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Environmental Risk Assessment Report: Dodecamethylcyclohexasiloxane

ea/br/e/sci/v1

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This report is the result of research commissioned and funded by the Environment Agency's Science Programme.

Published by:
Environment Agency, Rio House, Waterside Drive, Aztec West, Almondsbury, Bristol, BS32 4UD
Tel: 01454 624400 Fax: 01454 624409
www.environment-agency.gov.uk

ISBN: 978-1-84911-030-3

Further copies of this report are available from:
The Environment Agency's National Customer Contact Centre by emailing enquiries@environment-agency.gov.uk or by telephoning 08708 506506.

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Dissemination Status:
Publicly available / Released to all regions

Keywords:
Dodecamethylcyclosiloxane, siloxane

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Product code:
SCHO0309BPQY-E-P

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Steve Killeen
Head of Science

Executive Summary

The Environment Agency's risk assessment for dodecamethylcyclohexasiloxane (D6) is based on the methods outlined in the European Union (EU) Technical Guidance Document.

Persistent, bioaccumulative, and toxic assessment

D6 does not meet the screening criteria for a persistent, bioaccumulative, and toxic (PBT) substance on the basis of all the available measured and calculated data.

D6 is not readily biodegradable in a standard biodegradation test, and no biodegradation or biodegradation-simulation test results are available for it. Based on information for related substances, D6 is not expected to biodegrade rapidly in aquatic systems or to hydrolyse rapidly at near neutral pHs. D6 therefore has the potential to meet the screening persistent or very persistent (vP) criteria.

The bioconcentration factor (BCF) of D6 in fish is 1160 l/kg (determined experimentally). Thus it does not meet the bioaccumulative or very bioaccumulative (vB) criteria.

D6 causes no lethality in fish exposed over periods of up to 49 days and no adverse effects to the invertebrate *Daphnia magna* in a 21-day reproduction test. Based on predictions and comparison with the known toxicity of similar substances, D6 is also expected to show little or no toxic effect with algae at concentrations up to its water solubility. In addition, it is not classified as carcinogenic, mutagenic, or reprotoxic compound. Thus, D6 does not meet the screening criteria for toxicity.

The overall conclusions of the PBT assessment are that D6 does not meet the criteria for a PBT or a vPvB substance.

Quantitative risk assessment

The risks from the normal use of D6 to water, sediments, soil, and predators are assessed using standard models and the information available. The property data set is not complete and in some areas further information will be valuable. This assessment therefore makes recommendations about the significance of the data gaps and uncertainties, and suggests the focus for further research.

The main uses of D6 are as an intermediate in the production of other chemicals (silicone polymers) and in personal care products (e.g. cosmetic products, and skin- and hair-care products). Use as an intermediate to make silicone polymers effectively consumes the D6, although trace amounts are still present in the final products can be subsequently released to the environment. Use of D6 in personal care products results in widespread exposure in the environment.

Estimates of the potential emissions to the environment from D6'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. Using the available information, risk characterisation ratios could only be generated for predators and top predators. No risk characterisation ratios above one are identified for any of the scenarios considered (above one indicates an unacceptable risk to the environment). However, a lack of suitable toxicity data means it is not currently possible to assess fully the risks to freshwater sediment, soil, and marine sediment. An assessment of human exposure via the environment concludes that D6 is unlikely to pose a risk to human health.

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 risk assessment are:

- No risks are identified from the life-cycle stages considered.
- The screening assessments for soil and predators indicate that the risks from life-cycle stages of D6 are likely to be low, and so further work is not currently a priority.
- A lack of suitable toxicity data means it is not currently possible to assess the risks to the sediment (both freshwater and marine). Further toxicity testing with sediment-dwelling organisms is needed to address this, such as long-term toxicity tests with *Chironomus riparius*, *Lumbriculus variegatus*, and *Hyalella azteca* using spiked sediment.

Industry is undertaking a voluntary test programme to address some of these issues. It is understood that D6 studies currently being considered, or underway, are:

- evaluation of atmospheric degradation pathways;
- modelling of the environmental distribution and overall fate;
- sediment bioaccumulation study with *Lumbriculus* spp;
- sediment toxicity study with *Chironomus* spp*:*
- 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 program (of the related substances D4 and D5, but will probably provide useful information on D6) that is likely to include the:
    - time trends using freshwater and marine sediment cores from local, regional, and remote locations, and from 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 these studies;

In addition, further studies are currently being considered or are underway for D4 and D5 and may provide useful information to refine this assessment.

Contents

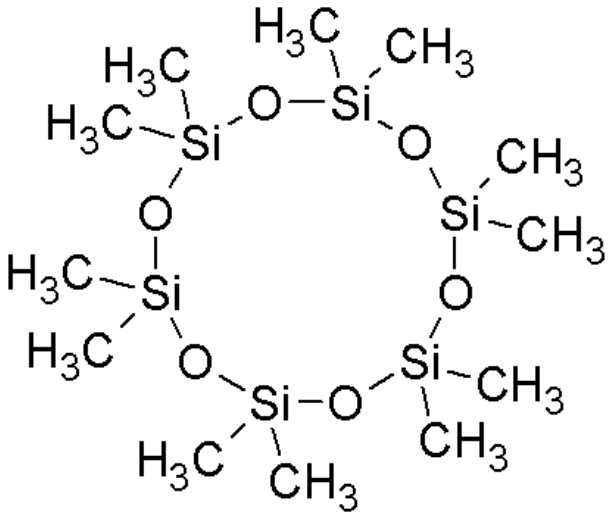
Acknowledgements

The Environment Agency would like to thank all contributors to this report:
Centre Européen des Silicones (CES)
Cosmetic, Toiletry & Perfumery Association (CTPA)
Dow Corning
Environment Canada
EVONIK Industries (formerly Degussa)
GE Bayer Silicones
Norwegian Pollution Control Authority (SFT)
Peter Fisk Associates
Proctor & Gamble
Swedish Chemicals Agency (KEMI)
Unilever
United States Environmental Protection Agency
Douglas Gray at the Health & Safety Executive produced the review of mammalian toxicity data and the human health-risk characterisation.

1 General substance information

1.1 Identification of the substance

- CAS No: 540-97-6
- EINECS No: 208-762-8
- EINECS Name: Dodecamethylcyclohexasiloxane
- Molecular formula: $C_{12}H_{36}O_6Si_6$
- Molecular weight: 444.9 g/mol
- Smiles notation: C[Si]1(O[Si](O[Si](O[Si](O[Si](C)(C)O[Si](O1)(C)C)(C)C)(C)C)(C)C)C
- Structural formula:



Other names, abbreviations, trade names, and registered trademarks for this substance in current use include the following (CES, 2005):

- cyclohexasiloxane[1]
- D6
- dodecamethylhexacyclosiloxane
- Dow Corning 246
- SF 1258.

In Europe, dodecamethylcyclohexasiloxane is commonly referred to as D6, 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 present 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, polydimethylsiloxy cyclics, polydimethylcyclosiloxane, and mixed cyclosiloxane. The D6 in cyclomethicone is accounted for in this assessment.

[1] Cyclohexasiloxane is the International Nomenclature Cosmetic Ingredient (INCI) name used to identify D6 used in cosmetic products.

1.2 Purity, impurity, and additives

1.2.1 Purity and impurities

The purity of the substance is generally >90 per cent (often higher than this). The main impurities are small amounts of hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and tetradecamethylcycloheptasiloxane (D7).

1.2.2 Additives

No additives are in the commercial substance.

1.3 Physicochemical properties

1.3.1 Physical state (at normal temperature and pressure)

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

1.3.2 Melting point

The melting point of D6 is –3°C (Merck, 1996; IUCLID, 2005). This value is used in the assessment.

1.3.3 Boiling point

Merck (1996) gives the boiling point as 245°C at atmospheric pressure and 128°C at a reduced pressure of 20 mmHg.
Chandra (1997) reviewed the available measured data and estimation methods available for D6 and reports that the measured boiling point was 245°C and the best estimate for the boiling point was 248°C. IUCLID (2005) also report the boiling point to be 245°C at atmospheric pressure.A boiling point of 245°C is used in the assessment.

1.3.4 Density

The relative density is 0.9762 (Merck, 1996). Chandra (1997) reviewed the measured data and estimation methods available for D6 and reports that the measured density at 20°C is 0.966 g/cm^3 and the best estimate for the density at 20°C is 0.959 g/cm^3. IUCLID (2005) gives the density as 0.963 g/cm^3 at 25°C. Where needed, a density of 0.963 g/cm^3 at 25°C is used in this assessment.

1.3.5 Vapour pressure

Flaningam (1986) measured the vapour pressure of D6 using an ebulliometer. The D6 tested was distilled prior to use and was 99.90 per cent pure. The vapour pressure of D6 was determined over a temperature range of 412–531 K (139–258°C). The corresponding pressure range was 4.1–135 kPa at these temperatures.

The data were fitted to the Antoine equation:

$$\ln P_v = A - B/(T + C) \quad (1.1)$$

where P_v is the vapour pressure (Pa), T is the temperature (K), A is a constant (= 20.4120 for D6), B is a constant (= 3572.15 for D6), and C is constant (= –116.144 for D6).
The standard deviation in the experimental vapour pressure for Equation (1.1) is given as 0.11 kPa. Using Equation (1.1), the vapour pressure of D6 can be estimated as 1.2 Pa at 20°C and 2.2 Pa at 25°C.

The vapour pressure data were also fitted to the AIChE DIPPR[2] equation. The root mean square percentage error in this method is given as 1.48 over the temperature range 284–645 K.

$$\ln P_v = A + B/T + C \times \ln(T) + D \times T^E \quad (1.2)$$

where P_v is the vapour pressure in Pa, T is the temperature (K), A is the constant (= 99.273 for D6), B is a constant (= –11,155 for D6), C is a constant (= –10.612 for D6), D is a constant (= 5.98667×10^{-18} for D6), and E isa constant = 6 for D6.
Using Equation (1.2), the vapour pressure of D6 can be estimated as 2.5 Pa at 20°C and 4.0 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 latter values are considered more reliable for use in this risk assessment.
Chandra (1997) reviewed the measured data and estimation methods available for D6 and reports that the measured vapour pressure at 25°C is 4 Pa (0.03 mmHg). Presumably this value refers to the extrapolated value above from the Flaningam (1986) data.
Another value for the vapour pressure for D6 of 4.6 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 –3 to 373°C. The actual data used in the correlation and the fitted parameters that result are not reported. However, as the temperature range covered appears to be larger than that in the Flaningam (1986) paper, this value is taken as the more reliable value (although there is very good agreement between the two studies).
The vapour pressure of D6 at 25°C is estimated as 4.73 Pa (0.0355 mmHg) using the 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 245°C.
The database within the EPI software also contains an experimental value for the vapour pressure of D6. This is 3.0 Pa (0.0225 mmHg) at 25°C and is referenced to Kochetkov *et al.* (2001). This value again appears to be derived from the Flaningam (1986) data. The estimated value above is in good agreement with this value.
A vapour pressure of 4.6 Pa at 25°C, as reported in IUCLID (2005), is used in the assessment for D6. 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 D6 using a slow-stirring method to avoid the formation of colloidal suspensions. The method involved adding the D6 to the surface of the water (1500 ml of water in a 2 l flask; sufficient D6 was added to cover the water) and gently stirring the water phase (avoiding cavitation and turbulence). The test was

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

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 D6. The definitive test determined the water solubility (mean ± standard deviation) to be 5.3 ± 0.48 µg/l at 23°C based on nine determinations.
Using the USEPA EPI (v3.12) estimation software a water solubility of 0.005 mg/l at 25°C can be estimated for D6 using an octanol–water partition coefficient (log K_{ow}, see Section 1.3.7) of 6.33 (the method applies a correction for cyclic siloxanes).
A second estimate for the water solubility of D6 of 0.002 mg/l at 25°C is also obtained using the USEPA EPI program. This value is estimated by a fragment approach.
Chandra (1997) reviewed the available measured data and estimation methods available for D6 and reports that the measured water solubility at room temperature is 5 µg/l [presumably based on the above experimental value from Varaprath *et al*. (1996)]. No estimated value is given.
A water solubility of 5.3 µg/l at 23°C is used in the risk 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 D6 to be 5.86 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} of D6 was also determined using the slow-stirring method (IUCLID, 2005). The test was carried out in line with the Organisation for Economic Co-operation and Development (OECD) draft guidelines (2002 version) using ^{14}C-labelled D6 (^{14}C-D6) at 22°C. The tests were carried out using around 800 ml of octanol-saturated water, and 50 ml of water-saturated octanol. A known mass of the radiolabelled D6 was added to the octanol phase, and then a further 50 ml of water-saturated octanol 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 to 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 ten days and the log K_{ow} value was 4.36 at 22.4°C.
However, D6 undergoes hydrolysis, albeit at a slow rate (see Section 3.2.2.1). 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 parent-compound analysis (this is especially important as the products of hydrolysis of D6 are likely to be more water soluble and less hydrophobic than D6 itself). Therefore there are currently some doubts over this value.
A log K_{ow} of 6.33 can be estimated for D6 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 D6 was undertaken on a voluntary basis by the industry (Xu *et al*., 2007). Preliminary results from some of this work were also made available in a poster presentation (Xu and Kozerski, 2007). The study investigated four different methods to estimate the log K_{ow} for D6. These were:

- a bond-contribution method based on directly measured values for log K_{ow} for two related substances (D4 and D5);
- correlation with HPLC retention times (HPLC method), taking into account the measured log K_{ow} for D4 and D5;
- linear extrapolation from the measured log K_{ow} values of D4 and D5 based on the number of –(CH_2)–Si–O– units;
- calculated based on linear free-energy relationships using measured solute descriptors for D6.

The values of log K_{ow} for D4 and D5 used in the analysis are 6.49 and 8.03, respectively (see Environment Agency, 2008a, 2008b). The linear free-energy relationship method was based on an approach by Abraham (1993) and Goss (2005). The method relates a general partition

property (K) to a linear combination of free-energy related product terms that quantify the contributions to log K from various types of solute–solvent interactions (including those that arise from van der Waals forces and hydrogen bonding). The descriptors used in the approach include McGowan's characteristic volume, the logarithm of the solute hexadecane–air partition coefficient, the solute excess molar refraction, the solute dipolarity and/or polarisability, the solute hydrogen-bond acidity, and the solute hydrogen-bond basicity. The values for the descriptors for D6 were determined by Ahmed *et al*. (2007) – the actual values were not given in the Xu *et al*. (2007) report.

The log K_{ow} values estimated using these methods are summarised as:

- bond contribution method, log K_{ow} = 9.57;
- HPLC retention-time method, log K_{ow} = 9.45;
- linear extrapolation method, log K_{ow} = 9.06;
- linear free-energy relationship method, log K_{ow} = 8.89.

Overall, there is good agreement between the values of log K_{ow} estimated for D6 using these four methods. Xu *et al*. (2007) recommend that a log K_{ow} value of 9.06 (as obtained from the linear extrapolation method) should be used for D6 as this value is close to the average log K_{ow} (9.24) from the four methods.

There is some discrepancy between the available log K_{ow} values for D6. For this risk assessment, particularly for soil and sediment, it is important to distinguish between log K_{ow} values >5 and log K_{ow} values <5. For D6, experimentally derived values both above and below five are reported; however, it is not possible to validate these data fully because a lack of experimental details. Recent predictions by Xu *et al*. (2007) suggest that the actual log K_{ow} is probably around 9.06, a value consistent with the known log K_{ow} values for both D4 and D5, and is also self-consistent with other partition coefficients used for D6.[3]

For the main assessment, the log K_{ow} value for D6 is taken as 9.06. However, to demonstrate the effects of the uncertainty in the value, the effect of using a lower log K_{ow} value of 5.86 on the overall conclusions of the risk assessment was investigated (results given in the Appendix).

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

1.3.8 Hazardous physicochemical properties

1.3.8.1 Flash point

The flash point of D6 is reported (IUCLID, 2005) as 91°C (closed cup) and 109°C (open cup).

1.3.8.2 Autoignition

The autoignition temperature is in the range 368–371°C (IUCLID, 2005).

1.3.8.3 Explosivity

No information is available.

1.3.8.4 Oxidising properties

No information is available, and D6 is not expected to have oxidising properties.

[3] Using the log K_{oa} of 5.76 at 24°C and the log K_{aw} of 3.30 at 25°C (see Section 1.3.9.3), the log K_{ow} can be estimated as 9.06.

1.3.9 Other relevant physicochemical properties

1.3.9.1 Granulometry

This property is not relevant as D6 is a liquid.

1.3.9.2 Surface tension

The surface tension of D6 is 19.2 mN/m at 20°C and 18.8 mN/m at 25°C (Dow Corning internal data; CES, 2005).

1.3.9.3 Henry's law constant

Kochetkov *et al*. (2001) determined the Henry's law constant of D6 using two different methods. The first was a static method in which a saturated solution of D6 in water was equilibrated with air in the headspace of a sealed container for 48 hours and then the equilibrium concentration of D6 in each phase determined. To avoid the formation of colloidal suspensions of D6 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 D6 directly to water (and hence avoiding any colloidal emulsion formation). In this method the vapour phase was essentially saturated with D6 by bubbling air though pure D6 and then a portion of this saturated vapour continuously circulated through water in a sealed system for 48 hours. At the end of this period the concentrations of D6 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 determined were 2.7 ± 0.2 (equivalent to a Henry's law constant of 6712 Pa m^3/mol) in the static method and 5.9 ± 2.9 (equivalent to a Henry's law constant of 14,667 Pa m^3/mol) in the vapour entry loop method. A reference substance (benzene) was also tested using the same methods. These gave dimensionless Henry's law constants of 0.25 and 0.19, respectively, which agree well with literature values (0.19–0.23).

The Henry's law constant can be estimated as 0.165 atm m^3/mol (16,719 Pa m^3/mol) using the Environmental Protection Agency (USEPA) Estimation Program Interface (EPI) (v3.12) estimation software. The value is estimated from the chemical structure using the bond-contribution method.

Using a water solubility of 0.0053 mg/l at 23°C and a vapour pressure of 4.6 Pa at 25°C, the Henry's law constant can be estimated as 386,140 Pa m^3/mol.

Further work to investigate the dimensionless Henry's law constant [or air–water partition coefficient (K_{aw})] for D6 was undertaken on a voluntary basis by industry (Xu *et al*., 2007). Preliminary results from some of this work were made available in a poster presentation (Xu and Kozerski, 2007). The study investigated four different methods to estimate log K_{aw} for D6. These are:

- a bond-contribution method based on the directly measured log K_{aw} for D4 and D5;
- calculated from the measured octanol–air partition coefficient (log K_{oa}) for D6 of 5.76 (see Section 1.3.10) and the estimated log K_{ow} for D6 of 9.45 obtained using the HPLC method (see Section 1.3.7);
- estimated from the measured log K_{oa} for D6 of 5.76 and the log K_{ow} for D6 of 9.06 estimated by linear extrapolation from the measured log K_{ow} of D4 and D5 based on the number of –(CH2)–Si–O– units (see Section 1.3.7);
- calculated based on linear free energy relationships using measured solute descriptors for D6 (further details of this method are given in Section 1.3.7 in relation to the estimation of log K_{ow}).

The values of log K_{aw} for D4 and D5 used in these methods are 2.69 and 3.13, respectively (see Environment Agency, 2008a, 2008b).

The resulting log K_{aw} values estimated at 25°C are:

- 3.57 by the bond contribution method;
- 3.69 estimated from log K_{oa} and log K_{ow};
- 3.30 by the linear extrapolation method;
- 3.08 by the linear free energy relationship method.

There is relatively good agreement between the log K_{aw} values estimated using these four methods. Xu *et al*. (2007) recommend a log K_{aw} value of 3.30 (K_{aw} = 1995; as obtained from the linear extrapolation method) for D6 as this value is close to the average log K_{aw} from the four methods (the average log K_{aw} is 3.41). A K_{aw} value of 1995 is equivalent to a Henry's law constant of around 4,943,000 Pa m^3/mol.

From the available data on the Henry's law constant it is apparent that the measured values [e.g. those from Kochetkov *et al*. (2001)] are significantly lower than predicted on the basis of water solubility and vapour pressure alone, whereas the recent estimates from Xu *et al*. (2007) are slightly higher than this predicted value. This implies inconsistency in these measured parameters and, therefore, 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 D6.

A Henry's law constant of 4,943,000 Pa m^3/mol at 25°C is considered in this risk assessment as it is consistent with the data available for both D4 and D5, and is self-consistent with the other partition coefficients estimated for D6.[4] However, this is a calculated value and some experimental data are considerably lower than it. 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 14,667 Pa m^3/mol at 26°C (dimensionless Henry's law constant of 5.9) on the conclusions of the risk assessment are also considered, based on the experiments by Kochetkov *et al*. (2001). This analysis is shown in the Appendix.

1.3.10 Octanol–air partition coefficient

Very recently, the results of a study to investigate the K_{oa} of D6 became available (Xu, 2006). The study was carried out using a mixture of ^{14}C-D4, ^{14}C-D5, and ^{14}C-D6, and the purity of the D6 was 99.5 per cent. Mixtures of the test substances in *n*-octanol were prepared [D6 concentrations between 6.2 and 445 ppm (mg/l) were tested; two concentrations were used for each temperature] and around 1–5 ml of this solution was added to 100 ml gas syringes. The syringes were incubated at–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 D6. The mean log log K_{oa} determined for D6 are 6.85 at –4°C, 6.49 at 5°C, 5.76 at 24°C, and 5.30 at 40°C. The temperature dependence of the log K_{oa} value was fitted to Equation (1.3):

$$\log K_{oa} = A + B/T \qquad (1.3)$$

where A and B are constants (B is related to the internal energy change for D6 that evaporates from the octanol to the air) and T = absolute temperature (K).

The heat of evaporation (ΔU) was calculated from the B value as 44.0 kJ mol^{-1} for D6.

Other values for the K_{oa} were reported in a poster presentation by Xu and Kozerski (2007). This reports a measured log K_{oa} value of 5.76 for dry octanol. The temperature of the determination is not stated and no further experimental details are available. It is likely that this value relates to the above study by Xu (2006), in which a similar log K_{oa} of 5.76 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 D6 predicted using this method are 6.26 for dry octanol and 6.05 for wet octanol. Few other details of these calculations are currently available.

[4] Using the log K_{oa} of 5.76 at 24°C (see Section 1.3.10) and the log K_{ow} of 9.06 at 25°C (see Section 1.3.7) the log K_{aw} is estimated as 3.30. This is the basis of method 3 above.

1.3.11 Summary of physicochemical properties

The physicochemical properties of D6 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	–3°C	
Boiling point	245°C	
Density	0.963 g/cm^3 at 25°C	
Vapour pressure	4.6 Pa at 25°C	
Water solubility	5.3 µg/l at 23°C	
Log K_{ow}	9.06	5.86
Henry's law constant	4,943,000 Pa m^3/mol at 25°C	14,667 Pa m^3/mol at 26°C
log K_{oa}	5.76 at 24°C	
Conversion factor for air	1 ppm = 18.2 mg/m^3 at 25°C	

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

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 D6, 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 D6 is as a monomer in the manufacture of polymeric materials. Such polymers could contain residual amounts of D6 (and, in some cases, could possibly break down to form small amounts of D6) and so the use of the polymeric materials could, in some cases, act as a source of release to the environment of D6.

Therefore this section provides a general overview of the silicone industry relevant to the cyclic organosiloxanes (including D6). The specific uses of D6 itself are considered in more detail in Section 2.3.

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

Chandra (1997) considers five basic groups of organosiloxanes (also known as silicones), which 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):

$(R_2SiO)_x$ are cyclic substances in which R is usually a methyl group, but can also be hydrogen, vinyl group, phenyl group, or a trifluoropropyl ($CF_3CH_2CH_2$–) group, and x = 3, 4, 5, 6, etc. (D6) falls into this group;

- $R_3SiO(SiR_2O)_nSiR_3$ are 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).

$$(CH_3)_2SiCl_2 + 2H_2O \rightarrow [(CH_3)_2Si(OH)_2] + 2HCl \rightarrow [(CH_3)_2SiO]_x + HO[Si(CH_3)_2O]_yH$$

where the products are cyclic siloxanes (x = 3, 4, 5, 6, etc.) and oligomeric siloxanols

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 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 (WWTP) or is reused in the hydrolysis process. The typical yield of cyclic oligomers is between 35 and 50 per cent, and consists mainly of octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane – D6 is only a small percentage of the products.

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 hydrolysis 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). Methyltrichlorosilane impurity in the starting material can produce significant amounts of trifunctional units in the resulting oligomers, which 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 process, the hydrolysate is depolymerised in strong bases or acids to give cyclic monomers, such as D4, D5, and D6, 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 use as site-limited intermediates in the production of polymeric siloxanes (Chandra, 1997). The remaining 13 per cent (amounting to around 20,000 tonnes) were used in personal care products (particularly the D4, D5, and D6 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) indicate that the functions of the cyclic siloxanes used in cosmetics in the United Kingdom (UK) are, in general, in the following three main areas (CTPA, personal communication):

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

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

2.1.2 Polymeric dimethylsiloxanes

More than 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

$HO[Si(CH_3)_2°]_nH$

where n = 5–6000 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 2.1.1. 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 (which 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 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, 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 that the numerous uses for PDMS, such as:

- a foaming agent in oil processing;
- a flow and gloss improver in alkyd paints and varnishes;
- a lubricant in polishes and maintenance products;
- in anti-adhesion coatings;
- in hydraulic, dielectric, and heat-transfer fluids and in diffusion pump oils;
- in barrier creams and lipstick, and in 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;
- 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 2.1.3) 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 further.

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 200–250°C thermal oxidation can occur and lead to the formation of formaldehyde, carbon dioxide (CO_2), water, and alkylsilicones.

PDMS is approved for food use in the UK (known as E900).[5]

Based on the above discussion 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 3.1.5.1). Furthermore, under certain conditions (elevated temperatures in the presence of acidic 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 D6.

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

2.1.3 Modified polymeric dimethylsiloxanes

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

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

or

$$X(CH_3)_2SiO(Si(CH_3)_2O)_m[Si(CH_3)_2O]_nSi(CH_3)_2X$$

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:

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

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:

$$y[X(CH_3)Si(OR)_2] + yH_2O \rightarrow [X(CH_3)SiO]_y + 2y\text{ROH}$$

cyclic

or

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

Linear

Hydrosilylation or nucleophilic substitution reactions are also used to synthesise modified PDMS.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 provides greater solvent and fuel resistance to the silicone rubber for use 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, which gives 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 D6.

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 in some trifluoropropyl or phenyl groups replace 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, and so 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, and methylethyloxime silanes. 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 one-part, cold-cured system is based on hydroxyl-terminated PDMS with methyltriacetoxysilane 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 by either a condensation reaction or an addition reaction. A condensation-cured two-part system is based on hydroxyl-terminated PDMS and ethyl silicate. An addition-cured two-part system is based on vinylated PDMS, PDMS, and a cross-linking agent. A heat-cured system is 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, as an alternative to aid subsequent processing, 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.

RTV silicones cure on exposure to atmospheric oxygen – the rate of cure depends 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 ether acetic acid or alcohols) and diol groups are formed 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 to those 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). After 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.

To make coated textiles and glass cloth the gum stock is dissolved in solvent and the rubber applied 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 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-ethyl titanate) 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 has 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 applications 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) list many possible uses for silicone rubbers (elastomers). One-component cold-cured rubbers are used as caulks and sealants for expansion joints and windows, for seals, gaskets, and shock-absorbing fixing in vehicles and domestic appliances, and in heat-resistant adhesives. Two-component cold-cured (addition cured) rubbers are used as dielectric gels, for electronic and electrical encapsulation, in fire-resistant cable coatings, in foamed sealants, and in resin casting moulds. Two-component cold-cured (condensation cured) rubbers are used as moulding compounds for furniture and construction, in paper anti-adhesion coatings, as electrical component sealants, as roofing membranes, and as window and curtain walling sealants. Heat-cured silicone rubbers are used in chemical-resistant and medical tubing and mouldings, and in 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 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 [clusters of quadrafunctional silicate groups (Q) end-capped with monofunctional trimethylsiloxy groups (M)] resins 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. Also, the industry is evolving towards products that can be cured by ultraviolet (UV) light.
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 D6.

2.1.6 Consumption of silicones

The Centre Européen des Silicones (CES) published figures on the total worldwide consumption of silicones in 2002.[6] 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) in North America, 28 per cent (560,000 tonnes) in Asia, and 5 per cent (100,000 tonnes) 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 for 2002 was:

- 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

Two companies produce or supply D6 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.

2.3 Uses

The uses of D6 can broadly be divided into three main areas:

- use as a site-limited chemical intermediate at the site of production;
- use as an off-site chemical intermediate;
- use in personal care products (e.g. cosmetic products, skin- and hair-care products).

CES provided information on the amounts of D6 supplied in the EU and the UK.

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

Some of these figures are confidential and are summarised in the confidential annex to this report. The non-confidential figures for D6 are summarised in Table 2.1.

Table 2.1 Uses of D6 in the UK and Europe

Life-cycle step	Amount used in Europe (tonnes/year)		Amount used in UK (tonnes/year)	
	2003	**2004**	**2003**	**2004**
Chemical intermediate – internal	Confidential	Confidential	Confidential	Confidential
Chemical intermediate – external (as a component of a D5–D6 blend)	0	41	0	41
Personal care	1858	1989	7	306
Total	**Confidential**	**Confidential**	**Confidential**	**Confidential**

Other uses of D6 reported in the Nordic Substances in Products in the Nordic Countries (SPIN) database include surface treatment, fillers, paints, lacquers, and varnishes (TemaNord, 2005). Environment Canada (2008) indicates that in Canada there may be some use of D6 in waxes and polishes (D6 content between 3 and 15 per cent) and in surfactants and defoamers (D6 content between 0.2 and 35 per cent). Such uses are not confirmed for the UK in the CES survey and so are not considered further here. It is possible that these figures may refer to uses of PDMS made from D6 rather than to a direct use of D6.

2.4 Life cycle

The overall life cycle of the various silicone products relevant to this project is summarised in Figure 2.1.

2.5 Trends

Based on the confidential information provided for this assessment, the production of D6 in the UK shows an increasing trend over recent years. Similarly, the off-site uses (off-site use as a chemical intermediate, use in personal care products) show a generally increasing trend in both the UK and the EU. However, this analysis is based on relatively few data points (in some cases only two years).

2.6 Legislative controls

There are no current European controls on D6.

In the USA, VMSs, including D6, are exempt from volatile organic compounds (VOCs) legislation because laboratory experiments by 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, 2005). 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 values for all four substances studied (hexamethyldisiloxane, D4, D5, and siloxanol) were close to zero, and so a similarly low value is also expected for D6 (CES, 2005).

In Germany, D6 is considered as a general organic substance in relation to limiting air emissions (CES, 2005). The emission limit according to TA Luft (based on total carbon) is 0.5 kg carbon/hour, which equates to an emission limit for D6 of 1.55 kg D6/hour or a maximum of 50 mg carbon/m^3 (= 155 mg D6/m^3). For indoor air, no specific Niedrigste Interessierende Konzentration (NIK) exists for D6. D6 is therefore included under the general category of other substances for which no NIK standard is derived, the sum of which must be <0.1 mg/m^3.

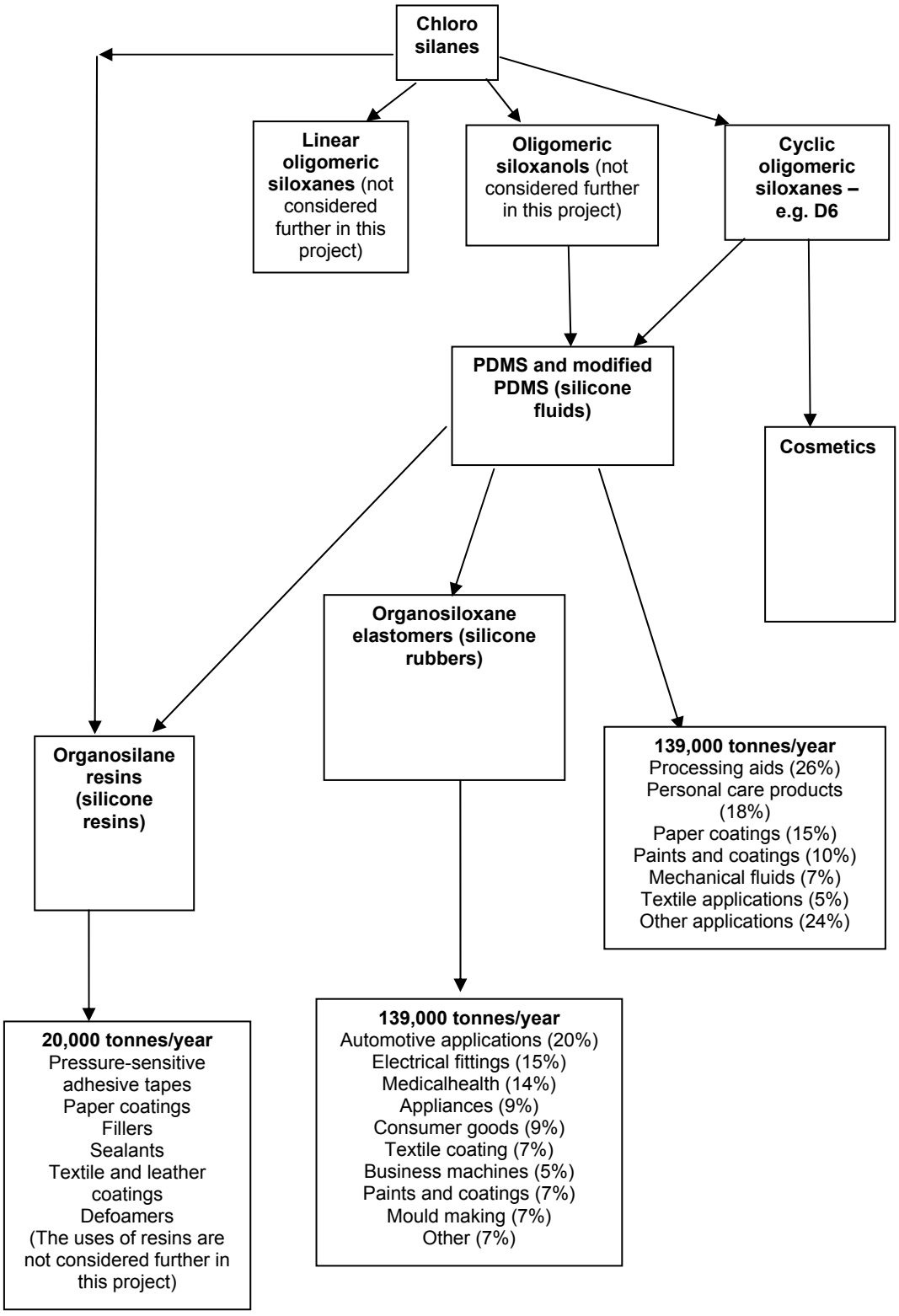


Figure 2.1 Western European usage of silicones

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, 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 D6 we have information on both the total EU volume and the volume used in the UK, and so, wherever possible, the B Tables for the UK volume are used to estimate the representative sizes for the sites in the UK.

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 figures, 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)] for D6 are:

- 0.00001 (0.001 per cent) to air
- 0.003 (0.3 per cent) to wastewater.

The number of days of release is 300 (from Table B1.6). The emissions estimated from these figures are confidential.

3.1.1.2 Other emission data

Information is available on the amounts of D4 and D5 in various effluent streams at the production sites in the EU, and is summarised in the risk assessment reports for D4 and D5 (Environment Agency, 2008a, 2008b). The data represent the emissions from the whole site and so include any on-site use of D4 and D5 as intermediates. Based on these figures, D4 and D5 emissions to water after waste treatment at the actual UK plant, estimated using the appropriate effluent flow data, are of the order 0.035–0.062 kg/day and 0.0024–0.0084 kg/day, respectively, . These data are based on measurements taken at around 2001. Using the 2001 production data for this site (confidential), an appropriate emission factor for D6 was derived (details of the calculation are given in the confidential annex, and is based on the releases of the other substances). This is used to estimate the emission of D6 from this UK production site (after wastewater treatment) as: 1.2 kg/year or 0.0039 kg/day.

3.1.1.3 Summary of emissions used in assessment

For the assessment, the emissions to water estimated in Section 3.1.1.2 are used, along with the default emissions estimated for air (see Section 3.1.1.1). 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 D6 used in this assessment are:

- local:
  - confidential to air
  - 1.2 kg/year or 0.0039 kg/day to surface water;
- total UK:
  - confidential to air
  - 1.2 kg/year to surface water;
- regional:
  - 58 kg/year to air
  - 1.2 kg/year 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 WWTP [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 is 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 D6 are (assuming MC = 3 as a default):

- 0.0001 (0.01 per cent) to air;
- 0.007 (0.7 per cent) to wastewater (wet process);
- 0 to wastewater (dry process).

CES (2005) recently completed the analysis of a questionnaire that requested further details of D6 emissions to water from UK and EU sites where D6 is used as an intermediate for off-site polymer synthesis. In the survey, a ‘dry process’ is defined as one that does not involve aqueous processing of D6 and therefore does not result in release of D6 to the aqueous effluent stream from the site.
The CES (2005) survey identified only a small amount of D6 used in the UK (with no other use in the EU) as an off-site intermediate to manufacture polymers. The D6 is part of D5–D6 blends used in dry processes (no pure D6 is used as an off-site intermediate). Therefore, no emissions to wastewater are expected from this use in the UK (and EU) and this is assumed here.

No further information on the actual emissions to air from the processes is provided. Therefore, the default emission factors outlined above are used here. For the sites that employ dry processes, the amount of D6 used on a site is estimated (using Table B3.2 of the TGD) as 27 tonnes/year over 27 days for polymer synthesis.

The estimated emissions to air and wastewater from off-site use of D6 as an intermediate in polymer synthesis are therefore:

- local (UK):
  - 2.7 kg/year or 0.1 kg/day to air
  - 0 kg/year to wastewater;
- local (EU), not relevant;
- total UK:
  - 4.1 kg/year to air
  - 0 kg/year to waste-water;
- regional:
  - 4.1 kg/year to air
  - 0 kg/year to wastewater;
- total EU:
  - 4.1 kg/year to air
  - 0 kg/year to wastewater.

The number of days of emission for the local site is 27.
The emissions to air estimated above using the default emission factors are highly uncertain. For this estimation, it is also relevant to consider the appropriate dilution factor when D6 is used as an intermediate in silicone production. The Emission Scenario Document for chemicals used in synthesis (reaction intermediates) in the TGD recommends an effluent flow rate of 10,000 m^3/day from the WWTP and a dilution factor of 40 for such sites. This is taken into account in the PEC calculations (although it is not important for the assessment as there are no emissions to the WWTP).

3.1.3 Use in personal care products

The relevant IC and UC for this use are IC = 5: Personal/Domestic and UC = 15 (Cosmetics).

3.1.3.1 Formulation

The default emissions from formulation of personal care products are estimated using Table A2.#[7] of the TGD. The relevant emission factors are summarised as:

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

As D6 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 D6 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 used. Using this figure and the amount of D6 supplied to the personal care industry in the UK, the following total amount of cosmetics and personal care products that are formulated in the UK and contain D6 can be estimated as 1020 tonnes/year.
Using these figures in Table B2.3 gives the amount of cosmetics and the amount of D6 formulated, on a worst-case local site over 300 days, as
1020 tonnes/year and 306 tonnes/year, respectively.

[7] This is how the Table is numbered in the TGD. The actual number is not clear.

CTPA surveyed cosmetic formulation sites in the UK. The amounts of D4, D5, and cyclomethicone (a general term used when mixtures of D4, D5, and D6) used at the sites were determined. No use of any of these substances was reported at 21 of these sites. The amounts used at the other sites are confidential, but it is 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, with many sites using much smaller volumes than this upper limit. Based on these data the appropriate size for a representative generic site is estimated at 25 tonnes/year of D6 over 300 days.
Using this value and the above default emission factors, the emissions of D6 from formulation can be estimated:

- local, generic site:
  - 5.0 kg/year or 0.017 kg/day to air
  - 22.5 kg/year or 0.075 kg/day to wastewater;
- total UK emission:
  - 56 kg/year to air
  - 275 kg/year to wastewater;
- regional:
  - 35.8 kg/year to air
  - 179 kg/year to wastewater;
- total EU emission:
  - 358 kg/year to air
  - 1790 kg/year to waste-water;

In addition, the CTPA survey allows us estimate the release of D6 from sites that use cyclomethicone. These calculations are confidential, but the local releases from UK sites are in the ranges
1.5×10^{-5} to 1.7×10^{-3} kg/day to air and 8.0×10^{-6} to 1.2×10^{-3} kg/day to wastewater.
The number of days of emission from the local site is 300 in all cases.
The generic estimate for a site that uses D6 and the estimates for UK sites that use D6 as a component of cyclomethicone are considered in this assessment.

3.1.4 Use by general public

The emissions to the environment through use by the general public are taken 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 occurs for products applied to the skin (e.g. skin creams, antiperspirants, etc.) and 100 per cent emission to waste water occurs for hair-care products (that 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 amount of D6 used to formulate personal care products in the EU and the UK are summarised in Section 2.3. However, CTPA indicate that companies 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 used in the UK that contain D6 are unknown, but as a first approximation 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 D6 (assuming a content of 30 per cent, as before) and of D6 itself used in the UK can therefore be estimated as 975 tonnes/year and 292 tonnes/year, respectively.
For the local assessment it is assumed that this tonnage is equally distributed about the UK. Using 60 million as the UK population, the average usage for D6 in personal care products can be estimated as
0.0049 kg/person/year.
Assuming a local site (in this case a WWTP) feeds 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 D6 are:

- local, 4.9 kg/year or 0.013 kg/day to wastewater;
- total UK:
  - 264,600 kg/year to air
  - 29,400 kg/year to wastewater;
- regional:
  - 88,200 kg/year to air
  - 9800 kg/year to wastewater;
- total EU:
  - 1,790,100 kg/year to air
  - 198,900 kg/year to wastewater.

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

3.1.5 Other sources of emission

3.1.5.1 Impurities in PDMS polymers

PDMS-based polymers may contain residual amounts of D6 which may subsequently be lost via volatilisation during the lifetime of these polymers. CES provided figures for the amounts of residual monomer in PDMS-based products, and these are summarised in Table 3.1 (EU) and Table 3.2 (UK).

Table 3.1 D6 impurities contained in silicone products (total EU)

Application	2004 EU sales (tonnes)	Residual monomer content (%)	Amounts of residual monomer (tonnes)
Sealants	210,000	0.048	101.4
Elastomers	139,000	0.081	112.9
Fluids and specialities	204,000	0.146	298.7
Silanes	60,000	0	0
Resins	20,000	0	0
Total	**633,000**		**513.0**

Table 3.2 D6 impurities contained in silicone products (UK)

Application	2004 UK sales (tonnes)[1]	Residual monomer content (%)	Amounts of residual monomer (tonnes)
Sealants		0.048	17.9
Elastomers		0.081	10.6
Fluids and specialities		0.146	54.6
Silanes		0	0
Resins		0	0
Total			**83.1**

Note: [1]Full figures are not available. Where data are missing they are 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.

Toub (2002) considered the factors that affect the levels of volatile products in fabricated silicone elastomers. 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 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 are 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 depends on the actual rubber formulation and the thickness of the article. The sheet exposure time is 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 are below the detection limit independent of the thickness of the article. Post-curing for two hours at 200°C also reduces significantly the residual amounts of D4 in the product. Similar reductions in residual levels are expected for D6.
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 D6 from this source can be estimated as:

- total UK, 83,100 kg/year to air
- regional, 51,300 kg/year to air
- total EU, 513,000 kg/year to air.

3.1.5.2 Breakdown of PDMS polymers

A number of literature sources indicate that D6 (and other cyclic oligomeric siloxanes) can form during the breakdown of PDMS. In this section we focus on the most relevant studies to investigate 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 5000–250,000 cst
- gums, kinematic viscosity >500,000 cst.

The relevant information on the identity of the substance (i.e. viscosity and other data) is given for each study wherever available.
Weschler (1988) showed that five main cyclic siloxanes are formed when samples of PDMS (viscosities between 20 and 30,000 cst) are pyrolysed at temperatures of between 700 and 980°C for one second (the atmosphere used in this study is not totally clear, but appears to have been helium). The relative abundances of the products formed are relatively constant over the range of PDMS products studied, with D3, D4, D5, D6, and D7 in the approximate ratio 100:36:13:8:6. No information is given on the yields of volatile products formed under these conditions. The author notes that this product distribution is 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 shows that the thermal degradation of PDMS end-blocked with $(CH_3)Si–$ groups in inert atmospheres (e.g. N_2) and under vacuum results 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 form. 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 further 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[8]]. Experiments were carried out in either a helium or air atmosphere in a glass container, and 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, then a 10°C/minute increase from 80°C to 400°C, and finally 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. The programmed temperature increase experiments show that the relative amounts of cyclic degradation products are 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 also form in smaller amounts. The actual absolute yields of the products are not given, but the paper indicates that the major volatile products from the experiments in air are water and CO_2 (and also silica), which result from the gas-phase oxidation of the volatile cyclic oligomers formed. The flash-pyrolysis experiments show that linear siloxane oligomers and rearranged siloxane compounds are formed along with the cyclic siloxane oligomers. Under these conditions D4 is the dominant cyclic oligomer (the relative abundance is 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 into CO_2, water, and silica is more limited under these conditions in the air atmosphere than in the slow heating experiments. Again, no information is given on the absolute yields of volatile products that form under these conditions.

Overall, Camino *et al.* (2002) conclude that thermal degradation of PDMS occurs through two competing mechanisms. The first is a molecular mechanism that forms 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 one that involves homolytic scission of the $Si–CH_3$ bond. Cross-links then form within the molecule, which in turn decrease the flexibility of the PDMS and hinder the splitting of the cyclic oligomers.

Lomakin *et al*. (2003) also found similar products in thermal degradation studies. 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. D6 accounts for 1.2 per cent at 300°C, 1.5 per cent at 400°C, 1.2 per cent at 500°C, 2.2 per cent at 600°C, 1.2 per cent at 700°C and 3.9 per cent, at 800°C of the total volatile products formed. D6 also forms in similar experiments using a blend of polystyrene and PDMS (80:20 ratio). The actual yields of volatile products at the different temperatures are not listed in the paper. The results of thermogravimetric analysis are given graphically and generally show little weight loss from the PDMS polymer alone in air at temperatures up to around 300°C, with around 50 per cent weight loss occurring by 500°C (no further weight loss appears to occur at higher temperature).

Nielsen (1979) reports that significant degradation of PDMS occurrs 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, 1000, or 10,000 cst) under a nitrogen atmosphere form both cyclic and linear volatile polysiloxanes (including D6). The actual yields of volatile products at the different temperatures are not listed in the paper. The results

[8] The viscosity is given in the paper as mPa, but 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 cst = 1 centipoise/specific gravity).

of thermogravimetric analysis are given graphically and generally show little weight loss from the PDMS polymer alone in air at temperatures up to around 300°C, with around 50 per cent weight loss occurring by 500°C (no further weight loss appears to occur at higher temperatures). The composition of the volatile products depends on the composition of the PDMS, and also changes with time as the composition of the residual PDMS fluid changes. For example, the 10,000 cst PDMS product gives only cyclic volatiles until much of the fluid is volatilised, whereas the 50–1000 cst PDMS substances evolve 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) thermally aged in inert gas atmospheres (argon), sometimes in the presence of moisture, at temperatures up to 190°C for 48 hours ([onger 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 are 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 is around 5.5 per cent of the initial weight of the polymer when the polymer is aged at 190°C in sealed containers, and 2.7 per cent of the initial weight when it is aged at 190°C in the open air (for comparison the amount of extractable matter from the virgin sample is 3 per cent of the initial weight of the polymer). The cyclic siloxanes contribute 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 is not clear). These substances are 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 for use at high temperatures for extended periods of time. The emission to air during post-curing of elastomers is considered in Section 3.1.5.1.

Although the results of thermal degradation studies show that D6 forms under certain high-temperature conditions, under the usual conditions of use PDMS polymers are known to possess a high degree of thermal stability. According to CES (2005), 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 should not exceed 300°C (for short periods of time). The available pyrolysis studies were carried out mainly at 300°C or higher and only limited information is available on the potential breakdown products formed at lower temperatures. (However, it is expected that PDMS and other silicone polymers become increasingly stable at lower temperatures. For example, although the above data show that D6 appears to make up a similar fraction of the total volatile products formed at each temperature, the amount of total volatile products formed varies with temperature and is likely to decrease with decreasing temperature below 300°C.) Overall, this means that the actual thermal breakdown of PDMS polymers during normal use is minimal, but it cannot be ruled out that D6 may form under some situations. It is not possible to quantify this potential source of D6 to air.

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 here.

Carpenter *et al*. (1995) studied the degradation of PDMS in a USEPA standard soil. 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 the three spiking methods the soil was slurried with:

- a solution of PDMS in hexane and the hexane 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 is 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 amounts of low molecular weight siloxanols formed. 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.
Carpenter *et al*. (1995) also carried out an experiment to investigate the formation of volatile products during the degradation. 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 formed under these conditions. The principal products in extracts from the soil were a series of linear silanol-terminated oligomers with seven siloxane units or less.
The mass balance reported in this study is relatively low for soils incubated for long periods. This indicates 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). These show that as the soil dries binding of dimethylsilanediol to soil increases (i.e. the dimethylsilanediol is no longer easily extracted with organic solvents such as tetrahydrofuran, but is readily extracted by dilute aqueous acid solution).
Lehmann *et al.* (1994) showed that ^{14}C-PDMS (200 cst viscosity, number average molecular weight 6642 g/mole) 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), 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 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, except that 5 g of soil in centrifuge tubes was used, a foam plug moistened with PDMS (350 cst viscosity) inserted into the neck of the tube (to trap volatiles), and the tubes 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 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 is generally very good (in the range 92.8–107.2 per cent), which indicates that all major degradation products are accounted for. When the soil was allowed to dry (from 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 dried 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. By day four the molecular weight distribution had decreased and a few water-soluble degradation products had formed. However, by day seven a significant breakdown of the PDMS to low molecular weight products had occurred and by day 14 the water-extractable and acid- extractable (0.1 M HCl) products accounted for around 18.2 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 is again very good (99.0–107.4 per cent).

Additional experiments on the microbial degradation of the low molecular weight products showed that dimethylsilanediol is the major ultimate degradation product.
Lehmann *et al.* (1994) conclude that the degradation of PDMS is probably not biological in origin, as it is 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, per centage organic matter, texture, mineralogy, and geographic origin demonstrates 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 is dimethylsilanediol. Other small silanols or cyclic siloxanes were either not detected or 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 is dimethylsilanediol for 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) formed. Taking these results, along with the earlier findings of Buch and Ingebrigtson (1979), it is concluded that the cyclic products formed are 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 a commercially available PDMS (viscosity of 350 cst) emulsion in field soils under natural conditions. 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 mg/kg (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 that remained. The concentration of PDMS 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 (found in most samples at <5 per cent of the original PDMS concentration). A further application of the medium treatment level was carried out in late August. This showed a slow degradation of PDMS during the cool, wet, autumn months followed by around 40 per cent degradation over the winter months, with further, extensive degradation in the summer of 1998. These findings are consistent with the results of the laboratory studies, but substances that volatilised from the soil were not collected in this study.

Stevens (1998) summarises the degradative behaviour of PDMS in soils . 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 slowly biodegradades into $^{14}CO_2$ and silicic acid [$SiOH)_4$] in soil, which thus provides a route for the ultimate mineralisation of PDMS.

Stevens (1998) also reports work by Carpenter (1996) that shows relatively slow degradation of ^{14}C-PDMS (viscosity 350 cst) in freshwater sediments. After one year around 5–10 per cent of the PDMS had 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 catalyse the degradation of ^{14}C-PDMS (viscosity 350 cst) when exposed at a relative humidity of 32 per cent. The more effective minerals are those with higher proportions of Al–OH functional groups on the surface, and the rate of degradation is also related to the specific surface area of the mineral.
Xu (1998) investigated further the effect of moisture levels and exchangeable cation on the degradation of PDMS fluids by clay minerals. ^{14}C-PDMS was tested, but no information on the viscosity is given (by comparison with other studies carried out by this author it is likely that the substance was of 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-PDMS solution was then added to each tube and the tubes 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 , which indicates that degradation to lower molecular weight products occurrs.

The main final degradation product 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 little or no volatile products 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 increases with the increase in polarising power of the exchangeable cation (i.e. Al^{3+} >> Ca^{2+} > Na^+) and decreased humidity.

Xu (1998) concludes that reaction proceeds 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, D5, etc. The actual products formed under any given conditions are thought to result from the relative rates at which the linear silanols from PDMS form and these two competing reactions. Conditions that best favour the formation of volatile cyclic products are 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 is 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 undergo degradation (see Section 3.2.3), and so the ultimate degradation product of PDMS in soil is likely to be dimethylsilanediol. The hydrolysis is thought to be catalysed by soil clays, with clay minerals of low pH, such as kaolinite and montmorillonite, the most effective. Traina *et al*. (2002) also investigated the degradation of PDMS in soil (a silt loam) under field conditions using test plots (5 m by 5 m) amended with anaerobically digested municipal biosolids. 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 are 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 concentration was >100 g/kg (10 per cent) over most of the test period. The half-life of PDMS was in the region 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 into 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 emission to the environment that results from such processes is very difficult, if not impossible, to estimate as the yield of such products depends on the specific conditions that the polymers are exposed to.

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 of 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 3.1.5.1). 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, which when spread onto soil is likely to provide a significant route of exposure. For example, Fendinger *et al*. (1997) measured PDMS concentrations of 290–5155 mg/kg in sewage sludge from eight WWTPs in North America, and found <0.41–10.4 mg/kg PDMS in soils from locations where sludge was applied. However, these conditions represent excessive loadings not normally found under field conditions, even where rates of sewage sludge application are very high (CES, 2005). The available information indicates that, although cyclic siloxanes can be formed from degradation of PDMS under some situations, they are generally not the major products 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 initial estimates of the possible magnitude of these emissionsbutthese estimates 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 provides estimates of the amounts of silicone products emitted to wastewater or disposed of as waste to landfill or incineration over the life cycle of the product. It includes possible emissions from both use and disposal of the substances, but excluded 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)[1]	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[2]	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]The consumption figures include the amounts used as site limited intermediates. Emissions from site limited intermediate use is not considered in the emission figures.
[2]PEMS is polyethermethylsiloxane.

For PDMS, Chandra (1997) indicates that the primary uses other than as site-limited intermediates, were in industrial applications (e.g. as antifoams, softeners, and wetting agents in textile manufacturing, and as transformer dielectric fluids and heat-transfer liquids) and in consumer applications (such as personal care, and as household- and automotive-care products, such as polishes). Chandra (1997) estimates that the main source of release to wastewater is from use in personal care products and various processing aids. At the end of the product life cycle it is estimated 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, it is estimated that around 13,380 tonnes/year disperses 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 are considered in the Chandra (1997) survey. Uses other than as site-limited intermediates uses 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 textile coatings, personal care products, household-care products, automotive-care products, and plastic modification.

The estimated emissions to wastewater are thought to come primarily from the uses of methyl(aminoalkyl)- or methyl(alkyl)siloxanes. The main sources to landfill and incineration are thought to be from uses such as textile coatings, high-temperature oil baths, wallboard coatings, rubber compounds, and powder treatment.
The main uses of polyethermethylsiloxanes, other than as site-limited intermediates, uses thought to lead to emissions to wastewater are from textile and personal care products. The main source for landfill and incineration is from use in urethane foam. In addition, a direct emission to soil of around 340 tonnes/year is estimated from use as an agricultural adjuvant.
The main uses of cured resins identified in the Chandra (1997) survey are as electrical varnishes, moulding compounds, components of decorative and high-temperature paints, abrasion-resistant coatings, laminating and adhesive materials, masonry water repellents, adhesive promoters, and components of silicone pressure-sensitive adhesives. Virtually all of the resin that enters the environment is thought to be disposed of by either landfill or incineration. However, it is also thought 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 is estimated that this may amount to around 310 tonnes/year.

The main uses of RTV elastomers considered in the Chandra (1997) survey are as sealants, encapsulants, foams coatings, caulking, and mould making. Heat-cured rubber applications include tubing, hoses, wire and cable insulation, penetration seals, laminates, release coatings, foams, and other moulded and extruded articles. Gel applications include electrical encapsulants and wound-dressing patches. It is estimated that virtually all of the elastomers are 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 are 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 emissions that result are summarised in Table 3.4. The assumptions made for these estimates are that the

- overall use pattern for PDMS-based products in the USA in 1993 is also applicable to the EU in 2004;
- 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];
- 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 used here 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 lifetime of ten years and is then disposed to landfill, there is no disposal over the first nine years, but from the tenth year onwards the amount disposed of corresponds to the amount produced in that year. A similar argument can be applied to substances and products continuously emitted during use and 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	N/A	N/A	N/A	N/A	N/A
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 D6 that may be emitted to the environment from the PDMS-based products.
Some products have structural differences to PDMS and therefore it may not be possible to estimate the amount of D6 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 is not clear whether the degradation of resins and elastomers in the environment is similar to that of PDMS. Both resins and elastomers are cross-linked, intractable solids. Chandra (1997) reports that silicone elastomers do not appear to degrade in landfills, possibly as a result of their limited bioavailability in the environment. Therefore biodegradation of both resins and elastomers is not considered a source of D6 in the environment from. The same considerations could also apply to sealants, which again have a degree of cross-linking in their cured state.
Therefore, in terms of potential for D6 to form from biodegradation, the emissions of PDMS fluids and specialities are likely to be the dominant source. As shown in Table 3.4, for the EU it is estimated that around 20,100 tonnes/year are emitted to wastewater, 36,800 tonnes/year are disposed of via landfill and incineration, and 19,800 tonnes/year are 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).
- The typical WWTP connection rate in the EU is 80 per cent (the default value from the TGD) and the majority of PDMS fluids that enter a WWTP adsorb onto the sludge and are subsequently applied to agricultural land. This then amounts to ~16,080 tonnes of PDMS fluids.
- Of the amount disposed of, 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.[9] Thus the

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

estimated amount of PDMS fluids landfilled in the EU is ~26,500 tonnes/year, with ~2600 tonnes/year incinerated.

- The amount of D6 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 degrades into cyclic siloxanes and other volatile products, the total amount of such products formed is estimated as around 179,500 kg/year. Thus the amount of this that could be D6 is estimated as around 44,875 kg/year. This represents a volatile loss from the soil and should be considered as an emission to air.
It is estimated that around 26,500 tonnes/year of PDMS fluids could be disposed of into landfills in the EU. The conditions in landfills are typically anaerobic in nature and little is information available on the degradation of PDMS under such conditions. If it is assumed again that the yield of cyclic siloxanes and other volatile products during degradation in landfills is around 0.5 per cent, with 25 per cent of this comprising D6, then the amount of D6 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 the direct uses of D6, these estimated emissions of 44,875–78,000 kg/year should be compared with the total estimated EU emissions to air. The total EU emission to air is confidential, but the estimated emission from PDMS breakdown is <2 per cent of this. Therefore, although there are large uncertainties in the approach used here to estimate the emissions from the degradation of PDMS polymers, this does not appear to be a major source of D6 in the environment when compared with the emissions from direct uses of D6 and so it is not considered again in theis assessment.
It is not currently possible to estimate the amount of D6 that may be the soil from the degradation of PDMS polymers. This is considered further 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 through degradation is much lower. However, little actual information appears to be available as to cyclic siloxanes form from such products under conditions found in landfills. Therefore it is not possible to evaluate fully this potential source here. This is considered in Section 3.1.5.3.
As well as by landfill, PDMS liquids and other polymeric siloxane products are also disposed of by incineration. It is not possible to estimate the amounts of cyclic siloxane products formed during high-temperature incineration processes. As noted above, a number of studies available show that cyclic siloxanes may be formed under high-temperature pyrolysis conditions, but the relevance of these studies to the conditions during incineration (i.e. in the presence of flames) is uncertain. However, it is thought that the conditions effectively destroy any cyclic products formed, and so the emissions of D6 from incineration are expected to be small compared with those from other sources emission This is considered further in Section 3.1.5.3.

3.1.5.3 Other sources

Some data reported in the literature suggest sources of emissions of D6 other than those considered above. These data are summarised here,, but in general information is scarce on the quality-control methods used in the analysis. While this in itself does not mean the data

are unreliable, there are potential problems from contamination in the analyses of D6 (see Section 3.3.1 for further details). It is therefore possible that some of the reported occurrences of D6 from these sources result from analytical artefacts and do not themselves represent significant sources of emission of D6 to the environment.

No data are available on the levels of D6 in flue gases from waste-incineration plants. As both D4 and D5 are detected in such gases (see Environment Agency, 2008a, 2008b), the potential for D6 emissions from this source is considered here. 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) without ash formation to form CO_2, water, and amorphous silica (Lipowitz and Ziemelis, 1976; Stevens. (1996). Siloxanes products (such as PDMS fluids and polymers) of higher boiling points 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 the emissions of D6 from waste incineration are likely to be low and so this potential source is not considered further here.

Schwarzbauer *et al.* (2002) found D6 was in landfill leachate at a sanitary landfill in Germany. The concentration is not given, but the detection limit of the analytical method used was around 50 ng/l. The source of D6 in the landfill is not known, but could include disposal of products that contain D6 (such as personal care products, etc.) or disposal of products that contain PDMS polymers with subsequent emission of unreacted D6 (see Section 3.1.5.1) or subsequent breakdown of the PDMS polymer to form D6 (see Section 3.1.5.2). It is not possible to quantify the actual amounts of D6 that may be emitted to leachate (and to air) 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.

Cao *et al*. (2007a, 2007b) report that D6 is 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 D6 in the samples.

Rosati *et al.* (2007) found that D6 is released during the cooking of some types of microwave popcorn. The quality-control procedures used in this study include the analysis of blanks daily, and it appears that D6 was not detectable in these blanks. The source of D6 in these experiments is unclear.

3.1.6 Summary of worst-case emission estimates

The preliminary worst-case emission estimates for D6 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 WWTP is assumed.

Table 3.5 Summary of emission estimates for D6

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 0.0039 to surface water	300	Confidential to air 1.2 to surface water	Not quantified
Chemical intermediate – off-site	0.1 to air 0 to wastewater	27	4.1 to air 0 to waste water	0 to air 0 to wastewater
Personal care products – formulation – UK site (cyclomethicone)	1.5×10^{-5} to 1.7×10^{-3} to air 8.0×10^{-6} to 1.2×10^{-3} to wastewater	300	35.8 to air 179 to wastewater	322 to air 1611 to wastewater
Personal care products – formulation – generic site	0.017 to air 0.075 to wastewater	300		
Personal care products – use	0.013 to wastewater	365	88,200 to air 9800 to wastewater	1,701,900 to air 189,100 to wastewater
Residual monomer in PDMS			51,300 to air	461,700 to air
Breakdown of PDMS			Not quantified	Not quantified
Total[a]			**Confidential to air 7983 to WWTP 1997 to surface water**	**2,169,922 to air 152,569 to WWTP 38,142 to surface water**

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

A further emission of 44,875–78,000 kg/year of D6 to air is estimated from the possible degradation of PDMS polymers in soil and landfills in the EU. However, this is subject to a large uncertainty and so is not taken into account in the total emission estimated in Table 3.5. It is also estimated that this source makes only a relatively small contribution to the total emissions to air, so it is not thought to impact significantly on the predicted environmental concentrations that result.

3.2 Environmental fate and distribution

3.2.1 Atmospheric degradation

3.2.1.1 Photo-oxidation

The rate constant for the reaction of D6 with atmospheric hydroxyl radicals is estimated as 1.80×10^{-12} cm^3/molecule^{-}/s using the AOP(v1.91) program, part of the USEPA EPI (v3.12) estimation software.

Whelan *et al.* (2004) assessed the atmospheric fate of VMSs and their degradation products. 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 are for only one cyclic VMS, the findings of the paper are equally applicable to other cyclic VMSs such as D6. The modelling is based on the work of Atkinson (1991) and Sommerlade *et al.* (1993) which demonstrates that siloxanes break down in the atmosphere

to form hydroxy-substituted silanols by reaction with atmospheric hydroxy 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 occur mainly in the vapour phase, with only relatively small amounts associated with the water and particulate phases (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 of the hydroxyl substitution are thought to be associated mainly with the dissolved and particulate phases. However, the decreasing concentration of precursor molecules as this degradation proceeds 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 siloxanediols in the precipitation are predicted to undergo further reaction via hydrolysis to give a mixture of siloxane 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}, the atmospheric half-life for D6 can be estimated as 8.9 days. The products from the reaction are expected to be silanols that are removed from the atmosphere by wet deposition. 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 carbon dioxide (CO_2) (Buch *et al.*, 1984; Chandra, 1997). D6 itself is expected to be present mainly in the vapour phase in the atmosphere.

3.2.1.2 Photolysis

No information is available on the direct photolysis of D6 in the atmosphere.

3.2.2 Aquatic degradation

3.2.2.1 Hydrolysis

No information is available on the hydrolysis of D6. By comparison with the hydrolysis data available for D3 (Dow Corning, 2004a), D4 (Environment Agency, 2008a), and D5 (Environment Agency, 2008b), which have hydrolysis half-lives at pH 7 and 25°C of 23 minutes, 69 hours, and 71 days, respectively, the hydrolysis half-life of D6 is expected to be >>71 days at pH7 and 25°C. Therefore it is concluded that hydrolysis of D6 in the environment is likely to be an insignificant process for D6 at near neutral pHs.

For D4 the kinetics of hydrolysis indicate a degree of reversibility in the reaction towards the end of the decay curve, although it is unclear whether this is caused by reversibility or by other factors [see Environment Agency (2008a) for a detailed discussion]. This possible reversibility is 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 D6 the initial step of the reaction is likely to form dodecamethyltetrasiloxane-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 is dependent on molecular properties (e.g. chain flexibility, distance between recombination sites, etc.) and so is most likely to be less favoured for D6 than for D4 (as the intermediate from D6 has a longer carbon chain than that from D4).

Therefore, although it is possible that the hydrolysis reaction of D6 could also have a degree of reversibility in the first step (as suggested for D4), this is probably not significant in terms of the actual hydrolysis of D6 in the environment and so is not considered further here.

3.2.2.2 Photolysis

No information is available on the direct photolysis of D6 in water.

3.2.2.3 Biodegradation

Springborn Smithers Laboratories (2005) studied the biodegradability of D6 using the draft OECD 310 methodology [ready biodegradability – CO_2 in sealed vessels (headspace test)]. The D6 tested was 99.6 per cent pure and sodium benzoate was used as a reference substance in the test. The inoculum was derived from activated sludge and sewage from a WWTP that received primarily domestic waste, and soil from a wooded area. The inoculum was added to the test medium at a concentration of 10 mg solids/l, D6 added at a concentration of 10 mg carbon/l and incubated in the dark at 22 ± 2°C. At intervals during the test the amount of CO_2 (measured by total carbon analysis) in the headspace was determined (four replicates were sampled on each occasion). A control (inoculum only), positive control (which contained sodium benzoate at a concentration of 10 mg carbon/l), and toxicity control (which contained sodium benzoate and D6, both at a concentration of 10 mg carbon/l) were also run.

The test showed 4.5 per cent degradation of D6 over the 28-day test period. The degradation in the positive control was 106 per cent after 28 days (with >60 per cent degradation within the ten-day window), which indicates that the inoculum used was viable, and the toxicity control showed that D6 was not toxic to the microorganisms present. However, the solubility of D6 is limited (5.3 µg/l), which possiblly may have reduced the bioavailability of D6 in this test. In addition, it is possible that D6 itself could have been in the headspace [the OECD 310 guideline suggests that this could be significant for substances with a Henry's law constant >50 Pa m^3/mol, and that for D6 is well above this value (4,943,000 Pa m^3/mol at 25°C)], and so could have contributed to the carbon measured in the headspace. Overall, based on these results, D6 is not considered to be readily biodegradable.

No other biodegradation tests are available for D6. Based on the available data for D6, and by comparison with D4 (Environment Agency, 2008a) and D5 (Environment Agency, 2008b), D6 is not readily biodegradable.

3.2.3 Degradation in soil

Xu (1999) investigated the degradation of D6 in soil. 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, and it was air dried before use. ^{14}C-D6 (radiochemical purity >99 per cent) 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 D6 added to the soil, and the tube flushed with air for two minutes. The initial target D6 concentrations were in the range 40–200 mg/kg dry weight. The spiked soil was then incubated in the closed tubes in the dark at room temperature for between ten minutes and seven days. At the end of the incubation period the soils were solvent extracted, and the D6 that remained and the degradation products determined. The overall recovery of total ^{14}C in the study was not given for D6, but as the recovery was very high for the more volatile D4 (recovery 98.7 per cent) and D5 (recovery 99 per cent), a similar high recovery is expected for D6 (CES, 2005).

D6 hydrolysis rapidly in the experiments, to form more polar products. For example, around 10 per cent of the D6 disappeared and eight hydrolysis products were evident after 0.5 hours incubation, and by 24 hours only two main hydrolysis products and D6 remained. The reaction was thought to proceed via ring-opening hydrolysis to form the linear dodecamethylhexasiloxanediol (hexamer diol), with subsequent loss of dimethylsilanediol to

form the decamethylpentasiloxanediol (pentamer diol), octamethyltetrasiloxanediol (tetramer diol), hexamethyltrisiloxanediol (trimer diol), tetramethyldisiloxanediol (dimer diol), and eventually dimethylsilanediol. 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 D6) 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 photodegraded to CO_2 and silicic acid and/or silica in the atmosphere. This, therefore, provides a complete degradation pathway for D6 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 in this soil were illite and chlorite. The other soil was a highly weathered soil (a clay oxisol), with a pH of 4.9 and 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 in this soil were kaolinite, gibbsite, and goethite.

Most of the tests were carried out with D4, but some tests were also carried out with D5 and D6. The general conclusions found with the experiments with D4 are also relevant for 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, 92, 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 is 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 incubated without capping.

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

The degradation is thought to result from hydrolysis reactions catalysed by the surface activity of soil clays. The increase in moisture of the soil is 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 carried out with D4 only in temperate soils. These show that loss through volatilisation from soil is a significant competing process for D4 in soils in open systems. At a relative humidity of around 50 per cent, volatilisation accounts for around

40 per cent of the total loss of D4, but loss through volatilisation is negligible compared to that throughdegradation in dry soils (relative humidity 32 per cent). In soils at high relative humidity (~100 per cent) loss through volatilisation is the dominant removal process e.g. 80 per cent loss through volatilisation over the incubation period compared with 5 per cent by degradation). These results are relevant for D6 but, given the higher log K_{ow} and lower vapour pressure[10] for D6 (log K_{ow} 9.06 and vapour pressure 4.6 Pa at 25°C) compared with those for D4 (log K_{ow} 6.49 and vapour pressure 132 Pa at 25°C; see Environment Agency, 2008a) the loss of D6 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 D6 occurs in the atmosphere by reaction with atmospheric hydroxyl radicals. Hydrolysis of D6 can also potentially occur, but this is thought to be relatively slow (half-life >>71 days) at near neutral pHs. No information is available on the potential for D6 to undergo direct photolysis reactions in the environment.

In summary, the following abiotic degradation rate constants are assumed in the assessment.

- atmospheric photooxidation, k_{OH} = 1.8 × 10–12 cm^3/molecule/s;
- photodegradation in air, k = 0;
- photodegradation in water, k = 0;
- hydrolysis (freshwater and marine), >>71 days.

3.2.4.2 Biodegradation

No standard ready and inherent biodegradation tests are available for D6. Based on information for D4 and D5, D6 is not expected to be readily biodegradable.

Degradation of D6 occurs in dry soils (most probably by an abiotic mechanism). However, moisture significantly reduces the rate of degradation such that when the dried soil is equilibrated to a 100 per cent relative humidity atmosphere essentially no degradation occurs. 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 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 situations is likely to be slow.

Another analysis of the soil degradation data for D6 as was carried out [Xu, personal communication, as reported by CES (2005) and 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 D4 are the same at any given moisture level in different soils;
- the rates of degradation of any given cyclic VMS are linearly related to water potential (which is, in turn, linearly related to log {relative humidity} as measured with Londo soil).

The estimated half-lives of D6 in two types of soil using this approach are summarised in Table 3.6 [the Xu and Chandra (1999) study was carried out at 22°C].

[10] Although D6 does have a slightly higher Henry's Law constant than D4 (4.94 × 10^6 Pa m^3/mol for D6 compared with 1.21 × 10^6 for D4).

Table 3.6 D4 half-lives for temperate and tropical soils

Relative humidity (%)	Half-lives (days)	
	Temperate soil	Tropical soil
50	158	1.8
70	179	2.3
90	202	3.0

The half-lives in Table 3.6 relate to a dry soil exposed in air of the stated relative humidity. CES (2005) indicate 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 115 days is estimated for a typical soil in the dry season in France [Xu, personal communication, as reported in CES (2005)]. In France the soil moisture content may regularly decline to between 5 and 10 per cent during the summer months.
The degradation in the soil studies with cyclic siloxanes parallels that of PDMS (see Section 3.1.5.2). The degradation of PDMS is also dependent on the soil moisture content (among other factors) and, although degradation generally slows as the water content of the soil increases, it still occurs. For representative soils, significant degradation of PDMS occurs 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 of the mechanisms of degradation of PDMS and D6 implies that degradation of D6 still occurs in wet soils. The available studies on cyclic siloxanes do not 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 cyclic siloxane is lost from the soil before degradation can occur).
The main degradation product of D6 in soils is eventually likely to be dimethylsilanediol. This is expected to undergo further degradation processes in the environment and ultimately form CO_2 and silica and/or silicic acid. This, therefore, provides a complete mineralisation pathway for D6 in soils in which such degradation occurs.
In terms of this assessment, it is assumed that D6 is not biodegradable as a worst case. However, in the environment D6 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 D6 can also be removed from soil by degradation under some situations, 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 115 days as estimated above for a typical soil in the dry season in France) on the PEC calculations that result is investigated (see Section 3.3.2.1). Also, under some conditions (e.g. particularly dry spells) the degradation of D6 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 1.2×10^6 l/kg can be estimated for D6 from its chemical structure using the USEPA EPI (v3.12) estimation software.
Chandra (1997) uses four different correlation equations (which relate K_{oc} to water solubility or log K_{ow}) to estimate K_{oc} for D6. The mean value for the K_{oc} estimated is 120,230 l/kg.

The partition coefficients in Table 3.7 are estimated using a log K_{ow} value of 9.06 and the methods outlined in the TGD. The equivalent values estimated using a lower log K_{ow} of 5.86 are also shown.

Table 3.7 Partition coefficients for D6 using K_{ow} values of 9.06 and 5.86

	log K_{ow} 9.06	**log K_{ow} 5.86**
Organic carbon–water partition coefficient (K_{oc})	2.75×10^7 l/kg	7.03×10^4 l/kg
Solids–water partition coefficient in soil (K_{soil})	5.5×10^5 l/kg	1.41×10^3 l/kg
Solids–water partition coefficient in sediment (K_{sed})	1.37×10^6 l/kg	3.52×10^3 l/kg
Solids–water partition coefficient in suspended matter (K_{susp})	2.75×10^6 l/kg	7.03×10^3 l/kg
Soil–water partition coefficient ($K_{soil–water}$)	8.25×10^5 m^3/m^3	2.11×10^3 m^3/m^3
Suspended matter–water partition coefficient ($K_{susp–water}$)	6.87×10^5 m^3/m^3	1.76×10^3 m^3/m^3
Sediment–water partition coefficient ($K_{sed–water}$)	6.87×10^5 m^3/m^3	1.76×10^3 m^3/m^3

Experimental values

No experimental values for the K_{oc} of D6 are available. However, recent studies with D4 and D5 determined the K_{oc} to be 1.7×10^4 for D4 and 1.5×10^5 for D5 using three different soils with organic carbon contents between 2 and 5.5 per cent by weight (Environment Agency, 2008a, 2008b). The K_{oc} values obtained in these studies are similar in all three soils, which implies that the majority of the adsorption measured was associated with the organic phase of the soil and so the log K_{ow} value should be a good measure of the relative adsorption of these substances. Using the log K_{ow} values for D4 (6.49), D5 (8.03), and D6 (9.06) it is possible to estimate that the actual K_{oc} value for D6 should be around 6.5×10^5 l/kg (by linear extrapolation). This value lies between the two estimates given above and is used in this assessment in preference to these because it is based on the known data for two related substances.

Summary of adsorption coefficients used in the risk assessment

The K_{oc} for D6 is taken as 6.5×10^5 l/kg based on extrapolation from the experimental data available for D4 and D5. The partition coefficients used in the assessment (calculated from this K_{oc} value using the methods outlined in the TGD) are:

- K_{oc}, 6.5×10^5 l/kg
- K_{soil}, 1.3×10^4 l/kg
- K_{sed}, 3.3×10^4 l/kg
- K_{susp}, 6.5×10^4 l/kg
- $K_{soil–water}$, 2.0×10^4 m^3/m^3
- $K_{susp–water}$, 1.6×10^4 m^3/m^3
- $K_{sed–water}$, 1.6×10^4 m^3/m^3.

3.2.5.2 Behaviour in wastewater treatment

The expected behaviour during wastewater treatment is estimated using the Simpletreat model within EUSES 2.0.3. The distribution that results is:

- percentage to air, 9.42 per cent
- percentage to sludge, 84.1
- percentage degraded, 0
- percentage to water, 6.48.

Therefore, the overall removal predicted is around 93.5 per cent. These values are used in the subsequent PEC calculations.

3.2.6 Adsorption

The K_{oc} of D6 is estimated as 6.5×10^4 l/kg, which means that D6 adsorbs 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 D6 (4.94×10^6 Pa m^3/mole at 26°C) means that it is likely to volatilise rapidly from water and soil. The rate constant for volatilisation from soil is estimated as 0.25/d/ for agricultural soil and 0.50/day for grassland using the methods outlined in the TGD. These rate constants correspond to volatilisation half-lives of 2.8 days and 1.4 days, respectively. These volatilisation half-lives are taken into account in the subsequent PEC calculations.
Another estimate for the volatilisation rate from water is obtained using the USEPA EPI estimation program. Using the Henry's law constant above, the volatilisation half-life for D6 is estimated as 2.2 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 200 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 D6 has a high volatility, it also has a high log K_{ow} and therefore, it may adsorb onto atmospheric aerosols. However, the available data for D6 [and other volatile cyclic methylsiloxanes such as D4 (Environment Agency, 2008a) and D5 (Environment Agency, 2008b)] indicate that, in the atmosphere, D6 is present almost entirely in the vapour phase (seeSection 3.2.1.1). This, coupled with the very low water solubility of D6, indicates that removal from the atmosphere by wet and dry deposition is likely to be minimal.

3.2.9 Bioaccumulation and metabolism

Several studies to investigate the accumulation and metabolism of D6 are available. ^{14}C-D6 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 D6 (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

Annelin and Frye (1989) studied the uptake of D6 from water by fish. The D6 used in this test was not radiolabelled and from a commercial source (no other information is 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 D6) to maintain a reasonably constant exposure concentration. The bioconcentration experiments were carried out with rainbow trout (*Oncorhynchus mykiss)* of approximately 0.7–2.3 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 35 days at 12°C. Both the water phase and the fish were analysed for D6 using a gas–liquid chromatography (GLC) method. After 35 days exposure, the concentration of D6 in the fish

reached 1–2 mg/kg. The concentration of D6 in the water phase was below the limit of detection (<1 µg/l). Based on these data it is possible to estimate the BCF for D6 as >1000 to >2000 l/kg based on parent-compound measurements.

The bioconcentration of D6 was also investigated using fathead minnows (*Pimephales promelas*) [Drottar (2005); IUCLID (2005)]. The study was carried out at 22°C according to OECD Guideline 305 using a flow-through system with a 49 day exposure period and a 98 day depuration period. The substance tested was ^{14}C-D6 with a radiochemical purity of 99.57 per cent. Two concentrations of D6 were tested [mean measured concentrations (± standard deviation) of 0.41 ± 0.029 µg/l and 4.4 ± 0.23 µg/l] and no treatment-related signs of toxicity occurred throughout the test. Stock solutions of the test substance were prepared in dimethylformamide (DMF) and 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 7.6–8.6) at a flow rate of 600 ml/minute). The concentration of DMF 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) were analysed for D6 by total radioactivity measurements. The tissue concentrations of D6 (measured as total radioactivity) reached steady state after 35 days of exposure [no statistically significant difference (p = 0.05) was found in the tissue concentrations measured on days 35, 42, and 49) and the steady-state BCF (based on total ^{14}C measurements) was 1160 l/kg for the 0.41 µg/l treatment and 240 l/kg for the 4.4 µg/l treatment, based on the mean tissue concentrations measured between day 35 and day 49. Around 79 per cent of the body burden was found to be present as the parent compound, which implies that the BCF based on parent compound may be lower than that based on total ^{14}C measurements. However, for this study the concentration in water was also based on total ^{14}C measurements, which may overestimate the concentration of the parent compound in the water phase if excreted metabolites are in the water (no information is available on the fraction of the radioactivity in the water phase that was parent compound). Thus, taking into account that 79 per cent of the radioactivity in the fish was parent compound, it is estimated that the BCF based on parent compound alone is ≥916 l/kg for the 0.41 µg/l treatment and ≥190 l/kg for the 4.4 µg/l treatment.

Depuration of the accumulated radioactivity was slow [the first-order rate constants for depuration ranged between 0.0233/day (0.41 µg/l treatment group) and 0.0260 day (4.4 µg/l treatment group)]. These are equivalent to depuration half-lives of 27–30 days. The corresponding first-order rate constants for the uptake phase of the study were 38.8/day (for the 0.41 µg/l treatment) and 8.29/day (for the 4.4 µg/l treatment). Based on the kinetic data, a BCF (based on total ^{14}C measurements) of 1660 l/kg (for the 0.41 µg/l treatment) and 319 (for the 4.4 µg/l treatment) is estimated (the equivalent BCFs corrected for the fraction of the total radioactivity in the fish that was parent compound is ≥1311 l/kg and ≥252 l/kg, respectively). These kinetic data support the BCFs above based on the steady-state measured body burdens. The fish used in this test had a mean lipid content [based on the analysis of a subset of six individuals (two each from the controls, and low- and high-treatment groups)] of 4.5 per cent (range 3.12–5.27 per cent) at day 0, 2.9 per cent (range 1.76–5.47 per cent) at the end of the uptake phase (day 49), and 4.5 per cent (range 3.05–6.17 per cent) at the end of the depuration phase (day 147).

The highest concentration tested in this study (4.4 µg/l) is very close to the water solubility of the test substance (5.3 µg/l). Although the test concentration was adequately maintained at this level, the analytical methodology 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 D6 and not necessarily dissolved concentrations only. It is therefore possible that, at the highest concentration tested, some of the D6 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 0.41 µg/l treatment (i.e. a BCF of 1160 l/kg based on total ^{14}C measurements) is considered to be the most representative value for the BCF of D6 from this study.

Opperhuizen *et al.* (1987) studied the uptake and elimination of D6 in guppies (*Poecilia reticulata*) and goldfish (*Carassius auratus*) through exposure via water or food. 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 and from commercial sources (no other information is available on the purity of the substances used). The analytical method used involved analysis of the parent compounds by gas chromatography equipped with a flame ionisation detector or a 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 concentrations in food that result 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, but when displayed graphically in the paper these concentrations appear to be around 1 mg/kg. No information is given in the paper 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 in the test vessels are not reported. The water-exposure experiments were only carried out with guppies.

The guppies used in the test had an average weight and lipid content of 0.17 g and 6.5 per cent, respectively, and for the goldfish these were 1.8 g and 2.3 per cent, respectively. The tests were carried out at 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 it 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 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 D6 the steady-state BCF was 1200 l/kg and the steady-state biomagnification factor (BMF) from the food experiment was 0.06 for guppies (similar results were stated for goldfish). These values are based on parent-compound analysis. The depuration half-life was around 4.3 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 exposing to either a single linear oligomer (hexadecylmethylheptasiloxane) or a single cyclic oligomer (D7). Some of these experiments provide evidence that cyclic siloxane products (ranging from D5 to D9) form in fish, but it cannot be established whether this was the result of impurities in the materials, or whether such materials were formed by transformation in the water phase followed by subsequent uptake or by metabolic processes in the fish.

Bruggeman *et al.* (1984) attempted to determine the dietary uptake of D6 by guppies (*Po. reticulata*). The substance tested was not radiolabelled and from a commercial source (no other information on the purity of the substance tested is given). The analytical method used in the study was gas chromatography with flame ionisation detection or mass spectrometric detection (parent-compound analysis). A standard mixture of linear and cyclic siloxane oligomers (including D6) together with several chlorinated benzenes and chlorinated biphenyls (as reference compounds) was prepared in toluene (concentration of each

component was 250 µg/ml). The spiked food (commercial dry fish food; lipid content 10 per cent of dry weight) was prepared by adding 3 ml of the toluene solution to food and evaporating the solvent. This lead to an initial measured concentration of D6 in the food of between 20 and 50 mg/kg food (the more volatile siloxanes tested completely evaporated from the food during sample preparation). The dietary exposure tests were carried out using 110 male guppies (*Po. reticulata*; lipid content 1.7 per cent of wet weight). These were fed the spiked food at a rate of ~20 mg dry food/g wet weight of fish each day for up to ten weeks. Samples of six fish were collected for analysis each week (after a period of two days without feeding). The detection limit for D6 in the fish was around 0.3 mg/kg wet weight. D6 was not detected in the fish during the course of this study and a magnification factor [defined as the concentration in fish (on a lipid basis) divided by the concentration in food (on a lipid basis)] was <0.03 based on parent-compound analysis.

There appear to be several shortcomings in this experiment, not least that preparation of the spiked food would have allowed loss via evaporation of D6 and, although the concentrations initially in the spiked food appear to be verified analytically, no details are given on the frequency of the preparation of the spiked food, the repeatability of the spiking of the food, or whether the concentration of D6 in the spiked food was maintained during any storage, etc. Therefore, there is a large amount of uncertainty over the actual exposure concentration of D6 during the course of this experiment.

The bioconcentration of D6 by invertebrates (*Daphnia magna*) was also investigated [unpublished; see IUCLID (2005)]. Few details of the test are currently available, but it appears to have been carried out over 32 days using a saturated solution of radiolabelled D6 prepared by a re-saturation system (the actual concentration of D6 in the solution is not given). The organisms used were reportedly a mixed-age culture and no control culture appears to have been used. The steady-state BCF for D6 was ~2400 l/kg. It is not clear if this value is based on total ^{14}C analysis or parent-compound analysis (as radiolabelled substance was used it is most likely to be based on total ^{14}C).

The available bioaccumulation data are summarised in Table 3.8. Overall, the steady-state BCF for fish of D6 is 1160 l/kg, a value considered suitable for use in this assessment. Other available studies support this value. A slightly higher level of accumulation was found in an invertebrate (*D. magna*). Uptake of D6 by fish from food was also demonstrated, but these feeding studies are not sufficiently accurate to allow a reliable accumulation factor to be determined.

Table 3.8 Summary of available bioaccumulation data for D6

Species	Exposure concentration	Value	Validity	Reference
Carassius auratus	306–425 mg/kg food (mixture of oligomers)	Value not given, but reported to be similar to that for *Po. reticulata* (BMF ~0.06)	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 ~1200)		
Daphnia magna	Saturated solution	BCF = 2400 l/kg	Use with care – full experimental details not yet available – basis for measurement (total ^{14}C or parent compound) is not clear (most probably total ^{14}C)	IUCLID (2005)
Oncorhynchus mykiss	<1 µg/l	BCF >1000 to >2000 l/kg	Invalid – exposure concentration not well	Annelin and Frye (1989)

Species	Exposure concentration	Value	Validity	Reference
			defined - based on parent compound	
Pimephales promelas	0.41 µg/l	BCF = 1160 l/kg	Valid – steady-state value based on total ^{14}C analysis – the estimated value based on parent compound is ≥916 l/kg	IUCLID (2005); Drottar (2005)
		BCF = 1660 l/kg	Use with care – kinetic value based on total ^{14}C analysis – supportive of steady-state value – the estimated value based on parent compound is ≥1311 l/kg	
	4.4 µg/l	BCF = 240 l/kg	Use with care – steady-state value based on total ^{14}C analysis – the concentration tested was very close to the water solubility – the estimated value based on parent compound is ≥190 l/kg	IUCLID (2005); Drottar (2005)
		BCF = 319 l/kg	Use with care – kinetic value based on total ^{14}C analysis – the concentration tested was very close to the water solubility – the estimated value based on parent compound is ≥252 l/kg	
Poecilia reticulata	1008–1044 mg/kg food (mixture of oligomers)	BMF = 0.06	Invalid – exposure concentration not well defined – based on parent compound	Opperhuizen *et al.* (1987)
	Saturated solution	BCF = 1200 l/kg		
	20–50 mg/kg food	BMF <0.03	Invalid – exposure concentration not well defined – based on parent compound	Bruggeman *et al*. (1984)

3.2.9.2 Calculated BCFs and BMFs

BCF values for fish and earthworms can be estimated from the log K_{ow} of 9.06 using the methods outlined in the TGD (the equivalent values using a log K_{ow} of 5.86 are also given):

- for log K_{ow} 9.06 the BCF for fish is 4870 l/kg and it is not possible to estimate[11] that for earthworms;
- for log K_{ow} 5.86 the BCF for fish is 19,100 l/kg and for earthworms it is 8690 l/kg.

The predicted value for fish is much higher than the experimental value, and so the latter is used in the assessment. No experimental value is available to compare with the predicted BCF for earthworms.

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

Using the experimentally determined BCF for fish of 1160 l/kg based on total ^{14}C measurements, the appropriate default BMFs from the TGD for the secondary poisoning assessment of D6 are:

- a BMF_1 for predators of 1
- a BMF_2 for top predators of 1.

3.2.9.3 Summary of bioaccumulation

The accumulation factors used in the assessment are:

- BCF for fish, 1160 l/kg
- BMF_1 for predators, 1
- BMF_2 for top predators, 1
- BCF for earthworms, not possible to estimate.

The most reliable value for the steady-state BCF determined is 1160 l/kg based on total ^{14}C measurements and this is used in the assessment. Although this value may contain a contribution from both metabolites and parent D6, parent-compound analysis indicates that a large proportion of the body burden (79 per cent) is parent compound. Therefore it is considered appropriate to use this value in the risk assessment as a realistic worst-case approach.

3.3 Environmental concentrations

In this we section outline the predicted and available measured concentrations in various environmental compartments. The predicted concentrations are 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 D6) and the use of D6 itself in personal care products mean the environmental samples can be contaminated during storage and handling in the laboratory and so measured concentrations may not reflect the actual environmental conditions. For example, Gasking (1988) reports that breakdown of septa used in gas chromatography could be a source of silicone oligomers. In a recent poster presentation Varaprath *et al.* (2005) highlighted the analytical problems that may be encountered when silicones are analysed. Therefore, to validate measured data for use in risk assessment, it is vital that the responses 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 D6 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, sample 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 inTable 3.9.

Table 3.9 Predicted concentrations in surface water, sediment, and wastewater treatment plants

Scenario	PEC		
	Surface water (µg/l)	Sediment (mg/kg wet weight)	Wastewater treatment plant (mg/l)
Production and on-site use as an intermediate	0.11	1.6	5.1×10^{-4}
Off-site use as an intermediate	8.3×10^{-3}	0.12	0
Personal care products – formulation – generic site	0.13	1.9	2.4×10^{-3}
Personal care products – formulation – UK sites – cyclomethicone	8.9×10^{-3}	0.13	1.1×10^{-5}
	8.4×10^{-3}	0.12	6.8×10^{-7}
	8.4×10^{-3}	0.12	4.2×10^{-7}
	8.6×10^{-3}	0.12	5.2×10^{-6}
	0.010	0.15	3.9×10^{-5}
	9.7×10^{-3}	0.14	2.6×10^{-5}
	9.4×10^{-3}	0.13	2.2×10^{-5}
	9.3×10^{-3}	0.13	1.9×10^{-5}
Personal care products – use by general public	0.030	0.42	4.2×10^{-4}
Regional	8.3×10^{-3}	0.24	

3.3.1.2 Measured environmental concentrations

Michael *et al*. (1991) analysed ten influent and ten effluent samples from municipal WWTPs in the Great Lakes basin area of the USA. The main focus of the analysis was to quantify a suite of 50 priority pollutants (not including D6) in these effluents; however the presence of other non-target chemicals was also reported. D6 was found in two of the samples analysed. The analytical procedure used included the analysis of blank samples and control samples, but these were related mainly to quantification of the priority pollutants; the blank response for the non-target species was not determined.

Fattore *et al.* (1998) identified D6 in a sample of groundwater from a heavily industrialised area near Milan, Italy. No quality-assurance details are reported.

Law *et al*. (1991) detected, but did not quantify, D6 in samples of unfiltered estuarine water from the River Tyne and River Tees, UK. However, D6 was not detected in estuarine water from other locations around the UK (River Humber, Liverpool Bay, and Plymouth Sound). Precautions were taken to avoid contamination in these analyses, including the analysis of a large number of blank samples.

Kaj *et al.* (2005) recently surveyed the levels of D6 in water and sediment in Sweden. The samples were collected during 2004 and 2005. The sampling and analytical methods used were designed to avoid both loss of D6 from the sample through volatilisation and contamination of the sample by D6. The concentrations found in this survey are summarised in Table 3.10. The samples were collected from sites both near to potential industrial point sources and in 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 D6 was actually used in these areas.

Overall, the concentrations in surface water found in this study appear to be generally low, but relatively few surface water samples were included, and these were generally taken from industrial areas in which it is unclear whether or not D6 was used at the time. D6 was found in only two of the sediment samples at concentrations up to 196 µg/kg dry weight.

Table 3.10 Concentration of D6 in water and sediment from Sweden (Kaj *et al.*, 2005)

Location	Measured concentration	Comment
Surface water (µg/l)		
Stenungsund	0.038	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	<0.06	Site near to potential point sources in an industrial area
	Sediment (ug/kg dry weight)	
Ö Gotlandsdjupet	<3	Background site
Ö Öland	<6	Background site
Norrköpingsdjupet	<2	Background site
Stenungsund	<6	Site near to potential point sources in an industrial area
Stenungsund	<6	Site near to potential point sources in an industrial area.
Stenungsund	<7	Site near to potential point sources in an industrial area
Bay outside Stockvik	<5	Site near to potential point sources in an industrial area
Bay outside Stockvik	<10	Site near to potential point sources in an industrial area
Bay outside Stockvik	<5	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	<7.2	
Lake Venjan	<18	
Gröpplebäcken	<6.1	
Hulingen	<17	
Verserum	<2.6	
Mouth of Emån	<5	
Ivösjön	<23	
Helsingborg	<6	
Hammarsjön	<8	
Storarydsdammen	<10	
Himmerfjärden	51	
St Envättern	<44	
Lake Vänern, Åsfjorden	196	
Lake Vänern, Kattfjorden	<8.8	
Skuten	<11	
Close to a pulp and paper production plant	<6.0	
Roxen	<17	
	Wastewater (ug/l)	
Influent to municipal WWTPs	0.06–0.27	Detected in samples from four out of four sewage treatment plants (detection limit 0.04 µg/l)
Effluent samples from municipal WWTPs	0.05–0.23	Detected in five out of twelve samples (detection limit was 0.04

Location	Measured concentration	Comment
		µg/l)
Industrial effluent	0.15	Effluent from a pulp- and-paper production plant
Industrial effluent	<0.06	Effluent from a factory (possibly a chemical plant, but it is not clear what was being manufactured)
Well water from factory site	<0.06	Well water from a factory (possibly a chemical plant, but it is not clear what was being manufactured)
Percolate waters from landfills	<0.04	Not detected in three samples

TemaNord (2005) measured the concentrations of D6 in wastewater (influent and effluent), surface water, and sediment in Nordic countries (including Denmark, Faroe Islands, Finland, Iceland, Norway, and Sweden) . The sampling and analytical methods used were designed to avoid both loss of D6 from the sample through volatilisation and contamination of the sample by D6. The samples were collected during 2004 and 2005. The results of the survey are summarised in Table 3.11. D6 was found in several influent (up to 3.8 µg/l) and effluent (up to 0.33 µg/l) samples from sewage treatment plants. In addition, D6 was detected in six sediment samples (including marine sediments) at concentrations up to 170 µg/kg dry weight.

Table 3.11 Concentration of D6 in water and sediment from Nordic countries (TemaNord, 2005)

Sampling location[1]		Concentration
		Water (µg/l)
Denmark	Coastal area, Kattegat	<0.02
	Coastal area, innerfjord, Roskilde	<0.02
	Coastal area, Øresund Lynetten, Kobenhavn	<0.02
	Kobenhavn, Lynetten STP influent	1.6
	Kobenhavn, Lynetten STP effluent	<0.02
	Roskilde, Bjergmarken STP influent	1.3
	Roskilde, Bjergmarken STP effluent	0.04
	Avedöre landfill leachate	<0.04
	Uggelöse landfill leachate	<0.04
Faroe Islands	Torshavn, Sersjantvikin STP effluent	0.33
	Torshavn, Húsarhaga landfill leachate	<0.05
Finland	Ämmässuo, landfill and waste tip leachate	1.7
	Influent to Nokia City Kulloonvuori STP (tyre industry wastewater)	3.7
	Influent to Nokia City Kulloonvuori STP (floor industry wastewater)	0.12
	Treated effluent, Kullonvuori STP	0.03
	Treated effluent, Kullonvuori STP	0.045
	Espoo City Suomenoja STP effluent	0.07
	Helsinki City Vilkinmäki STP effluent	<0.04
Iceland	Alfnes landfill runoff water	1.3
	Reykjavik, seawater	<0.03
	Reykjavik, seawater	<0.03
	Reykjavik, seawater	<0.03
	Reykjavik, seawater	<0.03
Norway	Arendal STP influent	3.8
	Arendal STP effluent	0.16
	Lake Bergsjøen (background area)	<0.04
	Lake Røgden (background area)	<0.05
	Outer Oslofjord (coastal background)	<0.04

Sampling location[1]		Concentration
	Inner Oslofjord (urban area)	<0.04
	Spillhaug landfill runoff water	<0.05
	Bölstad landfill runoff water	<0.04
	Grönmo landfill runoff water	<0.04
Sweden	River Nissan (upstream of storm water effluent)	<0.05
	River Nissan (storm water effluent)	<0.04
	River Nissan (downstream of storm water effluent)	0.064
	Högbytorp landfill (untreated percolate water)	<0.07
	Högbytorp landfill (treated percolate water)	<0.05
		Sediment (µg/kg dry weight)
Denmark	Coastal area, Kattegat	<1
	Coastal area, Øresund, Lynetten	<2
	Coastal area, Roskilde	170
Faroe Islands	Kaldbakfjordur (influence by pollution from unidentified sources)	<4
Finland	Helsinki, Vakal (Old City Bay – site influenced by historical pollution from a former hazardous waste combustion plant)	8.6
	Espoo coastal sea area	<8
Iceland	Sediment 1	<2
	Sediment 2	<1
	Sediment 3	4.0
	Sediment 4	<3
Norway	Lake Bergsjøen (background area)	<23
	Lake Bergsjøen (background area)	<25
	Lake Røgden (background area)	<19
	Lake Røgden (background area)	<17
	Leanbukta	<8
	Vrengansundet	<4
	Brödrene Sunde Verft	<13
Sweden	Gislaved, Nissan (storm water effluent)	0.89
	Gislaved, Nissan (downstream of storm water effluent)	<0.6
	Gislaved, Nissan (upstream of storm water effluent)	<1
	Stockholm, Essingen	25
	Stockholm, Riddarfjärden	10
	Ö Gotlandsdjupet	<9
	Ö Landsortsdjupet	<12

Note: [1]STP, sewage treatment plant.

Schlabach *et al*. (2007) followed up the TemaNord (2005) study. They investigated the concentrations of D6 in influent and effluent from two sewage treatment plants that discharge to the Inner Oslofjord in Norway (Bekkelaget STP and VEAS STP), as well as those in water and sediment from the Inner Oslofjord itself. The sampling and analytical methods used were designed to avoid both loss of D6 from the sample through volatilisation and contamination of the sample by D6. The samples were collected in September and October 2006, and the results are summarised in Table 3.12.

Table 3.12 Concentration of D6 in water and sediment from the Inner Oslofjord (Schlabach *et al*., 2007)

Sampling location[1]	Concentration
	Water (µg/l)
Bekkelaget STP influent	0.5
Bekkelaget STP effluent	<0.02
VEAS STP influent	1.0
VEAS STP effluent	0.1
Seawater, Bekkelaget	<0.02
Seawater, Lysaker	<0.02
Seawater, Vestfjord/Nesodden	<0.02
Seawater, Færder	<0.02
	Sediment (µg/kg dry weight)
Bekkelagsbassenget	100
Bekkelagsbassenget	72
Lysaker	27
Lysaker	<17
Vestfjord/Oslofj	24
Vestfjord/Oslofj	22

Note: [1]STP, sewage treatment plant.

D6 was in the influent from both sewage treatment plants, but was detected in measurable amounts in the effluent from only one sewage treatment plant. D6 was not detectable in seawater, but was present in five out the six sediment samples. The conccentrations in sediment where highest in the samples from Bekkelagsbassenget (concentration 72–100 µg/kg dry weight), which is near to the Bekkelaget sewage treatment plant.
Environment Canada (2008) report the results of an unpublished survey of the levels of D6 in the influent and effluent of WWTPs in Canada.. Nine WWTPs 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 concentrations of D6 were between 0.49 and 27 µg/l in the influent samples and between 0.97 and 2.7 µg/l in the effluent ones. Environment Canada (2008) indicates, for the lagoon samples only, some evidence for higher influent concentrations in the winter samples than in the samples taken in October (the levels found in the lagoon influent samples were not reported separately), but that effluent samples were generally higher in the winter samples than in the autumn (October) samples (range 0.97–1.0 µg/l in the October samples and 2.3–2.7 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, and therefore the significance of the apparently higher concentrations in winter compared with autumn (October) is unclear.
Powell and Kozerski (2007) report the results of a monitoring study to investigate the levels of D6 in sediments and sediment cores from Lake Ontario . 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 also collected at three of these sites (Rochester, Mississauga, and Niagara basins). D6 was detected at a concentration of 198 µg/kg dry weight (90 µg/kg wet weight) in surface sediment from Toronto harbour, but was not detected in surface sediments from the other (more remote) sites or sediment cores (no sediment core was taken from Toronto harbour). The method limit of detection was around 6.1 µg/kg dry weight for D6. The sample collection and analytical methodology used included comprehensive quality-assurance and quality-control procedures to prevent problems of contamination of the samples by D6 or loss of D6 during the analytical procedure.

3.3.1.3 Comparison of measured levels with predicted levels

A detailed comparison of the measured levels with the predicted levels is currently not possible for D6, as only very few data are available and details of the sources of D6 in the samples is unclear. However, the available data show that D6 is in the influent and effluent of some sewage treatment plants. The effluent concentrations measured (up to 0.33 µg/l) compare reasonably well with the concentrations predicted to occur in WWTP effluent for the scenario personal care products – use by the general public (predicted concentration 0.42 µg/l). In addition, the predicted concentrations for sediment are reasonably consistent with the measured data for sediment (<1–198 µg/kg dry weight).

3.3.2 Terrestrial compartment

3.3.2.1 Predicted environmental concentrations

The predicted concentrations in soil are summarised in Table 3.13**.**

Table 3.13 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	1.8×10^{-5}	1.8×10^{-5}	1.8×10^{-5}
Off-site use as an intermediate	1.8×10^{-5}	1.8×10^{-5}	1.8×10^{-5}
Personal care products – formulation – generic site	0.016	2.6×10^{-3}	5.4×10^{-4}
Personal care products – formulation – UK sites – cyclomethicone	8.6×10^{-5}	2.9×10^{-5}	2.0×10^{-5}
	2.2×10^{-5}	1.8×10^{-5}	1.8×10^{-56}
	2.0×10^{-5}	1.8×10^{-5}	1.8×10^{-5}
	5.0×10^{-5}	2.3×10^{-5}	1.9×10^{-5}
	2.7×10^{-4}	5.9×10^{-4}	2.6×10^{-5}
	1.8×10^{-4}	4.6×10^{-5}	2.3×10^{-5}
	1.6×10^{-4}	4.1×10^{-5}	2.2×10^{-5}
	1.4×10^{-4}	3.9×10^{-5}	2.2×10^{-5}
Personal care products – use by general public	2.7×10^{-3}	4.7×10^{-4}	1.1×10^{-4}

The regional (steady-state) concentrations are:

- agricultural soil, 0.041 mg/kg wet weight
- natural soil, 1.8×10^{-5} mg/kg wet weight
- industrial soil, 1.8×10^{-5} mg/kg wet weight.

The above regional concentrations are estimated assuming the substance is not degradable. As discussed in Section 3.2.4, the actual degradation half-life for D6 in soil is uncertain. Example calculations assume a degradation half-life of D6 of six months, one year, and ten years (all at 12°C), and a degradation half-life of 115 days at 22°C [equivalent to a half-life of around 270 days at 12°C, based on the analysis of soil degradation data carried out by Xu, as reported in CES (2005); see Section 3.2.4.2)]. The estimated calculations that result are given in Table 3.14 [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 3.14 Example estimated concentrations of D6 in soils

Half-life at 12°C	Scenario	D5 concentration (mg/kg wet weight)
6 months	local: personal care products – use	2.7×10^{-3}
	regional: agricultural soil	3.0×10^{-4}
	regional: natural soil	1.6×10^{-6}
270 days	local: personal care products – use	2.7×10^{-3}
	regional: agricultural soil	4.0×10^{-4}
	regional: natural soil	1.7×10^{-6}
1 year	local: personal care products – use	2.7×10^{-3}
	regional: agricultural soil	4.9×10^{-4}
	regional: natural soil	1.7×10^{-6}
10 years	local: personal care products – use	2.7×10^{-3}
	regional: agricultural soil	2.1×10^{-3}
	regional: natural soil	2.6×10^{-6}

As this example shows the predicted local concentration in soil is essentially independent of the degradation rate 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 D6 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 competes with the volatilisation (and degradation in the atmosphere) when longer timescales are considered. Overall, the local PECs calculated are relatively insensitive to the assumptions made in the assessment over the degradation rate of D6 in soil.

As discussed in Section 3.1.5.2, the breakdown of PDMS polymers in soil may provide another route for exposure of soil organisms to D6. It is not possible to estimate reliably the amount of D6 in soil from such a process. However, a very rough indication of the potential significance of the process can be made. 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 3.1.5.2). The same approach is used as that in Section 3.1.5.2 along with the emission rate of 0.5 per cent over 25 weeks for cyclic siloxanes and other volatiles from the Lehmann *et al.* (1994) study. With the assumptions that D6 accounts for 25 per cent of the cyclic siloxanes and other volatiles, and that, in this case, all of the D6 formed initially remains in the soil, a PDMS concentration of 5155 mg/kg sludge generates around 6 mg/kg sludge of D6 over the 25 week period, or an input of D6 via sludge into soil of 0.034 mg/kg sludge per day. With the default sludge application rate given in the TGD (0.5 kg sludge per m^2, depth of agricultural soil 0.2 m, density of soil 1,700 kg/m^3) this input rate converts into an equivalent input rate of 0.017 mg/m^2 per day or 5×10^{-5} mg/kg wet soil per 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 2×10^{-4} mg/kg wet weight (estimated using EUSES 2.0.3). This is well below the predicted regional concentration for D6 in agricultural soil.

3.3.2.2 Measured environmental concentrations

Kaj *et al.* (2005) report the results of a survey of levels of D6 in sewage sludge samples from Sweden. The sampling and analytical methods used were designed to avoid loss of D6 from the sample through volatilisation and contamination of the sample by D6. 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 in 2004 and D6 was detected in all 54 samples of municipal sludge at a concentration between 37 and 8400 µg/kg dry weight. The median and mean concentrations were 1300 and 1500 µg/kg dry weight, respectively. D6 was not detected (<16 µg/kg dry weight) in sewage sludge from an industrial sewage treatment plant associated with a car manufacturer.

Recently, TemaNord (2005) also studied the levels of D6 in sewage sludge from Nordic countries. The samples were collected during 2004 and 2005 and the sampling and analytical methods used were designed to avoid both loss of D6 from the sample through volatilisation and contamination of the sample by D6. D6 was found at concentrations of 0.22–11 mg/kg dry weight in the sewage sludge samples. Two soil samples collected from landfill sites were also analysed in this study and the concentration of D6 was below the limit of quantification (<2 to <4 µg/kg dry weight). The results of the study are summarised in 3.15.

Table 3.15 Concentration of D6 in sewage sludge and soil samples from Nordic countries (TemaNord, 2005)

Sampling location		**Concentration (µg/kg dry weight)**
Soil		
Faroe Islands	Havnardalur (disused landfill)	<4
	Husarhaga landfill (working landfill)	<2
Sewage sludge		
Denmark	Kobenhavn, Lynetten STP (primary sludge)	1100
	Kobenhavn, Lynetten (digested sludge)	2800
Faroe Islands	Torshavn, Sersjantvikin	1000
Finland	Nokia City, Kullonvuori STP (receives waste water from several industries)	3500
	Helsinki, Vilkinmäki STP (receives municipal, urban and industrial waste water)	2,200
	Espoo, Suomenoja STP (receives waste water from perfume manufacturer and leachate from a landfill)	11000
	Pormainen STP (receives municipal waste water)	3600
	Porvoo City, Kokonniemi STP (receives urban and industrial waste water)	1900
Iceland	Klettegardar STP	240
	Ananaust STP	220
Sweden	Skellefteå STP (digested sludge – no industrial inputs)	2400
	Floda STP	870
	Ellinge STP (digested sludge – inputs from the food industry)	700
	Tekniska verket	1800

In the follow-up study Schlabach *et al*. (2007) investigated the levels of D6 in sewage sludge from two sewage treatment plants that discharge to the Inner Oslofjord in Norway (Bekkelaget STP and VEAS STP). The sampling and analytical methods used were designed to avoid both loss of D6 from the sample through volatilisation and contamination of the sample by D6. The samples were collected in September 2006. The concentration of D6 in sewage sludge at the Bekkelaget STP was 14,000 µg/kg dry weight in inlet sludge and 960

µg/kg dry weight in outlet sludge. The concentration in sewage sludge at the VEAS STP was 3400 µg/kg dry weight in inlet sludge and 4700 µg/kg dry weight in outlet sludge. These concentrations compare with those from 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.

3.3.2.3 Comparison of measured levels with predicted levels

Only a few measured data relevant to the terrestrial compartment are available, and so a detailed comparison of the predicted with the measured levels is not possible at present. However, the concentrations predicted in sewage sludge for consumer use in personal care products (13.8 mg/kg dry weight) are is in good agreement with levels measured in sewage sludge from the available Nordic surveys.

3.3.3 Atmospheric compartment

3.3.3.1 Predicted environmental concentrations

The predicted concentrations in the air compartment are summarised in Table 3.16Table 3..

Table 3.16 Predicted concentrations in air

Scenario	Annual average PEC (mg/m^3)
Production and on-site use as an intermediate	5.5×10^{-5}
Off-site use as an intermediate	1.4×10^{-5}
Personal care products – formulation – generic site	1.6×10^{-5}
Personal care products – formulation – UK sites – cyclomethicone	1.2×10^{-5}
	1.2×10^{-5}
	1.2×10^{-5}
	1.2×10^{-5}
	1.2×10^{-5}
	1.2×10^{-5}
	1.2×10^{-5}
	1.2×10^{-5}
Personal care products – use by general public	1.2×10^{-5}
Regional	1.2×10^{-5}

3.3.3.2 Measured environmental concentrations

TemaNord (2005) and Kaj *et al.* (2005) report the results of a survey of indoor air levels from 400 homes in Sweden. D6 was found in 142 homes at concentrations between 0.6 and 164 µg/m^3 (the mean of the detected concentrations is 7.9 µg/m^3).
Recently, Kaj *et al.* (2005) studied the levels of D6 in air in Sweden. The samples were collected during 2004 and 2005. The sampling and analytical methods used were designed to avoid loss of D6 from the sample through volatilisation and contamination of the sample. The concentrations found in this survey are summarised in Table 3.17. 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 D6 was actually being used in the area sampled.

Table 3.17 Concentration of D6 in air from Sweden (Kaj *et al.*, 2005)

Location	Measured concentration (ng/m^3)	Comment
Råo	<12	Background site
Råo	11	Background site
Råo	77	Background site
Stenungsund	13	Site near to potential point sources in an industrial area
Stenungsund	27	Site near to potential point sources in an industrial area
Stenungsund	42	Site near to potential point sources in an industrial area
Stockvik	<12	Site near to potential point sources in an industrial area
Stockvik	38	Site near to potential point sources in an industrial area
Hudiksvallsgatan	21	Urban area of Stockholm
Hudiksvallsgatan	<12	Urban area of Stockholm
Hudiksvallsgatan	<12	Urban area of Stockholm

TemaNord (2005) carried out a further study of the levels of D6 in air in Nordic countrie . The samples were collected in 2004 and 2005 and the sampling and analytical methods used were designed to avoid contamination of the sample by D6. The results of this survey are summarised in Table 3.18. The concentrations of D6 are in the range 0.02–2.1 $\mu g/m^3$. The concentrations were generally elevated in urban areas and in areas close to sewage treatment plants compared to other areas.

Environment Canada (2008) gives the results of an unpublished study of the air levels of D6 in the Great Lakes region. The samples were collected during February and March 2006. In all, 18 outdoor samples were collected from urban and rural areas in Ontario and D6 was found “almost all of the samples” at concentrations <1 $\mu g/m^3$, with a concentration in one sample from an urban area of Toronto of ~16 $\mu g/m^3$. Environment Canada (2008) also indicates that the widespread detection of D6 in ambient air could, in part, be a result of sample contamination as the methodology to determine trace concentrations in air is still under development.

Wilkins *et al*. (1993) also report D6 in office-dust samples collected by vacuum cleaner from nine city hall buildings in Denmark. The samples were separated into the particle (<1 mm) and fibre fractions and siloxanes detected by a thermal desorption technique. D6 occurred at a concentration of ≥5 mg/kg in three of the nine samples analysed. No quality-assurance data are reported in the paper.

Table 3.18 Concentration of D6 in air from Nordic countries (TemaNord, 2005)

Sampling location		Concentration (µg/m^3)
Denmark	Jagtvejen	0.07
	Bjergmarken STP	0.17
	Sepstrup Sande	0.44
	H.C. Ørsted Institute	0.14
Faroe Islands	Torshavn, downtown	0.39
	Sersjantvikin STP	2.1
Finland	Nokia City STP	0.20
	Espoo landfill	0.09
Iceland	Reykjavik, urban	0.42
	Reykjavik, urban	0.34
	Reykjavik, urban	0.29
	Reykjavik, urban	0.08
Norway	Bekkelaget STP	0.57
	Bekkelaget STP	1.0
	Manglerud	0.82
	Oslo central station	0.87
Sweden	Högbytorp landfill (windside)	0.06
	Högbytorp landfill (windside)	0.02
	Mossarps recycling site	0.17
	Mossarps recycling site	0.24
	Göteborg, Kapellplatsen	0.08
	Göteborg, Kapellplatsen	0.05
	Stockholm, Hudiksvallsgatan	0.10
	Stockholm, Hudiksvallsgatan	0.11

3.3.3.3 Comparison of measured levels with predicted levels

The concentrations of D6 measured in air generally range between 0.02 and 2.1 µg/m^3 (2×10^{-5} and 2×10^{-3} mg/m^3). These measured values are usually higher than those predicted for D6 for the local scenarios, but the lower end of the measured data are similar to the predicted regional concentration. Possible explanations for this discrepancy could include underestimation of the loss from water, sediment, and soil through volatilisation, underestimation of the local and regional emissions to air, or overestimation of the rate of degradation of D6 in air when the concentrations in air are calculated, but at present it is not possible to determine which of these (or other possibilities) account for the discrepancy. Also, the available monitoring data are relatively limited in their coverage, and the sources of emission of D6 at the sampling sites is not always clear.

3.3.4Food chain exposure

3.3.4.1 Predicted environmental concentrations

The predicted concentrations in fish and earthworms for secondary poisoning are summarised in Table 3.19.

Table 3.19 Predicted concentrations in fish and earthworms[1]

Scenario	PEC (mg/kg)
	Fish
Production and on-site use as an intermediate	0.058
Off-site use as an intermediate	9.7×10^{-3}
Personal care products – formulation – generic site	0.068
Personal care products – formulation – UK sites – cyclomethicone	9.9×10^{-3}
	9.7×10^{-3}
	9.7×10^{-3}
	9.8×10^{-3}
	0.011
	0.010
	0.010
	0.010
Personal care products – use by general public	0.022

Note: [1]The calculation methods in the TGD 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.

The predicted concentrations in food for human consumption are summarised inTable 3.20.

Table 3.20 Predicted concentrations of D6 in food for human consumption

Scenario	PEC							Estimated total daily intake (mg/kg body weight/day)
	Fish (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	0.11	9.0×10^{-3}	1.5×10^{-4}	1.4×10^{-3}	4.4×10^{-4}	1.2×10^{-5}	5.5×10^{-5}	2.5×10^{-4}
Off-site use as an intermediate	9.7×10^{-3}	8.7×10^{-3}	3.8×10^{-5}	3.4×10^{-4}	1.1×10^{-4}	1.0×10^{-6}	1.4×10^{-5}	7.1×10^{-5}
Personal care products – formulation – generic site	0.13	1.3	4.3×10^{-5}	4.6×10^{-4}	1.5×10^{-4}	7.3×10^{-3}	1.6×10^{-5}	7.3×10^{-3}
Personal care products – formulation – UK sites – cyclomethicone	0.010	0.014	3.3×10^{-5}	3.0×10^{-4}	9.3×10^{-5}	1.1×10^{-6}	1.2×10^{-5}	1.0×10^{-4}
	9.7×10^{-3}	9.1×10^{-3}	3.2×10^{-5}	2.9×10^{-4}	9.2×10^{-5}	1.1×10^{-6}	1.2×10^{-5}	7.2×10^{-5}
	9.7×10^{-3}	8.9×10^{-3}	3.2×10^{-5}	2.9×10^{-4}	9.2×10^{-5}	1.0×10^{-6}	1.2×10^{-5}	7.1×10^{-5}
	9.9×10^{-3}	0.012	3.2×10^{-5}	2.9×10^{-4}	9.2×10^{-5}	1.1×10^{-6}	1.2×10^{-5}	8.5×10^{-5}
	0.012	0.029	3.3×10^{-5}	2.9×10^{-4}	9.3×10^{-5}	1.2×10^{-6}	1.2×10^{-5}	1.9×10^{-4}
	0.011	0.022	3.2×10^{-5}	2.9×10^{-4}	9.3×10^{-5}	1.2×10^{-6}	1.2×10^{-5}	1.5×10^{-4}
	0.011	0.020	3.2×10^{-5}	2.9×10^{-4}	9.3×10^{-5}	1.2×10^{-6}	1.2×10^{-5}	1.3×10^{-4}
	0.011	0.019	3.2×10^{-5}	2.9×10^{-4}	9.3×10^{-5}	1.1×10^{-6}	1.2×10^{-5}	4.0×10^{-5}
Personal care products – use by general public	0.034	0.23	3.3×10^{-5}	3.2×10^{-4}	1.0×10^{-4}	3.7×10^{-6}	1.2×10^{-5}	1.3×10^{-4}
Regional	9.7×10^{-3}	20.4	3.2×10^{-5}	1.8×10^{-3}	5.7×10^{-4}	3.5×10^{-6}	1.2×10^{-5}	0.11

3.3.4.2 Measured environmental concentrations

Kaj *et al.* (2005) recently studied the levels of D6 in fish from Sweden . The samples were collected during 2004 and 2005. The sampling method and analytical method used was designed to avoid loss of D6 from the sample by volatilisation and contamination of the sample. The concentrations found in this survey are summarised in Table 3.21. Fish muscle only was analysed in this study and D6 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 D6 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 3.21 Concentration of D6 in fish muscle from Sweden (Kaj *et al.*, 2005)

Location	Species	Measured concentration (µg/kg wet wt.)	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	

Kaj *et al.* (2005) also determined the levels of D6 in 49 samples of human breast milk. The detection limit for D6 in these samples was 2 µg/l, and D6 was found in four of the samples at concentrations of 2.5–4.8 µg/l.

TemaNord (2005) report concentrations of D6 of <5–74 µg/kg fresh weight in biota from Nordic countries. The concentrations are generally elevated in urban areas and in areas close to sewage treatment plants, and only a few background samples had detectable levels. The sampling and analytical methods used were designed to avoid loss of D6 from the sample through volatilisation and contamination of the sample by D6. The samples were generally collected between 2002 and 2004 (fish and marine mammals) or 2000 and 2005 (bird eggs). The full results of this survey are summarised in 3.22.

Table 3.22 Concentration of D6 in biota from Nordic countries (TemaNord, 2005)

Sample and location				Concentration (µg/kg wet weight)
Marine fish	Denmark	Roskildefjord	Three eelpout, liver	<5
		Øresund	Three flounder, liver	8.7[a]
		North Sea	Three flounder, liver	<5
		Wadden Sea	Three flounder, liver	<5
	Faroe Islands	Mylingsgrunnurin	Nine cod, liver	<5
		Kaldbaksfjøröur	Ten sculpin, liver	5.2
		Kaldbaksfjøröur	Nineteen flatfish (dab), liver	<5
	Norway	Lista/Farsund	Sixteen cod, liver	<5
		Indre Sørfjord	Ten cod, liver	6.7 [1]
		Ulsteinvik	Five cod, liver	6.1 [1]
		Indre Oslofjord	Four cod, liver	74
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	<5
		Old City Bay, Helsinki	Two pike, liver	<5
		Old City Bay, Helsinki	Two pike, liver	<5
		Cold Water Bay, Helsinki	Two pike, liver	<5
		Guard Village Bay, Helsinki	Two pike, liver	<5
	Norway	Lake Mjøsa	Five vendance, liver	<5
	Sweden	River Nissan, Skepshult	One pike, liver	<5
		River Nissan, Rydöbruk	One pike, liver	<5
Marine mammals	Denmark	Coastal area, Øresund	Five seals, blubber	<5
		Samsø	Five seals, blubber	<5
		Limfjorden	Five seals, blubber	<5
		Hesselø	Five seals, blubber	7.9[a]
	Faroe Islands	Sandangeröi	Ten pilot whales, blubber	<5
		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

Sample and location				Concentration (µg/kg wet weight)
		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.

In the follow-up study, Schlabach *et al*. (2007) investigated the levels of D6 in biota from the Inner Oslofjord in Norway [where the highest concentration of D6 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 method and analytical methods used were designed to avoid loss of D6 from the sample through volatilisation and contamination of the sample by D6. 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 depuration. The concentrations found are summarised in Table 3.23.

D6 was found in all the biota samples analysed. The highest concentrations were in cod liver, and the concentrations in cod liver (~110–150 µg/kg wet weight) compare with the those found in cod liver from the same area in the TemaNord (2005) survey (74 µg/kg wet weight; sample collected in 2004).

Table 3.23 Further study of the concentration of D6 in biota from the Inner Oslofjord (Schlabach *et al*., 2007)

Sample	Location	Concentration	
		µg/kg wet weight	µg/kg lipid
Common mussel	Færder	1.7	73.6
	Gressholmen	1.8	339
	Ormøya	1.3	132
Flounder liver	Frognerkilen	1.4	8.8
Flounder fillet	Frognerkilen	0.9	67.3
Cod liver (each sample is a pooled sample from five individual fish)	Nesodden/Vestfjord	130	829
	Nesodden/Vestfjord	152	611
	Nesodden/Vestfjord	109	328
Cod stomach content	Nesodden/Vestfjord	1.8	103
	Nesodden/Vestfjord	3.3	165
	Nesodden/Vestfjord	3.3	167

EVONIK Industries (2007) briefly reported in a slide presentation the results of a further survey of the levels of D6 in freshwater and marine fish from Europe. The analytical detection limit was 15 µg/kg wet weight. In the marine fish, D6 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. In the freshwater fish, D6 was not detectable in three species from Lake Nipgård, Denmark, and three species from Lake Constance, Germany. D6 was found at concentrations up to 0.1 mg/kg wet weight in one sample of eel from the River Rhine, Germany (close to the Dutch Border), but it was not detectable in other species of fish. The results included details of the species analysed are summarised inTable 3.24. Few other details of this study are currently available.

Table 3.24Concentration of D6 in freshwater and marine fish from Europe (EVONIK Industries, 2007)

Location	Species	Measured concentration (µg/kg wet weight)	Comment
River Rhine, Germany (close to Dutch border)	Roach (*Rutilus rutilus*)	<15	
	Ide (*Leuciscus idus*)	<15	Two samples analysed
	Eel (*Aguilla aguilla*)	<0.045–100	Two samples analysed and various tissues were also analysed separately; concentrations were <15 µg/kg in liver, <45 µg/kg in skin, 100 µg/kg in fatty tissue, and 100 µg/kg in muscle
Lake Constance, Germany	Lake white fish (*Coregonus* spp.)	<15	
	Alpine charr (*Salvelinus umbla*)	<15	
	Eel (*Aguilla aguilla*)	<15	
Lake Nipgård, Denmark	Perch (*Perca fluviatilis*)	<15	
	Roach (*Rutilus rutilus*)	<15	
	Pike (*Esox lucius*)	<15	
North East Atlantic	Atlantic salmon (*Salmo solar*)	<15	Sample from Denmark fjord
	Cod (*Gadus morhua*)	<15	
	Common sole (*Solea solea*)	<15	
	Pilchard (*Sardina pilcharus*)	<15	
	Redfish (*Sebastes marinus*)	<15	
	Wolffish (*Anarhichas lupus*)	<15	
	Mackerel (*Scomber scombrus*)	<15	
	Plaice (*Pleuronectes platessa*)	<15	
	Monkfish (*Lophius piscatorius*)	<15	
	Lemon sole (*Microstomus kitt*)	<15	
	Pollock (*Pollachius virens*)	<15	
Baltic Sea (close to mouth of Odra River, Germany)	Eel (*Aguilla aguilla*)	<15	
	Flounder (*Platichthys flesus*)	<15	
	Turbot (*Psetta maxima*)	<15	
	Perch (*Perca fluviatilis*)	<15	
	Pike-perch (*Stizostedion lucioperca*)	<15	
	Pike (*Esox lucius*)	<15	
Baltic Sea, Estonia	**3.3.5**Pike-perch (*Stizostedion lucioperca*)	<15	

Boehmer *et al*. (2007) carried out a preliminary screening study of the levels of D6 in mussels from the southern North Sea. The main purpose of the study was to develop methodologies for the collection, transportation, preparation, and analysis of mussel tissue samples for cyclic VMSs. The methodology was developed to prevent both contamination with D6 and loss of D6 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 (collected 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 to purge sediment particles 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 13.8 µg/kg. In all, 23 samples were analysed. The levels found (corrected for the levels of D6 in laboratory blank samples) are below the method detection limit (<6.6 µg/kg) in 22 samples, and between the method detection limit and the method limit of quantification in one sample (the estimated concentration was 5.0 µg/kg).
D6 was identified in drinking water from New Orleans and Seattle (USEPA, 1992). No details of the levels found are given.

3.3.5.1 Comparison of measured levels with predicted levels

The levels of D6 measured in biota are generally very low. The majority of the data show that D6 is not detectable in biota, but it has been found at up to 150 µg/kg wet weight in livers of some marine fish, 100 µg/kg wet weight in muscle and fatty tissue of an eel from the River Rhine, and up to 7.9 µg/kg wet weight in seal blubber. In addition D6 has been found at concentrations up to 4.8 µg/l in breast milk.
It is not possible to carry out a meaningful comparison of the predicted and measured levels as it is not clear how the samples relate to the scenarios considered in this assessment. The concentration of D6 measured in freshwater fish (<5 to <15 µg/kg wet weight) in general appears to be lower than that calculated for use of D6 in personal care products. However, higher concentrations (up to 100 µg/kg wet weight) have been measured in eels in the River Rhine and this compares reasonably well with the PECs estimated for fish for D6 (15–100 µg/kg wet weight).

3.3.6Marine compartment

3.3.6.1 Predicted environmental concentrations

The predicted concentrations relevant for the marine environment are summarised inTable 3.25. The calculations assume that the emissions to wastewater are not treated in a WWTP (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 WWTP and scenarios for personal care products – use (in which the WWTP is the local emission source).

Table 3.25 Predicted concentrations relevant for the marine environment

Scenario	PEC			
	Water (µg/l)	Sediment (mg/kg wet weight)	Predators (mg/kg)	Top predators (mg/kg)
Production and on-site use as an intermediate	3.6×10^{-3}	0.051	2.5×10^{-3}	1.5×10^{-3}
Off-site use as an intermediate	1.1×10^{-3}	0.015	1.2×10^{-3}	1.2×10^{-3}
Personal care products – formulation – generic site	0.19	2.7	0.092	0.019
Personal care products – formulation – UK sites – cyclomethicone	1.1×10^{-3}	0.016	1.3×10^{-3}	1.3×10^{-3}
	1.1×10^{-3}	0.015	1.3×10^{-3}	1.3×10^{-3}
	1.1×10^{-3}	0.015	1.3×10^{-3}	1.3×10^{-3}
	1.1×10^{-3}	0.016	1.3×10^{-3}	1.3×10^{-3}
	1.3×10^{-3}	0.018	1.3×10^{-3}	1.3×10^{-3}
	1.2×10^{-3}	0.017	1.3×10^{-3}	1.3×10^{-3}
	1.2×10^{-3}	0.017	1.3×10^{-3}	1.3×10^{-3}
	1.2×10^{-3}	0.017	1.3×10^{-3}	1.3×10^{-3}
Personal care products – use by general public	3.2×10^{-3}	0.045	2.5×10^{-3}	1.5×10^{-3}
Regional	1.1×10^{-3}	0.030		

3.3.6.2 Measured environmental concentrations

Measured data available for marine sediments (see Section 3.3.1.2) and marine biota (see Section 3.3.4.2) are limited. The concentrations of D6 found in marine sediments are up to around 170 µg/kg dry weight, and those in liver samples from marine fish are up to 150 µg/kg wet weight. However, in many samples D6 was not detectable.

3.3.6.3 Comparison of measured levels with predicted levels

It is not clear how the limited data available for the marine environment relate to the scenarios considered in this assessment. Therefore it is not possible to make a detailed comparison of the predicted and measured concentrations. However, the available measured data for marine sediment (up to 170 µg/kg wet weight) and marine fish liver (up to 150 µg/kg wet weight) are reasonably consistent with the predicted concentrations for some scenarios.

4 Effects assessment: hazard identification and dose (concentration) versus response (effect) assessment

4.1 Aquatic compartment (including sediment)

4.1.1 Toxicity to fish

4.1.1.1 Short-term studies

No experimental data appear to be available on the acute toxicity of D6 to fish.

4.1.1.2 Long-term studies

The long-term toxicity of D6 to fish was investigated as part of an unpublished 49 day bioconcentration study with fathead minnows (*P. Promelas*) [Drottar (2005); IUCLID (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 7.6–8.6 and a hardness of 109–151 mg/l as $CaCO_3$. ^{14}C-D6 with a radiochemical purity of 99.57 per cent was tested. Two exposure concentrations were used and the concentrations were verified by total radioactivity measurements. The mean measured concentrations (± standard deviation) during the 49 day exposure period were 0.41 ± 0.029 µg/l and 4.4 ± 0.23 µg/l in the two exposure groups. A cosolvent (DMF at a concentration of 0.1 ml/l) was also used (a solvent control was run). The dissolved oxygen concentration remained ≥5.5 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 49 day exposure period and the 98 day depuration period (during which the fish were not exposed to D6). The overall mortality was 8.3 per cent in the control, 11 per cent in the 0.41 µg/l treatment group, and 12 per cent in the 4.4 µg/l treatment group. The no observed effect concentration (NOEC) was therefore given as ≥4.4 µg/l. Further details of the bioconcentration study are reported in Section 3.2.9.

This test was actually a bioconcentration test and the only endpoints investigated were mortality and visual inspection for overt signs of toxicity. In addition, fish from the control and treatment groups were sacrificed at regular intervals during the test to investigate the uptake of D6. Therefore the test cannot be compared directly with standard long-term toxicity tests, such as the fish early-lifestage test. Therefore, although this test shows that no treatment-related mortalities were evident; these results need to be treated with caution as other endpoints were not considered.

4.1.2 Toxicity to aquatic invertebrates

4.1.2.1 Short-term studies

No short-term toxicity data for aquatic invertebrates are currently available for D6.

4.1.2.2 Long-term studies

Springborn Smithers Laboratories (2006) undertook a 21-day toxicity test of D6 in *D. magna* for D6. The test was carried out according to the OECD 211 test guideline using a semi-static test procedure (solutions were renewed every 24 hours). ^{14}C-D6 (radiochemical purity 98.1

per cent) mixed with unlabelled D6 (purity 99.6 per cent) was tested. This mixture was added to the test media as a solution in acetone (the final concentration of acetone was 0.1 µl/ml). In the study, juvenile *D. magna* (<24 hours old) were exposed for 21 days to mean measured concentrations of D6 of 0.27, 0.57, 1.2, 2.5, and 4.6 µg/l [based on ^{14}C analysis of the fresh solutions on days 0, 7, 14, and 20 and aged solutions (24 hour old) on days 1, 8, 15, and 21]. The mean measured concentrations were between 85 and 97 per cent of the nominal concentrations prepared (the nominal concentrations were 0.32, 0.64, 1.3, 2.6, and 5.1 µg/l), and the measurements were consistent at all time points monitored. A control and a solvent control were also run. The test water had a hardness of 170–190 mg $CaCO_3$/l. During the test the pH was maintained at 7.4–8.4, the temperature was generally maintained between 18 and 21°C (although it may have reached up to 24°C on one occasion) and the dissolved oxygen content was between 7.7 and 10 mg/l in the freshly prepared solutions and between 3.4 and 11 mg/l in the aged solutions at renewal.

The biological results are summarised in
Table 4.1. No mortality, no effects on reproduction rate, and no other biologically significant effects were seen in the exposure groups when compared with the pooled control group (statistical significance was determined at the p = 0.05 level). Therefore the NOEC is the highest concentration tested (NOEC ≥4.6 µg/l).

Table 4.1 Results of the 21 day reproduction test with *D. magna* (Springborn Smithers Laboratory, 2006)

Mean measured exposures concentration (µg/l)	Biological response				
	Parent survival (%)	Time to first brood (days)	Mean cumulative offspring per surviving female	Total body length at day 21 (mm)	Dry weight at day 21 (mg per daphnid)
0.27	100	8	158	4.86	1.10
0.57	90	8	151	4.85	1.15
1.2	100	8	141	4.84	1.11
2.5	100	8	149	4.84	1.17
4.6	100	8	155	4.91	1.18
Control	90	8	165	4.91	1.06
Solvent control	100	8	148	4.84	1.12
Pooled control	95		157	4.88	1.09

The study appears to be of good quality and the results can be considered reliable. The test report shows that the *D. magna* were fed an algal suspension during the test at a rate of 0.3 mg carbon per daphnid per day, which is slightly higher than the rate recommended in the test guideline (0.1–0.2 mg carbon per daphnid per day). In addition, the temperature fluctuated briefly outside of the range recommended in the test guidelines. However, it is thought that neither of these deviations unduly influenced the results of the test.

4.1.3 Toxicity to aquatic algae and plants

No toxicity data for aquatic algae and plants are currently available for D6.

4.1.4 Quantitative structure–activity relationships

Estimates for the toxicity of D6 are generated from the measured log K_{ow} value (log K_{ow} = 9.06) using the equations outlined in the TGD. The estimates obtained are summarised in Table 4.2. The equivalent values using a log K_{ow} of 5.86 are also shown.

Table 4.2 Estimates for the toxicity of D6 generated from log K_{ow} 9.06 and log K_{ow} of 5.86

		log K_{ow} = 9.06 (mg/l)	log K_{ow} = 5.86(mg/l)
Fish	96 hour LC_{50}	3.6×10^{-4}	0.19
	28–32 day NOEC	1.6×10^{-5}	0.012
Daphnids	48 hour EC_{50}	5.3×10^{-5}	0.058
	16 day NOEC	1.9×10^{-6}	0.004
Green algae	72–96 hour EC_{50}	2.3×10^{-5}	0.036

Note [1]LC_{50}, lethal concentration that kills 50 per cent of the population in the period given; EC_{50}, per cent effective concentration.

The equations in the TGD are applicable to chemicals that act by non-polar narcosis and are well validated. The relevant validation statistics [n is the number of chemicals used to derive the quantitative structure–activity relationships (QSARs) 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] are:
:

- 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).

The range of log K_{ow} values to which the equations apply is not given in the TGD, but it is questionable whether these estimates are valid for a substance with a log K_{ow} value of 9.06 and so they are not considered further here.
The toxicity of D6 to aquatic organisms is also estimated using the USEPA EPI (v3.12) software, which estimates the toxicity from the log K_{ow} value using various QSARs. A calculated log K_{ow} of 6.33 is used, as the original equations were developed using predicted rather than measured log K_{ow} values and this predicted log K_{ow} for D6 lies within the validity range of most of the estimation methods. (The QSARs for neutral organics are used in the estimates – these are reported to apply 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 4.3.

Table 4.3 Estimates for the toxicity of D6 generated from log K_{ow} 6.33 using USEPA EPI (v3.12) software

Fish	96 hour LC_{50}	0.028 (freshwater)
	96 hour LC_{50}	0.052 (saltwater)
	14 day LC_{50}	0.10
	30 day Chv[1]	0.007
Daphnids	48 hour LC_{50}	0.041
	16 day EC_{50}	0.014
Mysid shrimp	96 hour LC_{50}	0.00037
Green algae	96 hour EC_{50}	0.033
	96 hour Chv[1]	0.040

Note [1]Chronic value, which most probably represents the geometric mean of the lowest observed concentration (LOEC) and the NOEC.

The relevant validation statistics for the EPI (v3.12) methods are:

- fish, 96 hour log LC_{50} (freshwater) = –0.94 × log K_{ow} + 1.75 mmol/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);
- mysid shrimp, 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 D6 is around 0.0053 mg/l, and so the predicted toxicity values are all above its water solubility, except for mysid shrimp and the chronic values for fish and daphnia (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 D4 are not in agreement with the known acute toxicity of that substance to mysids (see Environment Agency (2008a)]. In addition the log K_{ow} used for D6 in the estimation (log K_{ow} 6.33) is outside the given validity range for the mysid shrimp QSAR. Therefore the reliability of this estimate in particular is uncertain.[12] Overall, the available estimates for toxicity suggest D6 is not toxic to aquatic organisms at concentrations up to its water solubility.

[12]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) are included in the chemicals used to construct this QSAR. This, therefore, casts further doubt on the applicability of this QSAR to D6.

4.1.5 Overall summary of standard endpoint toxicity data

Relatively few aquatic toxicity data are available for D6. It appears not to cause lethality in fish when exposed over periods of up to 49 days at concentrations close to its water solubility and no adverse effects occurred in a 21-day *D. magna* reproduction study at concentrations of up to 4.6 µg/l. No data are available for algae.
Predictions of toxicity suggest that D6 is not toxic to aquatic organisms at concentrations below its water solubility. However, some predictions are very close to the water solubility, and therefore are not conclusive in this respect.
Also relevant is the available toxicity data for the similar substance D5 (Environment Agency, 2008b). The solubility and fish BCF for D5 are higher (0.017 mg/l and ~7000 l/kg, respectively) than those for D6 (0.0056 mg/l and 1160 l/kg), and this substance showed no effects at concentrations up to its water solubility in acute and long-term toxicity tests with fish (although, again, the long-term fish tests appear to have considered mortality only and so are not comparable with a standard fish early-lifestage test), daphnia, and algae. Therefore, based on the data available for D5, it is expected that D6 will also not show toxicity to aquatic organisms at concentrations up to its water solubility as it has a lower solubility and lower accumulation potential than those of D5.

4.1.6 Endocrine disruption

No toxicity data are available for the effects of D6 on the endocrine system in aquatic organisms.

4.1.7 Wastewater treatment plant micro-organisms

No toxicity data are available for the effects of D6 on microorganisms.

4.1.8 Toxicity to sediment organisms

No toxicity data are available for the effects of D6 on sediment organisms.

4.1.9 Predicted no-effect concentration for the aquatic compartment

4.1.9.1 Surface water

No predicted no-effect concentration (PNEC) for surface water can be derived for D6. The information available (toxicity data for D6 itself, predictions, and data for similar substances) suggest D6 is not toxic to aquatic organisms at concentrations up to its water solubility, but some of the predicted NOECs are close to the solubility, and no long-term toxicity studies are available for algae. To carry out a screening assessment for the aquatic compartment an indicative concentration of one-tenth of the water solubility (i.e. 0.53 µg/l) is used in place of a PNEC for freshwater so that the significance of these data gaps can be assessed. For marine water a lower indicative concentration of 0.053 µg/l is assumed.

4.1.9.2 Microorganisms

No toxicity data are available and so it is not possible to derive a PNEC for this endpoint.

4.1.9.3 Sediment

It is currently not possible to derive a PNEC for sediment. Based on information for D4 and D5 (Environment Agency, 2008a, 2008b) toxic effects of D6 in sediment organisms cannot be ruled out.

As a screening approach, an indicative concentration for the sediment compartment is estimated from the indicative concentration for surface water (0.53 µg/l for freshwater and 0.053 µg/l for marine water) using the equilibrium partitioning approach. This gives an indicative concentration of 7.5 mg/kg wet weight for freshwater sediment and 0.75 mg/kg for

marine sediment, assuming a $K_{susp-water}$ of 1.6×10^4 m^3/m^3 estimated from the log K_{ow} value of 9.06. According to the TGD, risk characterisation ratios obtained using the equilibrium partitioning method should be increased by a factor of ten for substances with a log K_{ow} >5. This approach is highly speculative and the risk characterisation ratios that result should be treated with caution. However, in the assessment they are used as a screening approach to determine if further information or testing on this endpoint is justified.

4.2 Terrestrial compartment

4.2.1 Terrestrial toxicity data

A 14 day LC_{50} of 127 mg/kg dry weight soil for earthworms is estimated for D6 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 6.33 is again used). This software estimates the toxicity from the log K_{ow} value using a QSAR for neutral organics:

$$\log 14 \text{ day } LC_{50} = 1.405 - 0.308 \times \log K_{ow} \quad (4.1)$$

where 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 correlation coefficient (coefficient of determination) of the method (R^2) is 0.48.

The method is reported as valid for log K_{ow} up to 5.0. The log K_{ow} of D6 is outside this range (a predicted log K_{ow} = 6.33 is used in the estimation, and the actual log K_{ow} is much higher than this value, at 9.06). 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 longer than 14 days may be needed for these to express their toxicity.

Information on 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).[13] According to this report the five chemicals included in the training set used to derive the QSAR are 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 is between 1.0 and 4.3.

Given that the QSAR is derived using only a limit number of chemicals (five), the relatively poor R^2 value for and the unknown applicability of the method to D6, the LC_{50} estimated using this method is considered uncertain. However, few other QSAR methods to estimate the toxicity of chemicals such as D6 to terrestrial organisms are currently available.

4.2.2 PNEC for the soil compartment

Insufficient data are available to derive a PNEC for soil.

Using the QSAR value for toxicity to earthworms, an indicative value is estimated as 0.13 mg/kg dry weight using an assessment factor (AF) of 1000. This is equivalent to 0.11 mg/kg on a wet weight basis.

Another approach is to estimate an indicative value using the equilibrium partitioning approach based on the indicative value of 0.53 µg/l derived for water. Using the soil–water partition coefficient of 2.0×10^4 m^3/m^3 an indicative concentration for the soil compartment of 6.2 mg/kg wet weight is estimated. According to the TGD, risk characterisation ratios

[13] 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.

obtained using the equilibrium partitioning method should be increased by a factor of ten for substances with a log K_{ow} >5.
Given the uncertainty over the QSAR estimate for the toxicity of D6, the indicative value derived using the equilibrium partitioning method is used in the assessment as a screening approach. Given that the risk characterisation ratios obtained by this method are increased by a factor of ten, this approach results 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.

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

No data indicate the bioavailability of inhaled D6, but based on data for the related cyclosiloxanes D4 (Environment Agency, 2008a) and D5 (Environment Agency, 2008b) it is likely that no more than 3 per cent of inhaled D6 vapour is absorbed. D6 is only moderately bioavailable by the oral route [15 per cent (Dow Corning, 1985, 2004b)]. Negligible dermal absorption is expected [0.1 per cent (Dow Corning, 2002)]. Absorbed D6 distributes widely within the body and only a small proportion is metabolised. The identity of D6 metabolites is not known. Unlike D4 and D5, the majority of absorbed D6 is eliminated unchanged in exhaled air. It is not clear what impact this difference has on the toxicity of D6. The bioaccumulative potential has not been specifically studied. However, given that D6 is only moderately bioavailable by the oral route and that absorbed D6 is readily exhaled, biaccumulation is not considered to be a concern for D6.

4.4.2 Acute toxicity

There is no information on acute inhalation toxicity, but based on information for D4 (Environment Agency, 2008a) and D5 (Environment Agency, 2008b) this is predicted to be low. No overt toxicity occurred following a single oral or dermal dose of 2000 mg/kg D6 (NOTOX, 1999a, 1999b).

4.4.3 Irritation

NOTOX (1999c) found no evidence of skin irritation in a standard study in rabbits. In a standard eye-irritation study in rabbits, an initial reddening of the conjunctivae was reported which resolved by the 24-hour observation (NOTOX, 1999d). No reports of the irritancy of D6 to the respiratory tract are available. However, given the lack of skin and eye irritation and what is known about the related compounds D4 (Environment Agency, 2008a) and D5 (Environment Agency, 2008b), D6 is not expected to cause irritation in the respiratory tract.

4.4.4 Sensitisation

NOTOX (1999e) investigated the sensitising potential of D6 in a maximisation test in guinea pigs and negative results were obtained.

There is no information on the potential asthmagenicity of D6. However, given that the substance has no skin-sensitising properties and what is generally known about cyclosiloxanes, D6 is not predicted to show asthmagenic potential.

4.4.5 Repeated dose toxicity

There is no information on the effects on humans of repeated exposure to D6. The only animal data are from two oral studies. The most extensive study is a combined repeated dose–reproductive and developmental toxicity screening study in which groups of ten male and ten female Sprague Dawley rats were given 0, 100, 300, or 1000 mg/kg/day D6 in corn oil (Silicones Environmental Health and Safety Council, 2005). Animals in the toxicity segment of this study were treated daily for around 28 days. There were no clinical signs of toxicity, no effects on food consumption or body weight, and negative results are reported for functional observational battery and motor activity parameters.
The only organ weight change to show a consistent dose-related increase was liver weight in females. This only achieved statistical significance in animals treated with 1000 mg/kg/day (absolute liver weights were around 20 per cent greater than those of controls). Liver enlargement was observed after treatment with the related cyclosiloxanes D4 and D5, for which the respective no observed adverse effect level (NOAELs) for this effect were 25 and 5 mg/kg/day (Environment Agency, 2008a, 2008b). D4 causes phenobarbital-like enzyme induction in the liver and there is evidence [summarised in CES (2005)] that D5 induces a similar profile of enzymes. It is reasonable to assume that liver-weight increase after treatment with D6 occurs via the same mechanism. Although the increased liver weight is mediated by a phenobarbital-like pattern of liver enzyme induction, it is unclear whether or not this is adverse in humans. As it is unclear whether liver weight increase is related to tumour development, it is assumed for D4 and D5 that increases in liver weight greater than 10 per cent could be adverse in humans. For D4, although increases in liver weight are not accompanied by impaired liver function or adverse histopathological changes, very large increases in liver size occur (with a maximal increase of 80 per cent at 427 mg/kg/day). Increases in size of this magnitude could compress other abdominal organs and hence be of clinical significance for human health and so are expected to affect survival of animals in the wild.

However, in comparison to D4 and D5, after treatment with D6 the maximal increase in liver weight is relatively small and only occurs at the high dose of 1000 mg/kg/day. In addition, liver enlargement only occurs in females in the absence of any other effects. On this basis, liver enlargement after exposure to D6 is not considered as a concern to human health or for animals in the wild.

Histopathological examinations reveal an increase in periportal fat deposits in the liver of females at all dose levels. The finding has minimal severity in four controls and minimal-to-moderate severity in all treated females at the low and intermediate dose and nine out of ten females at the top dose. The toxicological significance of this is unclear, but may be related to the use of corn oil as the dosing vehicle. In the absence of evidence for liver damage the periportal fat deposits are not considered to be an adverse effect. No other effects are reported.

In a 28-day screening study with limited histopathological investigations (Dow Corning, 1990), groups of six male and six female Sprague Dawley rats received distilled water or 1500 mg/kg/day undiluted D6 five days per week. Investigations encompassed cage-side observations, body weights, food consumption, urinalysis, and organ weights for the liver, kidneys, testes, ovaries, brain, heart, and spleen. Subsequently, histopathological examinations were performed for these tissues. No deaths, signs of toxicity, effects on body weights, food consumption, or organ weights were observed. No histopathological changes are reported. On this basis, and given the lack of adverse effects in the Silicones

Environmental Health and Safety Council (2005) 28-day study, the NOAEL for the effects of repeated oral exposure to D6 is considered to be >1500 mg/kg/day.
There are no data on the effects of repeated inhalation or dermal exposure. Given the lack of systemic toxicity for D6 by the oral route, no systemic toxicity is anticipated through the inhalation or dermal routes.
In conclusion, there are no data from humans on the effects of repeated exposure to D6. The only data in animals are from oral dosing studies. No adverse effects are observed at the highest test dose of 1500 mg/kg/day. There is no information on the effects of repeated inhalation or dermal exposure. Systemic toxicity is not anticipated by either of these routes.

4.4.6 Mutagenicity

NOTOX (1999f) examined the potential mutagenicity of D6 in a reverse mutation assay using *Salmonella typhimurium* strains TA98, TA100, TA1535, and TA1537, and *Escherichia coli* strain WP2uvrA. The top dose used was 1000 µg/plate. At this concentration and above the test substance precipitated. There was no evidence for cytotoxicity. No increase in revertants was observed across the dose range. Positive controls reacted appropriately. This result is consistent with findings in mutagenicity tests in a range of assay systems for other cyclosiloxanes, which indicate that this class of compound does not possess mutagenic activity.

4.4.7 Carcinogenicity

There are no data on the carcinogenic potential of D6. Both D4 and D5 cause endometrial tumours in rats, but that the mechanism is not relevant to humans (Environment Agency, 2008a, 2008b). Since the tumours seen with D4 and D5 arise late in the rat life cycle they are unlikely to influence the sustainability of populations in the wild. On this basis, no concerns are identified for carcinogenicity in relation to D6.

4.4.8 Toxicity for reproduction

The only information on this endpoint is from a combined repeated dose–reproductive and developmental toxicity screening study (Silicones Environmental Health and Safety Council, 2005). Groups of ten male and female Sprague Dawley rats were treated with 0, 100, 300, or 1000 mg/kg/day D6 in corn oil for up to 45 consecutive days. No adverse reproductive or developmental effects are reported for D6. Investigations included an assessment of numbers of corpora lutea. A reduction in numbers of corpora lutea is a key event in the reproductive effects reported with D4. The lack of any effect on corpora lutea suggests that D6 does not have the same reproductive effects as D4. This may be because of lack of intrinsic hazard or that higher doses of D6 are needed to elicit effects. If D6 does possess the ability to affect reproduction, then the NOAEL would be >1000 mg/kg/day.

4.4.9 Summary of mammalian toxicity

It is likely that D6 vapour is poorly absorbed (<3 per cent) by inhalation. D6 is only moderately bioavailable by the oral route (15 per cent). Negligible dermal absorption (0.1 per cent) is anticipated. Any D6 that is absorbed is distributed widely within the body and a small proportion is metabolised. The identity of D6 metabolites is not known. D6 is not likely to biaccumulate.
D6 is of low acute toxicity via the oral and dermal routes, and it is anticipated that acute toxicity after inhalation exposure is also likely to be low.
D6 is not a skin or eye irritant and is not predicted to irritate the respiratory tract. Also, D6 is not a skin sensitiser and is not predicted to have asthmagenic potential.
There are no data from humans on the effects of repeated exposure to D6. The only data in animals derives from a 28-day oral dosing studies in rats in which the only effect seen was liver enlargement of up to 20 per cent above controls at 1000 mg/kg/day. This was not observed in another 28-day study in which rats were treated with up to 1500 mg/kg/day. As

the magnitude of liver enlargement was relatively small (compared to those for the related siloxanes D4 and D5), and only occurred after treatment with high doses in the absence of any other effects, this observation is not considered a concern for human health or for animals exposed via the environment.
D6 has been investigated for mutagenicity in one bacterial reverse mutation assay in which negative results were obtained. On the basis of this finding and the lack of evidence for mutagenic properties with the related cyclosiloxanes D4 and D5, there are no concerns for mutagenicity with D6.
There are no data on the carcinogenic potential of D6. It is possible that D6 might cause endometrial tumours (as do D4 and D5), but the mechanism for tumour formation is not relevant to human health. On this basis, no concerns are identified for carcinogenicity in relation to D6.
No adverse effects on fertility or development are reported from a combined repeated dose–reproductive and developmental toxicity screening study in which rats were treated with 0, 100, 300, or 1000 mg/kg/day oral D6 for up to 45 consecutive days.
Overall, no toxicological hazards are identified for D6.

4.4.10 Derivation of $PNEC_{oral}$

To derive $PNEC_{oral}$ two relevant NOAELs can be considered. The first is the 28-day NOAEL of ≥1500 mg/kg body weight per day. Using this value, a conversion factor of ten (for rats ≤6 weeks old) or 20 (for rats ≥6 weeks old) to convert from a daily dose to a concentration in food, and an AF of 300 (as recommended in the TGD), the $PNEC_{oral}$ is estimated as ≥50 to ≥100 mg/kg food, depending on the age of the rats used in the test.
The second NOAEL value is ≥1000 mg/kg body weight per day for reproduction. Using this value, and a conversion factor of 20 (for rats ≥6 weeks old) to convert from a daily dose to a concentration in food, and an AF of 30 (as recommended in the TGD for a chronic endpoint), the $PNEC_{oral}$ is estimated as 667 mg/kg food.
The PNEC of ≥50 mg/kg food, derived from the 28-day study, is used in the risk characterisation. This PNEC is lower than that derived from the NOAEL for reproductive effects of D6 and so is expected to be protective of such effects.

4.5 Classification for environmental hazard

D6 is not currently classified for environmental hazard.
it is not readily biodegradable, has a fish BCF of 1160 l/kg, and is thought not to be 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 D6 for surface water. It is thought that the substance is not toxic to aquatic organisms at concentrations up to its water solubility, and therefore no risks to surface water are expected. An indicative concentration of 0.53 µg/l is derived for D6 and a comparison of the PECs with this value are shown in Table 5.1. This comparison confirms that no risks to surface water are expected.

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	0.11	0.21
Off-site use as an intermediate	8.3×10^{-3}	0.016
Personal care products – formulation – generic site	0.13	0.25
Personal care products – formulation – UK sites – cyclomethicone	8.9×10^{-3}	0.017
	8.4×10^{-3}	0.016
	8.4×10^{-3}	0.016
	8.6×10^{-3}	0.016
	0.010	0.020
	9.7×10^{-3}	0.018
	9.4×10^{-3}	0.018
	9.3×10^{-3}	0.018
Personal care products – use by general public	0.030	0.056
Regional	8.3×10^{-3}	0.016

5.1.2 Risk characterisation ratios for wastewater treatment plant micro organisms

No PNEC can be determined for D6 for WWTPs. Based on comparison with the findings of the risk assessments for D4 and D5, no risk to WWTPs is expected for D6.

5.1.3 Risk characterisation ratios for sediment

No PNEC can be derived for sediment. Based on information for D4 and D5 (Environment Agency, 2008a, 2008b), toxic effects of D6 in sediment organisms cannot be ruled out. For example, the PNEC for D5 is 0.75 mg/kg wet weight. This value is of a similar order to the predicted levels of D6 in sediment for some scenarios.

An indicative concentration for D6 in sediment of 7.5 mg/kg wet weight is derived for D6. A comparison of the PECs with this value is shown in Table 5.2 (the ratios are increased by a factor of ten in line with the recommendations of the TGD for substances with log K_{ow} >5). Although it is recognised that this approach is highly uncertain, this comparison confirms that risks to freshwater sediment cannot currently be ruled out.

Table 5.2 Comparison of PECs with the indicative concentration for sediment

Scenario	PEC (mg/kg wet weight)	PEC/indicative concentration
Production and on-site use as an intermediate	1.6	2.1
Off-site use as an intermediate	0.12	0.16
Personal care products – formulation – generic site	1.9	2.5
Personal care products – formulation – UK sites – cyclomethicone	0.13	0.17
	0.12	0.16
	0.12	0.16
	0.12	0.16
	0.15	0.20
	0.14	0.18
	0.13	0.18
	0.13	0.18
Personal care products – use by general public	0.42	0.56
Regional	0.24	0.31

5.1.4 Uncertainties and possible refinements

Insufficient toxicity data are available for D6 to derive reliable PNEC values for surface water, WWTPs, and sediments. The available information on similar substances is suggests that D6 presents a low risk to aquatic organisms and wastewater treatment processes, but the possibility of risk to sediment-dwelling organisms cannot be ruled out currently.

Further long-term aquatic toxicity tests could be carried out to confirm that D6 does not cause effects within the range of its water solubility. However, such tests are very difficult because D6 is volatile and has a very low water solubility. In addition, as it has a high log K_{ow} value, to assess the risks to the aquatic compartment sediment is expected to be much more relevant than surface water. Therefore it is recommended that any refinement of the PNEC for sediment should take precedence over that for surface water. Long-term testing with sediment organisms is needed to define the PNEC for sediment.

Also, the default methods in the TGD are used to carry out some of the exposure assessment and the PEC calculations. Thus, further refinement of the PECs could also be investigated. In addition, the PECs for sediment depend crucially on the K_{oc} value for D6. At present this value is estimated from experimental data for D4 and D5 using a log K_{ow} that is also estimated from data on D4 and D5. Although this value is considered the best available estimate for the K_{oc} there are uncertainties in it. An analysis of the effect of using a lower log K_{ow} value (and hence K_{oc} value) on the risk assessment (see the Appendix) shows that the use of lower log K_{ow} and K_{oc} values results in similar conclusions. Therefore, it is unlikely that a measured K_{oc} value alone is sufficient to refine the risk characterisation for sediment.

5.1.5 Conclusions for the aquatic compartment

The risks to surface water and WWTPs are thought to be low based on the limited information currently available and on a default exposure estimate. The risks to the sediment compartment cannot be fully quantified because the lack of toxicity data for D6. Therefore sediment toxicity testing is needed to determine the risks of D6 to the aquatic compartment. As D6 has a high log K_{ow}, any future sediment toxicity testing should take account of the recommendation in the TGD that such tests be carried out without supplemental feeding.

5.2 Terrestrial compartment

5.2.1 Risk characterisation ratios

No PNEC can be derived for D6. An indicative value of 6.2 mg/kg wet weight is derived using the equilibrium partitioning method and a comparison of this value with the PECs is outlined in Table 5.3 (the ratios are increased by a factor of ten as recommended in the TGD). Based on this preliminary assessment, no risk characterisation ratios >1 are obtained. Therefore the scenarios considered indicate a low risk to soil.

Table 5.3 Comparison of PECs with the indicative concentration for soil

Scenario	PEC (mg/kg wet weight)	PEC/indicative concentration
Production and on-site use as an intermediate	1.8×10^{-5}	2.9×10^{-5}
Off-site use as an intermediate	1.8×10^{-5}	2.9×10^{-5}
Personal care products – formulation – generic site	0.016	0.0 25
Personal care products – formulation – UK sites – cyclomethicone	8.6×10^{-5}	1.4×10^{-4}
	2.2×10^{-5}	3.6×10^{-5}
	2.0×10^{-5}	3.3×10^{-5}
	5.0×10^{-5}	8.2×10^{-5}
	2.7×10^{-4}	4.3×10^{-4}
	1.8×10^{-4}	3.0×10^{-4}
	1.6×10^{-4}	2.5×10^{-4}
	1.4×10^{-4}	2.3×10^{-4}
Personal care products – use by general public	2.7×10^{-3}	4.4×10^{-3}
Regional – agricultural soil	0.041	0.065
Regional – natural soil	1.8×10^{-5}	2.9×10^{-5}
Regional – industrial soil	1.8×10^{-5}	2.9×10^{-5}

5.2.2 Uncertainties and possible refinements

There are considerable uncertainties over both the PECs and the PNECs used in the assessment, as the approach taken effectively represents a worst-case one. A number of possible refinements could be made as outlined below. However, as no risks are identified using this approach, further work to address these uncertainties and refinements is of low priority at this time.

The local PECs could be refined by obtaining further information on the exposure, particularly whether sewage sludge from WWTPs is spread onto agricultural land. The local PECs also depend on the emissions assumed for the WWTP and so further information on this aspect would also help to revise the PEC.

The PEC for soil is also dependent on the K_{oc} value. At present this value is estimated from experimental data for D4 and D5 using a log K_{ow} that is also estimated from data on D4 and D5. Although this value is considered to be the best available estimate for the K_{oc} there are uncertainties in it. The Appendix considers the use of a lower log K_{ow} (and hence K_{oc}) on the outcome of the risk assessment and shows that the assessment is relatively insensitive to the log K_{ow} (and K_{oc}) value used. No risk characterisation ratios above one are identified for any scenario except for the generic formulation of personal care products, for which the risk characterisation ratio is only just above one (ratio of 1.4). This scenario is not relevant to the UK.

The actual degradation rate in soil for this substance is uncertain. However, the effect of this on the local concentrations in soil is minimal and so does not significantly affect the conclusions that can be drawn. The uncertainty in the degradation rate in soil has an impact on the predicted regional concentrations only and, as no risk is predicted even assuming no degradation, similar conclusions are drawn for this endpoint if the substance degrades more quickly than is assumed.

A further consideration related to the spreading of sewage sludge is that, although a significant fraction of the substance is predicted to be adsorbed to sewage sludge during wastewater 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 more rapid hydrolysis of D6 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 predicted instantaneous concentration in sewage sludge during wastewater treatment may not reflect the actual concentration in sewage sludge applied to land. Actual measurements in sewage sludge may be useful in this respect.

Also, the PNEC for soil is based on the equilibrium partitioning method that uses an indicative concentration for water. It is possible to refine the PNEC for soil by carrying out long-term toxicity testing with soil organisms. However, soil toxicity testing is very difficult for D6 because of its high volatility.
It is possible that D6 could be formed in soil from the degradation of PDMS fluids and other siloxane polymers. A preliminary assessment of this potential source (see Section 3.1.5.2) indicates that the amounts of D6 that could be volatilised from soil through this process are likely to be small compared with other sources of D6. 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 landfill conditions. In addition, it is not currently possible to estimate the amount of D6 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 D6 from this source. This is beyond the scope of the current risk assessment.

5.2.3 Conclusions for soil

This preliminary assessment indicates a low risk to the soil compartment from the production and all uses of D6. Some uncertainties are associated with this assessment, but the present risk characterisation suggests that further work to address these uncertainties is not a priority at this time.

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.

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 50 mg/kg food. The risk characterisation ratios that result are summarised in Table 5.4.
Based on the information available, the risks from secondary poisoning from D6 appear to be low.

Table 5.4 Risk characterisation ratios for secondary poisoning[1]

Scenario	Fish	
	PEC (mg/kg)	Risk characterisation ratio
Production and on-site use as an intermediate	0.058	1.2×10^{-3}
Off-site use as an intermediate	9.7×10^{-3}	1.9×10^{-4}
Personal care products – formulation – generic site	0.068	1.4×10^{-3}
Personal care products – formulation – UK sites – cyclomethicone	9.9×10^{-3}	2.0×10^{-4}
	9.7×10^{-3}	1.9×10^{-4}
	9.7×10^{-3}	1.9×10^{-4}
	9.8×10^{-3}	2.0×10^{-4}
	0.011	2.1×10^{-4}
	0.010	2.1×10^{-4}
	0.010	2.0×10^{-4}
	0.010	2.0×10^{-4}
Personal care products – use by general public	0.022	4.4×10^{-4}

Note: [1]The calculation methods in the TGD 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.

5.4.2 Uncertainties and possible refinements

The methodology in the TGD to assess secondary poisoning via the earthworm food chain is not applicable for substances with log K_{ow} values >8.0. The analysis reported in the Appendix uses a lower log K_{ow} value and indicates that no risk for this food chain is expected, but the actual level of uptake into earthworms from soil is uncertain. It is possible to carry out a more reliable assessment of this route of exposure with further work to measure a bioaccumulation factor for earthworms in soil. However, given the very low concentrations of D6 predicted in soil, and the difficulties in carrying out such a test, such further work is not warranted at present.
Although it is potentially possible to further refine the PECs and PNECs for secondary poisoning, the worst-case risk assessment indicates no risk and so such further refinement is

considered unnecessary. The analysis reported in the Appendix indicates that the assessment for secondary poisoning is relatively insensitive to the log K_{ow} value used.

5.4.3 Conclusions for predators

The risk to fish-eating predators is low based on the worst-case assessment.
It is not currently possible to assess fully the risk to predators exposed via the earthworm food chain, and further work is not warranted at present.

5.5 Marine compartment

5.5.1 Risk characterisation ratios

A PNEC for the marine compartment can currently be derived for secondary poisoning of predators and top predators only. Using the PNEC of 50 mg/kg food the risk characterisation ratios that result are summarised in Table 5.5.
Based on the worst-case risk characterisation ratios the risk of secondary poisoning of marine predators and marine top predators is low.

Table 5.5 Predicted concentrations relevant for the marine environment

Scenario	Predators		Top predators	
	PEC (mg/kg)	Risk characterisation ratio	PEC (mg/kg)	Risk characterisation ratio
Production and on-site use as an intermediate	2.5×10^{-3}	4.9×10^{-5}	1.5×10^{-3}	3.0×10^{-5}
Off-site use as an intermediate	1.2×10^{-3}	2.5×10^{-5}	1.2×10^{-3}	2.5×10^{-5}
Personal care products – formulation – generic site	0.092	1.8×10^{-3}	0.019	3.9×10^{-4}
Personal care products – formulation – UK sites – cyclomethicone	1.3×10^{-3}	2.5×10^{-5}	1.3×10^{-3}	2.5×10^{-5}
	1.3×10^{-3}	2.5×10^{-5}	1.3×10^{-3}	2.5×10^{-5}
	1.3×10^{-3}	2.5×10^{-5}	1.3×10^{-3}	2.5×10^{-5}
	1.3×10^{-3}	2.5×10^{-5}	1.3×10^{-3}	2.5×10^{-5}
	1.3×10^{-3}	2.7×10^{-5}	1.3×10^{-3}	2.5×10^{-5}
	1.3×10^{-3}	2.6×10^{-5}	1.3×10^{-3}	2.5×10^{-5}
	1.3×10^{-3}	2.6×10^{-5}	1.3×10^{-3}	2.5×10^{-5}
	1.3×10^{-3}	2.6×10^{-5}	1.3×10^{-3}	2.5×10^{-5}
Personal care products – use by general public	2.5×10^{-3}	5.0×10^{-5}	1.5×10^{-3}	3.0×10^{-5}

An indicative concentration of 0.053 µg/l for marine water and 0.75 mg/kg wet weight for marine sediment is derived for D6. A comparison of the PECs with these values is given in Table 5.6 (the ratios for sediment are increased by a factor of ten in line with the recommendations of the TGD for substances with log K_{ow} values >5).
Based on this analysis, the PEC for marine water and marine sediment is greater than the indicative concentration for one generic scenario only (formulation of personal care products). This scenario is not relevant to the situation in the UK and the site-specific PECs for sites that formulate personal care products in the UK are below the indicative concentration. A similar situation exists for D5 (see Environment Agency, 2008b) for which site-specific information was also obtained for the majority of sites that formulate personal care products containing cyclic siloxanes in the EU outside of the UK. This information shows that the PECs for these sites are in all cases very much lower than that predicted for the generic site scenario (only one site was identified that emitted into the marine environment, and this had a PEC for marine water and marine sediment around 380 times lower than predicted for the generic site). The generic scenario is based on a size representative of a

relatively large formulation site (assumed to be using around 306 tonnes/year of D6). Based on the site-specific information for D6 for UK formulation sites, and the site-specific information for D5 for non-UK formulation sites, it is unlikely that a site of this size exists in the EU that is not already covered by the site-specific information. The available site-specific information is therefore preferable to that in this scenario.

Table 5.6 Comparison of PECs with indicative concentrations for marine water and marine sediment

Scenario	Marine water		Marine sediment	
	PEC (µg/l)	PEC/indicative concentration	PEC (mg/kg wet wt.)	PEC/indicative concentration
Production and on-site use as an intermediate	3.6×10^{-3}	0.069	0.051	0.69
Off-site use as an intermediate	1.1×10^{-3}	0.020	0.015	0.20
Personal care products – formulation – generic site	0.19	3.6	2.7	36
Personal care products – formulation – UK sites – cyclomethicone	1.1×10^{-3}	0.021	0.016	0.21
	1.1×10^{-3}	0.020	0.015	0.20
	1.1×10^{-3}	0.020	0.015	0.20
	1.1×10^{-3}	0.021	0.016	0.21
	1.3×10^{-3}	0.024	0.018	0.24
	1.2×10^{-3}	0.023	0.017	0.23
	1.2×10^{-3}	0.022	0.017	0.22
	1.2×10^{-3}	0.022	0.017	0.22
Personal care products – use by general public	3.2×10^{-3}	0.061	0.045	0.61
Regional	1.1×10^{-3}	0.020	0.030	0.40

5.5.2 Assessment against persistent, bioaccumulative, and toxic criteria

D6 is considered to be not readily biodegradable and so meets the screening persistent (P) or very persistent (vP) criteria. However, the it is not thought to be toxic to aquatic organisms at concentrations up to its water solubility, and has a fish BCF value of 1160 l/kg, although higher values (up to ~2400 l/kg) are found in aquatic invertebrates. On this basis D6 does not meet the screening bioaccumulative (B), very bioaccumulative (vB), and toxic (T) criteria. Recent modelling work by Xu (2007b, 2007c) suggests that only a very small fraction of D6 is likely be transported to remote regions, and that significant deposition in remote regions is unlikely. Therefore D6 has a low potential for long-range transport.

5.5.3 Uncertainties and possible refinements

It is currently not possible to complete the marine risk characterisation. Information on the toxicity to sediment organisms would be useful to define a PNEC for marine sediment. In addition, further exposure information would be useful to refine the PECs for the marine environment.

The log K_{ow} value and K_{oc} value for D6 uncertain. In the Appendix the effect of using a lower log K_{ow} value (and hence lower K_{oc} value) on the outcome for the marine compartment is considered. This approach again indicates a possible risk to the sediment compartment for the generic scenario for formulation of personal care products. Again, the available site-specific information is preferable to this scenario and shows no potential risks. In addition, a possible risk to marine sediment from the production and on-site use of D6 as an intermediate was obtained using a lower K_{oc} value.

In relation to the persistent, bioaccumulative, and toxic (PBT) assessment, although D6 meets P or vP screening criteria, it it is also lost rapidly from surface water by volatilisation.

Modelling work is currently being carried out for D5 to determine the effect of volatilisation on the half-life in sediment, which may be relevant here.

5.5.4 Conclusions for the marine compartment

Based on the information available, D6 is not a PBT or vPvB substance.
The risks to marine aquatic organisms and the risks of secondary poisoning in the marine environment are thought to be low. In addition, the risks to marine sediment organisms are thought to be low based on the best available estimate of the K_{oc} value. Any further sediment toxicity testing carried out for the freshwater compartment (see Section 5.1.5) would also be useful to confirm the conclusions for the marine sediment compartment.

5.6 Human exposure to D6 via the environment

No hazards of concern for human health are identified in relation to acute toxicity, irritation, skin sensitisation, repeat dose toxicity, mutagenicity, carcinogenicity, or reproductive toxicity. As a consequence, D6 is unlikely to pose a risk to human health in any exposure scenario.

5.7 Further testing currently underway

A number of further tests or studies of direct relevance to the conclusions of this assessment have been (or are in the process of being) commissioned by CES on a voluntary basis (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;
- further modelling of the environmental distribution and overall fate;
- sediment toxicity study with *Chironomus* species;
- further environmental monitoring (the focus of which is on D4 and D5, but useful information on D6 is likely to be provided) of air, sewage effluent, river water, sediment, and biota including:
    - Lake Pepin, MN, to look at historical deposition patterns to evaluate degradation in the environment,
    - CES mussel-screening program (preliminary results are included in this risk assessment),
    - River Nene to look at the distribution and persistence downstream from a known point source (monitoring and river die-away study),
    - long-term robust monitoring program to investigate the persistence and bioaccumulation potential in the field, but it has yet to be developed fully and agreed, although it is likely to include investigations of time trends (using freshwater and marine sediment cores from local, regional, and remote locations, and 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 to refine the current PECs used in the risk assessment;
- development of analytical methodology for water, sediment, soil, biota, sludge, and air to support these studies;
- in addition, further studies are currently being considered or are underway for D4 and D5 that may provide information useful to refine this assessment of D6.

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
EUSES	European Union System for the Evaluation of Substances
HAV	Heat Activated Vulcanising
IC	Industry Category
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
LC_{50}	Lethal concentration 50 – the concentration that kills 50 per cent of the population
LOEC	Lowest observed effect concentration
MC	Main Category
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)
NIK	Niedrigste Interessierende Konzentration
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
OECD	Organisation for Economic Co-operation and Development
PBT	Persistent, Bioaccumulative and Toxic
PDMS	Polydimethylsiloxane
PEC	Predicted environmental concentration
PNEC	Predicted no effect concentration
POCP	Photochemical Ozone Creation Potential
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

UC	Use Category
USEPA	United States Environmental Protection Agency
VMS	Volatile Methylsiloxanes
vPvB	Very Persistent, Very Bioaccumulative

Appendix: Sensitivity of the assessment to the log K_{ow} and Henry's law constant

As discussed in Section 1 of the main report, the values of some of the key physicochemical properties for D6 are uncertain. New values and/or estimates for log K_{ow} and Henry's law constant recently became available and are considered in the modelling for the PEC calculations in the main risk assessment report (used are a log K_{ow} of 9.06, a Henry's law constant of 4,943,000 Pa m^3/mol at 25°C, and a K_{oc} of 6.5×10^5). In this Appendix we consider the consequences of assuming lower values for log K_{ow} (5.86), Henry's law constant (14,667 Pa m^3/mol at 25°C), and K_{oc} (estimated from log K_{ow} as 7.0×10^4 l/kg) on the outcome of the risk assessment.
Both the log K_{ow} and Henry's law constant affect the predicted partitioning of D6 in the environment. The most important partition coefficients used in the assessment derived from these values are:

- $K_{oc} = 7.0 \times 10^4$ l/kg
- $K_{soil} = 1.4 \times 10^3$ l/kg
- $K_{sed} = 3.5 \times 10^3$ l/kg
- $K_{susp} = 7.0 \times 10^3$ l/kg
- $K_{soil–water} = 2.1 \times 10^3$ m^3/m^3
- $K_{susp–water} = 1.8 \times 10^3$ m^3/m^3
- $K_{sed–water} = 1.8 \times 10^3$ m^3/m^3
-

The expected behaviour during wastewater treatment is estimated using the Simpletreat model within EUSES 2.0.3 as:

- 29.7 per cent to air
- 66.3 per cent to sludge
- 0 per cent degraded
- 4.08 per cent to water.

Using the lower values for log K_{ow} and Henry's law constant results in a much higher percentage being released to air from wastewater treatment (29.7 per cent compared with 9.4 per cent in the main assessment), with lower releases to sludge (66.3 per cent compared with 84.1 per cent in the main assessment), and water (4.08 per cent compared with 6.48 per cent in the main assessment).

The log K_{ow} also affects any PNECs determined by the equilibrium partitioning method. For D6 no PNECs are derived for sediment and soil, but indicative concentrations are estimated using the equilibrium partitioning method. An equilibrium partitioning method using log K_{ow} of 5.86 results in indicative concentrations of 0.81 mg/kg wet weight in freshwater sediment, of 0.081 mg/kg wet weight in marine sediment, and an of 0.66 mg/kg wet weight in soil. In addition, an indicative concentration of 0.11 mg/kg wet weight for soil based on QSAR estimates (see Section 4.2.2) is also considered. The PECs, risk characterisation ratio,s and comparisons of PECs with indicative concentrations obtained using a log K_{ow} of 5.86 and a Henry's law constant of 14,667 Pa m^3/mol are summarised in Tables A1 to A6.

With the exception of soil and marine sediment from the generic scenario for formulation of personal care products, and sediment and marine sediment from the production and on-site use as an intermediate, this analysis does not identify any potential risks from D6. As discussed in the main risk assessment, the site-specific PECs for formulation of personal care products should overwrite this generic scenario. For the production and use as an intermediate scenario, a risk to freshwater sediment (but not to marine sediment) is also identified in the main risk assessment report using a higher K_{oc} value than that assumed here. As the PNEC for sediment is based on equilibrium partitioning it may be possible to refine further the PNEC by more toxicity testing with sediment-dwelling organisms.

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	0.19	0.36
Off-site use as an intermediate	0.013	0.025
Personal care products – formulation – generic site	0.15	0.28
Personal care products – formulation – UK sites – cyclomethicone	0.013	0.025
	0.013	0.025
	0.013	0.025
	0.013	0.025
	0.015	0.28
	0.014	0.026
	0.014	0.026
	0.014	0.026
Personal care products – use by general public	0.037	0.070
Regional	0.013	0.025

Note: [1]Indicative concentration is 0.53 µg/l.

Table A2 Comparison of PECs with the indicative concentration for sediment

Scenario	PEC (mg/kg wet weight)	PEC/indicative concentration[1]
Production and on-site use as an intermediate	0.30	3.7
Off-site use as an intermediate	0.019	0.23
Personal care products – formulation – generic site	0.23	2.8
Personal care products – formulation – UK sites – cyclomethicone	0.020	0.25
	0.020	0.25
	0.019	0.23
	0.020	0.25
	0.023	0.28
	0.021	0.26
	0.021	0.26
	0.021	0.26
Personal care products – use by general public	0.056	0.69
Regional	0.038	0.47

Note: [1]Indicative concentration is 0.81 mg/kg wet weight based on the equilibrium partitioning method. The ratios are increased by a factor of ten in line with the recommendations in the TGD.

Table A3 Comparison of PECs with the indicative concentration for the soil compartment

Scenario	PEC (mg/kg wet wt.)	PEC/indicative concentration	
		0.66 mg/kg wet weight[1]	0.11 mg/kg wet weight[2]
Production and on-site use as an intermediate	2.5×10^{-5}	3.8×10^{-4}	2.3×10^{-4}
Off-site use as an intermediate	6.6×10^{-6}	1.0×10^{-4}	6.0×10^{-5}
Personal care products – formulation - generic site	0.090	1.4	0.82
Personal care products – formulation – UK sites – cyclomethicone	2.7×10^{-4}	4.1×10^{-3}	2.5×10^{-3}
	2.1×10^{-5}	3.2×10^{-4}	1.9×10^{-4}
	1.5×10^{-5}	2.3×10^{-4}	1.4×10^{-4}
	2.0×10^{-4}	3.0×10^{-3}	1.8×10^{-3}
	1.5×10^{-3}	0.023	0.014
	9.7×10^{-4}	0.015	8.8×10^{-3}
	8.1×10^{-4}	0.012	7.4×10^{-3}
	7.3×10^{-4}	0.011	6.6×10^{-3}
Personal care products – use by general public	0.016	0.24	0.15
Regional – agricultural soil	0.011	0.17	0.10
Regional – natural soil	5.6×10^{-6}	8.4×10^{-5}	5.1×10^{-5}
Regional – industrial soil	2.6×10^{-6}	4.0×10^{-5}	2.4×10^{-4}

Notes: [1]Indicative concentration based on equilibrium partitioning. The ratios are increased by a factor of ten in line with the recommendations in the TGD.
[2]Indicative concentrationbased on QSAR estimates.

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	0.10	2.0×10^{-3}	0.035	7.0×10^{-4}
Off-site use as an intermediate	0.015	3.0×10^{-4}	0.035	7.0×10^{-4}
Personal care products – formulation – generic site	0.081	1.6×10^{-3}	0.22	4.4×10^{-3}
Personal care products – formulation – UK sites – cyclomethicone	0.015	3.0×10^{-4}	0.035	7.0×10^{-4}
	0.015	3.0×10^{-4}	0.035	7.0×10^{-4}
	0.015	3.0×10^{-4}	0.035	7.0×10^{-4}
	0.015	3.0×10^{-4}	0.035	7.0×10^{-4}
	0.016	3.2×10^{-4}	0.038	7.6×10^{-4}
	0.015	3.0×10^{-4}	0.037	7.4×10^{-4}
	0.015	3.0×10^{-4}	0.036	7.2×10^{-4}
	0.015	3.0×10^{-4}	0.036	7.2×10^{-4}
Personal care products – use by general public	0.028	5.6×10^{-4}	0.066	1.3×10^{-3}

Note: [1]PNEC is 50 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	3.5×10^{-3}	7.0×10^{-5}	1.8×10^{-3}	3.6×10^{-5}
Off-site use as an intermediate	1.4×10^{-3}	2.8×10^{-5}	1.4×10^{-3}	2.8×10^{-5}
Personal care products – formulation – generic site	0.16	3.2×10^{-3}	0.034	6.8×10^{-4}
Personal care products – formulation – UK sites – cyclomethicone	1.4×10^{-3}	2.8×10^{-5}	1.4×10^{-3}	2.8×10^{-5}
	1.4×10^{-3}	2.8×10^{-5}	1.4×10^{-3}	2.8×10^{-5}
	1.4×10^{-3}	2.8×10^{-5}	1.4×10^{-3}	2.8×10^{-5}
	1.4×10^{-3}	2.8×10^{-5}	1.4×10^{-3}	2.8×10^{-5}
	1.5×10^{-3}	3.0×10^{-5}	1.4×10^{-3}	2.8×10^{-5}
	1.4×10^{-3}	2.8×10^{-5}	1.4×10^{-3}	2.8×10^{-5}
	1.4×10^{-3}	2.8×10^{-5}	1.4×10^{-3}	2.8×10^{-5}
	1.4×10^{-3}	2.8×10^{-5}	1.4×10^{-3}	2.8×10^{-5}
Personal care products – use by general public	2.8×10^{-3}	5.6×10^{-5}	1.6×10^{-3}	3.2×10^{-4}

Note: [1]PNEC is 50 mg/kg food.

Table A6 Comparison of PECs with indicative concentrations for marine water and marine sediment

Scenario	Marine water		Marine sediment	
	PEC (µg/l)	PEC/indicative concentration[1]	PEC (mg/kg wet weight)	PEC/indicative concentration[2]
Production and on-site use as an intermediate	5.8×10^{-3}	0.11	8.8×10^{-3}	1.1
Off-site use as an intermediate	1.2×10^{-3}	0.023	1.8×10^{-3}	0.22
Personal care products – formulation – generic site	0.34	6.4	0.52	64
Personal care products – formulation – UK sites – cyclomethicone	1.2×10^{-3}	0.023	1.9×10^{-3}	0.23
	1.2×10^{-3}	0.023	1.8×10^{-3}	0.22
	1.2×10^{-3}	0.023	1.8×10^{-3}	0.22
	1.2×10^{-3}	0.023	1.8×10^{-3}	0.22
	1.4×10^{-3}	0.026	2.1×10^{-3}	0.26
	1.3×10^{-3}	0.025	2.0×10^{-3}	0.25
	1.3×10^{-3}	0.025	2.0×10^{-3}	0.25
	1.3×10^{-3}	0.025	2.0×10^{-3}	0.25
Personal care products – use by general public	3.6×10^{-3}	0.068	5.5×10^{-3}	0.68
Regional	1.2×10^{-3}	0.023	3.5×10^{-3}	0.43

Notes: [1]Indicative concentration is 0.053 µg/l.
[2]Indicative concentration is 0.081 mg/kg wet weight. The ratios are increased by a factor of ten in line with the recommendations in the TGD.