Not detected	Sampled at Koblenz
	6	Sampled at Köln
	Not detected	Sampled at Leverkusen
	91	Sampled at Krefeld
	Not detected	Sampled at Emmerich
	Not detected	Sampled at Hollands Diep
Hall Dike Creek	27, 40 and 42	3.5 km downstream of a WWTP[2]
Marine		
River Mersey (mouth)	39, 83, 45, 57, 61, and 33	Six samples collected January 2001
Cardiff Bay	250, 250, 230, 280, 120, and 240	Six samples collected February 2001
Coast of Scotland (LAS St. Abbs)	Not detected	Site previously used for sewage sludge disposal; three samples collected in July 2000
Coast of Scotland (Bell Rock)	Not detected	Site previously used for sewage sludge disposal; six samples collected

Notes: [1]The limit of detection was set at 1 µg/kg dry weight. The limit of quantification was set at three times this limit (i.e. 3 µg/kg dry weight).
[2]WWTP, wastewater treatment plant.

Hankemeier *et al*. (1999) detected D5 in a sample of river water from the River Meuse, but the amount was not quantified.

Law *et al*. (1991) detected, but did not quantify, D5 in samples of unfiltered estuarine water from the River Tyne and River Tees, UK. However, D5 was not detected in estuarine water from other locations around the UK (River Humber, Liverpool Bay, or Plymouth Sound). Precautions were taken to avoid contamination in these analyses, including the analysis of a large number of blank samples.

A survey of the levels of D5 in water and sediment in Sweden was undertaken recently (Kaj *et al.*, 2005). The samples were collected mainly during 2004. The sampling and analytical methods used were designed to avoid both loss of D5 from the sample by volatilisation and contamination of the sample. The levels found in this survey are summarised in Table 3.20. The samples were collected from sites both near to potential industrial point sources and more remote areas, and include both freshwater and coastal sites. However, few details of the potential point sources are given, and it is not clear if D5 was actually being used in the area.

Overall, the levels of D5 in surface water found in this survey appear to be generally low, but relatively few surface water samples were included, and these were generally taken from industrial areas where it was not clear whether or not D5 was being used at the time. D5 was found in only three of the sediment samples at levels up to 190 µg/kg dry weight, but the source of D5 in these samples is unclear.

Table 3.20 Levels of D5 in water and sediment from Sweden (Kaj *et al.*, 2005)

Location	Measured level	Comment
Surface water (µg/l)		
Stenungsund	<0.03	Site near to potential point sources in an industrial area
Stenungsund	<0.03	Site near to potential point sources in an industrial area
Stenungsund	<0.03	Site near to potential point sources in an industrial area
Bay outside Stockvik	<0.03	Site near to potential point sources in an industrial area
Sediment (µg/kg dry weight)		
Ö Gotlandsdjupet	<6	Background site
Ö Öland	<11	Background site
Norrköpingsdjupet	<4	Background site
Stenungsund	<7	Site near to potential point sources in an industrial area
Stenungsund	<7	Site near to potential point sources in an industrial area
Stenungsund	<9	Site near to potential point sources in an industrial area
Bay outside Stockvik	<6	Site near to potential point sources in an industrial area
Bay outside Stockvik	<11	Site near to potential point sources in an industrial area
Bay outside Stockvik	<6	Site near to potential point sources in an industrial area
Bay outside Stockvik	<6	Site near to potential point sources in an industrial area
Lake Bäsingen	<9.3	
Lake Venjan	<23	
Gröpplebäcken	17.2	
Hulingen	<22	
Verserum	<3.4	
Mouth of Emån	<6	
Ivösjön	<29	

Location	Measured level	Comment
Helsingborg	<8	
Hammarsjön	<10	
Storarydsdammen	<14	
Himmerfjärden	190	
St Envättern	<57	
Lake Vänern, Åsfjorden	37	
Lake Vänern, Kattfjorden	<11	
Skuten	26	
Close to a pulp and paper production plant	<7.8	
Roxen	<22	
Wastewater (µg/l)		
Influent to municipal wastewater treatment plants	0.1–1.1	Detected in samples from three out of four sewage treatment plants (detection limit was 0.04 µg/l)
Effluent samples from municipal wastewater treatment plants	0.051	Detected in one out of 12 samples (detection limit was 0.04 µg/l)
Industrial effluent	0.059	Effluent from a pulp and paper production plant
Industrial effluent	<0.03	Effluent from a factory (possibly a chemical plant, but it is not clear what is being manufactured)
Well water from factory site	<0.03	Well water from a factory (possibly a chemical plant, but it is not clear what is being manufactured)
Percolate waters from landfills	<0.04	Not detected in three samples

A survey of the levels of D5 in wastewater (influent and effluent), surface water, and sediment in Nordic countries (including Denmark, Faroe Islands, Finland, Iceland, Norway, and Sweden) was undertaken recently (TemaNord, 2005). The sampling and analytical methods used were designed to avoid both loss of D5 from the sample by volatilisation and contamination of the sample with D5. The samples were collected during 2004 and 2005. The results of the survey are summarised in Table 3.21.

D5 was found in several influent (up to 26 µg/l) and effluent (up to 5.2 µg/l) samples from sewage treatment plants in the survey. In addition, D5 was detected in sediment samples (including marine sediments) at concentrations up to 2000 µg/kg dry weight. The levels of D5 in surface water were found to be generally very low (not detectable).

Table 3.21 Levels of D5 in water and sediment from Nordic countries (TemaNord, 2005)

Sampling location[1]	Concentration
	Water (µg/l)

Sampling location[1]		Concentration
Denmark	Coastal area, Kattegat	<0.02
	Coastal area, innerfjord, Roskilde	<0.02
	Coastal area, Øresund Lynetten, Kobenhavn	<0.02
	Kobenhavn, Lynetten STP influent	26
	Kobenhavn, Lynetten STP effluent	0.063
	Roskilde, Bjergmarken STP influent	24
	Roskilde, Bjergmarken STP effluent	0.092
	Avedöre landfill leachate	<0.04
	Uggelöse landfill leachate	<0.04
Faroe Islands	Torshavn, Sersjantvikin STP effluent	5.2
	Torshavn, Húsarhaga landfill leachate	<0.05
Finland	Ämmässuo, landfill and waste tip leachate	3.9
	Influent to Nokia City Kulloonvuori STP (tyre industry wastewater)	5.3
	Influent to Nokia City Kulloonvuori STP (floor industry wastewater)	0.33
	Treated effluent, Kullonvuori STP	0.48
	Treated effluent, Kullonvuori STP	0.98
	Espoo City Suomenoja STP effluent	0.62
	Helsinki City Vilkinmäki STP effluent	0.29
Iceland	Alfnes landfill runoff water	5.4
	Reykjavik, seawater	<0.03
	Reykjavik, seawater	<0.03
	Reykjavik, seawater	<0.03
	Reykjavik, seawater	<0.03
Norway	Arendal STP influent	5.0
	Arendal STP effluent	0.72
	Lake Bergsjøen (background area)	<0.04
	Lake Røgden (background area)	<0.05
	Outer Oslofjord (coastal background)	<0.04
	Inner Oslofjord (urban area)	<0.04
	Spillhaug landfill runoff water	<0.05
	Bölstad landfill runoff water	<0.04
	Grönmo landfill runoff water	<0.04

Sampling location[1]		Concentration
Sweden	River Nissan (upstream of storm water effluent)	<0.04
	River Nissan (storm water effluent)	<0.04
	River Nissan (downstream of storm water effluent)	<0.04
	Högbytorp landfill (untreated percolate water)	<0.07
	Högbytorp landfill (treated percolate water)	<0.05
		Sediment (µg/kg dry weight)
Denmark	Coastal area, Kattegat	<2
	Coastal area, Øresund, Lynetten	<3
	Coastal area, Roskilde	2000
Faroe Islands	Kaldbakfjordur (influence by pollution from unidentified sources)	<5
Finland	Helsinki, Vakal (Old City Bay – site influenced by historical pollution from a former hazardous waste-combustion plant)	58.0
	Espoo coastal sea area	19.0
Iceland	Sediment 1	7.6
	Sediment 2	7.4
	Sediment 3	39
	Sediment 4	19
Norway	Lake Bergsjøen (background area)	<30
	Lake Bergsjøen (background area)	<30
	Lake Røgden (background area)	<30
	Lake Røgden (background area)	<30
	Leanbukta	12
	Vrengansundet	<5
	Brödrene Sunde Verft	96
Sweden	Gislaved, Nissan (storm water effluent)	1.8
	Gislaved, Nissan (downstream of storm water effluent)	<1
	Gislaved, Nissan (upstream of storm water effluent)	<1
	Stockholm, Essingen	130
	Stockholm, Riddarfjärden	77
	Ö Gotlandsdjupet	<10

Sampling location[1]		Concentration
	Ö Landsortsdjupet	<20

Note: [1]STP, sewage treatment plant.

A follow-up to the TemaNord (2005) study was undertaken by Schlabach *et al*. (2007). This study investigated the levels of D5 in influent and effluent from two sewage treatment plants discharging to the Inner Oslofjord in Norway (Bekkelaget STP and VEAS STP), as well as the levels in water and sediment from the Inner Oslofjord itself. The sampling and analytical methods used were designed to avoid loss of D5 from the sample by volatilisation and contamination of the sample by D5. The samples were collected in September and October 2006. The results are summarised in Table 3.22.

Table 3.22 Levels of D5 in water and sediment from the Inner Oslofjord (Schlabach *et al*., 2007)

Sampling location[1]	Concentration
	Water (µg/l)
Bekkelaget STP influent	9.8
Bekkelaget STP effluent	0.2
VEAS STP influent	12.0
VEAS STP effluent	1.0
Seawater, Bekkelaget	<0.02
Seawater, Lysaker	<0.02
Seawater, Vestfjord/Nesodden	<0.02
Seawater, Færder	<0.02
	Sediment (µg/kg dry weight)
Bekkelagsbassenget	920
Bekkelagsbassenget	690
Lysaker	200
Lysaker	93
Vestfjord/Oslofj	250
Vestfjord/Oslofj	280

Note: [1]STP, sewage treatment plant.

D5 was present in both the influent and effluent from the sewage treatment plants, but was not detectable in seawater. The levels in sediment were highest in the samples from Bekkelagsbassenget (concentration 690–920 µg/kg dry weight), which is near to the Bekkelaget sewage treatment plant.

Paxéus (2000) found D5 at a concentration of 0.1–0.4 µg/l in leachate from three landfill sites (two active landfills and one in operation from 1938 to 1978) in Sweden. No quality-assurance data are reported.

The results of an unpublished survey of the levels of D5 in the influent and effluent of wastewater treatment plants in Canada are reported by Environment Canada, 2008). A total of nine wastewater treatment plants were surveyed. The plants were located in large urban centres in southwestern Ontario and the survey included conventional secondary and tertiary water treatment plants and lagoons. The plants were sampled in October 2005 and in winter 2005. The concentration of D5 found was between 0.49 and 228 µg/l in the influent samples and 1.0–2.3 µg/l in the effluent concentrations. Environment Canada (2008) indicates some evidence for higher influent concentrations in the winter samples (range 8.0–228 µg/l) than in the samples taken in October (range 0.49–57 µg/l), but that this was not so evident in the effluent samples (range 1.0–1.3 µg/l in the October samples and 1.7–2.3 µg/l in the winter samples). No information on the number of samples analysed at each plant is given and no quality-assurance data reported; therefore the significance of the apparent higher concentrations in winter compared with those in autumn (October) is unclear.

The results of a monitoring study to investigate the levels of D5 in sediments and sediment cores from Lake Ontario are reported by Powell and Kozerski (2007) [the same results are also briefly reported in Plotzke (2007)]. Surface sediment samples (upper 5 cm) were collected from five sites (Toronto Harbour, Kinston Basin, Rochester Basin, Mississauga Basin, and Niagara Basin), with sediment cores collected at three of these sites (Rochester, Mississauga, and Niagara basins). D5 was detected at a concentration of 790 µg/kg dry weight (358 µg/kg wet weight) in surface sediment from Toronto harbour, but was not detected in surface sediments from the remaining (more remote) sites or sediment cores (no sediment core was taken from Toronto harbour). The method limit of detection was around 11.9 µg/kg dry weight for D5. The sample collection and analytical methodology used included comprehensive quality-assurance and quality-control procedures to prevent problems from contamination of the samples by D5 or loss of D5 during the analytical procedure.

3.3.1.3 Comparison of measured levels with predicted levels

Monitoring data are available for the levels of D5 in surface water downstream of a silicones production site in the UK. The measured levels found downstream of the plant (around 0.4 µg/l) compare well with the predicted levels of 0.52 µg/l.

Measured data are available for municipal wastewater treatment plants in Europe. These data can be compared with the scenarios that consider the use of D5 by the general public (in particular, use of personal care products and of household products). The available monitoring data from such plants indicate that the influent concentration of D5 is in the range 1–50 µg/l, with the highest level in a plant in the UK. This can be compared with the predicted influent concentrations to the wastewater treatment plant of around 60 µg/l for use of personal care products and 3 µg/l for use of household products. There is, therefore, good agreement between the predicted concentrations for these scenarios and the levels actually found in municipal wastewater treatment plants (although the water solubility of D5 is exceeded in some cases in the influent, based on both measured and predicted values). Similarly, the measured effluent concentrations from such plants are in the range 0.1–5.2 µg/l, which again compares favourably with the effluent concentrations predicted for personal care products (around 2.8 µg/l) and household products (around 0.14 µg/l).

For sediment direct comparison between the predicted and measured concentrations is not possible as the levels predicted depend on the organic carbon content of the sediment and the conversion from wet weight to dry weight requires knowledge of the actual water contents of the sediments. D5 has been found in sediments at some locations in the UK and EU (e.g. concentrations of up to 91 µg/kg dry weight were measured in the River Rhine, up to 250 µg/kg dry weight in Cardiff Bay, and up to 2000 µg/kg dry weight in Nordic countries). Using the default water contents for sediment given in the TGD, concentrations of 0.091, 0.250,

and 2000 mg/kg dry weight are equivalent to concentrations of 0.02, 0.054, and 0.43 mg/kg on a wet weight basis. These are similar to, but slightly lower than, those predicted for the scenarios that relate to the use of D5 by the general public and the regional scenario. However, it is not possible to make a more meaningful comparison directly with the scenarios considered in this assessment as the levels in the areas sampled may be influenced by a number of sources.

Confirmation of the presence of D5 in sediments in the environment is of interest in relation to the general persistence of the substance in the environment. This is considered further in relation to the PBT properties of this substance (see Section 5.5.2).

3.3.2 Terrestrial compartment

3.3.2.1 Predicted environmental concentrations

The predicted concentrations in soil are summarised in Table 3.23.

Table 3.23 Predicted concentrations in soil

Scenario	**PEC**		
	Agricultural soil, 30 day average (mg/kg wet weight)	**Agricultural soil, 180 day average (mg/kg wet weight)**	**Grassland, 180 day average (mg/kg wet weight)**
Production and on-site use as an intermediate	1.3×10^{-5}	1.3×10^{-5}	1.3×10^{-5}
Off-site use as an intermediate – wet process (non-UK)	7.2×10^{-6}	7.2×10^{-6}	7.2×10^{-6}
Off-site use as an intermediate – dry process (non-UK)	9.5×10^{-6}	9.5×10^{-6}	9.5×10^{-6}
Personal care products – formulation – UK sites	7.2×10^{-4}	1.3×10^{-4}	3.1×10^{-5}
	2.3×10^{-3}	3.8×10^{-4}	8.4×10^{-5}
	7.0×10^{-5}	1.8×10^{-5}	9.2×10^{-6}
	2.1×10^{-3}	3.5×10^{-4}	7.6×10^{-5}
	0.014	2.4×10^{-3}	4.8×10^{-4}
	2.1×10^{-3}	3.6×10^{-4}	7.8×10^{-5}
	1.6×10^{-3}	2.8×10^{-4}	6.1×10^{-5}
	3.0×10^{-3}	5.1×10^{-4}	1.1×10^{-4}
	2.5×10^{-4}	4.7×10^{-5}	1.5×10^{-5}
	0.016	2.7×10^{-3}	5.4×10^{-4}
	0.012	2.1×10^{-3}	4.2×10^{-4}
	6.2×10^{-3}	1.0×10^{-3}	2.1×10^{-4}
	1.2×10^{-3}	2.0×10^{-4}	4.6×10^{-5}

Scenario	PEC		
	Agricultural soil, 30 day average (mg/kg wet weight)	**Agricultural soil, 180 day average (mg/kg wet weight)**	**Grassland, 180 day average (mg/kg wet weight)**
	1.9×10^{-4}	3.7×10^{-5}	1.3×10^{-5}
	7.5×10^{-6}	7.2×10^{-6}	7.2×10^{-6}
	4.5×10^{-4}	8.1×10^{-5}	2.2×10^{-5}
	5.3×10^{-4}	9.4×10^{-5}	2.5×10^{-5}
	0.013	2.2×10^{-3}	4.4×10^{-4}
Personal care products – formulation – generic site[1]	0.050	8.3×10^{-3}	1.7×10^{-3}
Personal care products – use by general public	7.7×10^{-3}	1.3×10^{-3}	2.7×10^{-4}
Household products – formulation	7.2×10^{-6}	7.2×10^{-6}	7.2×10^{-6}
Household products – use	3.9×10^{-4}	7.2×10^{-5}	2.0×10^{-5}
Industrial/institutional cleaning – use	7.5×10^{-6}	7.5×10^{-6}	7.5×10^{-6}

Note: [1]See Appendix B for site-specific calculations for non-UK formulation sites.

The regional (steady state) concentrations are:

- agricultural soil, 0.11 mg/kg wet weight
- natural soil, 7.1×10^{-6} mg/kg wet weight
- industrial soil, 7.1×10^{-6} mg/kg wet weight.

The above regional concentrations were estimated assuming the substance was not degradable. As discussed in Section 3.2.3, there is some uncertainty over the actual degradation half-life for D5 in soil. Example calculations assumed a degradation half-life for D5 of six months, one year, and ten years (all at 12°C), and a degradation half-life of 5.7 days at 22°C [equivalent to a half-life of around 13 days at 12°C, based on the analysis of the soil degradation data carried out by Xu, as reported in CES (2005b), see Section 0]. The estimated concentrations are given in Table 3.24 [example calculations are given for one local scenario (personal care products – use by the general public; value given is the 30 day average value) and for the regional scenarios for agricultural soil and natural soil (this latter value is important as it acts as the regional background for the local soil concentrations)].

Table 3.24 Example estimated concentrations of D5 in soils

Half-life at 12°C	Scenario	D5 concentration (mg/kg wet weight)
13 days	Local: personal care products – use	7.2×10^{-3}

	Regional: agricultural soil	1.8×10^{-4}
	Regional: natural soil	1.2×10^{-6}
6 months	Local: personal care products – use	7.7×10^{-3}
	Regional: agricultural soil	1.2×10^{-3}
	Regional: natural soil	1.5×10^{-6}
1 year	Local: personal care products – use	7.7×10^{-3}
	Regional: agricultural soil	1.8×10^{-3}
	Regional: natural soil	1.6×10^{-6}
10 years	Local: personal care products – use	7.7×10^{-3}
	Regional: agricultural soil	6.3×10^{-3}
	Regional: natural soil	1.9×10^{-6}

As this example shows the predicted local concentration in soil is essentially independent of the degradation rate assumed, until a very rapid degradation rate is used. The reason is that at the local level removal by volatilisation is dominant over the relatively short timescale considered in the calculations. However, at the regional level, a steady-state model is used whereby substance that is volatilised from soil can subsequently be re-deposited by wet or dry deposition processes. Therefore, according to this model, re-deposition and degradation of the substance in soil compete with the volatilisation (and degradation in the atmosphere) when longer timescales are considered.

When a rapid rate of degradation for D5 (as may be expected under dry soil conditions) is included in the model, the predicted local concentration is reduced by a factor much less than two from the situation when no degradation in soil is assumed. This is considered in relation to the risk characterisation for the terrestrial compartment.

As discussed in Section 3.1.7.2, the breakdown of PDMS polymers in soil may provide another route of exposure of soil organisms to D5. It is not possible to reliably estimate the amount of D5 in soil from such a process. However, a very rough indication of the potential significance of the process can be made using the approach described here.

Based on the monitoring data of Fendinger *et al.* (1997) a PDMS concentration of 5155 mg/kg sludge is likely to be towards the upper end of the actual PDMS concentrations in sewage sludge (see Section 3.1.7.2). The same approach as that in Section 3.1.7.2 and the emission rate of 0.5 per cent over 25 weeks for cyclic siloxanes and other volatiles from the Lehmann *et al.* (1994) study are used. With the assumptions that D5 accounts for 25 per cent of the cyclic siloxanes and other volatiles and, in this case, that all of the D5 formed initially remains in the soil, a PDMS level of 5155 mg/kg sludge would generate around 6 mg/kg sludge of D5 over the 25 week period, or an input of D5 via sludge into soil of 0.034 mg/kg sludge per day. Using the default sludge application rate given in the TGD (0.5 kg sludge/m^2, depth of agricultural soil 0.2 m, and density of soil 1700 kg/m^3) this input rate can be converted into an equivalent input rate of 0.017 mg/m^2 soil/day or 5×10^{-5} mg/kg wet soil/day. This input can then be treated as a continuous input to soil using the methods outlined in the TGD (or input into the EUSES 2.0.3 program as a daily flux to soil), which then

takes into account the subsequent volatilisation from soil. The resulting PEC for soil (averaged over 30 days) is around 7×10^{-5} mg/kg wet weight (estimated using EUSES 2.0.3). This is well below the predicted regional concentration for D5 in agricultural soil.

3.3.2.2 Measured environmental concentrations

The major route of D5 to soil is likely to be from the spreading of sewage sludge that contains D5 onto agricultural land, so it is relevant to consider the available data on its actual levels in sewage sludge.

D5 has been detected at levels of 0.1–2.3 mg/kg dry weight in samples of sludge from three municipal wastewater treatment plants in Germany (Boehmer and Gerhards, 2003). The samples were collected in spring and summer 2000.

Kaj *et al.* (2005) report the results of a survey of levels of D5 in sewage-sludge samples from Sweden. The sampling and analytical methods used were designed to avoid both loss of D5 from the sample by volatilisation and contamination of the sample with D5. The sewage-sludge samples were collected from the anaerobic chambers of three large municipal sewage treatment plants in Stockholm, Gothenburg, and Borås, 51 further municipal sewage treatment plants from all over Sweden, and one industrial sewage treatment plant. The samples were collected during 2004. D5 was detected in all 54 samples. The levels found ranged between 54 and 54,000 µg/kg dry weight, with median and mean values of 9500 and 11,000 µg/kg dry weight, respectively. D5 was not detected (<28 µg/kg dry weight) in the sewage sludge from an industrial sewage treatment plant associated with a car manufacturer.

A recent paper by Dewil *et al*. (2007) reports that D5 was measured at concentrations up to 30 mg/kg dry weight in samples of secondary sewage sludge from wastewater treatment plants in the UK. The results are taken from an unpublished study by Griffin (2004).

A further study of the levels of D5 in sewage sludge from Nordic countries was published recently (TemaNord, 2005). The samples were collected during 2004 and 2005 and the sampling method and analytical method used were designed to avoid both loss of D5 from the sample by volatilisation and contamination of the sample with D5. The levels of D5 found in the sludge samples were in the range 1.1–89 mg/kg dry weight. Two soil samples from landfill sites were also analysed and the level of D5 was below the limit of quantification (<3 to <5 µg/kg dry weight) in these samples. The results of the study are summarised in Table 3.25.

Table 3.25 Levels of D5 in sewage sludge and soil samples from Nordic countries (TemaNord, 2005)

Sampling location[1]		Concentration (µg/kg dry weight)
Soil		
Faroe Islands	Havnardalur (disused landfill)	<5
	Husarhaga landfill (working landfill)	<3
Sewage sludge		
Denmark	Kobenhavn, Lynetten STP (primary sludge)	27,000

	Kobenhavn, Lynetten (digested sludge)	50,000
Faroe Islands	Torshavn, Sersjantvikin	4300
Finland	Nokia City, Kullonvuori STP (receives wastewater from several industries)	30,000
	Helsinki, Vilkinmäki STP (receives municipal, urban. and industrial wastewater)	21,000
	Espoo, Suomenoja STP (receives wastewater from perfume manufacturer and leachate from a landfill)	89,000
	Pormainen STP (receives municipal wastewater)	31,000
	Porvoo City, Kokonniemi STP (receives urban and industrial wastewater)	25,000
Iceland	Klettegardar STP	1600
	Ananaust STP	1100
Sweden	Skellefteå STP (digested sludge – no industrial inputs)	21,000
	Floda STP	5800
	Ellinge STP (digested sludge – inputs from the food industry)	4500
	Tekniska verket	11,000

Note: [1]STP, sewage treatment plant.

In the follow-up study Schlabach *et al*. (2007) investigated the levels of D5 in sewage sludge from the two sewage treatment plants (Bekkelaget STP and VEAS STP). The sampling and analytical methods used were designed to avoid loss of D5 from the sample by volatilisation and contamination of the sample by D5. The samples were collected in September 2006. The concentration of D5 in sewage sludge at the Bekkelaget STP was 130,000 µg/kg dry weight in inlet sludge and 1900 µg/kg dry weight in outlet sludge. The concentration in sewage sludge at the VEAS STP was 25,000 µg/kg dry weight in inlet sludge and 62,000 µg/kg dry weight in outlet sludge. These concentrations are comparable with those found in the TemaNord (2005) study. The influent and effluent water concentrations were also monitored at these plants, along with sediment concentrations close to the plants. The results of these analyses are summarised in Section 3.3.1.2.

Labban *et al.* (2006) detected D5 in a sample of air dried and powdered (<38 µm) surface soil from the USA. The level found was not stated.

3.3.2.3 Comparison of measured levels with predicted levels

The available data for D5 in sewage sludge show the substance was present at levels of 0.1–2.3 mg/kg dry weight in municipal wastewater treatment plants in Germany, and higher levels of 1.1–130 mg/kg are reported in a recent survey of Nordic countries. The predicted levels of D5 in sewage sludge that results from consumer use in personal care products and household cleaning products are 111 mg/kg dry weight and 5.6 mg/kg dry weight, respectively, which are in reasonably good agreement with, but towards the upper end of, the available measured data. The available levels of D5 measured in soil are all very low, but

details of the sampling locations in relation to the scenarios being considered here are currently unknown.

The lower measured levels in some soil- and sewage-sludge samples compared with the predicted concentrations could indicate that D5 is volatilised from sewage sludge during its collection and treatment (the calculations in EUSES assume that no further removal of D5 occurs once it is adsorbed onto the sludge, which may not be correct for a substance of high volatility). Alternatively, relatively few measured data points are available and the treatment plants for which samples are available are not necessarily those for which the highest D5 concentrations in influent were measured (see Table 3.18 in Section 3.3.1.2; the highest influent concentrations were measured in UK plants, for which the corresponding sewage-sludge levels were not measured). If further volatilisation of D5 during the subsequent handling, transport, and spreading of sewage sludge does occur to a significant extent, this would have implications for the PECs for soil as not all the D5 initially adsorbed onto the sludge during wastewater treatment would be subsequently applied to land. This is considered further in Section 5.2.

3.3.3 Atmospheric compartment

3.3.3.1 Predicted environmental concentrations

The predicted concentrations in the air compartment are summarised in Table 3.26.

Table 3.26 Predicted concentrations in air

Scenario	Annual average PEC (mg/m^3)
Production and on-site use as an intermediate	1.3×10^{-3}
Off-site use as an intermediate – wet process (non-UK)	9.8×10^{-5}
Off-site use as an intermediate – dry process (non-UK)	6.1×10^{-4}
Personal care products – formulation – UK sites	1.0×10^{-4}
	3.5×10^{-4}
	8.8×10^{-5}
	1.2×10^{-4}
	9.7×10^{-5}
	8.8×10^{-5}
	9.9×10^{-5}
	8.8×10^{-5}
	8.6×10^{-5}
	9.9×10^{-5}
	9.6×10^{-5}
	9.1×10^{-5}
	8.7×10^{-5}

Scenario	Annual average PEC (mg/m^3)
	9.0×10^{-5}
	8.6×10^{-5}
	1.1×10^{-4}
	8.6×10^{-5}
	9.6×10^{-5}
Personal care products – formulation – generic site (non-UK)[1]	1.3×10^{-4}
Personal care products – use by general public	9.3×10^{-5}
Household products – formulation	9.1×10^{-5}
Household products – use	8.6×10^{-5}
Industrial/institutional cleaning – use	1.6×10^{-4}
Regional	8.6×10^{-5}

Note: [1]See Appendix B for site-specific calculations for non-UK formulation sites.

3.3.3.2 Measured environmental concentrations

IUCLID (2005) reports the results of two studies in which D5 was measured in biogas from sewage treatment plants in Germany. In the first study the concentration of D5 was in the range ~10–23 mg/m^3 biogas from three plants (Hagmann *et al*., 1999) and in the second study D5 was found in the range ~2.8–9.7 mg/m^3 biogas from two plants (Schweigkofler and Niessner, 1999). These concentrations relate to the concentration in the biogas itself rather than to the resulting concentration in the outdoor air.

A study on the levels of D5 in various air samples in the EU was undertaken by Boehmer *et al*. (2001). The areas sampled included sites close to silicone production and/or use plants in Germany, France, and the UK, inside and around buildings in Germany, cities (Munich and Essen), and a rural area. The analytical method used had a detection limit of around 0.01 µg/m^3. Field blank samples were run at regular intervals. On occasions, traces of D5 were found in the blank analyses. In these cases the average blank value was subtracted from the field values, and the detection limit was then set as twice the average blank value. The recovery of the method was in the range 121–125 per cent for D5 concentrations in the range 0.52– 5.2 µg/m^3, which was considered acceptable given the low concentrations. The results of the analyses are summarised in Table 3.27.

Table 3.27 Levels of D5 in air samples (Boehmer *et al.,* 2001)

Sample type	Total number of samples	D5 concentration (µg/m^3)			
		Minimum	Maximum	Median	90 percentile
Close to silicone plants (six locations)	58	<0.1	20	0.4	13
Inside and around buildings (three locations)	18	<0.1	79.5	0.3	17.5
City areas (two locations)	18	<0.1	0.5	0.2	0.4

Rural area	6	<0.1	0.1	<0.1	<0.1

The levels of D5 in outdoor air in three cities in China (Guangzhou, Macau, and Nanhai) were determined by Wang *et al*. (2001). The samples were all collected between 9:00 am and 2:00 pm over a 20 minute period at a height of 1.2 m above ground. A blank sample was analysed with each batch of samples and the analysis was considered acceptable when none of the target compounds were detected when the zero air test was performed. The sampling sites in Guangzhou included urban mixed areas (32 samples), industrial areas (eight samples), a landfill (12 samples), a wastewater treatment plant (four samples), suburban areas (18 samples), and a forest park (two samples). Sampling sites in Macau include the Macau Peninsula (ten samples), a university campus (two samples), and a coastal beach (two samples). The sampling sites in Nanhai included three small industrial towns and a rural area (a total of 24 samples). D5 was found at only trace concentrations in a few of the samples (it was not detected in most of the samples). Details of the number of positive samples or detection limit of the method used are not given in the paper.

Shields *et al.* (1996) investigated the levels of D5 in indoor air in three types of commercial buildings located throughout the USA. The buildings sampled included 50 telecommunications offices that were sparsely occupied, nine data centres with variable occupancy, and 11 densely occupied administrative offices. The samples were collected using passive diffusion samplers over a six week period from 18th March until 29th April 1991. Outdoor samples were collected from around the buildings at the same time. A total of three indoor and three outdoor samples were analysed at each location. Field blank and laboratory blank samples were also included. Occasionally D5 was found in the blanks (the source of this contamination was thought to be from the carbon-impregnated Teflon pad associated with the passive sampler). Where this occurred, corrections were applied based on the field blanks. The absolute detection limit for the analytical method used was around 0.05 $\mu g/m^3$, but the limit of quantification was set to 0.5 $\mu g/m^3$ (and any substance below this level was deemed to be 'not detectable'). The relative standard deviation of the method was typically 6–10 per cent. D5 was found in 49 out of 50 telecommunications offices at a geometric mean level of 7.0 $\mu g/m^3$, all nine data centres at a geometric mean level of 26.1 $\mu g/m^3$, and all 11 administration offices at a geometric mean level of 39.6 $\mu g/m^3$. D5 was also found in 64 per cent of the 70 outdoor air samples at a geometric mean level of 0.5 $\mu g/m^3$. A positive correlation between the D5 level in indoor air and the occupancy of the office was found, which indicates that use of D5 in personal care products was a major source of D5 in office air. The levels in outdoor air were thought to reflect the influence of the building exhaust on the air levels close to the building rather than the general background concentration in air.

The effect of ventilation rate on the concentrations of D5 in an office building was studied by Hodgson *et al*. (2003). The building used was a call centre in the San Francisco Bay area of the USA. The office was on two floors and had a total floor area of 4600 m^2 (divided into four interior zones that ranged in size from 840 m^2 to 1460 m^2. The total occupant density during the study was around five people per 100 m^2. Duplicate air samples (both indoor and outdoor) were collected over a five hour period on seven days during the thirteen-week experimental period. The ventilation rate of the building was varied for each sampling occasion via the mechanical ventilation system of the building. Blank samples were collected on a weekly basis. The concentration of D5 measured in indoor air was in the range 1.1–7.4 ppb (~17–112 $\mu g/m^3$) with a geometric mean of 2.5 ppb (~38 $\mu g/m^3$). The concentration of D5 in outdoor air was in the range 0.03–0.08 ppb (~0.5–1.2 $\mu g/m^3$), with a geometric mean of 0.05 ppb (~0.8 $\mu g/m^3$). The concentration of D5 measured in the indoor air was generally inversely related to the ventilation rate. Based on these data the geometric mean emission rate of D5 from the building to outdoor air was estimated as around 220 µg/m/h (range 114–330 µg/m/h). Assuming that the main source of D5 in indoor air was from the use of personal

care products, an average per occupant emission rate for D5 of ~3–6 mg/h was estimated from the data.

TemaNord (2005) and Kaj *et al.* (2005) report the results of an unpublished survey of indoor air levels from 400 homes in Sweden. D5 was found in 250 homes at a concentration between 0.5 and 79.4 µg/m^3 (the mean of the detected concentrations was 9.7 µg/m^3).

A survey of the levels of D5 in air in Sweden was recently undertaken (Kaj *et al.*, 2005). The samples were collected during 2004 and 2005. The sampling and analytical methods used were designed to avoid contamination of the sample by D5. The levels found in this survey are summarised in Table 3.28. Although some of the samples were collected from industrial areas, few details of the potential point sources are given, and it is not clear if D5 was actually being used in the area sampled.

Table 3.28 Levels of D5 in air from Sweden (Kaj *et al.*, 2005)

Location	Measured level (ng/m^3)	Comment
Råo	9	Background site
Råo	30	Background site
Råo	170	Background site
Stenungsund	37	Site near to potential point sources in an industrial area
Stenungsund	95	Site near to potential point sources in an industrial area
Stenungsund	140	Site near to potential point sources in an industrial area
Stockvik	19	Site near to potential point sources in an industrial area
Stockvik	40	Site near to potential point sources in an industrial area
Hudiksvallsgatan	54	Urban area of Stockholm
Hudiksvallsgatan	<13	Urban area of Stockholm
Hudiksvallsgatan	<13	Urban area of Stockholm

A further survey of the levels of D5 in air in Nordic countries was carried out by TemaNord (2005). The samples were collected in 2004 and 2005. The sampling and analytical methods used were designed to avoid contamination of the sample with D5. The results of the survey are summarised in Table 3.29. The concentration of D5 found was in the range 0.05–19 µg/m^3. The concentrations were generally elevated in urban areas and in areas close to sewage treatment plants compared to other areas.

Table 3.29 Levels of D5 in air from Nordic countries (TemaNord, 2005)

Sampling location		Concentration (µg/m^3)
Denmark	Jagtvejen	0.19
	Bjergmarken STP	1.3
	Sepstrup Sande	0.95
	H.C. Ørsted Institute	0.31
Faroe Islands	Torshavn, downtown	0.93
	Sersjantvikin STP	2.4
Finland	Nokia City STP	1.3
	Espoo landfill	0.23
Iceland	Reykjavik, urban	1.5
	Reykjavik, urban	1.6
	Reykjavik, urban	0.73

Sampling location		Concentration (µg/m^3)
	Reykjavik, urban	0.13
Norway	Bekkelaget STP	19
	Bekkelaget STP	12
	Manglerud	2.5
	Oslo central station	0.89
Sweden	Högbytorp landfill (windside)	0.06
	Högbytorp landfill (windside)	0.05
	Mossarps recycling site	0.29
	Mossarps recycling site	0.52
	Göteborg, Kapellplatsen	0.10
	Göteborg, Kapellplatsen	0.05
	Stockholm, Hudiksvallsgatan	0.18
	Stockholm, Hudiksvallsgatan	0.20

Environment Canada (2008) gives the results of an unpublished study of the air levels of D5 in the Great Lakes region. The samples were collected during February and March 2006. A total of 18 outdoor samples were collected from urban and rural areas in Ontario and D5 was found in 'almost all of the samples' at concentrations <1 µg/m^3, with one sample from an urban area of Toronto showing a level of ~20.5 µg/m^3. Environment Canada (2008) also indicates that the widespread detection of D5 in ambient air could, in part, be a result of sample contamination as the methodology for to determine trace concentrations in air is still under development.

D5 is also reported to occur in office-dust samples (Wilkins *et al*., 1993). The samples of floor dust were collected by vacuum cleaner from nine city-hall buildings in Denmark. The samples were separated into the particle (<1 mm) and fibre fractions and the presence of siloxanes was analysed by a thermal desorption technique. D5 was detected in three of the nine samples analysed (the actual levels were not given). No quality-assurance data were reported in the paper.

3.3.3.3 Comparison of measured levels with predicted levels

From the data available the measured concentrations of D5 in air close to silicone plants are up to around 20 µg/m^3 (median 0.4 µg/m^3). The predicted concentration for the UK site (1.3 µg/m^3) fits within this range.

At a regional level the concentrations of D5 found in city areas in the EU are generally up to around <0.1–2 µg/m^3, with the levels in rural areas being up to a maximum of around 0.2 µg/m^3. These data, although slightly higher than predicted, compare reasonably well with the predicted levels for use of D5 by the general public (personal care products – 0.09 µg/m^3, household products – 0.09 µg/m^3) and regional sources (0.09 µg/m^3), particularly when it is considered that the levels in cities reflect the contributions from all uses by the general population. This indicates that all significant sources and removal mechanisms of D5 in air appear to be accounted for in the assessment.

Several studies also investigated the levels of D5 inside buildings. These levels are generally higher than found in the outdoor environment. However, such levels are not relevant to this assessment.

3.3.4 Food chain exposure

3.3.4.1 Predicted environmental concentrations

The predicted concentrations in fish for secondary poisoning are summarised in Table 3.30 (the methodology used in the TGD to estimate the concentrations in earthworms is not applicable to substances with very high log K_{ow} values).

For the concentration in fish, a measured BCF of 7060 l/kg is used in the calculations. The TGD indicates that, as well as the bioconcentration, the BMF for fish should be considered in the calculation of PEC for secondary poisoning, i.e.

$$PEC_{oral} = PEC_{water} \times BCF \times BMF$$

In addition, the TGD suggests that the BMF value should be expressed on a lipid-normalised basis. As discussed in Section 3.9, a growth-corrected kinetic BMF of 3.9 on a lipid-normalised basis was determined for D5 in a fish feeding study and this value is used for the calculation here.

The above equation given in the TGD is not appropriate when considering actual data from laboratory feeding studies as the default BMF values used in the TGD method are not necessarily equivalent to those obtained in feeding studies. One of the intentions in the TGD is to model the concentration in fish that results from simultaneous exposure via both water and food, which is represented by Figure 3.4 and Equation (3.1).

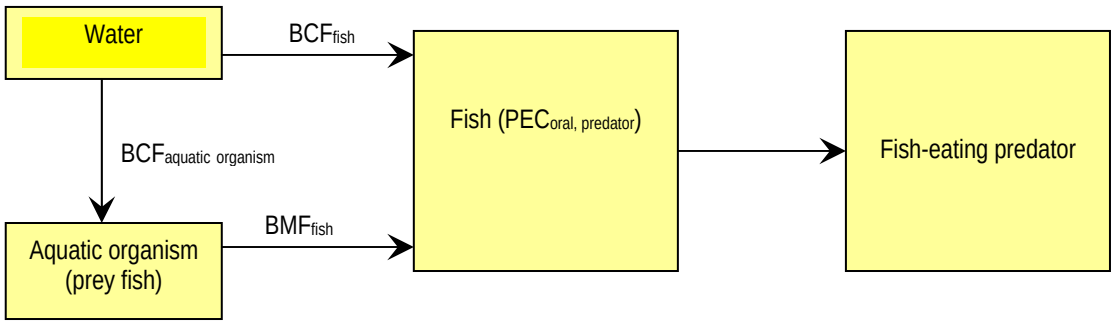


Figure 3.4 Model of the concentration in fish from simultaneous exposure via both water and food

$$PEC_{oral,\ predator} = (PEC_{water} \times BCF_{aquatic\ organism} \times BMF_{fish}) + (PEC_{water} \times BCF_{fish}) \quad (3.1)$$

Assuming that the 'aquatic organism' in the food chain is also a fish, this equation simplifies to:

$$PEC_{oral,\ predator} = PEC_{water} \times BCF_{fish} \times (1 + BMF_{fish}) \quad (3.2)$$

Using a BMF of 3.9 for D5, the resulting PECs in predatory fish using Equation (3.2), and assuming that 50 per cent of the exposure comes from local sources and 50 per cent regional sources (the default assumption in the TGD) are shown in Table 3.30. There has been no formal discussion (or agreement) of this method of calculation at Technical Committee Meeting level. Also, this calculation should not be confused with the possibility of increasing concentrations found in sequential trophic levels (i.e. biomagnification) in the environment because the simplistic calculations used here neglect that the prey fish and/or organism in the calculations will also have a contribution from food. The calculation here simply takes into account that any given aquatic organism can be exposed both via water and food, and does not give any indication of possible trends in concentrations with increasing trophic level.

Table 3.30 Predicted concentrations in fish

Scenario	PEC in fish[1,2] (mg/kg)
Production and on-site use as an intermediate	9.4
Off-site use as an intermediate – wet process (non-UK)	3.5
Off-site use as an intermediate – dry process (non-UK)	3.5
Personal care products – formulation – UK sites	3.8
	4.8
	3.5
	4.3
	9.4
	4.4
	4.1
	4.7
	3.6
	10
	8.6
	6.0
	4.0
	3.5
	3.5
	3.6
	3.7
	8.9
Personal care products – formulation – generic site (non-UK)[3]	24
Personal care products – use by general public	7.4
Household products – formulation	3.5
Household products – use	3.7
Industrial/institutional cleaning – use	3.5

Notes: [1]The calculations for fish include a BMF of 3.9.

[2]Using the regional water concentration alone (0.10 µg/l) the concentration in fish would be 3.5 mg/kg wet weight. Therefore many of the predicted local concentrations are dominated by the regional contribution.

[3]See Appendix B for site-specific calculations for non-UK formulation sites.

The predicted concentrations in food for human consumption are summarised in Table 3.31 (no BMF value is used in these calculations, in line with the methodology outlined in the TGD).

Table 3.31 Predicted concentrations of D5 in food for human consumption

Scenario	PEC							Estimated total daily intake (mg/kg bw/day)
	Fish[1] (mg/kg)	Root crops (mg/kg)	Plant leaves (mg/kg)	Meat (mg/kg)	Milk (mg/kg)	Drinking water (mg/l)	Air (mg/m^3)	
Production and on-site use as an intermediate	3.2	2.7×10^{-3}	5.7×10^{-4}	0.016	5.1×10^{-3}	5.6×10^{-5}	1.3×10^{-3}	5.7×10^{-3}
Off-site use as an intermediate – wet process (non-UK)	0.71	1.6×10^{-3}	4.2×10^{-5}	1.2×10^{-3}	3.9×10^{-4}	1.3×10^{-5}	9.8×10^{-5}	1.2×10^{-3}
Off-site use as an intermediate – dry process (non-UK)	0.71	2.1×10^{-3}	2.6×10^{-4}	7.4×10^{-3}	2.3×10^{-3}	1.3×10^{-5}	6.1×10^{-4}	1.4×10^{-3}
Personal care products – formulation – UK sites	0.83	0.027	4.3×10^{-5}	1.3×10^{-3}	4.0×10^{-4}	1.5×10^{-5}	1.0×10^{-4}	1.6×10^{-3}
	1.2	0.083	1.5×10^{-4}	4.2×10^{-3}	1.3×10^{-3}	2.2×10^{-5}	3.5×10^{-4}	2.6×10^{-3}
	0.72	3.8×10^{-3}	3.8×10^{-5}	1.1×10^{-3}	3.5×10^{-4}	1.3×10^{-5}	8.8×10^{-5}	1.2×10^{-3}
	1.1	0.076	5.4×10^{-5}	1.6×10^{-3}	5.0×10^{-4}	1.9×10^{-5}	1.2×10^{-4}	2.2×10^{-3}
	3.1	0.51	4.2×10^{-5}	1.4×10^{-3}	4.5×10^{-4}	5.6×10^{-5}	9.7×10^{-5}	8.0×10^{-3}
	1.1	0.078	3.8×10^{-5}	1.1×10^{-3}	5.6×10^{-4}	1.9×10^{-5}	8.8×10^{-5}	2.2×10^{-3}
	0.98	0.060	4.2×10^{-5}	1.3×10^{-3}	4.0×10^{-4}	1.7×10^{-5}	9.9×10^{-5}	2.0×10^{-3}
	1.2	0.11	3.8×10^{-5}	1.2×10^{-3}	3.7×10^{-4}	2.2×10^{-5}	8.8×10^{-5}	2.7×10^{-3}
	0.75	0.010	3.7×10^{-5}	1.1×10^{-3}	3.4×10^{-4}	1.3×10^{-5}	8.6×10^{-5}	1.3×10^{-3}
	3.5	0.58	4.2×10^{-5}	1.5×10^{-3}	4.7×10^{-4}	6.2×10^{-5}	9.9×10^{-5}	8.9×10^{-3}
	2.8	0.44	4.1×10^{-5}	1.4×10^{-3}	4.4×10^{-4}	5.0×10^{-5}	9.6×10^{-5}	7.1×10^{-3}
	1.8	0.22	3.9×10^{-5}	1.2×10^{-3}	3.9×10^{-4}	3.1×10^{-5}	9.1×10^{-5}	4.2×10^{-3}
	0.91	0.043	3.7×10^{-5}	1.1×10^{-3}	3.5×10^{-4}	1.6×10^{-5}	8.7×10^{-5}	1.8×10^{-3}
	0.74	8.0×10^{-3}	3.9×10^{-5}	1.1×10^{-3}	3.6×10^{-4}	1.3×10^{-5}	9.0×10^{-5}	1.3×10^{-3}
	0.71	1.6×10^{-3}	3.7×10^{-5}	1.1×10^{-3}	3.4×10^{-4}	1.3×10^{-5}	8.6×10^{-5}	1.2×10^{-3}
	0.78	0.018	4.9×10^{-5}	1.4×10^{-3}	4.5×10^{-4}	1.4×10^{-5}	1.1×10^{-4}	1.4×10^{-3}
	0.80	0.020	3.7×10^{-5}	1.1×10^{-3}	3.5×10^{-4}	1.4×10^{-5}	8.6×10^{-5}	1.5×10^{-3}
	2.9	0.47	4.1×10^{-5}	1.4×10^{-3}	4.4×10^{-4}	5.2×10^{-5}	9.6×10^{-5}	7.4×10^{-3}
Personal care products – formulation – generic site (non-UK)[21]	9.2	1.8	5.4×10^{-5}	2.3×10^{-3}	7.1×10^{-4}	1.6×10^{-4}	1.3×10^{-4}	0.025[1]
Personal care products – use by general public	2.3	0.28	4.0×10^{-5}	1.3×10^{-3}	4.1×10^{-4}	4.1×10^{-5}	9.3×10^{-5}	5.4×10^{-3}

Scenario	PEC							Estimated total daily intake (mg/kg bw/day)
	Fish[1] (mg/kg)	Root crops (mg/kg)	Plant leaves (mg/kg)	Meat (mg/kg)	Milk (mg/kg)	Drinking water (mg/l)	Air (mg/m^3)	
Household products – formulation	0.71	1.6×10^{-3}	3.9×10^{-5}	1.1×10^{-3}	3.6×10^{-4}	1.3×10^{-5}	9.1×10^{-5}	1.2×10^{-3}
Household products – use	0.79	0.015	3.7×10^{-5}	1.1×10^{-3}	3.5×10^{-4}	1.4×10^{-5}	8.6×10^{-5}	1.4×10^{-3}
Industrial/institutional cleaning – use	0.71	1.6×10^{-3}	6.9×10^{-5}	2.0×10^{-3}	6.3×10^{-4}	1.3×10^{-5}	1.6×10^{-4}	1.2×10^{-3}
Regional	0.71	25	3.7×10^{-5}	5.3×10^{-3}	1.6×10^{-3}	4.1×10^{-5}	8.6×10^{-5}	0.14

Notes: [1]The calculations for fish follow the methods given in the TGD and do not include a BMF.

[12] Value given is estimated using a generic (default) scenario. Site-specific information is available for non-UK formulation sites (see Appendix B), and using this data the predicted daily human intake would be in the range 1.2×10^{-3} to 0.012 mg/kg bw/day.

3.3.4.2 Measured environmental concentrations

A survey of the levels of D5 in fish from Sweden was recently undertaken (Kaj *et al.*, 2005). The samples were collected during 2004 and 2005. The sampling and analytical methods used were designed to avoid both loss of D5 from the sample by volatilisation and contamination of the sample. The levels found in this survey are summarised in Table 3.32. The Fish muscle only was analysed in this study and D5 was not detected in any of the samples. Although some of the samples were collected from industrial areas, few details of the potential point sources are given, and it is not clear if D5 was actually being used in the area sampled. Sediment samples were also analysed from several of these locations. The sediment levels are reported in Section 3.3.1.2.

Table 3.32 Levels of D5 in fish muscle from Sweden (Kaj *et al.*, 2005)

Location	Species	Measured level (µg/kg wet weight)	Comment
V. Fladen	Herring	<5	Background site
Ångsskärsklubb	Baltic herring	<5	Background site
Landsort	Baltic herring	<5	Background site
Stenungsund	Eelpout (females)	<5	Site near to potential point sources in an industrial area
	Eelpout (males)	<5	
	Eelpout (juveniles)	<5	
Sundsvall bay	Baltic herring	<5	Site near to potential point sources in an industrial area
	Herring	<5	
	Salmon	<5	
Lake Bäsingen	Not given	<5	
Lake Venjan	Not given	<5	
Ivösjön	Perch	<5	
Helsingborg	Flounder	<5	
Hammarsjön	Flounder	<5	
Storarydsdammen	Perch	<5	
Himmerfjärden	Perch	<5	
St Envättern	Perch	<5	
Lake Vänern, Åsfjorden	Perch	<5	
Lake Vänern, Kattfjorden	Perch	<5	

The results of a further survey of the levels of D5 in freshwater and marine fish from Europe were briefly reported in a slide presentation (EVONIK Industries, 2007). 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 River, and one species from the Baltic Sea close to Estonia. For the freshwater fish, D5 was not detectable in three species from Lake Nipgård, Denmark, and two out of three species from Lake Constance, Germany. D5 was detected in an eel sample from Lake Constance, but the level was below the limit of quantification of the analytical method (<30 µg/kg wet weight). In contrast to this, D5 was present at concentrations between 150 and 2600 µg/kg wet weight in fish from the River Rhine, Germany (close to the Dutch Border). The results, including details of the species analysed, are summarised in Table 3.33. Few other details of this study are currently available.

Table 3.33 Levels of D5 in freshwater and marine fish from Europe (EVONIK Industries, 2007)

Location	Species	Measured level (µg/kg wet weight)	Comment
River Rhine, Germany (close to Dutch border)	Roach (*Rutilus rutilus*)	1000	
	Ide (*Leuciscus idus*)	150–700	Two samples analysed.
	Eel (*Aguilla aguilla*)	1600–2600	Two samples analysed. Various tissues were also analysed separately. The levels found were 150–180 µg/kg in liver, 700 µg/kg in skin, 2500 µg/kg in fatty tissue, and 2000 µg/kg in muscle.
Lake Constance, Germany	Lake white fish (*Coregonus* spp.)	<10	
	Alpine charr (*Salvelinus umbla*)	<10	
	Eel (*A. aguilla*)	<30	Detectable, but below the limit of quantification of the analytical method.
Lake Nipgård, Denmark	Perch (*Perca fluviatilis*)	<10	
	Roach (*R. rutilus*)	<10	
	Pike (*Esox lucius*)	<10	
North East Atlantic	Atlantic salmon (*Salmo solar*)	<10	Sample from Denmark fjord.
	Cod (*Gadus morhua*)	<10	
	Common sole (*Solea solea*)	<10	
	Pilchard (*Sardina pilcharus*)	<10	
	Redfish (*Sebastes marinus*)	<10	
	Wolffish (*Anarhichas lupus*)	<10	
	Mackerel (*Scomber scombrus*)	<10	
	Plaice (*Pleuronectes platessa*)	<10	
	Monkfish (*Lophius piscatorius*)	<10	
	Lemon sole (*Microstomus kitt*)	<10	
	Pollock (*Pollachius virens*)	<10	
Baltic Sea (close to mouth of Odra River, Germany)	Eel (*A. aguilla*)	<10	
	Flounder (*Platichthys flesus*)	<10	
	Turbot (*Psetta maxima*)	<10	
	Perch (*Pe. fluviatilis*)	<10	
	Pike-perch (*Stizostedion lucioperca*)	<10	
	Pike (*E. lucius*)	<10	
Baltic Sea, Estonia	Pike-perch (*S lucioperca*)	<10	

Kaj *et al.* (2005) also determined the levels of D5 in 49 samples of human breast milk. The detection limit for D5 in these samples was 2 µg/l, and D5 was found in eight of the samples at a concentration of 2.1–4.5 µg/l.

TemaNord (2005) reports levels of D5 of <5–2200 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 a few background samples show detectable levels. The sampling and analytical methods used were designed to avoid loss of D5 from the sample by volatilisation and contamination of the sample by D5. The samples were generally collected between 2002 and 2004 (fish and marine mammals) or 2000 and 2005 (birds eggs). The full results of this survey are summarised in Table 3.34.

In the follow-up study Schlabach *et al*. (2007) investigated the levels of D5 in biota from the Inner Oslofjord in Norway [where the highest concentration of D5 was found in cod liver in the TemaNord (2005) study]. The samples investigated included common mussels, flounder fillet, flounder liver, cod liver, and cod stomach content (mainly krill, shrimp, and small crabs). The sampling and analytical methods used were designed to avoid loss of D5 from the sample by volatilisation and contamination of the sample by D5. All samples were collected between September and November 2006. The mussels were immersed in clean water for one hour prior to analysis to allow detrital material to depurate. The levels found are summarised in Table 3.35.

D5 was found in all the biota samples analysed. The highest levels found were in cod liver, where the concentrations (~1500–2000 µg/kg wet weight) were comparable with those found in cod liver from the same area in the TemaNord (2005) survey (2200 µg/kg wet weight; sample collected in 2004). The results also suggest that biomagnification could be occurring as the concentrations (on both a wet-weight basis and lipid-weight basis) in cod liver are generally higher than those found in organisms lower down the food chain. However, the levels in stomach content of cod are similar to, or slightly lower than, those in cod when compared on a lipid-weight basis (e.g. the average of the three stomach content samples is around 4400 µg/kg lipid compared with the average cod liver concentration of 7200 µg/kg lipid). As only very few samples were analysed in this study, and many of these were from different areas, it is difficult to draw firm conclusions either way on the biomagnification potential of D5 from these data.

Table 3.34 Levels of D5 in biota from Nordic countries (TemaNord, 2005)

Sample type and location				**Concentration (µg/kg wet weight)**
Marine fish	Denmark	Roskildefjord	Three eelpout, liver	<5
		Øresund	Three flounder, liver	52
		North Sea	Three flounder, liver	<5
		Wadden Sea	Three flounder, liver	33
	Faroe Islands	Mylingsgrunnurin	Nine cod, liver	<5
		Kaldbaksfjøröur	Ten sculpin, liver	<5
		Kaldbaksfjøröur	19 flatfish (dab), liver	<5
	Norway	Lista/Farsund	16 cod, liver	26
		Indre Sørfjord	Ten cod, liver	61
		Ulsteinvik	Five cod, liver	46
		Indre Oslofjord	Four cod, liver	2200
Freshwater fish	Faroe Islands	Lake A Myranar	Ten Arctic char, liver	<5
		Lake A Myranar	Seven brown trout, liver	<5
	Finland	Old City Bay, Helsinki	Two pike, liver	20
		Old City Bay, Helsinki	Two pike, liver	33
		Old City Bay, Helsinki	Two pike, liver	84
		Cold Water Bay, Helsinki	Two pike, liver	22
		Guard Village Bay, Helsinki	Two pike, liver	6.5[1]
	Norway	Lake Mjøsa	Five vendance, liver	21
	Sweden	River Nissan, Skepshult	One pike, liver	<5
		River Nissan, Rydöbruk	One pike, liver	<5

Sample type and location				Concentration (µg/kg wet weight)
Marine mammals	Denmark	Coastal area, Øresund	Five seals, blubber	24
		Samsø	Five seals, blubber	20
		Limfjorden	Five seals, blubber	17
		Hesselø	Five seals, blubber	22
	Faroe Islands	Sandangeröi	Ten pilot whales, blubber	10 [1]
		Gøtu	Ten whiteside dolphins	<5
	Iceland		Five common porpoise	<5
Seabird eggs	Faro Islands	Skúvoy	Ten fulmar eggs	<5
		Koltur/Skúvoy	Ten black guillemot eggs	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
		Viöareiöi	One fulmar egg	<5
	Sweden	Söderskäretskan	One herring gull egg	<5
		Svartlögafjorden	One herring gull egg	<5
		Svartlögafjorden	One herring gull egg	<5
		Svartlögafjorden	One herring gull egg	<5
		Svartlögafjorden	One herring gull egg	<5
		Svartlögafjorden	One herring gull egg	<5

Note: [1]Concentrations are above the limit of detection, but below the limit of quantification.

Table 3.35 Further study of the levels of D5 in biota from the Inner Oslofjord (Schlabach *et al*., 2007)

Sample	Location	Concentration	
		µg/kg wet weight	µg/kg lipid
Common mussel	Færder	5.6	244
	Gressholmen	8.7	1624
	Ormøya	3.3	337
Flounder liver	Frognerkilen	27.1	172
Flounder fillet	Frognerkilen	3.4	248
Cod liver (each sample is a pooled sample from five individual fish)	Nesodden/Vestfjord	1503	9607
	Nesodden/Vestfjord	1491	6011
	Nesodden/Vestfjord	1979	5943
Cod stomach content	Nesodden/Vestfjord	22.9	1289
	Nesodden/Vestfjord	85.3	4269
	Nesodden/Vestfjord	149.3	7637

A preliminary screening study of the levels of D5 in mussels from the Southern North Sea was carried out by Boehmer *et al*. (2007). The main purpose of the study was to develop methodologies to collect, transport, prepare, and analyse mussel tissue samples for cyclic VMSs. The methodology was developed to prevent contamination with D5, and to prevent loss of D5, during the collection and analytical procedure. Around 30–50 blue mussels (*Mytilus edulis*) were collected from the intertidal areas from sites at Rømø and Ho Bugt (Denmark), Norderney (Germany), Ameland (the Netherlands), and Ambleteuse and Cap Gris Nez (France). Samples of sediment (three samples of the top 5 cm from each location) and surface water (from shallow puddles) were also collected at the same locations as the mussels. The mussels were placed in clean water for 24–40 hours prior to analysis for

sediment particles to be purged from the mussels. Samples of mussels (total weight 10 g, each sample consisting of 2–6 individuals) were then analysed. The method detection limit was 6.6 µg/kg, and the method limit of quantification was 19.5 µg/kg. In all, a total of 23 samples were analysed. The levels found (corrected for the levels of D5 found in laboratory blank samples) 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 reported were in the range 8.8–19.3 µg/kg), and above the method limit of quantification in four samples (the concentrations reported were in the range 24.7–33.1 µg/kg).

A survey of the levels of D5 in livers of seabirds from Bjørnøya (Svalbard; 74°30´N, 19°01´E) was 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 glaucous gulls were randomly selected for analysis of D5. D5 was found in all of the ten samples analysed at a concentration of between 32.2 µg/kg and 68.8 µg/kg wet weight.

D5 was identified in drinking water from New Orleans and Cincinnati (USEPA, 1992). No details of the levels found are given.

3.3.4.3 Comparison of measured levels with predicted levels

Relatively few data are available for the measured levels of D5 in biota. D5 is not detectable in many of the fish samples, birds' eggs, and bird liver samples analysed. However, D5 was detected at concentrations up to 2200 µg/kg wet weight in livers of some marine and freshwater fish, and up to 24 µg/kg wet weight in blubber of marine mammals (seals and whales). Another survey reports levels up to 2600 µg/kg wet weight in freshwater fish from the River Rhine, but found that D5 was not detectable in marine fish. A recent survey also found D5 in livers of glaucous gulls at a concentration of up to 69 µg/kg wet weight.

The predicted levels of D5 for secondary poisoning in fish appear to be generally higher than the measured data. There may be several explanations for this. For example, it may be that the PECs for water are overestimated, the samples were taken from locations away from point sources of release, and/or the use of a BMF of 3.9 in the calculation for D5 is inappropriate. The most relevant data with which to compare the PECs are probably the recent data available for fish from the River Rhine, as these are likely to be influenced by local sources of release. The levels found in this survey are up to 2600 µg/kg wet weight, which is comparable to, but slightly lower than, the PECs predicted in fish for the majority of the local scenarios (PECs are generally in the range 3500–10,000 µg/kg wet weight excluding the generic scenario for formulation of personal care products).

3.3.5 Marine compartment

3.3.5.1 Predicted environmental concentrations

The predicted concentrations relevant for the marine environment are summarised in Table 3.36. The calculations assume that the emissions to wastewater are not treated in a wastewater treatment plant (this is the default assumption for the marine risk assessment in the TGD). An exception is for scenarios in which site-specific information is available that shows the effluent from the site does pass through a wastewater treatment plant and the

personal care products use (personal and household products) scenarios (where the wastewater treatment plant is the local emission source).

Similar to the situation for secondary poisoning in Section 3.3.4.1, the methodology in the TGD was modified to allow the actual BMF data from the feeding study to be used. The intention in the TGD is to model the concentration in fish that results from simultaneous exposure via both water and food in a simplified food chain. An example scheme that can utilise the available food uptake data is presented in Figure 3.5. This scheme differs from that in the TGD, in which the top predator could be a predatory mammal or bird that feeds on other marine mammals or birds (a different equation needs to be constructed for such food chains). However, the scheme in Figure 3.5 does allow the available food uptake data for D5 by fish to be utilised in an extended food chain.

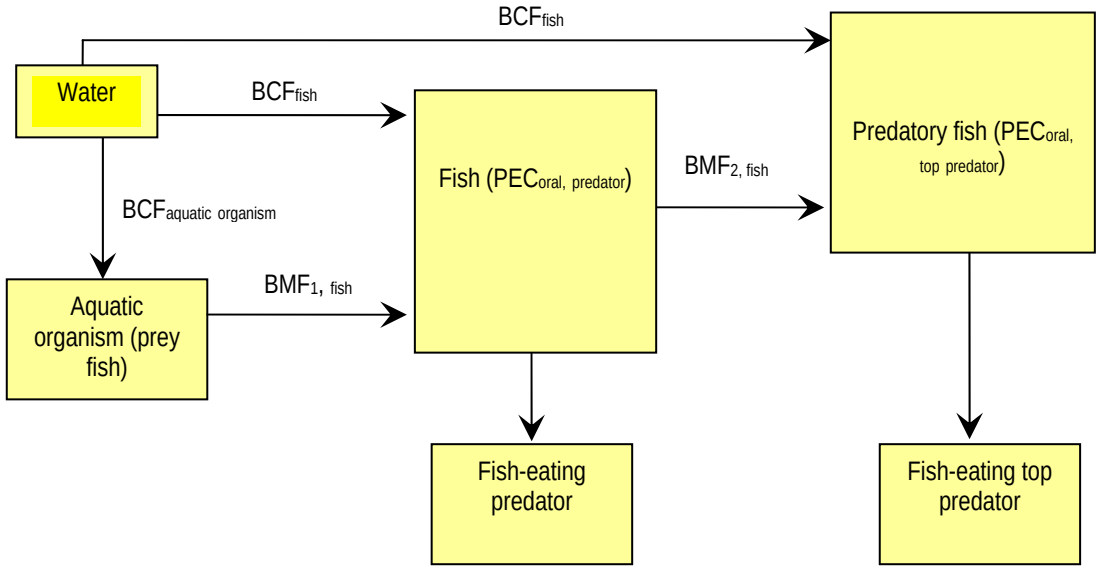


Figure 3.5 Model of the concentration in fish from simultaneous exposure via both water and food in a simplified food chain

Assuming that the 'aquatic organism' in the food chain is also a fish, the appropriate equations for this scheme are:

$$PEC_{oral,\ predator} = (PEC_{water} \times BCF_{aquatic\ organism} \times BMF_{1\ fish}) + (PEC_{water} \times BCF_{fish}) \quad (3)$$

$$PEC_{oral,\ top\ predator} = (1 + BMF_{1,\ fish}) \times (1 + BMF_{2,\ fish}) \times BCF_{fish} \times PEC_{water} \quad (3.4)$$

Using a BMF of 3.9, as before, for both BMF_1 and BMF_2, the resulting PECs for predators and top predators using Equations 3.3 and 3.4, respectively, are shown in Table 3.36. These calculations still assume that 50 per cent of the exposure comes from local sources and 50 per cent from regional sources for predators, and that 10 per cent of the exposure comes from local sources and 90 per cent from regional sources for top predators (the TGD defaults).

Table 3.36 Predicted concentrations relevant for the marine environment

Scenario	PEC

	Water (µg/l)	Sediment (mg/kg wet weight)	Predators[1] (mg/kg)	Top predators[1] (mg/kg)
Production and on-site use as an intermediate	0.020	0.067	0.49	1.8
Off-site use as an intermediate – wet process (non-UK)	9.8×10^{-3}	0.032	0.34	1.7
Off-site use as an intermediate – dry process (non-UK)	9.8×10^{-3}	0.032	0.34	1.7
Personal care products – formulation – UK sites	0.012	0.039	0.37	1.7
	0.017	0.054	0.34	1.8
	0.010	0.033	0.34	1.7
	0.016	0.052	0.43	1.8
	0.052	0.17	0.94	2.3
	0.016	0.053	0.43	1.8
	0.015	0.048	0.41	1.7
	0.019	0.061	0.47	1.8
	0.011	0.034	0.35	1.7
	0.058	0.19	1.0	2.3
	0.046	0.15	0.86	2.2
	0.028	0.092	0.60	1.9
	0.013	0.043	0.39	1.7
	0.010	0.034	0.35	1.7
	9.8×10^{-6}	0.032	0.34	1.7
	0.011	0.036	0.36	1.7
	0.011	0.037	0.36	1.7
	0.048	0.16	0.88	2.2
Personal care products – formulation – generic site (non-UK)[2]	3.2	10	45	45
Personal care products – use by general public	0.033	0.11	0.74	2.1
Household products – formulation	9.8×10^{-3}	0.032	0.34	1.7
Household products – use	0.011	0.036	0.36	1.7
Industrial/institutional cleaning – use	9.8×10^{-3}	0.032	0.34	1.7
Regional	9.8×10^{-3}	0.063		

Notes: [1]For both predators and top predators the value for BMF_1 and BMF_2 is 3.9.
[2]See Appendix B for site specific calculations for non-UK formulation sites.

3.3.5.2 Measured environmental concentrations

The available measured levels of D5 in marine water are given in Section 3.3.1.2. Only relatively few data are available, but these show that the levels in marine water taken from the mouth of the River Mersey and from Cardiff Bay were below the detection limit (0.2 and

0.04 µg/l, respectively). D5 was, however, found in marine sediment samples at concentrations of 0.033–0.083 mg/kg dry weight (mouth of River Mersey) and 0.12–0.25 mg/kg dry weight (Cardiff Bay). More recent data from Nordic countries show D5 in marine sediments at concentrations up to 2000 µg/kg dry weight, but it was generally not detectable in marine waters.

The available monitoring data for marine biota are given in Section 3.3.4.2. D5 was detected at concentrations up to 2200 µg/kg wet weight in livers of some marine fish, and up to 24 µg/kg wet weight in blubber of marine mammals (seals and whales). In contrast, D5 was not detected in seabirds' eggs.

3.3.5.3 Comparison of measured levels with predicted levels

Relatively few data are available on the levels of D5 in marine waters. As discussed in Section 3.3.1.3 levels of D5 of 0.25 mg/kg dry weight are equivalent to a concentration of around 0.054 mg/kg on a wet-weight basis using the default value for the water content of sediment from the TGD. This level is reasonably consistent with some of the values predicted. However, recent monitoring data from Nordic countries show a higher level of 2 mg/kg dry weight (equivalent to 0.43 mg/kg wet weight) in marine sediment. It is not possible to make a more meaningful comparison directly with the concentrations predicted in this assessment as it is not always clear how the areas sampled relate to the scenarios considered in this assessment.

For the marine biota, the higher levels measured in fish livers (up to 2200 µg/kg wet weight) appear to be of a similar order of magnitude to the concentrations predicted in the food for predators and top predators, but the predicted concentrations relate to whole-body concentrations rather than concentrations in specific organs. Although D5 was found in some samples of fish, a large proportion of the samples had no detectable D5 present. Again, it is not possible to make a more meaningful comparison of the predicted and measured levels as it is not clear how the areas sampled relate to the scenarios considered in this assessment.

4 Effects assessment: Hazard identification and dose (concentration) – response (effect) assessment

4.1 Aquatic compartment (including sediment)

4.1.1 Toxicity to fish

The acute toxicity to fish of D5 is summarised in Table C1 (short-term studies) and (long-term studies) in Appendix C.

4.1.1.1 Short-term studies

The acute toxicity of D5 to carp (*Cyprinus carpio*) was determined in an unpublished study, some details of which are given in IUCLID (2005). The test was carried out using a water-accommodated fraction prepared by stirring D5 (at a loading rate of 1 g/l) with tap water for 18 hours and then filtering the solution. The test was carried out under semi-static conditions (a fresh-water-accommodated fraction solution was prepared each day). No mortality was seen over the 96 hour test when the fish were exposed to the water-accommodated fraction directly. IUCLID (2005) indicates that the homogeneity and stability (over 24 hours) of the test solutions prepared in this way were not reproducible and so there are large uncertainties over the actual concentrations the organisms were exposed to over the course of this study. Therefore, the results of this test are of limited use for this risk assessment.

IUCLID (2005) reports the results of three unpublished, prolonged (14 day) acute studies with rainbow trout (*O. mykiss*).

The first test was carried out using an open flow-through system in which D5 was dosed into the water (as a solution in acetone) every 27 seconds to maintain a constant nominal concentration of 5 mg/l. No mortality was seen in this test. The nominal concentrations used were well above the water-solubility limit of D5 and so a substantial amount of the D5 would be present as undissolved material or emulsions and/or suspensions. Therefore, although there are some uncertainties as to the actual true (dissolved) exposure concentration in this test, these results are probably best interpreted as that D5 shows no toxic effects at the limit of solubility in the test-system used.

The second 14 day acute-toxicity test again used a flow-through system, but in this test the highest concentration tested was below the water-solubility limit of D5, and the exposure concentrations were verified by analytical measurements. D5 was added to the test system as a solution in acetone. The flow rate used was 90 ml/minute (as the volume of the test vessels was 9.6 l, this flow rate gave around 36 volume changes per day). No treatment-related mortality was seen in the test (no mortality was seen at 2.1, 3.1, and 16 µg/l, 10 per cent mortality was seen at 5.0 µg/l, and 15 per cent mortality was seen at 8.6 µg/l; the control mortality was 10 per cent in the control and 5 per cent in the solvent control) and so the 14d-LC_{50} was >16 µg/l (the highest concentration that could be tested).

The third study was a flow-through one in which a single concentration of D5 of 2.4 µg/l was used. This study was carried out in a sealed system to prevent loss of D5 through volatilisation. No treatment-related effects were seen in the test.

Taken overall, the available acute- and prolonged acute-toxicity data show that D5 is not acutely toxic at concentrations up to its water-solubility limit over time periods of up to 14 days.

4.1.1.2 Long-term studies

The long-term toxicity of D5 to fish was investigated as part of an unpublished 35 day bioconcentration study with fathead minnows (*P. promelas*; IUCLID, 2005; Drottar, 2005). The test was carried out according to OECD guideline 305 using a flow-through system at 22°C. The water used in the test was dechlorinated municipal water with a pH of 6.3–7.6 and a hardness of 99–134 mg/l as $CaCO_3$. The substance tested was ^{14}C-labelled D5 with a radiochemical purity of 98.48 per cent. Two exposure concentrations were used, and the concentrations were verified by total radioactivity measurements. The mean measured concentrations (± standard deviation) during the 35 day exposure period were 1.1 ± 0.11 and 15 ± 0.60 µg/l. A co-solvent (dimethylformamide at a concentration of 0.1 ml/l) was also used (a solvent control was run). The dissolved oxygen concentration remained at ≥5.2 mg/l throughout the test. No acute effects (e.g. mortality) and no overt signs of sub-lethal toxicity were seen in this test, either during the 35 day exposure period or the 70 day depuration period (during which the fish were not exposed to D5). The overall mortality seen in the test was 7.6 per cent in the control, 12 per cent in the 1.1 µg/l treatment group, and 4.2 per cent in the 15 µg/l treatment group. The no observed effect concentration (NOEC) was therefore given as ≥15 µg/l. Further details of the bioconcentration study are reported in Section 3.2.9.

Similar to above, no mortalities were seen in the 28 day bioconcentration study by Annelin and Frye (1989) with D5 in rainbow trout (see Section 3.2.9.1 for further details). For mortality a 28 day NOEC of 5.8 µg/l can be derived from this study (IUCLID, 2005).

A further indication of the possible long-term toxicity of D5 to fish is obtained from the recent study to investigate the uptake of D5 from food (Dow Corning, 2006b). Briefly, rainbow trout (*O. mykiss*) with an average weight of 1.2 g at the start of the test were fed a diet that contained 458 mg/kg of D5 for 35 days (this was followed by a 42 day depuration period in which the fish were fed a clean diet). One fish died during the study, but this was not thought to be treatment related. All other fish appeared normal and healthy during the study. Full details of the methodology used in this study are reported in Section 3.2.9. Therefore, based on these data, a concentration of D5 of 458 mg/kg in the diet had no adverse effects on the survival of rainbow trout.

Although the results from the Dow Corning (2006b) study cannot be compared directly with the results of the available toxicity studies using water exposure, it is possible to make an indirect comparison. The steady-state concentration of D5 found in the uptake part of the feeding study was around 102 mg/kg wet weight (see Section 3.2.9). Given that the fish BCF for D5 is around 5250 l/kg an internal concentration in fish of 102 mg/kg wet weight is expected to occur after a water-only exposure of 102/5250 = 0.019 mg/l, which is close to, but slightly above, the water solubility of D5 (0.017 mg/l). Therefore, based on this calculation, no effects on mortality are expected to occur after long-term exposure to concentrations of D5 up to its water-solubility limited.

Importantly, the long-term fish tests reported above are actually bioconcentration and accumulation tests, and the only endpoints investigated in the original test reports were mortality and visual inspection for overt signs of toxicity. In addition, fish from the control and treatment groups were sacrificed at regular intervals in the studies, which means that the exposed populations decrease with time. Therefore the test cannot be compared directly with

standard long-term toxicity tests, such as the fish early life-stage test. Although these data indicate that D5 does not cause mortality to fish over long-term exposure to concentrations below its solubility limit, the results need to be treated with caution as some important toxicological endpoints were not considered.

Although not considered in the original test reports, both the Drottar (2005) and Dow Corning (2006b) studies include information on the weights of fish during the study. These data are analysed to determine whether any effects on growth can be seen in the studies. The sample size of the weight data was generally small [typically four data points per treatment group at each sampling interval for the Drottar (2005) study and six data points per treatment group at each sampling interval for the Dow Corning (2006b) study], and so the Drottar (2005) data in particular generally show a higher variability than might be expected in a study purposely designed to investigate growth. In addition, the Drottar (2005) study used effectively adult fish that generally showed only a small amount of growth over the study. Therefore the power of this analysis to detect any small changes in growth is probably limited. The growth data are summarised in Table 4.1.1(Drottar, 2005) and

Table 4.2 (Dow Corning, 2006b). The analysis of the fish-weight data shows no apparent effect of on growth from exposure to D5 in these accumulation studies.

Table 4.1.1 Analysis of growth (weight) data from the bioconcentration study with *Pimephales promelas* [raw data taken from Drottar (2005)]

Sampling time (days)	Fish fresh weights (g, mean ± standard deviation)		
	Control group	1.1 µg/l treatment group	15 µg/l treatment group
Uptake phase			
0	1.233 ± 0.188	1.461 ± 0.364	1.314 ± 0.192
3	1.157 ± 0.173	1.052 ± 0.317	1.122 ± 0.225
7	1.488 ± 0.195	1.342 ± 0.314	1.147 ± 0.090
14	1.312 ± 0.230	1.206 ± 0.342	1.264 ± 0.338
21	1.462 ± 0.257	1.268 ± 0.240	1.518 ± 0.281
28	1.021 ± 0.141	1.679 [1] ± 0.087	1.518 ± 0.409
35	1.425 ± 0.334	1.343 ± 0.168	1.343 ± 0.264
Depuration phase			
36	1.254 ± 0.258	1.126 ± 0.240	1.457 ± 0.300
38	1.471 ± 0.293	1.726 ± 0.192	1.404 ± 0.415
42	1.531 ± 0.492	1.701 ± 0.294	1.230 ± 0.156
45	1.670 ± 0.241	1.416 ± 0.215	1.378 ± 0.269
49	1.123 ± 0.385	1.145 ± 0.221	1.322 ± 0.282
56	1.318 ± 0.361	1.289 ± 0.103	1.082 ± 0.264
63	1.496 ± 0.340	1.468 ± 0.323	1.369 ± 0.096
70	1.305 ± 0.233	1.174 ± 0.279	1.565 ± 0.307
84	1.380 ± 0.210	1.305 ± 0.241	1.307 ± 0.385
105	1.661 ± 0.310	1.503 ± 0.358	1.233 ±0.148

Note: [1]Statistically significantly different from control group at p = 0.05 level. As the weight of the exposed population was actually higher than the control population it can be concluded that this difference was not of toxicological significance.

Table 4.2 Analysis of growth (weight) data from the bioconcentration study with *Oncorhynchus mykiss* [raw data taken from Dow Corning (2006b)]

Sampling time (days)	Fish fresh weights (g, mean ± standard deviation)	
	Control group	Treatment group (fed D5 at 458 mg/kg food during uptake phase)
Uptake phase		
1	1.244 ± 0.242	1.286 ± 0.233
3	1.364 ± 0.196	1.356 ± 0.428
7	1.876 ± 0.276	1.861 ± 0.268
10	1.959 ± 0.491	1.763 ± 0.419
14	2.094 ± 0.254	2.132 ± 0.200
21	2.804 ± 0.629	2.801 ± 0.301
35	4.326 ± 0.470	4.821 ± 0.799
Depuration phase		
36	5.062 ± 0.871	4.726 ± 1.102
37	4.839 ± 0.622	5.007 ± 0.872
39	5.859 ± 1.599	5.559 ± 0.961
42	5.882 ± 0.927	4.938 ± 0.409
49	7.077 ± 1.090	7.037 ± 1.474
63	11.681 ± 4.038	9.420 ±1.223
77	16.250 ± 2.983	13.487 ± 1.021

Overall, the available long-term toxicity data for D5 suggest that no mortality or effects on growth of fish are expected over long-term exposure to concentrations below its solubility limit. However, the available studies have limitations, and results from such studies cannot be compared directly with the results from more standard long-term toxicity test such as a fish early life-stage study. Some uncertainty remains over the potential for D5 to cause adverse effects in fish over long-term exposure. Given the high BCF for D5 in fish, and the recent results from the fish feeding study that indicate a long depuration half-life in the liver of fish, this is an important gap in the database for D5. This is considered further in Section 4.1.9 in relation to the predicted no effect concentration (PNEC) for D5 and in Section 5.5.2 in relation to the PBT assessment for D5.

4.1.2 Toxicity to aquatic invertebrates

The toxicity of D5 to aquatic invertebrates is summarised in

Table C3 (short-term studies) and Table C4 (long-term studies) of Appendix C.

4.1.2.1 Short-term studies

The results from three unpublished short-term toxicity studies with *Daphnia magna* are reported in IUCLID (2005).

The first study is a flow-through study that used five concentrations of D5. The test substance was added to the media as a solution in acetone. The nominal D5 concentrations tested were 2.2, 3.7, 6.1, 10, and 17 µg/l, but the mean measured concentrations found in these treatments during the test were 2.1, 1.6, 1.8, 2.5, and 2.9 µg/l, respectively, which indicates that only a very narrow range of exposure concentrations were actually tested. No treatment-related effects on the *Daphnia* were seen in this study and so the 48 hour 50 per cent effect concentration (EC_{50}) was given as >2.9 µg/l.

In the second (24 hour) study the 24 hour EC_0 and 24 hour EC_{100} were reported to be 4.4 mg/l and >400 mg/l, respectively. The very high concentrations that appear to have been used in this study mean the results are of limited use in this risk assessment.

The third study (48 hour static one) used the water-accommodated fraction derived from stirring 1 g/l of D5 with tap water for 18 hours, followed by filtering the solution. This stock solution was then diluted (nine parts stock solution in ten parts total volume) for use in the test. No treatment-related effects were seen in this test. However, the actual exposure concentrations in this test are unclear, and the test system was static, which means loss by volatilisation may have occurred. Insufficient detail is reported in IUCLID (2005) to validate these parts of the test.

Taken overall, the 48 hour EC_{50} for D5 with *D. magna* is >2.9 µg/l.

4.1.2.2 Long-term studies

The long-term toxicity of D5 to *D. magna* was determined in an unpublished study, full details of which are reported in IUCLID (2005). The test was carried out under static renewal conditions (the test solution was renewed every 24 hours) using sealed vials with no headspace to minimise loss of D5 from volatilisation. The substance tested was ^{14}C-labelled D5 with a radiochemical purity of 100 per cent. A total of five exposure concentrations were tested (the time-weighted mean measured concentrations were determined as 1.0, 1.7, 3.5, 7.2, and 15 µg/l). A control and solvent control (acetone at a concentration of 0.1 ml/l) were also used. No significant (p = 0.05) differences were seen in the response of the two control groups, and no significant differences were seen between any of the treatment groups and control groups for parent survival (95 per cent the pooled controls; 100 per cent in all treatment groups), mean cumulative number of offspring released per female (146 in the pooled controls, 138–150 in the treatment groups), or growth of the parent [as measured by both mean body length (4.99 mm in the pooled controls, 4.99–5.05 in the treatment groups) and dry weight (1.12 mg in the pooled controls, 1.15–1.20 in the treatment groups)]. Therefore the 21 day NOEC from this study is ≥15 µg/l (the highest concentration tested).

4.1.3 Toxicity to aquatic algae and plants

Two unpublished algal toxicity studies were carried out with D5, details of which are given in IUCLID (2005). The first test was an OECD 201 test with *Pseudokirchneriella subcapitata*. The test was carried out using sealed containers with no headspace (sodium bicarbonate was added to the test medium to ensure sufficient algal growth; the control response was satisfactory). A single test concentration of D5 was used (the initial mean measured concentration was 12 µg/l) and the test substance was added to the medium as a solution in

acetone. No effects were seen on either growth rate or biomass. The 72 hour NOEC was therefore determined as ≥12 µg/l. This result is based on the initial measured concentration of D5 in the test. No information on concentrations of D5 at other time points during the test was given.[19]

The second test was with *Scenedesmus subspicatus.* This test used a water-accommodated fraction derived from stirring 1 g/l of D5 with tap water for 18 hours, followed by filtering the solution. This stock solution was then diluted (nine parts stock solution in ten parts total volume) for use in the test. No treatment-related effects were seen. However, the actual exposure concentrations in this test are unclear, and the test system appears to have been an open static system, which means loss by volatilisation may have occurred. Insufficient detail is reported in IUCLID (2005) to allow these parts of the test to be validated.

4.1.4 Quantitative structure–activity relationships

Estimates for the toxicity of D5 were generated from the measured log K_{ow} value (log K_{ow} = 8.03) using the equations outlined in the TGD. The estimates obtained are summarised in Table 4.3. The equivalent estimates using a log K_{ow} of 5.2 are also given in Table 4.3.

Table 4.3 Estimates for the toxicity of D5 generated from log K_{ow} 8.03 and log K_{ow} of 5.2

	Toxicity test	**log K_{ow} = 8.03**	**log K_{ow} = 5.2**
Fish	96 hour LC_{50}	2.3×10^{-3} mg/l	0.57 mg/l
	28–32 day NOEC	1.1×10^{-4} mg/l	0.038 mg/l
Daphnids	48 hour LC_{50}	4.2×10^{-4} mg/l	0.20 mg/l
	16 day EC_{50}	1.9×10^{-5} mg/l	0.018 mg/l
Green algae	72–96 hour EC_{50}	2.0×10^{-4} mg/l	0.14

The equations in the TGD are applicable to chemicals that act by non-polar narcosis and are well validated. The relevant validation statistics are[*n* is the number of chemicals used to derive the quantitative structure–activity relationships (QSAR) equation, R^2 is the correlation coefficient (coefficient of determination), Q^2 is the cross-validated correlation coefficient, and s.e. is the standard error of estimate]:

- fish, 96 hour log LC_{50} = –0.85 × log K_{ow} – 1.39 mol/l (n = 58, R^2 = 0.94, Q^2 = 0.93, s.e. = 0.36);
- fish, 28–32 day log NOEC = –0.90 × log K_{ow} – 2.30 mol/l (n = 27, R^2 = 0.92, Q^2 = 0.91, s.e. = 0.33);
- daphnids,48 hour log EC_{50} = – 0.95 × log K_{ow} – 1.32 mol/l (n = 49, R^2 = 0.95, Q^2 = 0.94, s.e. = 0.34);
- daphnids, 16 day log NOEC = –1.05 × log K_{ow} – 1.85 mol/l (n = 10, R^2 = 0.97, Q^2 = 0.95, s.e. = 0.39);
- green algae, 72–96 hour log EC_{50} = –1.00 × log K_{ow} – 1.23 mol/l (n = 10, R^2 = 0.93, Q^2 = not determined, s.e. = 0.17).

[19] Environment Canada (2008) indicates that the concentration had fallen to ~2 µg/l at the end of the test. This would give a mean exposure concentration over the 96 hour period of 7 µg/l.

The range of log K_{ow} values to which the equations are applicable are not given in the TGD, but it is questionable whether these estimation methods are valid for a substance with a log K_{ow} value of 8.03 and so they are not considered further here.

The toxicity of D5 to aquatic organisms was also estimated using the USEPA EPI (v3.12) software. This software estimates the toxicity from the log K_{ow} value (a calculated log K_{ow} of 5.71 was used, as the equations were developed using predicted rather than measured log K_{ow} values and this predicted log K_{ow} for D5 lies within the validity range of most of the methods) using various QSARs (the QSARs for neutral organics were used – these are reported to be applicable to non-reactive, non-ionisable compounds such as alcohols, ketones, ethers, alkyl halides, aryl halides, aromatic hydrocarbons, halogenated aromatic and aliphatic hydrocarbons, and sulfides and disulfides). The results are given in Table 4.4.

Table 4.4 Estimates for the toxicity of D5 generated from log K_{ow} 5.71 using USEPA EPI (v3.12) software

	Toxicity test	**log K_{ow} = 5.71**
Fish	96 hour LC_{50}	0.089 mg/l (freshwater)
	96 hour LC_{50}	0.12 mg/l (saltwater)
	14 day LC_{50}	0.29 mg/l
	30 day Chv[1]	0.021 mg/l
Daphnids	48 hour LC_{50}	0.12 mg/l
	16 day EC_{50}	0.032 mg/l
Mysid shrimp	96 hour LC_{50}	0.0018 mg/l
Green algae	96 hour EC_{50}	0.096 mg/l
	96 hour Chv	0.082 mg/l

Note [1]Chronic value, which most probably represents the geometric mean of the lowest observed concentration (LOEC) and the no observed effect concentration (NOEC).

The relevant validation statistics for the EPI (v3.12) methods are [*n* is the number of chemicals used to derive the QSAR equation and R^2 is the correlation coefficient (coefficient of determination)]:

- fish, 96 hour log LC_{50} (freshwater) = –0.94 × log K_{ow} + 1.75mmol/l (*n* = 60, R^2 = 0.94, applicable to log K_{ow} up to 5.0);
- fish, 96 hour log LC_{50} (saltwater) = –0.73 × log K_{ow} + 0.69 mmol/l (*n* = 37, R^2 = 0.66, applicable to log K_{ow} up to 5.0);
- fish, 14 day log LC_{50} = –0.871 × log K_{ow} + 1.87 mmol/l (*n* = 50, R^2 = 0.98, applicable to log K_{ow} up to 8.0);
- fish, 30 day log Chv = –0.87 × log K_{ow} + 0.72 mmol/l (*n* = 20, R^2 = 0.91, applicable to log K_{ow} up to 8.0);
- daphnids, 48 hour log LC_{50} = –0.91 × log K_{ow} + 1.72 mmol/l (*n* = 19, R^2 = 0.99, applicable to log K_{ow} up to 5.0);
- daphnids, 16 day log EC_{50} = –0.72 × log K_{ow} + 0.05 mmol/l (*n* = 5, R^2 = 0.99, applicable to log K_{ow} up to 8.0);

- mysid shrimp, 96 hour log LC_{50} = –1.25 × log K_{ow} + 1.83 mmol/l (n = 17, R^2 = 0.71, applicable to log K_{ow} up to 5.0);
- green algae, 96 hour log EC_{50} = –0.885 × log K_{ow} + 1.466 mmol/l (n = 7, R^2 = 0.91, applicable to log K_{ow} up to 6.4);
- green algae, 96 hour log Chv = –0.634 × log K_{ow} – 0.036 mmol/l (n = 7, R^2 = 0.99, applicable to log K_{ow} up to 8.0).

The water solubility of D5 is around 0.017 mg/l and so these predicted toxicity values are all above the water solubility of the substance, with the exception of mysid shrimp and the chronic values for fish and daphnids (these latter values are very close to the water solubility). The predictions for mysid shrimp are generally not consistent with those obtained for fish, daphnids, and algae [and the predictions for mysid shrimp for the related substance D4 are not in agreement with the known acute toxicity of that substance to mysids (see Environment Agency, 2008) and the log K_{ow} value used for D5 in the prediction is outside the stated validity range of the method] and so the reliability of this estimate is uncertain.[20] Overall, the available estimates for toxicity suggest that D5 will not be toxic to aquatic organisms at concentrations up to its water solubility, and are in agreement with the available experimental data for D5.

4.1.5 Overall summary of standard endpoint toxicity data

The available acute, prolonged acute, and chronic toxicity data for D5 show that it does not cause toxic effects at concentrations up to its water solubility. This finding is supported by the results of QSAR analysis.

However, the available long-term fish-toxicity data do not consider possible sensitive life stages (the tests are not comparable with a fish early life stage test, for example). Given the high BCF value for fish D5 and the recent results from the fish feeding study that indicate a long depuration half-life in liver of fish, this is an important gap in the database for D5. The available QSAR estimates point to the NOEC for this type of study being close to, but slightly above, the actual water solubility of D5.

4.1.6 Endocrine disruption

No data are available for investigations into the effects of D5 on the endocrine system in aquatic organisms.

4.1.7 Wastewater treatment plant micro-organisms

The 3 hour EC_{50} for D5 within domestic activated sludge was reported as >2000 mg/l in an unpublished OECD 209 activated sludge respiration inhibition test (IUCLID, 2005).

[20] Details of the chemicals included in the training set for the mysid shrimp QSAR are given in Clements *et al.* (1988). As well as neutral organics, it appears that several pesticides, including an organophosphorous insecticide (leptophos) and a pyrethroid insecticide (fenvalerate), were included in the chemicals used to construct this QSAR. This, therefore, casts further doubt on the applicability of this QSAR to D5.

4.1.8 Toxicity to sediment organisms

The toxicity of D5 to *Ch. riparius* is reported in an unpublished study (Putt, 2003). The details of the study are also summarised in IUCLID (2005).

The substance tested was ^{14}C-labelled D5 mixed with unlabelled D5, which had a purity of 99.35 per cent. The test sediments were prepared by firstly adding the appropriate amounts of a solution of both the labelled (as a solution in acetone) and unlabelled D5 (as a neat liquid) to 75 g of alpha-cellulose and then mixing for five minutes with a glass rod. The alpha cellulose was then added to a mixture of 300 g of clay and 1125 g of premoistened sand and mixed for ten minutes (this mixture corresponds to the artificial sediment used in OECD test guideline 219). This mixture was added to the replicated test vessels. The sediment had an organic carbon content of 2 per cent, a pH of 7.2, and a particle distribution of 79 per cent sand, 4 per cent silt, and 17 per cent clay.

The test vessels used were 600 ml beakers. The prepared sediment (95 g dry weight, to give a 1.5 cm deep layer) and overlying water (300 ml, to give a 6 cm deep layer) were added to the beakers 24 hours prior to the start of the test. The ratio of sediment to water was 1:4. The initial water level in the beaker was marked to evaluate evaporation and each test vessel was covered with a clear plastic plate to minimise evaporation and to trap the emerging midges. The water was gently aerated (1–3 bubbles per second) throughout the experiment. At the start of the test, 20 midge larvae were added to each replicate test vessel.

A total of 11 replicate exposure vessels were used for each treatment and control. Five nominal D5 test concentrations (45, 100, 220, 500, and 1100 mg/kg dry weight) were prepared in this way, along with a solvent control sediment. The actual concentrations of D5 present in the sediments were determined on days zero, ten, and 28 of the study. The mean measured concentrations were 13, 30, 73, 180, and 580 mg/kg dry weight based on day zero and ten analyses, and 12, 30, 69, 180, and 570 mg/kg dry weight based on day zero, ten, and 28 analyses. These data show that, although the actual concentrations were much lower than the nominal concentrations (presumably as a result of volatile loss of D5 during the sediment spiking procedure used), they actual concentrations were stable during the course of the study.

The larval survival and larval growth were evaluated after ten days exposure. After 28 days exposure the midge emergence and midge development rate were determined. The results for these endpoints are summarised in Table 4.5 and the derived data in Table 4.6.

Table 4.5 Effects of D5 on *Chironomus riparius* (Putt, 2003)

Mean exposure concentration (mg/kg dry weight)		Endpoints determined at day ten		Endpoints determined at day 28		
Days 0–10	Days 0–28	Larval survival (%)	Mean larval wet weight (mg)	Emergence (%)	Mean development rate	
					Males	Females
13	12	100	5.59	90	0.0697	0.0627
30	30	97	5.65	91	0.0695	0.0630
73	69	98	4.77	83	0.0688	0.0628
180	180	97	4.44 [1]	89	0.0659 [1]	0.0622
580	570	27 [1]	1.36 [1]	18 [1]	0.0528 [1]	0.0573 [1]
Control		95	5.04	85	0.0694	0.0610
Solvent control		98	5.44	89	0.0684	0.0611
Pooled control		97	5.24	87	0.0689	0.0610

Note: [1]Statistically significant difference (p = 0.05) from pooled control.

Table 4.6 Data derived from results in Table 4.5

Parameter	Value (mg/kg dry weight)
10 day LC_{50} larval survival	450
10 day EC_{50} larval growth (wet weight)	410
10 day NOEC larval growth	73
10 day LOEC larval growth	180
28 day EC_{50} emergence	420
28 day EC_{50} development rate	>570
28 day NOEC development rate	69
28 day LOEC development rate	180

An expert review of this toxicity study was carried out by Maycock *et al.* (2005) and CES (2005b). The review indicates that the study was compromised by the methodology used to spike the D5 onto the sediment (i.e. direct addition to the organic carbon fraction and subsequent mixing of this into the bulk sediment). It is argued that, given the properties of D5, it is highly likely that the majority of D5 not lost by volatilisation during the sediment preparation would remain adsorbed to the alpha cellulose during the preparation of the sediment, and for a significant period thereafter. As only 24 hours was allowed in the test prior to the addition of the test organisms, this may not have been sufficient time for D5 to equilibrate within the various phases of the sediment that occurred. This is thought to be an important consideration as chironomids preferentially select organic matter for both tube building and as a food source, and may therefore be exposed to much higher concentrations of D5 than the bulk sediment analysis indicates.

A counter argument to this is that the high log K_{ow} value for D5 suggests that the majority of D5 added to a sediment is associated with the organic carbon and so the concentration in the organic carbon phase is expected to be much higher than indicated in the bulk sediment phase regardless of how the D5 was added to the sediment. In addition, any lack of equilibrium between the organic carbon content and the pore water at the start of the test would have resulted in a reduced exposure via the pore water at the start of the test. Also, this test was carried out with supplemental feeding (and so the food added was not contaminated with D5). The TGD now recommends that sediment toxicity tests should be carried out, wherever possible, without supplemental feeding, and so exposure via the food may be an important source of exposure for this organism that was not considered in the study. The effect of the supplemental feeding on the result of the study is unknown.

Another criticism of this study put forward by Maycock *et al.* (2005) and CES (2005b) is that the D5 concentrations measured in pore water are significantly greater (in some cases up to 1000 fold) than the water solubility of D5 (the actual pore-water concentrations measured were 0.14–0.25, 0.27–1.5, <0.78–0.82, 1.3–<1.8, and 19–53 mg/l in the five treatment groups, respectively). Thus it is clear that the organisms were exposed to very high concentrations (i.e. particulate-bound as well as dissolved) via the pore water. However, the report by Putt (1993) indicates that the high pore-water concentrations measured were a result of the extraction (centrifugation of the sediment) method used. This caused the various phases of the sediment to separate and it was reported to be difficult to remove the alpha-cellulose fraction from the pore water after centrifugation. Thus, the levels reported reflect the

concentrations measured in pore water contaminated with alpha-cellulose as a result of the extraction process, rather than the actual pore-water concentration in the sediment *in-situ*. The true pore-water concentrations in this study are unknown.

On the basis of these concerns, CES (2005b) suggests that the results from this study be considered as an extreme worst case when considering a NOEC for use in the risk assessment. However, although there are some legitimate uncertainties, it is by no means clear that these lead to an unrealistically high exposure of the organisms in this study. Therefore, it is considered that the study design reflects the best technically possible at that time with a highly volatile substance such as D5, and that the results are suitable for use in the risk assessment, recognising that there are some uncertainties associated with the study.

In light of these, the industry has voluntarily carried out further studies on the toxicity of D5 to sediment organisms. A repeat study using *Ch. riparius* was recently completed (Krueger *et al.*, 2008). The D5 tested had a purity of 99.19 per cent. An artificial sediment was used (based on the recommendations in OECD test guideline 218) that consisted of 10 per cent sphagnum peat moss, 20 per cent silt and clay, and 70 per cent industrial quartz sand. The sediment used had an organic carbon content of 3.2 per cent and a pH of 6.6. D5 was added to the sediment in a two-stage process. Firstly, neat test material was added to air-dried peat and mixed overnight. Secondly, the formulated sediment was added to the peat and mixed for 30–40 minutes. A 28 day ration of food was mixed into the sediment prior to addition of the water (well water was used). The test vessels used were 2 litre glass beakers that contained a 2 cm depth of sediment and an 8 cm depth of overlying water.

The nominal test concentrations prepared were 156, 259, 432, 720, 1200, and 2000 mg/kg dry weight plus a control, and a total of eight replicates were prepared – four to evaluate the biological endpoints, three for analytical confirmation of the sediment concentrations on days zero, seven, and 24, and one for water-quality measurements on day zero. Further water-quality measurements were taken from the replicates during the test. The sediments were allowed to equilibrate for 48 hours prior to the addition of the test organism. At test initiation 20 midges per replicate were introduced (a total of 80 midges per treatment) and the sediments incubated at 20°C for 28 days. During the incubation, the test chambers were covered with loose-fitting lids and the water phase was continuously aerated (the aeration rate was such as to avoid disturbance of the sediment).

The concentrations of D5 present in the sediment phase were determined on day zero, day seven, and day 28 of the test. The mean measured concentrations found were 35, 70, 160, 248, 390, and 759 mg/kg dry weight for the nominal 156, 259, 432, 720, 1200, and 2000 mg/kg dry weight treatment groups, respectively. The measured concentrations were therefore much lower than the nominal concentrations (range was 22–38 per cent of nominal), which most probably reflects loss during the sediment preparation as the measured concentrations appeared to be reasonably constant over the three sampling periods (although there was some variation in the data; see Table 4.6).

During the test the dissolved oxygen concentration in the water phase was ≥7.4 mg/l, the pH was between 8.0 and 8.4, and the hardness was 136–160 mg/l as $CaCO_3$. The level of ammonia in the water phase was monitored at weekly intervals during the test and was above 4 mg/l on days seven, 14, and 21 (generally similar levels were present in the control and treatment groups). As a result, the overlying water was partially replaced on these days to minimise potential toxicity from ammonia.

The biological results are summarised in Table 4.7.

Table 4.7 Effects of D5 on *Chironomus riparius* (Krueger *et al.*, 2008)

Measured exposure concentration (mg/kg dry weight)				Biological endpoints (at 28 days)			
Day 0	Day 7	Day 28	Mean	Mortality (%)	Mean development time (days)	Mean emergence ratios	Mean development rate
29.3	52.1	23.9	35	15	16.7	0.85	0.0629
72.8	89.3	48.1	70	16	17.5	0.88	0.0601
77.4	172	230	160	29	18.5	0.71	0.0562 [1]
239	299	206	248	49	21.4 [1]	0.53 [1]	0.0489 [1]
358	531	280	390	69	21.9 [1]	0.31 [1]	0.0476 [1]
997	611	670	759	75	23.5 [1]	0.26 [1]	0.0441 [1]
Control				13	16.2	0.88	0.0640

Note: [1]Statistically significant difference (p=0.05) from control.

Emergence was first seen on day 14 of the test. A dose-related increase in mortality at 28 days (mortality included organisms that died in the pupal and larval stages, organisms that emerged and died, and organisms that did not emerge by day 28) was evident in the test and the 28 day LC_{50} was 257 mg/kg dry weight (95 per cent confidence limits of 213 and 318 mg/kg dry weight). The LOECs and NOECs for the other endpoints studied (development time, emergence ratio, and development rate) are given in Table 4.8 (note that in this study the development rate was not determined separately for males and females, as done in the previous study)

Table 4.8 Data derived from results in Table 4.7

Parameter	Value (mg/kg dry weight)
28 day LC_{50} mortality	257
28 day NOEC development time	160
28 day LOEC development time	248
28 day NOEC emergence ratio	160
28 day LOEC emergence ratio	248
28 day NOEC development rate	70
28 day LOEC development rate	160

Overall, the NOEC from this study was 70 mg/kg dry weight based on development rate. This is based on the mean measured concentration during the test. As Table 4.7 shows, there is some variation in the levels measured during the test, but the results are considered reliable and generally confirm the results from the earlier study by Putt (2003) with this species. However, as the Krueger *et al*. (2008) study was carried out without supplemental feeding, considers survival after 28 days rather than ten days, and, as discussed above, there may be further limitations with the Putt (2003) study, the results from Krueger et al. (2008) are considered in the PNEC derivation in preference to those of Putt (2003).

The results of a study to investigate the toxicity of D5 to *Lumbriculus variegatus* were also provided for this assessment (Krueger et al., 2006). The test substance was unlabelled D5 with a purity of 99.19 per cent. The sediment used consisted of 13 per cent peat, 10 per cent

kaolin clay, and 77 per cent industrial quartz sand (this mixture corresponds to the artificial sediment used in the OECD test guideline 218). The sediment was spiked by firstly mixing the peat and the sand. The peat was then mixed with the neat test substance and then the spiked peat was mixed into the clay–sand. The final sediment had a pH of 7.1 and an organic carbon content of 3.7 per cent. A total of six nominal test concentrations (63, 15, 250, 500, 1000, and 2000 mg/kg dry weight) were prepared, along with a control sediment.

The test system used was a flow-through system. The chambers were 300 ml glass beakers with stainless steel mesh-covered holes on opposite sides. Each chamber contained 100 ml of dry sediment, a 28 day ration of food (approximately 200 mg of salmon starter mixed into the sediment before the addition of the water), and 150 ml of well water (hardness 116–132 mg/l as $CaCO_2$, pH = 7.9–8.3). The depths of sediment and overlying water in a representative chamber were 3.8 cm and 5.4 cm, respectively. The flow rate of the overlying water was then adjusted to allow two volume additions per day (the water was added over a three minute period twice a day). The chambers were incubated at 23°C and allowed to acclimate for approximately 48 hours prior to the addition of the test organisms. A total of eight replicate chambers, each of which contained ten organisms, were prepared to evaluate the survival and growth in each treatment group and the control group. Additional chambers were prepared to determine analytically the concentration in sediment. No supplementary feeding was carried out during the test. The dissolved oxygen concentration was ≥76 per cent of saturation throughout the test.

During the test the chambers were observed daily and a visual assessment of any abnormal behaviour (such as leaving the sediment or climbing the walls of the test chamber) was made. The number of live or dead worms was determined at the end of the 28 day exposure period (as it is not possible to differentiate between young and adults for this species, survival and reproduction were considered as one endpoint). Growth was assessed on the basis of dry weight measurements on day 28.

The concentration of D5 in the sediment phase was determined analytically on day zero (just after addition of the organisms), day seven, and day 28 of the test. The measured concentrations for the nominal 63, 125, 250, 500, 1000, and 2000 mg/kg dry weight treatment groups were 19.0, 33.8, 90.6, 204, 522, and 1325 mg/kg dry weight, respectively, at day zero; at day seven they were 20.4, 39.6, 79.6, 262, 631, and 1350 mg/kg dry weight, respectively; and at day 28 they were 33.0, 64.2, 111, 211, 311, and 1141 mg/kg dry weight, respectively. From these results it can be seen that the concentration present in sediment remained constant over the 28 day test period,[21] but that loss of D5 occurred during the preparation of the sediment. The mean measured concentrations in the six treatment groups over the 28 day exposure period were 24, 46, 94, 226, 495, and 1272 mg/kg dry weight, respectively. As these concentrations are lower than the expected nominal concentrations (around 37–64 per cent of the nominal) the results are based on the mean measured concentrations over the test period.

No treatment-related abnormal behaviour was observed in the organisms throughout the test. The mean (± standard deviation) number of worms per replicate at day 28 was 26 ± 5 in the control group and 33 ± 12, 30 ± 7, 31 ± 12, 21 ± 14, 19 ± 5, and 26 ± 15 in the 24, 46, 94, 226, 495, and 1272 mg/kg treatment groups, respectively. No statistically significant differences ($p < 0.05$) were seen between the treatment groups and the control group. The mean (± standard deviation) dry weight per worm in the control group at the end of the test

[21] The test chambers do not appear to have been sealed (and so volatilisation could have occurred from the water phase during the test). In addition the pH of the overlying water was around 7.9–8.3 and under these conditions it is expected that D5 in the water may have hydrolysed (a hydrolysis half-life of around 9 days is expected for D5 at pH of around 8; see Section 3.2.2.1). Therefore, the concentration of D5 in the sediment phase remained reasonably constant over the 28 day period, which provides further supporting evidence that D5 may be more persistent in sediment than expected from its volatility and rate of hydrolysis (see Section 5.5.2.1).

was 0.92 ± 0.7 mg. The mean dry weight per worm in the 24, 46, 94, 226, 495, and 1272 mg/kg treatment groups was 0.94 ± 0.07, 0.92 ± 0.08, 0.99 ± 0.11, 1.19 ± 0.27, 1.03 ± 0.22, and 1.12 ± 0.21 mg, respectively. No statistically significant difference was seen in the mean dry weight per worm for any of the treatment groups compared with the control groups.

Overall, this study appears to be reliable and the NOEC from the study is ≥1272 mg/kg dry weight.

4.1.9 Predicted no effect concentration for the aquatic compartment

4.1.9.1 Surface water

Based on the available toxicity data, D5 does not cause adverse effects in fish, daphnids, and algae at concentrations close to its water solubility for both short-term and long-term exposure. No PNEC can therefore be derived for D5 for surface water or marine water.

However, there is an important gap in the database of D5 in that the available long-term toxicity data for fish are taken from bioconcentration studies which do not consider possible sensitive life stages. The substance has a high BCF value and results from a fish feeding study indicate a long depuration half-life in liver of fish. Therefore there are uncertainties over the potential for D5 to cause adverse effects in sensitive fish life stages following long-term exposure. QSAR estimates indicate that the NOEC for fish from standard long-term toxicity studies is expected to be close to, but just above, the solubility limit of D5 in water.

To try to assess the significance of this data gap, an indicative concentration of 1.7 µg/l (i.e. one-tenth of the water solubility[22]) is used in place of the PNEC for freshwater to establish if further testing is warranted to determine a more reliable long-term NOEC for fish. For marine water a lower indicative concentration of 0.17 µg/l is assumed.

For a related substance (D4; see Environment Agency, 2008) a PNEC of 0.44 µg/l was determined based on the results of both a 14 day study with fish and a 93 day fish early life-stage study. Using the BCF value for D4 (BCF of 12,400 l/kg) it is possible to estimate an internal body concentration that is equivalent to the PNEC of 5456 µg/kg or 18 µmol/kg. If it is assumed that D5 shows a similar level of toxicity to D4 in long-term exposure of fish, the concentration in water equivalent to an internal body concentration of 18 µmol/kg for D5 (using a BCF of 7060 l/kg) would be around 1 µg/l. This is similar to the indicative concentration outlined above.

4.1.9.2 Microorganisms

An EC_{50} of >2000 mg/l was found for D5 in an activated sludge respiration inhibition test. A PNEC for wastewater treatment microorganisms of >20 mg/l can be derived from this value using an assessment factor (AF) of 100.

4.1.9.3 Sediment

Long-term sediment toxicity results are available for two species (*Ch. riparius* and *Lu. variegatus*). The lowest NOEC from these studies is 70 mg/kg dry weight, obtained in a 28 day study with *Ch. riparius.* The sediment used had an organic carbon content of 3.2 per

[22] This can be considered as applying an assessment factor of ten to the long-term NOEC for fish estimated from QSARs, taking into account the actual water solubility of the substance. For marine water an assessment factor 100 can be applied to the estimated NOEC.

cent. Normalising this value to a standard organic carbon content of 5 per cent (as recommended in the TGD) gives a $NOEC_{standard}$ of 109 mg/kg dry weight.

According to the TGD an AF of 50 is applied to the result from two long-term toxicity tests with sediment organisms. This gives a $PNEC_{sediment}$ of 2.2 mg/kg dry weight or 0.48 mg/kg wet weight [as calculated by EUSES using the default water content of sediment given in the TGD (approximately 79 per cent by weight)].

For the marine assessment, the appropriate AF for the available data is 500. This gives a $PNEC_{marine\ sediment}$ of 0.22 mg/kg dry weight or 0.048 mg/kg wet weight.

4.2 Terrestrial compartment

4.2.1 Terrestrial toxicity data

A 14 day EC_{50} of 164 mg/kg dry soil for earthworms can be estimated for D5 using the USEPA EPI (v3.12) estimation software [similar to the predictions for aquatic toxicity (see Section 4.1.4) a predicted log K_{ow} of 5.71 is used in the estimates as the equation was developed using mainly predicted rather than measured log K_{ow} values]. This software estimates the toxicity from the log K_{ow} value using a QSAR for neutral organics. The QSAR used in the software is:

$$\log \text{14 day } LC_{50} = 1.405 - 0.308 \times \log K_{ow}$$

where the LC_{50} is estimated in units of mmol/kg dry soil.

The QSAR was developed using experimental data from Neuhauser *et al.* (1985, 1986) and appears to be based on five data points only. The coefficient of determination of the method (R^2) is 0.48.

The method used is reported to be valid for log K_{ow} up to 5.0. The log K_{ow} of D5 is outside this range (a predicted log K_{ow} of 5.71 is used in the estimation, but the actual log K_{ow} is much higher than this value, at 8.03). According to the help files within EPI (v3.12) one of the limitations of the method for substances with log K_{ow} >5.0 is that a test duration of longer than 14 days may be needed for such substances to express their toxicity.

Details of the chemicals used to derive the QSAR are not given within the EPI (v3.12) program. However, further details of the method are given in Clements *et al.* (1988).[23] According to this report the five chemicals included in the training set used to derive the QSAR were 2-chlorovinyl ether, nitrobenzene, 1,2-dichloropropane, fluorene, and 1,2,4-trichlorobenzene. The range of log K_{ow} values covered by the training set was from 1.0 and 4.3.

Given that the QSAR was derived using only a limit number of chemicals (five), the relatively poor R^2 value for the method, and the unknown applicability of the method to D5, the LC_{50} estimated using this method is considered to be uncertain. However, few other QSAR methods are currently available for estimating the toxicity of chemicals such as D5 to terrestrial organisms.

4.2.2 PNEC for the soil compartment

Insufficient data are available to derive a PNEC for soil.

[23] In Clements *et al.* (1988) the same QSAR equation is given, but the units of the predicted LC_{50} are stated to be mmol/l rather than mmol/kg dry soil. It is assumed here that the correct units are incorporated into the EPI (v3.12) software.

Using the QSAR value for toxicity to earthworms, an indicative value is estimated as 0.16 mg/kg dry weight using an AF of 1000. This is equivalent to a value of 0.15 mg/kg on a wet weight basis.

Another approach that can be taken is to estimate an indicative value using the equilibrium partitioning approach based on the indicative value of 1.7 µg/l derived for water. Using the soil–water partition coefficient of 4.8×10^3 m^3/m^3 estimated for D5 from the measured K_{oc} value of 1.5×10^5 l/kg, an indicative value for the soil compartment of 4.8 mg/kg wet weight is estimated. According to the TGD, risk characterisation ratios obtained using the equilibrium partitioning method should be increased by a factor of 10 for substances with a log K_{ow} >5.

Given the uncertainty over the QSAR estimate of the toxicity of D5, the indicative value of 4.8 mg/kg wet weight derived using the equilibrium partitioning method is used in the assessment as a screening approach, because it is based on the known partitioning behaviour of D5 (i.e. a measured K_{oc} value). The risk characterisation ratios obtained by this method are increased by a factor of ten, which will result in risk characterisation ratios of a similar order of magnitude as those obtained if the indicative concentration based on the QSAR estimate is used.

4.3 Atmospheric compartment

4.3.1 Toxicity data relevant to the atmospheric compartment

No toxicity data are available relevant to the atmospheric compartment.

D5 is very volatile and reacts readily with hydroxyl radicals in the atmosphere. Therefore the potential for D5 to contribute to low-level photochemical smog formation is evaluated. A series of experiments with D5 in simplified model photochemical smog chambers were conducted (Chandra, 1997). The experiments consisted of repeated six hour irradiations of a standard mixture of photochemical smog precursors with various amounts of D5. D5 strongly inhibit the formation of ozone in these experiments. Further, model simulations using airshed models to represent 39 different urban areas in the USA, and also a trajectory model to simulate a pollution episode in Europe, also predict that D5 inhibits ozone formation. Although it is recognised that the overall mechanism for photochemical smog formation is very complicated, and depends on numerous variables (and so it is impractical to address all of these in laboratory simulations), it can be concluded that D5 does not contribute (indeed, appears to inhibit) the low-level formation of atmospheric ozone during photochemical smog episodes.

As the main products of atmospheric degradation of D5 appear to be hydroxylated products (see Section 3.2.1.1) which have lower vapour pressures than D5 itself, it is possible that if these products are not removed rapidly from the atmosphere by wet or dry deposition, they could condense onto aerosol particles already present in the atmosphere. Chandra (1997) reports the results of a series of screening experiments to investigate the potential for D5 to contribute to aerosol formation in the atmosphere using a similar photochemical smog chamber as above. No enhancement of aerosol formation was observed when D5 was added to the chambers at concentrations of ~0.1–0.9 ppm_V. Therefore based on these results it is unlikely that the degradation products from D5 contribute significantly to atmospheric aerosol formation (although, again, atmospheric aerosol formation depends on many factors and it is impractical to investigate all these factors in a laboratory setting).

4.3.2 PNEC for the atmospheric compartment

No PNEC can be derived for the atmospheric compartment.

4.4 Mammalian toxicity

4.4.1 Toxicokinetics

Mass balance studies in animals show that around 3 per cent of inhaled D5 is absorbed (Battelle, 2001a, 2001b). Around 20 per cent of an oral dose given in corn oil is absorbed (CES, 2005c). Studies *in vitro* and *in vivo* in rats and humans indicate that 0.1–1 per cent of the applied dose of D5 is absorbed across the skin, with D5 preferentially evaporating from the skin (Plotzke *et al*., 1994; Dow Corning, 1996a, 1996b, 1999b; University of Rochester Medical Center, 2001). Absorbed D5 distributes widely with peak radiolabel concentrations in most tissues reached at 1 hour post-exposure (Battelle, 2001b). With the exception of fat, radioactivity in most tissues decreases rapidly with time. There is evidence that fat acts as a depot in the body for D5. However, there is limited potential for bioaccumulation in rats because liver enzyme induction leads to enhanced excretion.

Differences in distribution may arise when D5 is given orally rather by inhalation (CES, 2005c). When D5 is given orally, higher concentrations are located within the liver and spleen compared with the amounts found following inhalation. This is attributed to the oral administration of D5 in corn oil leading to absorption as chylomicrons via the lymphatic system. Chylomicrons are removed from the bloodstream and broken down by the reticuloendothelial system in the liver and spleen, and hence a lower proportion of the absorbed dose is available for systemic distribution.

D5 is metabolised, although the complete metabolic pathway is not yet determined. However, analysis of urine identified many of the same metabolites that occur after treatments with the related cyclosiloxane D4 (Dow Corning, 1999a; Varaprath *et al*., 2000). Around 75 per cent of total urinary radioactivity are accounted for by the two major metabolites dimethylsilanediol [$Me_2Si(OH)_2$] and methylsilanetriol [$MeSi(OH)_3$]. The methylsilanetriol moiety is linked with the liver weight increases seen with D4. A further ten minor metabolites were identified for D5.

D5 and/or its metabolites are eliminated in exhaled air, urine, and faeces. The urine and faeces appear to be the main routes of elimination when D5 is inhaled. When D5 is given orally, the greatest proportion of absorbed D5 is eliminated unchanged in exhaled air (CES, 2005c).

4.4.2 Acute toxicity

No single exposure data are available for humans. Studies in animals show that D5 is of low acute toxicity by all routes. The no observed adverse effect level (NOAEL) for single four hour inhalation exposures in the rat is 4.62 mg/l based on decreased food consumption and body weight at 6.73 mg/l (Dow Corning, 1994). A four hour LC_{50} value of 8.67 mg/l was obtained in this study. Few details are available from single oral and dermal dosing studies, although no overt signs of toxicity are reported in rats given 5000 mg/kg by the oral route (Löser, 1984; Toxikon Corporation, 1990a) or 2400 mg/kg by the dermal route (Ramm, 1985).

4.4.3 Irritation

There is no evidence from several studies that involved single and repeated semi-occlusive or occlusive dermal applications that D5 irritates rat, rabbit, or human skin (Huntingdon Research Centre, 1979; Suberg 1983a, 1983b; Dow Corning, 1986; Toxikon Corporation 1990b). Minimal transient reddening of the eyelids was the only finding in eye irritation studies (Carnegie-Mellon Institute of Research, Chemical Hygiene Fellowship, 1976; Suberg 1983c; Toxikon Corporation 1990c). No studies have been conducted to investigate sensory irritation in the respiratory tract, but given that skin and eye irritation have not been observed, this property is not predicted for D5.

4.4.4 Sensitisation

Data are available from human volunteers in whom 0.05 ml D5 was applied undiluted three times per week for a total of nine applications followed by a challenge application of 0.05 ml (Dow Corning, 1986). In all cases exposures were for 24 hours under an occlusive dressing. There was no evidence that D5 had sensitising properties. Negative results were also obtained in a guinea pig maximisation test and a Buehler test, also in the guinea pig (Schmidt, 1985; Toxikon Corporation, 1991).

No studies have been conducted to investigate the potential asthmagenicity of D5. However, given that the substance is not a skin sensitiser, D5 is not predicted to show asthmagenic potential.

4.4.5 Repeated dose toxicity

There is no information about the effects of repeated exposure to D5 on humans. Repeated exposure studies in animals are available for all relevant routes of exposure.

4.4.5.1 Inhalation

Data from inhalation studies in rats are available and cover exposure periods of up to two years and concentrations of D5 up to 3591 mg/m^3 (Dow Corning, 1990a; RCC, 1995; Burns-Naas *et al.*, 1998a, 1998b). No effects on food consumption or bodyweight gains were reported. The key findings were changes in the respiratory tract, consistent with a mild irritant response, and increases in liver weights.

Site-of-contact effects in the respiratory tract

The key site-of-contact findings in the respiratory tract were proliferation of goblet cells in the nasal cavity. This was accompanied by submucosal inflammation, focal macrophage accumulation, and minimal to slight interstitial inflammation in the lungs

In a 28 day study, Fischer 344 rats were exposed (whole body) to 0 ppm, 10 ppm (152 mg/m^3), 25 ppm (380 mg/m^3), 75 ppm (1140 mg/m^3) or 160 ppm (2432 mg/m^3) of D5 for six hours per day, seven days per week (Burns-Naas *et al.*, 1998a). Goblet cell proliferation and submucosal inflammation in the nasal cavity were apparent at concentrations of 75 ppm or more. Mild inflammation in the lungs was also observed at 160 ppm. From this study the NOAEL effect is 25 ppm.

Goblet cell proliferation was not recorded in a 90 day inhalation study in F344 rats exposed to 0 ppm, 28 ppm (435 mg/m^3), 49 ppm (757 mg/m^3), 88 ppm (1337 mg/m^3) or 233 ppm (3542 mg/m^3) of D5 for six hours per day, five days per week (Burns-Naas *et al.*, 1998b). However, in both sexes at the highest concentration, and in males at 88 ppm, the incidence

and severity of foci of alveolar macrophage accumulation and focal interstitial inflammation increased. These effects had not completely resolved by the end of the one month recovery period.

In a separate 90 day inhalation study in Sprague-Dawley rats no changes were seen in the respiratory tract at any concentration, with the highest concentration being 120 ppm (182 mg/m^3) (Dow Corning, 1990a).

On the basis that submucosal histopathological changes that indicate mild inflammation are reported in the nasal cavity of animals that inhale 75 ppm (1140 mg/m^3) and above, the NOAEL for site-of-contact effects in the respiratory tract is considered to be 25 ppm (380 mg/m^3).

Systemic effects

The only systemic effect observed after repeated inhalation exposure to D5 is increased liver weight and associated hypertrophy. Females are more sensitive to increases in liver weight than males. It is assumed that increases in liver weight greater than 10 per cent lie outside the range for natural variation and could be considered as potentially adverse.

The maximum reported increase in liver weight occurred in a 28 day study in which the liver weights of females exposed to the highest doses of 197 or 151 ppm (2.29 or 3.71 mg/l) for six hours per day, seven days per week, were 30 per cent greater than those of the controls (RCC, 1995). This was associated with slight hepatocellular hypertrophy. Liver weight increases were below 10 per cent at the next lowest dose of 96 ppm (1.50 mg/l), which was not accompanied by hypertrophy. Liver weight increases in males remained ≤10 per cent at all dose levels in this study.

In a second 28 day study, Fischer 344 rats were exposed (whole body) to 0 ppm, 10 ppm (152 mg/m^3), 25 ppm (380 mg/m^3), 75 ppm (1140 mgm^3), or 160 ppm (2432 mg/m^3) of D5 for six hours per day, seven days per week (Burns-Naas *et al*., 1998a). A statistically significant increase in liver weight of 15 per cent above controls was observed in females exposed to 160 ppm. In females exposed to lower concentrations, and in all male exposure groups, liver weight increases were ≤10 per cent. There were no signs of treatment-related pathology in the liver. The immunological function was also assessed in exposed animals in this study. There was no indication of an effect on humoral immunity based on measurements of the antibody-forming cell response in a standard plaque assay and enzyme-linked immunosorbent assay (ELISA).

In a 90 day study, Fischer 344 rats (20–30 per group) were exposed to 0 ppm, 28 ppm (435 mg/m^3), 49 ppm (757 mg/m^3), 88 ppm (1337 mg/m^3), or 233 ppm (3542 mg/m^3) of D5 for six hours per day, five days per week (Burns-Naas *et al*., 1998b). Liver weights increased by <10, <10, 15, 8, and 16 per cent in female rats at 0, 28, 49, 88, and 233 ppm, respectively. Increased liver weight was accompanied by raised gamma-glutamyl transferase levels at 49 ppm and above. Increases in liver weight were not observed in animals treated with 233 ppm (ten per group per sex) one month after the cessation of treatment. No toxicologically significant liver weight increases or biochemical changes occurred in males. There was no evidence for tissue damage in the liver in either study. The most likely explanation for increased liver weight is enzyme induction, which is discussed further below. The NOAEL from this study was 28 ppm based on increased liver weight (15 per cent) and increased gamma-glutamyl transferase levels at 49 ppm.

In a GLP-compliant two year rat bioassay, groups of 96 animals were exposed to 0 ppm, 10 ppm (152 mg/m^3), 40 ppm (608 mg/m^3), or 160 ppm (2432 mg/m^3) of D5 for six hours per day for five days per week for up to 24 months (Dow Corning, 2005b). Rats were sacrificed after six months (six males, six females), 12 months (ten males, ten females), or 24 months (60 males, 60 females). An additional group of rats (20 males, 20 females) were exposed to D5 for 12 months only and sacrificed at 24 months. At six months, increases in the liver to

body weight ratio were seen in females exposed to 160 ppm (11.6 per cent) only. At one year, absolute liver weights were increased in females exposed to 10 ppm (12.6 per cent) and 160 ppm (10.9 per cent), but not increased in those exposed to 40 ppm. There were no histopathological changes in the liver. Increases in liver weight were not seen in females exposed for two years. No significant increase in liver weight (>10 per cent) was noted in males at any time point. Although increases in liver weight were seen in females after six and 12 months of treatment, there was no clear indication of a dose response and therefore these effects are likely to be incidental and not treatment related. The lack of effect in this chronic study indicates that increased liver weight in rats occurs after short-term exposure (up to three months and less than six months) and is reversible.

Overall, liver weight increase and associated hypertrophy is the key form of systemic toxicity observed in inhalation studies in rats. A NOAEL of 28 ppm (435 mg/m^3) can be identified based on a 15 per cent increase in liver weight and raised gamma-glutamyl transferase at the next highest concentration of 49 ppm (757 mg/m^3) from a 90 day rat study.

4.4.5.2 Oral

Repeated oral dosing studies in rats are available and cover doses up to 1600 mg/kg/day and dosing periods of up to 13 weeks. The volatility of D5 makes it difficult to administer via the food, so oral treatment in most studies was via gavage. In rats, the key systemic effect after oral treatment with D5 was increased liver weight and liver enzyme induction.

Evidence is available to show that the profile of enzymes induced by D5 is similar to that induced by phenobarbital. In Sprague-Dawley rats (three or four per group) treated with 1, 5, 20, or 100 mg/kg/day of D5 for four days, enzymes induced were similar to those induced by phenobarbital (CYP2B1/2, PROD, EROD, CYP3A1/2) (Zhang *et al.*, 2000). The lowest dose to produce a measurable enzyme induction was 5 mg/kg/day, with a NOEL of 1 mg/kg/day. In this study, there were also increases in relative liver weight of around 15 per cent or more in females at 20 mg/kg/day and above and of around 40 per cent in males at 100 mg/kg/day. Although a NOAEL of 5 mg/kg/day and a lowest observed adverse effect level (LOAEL) of 20 mg/kg/day can be identified from this study for liver weight increases, they are not used in this risk assessment because of limitations in the study. This is primarily because of the low numbers of animals used per group, the absence of GLP, and the limited data presented (liver weights are in graphical form; individual animal data are not given). The results of this study are, however, considered to support enzyme induction as the most likely explanation for increases in liver weight.

Consistent with the findings in the inhalation studies, females are more sensitive than males to the effects of D5. In a 14 day study, liver weights in females from the 25, 100, 400, and 1600 mg/kg/day dose groups were 13, 34, 33, and 50 per cent greater than control weights, respectively (Dow Corning, 1990b). Liver weights were also slightly raised (15 per cent) in males from the 1600 mg/kg/day group. No histopathological examinations were performed. No NOAEL could be identified in this study as a 13 per cent increase in liver weight was observed at the lowest dose of 25 mg/kg/day (LOAEL).

In a 90 day study, liver weights in females from the 100, 330, and 1,000 mg/kg/day dose groups were 42, 53, and 62 per cent greater than control weights, respectively (Jäger and Hartmann, 1991). Liver weights did not increase in males. The only treatment-related histological finding was a change in the appearance of hepatocyte cytoplasm in four out of ten male and eight out of ten female rats at 1000 mg/kg/day. This may reflect the presence of test substance within hepatocytes. There was no indication that this was an adverse effect. No histological changes were present in animals from the lower dose groups despite the large increases in liver weights reported.

In summary, liver enlargement is the principal adverse effect after oral treatment with D5. A consistent NOAEL could not be identified following oral exposure. However, a LOAEL of 25 mg/kg/day could be identified from a 14 day study in rats on the basis of a 13 per cent increase in liver weight.

4.4.5.3 Dermal

No adverse effects were reported in a 28-day dermal exposure study in which ten male and ten female Sprague-Dawley rats received a dermal application of up to 1600 mg/kg/day neat D5 under an occlusive dressing for six hours per day, seven days per week, for 28 days (Dow Corning, 1990c). These findings are consistent with two additional three week dosing studies in which rabbits received up to 1000 mg/kg/day (Huntingdon Research Centre, 1979; Krötlinger, 1988). The lack of any findings from dermal exposure studies is consistent with the minimal dermal penetration measured for this substance (0.1–1 per cent). The NOAEL for the effects of repeated dermal exposure is >1600 mg/kg/day.

4.4.5.4 Summary

The effects of repeated exposure to D5 were studied by all relevant routes. Inhalation of D5 produced local effects in the respiratory tract that indicate a mild irritant response at concentrations of 75 ppm (1140 mg/m^3) or more. A NOAEL of 25 ppm (380 mg/m^3) was identified, which can be used for the human health risk-characterisation of local effects on the respiratory tract following repeated inhalation exposure to D5.

In relation to systemic effects, the key concern is liver enlargement and associated hypertrophy caused by phenobarbital-type enzyme induction. Liver enlargement occurs after both oral and inhalation exposures in rats. This effect is considered to be relevant to human health as liver enzyme induction and liver enlargement do occur in humans who receive therapeutic doses of phenobarbital. As increases in liver weight greater than 10 per cent lie just outside the range of normal human variation, any such increases are considered to have adverse consequences to health. Furthermore, very large increases in liver size could compress other abdominal organs, and enzyme induction could impair the normal response to other xenobiotics. Liver enlargement (≥10 per cent) was seen in studies with exposures of four days up to 90 days, but not in a chronic inhalation study after six, 12, or 24 months of exposure. This suggests that liver enlargement after treatment with D5 is a short-term, reversible effect. A NOAEL of 28 ppm (435 mg/m^3) was identified for the inhalation route from a 90 day study in rats (based on a 15 per cent increase in relative liver weight and raised gamma-glutamyl transferase at the next concentration of 49 ppm) and a LOAEL of 25 mg/kg/day was identified for the oral route from a 14 day study in rats (based on a 13 per cent increase in liver weight).

No adverse effects are reported in repeated dermal dosing studies at concentrations of up to 1600 mg/kg/day, this being the highest dose tested in any study.

4.4.6 Mutagenicity

D5 was tested in a variety of *in vitro* assays in the presence and absence of rat liver S9 (Litton Bionetics, 1978; Isquith *et al.*, 1988; Dow Corning, 2003; CES, 2005c). These include bacterial reverse mutation assays and, in mammalian cells, chromosome aberration tests, gene mutation tests, a sister chromatid exchange test, and a DNA damage and repair assay. A DNA-damage and mitotic recombination assay in the yeast *Saccharomyces cerevisiae* was also conducted. Negative results were obtained in all tests.

The genotoxic potential of D5 was also assessed *in vivo* in unscheduled DNA synthesis (UDS) and micronucleus assays (CES, 2005c). Fischer rats were whole body exposed to 0 or 160 ppm of D5 vapour for six hours per day for seven consecutive days. No evidence of genotoxic potential was found in either assay. Based on information from toxicokinetics studies, it is expected that the relevant target tissues were exposed in each assay.

D5 is not considered to be an *in vivo* mutagen.

4.4.7 Carcinogenicity

There are no carcinogenicity data for D5 from humans. The carcinogenic potential of D5 was assessed in F344 rats in a single inhalation study (CES, 2005c; Dow Corning, 2005b). In a two year rat bioassay, animals were exposed to 0 ppm, 10 ppm (152 mg/m^3), 40 ppm (608 mg/m^3), or 160 ppm (2432 mg/m^3) of D5 for six hours per day for five days per week. Rats were sacrificed after six months (six males, six females), 12 months (ten males, ten females), 12 months plus a 12 month exposure-free period (20 males, 20 females), or after 24 months (60 males, 60 females). No neoplastic changes were reported in the respiratory tract or in the liver at any time point. These sites were identified as target tissues in repeated exposure studies. Exposure to D5 did, however, lead to an increased incidence of uterine endometrial adenomas and adenocarcinomas.

An increase in endometrial adenocarcinoma was seen in rats exposed to 160 ppm D5. In rats exposed to D5 for two years, adenocarcinomas were observed in 0/60, 1/60, 0/60, and 5/60 females exposed to 0, 10, 40, and 160 ppm, respectively. Adenocarcinomas were also observed in females exposed for one year with a one year recovery period at incidences of 1/20, 1/20, 0/20, and 2/20 at 0, 10, 40, and 160 ppm, respectively. One adenoma was observed in one rat exposed to 10 ppm for two years. A NOAEL of 40 ppm was identified.

Mechanistic studies indicate that uterine tumours arise because D5 acts as a dopamine agonist (Jean *et al.*, 2005, cited in CES, 2005c). By maintaining dopaminergic inhibition of prolactin secretion, female reproductive senescence is delayed, which leads to prolonged stimulation of the endometrium and eventually tumours. This mechanism was also identified as the basis for the endometrial tumours seen in female rats that inhale D4 for up to two years (CES, 2005d). Differences in the reproductive ageing process between humans and rodents mean that this mechanism is not relevant to humans (CES, 2005d). It is not clear whether tumours seen in rats after D5 exposure are relevant to other animal and bird species. However, because the carcinogenic effect occurs late in life, it is not an effect that influences the sustainability of a population. It is therefore not necessary to take the carcinogenicity of D5 into account in a risk assessment for secondary poisoning of wildlife exposed via the food chain.

4.4.8 Toxicity for reproduction

The potential reproductive toxicity of D5 was examined in a one-generation range-finding study (WIL Research Laboratories Inc., 1996) and a two-generation reproductive study that included developmental neurotoxicity evaluations in F_2 pups (WIL Research Laboratories Inc., 1999; Stump *et al*., 2000).

In a one-generation inhalation study, Sprague-Dawley rats were exposed to 0, 26, or 132 ppm of D5 vapour for six hours per day, seven days per week for 28 days prior to mating. No adverse effects on fertility were reported.

In a two-generation inhalation study, Sprague-Dawley rats were exposed to 0, 30, 70, or 160 ppm of D5 vapour for six hours per day, seven days per week for at least 70 days prior to mating. No adverse treatment-related effects were reported. Based on the results of these

studies, no significant signs of parental toxicity, reproductive toxicity, neonatal toxicity, or developmental neurotoxicity were observed at the highest concentration tested of 160 ppm.

It is notable that adverse reproductive effects are reported for the related cyclosiloxane D4. In inhalation reproductive toxicity studies at concentrations of 500 ppm and above, D4 causes a reduction in the numbers of corpora lutea that manifest as reduced litter sizes. This is likely to occur via inhibition of the luteinising hormone (LH) surge. The siloxanes industry proposes that the mechanism of action is not of relevance to humans. The mechanism by which the reproductive effect occurs was discussed by specialised experts in the context of classification and labelling for D4. The expert group concluded that the mechanism behind the reproductive effects of D4 could be relevant to human health and that Category 3 was appropriate.

Reproductive toxicity studies with D5 were conducted at concentrations below the NOAEL identified for D4 and, given the similarities between D4 and D5, it is possible that positive findings might be obtained for D5 if higher systemic doses are achieved, for example after oral dosing. This raises a concern that D5 may have the potential to cause adverse reproductive effects that are possibly relevant to human health. However, liver enlargement is the most sensitive effect and a NOAEL for effects on reproduction is likely to be higher than that set for liver enlargement, and therefore any possible adverse effect on fertility should be protected against.

4.4.9 Summary of mammalian toxicity

Animal studies show that around 3 per cent of inhaled D5 is absorbed and around 20 per cent of an oral dose given in corn oil is absorbed. In rats and humans only around 0.1–1 per cent of the applied dose of D5 is absorbed across the skin, with absorption being limited by evaporation from the skin. Given orally, higher concentrations of D5 are located within the liver and spleen compared with those following inhalation exposures. Absorbed D5 is distributed widely throughout the body with some preferential storage in fat. However, the potential for bioaccumulation in rats is limited because enzyme induction leads to enhanced excretion. The urine is the major route of excretion of D5 and its metabolites.

D5 is of low acute toxicity. The NOAEL for single four hour inhalation exposures in the rat is 4.62 mg/l based on decreased food consumption and body weight at 6.73 mg/l. The oral LD_{50} value in the rat lies above 5000 mg/kg and the dermal LD_{50} value in the rat lies above 2400 mg/kg.

D5 is not a skin irritant in humans and is not a skin or eye irritant in animals. It is not expected to be a sensory irritant. D5 is not a skin sensitiser and is not predicted to show asthmagenic potential.

The effects of repeated exposure to D5 by all relevant routes have been studied. Inhalation of D5 causes respiratory tract irritation in rats at 75 ppm and above. A NOAEL of 25 ppm for this effect was identified in a 90 day study, which can be used in the human health-risk assessment for the respiratory effects of repeated inhalation of D5.

No adverse effects are reported in repeated dermal dosing studies at concentrations of up to 1600 mg/kg/day, this being the highest dose tested in any study.

In relation to systemic effects, the main concern is liver enlargement and associated hypertrophy caused by phenobarbital-type enzyme induction (see Section 4.4.5.4). A NOAEL of 28 ppm (435 mg/m^3) was identified for the inhalation route from a 90 day study in rats and a LOAEL of 25 mg/kg/day was identified for the oral route from a 14 day study in rats.

Although no consistent NOAEL could be identified for liver enlargement after oral exposure, the inhalation NOAEL of 28 ppm should be relevant for both oral and inhalation routes as it

equates to an extrapolated oral NOAEL of 19 mg/kg/day (see next paragraph), which is below the oral LOAEL of 25 mg/kg/day. Although this NOAEL is very close to the LOAEL, it is an appropriate point for the risk assessment as the adverse effects seen at the LOAEL are marginal. Additionally, inhalation exposure compared to gavage administration more closely reflects the likely exposure conditions of humans exposed via the environment. Environmental exposures are low-level continuous ones rather than high-peak daily doses.

As the oral route contributes by far the most significant fraction to the total dose to which humans via the environment are exposed, it is necessary to convert the inhalation NOAEL into an oral equivalent. Based on a conversion factor of 1 ppm = 15.2 mg/m^3, the NOAEL of 28.6 ppm (six hours per day, five days per week) equates to 434.72 mg/m^3. The ventilation rate for the rat given in the EU TGD is 0.8 l/min/kg. Assuming that 3 per cent of an inhaled concentration is retained, the equivalent internal systemic dose is 3.75 mg/kg/day. Since 20 per cent of an oral dose is absorbed, the external oral dose that equates to this inhalation NOAEL is 19 mg/kg/day.

D5 is not considered to have mutagenic potential either *in vitro* or *in vivo*.

D5 causes uterine tumours in F344 rats, but the underlying mechanism is not relevant to humans. Since the carcinogenic effect occurs late in life, it is not an effect that influences the sustainability of a population. It is therefore not necessary to take the carcinogenicity of D5 into account in a risk assessment for secondary poisoning of wildlife exposed via the food chain.

No adverse effects on fertility were seen in the two reproductive toxicity studies conducted for D5 at up 160 ppm, the highest dose tested. An impairment of female fertility was reported for the related cyclosiloxane D4. Reproductive toxicity studies with D5 were conducted at concentrations below the NOAEL for fertility effects identified for D4 and, given the similarities between D4 and D5, it is possible that positive findings might be obtained for D5 if higher systemic doses had been achieved. On this basis, reproductive toxicity is of concern for the risk assessments to human health. The highest dose tested of 160 ppm is adopted as a surrogate for a NOAEL (equivalent to an extrapolated oral NOAEL of 105 mg/kg/day).

Overall, the critical effects are chronic respiratory tract irritation after inhalation exposure, liver weight increases after repeated exposure, and, by analogy with D4, a potential concern for fertility. In relation to the local effects on the respiratory tract, a NOAEL of 25 ppm is derived from a 90 day rat study. In relation to the systemic effects on the liver after repeated exposure a NOAEL of 19 mg/kg/day is derived from a 90 day rat study. For the potential effects on fertility a NOAEL of 105 mg/kg/day from a two generation study in rats is selected. As discussed above, the mechanism behind the reproductive effects of D4 could be relevant to human health. However, these potential effects on fertility occur at higher dose levels (>105 mg/kg/day) than those at which a toxicologically significant liver enlargement is seen, so liver enlargement is the lead systemic health effect to drive the risk characterisation regardless of whether or not the fertility effects are judged to be relevant to humans.

4.4.10 Derivation of $PNEC_{oral}$

The lowest NOAEL for D5 relevant for secondary poisoning is 19 mg/kg bw/day for effects on liver after repeated exposure. Although the NOAEL was determined in a 90 day study it is considered that this NOAEL is also appropriate for longer term exposures.

Based on these effects and using a conversion factor of 20 (for rats >6 weeks old) and an AF of 30, a PNEC of 13 mg/kg food can be estimated for D5.

4.5 Classification for environmental hazard

D5 is not currently classified for environmental hazard.

It is not readily biodegradable, has a fish BCF of 7060 l/kg, and is not toxic to aquatic organisms at concentrations up to its water solubility. Therefore, on this basis, no classification for environmental hazard is warranted.

5 Risk characterisation

5.1 Aquatic compartment

5.1.1 Risk characterisation ratios for surface water

No PNEC can be determined for D5 for surface water as the available studies show that it is not toxic to aquatic organisms at concentrations up to its water solubility. However, as discussed in Section 4.1.9, there are uncertainties over the potential for D5 to cause adverse effects in sensitive life stages of fish after long-term exposure, and an indicative concentration of 1.7 µg/l was derived for D5 to determine if further work is needed to determine a more reliable long-term NOEC for fish.

A comparison of the PECs with this indicative concentration is shown in Table 5.1.

Table 5.1 Comparison of PECs with the indicative concentration for surface water

Scenario	PEC (µg/l)	PEC/indicative concentration
Production and on-site use as an intermediate	0.52	0.31
Off-site use as an intermediate – wet process (non-UK)	0.10	0.059
Off-site use as an intermediate – dry process (non-UK)	0.10	0.059
Personal care products – formulation – UK sites	0.12	0.071
	0.19	0.11
	0.10	0.060
	0.16	0.095
	0.52	0.031
	0.16	0.096
	0.15	0.087
	0.19	0.11
	0.11	0.063
	0.58	0.34
	0.46	0.27
	0.28	0.17
	0.13	0.079
	0.11	0.062
	0.10	0.059
	0.11	0.067
	0.12	0.068
	0.48	0.28
Personal care products – formulation – generic site (non-UK)	1.6	0.92
Personal care products – formulation – specific sites (non-UK)	0.10–0.86 (see Appendix B)	0.059–0.51 (see Appendix B)
Personal care products – use by general public	0.33	0.19
Household products – formulation	0.10	0.059
Household products – use	0.11	0.066
Industrial/institutional cleaning – use	0.10	0.059
Regional	0.10	0.059

The ratios of PEC to indicative concentration are <1 for all endpoints considered. Similar ratios[24] are also obtained if a lower indicative concentration of 1 µg/l is used (as estimated by extrapolation from the PNEC for the related substance D4; see Section 4.1.9.1). This indicates that no risks to surface water is expected from production and use of D5, and that further work to determine a more reliable long-term NOEC for fish is probably not required to define a more reliable PNEC.

5.1.2 Risk characterisation ratios for wastewater treatment plant micro-organisms

For wastewater treatment plants a derived PNEC of >20 mg/l is used (see Section 4.1.9.2). The worst-case risk characterisation ratios are summarised in Table 5.2**.**

Table 5.2 Risk characterisation ratios for wastewater treatment plants

Scenario	PEC (mg/l)	Risk characterisation ratio
Production and on-site use as an intermediate	1.3×10^{-3}	$<6.5 \times 10^{-5}$
Off-site use as an intermediate – wet process (non-UK)	4.6×10^{-10}	$<2.3 \times 10^{-1}$
Off-site use as an intermediate – dry process (non-UK)	0	<<1
Personal care products – formulation – UK sites	2.6×10^{-4}	$<1.3 \times 10^{-5}$
	8.2×10^{-4}	$<4.1 \times 10^{-5}$
	2.3×10^{-5}	$<1.1 \times 10^{-6}$
	7.5×10^{-4}	$<3.7 \times 10^{-5}$
	5.2×10^{-3}	$<2.6 \times 10^{-4}$
	7.7×10^{-4}	$<3.9 \times 10^{-5}$
	5.9×10^{-4}	$<2.9 \times 10^{-5}$
	1.1×10^{-3}	$<5.5 \times 10^{-5}$
	8.7×10^{-5}	$<4.3 \times 10^{-6}$
	5.9×10^{-3}	$<2.9 \times 10^{-4}$
	4.4×10^{-3}	$<2.2 \times 10^{-4}$
	2.3×10^{-3}	$<1.1 \times 10^{-5}$
	4.2×10^{-4}	$<2.1 \times 10^{-5}$
	6.6×10^{-5}	$<3.3 \times 10^{-6}$
	1.4×10^{-7}	$<7.1 \times 10^{-9}$
	1.6×10^{-4}	$<8.0 \times 10^{-6}$
	1.9×10^{-4}	$<9.5 \times 10^{-6}$
	4.7×10^{-3}	$<2.3 \times 10^{-4}$
Personal care products – formulation – generic site (non-UK)	0.018	$<9.0 \times 10^{-4}$
Personal care products – use by general public	2.8×10^{-3}	$<1.4 \times 10^{-4}$
Household products – formulation	0	<<1
Household products – use	1.4×10^{-4}	$<7.0 \times 10^{-6}$
Industrial/institutional cleaning – use	2.0×10^{-9}	$<9.9 \times 10^{-1}$

Based on this worst-case assessment no risks to wastewater treatment plants are expected from the production and use of D5.

[24] In this case the generic scenario for formulation of personal care products leads to a ratio >1, but this scenario is not relevant to the UK, and site-specific information is available for most other formulation sites in the EU, which give ratios <1.

5.1.3 Risk characterisation ratios for sediment

A $PNEC_{sediment}$ of 2.2 mg/kg dry weight or 0.48 mg/kg wet weight was derived for D5 (see Section 4.1.9.3). The resulting worst-case risk characterisation ratios are summarised in Table 5.3.

Table 5.3 Risk characterisation ratios for sediment

Scenario	PEC (mg/kg wet weight)	Risk characterisation ratio
Production and on-site use as an intermediate	1.7	3.6
Off-site use as an intermediate – wet process (non-UK)	0.33	0.69
Off-site use as an intermediate – dry process (non-UK)	0.33	0.69
Personal care products – formulation – UK sites	0.39	0.81
	0.63	1.3
	0.33	0.69
	0.53	1.1
	1.7	3.5
	0.53	1.1
	0.48	1.0
	0.62	1.3
	0.35	0.73
	1.9	4.0
	1.5	3.2
	0.92	1.9
	0.44	0.92
	0.34	0.71
	0.33	0.69
	0.37	0.77
	0.38	0.80
	1.6	3.4
Personal care products – formulation – generic site (non-UK)	5.1	11
Personal care products – formulation – specific non-UK sites	0.33–2.8 (see Appendix B)	0.69–5.9 (see Appendix B)
Personal care products – use by general public	1.1	2.3
Household products – formulation	0.33	0.69
Household products – use	0.36	0.76
Industrial/institutional cleaning – use	0.33	0.69
Regional	0.65	1.4

Based on this worst-case analysis, risk characterisation ratios above one are obtained for several scenarios. These include production and on-site use as an intermediate, personal care formulation sites (both UK and non-UK), and use of personal care products by the general public and at the regional level.[25] Therefore it is concluded that a risk to sediment organisms from production and some uses of D5 cannot currently be ruled out.

[25] The regional sediment concentration is calculated using EUSES and represents the steady-state concentration. The local PECs for sediment are calculated from the local water PECs using the equilibrium partition approach. They are not calculated by adding the regional sediment concentration to the local contribution. Hence it is possible to have ratios below one for individual scenarios when the regional ratio is above one. For comparison, if the regional sediment concentration is estimated

5.1.4 Uncertainties and possible refinements

It is not possible to derive a PNEC for D5 for surface water. The available information indicates that the substance presents a low risk to aquatic organisms. It may be possible to carry out a long-term fish early life-stage test to confirm that D5 does not give rise to toxic effects at the water solubility limit. However, such a test is very difficult to carry out (D5 is volatile and has a very low water solubility). In addition, as D5 has a high log K_{ow} value, the sediment compartment is expected to be much more relevant than surface water for assessing the risks to the aquatic compartment. Therefore, it is recommended that any refinement considered necessary for the sediment should take precedence over that for surface water.

As discussed in Section 1.3.7, some uncertainty exists over log K_{ow} value for D5. An analysis of the effect of using a lower log K_{ow} value on the risk assessment (see Appendix A) shows that the use of a lower log K_{ow} value has little effect on the outcome of the risk assessment.

Further information on the release to the environment from production and on-site use as an intermediate, personal care formulation sites, and use of personal care products by the general public would be useful to refine the PEC estimates. However, some of the emission estimates for scenarios are already based on the best information currently available rather than on default release values.

It is also possible to refine the PNEC for sediment by carrying out further long-term toxicity testing with sediment organisms.

5.1.5 Conclusions for the aquatic compartment

The risks to surface water and waste-water treatment plants are thought to be low based on the information currently available and a default exposure estimate.

For sediment a possible risk is identified from production and on-site use as an intermediate, personal care formulation sites (both UK and non-UK), and use of personal care products by the general public and at a regional level. Further information on the emissions to water from these processes would be useful to refine the PECs for these scenarios. In addition, further toxicity data for sediment-dwelling organisms would be useful to refine the PNEC for sediment.

5.2 Terrestrial compartment

5.2.1 Risk characterisation ratios

No PNEC can be derived for D5. An indicative value of 4.8 mg/kg wet weight was derived (see Section 4.2.2) and a comparison of this value with the PECs is given in

Table 5.4. As the indicative value is derived using the equilibrium partitioning approach the risk characterisation ratios are increased by a factor of ten in line with the recommendations in the TGD.

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from the regional water concentration using the equilibrium partitioning approach, the regional sediment concentration would be 0.33 mg/kg wet weight, which does not lead to a risk characterisation ratio above one.

Table 5.4 Risk characterisation ratios for the terrestrial compartment

Scenario	PEC (mg/kg wet weight)	Risk characterisation ratio
Production and on-site use as an intermediate	1.3×10^{-5}	2.7×10^{-5}
Off-site use as an intermediate – wet process (non-UK)	7.2×10^{-6}	1.5×10^{-5}
Off-site use as an intermediate – dry process (non-UK)	9.5×10^{-6}	2.0×10^{-5}
Personal care products – formulation – UK sites	7.2×10^{-4}	1.5×10^{-3}
	2.3×10^{-3}	4.7×10^{-3}
	7.0×10^{-5}	1.5×10^{-4}
	2.1×10^{-3}	4.3×10^{-3}
	0.014	0.030
	2.1×10^{-3}	4.5×10^{-3}
	1.6×10^{-3}	3.4×10^{-3}
	3.0×10^{-3}	6.3×10^{-3}
	2.5×10^{-4}	5.1×10^{-4}
	0.016	0.034
	0.012	0.026
	6.2×10^{-3}	0.013
	1.2×10^{-3}	2.4×10^{-3}
	1.9×10^{-4}	3.9×10^{-4}
	7.5×10^{-6}	1.6×10^{-5}
	4.5×10^{-4}	9.4×10^{-4}
	5.3×10^{-4}	1.1×10^{-3}
	0.013	0.067
Personal care products – formulation – generic site	0.050	0.10
Personal care products – formulation – specific non-UK sites	<1 (see Appendix B)	<1 (see Appendix B)
Personal care products – use by general public	7.7×10^{-3}	0.016
Household products – formulation	7.2×10^{-6}	1.5×10^{-5}
Household products – use	3.9×10^{-4}	8.2×10^{-4}
Industrial/institutional cleaning – use	7.5×10^{-6}	1.6×10^{-5}
Regional – agricultural soil	0.11	0.23
Regional – natural soil	7.1×10^{-6}	1.5×10^{-5}
Regional – industrial soil	7.1×10^{-6}	1.5×10^{-5}

Based on this worst case analysis, risk characterisation ratios <1 are for all scenarios. Therefore it is concluded that the risk to soil organisms from production and all uses of D5 in the UK and EU is low.

5.2.2 Uncertainties and possible refinements

For the soil compartment considerable uncertainties exist over both the PECs and the PNEC.

The local PECs for the generic scenario can be further refined by obtaining information on the exposure, particularly whether sewage sludge from wastewater treatment plants is spread onto agricultural land at sites where D5 is used. This information was made available for a number of sites using D5, but where such information is not available the assessment

currently assumes that sewage sludge is applied to agricultural land as a worst case. However, given that even with this worst-case assumption no risks to soil are identified, to obtain such information is not a priority.

As discussed in Section 3.3.4.2, there is some uncertainty over the actual degradation rate in soil for D5. The effect of this uncertainty on the local concentrations in soil is generally small (much less than a factor of 2; see Section 3.3.2.1). The uncertainty in the degradation rate in soil also impacts on the predicted regional concentrations. However, as no risk is predicted, even assuming no degradation, similar conclusions would be drawn for this endpoint even if the substance degrades faster than assumed.

A further consideration related to the spreading of sewage sludge is that, although a significant fraction of D5 is predicted to be adsorbed into sewage sludge during waste-water treatment, some of this could be lost (e.g. by volatilisation or hydrolysis) during subsequent treatment and handling of the sludge prior to application to land. For example, stabilisation of the sludge with lime (which can raise the pH to around 12, conditions under which rapid hydrolysis of D5 may occur) or pasteurisation (by heating to 55–70°C for 30 minutes to four hours) may be carried out. Several other treatments are also commonly used (e.g. mesophilic anaerobic digestion, thermophilic aerobic digestion, composting, dewatering, and storage) whereby the sludge is treated and/or stored for several days [typically 7–14 days, but up to three months for liquid storage, sometimes at elevated temperatures (35–55°C)] prior to spreading on land. Therefore the instantaneous concentration in sewage sludge predicted during wastewater treatment may not reflect the actual concentration in sewage sludge that is applied to land. Actual measurements in sewage sludge as applied may be useful in this respect.

Some uncertainty exists over log K_{ow} for D5. In Appendix A the use of a lower log K_{ow} on the outcome of the risk assessment for soil is considered and again no risks for any scenario identified.

It is also possible to refine the PNEC for soil through long-term toxicity testing with soil organisms. However, as no risk is currently identified this is not a priority.

It is possible that D5 could be formed in soil from the degradation of PDMS fluids and other siloxane polymers. A preliminary assessment of this potential source (see Section 3.1.7.2) indicates that the amounts of D5 that could be volatilised from soil through this process are likely to be small compared with other sources of D5. However, there are considerable uncertainties and simplifications in the approach taken and little or no information is available on the breakdown of PDMS fluids and other siloxane polymers in landfills (landfills appear to be a major route of disposal for some of these polymers). It is currently assumed that such products are relatively stable under landfills conditions. In addition, it is not currently possible to estimate the amount of D5 that could be present in the soil itself as a result of these processes. A further, in-depth, assessment of the use pattern, emission sources, and fate of PDMS and other siloxane polymers is needed to provide a more refined estimate of the potential emissions of D5 from this source. This is beyond the scope of the current risk assessment.

5.2.3 Conclusions for soil

Based on this worst-case assessment, no risk to soil is identified from the production and use of D5 in the UK and EU.

5.3 Atmospheric compartment

5.3.1 Conclusions for the atmosphere

No PNEC can be derived for the atmospheric compartment. The predicted concentrations in the atmosphere are generally low and so direct toxic effects are not expected.

Although D5 is reactive in the atmosphere, the half-life for the reaction is sufficiently long (estimated to be around 10.4 days) that transport to remote regions could occur. This, coupled with the high BCF for fish (BCF = 7060 l/kg), the lack of biodegradability, and the relatively long hydrolysis half-life (particularly at near neutral pH), means that the substance could possibly meet at least some of the screening criteria in relation to persistent organic pollutants (POPs). For example, the Stockholm Convention (UNEP, 2004) screening criteria (among others) are:

- Persistence: evidence that the half-life of the chemical in water is greater than two months, or that its half-life in soil is greater than six months, or that its half-life in sediment is greater than six months.
- Bioaccumulation: evidence that the BCF or bioaccumulation factor in aquatic species for the chemical is greater than 5000 or, in the absence of such data, that log K_{ow} is greater than five.
- Potential for long-range environmental transport: environmental fate properties and/or model results that demonstrate the chemical has a potential for long-range environmental transport through air, water, or migratory species, with the potential for transfer to a receiving environment in locations distant from the sources of its release. For a chemical that migrates significantly through the air, its half-life in air should be greater than two days.
- Adverse effects: toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.

Further consideration of these aspects in relation to the PBT assessment is given in Section 5.5.2. This indicates that, although D5 has the potential to be transported long-distances in the atmosphere, the very high Henry's law constant coupled with the fact that the vast majority of D5 in the atmosphere is present in the gaseous phase means that it has a very low potential for redeposition to surface media in remote regions. Therefore, on this basis, D5 is considered unlikely to meet the POPs criteria.

5.4 Non-compartment specific effects relevant to the food chain (secondary poisoning)

5.4.1 Risk characterisation ratios

The PNEC for secondary poisoning is estimated as 13 mg/kg food. The resulting risk characterisation ratios are summarised in

Table 5.5.

It is not possible to carry out a risk characterisation for the earthworm food chain because of the lack of a suitable methodology to predict the concentrations in earthworms.

For the fish food chain, most scenarios lead to risk characterisation ratios <1. The only exception is the generic scenario for formulation of personal care products and the site-specific calculation for one of the non-UK personal care formulation sites. Neither of these scenarios is relevant to the UK and it is likely that both could be refined if further exposure information was obtained.

Recent monitoring data from the River Rhine shows concentrations up to 2.6 mg/kg wet weight in fish. These concentrations are below the PNEC for secondary poisoning. However, the number of samples analysed was relatively limited and so it is not possible to draw any general conclusions from these data as to whether there is or is not a risk from secondary poisoning in industrial and/or heavily populated areas.

5.4.2 Uncertainties and possible refinements

A large uncertainty exists over the BMF used for the fish food chain. The default value is 10, but this is not thought to be appropriate for D5. The BMF value of 3.9 used in the assessment for D5 is obtained from a dietary study with fish and the value is both growth corrected and lipid normalised. Lower BMFs for D5 are obtained without these corrections, and result in lower risk characterisation ratios. The TGD recommends that the BMF used should be lipid normalised, but gives no guidance on whether or not the BMF should be growth corrected.

Table 5.5 Risk characterisation ratios for secondary poisoning[1]

Scenario	Fish[2]	
	PEC (mg/kg)	Risk characterisation ratio
Production and on-site use as an intermediate	9.4	0.72
Off-site use as an intermediate – wet process (non-UK)	3.5	0.27
Off-site use as an intermediate – dry process (non-UK)	3.5	0.27
Personal care products – formulation – UK sites	3.8	0.29
	4.8	0.37
	3.5	0.27
	4.3	0.33
	9.4	0.72
	4.4	0.34
	4.1	0.32
	4.7	0.36
	3.6	0.28
	10	0.77
	8.6	0.66
	6.0	0.46
	4.0	0.31
	3.5	0.27
	3.5	0.27
	3.6	0.28
	3.7	0.28
	8.9	0.68
Personal care products – formulation – generic site (non-UK)	24	1.8
Personal care products – formulation – specific non-UK sites	3.5–14 (see Appendix B)	0.27–1.1 (see Appendix B)
Personal care products – use by general public	7.4	0.57
Household products – formulation	3.5	0.27
Household products – use	3.7	0.28
Industrial/institutional cleaning – use	3.5	0.27
Regional sources	3.5	0.27

Note: [1]The methodology used in the TGD for estimating the concentrations in earthworms is not applicable to substances with very high log K_{ow} values.
[2]The calculations for fish include a BMF of 3.9.

For the PNEC, it is not straightforward to interpret the effects seen with D5 in the available mammalian toxicity studies using oral exposure. The majority of the effects seen at lower doses are not thought to be toxicologically significant for humans or not related to a toxic effect of D5, and this is reflected in the PNEC chosen to derive the risk characterisation ratios. The PNEC is derived on the basis of enlargement of the liver through oral exposure in rats. This liver weight increase occurs without any evidence of any accompanying liver damage and the approach used here assumes that an increase in liver weight alone may impair survival in the wild if the increase is sufficiently large.

A limited amount of monitoring data is available for the levels of D5 in biota. These show that although D5 is found in some biota (notably some fish livers and blubber of marine mammals), the levels found in fish are generally much lower than predicted here. This raises some uncertainty as to the reliability of the PECs estimated in this assessment. However, it is not clear how much of the monitoring data relate to the scenarios considered here.

There is also some uncertainty over log K_{ow} for D5. When a lower log K_{ow} is considered in the assessment (see Appendix A) the risk characterisation ratios for the fish food chain are similar to those obtained above.

Uncertainties exist over the prediction of the concentrations of D5 in earthworms using the methods in the TGD because of the high log K_{ow} value for D5. At present it is not possible to assess fully the risk from this route of exposure. Appendix A considers the effect of using a lower log K_{ow} on the risk characterisation ratios and indicates there is likely to be little or no risk from secondary poisoning via the earthworm food chain. It is possible to produce a more reliable assessment of this route of exposure if further work is carried out to measure a bioaccumulation factor for earthworms in soil. However, given the very low concentrations of D5 predicted in soil and the difficulties in carrying out such a test, further testing is not warranted at present.

5.4.3 Conclusions for predators

The worst-case risk characterisation ratios for the fish food chain indicate no risk of secondary poisoning from fish through production and all uses of D5 in the UK. Two scenarios related to the formulation of personal care products at sites outside the EU lead to risk characterisation ratios >1, but it is likely that these scenarios could be refined by obtaining further exposure information if desired.

The risk to predators exposed via the earthworm food chain cannot be fully assessed based on the current dataset. Further work can carried out to measure a bioaccumulation factor for earthworms in soil, but such further testing is not warranted at present.

5.5 Marine compartment

5.5.1 Risk characterisation ratios

Currently a PNEC for the marine compartment can only be derived for sediment (PNEC = 0.048 mg/kg wet w**eight**) and secondary poisoning (PNEC = 13 mg/kg food). The resulting risk characterisation ratios are summarised in Table 5.6. For marine water, the PECs are compared with the indicative concentration of 0.17 µg/l.

Based on this worst-case analysis one generic scenario (formulation of personal care products) leads to predicted risk characterisation ratios >1 for marine water sediment,

predators, and top predators. In addition, risk characterisation ratios of one and above are indicated for sediment for the production and on-site use as an intermediate, ten UK personal care products formulation sites, use of personal care products by the general public, and the regional scenario.

The generic scenario for formulation of personal care products is not relevant to the situation in the UK because site-specific risk characterisation ratios are derived for sites in the UK. In addition, site-specific information has been obtained for EU personal care product formulation sites outside the UK. These sites cover around 80 per cent of the total EU market, and risk characterisation ratios <1 are obtained for all of them. The generic scenario is based on a size representative of a relatively large formulation site (assumed to be using around 255 tonnes/year of D5). Based on the site-specific information for both the UK and non-UK formulation sites it is unlikely that a site of this size in the EU is not already covered by site-specific information. The available site-specific information for UK and EU sites is thus preferable to this scenario.

Based on the above analysis, the risk to marine water, predators, and top predators appears to be low, but a possible risk to marine sediment from the production and on-site use of D5 as an intermediate, some sites for formulating person care products, the use of personal care products by the general public, and regional sources cannot be currently ruled out.

Table 5.6 Risk characterisation ratios for the marine environment

Scenario	Water		Sediment		Predators[1]		Top predators[2]	
	PEC (µg/l)	PEC/indicative concentraiton	PEC (mg/kg wet weight)	RCR	PEC (mg/kg)	RCR	PEC (mg/kg)	RCR
Production and on-site use as an intermediate	0.020	0.12	0.067	1.4	0.49	0.038	1.8	0.14
Off-site use as an intermediate – wet process (non-UK)	9.8×10^{-3}	0.058	0.032	0.67	0.34	0.026	1.7	0.13
Off-site use as an intermediate – dry process (non-UK)	9.8×10^{-3}	0.058	0.032	0.67	0.34	0.026	1.7	0.13
Personal care products – formulation – UK sites	0.012	0.070	0.039	0.82	0.37	0.028	1.7	0.13
	0.017	0.097	0.054	1.1	0.34	0.026	1.8	0.14
	0.010	0.059	0.033	0.69	0.34	0.026	1.7	0.13
	0.016	0.094	0.052	1.1	0.43	0.033	1.8	0.14
	0.052	0.31	0.17	3.6	0.94	0.072	2.3	0.18
	0.016	0.095	0.053	1.1	0.43	0.033	1.8	0.14
	0.015	0.086	0.048	1.0	0.41	0.032	1.7	0.13
	0.019	0.11	0.061	1.3.111.3	0.47	0.036	1.8	0.14
	0.011	0.062	0.034	0.71	0.35	0.027	1.7	0.13
	0.058	0.34	0.19	1.3.124.0	1.0	0.076	2.3	0.18
	0.046	0.27	0.15	1.3.133.2	0.86	0.066	2.2	0.17
	0.028	0.17	0.092	1.3.141.9	0.60	0.046	1.9	0.15
	0.013	0.078	0.043	0.90	0.39	0.030	1.7	0.13
	0.010	0.061	0.034	0.71	0.35	0.027	1.7	0.13
	9.8×10^{-6}	0.058	0.032	0.67	0.34	0.026	1.7	0.13

Scenario	Water		Sediment		Predators[1]		Top predators[2]	
	PEC (µg/l)	PEC/indicative concentraiton	PEC (mg/kg wet weight)	RCR	PEC (mg/kg)	RCR	PEC (mg/kg)	RCR
	0.011	0.065	0.036	0.76	0.36	0.028	1.7	0.13
	0.011	0.067	0.037	0.78	0.36	0.028	1.7	0.13
	0.048	0.28	0.16	1.3.153.4	0.88	0.068	2.2	0.17
Personal care products – formulation – generic site (non-UK)	3.2	19	10	1.3.16210	45	3.5	45	3.5
Personal care products – formulation – specific non-UK sites	9.8×10^{-3} (see Appendix B)	0.058 (see Appendix B)	0.032 (see Appendix B)	0.67 (see Appendix B)	0.34 (See Appendix B)	0.026 (see Appendix B)	1.7 (see Appendix B)	0.13 (see Appendix B)
Personal care products – use by general public	0.033	0.19	0.11	1.3.172.3	0.74	0.057	2.1	0.16
Household products – formulation	9.8×10^{-3}	0.058	0.032	0.67	0.34	0.026	1.7	0.13
Household products - use	0.011	0.064	0.036	0.76	0.36	0.028	1.7	0.13
Industrial/institutional cleaning – use	9.8×10^{-3}	0.058	0.032	0.67	0.34	0.026	1.7	0.13
Regional	9.8×10^{-3}	0.058	0.063	1.3.181.3	0.34	0.026	1.7	0.13

Notes: [1]The values for predators use a BMF_1 of 3.9.
[2]The values for top predators use a BMF_1 and a BMF_2 of 3.9.

5.5.2 Assessment against PBT criteria

5.5.2.1 Persistence

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. The data available from a preliminary study indicate that the hydrolysis half-life is 60 days [the cut-off for the persistent (P) or very persistent (vP) criterion] or longer at different temperatures and within the pH ranges (see Section 3.2.4.1).

- 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

According to the TGD, the relevant environmental conditions for marine waters are a pH of around 8 and a temperature of around 9°C. Under these conditions, the hydrolysis half-life of D5 is >60 days (actually around 64 days) and so D5 would be considered a P or vP substance. However, there are also water bodies within the UK (and EU) in which the hydrolysis half-life is >>60 days, and others in which the hydrolysis half-life is <60 days. It is therefore concluded that D5 meets the screening criteria for P and vP under some circumstances.

Important to the screening criteria for P and vP is that D5 is highly volatile and so can be lost from water by this mechanism (this may be the primary loss process of D5 from some water bodies). A further consideration in this respect is that D5 has a high log K_{ow} value (log K_{ow}) and so any substance present in water may adsorb onto sediments or suspended sediments [D5 was detected in samples of sediments from the environment (see Section 3.3.1.2)]. The effect of this on the hydrolysis rate is unknown (which is also expected to moderate the volatilisation from water). To account for these factors, it is necessary to consider the persistence of the substance in the whole environment rather than just in the water compartment. In the TGD there is currently no agreed methodology for carrying out such an analysis. However, a number of approaches and models (as discussed below) are used here for D5. The models were generally run using the in-build default compartment sizes and properties, as the intention is to investigate the predicted distributions and behaviours rather than absolute concentrations. Unless otherwise stated, no attempts were made to modify the models to typical European conditions.

New data on the physico-chemical properties of D5, particularly log K_{ow}, Henry's law constant, and K_{oa} have become available recently. These data are discussed in detail in Section 1. Much of the modelling work outlined below was carried out before these new data became available and so use a log K_{ow} of around 5.2 and a Henry's law constant of around 3.23×10^4 Pa m^3/mol (these are the alternative values listed in Table 1.1). However, two studies were carried out more recently using the higher log K_{ow} of 8.03 and a Henry's law constant of 3.34×10^6 Pa m^3/mol. The text indicates the studies in which these new values are used (where there is no indication then the alternative values from Table 1.1 are generally used). The findings using both sets of physico-chemical properties are broadly in agreement.

The first model investigated was the EQC model. This is a regional multimedia fugacity model and takes into account volatilisation and adsorption to sediment. The default environmental compartment sizes and properties within the model are used for this simulation. These have a higher proportion of freshwater than found in typical multimedia models representative of the EU. The level III model was run assuming a release of 69 kg/hour into air, 20 kg/hour to water, and 11 kg/hour to soil. These are based on the worst-case default emission estimates given in the confidential Annex and take into account the distribution in the wastewater treatment plant (the actual emissions used in this risk assessment for the PEC calculations are generally lower than these values). The model was run three times [the atmospheric degradation half-life was assumed to be 250 hours (10.4 days) in all cases] using the hydrolysis rates:[26]

- 61 days (i.e. close to the half-life at pH 8 and 9°C),
- 90 days (i.e. close to the half-life at pH 7 and 25°C),
- 324 days (i.e. close to the half-life at pH 7 and 12°C).

The overall residence time is estimated to be between 10.7 and 11.4 days irrespective of the hydrolysis time used. The main loss from the system is predicted to be via transport in air flowing from the region, followed by degradation in air. The predicted steady-state distribution of D5 within the model environment is around 28 per cent in air, around 16 per cent in soil, around 20 per cent in water, and around 36 per cent in sediment.

A similar model for D5 was used by Cousins and Prevedouros (2005). This modelling exercise was carried out as a blind trial in that the authors were not provided with the identity of the substance being modelled, but with only the basic physico-chemical properties and degradation rates of the chemical (taken from this assessment) were provided. The model used is a modified version of ChemCAN 4, which is a steady-state level III model originally developed to describe the regional fate and behaviour of substances in Canada. The model comprises eight environmental compartments (air, fresh, ground, and marine water, soil, freshwater sediments, terrestrial plants, and animals), but for this example the model was modified by adding a marine sediment compartment and setting the volumes of the groundwater and terrestrial plant and animals compartments to zero. The model was run for a generic (100,000 km^2) area similar to that within the EQC model at a temperature of 12°C. The model uses emission rates to air, water, and soil based on the default calculations in this assessment (the actual emission rates are confidential). The results of the modelling predict D5 to partition to freshwater (around 23 per cent of total), freshwater sediments (around 36 per cent of total), soil (around 21 per cent of total), and air (around 15 per cent of total), with smaller amounts predicted to partition into marine water and marine sediments (<5 per cent). The most important loss process in the model is advection out of the region. The overall residence time, taking into account advection and degradation, is 7.4 days, with loss from the model dominated by advection. These results are similar to those obtained above using the EQC model.

Also of interest here is that, although a relatively short overall residence time is predicted using both the EQC and ChemCAN 4 model, the models predict that in a steady-state around 36 per cent of the total D5 in the system is associated with sediment and around 16–21 per cent is associated with soil.

Cousins and Prevedouros (2005) also investigated the sensitivity of the model to individual model input parameters. All the input parameters were varied by ±10 per cent of their initial values and the effect of this on a number of model output parameters examined. In this

[26] These half-lives are chosen based on the results of the preliminary hydrolysis study. Results from the definitive hydrolysis study are now available and lead to half-lives of a similar order (see Section 3.2.4.1).

respect the model outputs appear to be most sensitive to changes in K_{oc}, Henry's law constant, and the emissions. The concentrations in air are mainly driven by K_{oc} and the emissions to air, the concentrations in freshwater are driven mainly by the emissions to water (the freshwater sediment levels are also driven by K_{oc}), and the concentrations in soil are driven by K_{oc}, Henry's law constant, and emissions to soil (via sewage sludge). The coastal water levels are driven by the emissions to freshwater, freshwater residence time, and coastal water degradation half-life.

The model outputs (both the predicted concentrations and the compartmental distribution) appear to be relatively insensitive to the media-specific degradation rates used (presumably because loss from the model is driven by advective rather than degradative processes).

It is also possible to obtain a predicted steady-state distribution of D5 from the regional model within EUSES 2.0.3. The model was run using the same emission estimates, physico-chemical properties, and degradation rates as assumed in the main risk assessment for the PEC calculations. Based on the total mass of D5 in the regional model, most of the chemical is predicted to occur in the agricultural soil compartment (around 97 per cent), with around 1.6 per cent predicted to be in the sediment compartment and 1.4 per cent in the air compartment. The regional model in EUSES differs from the EQC and ChemCAN 4 models in that it includes spreading of sewage sludge onto agricultural land (which may explain the higher predicted distribution to soil in EUSES compared with the EQC and ChemCan 4 estimates above) as well as different relative proportions of land and water surfaces. Of interest here is that the EUSES regional model predicts that, at steady state, the percentages of the total D5 in the region that occurs in sediment and air are broadly similar. This is in line with the relative distributions to air and sediment in the EQC and ChemCAN 4 estimates above.

The predicted steady-state behaviour of D5 at a regional level was also investigated using the level III steady state model in the EPI-WIN software (Whelan, 2006a). This study is considered as 'work in progress, but the initial results were made available for this report. The model used is based on the EQC model (see above) and various combinations of degradation half-lives in air, water, sediment, and soil are investigated along with combinations of emissions to air, water, and soil. In all scenarios advective losses are minimised by setting advection times to ten years in all media. Where emissions are assumed to occur to air only, a very high proportion (>97 per cent) of the total steady-state mass of D5 is predicted to reside in the air and the overall residence time of D5 is predicted to be <15 days. Where emissions to water are assumed a significant fraction (up to around 50 per cent based on 10 per cent of the total emission being to water) of the total steady-state mass is predicted to end up in sediment, which again indicates that, despite a relatively short overall residence time, a substantial fraction of the steady-state burden may be associated with the sediment phase.

Long-range transport models can also provide useful information on the overall persistence of D5 in the environment. Similar to EQC, these models take into account both volatilisation and partitioning between water and sediment, but the persistence is considered on a global rather than regional scale. Thus, the persistence in air (and water) in these models is not limited by transport out of the model, and so they give a more reliable picture of the overall persistence of the chemical. A number of such models were used with D5 to investigate the effect of varying the hydrolysis half-life on the overall environmental persistence. The same hydrolysis and atmospheric degradation half-lives as used in the EQC model above are used in this exercise. The necessary physico-chemical properties for D5 are taken from Section 1.3. The default values for any other parameters required by the model are used. The results of the model are summarised as:

- TaPL3 is a long-range transport and persistence model (a level III fugacity model) developed by the Canadian Environmental Modelling Centre. It is based on a

publication by Beyer *et al.* (2000). The model gives an overall persistence in the environment and a long-range transport distance for both emissions to air and emissions to water. The default compartments within the model are used for the simulation. The simulations were run twice, firstly assuming a hypothetical emission rate of 1000 kg/hour to water and secondly assuming a hypothetical emission rate of 1000 kg/hour to soil. The results are summarised in

- Table 5.7.

Table 5.7 Results of TaPL3 model

Hydrolysis half-life assumed (days)	Overall persistence[1] (days)		Overall half-life (days)		Long-range transport distance (km)	
	Emission to air	Emission to water	Emission to air	Emission to water	Emission to air	Emission to water
61	15	75	10.4	55	5195	1234
90	15	79	10.4	52	5195	1303
324	15	86	10.4	60	5195	1422

Note: [1]Overall persistence (P) is defined as the (total steady-state chemical mass in the system)/(total loss rates from all compartments). An equivalent half-life (HL) can be estimated from HL = ln(2) × P.

- ChemRange 2.1 is a multimedia transport model developed by the Swiss Federal Institute of Technology (ETH), Zurich to calculate persistence and spatial range of organic chemicals. The model was run without modification, assuming a hypothetical release rate of 11 kg/day to soil, 20 kg/day to water, and 69 kg/day to air. These are based on an approximate estimate of the relative fraction of D5 released to soil, water, and air (i.e. 11:20:69) based on an earlier estimate of the emissions of D5 in the EU carried out as part of this assessment at the time of the simulation. The model calculates the percentage of the earth's circumference to which a substance is transported. For D5 this is estimated at 24 per cent of the earth's circumference using a hydrolysis half-life of 324 days. Assuming the earth's circumference is 40,076 km, this corresponds to a transport distance of 9618 km.

- ELPOS (Environmental Long-range Transport and Persistence of Organic Substances Model) is a multimedia chemical fate model financed by the German Federal Environmental Agency. It is based on the regional part of the SimpleBox model within EUSES. The model was run without modification, assuming an emission pattern of 69 per cent to air, 20 per cent to water, and 11 per cent to soil (see above). Using this model the overall persistence in the environment is estimated as (both based on a hydrolysis half-life of 324 days):

  - emission to air: overall persistence 16 days (half-life 11 days), travel distance 5185 km in air;

  - emission to water: overall persistence 43 days (half-life 30 days), travel distance 11 km in water.

The overall environmental fate of D5 is also being investigated by other workers using similar global models (Whelan, 2006a). The study is 'work in progress' but the preliminary findings were made available for this assessment. Assessments of the long-range transport potential are made using the ChemRange, ELPOS, BETR (assuming 100 per cent release to the atmosphere), and GLOBOPOP (assuming an equal release to air, water, and soil) models. It is concluded that the properties of D5 mean that that it partitions readily into the atmosphere

where it remains until degraded. The relatively long atmospheric half-life means that the substance has a high potential for long-range transport to occur, but it will not be redeposited to surface media in remote regions. Values of the Arctic Contamination Potential of D5 (Wania, 2003) based on predictions made using the GLOBOPOP model are relatively low.

Based on the modelling results outlined above, a clear picture emerges as to the overall environmental behaviour of D5. When released to air, the overall environmental half-life for D5 is related to its reactivity in the atmosphere, and is around 10–11 days. When released to water, the overall environmental half-life is longer (around 30–60 days) and is relatively independent of the hydrolysis rate assumed. This implies that the actual fate of D5 in water is governed mainly by the partitioning behaviour between sediment, water, and air rather than degradation by hydrolysis. Therefore it is very important to take these processes into account when the overall persistence in the environment is considered.

Although from the available modelling data it appears that the overall half-life of D5 in the environment is <60 days, it is difficult to compare these overall environmental half-lives directly with the P and vP criteria given in the TGD. This is because the criteria in the TGD refer to only one compartment (either water or sediment) rather than to the whole environment. Further, the criteria given in the TGD for water and sediment are different. However, the available modelling results (which also take into account adsorption onto sediment) generally show that the substance is lost from aquatic systems mainly by volatilisation to the atmosphere (coupled with hydrolysis in water) and so, although the screening P and vP criteria appear to be met for water, there is a plausible loss process for D5 that means the substance will not persist in the aquatic (water) environment.

Furthermore, most river networks have advective residence times for water and solutes of the order of a few days. Even for longer rivers such as the Rhine, typical water residence times are likely to be of the order of 2–3 weeks for the whole river length. Combined with the relatively high rate of volatilisation expected from shallow water bodies, such as rivers, these time scales imply that longer hydrolysis half-lives (e.g. 60 days) are not particularly meaningful for understanding the fate of D5 in these systems.

However, the above modelling approaches do indicate the half-life of D5 in the sediment compartment specifically. This is an important point in relation to the P or vP criteria. To investigate the half-life in sediment further modelling studies were carried out.

Whelan (2006c) explored the fate of D5 in a hypothetical lake system using a slightly modified version of the Quantitative Water Air Sediment Interaction (QWASI) steady-state model (Mackay *et al.*, 1983a, 1983b), with a specific focus on the role of volatility in controlling persistence and concentration. QWASI v2.8[27] was used in a number of scenarios that combined water depth, degradation rate in the water column, assumed degradation rate in sediment, and K_{aw}. QWASI was applied previously to explore the fate of a range of different chemicals in different lake systems and its predictions match observations well (e.g. Mackay, 1989; Mackay and Diamond, 1989; Diamond *et al.*, 1994, 1996; Lun *et al.*, 1998; Woodfine *et al.*, 2000; Mackay and Hickie, 2000). In all scenarios the common assumptions applied are:

- Log K_{OW} = 5.2 (i.e. appropriate for D5).
- Half-life in sediment = 3 × half-life in water (no empirical information on sediment fate is currently available). This is consistent with the PBT criteria for half-lives in water and sediment defined within the TGD.

[27] Model available from http://www.trentu.ca/cemc/models/models.html.**Error! Hyperlink reference not valid.**.

- Sediment deposition, sediment re-suspension, and sediment burial and advection of water and sediment into and out of the lake system are minimised to negligible levels. Chemical exchanges between the water column and the sediment are effectively restricted to diffusion only. This simplifying assumption is conservative with respect to persistence and facilitates interpretation of the results but does not affect the overall conclusions.
- The calculation of persistence metrics uses only terms which represent net losses for the whole water and sediment system. The basic equations that describe chemical fate and partitioning in the model are not changed in any way.
- Two different values of K_{aw} (dimensionless Henry's Law constant) were used: 13 [the measured value for D5 (Kochetkov *et al.*, 2001)] and 0.0001 which is intended to serve as a non-volatile contrast for D5.
- The effect of temperature is included only as a determinant of degradation half-life (water and sediment). Its potential effects on other processes are not taken into account, but are not likely to be important for the overall conclusions.
- Estimated hydrolysis half-lives in water at pH 7 only are considered. Much lower half-lives at pH values higher and lower than seven have been observed.
- In all cases emission is arbitrarily set at 100 kg/hour (the emission is assumed to enter into the water phase), although importantly the persistence is completely independent of emission.

In QWASI, complete and instantaneous mixing of emitted material is assumed. This assumption may not be valid for large (deep and or expansive) water bodies.

Six scenarios were run at each of three water temperatures (25, 12, and 9°C). In each scenario identical chemical-specific parameters are assumed,[28] except for the degradation rate. The half-lives in water used (90, 255, and 324 days) are the hydrolysis half-lives in water estimated at pH 7 at 25, 12, and 9°C respectively (based on the results of the preliminary hydrolysis study; see Section 3.2.4). The influence of water column depth on volatilisation required three different lake depths to be considered (1 m, 10 m, and 100 m).

A summary of the predicted half-lives of D5 (K_{aw} = 13) in water, sediment, and overall are shown in

[28] The K_{aw} is likely to vary with temperature. However, for this exercise the same K_{aw} value was assumed at each temperature. This assumption does not affect the key finding of this study that volatilisation has little or no effect on the half-life in sediment.

Table 5.8. The assumed degradation half-lives in water and sediment are HL_w and HL_s, respectively, and z is the depth of the water column. Experimentally derived hydrolysis half-lives at pH 7 are used for HL_w. Currently there are no observed half-life values for sediment. Values of HL_s are assumed to be three times HL_w and the predicted half-lives in sediment reflect this assumption. The equivalent predicted half-lives when a much lower K_{aw} of 0.0001 is used are also shown in

Table 5.8 for comparison.

The following observations can be made from the results for D5:

- predicted half-life in water and predicted overall half-life are significantly reduced by volatilisation, even when depth is great;
- predicted values of half-life in water can be very short, even when the assumed degradation half-life is relatively large;
- values of the half-life in water and overall half-life increase with increasing water depth;
- values of the half-life in sediment are insensitive to volatility and water depth.

Table 5.8 QWASI-predicted half-lives in water, sediment, and overall for a hypothetical lake system with advection and sediment exchanges switched off

Conditions	Predicted half-life in water (days)	Predicted half-life in sediment (days)	Predicted overall half-life (days)
Predictions for D5 (K_{aw} = 13)			
25 °C, z = 1 m, HL_w = 90 days, HL_s = 270 days	3	270	13
25 °C, z = 10 m, HL_w = 90 days, HL_s = 270 days	22	270	29
25 °C, z = 100 m, HL_w = 90 days, HL_s = 270 days	69	270	71
12 °C, z = 1 m, HL_w = 255 days, HL_s = 765 days	3	765	19
12 °C, z = 10 m, HL_w = 255 days, HL_s = 765 days	26	765	40
12 °C, z = 100 m, HL_w = 255 days, HL_s = 765 days	135	765	142
9 °C, z = 1 m, HL_w = 324 days, HL_s = 972 days	3	972	20
9 °C, z = 10 m, HL_w = 324 days, HL_s = 972 days	27	972	42
9 °C, z = 100 m, HL_w = 324 days, HL_s = 972 days	153	972	160
Example predictions for a substance with a lower K_{aw} of 0.0001			
25 °C, z = 1 m, HL_w = 90 days, HL_s = 270 days	69	270	168
25 °C, z = 10 m, HLw = 90d, HLs = 270 days	87	270	107
25 °C, z = 100 m, HL_w = 90 days, HL_s = 270 days	90	270	92
12 °C, z = 1 m, HL_w = 255 days, HL_s = 765 days	136	765	453
12 °C, z = 10 m, HL_w = 255 days, HL_s = 765 days	234	765	313
12 °C, z = 100 m, HL_w = 255 days, HL_s = 765 days	253	765	262
9 °C, z = 1 m, HL_w = 324 days, HL_s = 972 days	153	972	553
9 °C, z = 10 m, HL_w = 324 days, HL_s = 972 days	292	972	396
9 °C, z = 100 m, HL_w = 324 days, HL_s = 972 days	320	972	333

Although the predicted persistence in sediment is not affected by volatility, the predicted concentration in sediment is significantly reduced as a consequence of the reduced water-column concentrations that result from high K_{aw}. Predicted concentrations in both water and sediment are significantly lower when volatility is considered (K_{aw} = 13) compared to when it is not. Furthermore, although persistence is predicted to increase with increasing water-body depth, the predicted concentration in both water and sediment decrease with increasing water depth. The QWASI model considers processes that operate at a local scale. However, similar conclusions about the effect of volatility on water and sediment concentrations can be reached using regional scale models of chemical fate (such as that implemented within EUSES).

The available models suggest that D5 could undergo long-range transport via the atmosphere. The key consideration here is whether the substance remains in the atmosphere (where it is effectively degraded) or is re-deposited in cold regions (and so can enter the aquatic food chain). Klasmeier *et al*. (2004) suggest that the potential for re-deposition depends on a combination of increased net deposition rate and decreased degradation rate at colder temperatures. Based on these assumptions they considered a screening approach in which the characteristic travel distances estimated at 10°C and 5°C using the ELPOS model could be used to identify chemicals with a potential for re-deposition in colder regions. They defined the cold-condensation potential as the ratio of the characteristic travel distance at 10°C to the characteristic travel distance at 5°C. A cold-condensation potential >1 implies that re-deposition in cooler regions could occur, whereas a cold-condensation potential <1 indicates the substance has a low potential for re-deposition in colder regions. This approach was tested for a group of 53 chemicals. The analysis shows that the characteristic travel distance alone does not imply a high potential for cold

condensation. Volatile chemicals with a liquid-phase vapour pressure above 1 Pa at 25°C have a low cold-condensation potential irrespective of the characteristic travel distance.

To carry out such an analysis for D5, information on the temperature dependence of the atmospheric degradation rate and various partition coefficients (air–water, octanol–water, and octanol–air[29]) are needed to calculate the appropriate values at 10°C and 5°C. However, based on the findings from the Klasmeier *et al.* (2004) study, the vapour pressure for D5 is probably high enough for it to remain mainly in the atmosphere, even in cold regions, where it eventually degrades. In addition, as discussed above, the accumulation potential for D5 in animals when inhaled appears to be low.

A low Arctic contamination potential for D5 is also predicted using a similar analysis based on the 'target-oriented' Arctic contamination potential developed by Wania (2003). The study is currently 'work in progress', but the results were made available for this assessment (Whelan, 2006a). The properties of D5 are such that for emissions to air, water, or soil the predicted Arctic contamination potential for D5 is low and it is unlikely to accumulate in surface media in remote regions.

Di Toro and Hellweger (1999) carried out an investigation into the role of Henry's law constant in long-range transport and subsequent deposition in remote areas. D4 was used as an example substance in the report. The report concluded that substances with high Henry's law constants (>1 on a dimensionless basis) are unlikely to be deposited in remote regions, even if they have very long degradation half-lives (up to three years), as most of the mass (around 99 per cent) remains in the atmosphere. The dimensionless Henry's law constant for D5 is around 13 at 26°C.

The long-range transport potential of D5 was also studied using the OECD Tool (version 2) model (Plotzke, 2007). The model is a global average steady-state model. A Monte Carlo simulation was used to investigate the most important factors to influence the predicted behaviour of D5 in the model. For this simulation, log K_{aw} was varied between 1.72 and 3.2, log K_{ow} was varied between 7.81 and 8.4, the half-life in air was varied between 73 and 416 hours (3.0–17.3 days), the half-life in soil was varied between 65 and 1986 hours (2.7–82.8 days), and the half-life in water was varied between 836 and 3562 hours (34.8–148 days). The chemical emission rates used in the simulation are not given. This model found that the most important factors to influence the predicted behaviour in the model are the half-life in air and the half-life in water. Using a log K_{aw} of 2.43, a log K_{ow} of 8.03, a half-life in air of 161 hours, a half-life in soil of 302 hours, and a half-life in water of 1702 hours, Plotzke (2007) estimated the overall persistence of D5 to be 23 days, with a characteristic travel distance of 3300 km and a transfer efficiency of 2×10^{-6} per cent. This places D5 in the low priority category for long-range transport within this modelling framework. Few other details of this study are currently available.

A similar study using the OECD Tool (version 2) model was carried out by Xu and Kozerski (2007). In this series of simulations, log K_{aw} was varied between 0.74 to 3.07 and log K_{ow} was varied between 5.2 and 8.03. The simulations were carried out assuming a rate constant for reaction with atmospheric hydroxyl radicals of 1.55×10^{-12} cm^3/molecule/s, a half-life in soil of 302 hours (12.6 days), a half-life in water of 1702 hours (70.9 days), and a half-life in sediment of five years. The emissions assumed in the simulation are 30,000 tonnes/year for ten years, with 80 per cent of the emissions to the northern temperate environment, 15 per cent of the emissions to the northern subtropic environment, and 5 per cent of the emissions to the northern tropic environment. The study found that varying log K_{aw} and log K_{ow} has little or no effect on the characteristic transport distance. Increasing the log K_{ow} from 5.2 to 8.03 increases the overall persistence lifetime from 63 days to 91 days. Increasing the log K_{aw}

[29] Data are now available on the temperature dependence of the octanol–air partition coefficient (see Section 1.3.9.4), but these arrived too late to be included in the modelling work carried out so far.

from 0.74 to 3.07 decreases the transfer efficiency by up to around 80 per cent. In all cases the estimated characteristic travel distance and transfer efficiency placed D5 in the low priority category for long-range transport. Few other details of this study are currently available.

Xu and Kozerski (2007) also considered the effect of varying log K_{aw} and log K_{ow} on the predicted distribution of D5 obtained using the GLOBOPOP model (version 1.1). Simulations were carried out using two combinations for these properties. The first set of simulations assumed a log K_{ow} of 5.2 and a log K_{aw} of 0.74 and the second set of simulations assumed a log K_{ow} of 8.03 and a log K_{aw} of 3.07. The simulations were carried out four times in each case, assuming 100 per cent emission to air, 100 per cent emission to soil, 100 per cent emission to water, or 97 per cent to air with 1.5 per cent to soil and 1.5 per cent to water. The study found that the majority of D5 predicted to occur in the Arctic is associated with the air compartment, but the fraction predicted is low (and is reduced further if the emission is to water or soil rather than to air). The higher log K_{ow} and log K_{aw} values result in a shift in the predicted distribution from water to sediment (although the fraction predicted in each of these two compartments is very low). The fraction of D5 predicted in Arctic sediments is negligible.

Similar conclusions that the properties of D5, although it can be transported to remote regions via the atmosphere, make it unlikely to be deposited in remote regions can be drawn from the recent work by Fenner *et al.* (2005) and Klasmeier *et al.* (2006). This work considered eight publicly available multimedia models and used a series of reference chemicals with well-known environmental fates to identify the key properties of chemicals of both high and low concern with regards to overall persistence in the environment and the potential for long-range transport. Wania (2006) also reached a similar conclusion for D5 using the Globo-POP model.

In relation to long-range atmospheric transport it is also relevant to consider the possibility of adsorption to atmospheric particulates with subsequent wet and dry deposition of particle-bound D5. The available information reported in Section 3.2.1.1 indicates that, in air, D5 is expected to be mainly in the vapour phase, with only a small fraction associated with the particulate and aerosol phases. On this basis wet and dry deposition of particle-bound D5 are likely to be minor processes only.

As discussed at the start of this section, most of the modelling work was carried out using the 'alternative' physico-chemical properties from Table 1.1. Recently, two new modelling studies were carried out by Xu (2007b, 2007c) using the latest values for log K_{ow} and Henry's law constant. The results of this modelling are summarised below.

The first model investigated was the OECD Pov and LRTP screening tool (Xu, 2007b). The properties (all at 25°C) for D5 assumed in the simulation are a log K_{aw} of 3.13, log K_{ow} of 8.03, half-life in air of 161 hours, half-life in water of 1702 hours, half-life in soil of 302 hours [estimated for a temperate soil at a dryness equivalent to 90 per cent relative humidity, based on Xu (2007a); see Section 3.2.3). The model default values are used for compartment dimensions and properties and various emission patterns are considered. These assume, firstly, 100 per cent emission to either air, water, or soil, then equal emissions to air, water, and soil, and finally (considered to be more realistic) 95 per cent of the total emission to air, 0.1 per cent to water, and 4.9 per cent to soil.

The outputs from the models include the overall persistence, characteristic travel distance, and transfer efficiency. These are then used to determine the priority of the chemical in terms of long-range transport potential.

The maximum values for the overall persistence, characteristic travel distance, and transfer efficiency found in the various simulations are 91.4 days (when 100 per cent release to water is assumed), 3335 km (when 100 per cent release to air is assumed) and 6.5×10^{-3} per cent

(when 100 per cent release to air is assumed) respectively. Regardless of the release scenario chosen, D5 is always identified as a low priority chemical based on the criteria used in the OECD screening tool.

The second model considered was the GLOBOPOP model (Xu, 2007c). The same physico-chemical properties and degradation rates as above are assumed, but additionally a degradation half-life of 43,800 hours (1825 days) in sediments is also used. All simulations were carried out using the model default values for the compartment dimensions and properties. The total D5 emission rate assumed is 3×10^7 kg/year, with an assumed 80 per cent released from the northern temperate climate zone, 15 per cent from the northern subtropical zone, and 5 per cent from the northern tropical zone. Within each climate zone, the release is estimated to be 95 per cent to air, 0.145 per cent to freshwater, and 4.9 per cent to agricultural soil (this is considered to be a realistic emission scenario based on the known uses of D5). No seasonal variation of emission was assumed.

The time to reach steady state within the model is estimated as 2–4 years for air and soil, but much longer for water and sediment (15–25 years for water and 20–25 years for sediment). The relative Arctic contamination potential is found to be low (around 0.033 per cent after ten years continuous release; this value is around 0.008 that of hexachlorobenzene and 0.011 that of PCB-101). The absolute Arctic contamination potential after ten years continuous release is 8×10^{-4} per cent (this value is around 0.0004 that of hexachlorobenzene and 0.0004 that of PCB-101. It is also predicted that the amount of D5 that would accumulate in polar surface media is very low (0.008 per cent of the total release in any time period), and the amount of D5 remaining in polar surface media at any one time is also low (<0.04 per cent of the total D5 that remains in the model). It is also estimated that around 94 per cent of the D5 is degraded after four years continuous release and close to 98 per cent of D5 is degraded after ten years of continuous release. After ten years continuous release it is predicted that the majority (93 per cent) of the D5 that remains within the system is in the air compartment and, of the remaining 7 per cent in surface media, the majority of this (96.6 per cent) is in the soil and sediment compartments of the three source zones (northern temperate, northern subtropical, and northern tropical zones).

Overall these new studies give broadly similar findings to previous studies on the long-range transport potential for D5 – that is, although it can be transported to remote regions via the atmosphere, significant deposition in remote regions is unlikely.

5.5.2.2 Bioaccumulation

For the bioaccumulation criterion, the substance has a measured fish BCF of 7060 l/kg and so clearly meets the very bioaccumulative (vB) criterion (although this BCF is based on total ^{14}C-measurements, the BCF based on parent compound alone would still be >5000 l/kg; see Section 3.2.9.1).

A fish feeding accumulation was also completed for D5. Full details of the study are given in Section 3.2.9.1 and the BMFs determined are summarised as:

- BMF of 0.22, the steady-state value on a (wet weight fish)/(wet weight food) basis;
- BMF of 0.63, steady-state value on a lipid-normalised basis;
- BMF of 1.39, kinetic growth-corrected value on a (wet weight fish)/(wet weight food) basis;
- BMF of 3.9, kinetic growth-corrected value on a lipid-normalised basis.

These data show that uptake into fish can occur from both food and water. Although the steady-state BMF is <1, much of the depuration seen in the fish in this study results from growth dilution. Therefore, in fish that are not growing rapidly, the BMF for D5 could be above one (as shown by the kinetic growth-corrected values). In addition to this, the study found that, although there is evidence of metabolism of D5 in the fish, the growth-corrected depuration half-live 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. These data therefore provide supporting evidence that D5 may be bioaccumulative, particularly in slow-growing fish.

In contrast to the high bioaccumulation potential in fish, the bioaccumulation potential for D5 in top predators (e.g. birds and mammals) appears to much lower than may be expected based on the high fish BCF (or log K_{ow}) alone, particularly in relation to inhalation exposure (see Section 3.2.9). This probably relates to the more rapid elimination kinetics (via respired air) and more rapid metabolism in rodents compared with those in fish. The toxicokinetics of D5 in mammals exposed via oral routes appear to be more complicated than for those for inhalation exposure. Here, the actual fate of D5 is a little less clear than that 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 lipid compartments in the animal. 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 lipid fractions in the body is actually biologically active.

Kelly *et al.* (2004) reviewed methods for predicting intestinal absorption and biomagnification of organic contaminants in fish, wildlife, and humans, and conclude that the emerging evidence indicates the currently used K_{ow}-based classification methods to identify potentially bioaccumulative substances are not adequate for mammals, birds, and humans. They also conclude that the log K_{oa} value is also an important consideration for assessing bioaccumulation potential in such species, whereas the log K_{ow} alone is a good indicator of bioaccumulation potential in aquatic organisms. It is argued that for air-breathing organisms, respiratory elimination occurs via lipid–air exchange, and that such exchange declines with increasing K_{oa}, with biomagnification predicted to occur in many mammals at log K_{oa} >5. This biomagnification potential can be mediated only if the substance is rapidly eliminated in urine (i.e. has a log K_{ow} of around two or less) or is rapidly metabolised. Thus, the bioaccumulation potential in air-breathing organisms is a function of both log K_{ow} and log K_{oa}. In contrast to this, for fish, respiratory elimination occurs to water via gill ventilation, which is known to be inversely related to log K_{ow} (hence an increase in log K_{ow} results in a decrease in the rate of elimination and hence increase in the accumulation potential). Similar conclusions are also reached by Gobas *et al*. (2003).

Based on these findings, Kelly *et al.* (2004) propose that chemicals can be classified into four groups based on their potential to bioaccumulate in air-breathing organisms:

- Polar volatiles (low log K_{ow} and low log K_{oa}). These substances have low potential for bioaccumulation in air-breathing organisms or aquatic organisms.
- Non-polar non-volatiles (high log K_{ow} and high log K_{oa}). This group represents themajority of POPs such as PCBs and some organochlorine pesticides. These substances have a high bioaccumulation potential in both air-breathing organisms and aquatic organisms.
- Polar non-volatiles (low log K_{ow} and high log K_{oa}). This group of substances has a low bioaccumulation potential in aquatic organisms, but a high bioaccumulation potential in air-breathing organisms (unless they are rapidly metabolised).

- Non-polar volatiles (high log K_{ow} and low log K_{oa}). This group of substances have a high accumulation potential in aquatic organisms, but a low accumulation potential in air-breathing mammals.

In this respect D5 can be considered to have a high log K_{ow} (5.2). The K_{oa} value can be estimated from the K_{ow} value and the dimensionless Henry's law constant (13 for D5, in effect, K_{aw}). Thus

K_{oa} = K_{ow}/Henry's law constant = $1.58 \times 10^5/13 = 1.22 \times 10^4$.

Thus log K_{oa} for D5 is 4.1,[30] which is below the cut-off of five for which significant bioaccumulation in air-breathing organisms is expected to occur. Consequently, D5 appears to fit in the non-polar volatiles group outlined above. This finding is entirely consistent with the available uptake and accumulation data for fish and laboratory mammals presented in Section 3.2.9). In addition, D5 also appears to be metabolised in mammals (particularly via inhalation exposure), which further reduces its potential to accumulate at the top of the food chain.

A similar conclusion is reached in a 'work in progress' study for D5 related to bioaccumulation in humans exposed via the food chain in remote regions (Whelan, 2006a). The study considered the Environmental Bioaccumulation Potential (EBAP) proposed by Czub and McLachlan (2004a). EBAP is generated from a human dynamic bioaccumulation model [ACC-Human (Czub and McLachlan, 2004b)] which predicts the concentrations of a given chemical in different stages of the marine and terrestrial food chains, and the chemical accumulation in humans that results from the consumption of a given dietary mix. The model has, thus far, been applied to Arctic and Swedish populations. In each case, the EBAP predicted for D5 is relatively low compared to chemicals known to be confirmed POPs.

However, much of the information on the metabolism and elimination of D5 from mammals is derived from experiments with laboratory animals. The metabolism of D5 in Arctic air-breathing organisms has not been studied.

5.5.2.3 Toxic

D5 is not thought to be toxic to aquatic organisms at concentrations up to its water solubility. It is not classified on the basis of carcinogenicity, mutagenicity, or reproductive toxicity. Therefore

it does not meet the toxic criterion based on the available ecotoxicological effects data or classification.

However, the available long-term fish-toxicity data may not cover all of the relevant toxicological endpoints and so there are doubts over whether or not D5 has the potential to cause effects in fish over long-term exposure. For example, a recent accumulation study with fish shows only slow depuration of accumulated D5 from liver, and the long-term impact of the accumulation in liver of fish is not known.

Also, the main mammalian toxicological effect of concern for the secondary poisoning assessment is 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 thought to be relevant to wildlife (see Section 4.4.5.2). The NOAEL for these effects is 5 mg/kg bw/day. Although they do not lead to classification for human health (as

[30] As discussed in Section 1.3.9.4 log K_{oa} values for D5 obtained by direct measurement became available very recently. The values determined are ~5.93 at 4°C, ~5.63 at 5°C, 4.96 at 24°C, and 4.58 at 40°C. As the body temperature of mammals is relatively high (e.g. between around 34 and 40°C), these data also support the fact that log K_{oa} is <5 at temperatures relevant for mammals.

the mechanism is not relevant), the NOAEL is low enough for it to be considered a similar level of concern to wildlife as is a substance with a R48 classification. This would then mean that D5 could be considered a toxic substance within the PBT assessment. It also needs to be recognised that no functional or histopathological changes to the liver accompany the liver weight changes. Therefore, it is not clear whether the liver weight changes alone warrant D5 being considered as a toxic substance within the PBT assessment.

Overall, the available data suggest that D5 does not meet the toxic criterion. However, there are uncertainties in the available database.

5.5.2.4 Conclusion

Based on the lack of ready biodegradability and the preliminary results of the hydrolysis test, it appears that D5 does meet the screening criteria for vPvB. Depending on how the available mammalian toxicity data are interpreted, it D5 could also meet the criteria for a toxic substance. In addition, the available long-term toxicity data for fish may not cover all relevant toxicological endpoints.

However, several mitigating factors should be taken into account in this respect. In particular, D5 is highly volatile and so transfers readily from the aquatic compartment to the atmosphere where it degrades. This process is attenuated to some extent by adsorption onto sediments, and the modelling results available so far suggest that a substantial fraction 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. In addition, that the hydrolysis rate for the substance is highly pH-dependent needs to be considered. Under many pH conditions the actual hydrolysis rate is below the 60 day half-life cut-off criterion given in the TGD. Furthermore, emissions to rivers are likely to result in relatively rapid losses of D5 by advection to the marine environment, where the hydrolysis half-life is expected to be lower than 60 days. Finally, the bioaccumulation potential for D5 in mammals appears to be lower than might be expected based on its high log K_{ow} or high BCF value.

Although, based on the available data, the substance is considered to meet the screening vPvB criteria, a number of factors are also relevant when considering the status of D5. In particular, the high volatility of the substance means significant (and rapid) removal from the water phase is likely (which leads to relatively low concentrations in this phase). Despite this, D5 has been detected in the livers of marine fish, and in the blubber of marine mammals in the environment.

In relation to the PBT assessment the long-range transport potential of D5 is also relevant, as the atmosphere is a potentially important environmental compartment for this substance. The available information indicates 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 redeposition to surface media in remote regions. Therefore, on this basis, D5 is considered unlikely to meet the POPs criteria outlined in Section 5.3.

5.5.3 Uncertainties and possible refinements

As for the freshwater assessment, there are uncertainties over both the PECs and PNECs for marine sediment. The analysis carried out in Appendix A indicates that the assessment for the marine sediment compartment is independent of the log K_{ow} value assumed. Any further work carried out to refine the PNEC for freshwater sediment would also be useful to refine the PNEC for marine sediment. In addition, it would be useful to obtain further information on the potential for release to the marine environment from sites that formulate personal care products in the UK.

Also, uncertainties remain in the toxicological database for D5 in relation to the toxic criterion for the PBT assessment. In particular the available long-term fish toxicity data may not cover all relevant toxicological endpoints, and there are also some issues over how the effects on liver weight seen in rats should be interpreted in terms of the toxicity criterion.

Further work is on-going that is relevant to the discussion of the PBT properties of D5 and may have some impact on the final conclusions drawn for D5. This work includes:

- further modelling work to better define the actual half-life of D5 in sediment;
- modelling of the bioaccumulation potential in fish and other species;
- investigation into the actual rate of desorption and/or loss of the substance from sediment–water systems;
- further environmental monitoring.

5.5.4 Conclusions for the marine compartment

Based on the information above D5 appears to meet the screening criteria for a vPvB substance. However, several mitigating factors should be taken into account, including the high volatility of the substance and the low potential for accumulation in mammals. Despite this, D5 has been detected in the livers of marine fish and in blubber of marine mammals in the environment.

The risk characterisation ratios obtained for the marine environment are <1 for production and all uses of D5 in the EU for marine water, predators, and top predators. Therefore D5 presents a low risk to these endpoints using the standard risk-assessment methodology. However, risk characterisation ratios >1 are obtained for marine sediments for scenarios that consider the production and on-site use of D5, formulation of personal care products in the UK, the use of personal care products, and regional releases. Any further work carried out to refine the PNEC for freshwater sediment would also be useful to refine the PNEC for marine sediment. In addition, it would be useful to obtain further information on the potential for release to the marine environment from these sources.

5.6 Humans exposed to D5 via the environment

For humans exposed to D5 via the environment, the local effects on the respiratory tract are not critical as inhalation exposures are low when D5 is dissipated through the environment. Therefore, the lead health effect is liver enlargement after repeated exposure. A NOAEL of 19 mg/kg/day was identified for this effect from a 90 day inhalation study in rats, based on a 15 per cent increase in liver weight at the next highest dose of 35 mg/kg/day.

This NOAEL is the toxicological starting point for the risk characterisation of D5, so extrapolation from rats to humans is needed. The available evidence indicates that it is unlikely that humans are more sensitive than rats to phenobarbital-like enzyme induction and subsequent liver enlargement. In studies of epilepsy patients treated with therapeutic doses of phenobarbital equivalent to those that cause large increases in liver weight in rats, no significant increase in liver pathology, incidence of significant abdominal organ compression caused by increased liver weight ,or toxicity was noted (Olsen *et al*., 1989). On this basis, an AF for interspecies differences of one seems appropriate. However, given the limitations of these human data (no accurate quantitative information on the magnitude of the effects and lack of detailed investigations), a more conservative interspecies AF of two is selected here.

In relation to intraspecies differences, phenobarbital-like liver enzyme induction and subsequent liver enlargement (from 10 per cent and above) are likely to have adverse consequences only in the most susceptible individuals of the population. Therefore, it is deemed that the default intraspecies AF of ten can be lowered to five.

Finally, although the starting point for the risk characterisation is identified from a 90 day study, an additional AF to account for subchronic to chronic extrapolation is not needed as the effect is a short-term, reversible one, the severity of which does not increase with increases in the duration of exposure.

An overall minimal margin of safety (minMOS) of 10 ($2 \times 5 \times 1$) is therefore established for this effect. There is concern when the MOS is lower than the minMOS.

5.6.1 Local exposure

The maximum continuous human exposure from local environmental sources predicted by EUSES is 0.025 mg/kg bw/day in the formulation of personal care products at a generic site not within the UK. The MOS between the NOAEL for liver enlargement (19 mg/kg/day) and this exposure level is 760.

This MOS is significantly greater than the minMOS of ten. Therefore there is no concern for local exposure.

5.6.2 Regional exposure

The value for human exposure from regional environmental sources predicted by EUSES is 0.14 mg/kg bw/day. The MOS between the NOAEL for liver enlargement (19 mg/kg/day) and this exposure level is 136, which is greater than the minMOS. However, the validity of this exposure estimate is questionable as it is dominated by the concentration in root crops (the estimated concentration in root crops is 25 mg/kg, and this source of exposure is estimated to account for 99.1 per cent of the total dose). The methodology used in the TGD to estimate the concentration in root crops may not be appropriate for a substance with a high log K_{ow} of 8.03. Given the high volatility of D5 from soils, it is considered highly unlikely that such high concentrations in root crops are achieved in practice. If the contribution from root crops is ignored, the total human exposure from regional sources is 1.2×10^{-3} mg/kg bw/day, which is considered a more reliable estimate for the regional exposure of humans via the environment. The MOS between the NOAEL for liver enlargement (19 mg/kg/day) and this exposure level is 1.6×10^{4}. This MOS is three orders of magnitude greater than the minMOS of ten. Therefore there is no concern for regional exposure.

5.7 Further testing currently underway

It is understood that a number of further tests or studies of direct relevance to the conclusions of this assessment of D5 have been (or are in the process of being) commissioned by CES (2007). The studies include:

- atmospheric degradation – evaluation of additional degradation pathways to better understand the degradation in the atmosphere and long-range transport potential;
- degradation in a wastewater treatment plant and sludge;
- degradation in sediment under aerobic and anaerobic conditions (modified OECD 308 method);

- further modelling of the environmental distribution and overall fate;
- sediment bioaccumulation study with *Lumbriculus* spp;
- further sediment toxicity study with *Hyalella azteca*;
- bioaccumulation – physiologically based pharmacokinetic (PBPK) modelling of fish;
- bioaccumulation – extension of PBPK model from fish and mammals to other environmental species;
- environmental monitoring of air, sewage effluent, river water, sediment, and biota including:
    - Lake Pepin, MN – objective is to look at historical deposition patterns to evaluate degradation in the environment.
    - CES mussel-screening program – preliminary results from this study are included in this risk assessment.
    - River Nene – objective is to look at the distribution and persistence downstream from a known point source (monitoring and river die-away study).
    - Long-term effective monitoring program – the objective is to investigate the persistence and bioaccumulation potential in the field. The program has yet to be fully developed and agreed, but is likely to include investigations of time trends (using freshwater and marine sediment cores from local, regional, and remote locations, and from archived biota samples), spatial distributions (sampling sediment and biota along transects of freshwaters from local, regional, and remote locations), and air samples (from local, regional, and remote locations).
    - Site-specific monitoring – the objective is to carry out monitoring to refine the current PECs used in the risk assessment.
- analytical methodology development for water, sediment, soil, biota, sludge, and air to support the above studies.

The results of this testing would allow several endpoints considered in this assessment to be refined.

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List of abbreviations

AIChE	American Institute of Chemical Engineers
BCF	Bioconcentration factor
BMF	Biomagnification factor
CES	Centre Européen des Silicones
cst	Centistokes
CTPA	Cosmetic, Toiletry and Perfumery Association
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6	Dodecamethylcyclohexasiloxane
D7	Tetradecamethylcycloheptasiloxane
DIPPR	Design Institute for Physical Property Data
EC_{50}	50 per cent effect concentration
EBAP	Environmental bioaccumulation potential
EPICS	Equilibrium partitioning in closed systems
ETH	Swiss Federal Institute of Technology
EUSES	European Union System for the Evaluation of Substances
GLP	Good laboratory practice
HAV	Heat activated vulcanising
IC	Industry category
ITC	Interagency Testing Committee
IUCLID	International Uniform Chemical Information Database
K_{aw}	Air–water partition coefficient
K_{oa}	Octanol–air partition coefficient.
K_{ow}	Octanol–water partition coefficient
K_{sed}	Solids–water partition coefficient in sediment
$K_{sed–water}$	Sediment–water partition coefficient
K_{soil}	Solids–water partition coefficient in soil
$K_{soil–water}$	Soil–water partition coefficient
K_{susp}	Solids–water partition coefficient in suspended matter
$K_{susp–water}$	Suspended matter–water partition coefficient (
LOAEL	Lowest observed adverse effect level
LOEC	Lowest observed effect concentration
MC	Main category
INCI	International Nomenclature Cosmetic Ingredient
MQ resins	MQ resins are composed of clusters of quadrafunctional silicate groups (commonly termed Q groups) end-capped with monofunctional trimethylsiloxy groups (commonly termed M groups)
LC_{50}	Lethal concentration 50 – the concentration that kills 50 per cent of the population
LOAEL	Lowest observed adverse effect level
NIK	Niedrigste interessierende konzentration
NOAEL	No observed adverse effect level
NOEC	No observed effect concentration
OECD	Organisation for Economic Co-operation and Development
PBPK	Physiologically based pharmacokinetic
PBT	Persistent, bioaccumulative and toxic
PDMS	Polydimethylsiloxane
PEC	Predicted environmental concentration
PNEC	Predicted no effect concentration
POCP	Photochemical ozone creation potential
POP	Persistent organic pollutant
ppm	Parts per million
ppm_v	Parts per million by volume

ppb	Parts per billion
ppb_v	Parts per billion by volume
RTV	Room temperature vulcanising
TD resins	TD resins contain difunctional dimethylsiloxy groups (commonly termed D groups) and trifunctional methylsiloxy groups (commonly termed T groups)
TGD	Technical Guidance Document
TSCA	Toxic Substances Control Act
UC	Use category
USEPA	United States Environmental Protection Agency
VMS	Volatile methylsiloxanes
vPvB	Very persistent, very bioaccumulative

Appendix A: Sensitivity of the assessment to values of log K_{ow} and Henry's law constant

As discussed in Section 1 of the main report, new values for the log K_{ow} and Henry's law constant for D5 became available recently. Few experimental details are currently available as to how these values were determined and so, at this stage, it is not possible to conclude which value is most reliable for these parameters. The main risk assessment was carried out using a log K_{ow} value of 8.03 and a Henry's law constant of 3.24×10^6 Pa m^3/mol at 25°C. This Appendix considers the consequences of assuming the lower values for the log K_{ow} (5.2) and Henry's law constant (32,317 Pa m^3/mol at 26°C) on the outcome of the risk assessment.

The EUSES model was run for the generic scenarios using the following input parameters.

- log K_{ow} = 5.2
- Henry's law constant = 32,317 Pa m^3/mol
- $K_{oc} = 1.5 \times 10^5$ l/kg
- Fish BCF = 7060 l/kg
- BMF = 3.9.

As the K_{oc}, BCF, and BMF were measured for D5, and the values are considered to be reliable, these measured values are used in the analysis here rather than estimates of the values from log K_{ow}.

Both K_{oc} and Henry's law constant affect the predicted partitioning of D5 in the environment. The most important partition coefficients used in the assessment derived from these values are:

- $K_{oc} = 1.5 \times 10^5$ l/kg
- $K_{soil} = 3.0 \times 10^3$ l/kg
- $K_{sed} = 7.5 \times 10^3$ l/kg
- $K_{susp} = 1.5 \times 10^4$ l/kg
- $K_{soil–water} = 4.5 \times 10^3$ m^3/m^3
- $K_{susp–water} = 3.8 \times 10^3$ m^3/m^3
- $K_{sed–water} = 3.8 \times 10^3$ m^3/m^3.

With the exception of $K_{soil–water}$, these derived partition coefficients are the same as those used in the main assessment ($K_{soil–water}$ has a small dependence on Henry's law constant).

The expected behaviour during wastewater treatment is estimated using the Simpletreat model within EUSES 2.0.3, and is identical to that estimated in the main report:

- percentage to air = 22.1 per cent

- percentage to sludge = 73.2 per cent
- percentage degraded = 0 per cent
- percentage to water = 4.7 per cent

The log K_{ow} potentially affects any PNECs determined by the equilibrium partitioning method. For D5 only the indicative concentration for soil is estimated using this method, and it depends on $K_{soil-water}$). The effect on the indicative concentration for soil of using a lower Henry's law constant and log K_{ow} is only very minor as $K_{soil-water}$ is reduced from 4.8×10^3 m^3/m^3 to 4.5×10^3 m^3/m^3, since it is estimated based on the measured K_{oc} value. The indicative concentration for soil estimated using the lower $K_{soil-water}$ value is 4.5 mg/kg wet weight.

Based on the above, use of the alternative log K_{ow} and Henry's law constant is expected to have only a very minor impact on the outcome of the risk assessment. The PECs, risk characterisation ratios, and comparisons of PECs with indicative concentrations obtained using a log K_{ow} of 5.2 and a Henry's law constant of 3.24×10^6 Pa m^3/mol are summarised in Tables A1 to A6.

Table A1 Comparison of PECs with the indicative concentration for surface water

Scenario	PEC (µg/l)	PEC/indicative concentration[1]
Production and on-site use as an intermediate	0.52	0.31
Off-site use as an intermediate – wet process (non-UK)	0.10	0.059
Off-site use as an intermediate – dry process (non-UK)	0.10	0.059
Personal care products – formulation – generic site (non-UK)	1.6	0.93
Personal care products – use by general public	0.33	0.20
Household products – formulation	0.10	0.059
Household products – use	0.11	0.066
Industrial/institutional cleaning – use	0.10	0.059
Regional	0.10	0.059

Note: [1]Indicative concentration is 1.7 µg/l.

Table A2 Risk characterisation ratios for sediment

Scenario	PEC (mg/kg wet weight)	Risk characterisation ratio[1]
Production and on-site use as an intermediate	1.7	3.6
Off-site use as an intermediate – wet process (non-UK)	0.33	0.69
Off-site use as an intermediate – dry process (non-UK)	0.33	0.69
Personal care products – formulation – generic site (non-UK)	5.2	11
Personal care products – use by general public	1.1	2.3
Household products – formulation	0.33	0.69
Household products – use	0.36	0.76
Industrial/institutional cleaning – use	0.33	0.69
Regional	0.65	1.4

Note: [1]PNEC is 0.48 mg/kg wet weight.

Table A3 Comparison of PECs with the indicative concentration for the soil compartment

Scenario	PEC (mg/kg wet weight)	PEC/indicative concentration[1]
Production and on-site use as an intermediate	5.5×10^{-4}	1.2×10^{-3}
Off-site use as an intermediate – wet process (non-UK)	1.3×10^{-5}	2.8×10^{-5}
Off-site use as an intermediate – dry process (non-UK)	2.4×10^{-4}	5.2×10^{-4}
Personal care products – formulation – generic site (non-UK)	1.0	2.3
Personal care products – use by general public	0.16	0.35
Household products – formulation	9.3×10^{-6}	2.1×10^{-5}
Household products – use	7.9×10^{-3}	0.018
Industrial/institutional cleaning – use	4.0×10^{-5}	9.0×10^{-5}
Regional – agricultural soil	0.11	0.24
Regional – natural soil	7.1×10^{-6}	1.6×10^{-5}
Regional – industrial soil	7.1×10^{-6}	1.5×10^{-5}

Note: [11]ndicative concentration is 4.5 mg/kg wet weight. The ratios are increased by a factor of 10 in line with the recommendations in the TGD.

Table A4 Risk characterisation ratios for secondary poisoning

Scenario	Fish		Earthworms	
	PEC (mg/kg)	Risk characterisation ratio[1]	PEC (mg/kg)	Risk characterisation ratio[1]
Production and on-site use as an intermediate	9.4	0.72	0.041	3.2×10^{-3}
Off-site use as an intermediate – wet process (non-UK)	3.5	0.27	0.041	3.2×10^{-3}
Off-site use as an intermediate – dry process (non-UK)	3.5	0.27	0.041	3.2×10^{-3}
Personal care products – formulation – generic site (non-UK)	25	1.9	0.28	0.022
Personal care products – use by general public	7.5	0.58	0.078	6.0×10^{-3}
Household products – formulation	3.5	0.27	0.041	3.2×10^{-3}
Household products – use	3.7	0.28	0.043	3.3×10^{-3}
Industrial/institutional cleaning – use	3.5	0.27	0.041	3.2×10^{-3}

Note: [1]PNEC is 13 mg/kg food.

Table A5 Risk characterisation ratios for secondary poisoning for the marine environment

Scenario	Predators		Top predators	
	PEC (mg/kg)	Risk characterisation ratio[1]	PEC (mg/kg)	Risk characterisation ratio[1]
Production and on-site use as an intermediate	0.49	0.038	1.8	0.14

Scenario	Predators		Top predators	
	PEC (mg/kg)	Risk characterisation ratio[1]	PEC (mg/kg)	Risk characterisation ratio[1]
Off-site use as an intermediate – wet process (non-UK)	0.34	0.026	1.7	0.13
Off-site use as an intermediate – dry process (non-UK)	0.34	0.026	1.7	0.13
Personal care products – formulation – generic site (non-UK)	45	3.5	46	3.5
Personal care products – use by general public	0.74	0.057	2.1	0.16
Household products – formulation	0.34	0.026	1.7	0.13
Household products – use	0.36	0.028	1.7	0.13
Industrial/institutional cleaning – use	0.34	0.026	1.7	0.13

Note: [1]PNEC is 13 mg/kg food.

Table A6 Comparison of PECs with indicative concentrations for marine water and risk characterisation ratios for marine sediment

Scenario	Marine water		Marine sediment	
	PEC (µg/l)	PEC/indicative concentraiton[1]	PEC (mg/kg)	Risk characterisation ratio[2]
Production and on-site use as an intermediate	0.020	0.12	0.067	1.4
Off-site use as an intermediate – wet process (non-UK)	9.8×10^{-3}	0.058	0.032	0.67
Off-site use as an intermediate – dry process (non-UK)	9.8×10^{-3}	0.058	0.032	0.67
Personal care products – formulation – generic site (non-UK)	3.2	19	10	210
Personal care products – use by general public	0.033	0.19	0.11	2.3
Household products – formulation	9.8×10^{-3}	0.058	0.032	0.67
Household products – use	0.011	0.065	0.036	0.76
Industrial/institutional cleaning – use	9.8×10^{-3}	0.058	0.032	0.67
Regional	9.8×10^{-3}	0.058	0.063	1.3

Note: [1]Indicative concentration is 0.17 µg/l.
[2]PNEC is 0.048 mg/kg wet weight.

This analysis leads to essentially the same PECs and conclusions as in the main risk assessment for all endpoints. It also shows that the risk from secondary poisoning via earthworms is likely to be small.

Appendix B: Site-specific assessment for non-UK personal care product formulation sites

Site-specific information (mainly amounts of D5 used and details of the effluent treatment and water flows at the sites) has been received for non-UK personal care product formulations sites in the EU. The survey covered the 36 non-UK formulations sites of the major multinational European personal care product formulators. These companies represent around 80 per cent of the total EU personal care product market. The information confidential, but the resulting PECs and risk characterisation ratios obtained using this information are summarised in this Appendix. The approach taken to calculate the PECs for these sites follows closely the methodology outlined in the TGD, including the use of the default emission factors to estimate the emissions to air and water where actual data are not available. However, several sites treat the effluent in a physico-chemical treatment process prior to discharge. As no information is available from which to estimate the removal of D5 from the effluent stream during physico-chemical treatment, as a worst case no removal is assumed during this treatment. Given the properties of D5 (high log K_{ow}, low water solubility, high volatility) a significant removal could be expected during certain types of physico-chemical wastewater treatment (such as filtration, air floatation, oil-skimming, etc.) and so the PECs calculated may overestimate the actual concentration in the receiving media.

The PECs estimated for surface water are summarised in Table B1. No PNEC can be determined for D5 for surface water as it is not toxic to aquatic organisms at concentrations up to its water solubility in the tests available. An indicative concentration of 1.7 µg/l is derived for D5 to account for an important gap in the database for D5 and the ratios of the PECs to this indicative concentration are shown in Table B1. These ratios indicate a low risk to the surface water from all sites.

Table B1 PECs for surface water

Site	PEC (µg/l)	PEC/indicative concentration
1	<0.67	<0.40
2	<0.13	<0.076
3	<0.22	<0.13
4	0.10	0.060
5	0.12	0.071
6	0.36	0.21
7	0.52	0.31
8	0.11	0.062
9	0.68	0.40
10	0.10	0.059
11	0.86	0.51
12	0.11	0.065
13	0.73	0.43
14	0.16	0.096
15	0.10	0.059
16	0.13	0.079
17	0.12	0.072
18	0.10	0.059
19	0.10	0.059
20	0.12	0.070
21	0.37	0.22
22	0.33	0.19
23	0.33	0.19
24	0.11	0.066
25	0.27	0.16
26	0.15	0.086
27	0.23	0.13
28	0.11	0.064
29	0.10	0.059
30	0.42	0.25
31	0.11	0.062
32	0.13	0.075
33	0.13	0.073
34	0.11	0.062
35	Negligible	<1
36	Negligible	<1

The PECs and risk characterisation ratios for sediment are summarised in Table B2. A PNEC of 0.48 mg/kg wet weight is used for this comparison. As can be seen, the risk characterisation ratios are >1 for some of the sites, which indicates a possible risk to sediment.

Table B2 PECs and risk characterisation ratios for sediment

Site	PEC (mg/kg wet weight)	Risk characterisation ratio
1	<2.2	<4.6
2	<0.42	<0.88
3	<0.70	<0.1.5
4	0.33	0.69
5	0.39	0.82
6	1.2	2.5
7	1.7	3.6
8	0.35	0.73
9	2.2	4.6
10	0.33	0.69
11	2.8	5.9
12	0.36	0.76
13	2.4	5.0
14	0.53	1.1
15	0.33	0.69
16	0.44	0.92
17	0.40	0.84
18	0.33	0.69
19	0.33	0.69
20	0.39	0.82
21	1.2	2.5
22	1.1	2.3
23	1.1	2.3
24	0.36	0.76
25	0.87	1.8
26	0.48	1.0
27	0.74	1.6
28	0.36	0.76
29	0.33	0.69
30	1.4	2.9
31	0.34	0.71
32	0.41	0.86
33	0.41	0.86
34	0.35	0.74
35	Negligible	<1
36	Negligible	<1

The PECs and risk characterisation ratios for the terrestrial compartment are summarised in Table B3. No PNEC can be derived for the terrestrial compartment for D5 and so an indicative value of 4.8 mg/kg wet weight is used here. As this is based on the equilibrium partitioning approach, the resulting risk characterisation ratios are increased by a factor of ten in line with the recommendations in the TGD.

For the terrestrial compartment, the risk characterisation ratios are all <1. Therefore it is concluded that the risk to the terrestrial compartment is low from all of the sites.

Table B3 PECs and risk characterisation ratios for the terrestrial compartment

Site	PEC (mg/kg wet weight)	Risk characterisation ratio
1	<0.019	<0.040
2	$<9.7 \times 10^{-4}$	2.0×10^{-3}
3	$<3.9 \times 10^{-3}$	8.1×10^{-3}
4	8.4×10^{-6}	1.8×10^{-5}
5	7.1×10^{-4}	1.5×10^{-3}
6	1.7×10^{-3}	3.4×10^{-3}
7	1.4×10^{-3}	3.0×10^{-3}
8	2.1×10^{-4}	4.5×10^{-4}
9	0.020	0.041
10	7.3×10^{-6}	1.5×10^{-5}
11	0.017	0.035
12	2.3×10^{-3}	4.8×10^{-3}
13	7.3×10^{-6}	1.5×10^{-5}
14	7.3×10^{-6}	1.5×10^{-5}
15	6.3×10^{-3}	0.013
16	1.2×10^{-3}	2.4×10^{-3}
17	7.8×10^{-4}	1.6×10^{-3}
18	7.2×10^{-6}	1.5×10^{-5}
19	9.6×10^{-6}	2.0×10^{-5}
20	6.3×10^{-4}	1.3×10^{-3}
21	9.0×10^{-3}	0.019
22	7.7×10^{-3}	0.016
23	7.7×10^{-3}	0.016
24	7.2×10^{-6}	1.5×10^{-5}
25	5.6×10^{-3}	0.012
26	1.6×10^{-3}	3.3×10^{-3}
27	4.3×10^{-3}	8.9×10^{-3}
28	3.2×10^{-4}	6.6×10^{-4}
29	1.7×10^{-5}	3.6×10^{-5}
30	7.1×10^{-6}	1.5×10^{-5}
31	6.8×10^{-4}	1.4×10^{-3}
32	9.1×10^{-4}	1.9×10^{-3}
33	8.4×10^{-4}	1.8×10^{-3}
34	2.0×10^{-4}	4.2×10^{-4}
35	Negligible	<1
36	Negligible	<1

The PECs and risk characterisation ratios for secondary poisoning are summarised in Table B4. The PECs are calculated using the alternative method outlined in the main report, with a BCF of 7060 l/kg and a BMF of 3.9. The PNEC for secondary poisoning is taken to be 13 mg/kg food.

Table B4 PECs and risk characterisation ratios for secondary poisoning[31]

Site	Fish food chain	
	PEC (mg/kg)	Risk characterisation ratio
1	<12	<0.92
2	<3.9	<0.3
3	<5.1	<0.39
4	3.5	0.27
5	3.8	0.29
6	7.1	0.55
7	9.5	0.73
8	3.5	0.27
9	12	0.92
10	3.5	0.27
11	14	1.1
12	3.6	0.27
13	12	0.92
14	4.4	0.34
15	3.5	0.27
16	3.9	0.30
17	3.8	0.29
18	3.5	0.27
19	3.5	0.27
20	3.7	0.28
21	7.3	0.56
22	6.7	0.52
23	6.7	0.52
24	3.6	0.28
25	5.8	0.45
26	4.1	0.32
27	5.3	0.41
28	3.6	0.28
29	3.5	0.27
30	8.1	0.62
31	3.5	0.27
32	3.8	0.29
33	3.8	0.29
34	3.5	0.27
35	Negligible	<1
36	Negligible	<1

The risk characterisation ratios obtained for the fish food chain are all <1 except for at one site, which indicates a possible risk at the site.

For the marine environment, the survey identified only one site that eventually discharged into the marine environment. The PECs and risk characterisation ratios for this scenario (using the PNEC for marine sediment of 0.075 mg/kg wet weight and a PNEC for secondary poisoning of 13 mg/kg food) are given in Table B5.

[31] [1]The calculation methods in the TGD for the earthworm food chain are not valid for substances with a very high log K_{ow}. Therefore it is not possible to estimate the concentration in earthworms in this case.

Table B5 PECs and risk characterisation ratios for one marine environment scenario

	PEC	Risk characterisation ratio
Marine water	9.8×10^{-3} µg/l	0.058[1]
Marine sediment	0.032 mg/kg wet weight	0.67
Predators (alternative method)	0.34 mg/kg	0.026
Top predators (alternative method)	1.7 mg/kg	0.13

Note: [1]No PNEC can be derived for marine water. Ratio estimated using an indicative concentration of 0.17 µg/l for marine water.

Appendix C: Summary of ecotoxicity data

This Appendix contains summary tables of the available ecotoxicity data. Where possible, a validity marking is given for each study (this appears in the summary tables within each Section). The validity markings used are:

- **1 – Valid without restriction**. The test is carried out to internationally recognised protocols (or equivalent protocols) and all or most of the important experimental details are available.
- **2 – Use with care**. The test is carried out to internationally recognised protocols (or equivalent protocols), but some important experimental details are missing, or the method used or endpoint studied in the test means that interpretation of the results is not straightforward.
- **3 – Not valid**. There is a clear deficiency in the test that means the results cannot be considered as valid.
- **4 – Not assignable.** Insufficient detail is available on the method used to allow a decision to be made on the validity of the study.

These validity codes are based on the Klimisch codes used by the OECD.

Table C1 Summary of short-term (acute and prolonged acute) toxicity to freshwater fish[1]

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Hard.	pH	Static/ flow	D.O.					
Cyprinus carpio	OECD 203	Ten	0.23 g	Water-accommodated fraction: initial loading 1 g/l.	M	Tap water	19.1–20.5	12.5	8.0–8.3	Semi-static	95–100 %	Mortality		No effects seen	IUCLID, 2005	**3**
Oncorhynchus mykiss	OECD 204	Ten	4.5 g	5 mg/l [a solvent control (acetone) was run]	N					Flow		Mortality		14d-LC_{50} >5 mg/l 14d-NOEC ≥5 mg/l	IUCLID, 2005	**4**
	OECD 204	Ten per replicate, two replicates per treatment	2.3 g, 61 mm	2.1, 3.1, 5.0, 8.6, and 16 µg/l (a control and solvent control was also run)	M	Well water	13–15	32–36	6.2–7.7	Flow	7.4–9.3 mg/l	Mortality	10% in control, 5% in solvent control	14 day LC_{50} >16 µg/l 14 day NOEC ≥16 µg/l	IUCLID, 2005	**1**
			43 mm	2.4 µg/l						Flow				14d-LC_{50} >2.4 µg/l 14d-NOEC ≥2.4 µg/l	IUCLID, 2005	**4**

Notes [1]N or M, nominal or measured concentration; Temp., temperature; Hard., water hardness as mg $CaCO_3$/l; D.O., dissolved oxygen (either as percentage saturation or as mg O_2/l); Val., validity marking.

Table C2 Summary of long-term toxicity to freshwater fish[1]

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Hard.	pH	Static/ flow	D.O. (mg/l)					
Pimephales promelas	OECD 305 (bioconcentration study)	Initially 60 per replicate, two replicates per treatment (fish sacrificed at intervals during the test)	49–60 mm 0.71–2.1 g	1.1 and 15 µg/l plus solvent control (dimethyl formamide at 0.1 ml/l)	M	Tap water	22	99–134	6.3–7.6	Flow	>5.2	Acute effects and overt signs of sublethal effects (and body weight)		35 day NOEC ≥15 µg/l	IUCLID, 2005 Drottar, 2005	**2**
Oncorhynchus mykiss	Bioconcentration study		1.31 g		M			104	7.6	Flow	8.0	Mortality		28 day NOEC ≥5.8 mg/l	Annelin and Frye, 1989 IUCLID, 2005	**2**
	Accumulation from food study	Initially70 per replicate, two replicates per treatment (fish sacrificed at intervals during the test)	1.2 g at start of study	458 mg/kg feed plus control	M	Tap water	12	113	6.8–8.4	Flow	>5.9	Mortality and overt signs of sublethal effects (and body weight)		No effects seen at 458 mg/kg feed	Dow Corning, 2006b	**2**

Notes [1]N or M, nominal or measured concentration; Temp, temperature; Hard, water hardness as mg $CaCO_3$/l; D.O., dissolved oxygen (either as percentage saturation or as mg O_2/l); Val., validity marking.

Table C3 Summary of short term toxicity to freshwater invertebrates[1]

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Hard.	pH	Static/ flow	D.O. (mg /l)					
Daphnia magna	OECD 202	Ten per replicate, two replicates per treatment	<24 hours	2.1, 1.6, 1.8, 2.5, and 2.9 [a control and solvent control (acetone) were also run]	M	Well water	20-21	170	7.8–8.0	Flow	7.2–9.1	Immobility	10% immobilisation	48 hour EC_{50} >2.9 µg/l	IUCLID, 2005	**1**
	UBA				N							Immobility		24 hour EC_0 = 4.4 mg/l 24 hour EC_{100} >100 mg/l	IUCLID, 2005	**3**
	OECD 202	Five per replicate, four replicates per treatment		Water accommodated fraction (initial loading 1 g/l) (a control was also run)	M	Tap water				Static				No effects seen	IUCLID, 2005	**4**

Notes [1]N or M, nominal or measured concentration; Temp., temperature; Hard., water hardness as mg $CaCO_3$/; D.O., dissolved oxygen (either as percentage saturation or as mg O_2/l); Val., validity marking.

Table C4 Summary of long-term toxicity to freshwater invertebrates[1]

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions						Endpoint	Control response	Effect concentration	Reference	Val.
						Media	Temp. (°C)	Hard.	pH	Static/ flow	D.O. (mg /l)					
Daphnia magna	OECD 211	One per replicate, Ten replicates per treatment	<24 hours	1.1, 1.7, 3.5, 7.2, and 15 µg/l (a control and solvent control [acetone, 0.1 ml/l) were also run]	M	Well water	20–23	160–170	7.9	Semi-static	9.4–9.8	Mortality	10% (control) 0% (solvent control)	21 day EC_{50} >15 µg/l 21 day NOEC ≥15 µg/l	IUCLID, 2005	**1**
												Reproduction (cumulative offspring per female)	148 (control) 145 (solvent control)	21 day EC_{50} >15 µg/l 21 day NOEC ≥15 µg/l		
												Growth (body length)	5.01 mm (control) 4.97 mm (solvent control)	21 day EC_{50} >15 µg/l 21 day NOEC ≥15 µg/l		
												Growth (dry weight)	1.16 mm (control) 1.08 mm (solvent control)	21 day EC_{50} >15µg/l 21 day NOEC ≥15 µg/l		

Note: [1]N or M, nominal or measured concentration; Temp, temperature; Hard., water hardness as mg $CaCO_3$/l D.O., dissolved oxygen (either as percentage saturation or as mg O_2/l); Val., validity marking.

Table C5 Summary of short-term toxicity to freshwater algae and plants[1]

Species	Test guideline	Initial inoculum concentration	Concentrations tested	N or M	Test conditions					Endpoint	Control response	Effect concentration	Reference	Val.
					Media	Temp. (°C)	Hard.	pH	Static/flow					
Scenedesmus subspicatus	OECD 201		Water-accommodated fraction from initial loading of 1 g/l plus control	Y	Tap water			8.5–9.5		Growth rate		No effects seen	IUCLID, 2005	**1.3.19**
Pseudokirchneriella subcapitata	OECD 201	1.0 10^4 cells/ml	12 µg/l [concentration as initial mean measured concentration – a control and solvent control (acetone) were also run]	M	Algal assay procedure	24			Static	Biomass (cell density)	270×10^4 (control) and 269×10^4 (solvent control) cells/ml at 96 hours	96 hour NOEC ≥12 µg/l 96 hour EC_{50} >12 µg/l	IUCLID, 2005	**2**
										Growth rate	1.61/day (control) and 1.62/day (solvent control) over 0–72 hours	72 hour NOEC ≥12 µg/l 72 hour EC_{50} >12 µg/l		

Notes: [1]N or M, nominal or measured concentration; Temp., temperature; Hard., water hardness as mg $CaCO_3$/l; D.O., dissolved oxygen (either as percentage saturation or as mg O_2/l); Val., validity marking.
[2] Formerly *Selenastrum capricornutum*.

Table C6 Summary of sediment toxicity data

Species	Test guideline	Number of animals/treatment	Age/ size	Concentrations tested	N or M	Test conditions			Endpoint	Control response	Effect concentration	Reference	Val.
						O.C. (%)	Hard.	pH					
Chironomus riparius	OECD 218 (draft)	20 per replicate, 11 replicates per treatment	2-day-old	13, 30, 73, 180, and 580 mg/kg dry weight (days 0–10), and 12, 30, 69, 180, and 570 mg/kg dry weight (days 0–28) – a control and solvent control were also run	M	2	30–60	6.6–7.6	Larval survival	97% survival in pooled control	10 day LC_{50} = 450 mg/kg dry weight 10 day NOEC = 180 mg/kg dry weight	IUCLID, 2005 Putt, 2003	**2**
									Larval wet weight	Mean 5.24 mg in pooled control	10 day EC_{50} = 410 mg/kg dry weight 10 day NOEC = 73 mg/kg dry weight		
									Emergence	87% in pooled control	28 day EC_{50} = 420 mg/kg dry weight 28 day NOEC = 180 mg/kg dry weight		
									Development rate	0.0689 (males) and 0.0610 (females) on pooled control	28 d-ay C_{50} = >570 mg/kg dry weight 28 day NOEC = 69 mg/kg dry weight		
	OECD 218	20 per replicate, four replicates per treatment	1–4 day old	35, 70, 160, 248, 390, and 759 mg/kg dry weight plus a control	M	3.2	136–160	8.0–8.4	Survival	87% survival in control	28 day LC_{50} = 257 mg/kg dry weight	Krueger *et al.*, 2006	**1**
									Development time	Mean 16.2 days	28 day NOEC = 160 mg/kg dry weight		
									Emergence ratio	Mean 0.88	28 day NOEC = 160 mg/kg dry weight		
									Development rate	Mean 0.0640	28 day NOEC = 70 mg/kg dry weight		
Lumbriculus variegatus	OPPTs 850 1735	10 per replicate, eight replicates per treatment	mean dry weight 0.51 mg	24, 46, 94, 226, 495, and 1272 mg/kg dry weight plus control	M	3.7	116–132	7.9–8.3	Survival and reproduction	Mean 26 per replicate	28 day NOEC ≥1272 mg/kg dry weight	Krueger *et al.*, 2006	**1**
									Growth (mean dry weight/worm)	Mean 0.92 mg	28 day NOEC ≥1272 mg/kg dry weight		

Note: [1]N or M, nominal or measured concentration; Temp., temperature; Hard., water hardness as mg $CaCO_3$/l; O.C., organic carbon content; Val, validity marking.