

Hexamethyldisiloxane (HMDS)¹



OSPAR Commission
2004

¹ OSPAR 2007 agreed to deselect Hexamethyldisiloxane (HMDS) from the List of Chemicals for Priority Action (OSPAR 07/24/1, §8.3).

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the “OSPAR Convention”) was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

La Convention pour la protection du milieu marin de l'Atlantique du Nord-Est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par la Communauté européenne et l'Espagne.

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Executive summary

Hexamethyldisiloxane (CAS No. 107-46-0)) was included on the OSPAR List of Chemicals for Priority Action at OSPAR 2000. HMDS is a siloxane, used as an internal synthesis intermediate and as an ingredient in personal care products and solvent.

The total production of HMDS in the European Union was 4025 tonnes in 2000 (including import and export data of the substance). HMDS is also formed as a by-product from the use of several other silicone containing intermediates, such as in the manufacturing of penicillin and other pharmaceuticals and in the production of silicone rubbers. HMDS may be released to the environment from production, import and use of HMDS, from production of other silicone substances, from reprocessing of HMDS-containing waste, and from landfill gas.

HMDS has a very low water solubility and is highly volatile. It is therefore difficult to perform biodegradability and toxicity tests. Experimental data on degradation in water are not available. Based on chemical structure, no aerobic biodegradation of HMDS in water is expected. The half-life of HMDS in marine water is thus expected to be more than 60 days and the persistence (P) criterion is fulfilled. HMDS has not been detected in any fresh or marine waters. Experimental data and QSAR calculations both give a bioconcentration factor below the EU TGD cut-off value of 2000. The TGD bioaccumulation (B) criterion is therefore not fulfilled. The lowest reported experimental data on chronic toxicity is the $NOEC_{daphnia}$ (21d) = 0,08 mg/l. Hence, the EU TGD toxicity (T) criterion is not fulfilled. In conclusion HMDS cannot be considered a PBT substance as defined in the EU TGD. The environmental risk assessment of HMDS concludes that HMDS poses no risk to the marine environment at the regional scale, but that there is a hypothetical risk on the local scale (as none of the sites are located on the coast).

The actions recommended are: The PEC/PNEC ratios need to be refined, especially the PEC values calculated for penicillin and pharmaceuticals manufactures, for fresh and marine water compartments; Contracting Parties who are also EU Member States should support the ongoing development of the Risk Assessment Review and provide new information, if available, on exposure, discharges, emissions and losses, which would enable the PEC/PNEC ratios to be refined; OSPAR should re-evaluate the risks posed by HMDS releases when further information has been collected; OSPAR should communicate this Background Document to the European Commission and to other appropriate international organisations which deal with hazardous substances to promote action to take account of this Background Document in a consistent manner. Special care should be taken in future in developing new manufacturing installations for HMDS near the coast.

Récapitulatif

L'hexaméthylidisiloxane (N° CAS. 107-46-0) a été inscrit sur la liste OSPAR des produits chimiques devant faire l'objet de mesures prioritaires à OSPAR 2000. Le HMDS est un siloxane, utilisé comme intermédiaire interne de synthèse ainsi que comme ingrédient de produits d'hygiène corporelle et comme solvant.

En 2000, la production totale de HMDS dans l'Union européenne s'est élevée à 4025 tonnes (chiffre comprenant les statistiques d'importation et d'exportation de cette substance). Le HMDS se forme également comme un sous-produit de l'utilisation de plusieurs autres intermédiaires contenant des silicones, comme dans la fabrication de la pénicilline et autres produits pharmaceutiques, de même que dans la fabrication des caoutchoucs silicones. Du HMDS peut être libéré dans l'environnement aux stades de sa fabrication, de son importation et de son utilisation, de la fabrication d'autres substances au silicone, du retraitement des déchets contenant du HMDS, et enfin du fait du gaz qui se dégage des décharges publiques.

Le HMDS est très peu soluble dans l'eau et est hautement volatile. Il est par conséquent difficile de procéder à des tests de biodégradabilité et de toxicité. L'on ne dispose d'aucune donnée expérimentale relative à sa dégradation dans l'eau. Compte tenu de sa structure chimique, aucune biodégradation aérobie du HMDS dans l'eau ne devrait se produire. La demi-vie du HMDS dans l'eau de mer devrait par conséquent être supérieure à 60 jours, et le critère de la persistance (P) est rempli. Le HMDS n'a pas été décelé dans des eaux douces ni dans l'eau de mer. Les données expérimentales et les calculs QSAR donnent un coefficient de bio-concentration inférieur au seuil de coupure de 2000 fixé dans le DOT de l'Union européenne. Par conséquent, le critère de bio-accumulation (B) du DOT n'est pas rempli. En ce qui concerne la toxicité chronique, les données expérimentales les plus basses qui aient été communiquées correspondent à $NOEC_{daphnie}(21d) = 0,08 \text{ mg/l}$. Par conséquent, le critère de toxicité (T) fixé dans le DOT de l'Union européenne n'est pas rempli. En conclusion, le HMDS ne peut être considéré comme une substance PBT telle que la définit le DOT de l'Union européenne. L'évaluation du risque environnemental suscité par le HMDS a conclu que celui-ci ne présentait pas de risques pour le milieu marin à l'échelon régional, mais qu'il existait un risque hypothétique à l'échelle locale (ceci car aucun des sites n'est situé sur la côte).

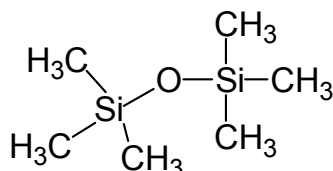
Les actions recommandées sont les suivantes : il est nécessaire de raffiner les ratios PEC/PNEC, surtout les valeurs PEC calculées pour la fabrication de la pénicilline et des produits pharmaceutiques, ceci dans les compartiments eaux douces et eau de mer ; il convient que les Parties contractantes qui sont également des Etats membres de l'Union européenne apportent leur soutien à la réalisation actuelle du réexamen de l'évaluation des risques, et qu'elles communiquent de nouveaux éléments d'information, si elles en disposent, sur l'exposition, les rejets, les émissions et les pertes, qui permettront de raffiner les ratios PEC/PNEC ; il conviendrait qu'OSPAR réévalue les risques que présentent les émissions de HMDS, ceci lorsque de plus amples renseignements auront été recueillis, qu'OSPAR communique le présent document de fond à la Commission européenne et à d'autres organisations compétentes traitant des substances dangereuses, ceci afin de favoriser la prise en compte du présent document de fond dans des conditions cohérentes. Il conviendrait en outre de prendre des précautions particulières dans l'avenir dans la création des nouvelles installations de fabrication du HMDS qui se trouveraient à proximité de la côte.

I. Environmental properties

I.1. General substance information (physico-chemical properties)

Hexamethyldisiloxane (CAS number: 107-46-0) is a low molecular weight linear siloxane (162,38 g/mol). Siloxanes are compounds of low aqueous solubility and are highly hydrophobic.

Formula: $C_6H_{18}Si_2O$



I.1.1. Melting point

IUCLID (2002) reports several values for the melting point of hexamethyldisiloxane. Most of them are close to -68°C . No further details on the methodology and conditions of tests are available. The melting point value used in this risk assessment will be -68°C .

I.1.2. Boiling point

IUCLID (2002) reports several values for the boiling point in the range 90 to $100,5^{\circ}\text{C}$. The first one is not an exact value (ca. 90°C) and the others are very close ($100,1$ and $100,5^{\circ}\text{C}$). No details on the methods used are available. The value of $100,5^{\circ}\text{C}$ at 1013 hPa (Dow Corning, 1985) will be chosen for the risk assessment.

I.1.3. Vapour pressure

One measured value of 54,9 hPa at 25°C (Flaningam, 1986) is reported in IUCLID (2002). In this study the authors have measured the vapour pressures of polydimethylsiloxanes among which HMDS. Vapour pressures measurements were made in an ebulliometer with reference compounds first (water, methylcyclohexane and diphenyl ether) in order to check the validity of the method. Eight measurements were made on each compound over a range of pressures from 4 to 101 kPa. Experimental vapour pressures reproduces literature values to within $\pm 0,07\%$. All the boiling points are the average of at least 3 readings at varied heat inputs to assure that the temperature is not below the true boiling point and the sample is not superheated. A least-squares fit of experimental measurements was made to the Antoine equation. This study is considered valid with restriction. Mazzoni et al (1997) reports a similar value of 56,3 hPa at 25°C however, no details on the methodology used are available. Kohn (2001) reports a value of 63,75 hPa at 20°C (arithmetic mean of two tests). The vapour pressure was determined in a static system with a pressure transducer. The sample was placed in a bath at 20°C and the pressure reading was made after an equilibration time of 20 minutes. The entire process was repeated until two pressure values that were nearly the same. The study is considered valid.

The vapour pressure value of 6375 Pa at 20°C will be used in the following risk assessment.

I.1.4. Solubility

HMDS is of very low aqueous solubility. IUCLID (2002) reports several values of water solubility in the range of 642 to 964 $\mu\text{g/l}$ at 20°C . No detail on the method used is available or sufficient. Varaprath *et al.* (1996) report a value of $930,66 \pm 33,7$ $\mu\text{g/l}$ at 23°C . With the view to avoid problems of colloidal emulsions due to vigorous stirring and by that the determination of higher solubility, the authors propose the use of a non-turbulent determination method. They simply stirred very gently a volume of water beneath a surface layer of the test substance at room temperature. Samples of water were taken at regular intervals up to saturation. Aqueous samples were then analysed by purge and trap GC-MS. The close solubility values obtained over a long period of time suggest that this non-turbulent method yields true water solubility. Moreover, the value determined by this method for hexamethyldisiloxane is in the range of other values quoted before. Therefore the study is considered valid.

Hence, a water solubility value of 930 $\mu\text{g/l}$ (at 23°C) will be used in this risk assessment.

I.1.5. Partition coefficient

a) Air-water partition constant (Henry's law constant)

Kochetkov *et al.* (2001) report two values of the dimensionless form of the Henry's law constant (H_c) for HMDS determined according to two different methods: a static head space (HS) method and a newly developed vapour entry loop method (VEL). A description of both methods is provided in Appendix 1. The air-water partition constant was determined for six volatile methyl siloxanes (three cyclic and three linear siloxanes including HMDS). The determined constant values for HMDS are $1,3 \pm 0,2$ for the head space method and $2,4 \pm 0,2$ for the VEL method.

David *et al.* (2000) report also values of the dimensionless Henry's law constant. The EPICS (equilibrium partitioning in closed system) static method was used to estimate the constant of compounds. Due to the low water solubility of HMDS high variability in the use of the EPICS method was observed. Therefore, the method was modified for this chemical in order to increase its water solubility. Pure water was replaced by a certain amount (from 25 to 50%) of 2-propanol. The mean calculated constant at each point was then regressed over percent 2-propanol and extrapolated to the Y axis intercept which represents pure water. This value (530) was taken to be the estimated dimensionless Henry's law constant of HMDS.

In the experiment reference compounds (methylene chloride, chloroform, TCE and toluene) were used in order to validate the method. The results obtained with these compounds were consistent with what was expected.

Another way to achieve the Henry's constant is to calculate the ratio of the vapour pressure and the solubility of the substance. The dimensionless calculated value obtained is of 365 (with a vapour pressure of 49,51 hPa and a solubility of 930 $\mu\text{g/l}$ at 23°C) which is far from the first two measured values and closer to the last one. This difference with the two first values is explained by Kochetkov *et al.* (2001). In the experiment this difference was not observed for all the tested compounds (e.g. the Henry's constant calculated values for the benzene is 0,22) and it seems that for siloxanes the ratio of vapour pressure to aqueous solubility is invalid because it assumes that the solubility limit of siloxanes will not be exceeded at the pure component vapour pressure. This comes from the fact that for siloxanes the activity coefficient at saturation concentration in the aqueous phase is not similar to that at infinite dilution. Therefore a correction coefficient is needed in order to have a ratio valid (for benzene this correction coefficient is near unity). This percentage correction increases as the compound hydrophobicity increases.

Furthermore even if the value obtained by David *et al.* (2000) is close to the calculated value, the method used by these authors can not be validated as it seems to be not adapted to HMDS and use a lot of extrapolations in opposition to the VEL and HS method which were developed specifically for HMDS. Therefore the result obtained with the EPICS method will be considered invalid.

Calculated value of the dimensionless Henry's law constant can also be obtained by modelling with QSAR. The estimate QSAR value is of 12,4 which is closer to the experimental values obtained by the VEL and HS method.

Considering the fact that both experimental values (Kochetkov *et al.*, 2001) are valid and in the same range, we propose to use the experimental value (obtained with the VEL method specifically developed for HMDS) of air-water partition coefficient of 2,4 (at 28°C) in the risk assessment.

b) Octanol-water partition coefficient (K_{ow})

Bruggeman *et al.* (1984) have determined octanol-water partition coefficient for several polydimethylsiloxanes (PDMS). The apparent hydrophobicity of HMDS was measured by corrected retention times in reversed-phase high performance liquid chromatography on an octadecylsilica (C18) column with methanol/water (90:10) as eluent. Apparent log K_{ow} values were determined from retention indices using a homologous series of n-alkylbenzenes as reference compounds. The apparent log K_{ow} determined for HMDS is of 4,2.

QSAR give an estimated value of log K_{ow} of 4,76 that is in the range of the experimental value.

Hence a log K_{ow} of 4,2 will be used in the risk assessment.

c) Organic-carbon partitioning coefficient (K_{oc})

In the experiment by David *et al.* (2000) an organic-carbon partitioning coefficient of 29 000 l/kg (log K_{oc} = 4,46) is reported. K_{oc} values were determined on the basis of a model describing partitioning between the vapour, liquid, and liquid-phase organic carbon and a statistical analysis. Dimensionless Henry's law constant were determined both in pure water and in raw wastewater. As said in I.1.5.a), the reported Henry's law constant values are not considered valid. Therefore the resulted K_{oc} will not be used in the risk assessment.

The Koc can also be derived by using QSAR equation (E.U., 2003).

$$\text{Log Koc} = 0,52 \log \text{Kow} + 1,02 = 3,2.$$

Hence, the QSAR estimate of log Koc = 3,2 will be used in the risk assessment.

1.1.6. Summary

The physico-chemical properties used in this risk assessment are summarised in Table I-1.

Table I-1. Physico-chemical properties of HMDS

Properties	Value
Molecular weight (g/mol)	162,38
Melting point (°C)	-68 ¹
Boiling point (°C at 1013 hPa)	100,5 ¹
Vapour pressure (hPa at 25°C)	63,75 ¹
Partition coefficient octanol-water (Log Kow)	4,2 ¹
Water solubility (mg/l at 23°C)	0,93 ¹
$K_{\text{air-water}}$	2,4 ¹
Partition coefficient organic carbon-water : log Koc (l.kg ⁻¹)	3,2

1.2. Degradation

1.2.1. Abiotic degradation

a) Photochemical reactions in the atmosphere

Due to a high Henry's law constant, HMDS released to water is expected to rapidly volatilise to the atmosphere. The most effective elimination process in the troposphere results from reaction with photochemically generated species like OH radicals, ozone and nitrate radicals. The specific first order degradation rate constant of the HMDS with OH-radicals (k_{OH}) was determined by Markgraf & Wells (1997). Hexamethyldisiloxane and OH radicals were put together in an irradiated reaction chamber. OH radicals were generated from the photolysis of methyl nitrite (CH_3ONO) in the presence of nitric oxide in air. Reference compounds (cyclohexane and hexane) were employed to determine the OH rate constants. A more detailed explanation is available in Appendix 1.

The results showed no detectable loss of the test substance or the reference products over the experiment. The slope of the linear least-squares analysis with 95% confidence analysis is $0,231 \pm 0,008$. The OH rate constant for hexane is $5,61 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which yields to a k_{OH} value for HMDS of $1,32 \pm 0,05 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is in agreement with previous values measured by Atkinson (1991) and Sommerlade *et al.* (1993), of respectively $1,38 \pm 0,05 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $1,19 \pm 0,30 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Moreover, these values are consistent with the OH rate constant calculated by QSAR of $0,8976 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

A pseudo-first order rate constant for degradation in air of the hexamethyldisiloxane can then be determined with an average estimated concentration of OH-radicals in atmosphere of $5 \cdot 10^5 \text{ molecules} \cdot \text{cm}^{-3}$.

$$k_{\text{deg air}} = k_{\text{OH}} \cdot \text{OHCONC}_{\text{air}} \cdot 24 \cdot 3600 = 0,057 \text{ d}^{-1}$$

An estimated half-life in the atmosphere of 12 days is expected for the HMDS.

The main degradation product observed in the experiment of Markgraf & Wells (1997) in the atmosphere is pentamethyldisiloxanol (MDOH), but experiments made by Atkinson *et al.* (1995) conclude that MDOH is a "second generation" product of water reacting with a siloxane ester product. However, due to the water in

¹ Experimental value

the atmosphere MDOH is most likely an important component in determining the atmospheric assessment of HMDS. This is supported by a yield of MDOH in the experiment of ca. 70% [Markgraf, 1997 #5].

b) *Hydrolysis*

No detailed study on hydrolysis of HMDS is currently available. An hydrolysis study is in progress and should be available but technical problems associated with low solubility and poor recovery have delayed completion of the work. It has been reported that methyl siloxanes are stable to hydrolysis in water (Frye, 1988). However it should be recognised that in protic solvents such as water, HMDS will exist in equilibrium with trimethylsilanol. Nevertheless the rate of hydrolysis has not yet been determined as said before.

In soil, analogy with low molecular weight cyclic siloxanes and also longer chain polydimethylsiloxanes (Xu *et al.*, 1998) suggest that HMDS will hydrolyse. Experiments with PDMS (Xu *et al.*, 1998) show that the degradation process in soil seems to be moisture sensitive and in moist proceeds at a slow rate. As the soil gradually dries from moist to air-dry, the siloxane polymers rapidly hydrolyse to oligomeric silanols and eventually to a water soluble monomer: dimethylsilanediol. This process seems to be catalysed by the presence of clay minerals in the soil which are very reactive constituents. It is not yet clear which soil mineral or minerals are responsible for catalysing PDMS degradation however, in the absence of clay minerals PDMS is stable under mild environmental conditions.

c) *Photolysis*

No studies on photolysis of HMDS in water are available. Observations made during the algal toxicity test suggest that HMDS might be subject to photodegradation in water. In a recent experiment no photolysis of HMDS was however observed during a 24 hour exposure to UV radiation of the parent compound (Böhmer, 2002).

1.2.2. Biodegradation

As hexamethyldisiloxane, is a poorly water soluble and highly volatile substance, the conventional OECD tests for ready biodegradability are very difficult to perform. Typically, organosilicon materials exhibit no BOD in tests for ready biodegradability; exceptions to this include alkoxysilanes, which hydrolyse, to form alcohols that are biodegradable. Based on chemical structure, no aerobic biodegradation of HMDS is expected in water.

Analogy with other silicones suggests that HMDS may be removed from waste water by adsorption onto sewage sludge (Stevens et Annelin, 1997). If sewage sludge is subsequently mixed with soil, it is expected that HMDS will hydrolyse to form dimethylsilanediol (as indicated above). Dimethylsilanediol has been shown to be metabolised by soil microorganisms (Sabourin *et al.*, 1996).

1.3. Bioaccumulation

Only one study reports an experimental value of bioconcentration factor (BCF) of hexamethyldisiloxane. Annelin (1990a) reports a BCF of 1300 for the fish *Pimephales promelas*. The test was run for 14 days as part of an aquatic toxicity test under flow-through saturated conditions. No mortality caused by the HMDS were recorded at the test concentration used for BCF ($93 \pm 11 \mu\text{g/l}$). There is no indication that a steady state was achieved during the test to permit the determination of a realistic BCF. The BCF value was obtained from the ratio of measured levels of HMDS in water and in fish. The study is considered valid with restriction as it is difficult to know if the steady state was achieved.

An other study from the same author (Annelin, 1990b) with the Rainbow trout (*Onchorhynchus mykiss*) is considered as non valid. The test substance appears to be toxic to the fish at approximately $100 \mu\text{g/l}$ under flow-through conditions.

The BCF value can also be extrapolated from the log Kow by using QSAR equation as proposed in the TGD (E.U., 2003).

$$\text{Log BCF} = 0,85 \log \text{Kow} - 0,70 = 741.$$

The calculated BCF value is lower than the experimental value therefore, in order to be protective, the experimental value of 1300 will be used in the risk assessment. The BCF value is higher than 100, therefore there is a potential of bioaccumulation of HMDS along the trophic chain.

1.4. Aquatic toxicity

1.4.1. Water organisms

Very few ecotoxicological studies for aquatic organisms are available for hexamethyldisiloxane. The low water solubility of the substance, combined with its volatility seems to be a major problem in the use of

standardised tests in most of the cases. Only ecotoxicological studies for freshwater organisms are available.

a) *Acute toxicity*

Grau (1991) reports a 96 hour LC50 of 3,02 mg/l with a NOEC of 0,28 mg/l for *Onchorhynchus mykiss* (rainbow trout). The acute toxicity was determined in a flow-through system according to the OECD guideline for testing chemicals n° 203 (OECD, 1992). The results are expressed as nominal concentrations. Some of the test concentrations were above the water solubility of the substance in the test (measured concentration of 650 µg/l at 20°C). The measured concentrations were far lower than the nominal concentrations. Hence, the study was reviewed in 2000 and the LC50 value was recalculated with the measured concentrations (arithmetic mean of the measured concentration on day 0 and the measured concentration on day 4). The final LC50 (96 hours) calculated for *Onchorhynchus mykiss* is 0,46 mg/l (with a NOEC of 0,37 mg/l). The study is considered valid with restriction.

The toxicity of HMDS to algae was tested by Oldersma *et al.* (2003) in a 95-hours growth inhibition test with *Selenastrum capricornutum* according to OECD guideline 201 (OECD, 1984b) extended to 4 days to include requirements given in EPA Guideline EG8 (US-EPA, 1996). The test was conducted in closed filled test vials silanized prior to the test to prevent adsorption of the substance on the tests vials. Modifications according to Mayer *et al.* (2001) were made (reduced initial algae density, increased NaHCO₃ concentration and reduced medium pH) with the aim of meeting the algae biomass increase criteria. Due to the low water solubility of the substance tertiary butyl alcohol (TBA) was used as a solvent carrier for the preparation of the stock solution. A solvent control was therefore included in the test programme. The substance concentrations tested were 0, 0,10, 0,33, 1,0, 1,8 and 3,3 mg/l.

The concentrations in the test medium were measured at the beginning and end of the test (t=95 hours). It should be noted that the pH increased with algae density during the test from 7,4 at the start of the test to 7,4-7,9 after 70h incubation and 8,4-10,0 after 95h.

Effect concentration with regard to the growth rate (E_rC) and to the area under the growth curve (E_bC , biomass) were determined at 70 and 95 hours. The following values (expressed as the geometric mean of the measured concentrations of the test substance at the beginning and end of the test) are reported at 70 hours: $E_rC50 > 0,55$ mg/l and $E_bC50 = 0,18$ mg/l. The values reported at 95 hours are higher than those reported at 70 hours. As the recommended duration of the algal test is 72 hours, values reported at 70 hours will be used. The study is considered valid.

b) *Chronic toxicity*

A chronic daphnia study, according to OECD Guideline 211 (OECD, 1998) was performed by Hoofman *et al.* (2003). Three NOECs were determined depending on the effect measured, i.e. reproduction, condition (colour and swimming behaviour) and mortality. Due to the high volatility and the potential of adsorption of HMDS onto the glass walls of the test vessels, the test was carried out in closed silanized glass vessels. HMDS was added to the test vessels in TBA. The following six nominal concentrations of hexamethyldisiloxane were tested : 0,10, 0,18, 0,32, 0,56, 1,0 and 1,8 mg/l as well as a solvent control with TBA. The exposure time was 21 days and the test solutions were renewed every Monday, Wednesday and Friday. pH values, oxygen concentrations and temperatures were measured weekly. The actual concentrations of HMDS were measured at several days during the exposure time. Low oxygen concentrations (less than 3 mg/l) were measured several times but this was unavoidable due to the closed filled bottles. It is underlined that daphnia can withstand these oxygen concentrations. The results are expressed as measured concentrations of the arithmetic mean of two replicates: NOEC (mortality) = 0,32 mg/l; NOEC (condition) = 0,25 mg/l and NOEC (reproduction) = 0,08 mg/l. The study is considered valid.

Long-term toxicity studies are available on two species of fish: *Pimephales promelas* and *Onchorhynchus mykiss*. Survival, length and weight of tested fish were followed in both studies. In the first one, Annelin (1990b) in a 14 days test under flow-through conditions showed no mortalities of fish (*Pimephales promelas*) exposed to HMDS at 93 µg/l (measured concentration) for fourteen days. In the second one, Annelin (1990a) reports a 9 day exposure test on *Onchorhynchus mykiss* under flow through conditions at a nominal concentration of 930 µg/l (limit of solubility). No mortality was observed until day 8, however on day 9, twenty percent mortality was recorded. The measured concentration in the aquarium was approximately 95 µg/l during the 9-day period. The studies are considered valid with restriction.

Oldersma *et al.* (2003) report chronic values for algae. The method used is described in I.4.1.a). The EC10 (expressed as the geometric mean of the measured concentrations at the beginning and end of the test) reported at 70 hours are: E_rC10 (70h) = 0,09 mg/l and E_bC10 (70h) = 0,01 mg/l. The 70-hour EC10 = 0,09 mg/l based on the growth rate will be used in the determination of the PNEC for aquatic organisms.

1.4.2. Sediment-dwelling organisms

There is no study available on sediment dwelling organisms.

1.4.3. Terrestrial compartment

There is no study available on organisms in soil.

1.4.4. Ecotoxicity to micro-organisms

Mayer *et al.* (2001) studied the effects of hexamethyldisiloxane on activated sludge from an oxidation ditch, treating domestic sewage only. Effects were determined in a respiration inhibition test according to the OECD guideline 209 (OECD, 1984a). The nominal concentrations of HMDS tested were: 0, 0,10, 0,32, 1,0, 3,2, 11, 39 and 100 mg/l. Due to the low solubility of the substance, the test concentrations were prepared by addition of a solution of TBA (tertiary butyl alcohol) with the exception of the two highest concentrations which were added directly to the test medium without explanation.

The aerated sludge, the synthetic sewage feed and the test substance were aerated for three hours at 20°C.

The test control performed with a reference substance (3,5-dichlorophenol) yielded an EC50 value of 13,1 mg/l and the difference between the respiration rates of the two controls of the test was amounted to 2,6 %. Hence the validity criteria of the method are fulfilled. However the concentrations tested were not followed analytically during the test.

No inhibition of the respiration rate was observed within the tested concentration range. The EC50 is therefore assessed to be >> 100 mg/l. The study is considered valid with restriction.

1.4.5. Summary

The ecotoxicological studies available for the HMDS are summarised in Table I-2.

Table I-2: Ecotoxicological data

Organisms	Species	Test type	Endpoint	Value (mg/l)	Comments (reliability)	Reference
Algae	<i>Selenastrum capricornutum</i>	OECD 201, US EPA 40 CFR 797.1050	E _r C50 (70h)	>0,55	Valid (1)	(Oldersma <i>et al.</i> , 2003)
			E _b C50 (70h)	0,18		
	<i>Selenastrum capricornutum</i>	OECD 201, US EPA 40 CFR 797.1050	E _r C10 (70h)	0,09	Valid (1)	(Oldersma <i>et al.</i> , 2003)
			E _b C10 (70h)	0,01		
Crustacean	<i>Daphnia magna</i>	OECD 211	NOECr (21 d)	0,08	Valid (1)	(Hoofman <i>et al.</i> , 2003)
Fish	<i>Onchorhynchus mykiss</i>	Flow-through	LC50(96h)	0,46	Valid with restriction (2)	(Grau, 1991)
	<i>Pimephales promelas</i>	Flow-through	NOEC(14 d)	>0,093	Valid with restriction (2)	(Annelin, 1990b)
	<i>Onchorhynchus mykiss</i>	Flow-through	NOEC(8 d)	0,095	Valid with restriction (2)	(Annelin, 1990a)
Micro-organisms	Domestic sewage sludge	OECD 209	LC50	>>100	Valid with restriction (2)	(Mayer <i>et al.</i> , 2001)

1.5. Toxicological properties

1.5.1. Reproduction studies

No effects were observed in a one-generation reproductive assay in rats (IUCLID, 2002).

1.5.2. Mutagenicity studies

HMDS shows no evidence of mutagenic effects in vitro or in vivo (IUCRID, 2002). HMDS did not cause a positive response in any of the bacterial or yeast tester strains, either with or without metabolic activation.

1.5.3. Carcinogenic potential

A carcinogenicity study has been completed but the final report is not yet available. HMDS was subjected to a two-year combined chronic/carcinogenicity whole-body vapour inhalation study. Prior data generated on HMDS indicated that this substance is non-genotoxic and is of very low acute oral, inhalation, and dermal toxicity.

In the two year life-span study, rats were exposed to 0, 100, 400, 1600 or 5000 ppm of HMDS, 6 hours/day, 5 day/week for up to two years. The results of the inhalation study are detailed in Appendix 2.

And on this basis the conclusion is that the observed effects in the two-year combined chronic/carcinogenicity study are rat-specific and are not relevant to humans or other species. Therefore the substance seems to have no carcinogenic potential.

1.6. PBT assessment

HMDS was selected as a priority substance according to the OSPAR DYNAMEC criteria. In this background document, revision of data and application of the risk assessment based on the criteria outlined in the Technical Guidance Document (E.U., 2003) have led to the following assessment of the substance.

Persistence: No aerobic biodegradation of HMDS is expected in water and the substance seems to be stable in water. The half-life of HMDS in marine water is thus expected to be more than 60 days. Therefore the P criterion is fulfilled.

Bioaccumulation: The reported BCF for fish is 1300. As the trigger value is 2000, the B criterion is not fulfilled. However the steady state was not achieved during the test. Therefore it is difficult to conclude only on this basis on the potential of bioaccumulation of HMDS. However, QSAR calculation gives a BCF value lower (741) than the experimental value and HMDS has not been detected in any fresh or marine waters. Therefore it may be expected that the BCF is less than 2000 and that the B criterion is not fulfilled. As the BCF is higher than 100 the risk of secondary poisoning will however be assessed as the substance is potentially bioaccumulable.

Toxicity: The lowest reported chronic data is the NOEC_{daphnia} (21d) = 0,08 mg/l. A substance is considered to fulfil the toxicity criterion when the long-term NOEC for marine or freshwater organisms is less than 0,01 mg/l. Hence, the T criterion is not fulfilled.

Conclusion on the PBT assessment

According to the EU – PBT criteria, only the P criterion seems to be fulfilled as no aerobic biodegradation of the chemical is expected in water. However due to the high volatility of the chemical, HMDS was almost never detected (see section III) in the water or the sediment (in freshwater as well as in marine waters). The B and the T criteria are not fulfilled. Moreover EU-PBT-TM meeting agreed on the fact that HMDS is not a PBT chemical. Therefore HMDS can not be considered as a PBT substance as defined in the TGD (E.U., 2003) and there is a need to perform an environmental risk assessment of HMDS.

II. Information on sources of HMDS (production and uses)

Five processes involving HMDS that give rise to emissions to the environment have been identified:

- Production and import;
- Generation as a by-product during synthesis of other substances (e.g. from the use of Trimethylsilylchloride (TMCS) and bis(bis(trimethylsilyl))urea (TMSU) for penicillin manufacturing, and Hexamethyldisilazane (HMDZ) for silica treatment in the manufacture of silicone rubbers);
- Reprocessing of HMDS-containing wastes and by-products;
- Use of the substance itself, in several application areas, by companies that are not involved in manufacturing;
- Release from landfill gas.

These processes are analysed in the sub-sections that follow. The diagram overleaf (figure 1) describes the life cycle of HMDS. The diagram should not be over-interpreted, nor should it be assumed that every

location conforms to this picture, which is intended only to summarise the broad mass flows that occur. Waste management via incineration is not shown.

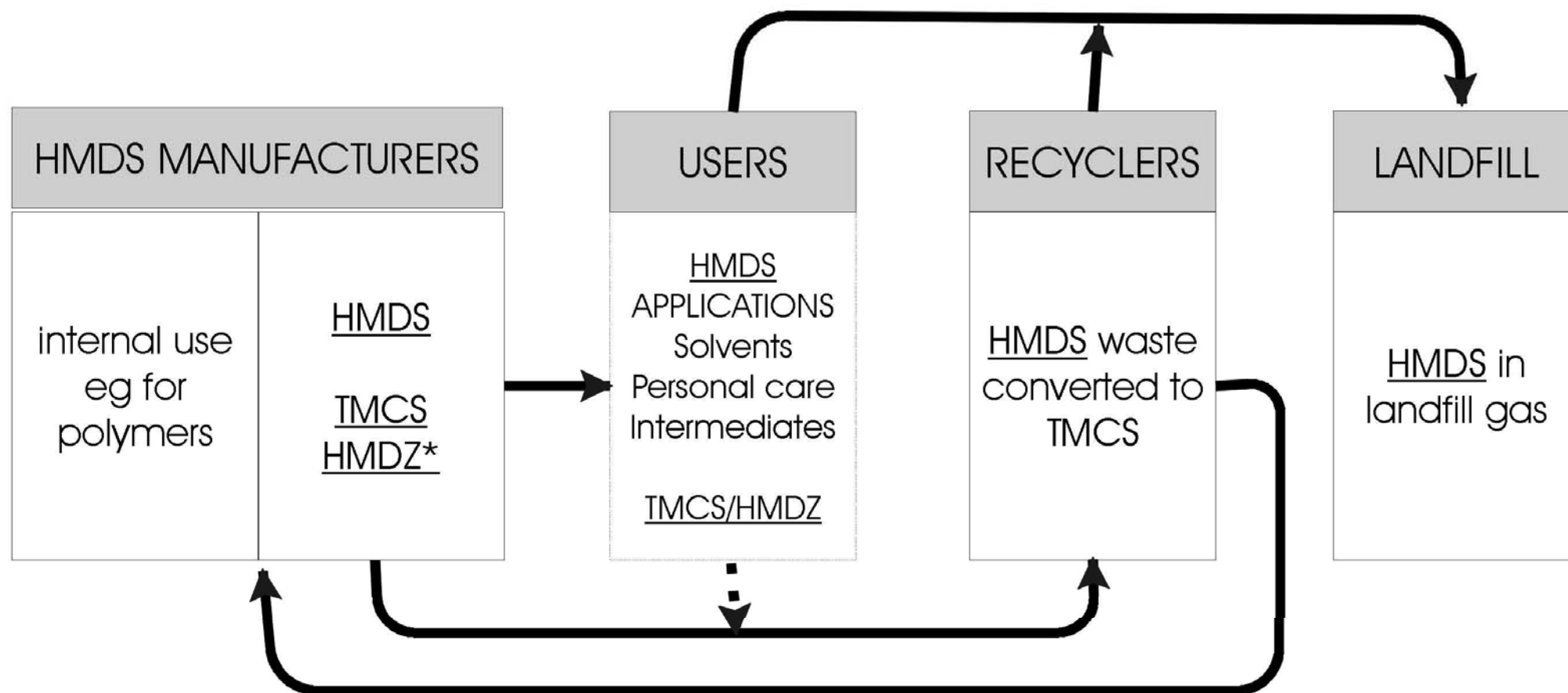
As stated in the introduction, the industry operational data forming the basis of this exposure assessment are commercially sensitive. Therefore every effort has been made to present the information in such a way as to preserve anonymity both of sites at which different processes occur and the localities in which the sites are located. Specific localities have been identified as separate regions (in the TGD sense of that word).

Appendix 4 tabulates the processes by site and region, all of which are indicated using codes only throughout the document.

A number of assumptions operate in respect of the data analysis:

- a. Whilst use tonnage inevitably vary from year to year, we have had access to only a little historic data; however, the evidence is that in most respects the pattern is stable from year to year.
- b. For the silicone production and processing sectors, 300 days activity per year is assumed where no specific pattern is available. This is consistent with TGD defaults in the main.
- c. The extensive consultation undertaken suggests that a high level of mass balance has been achieved. It should be noted that the tonnage data are for 2000, but questionnaires and other research have been realised in 2001. Hence, some changes in the use are being detected; for example, some users in the personal care sector are moving away from HMDS, and more penicillin manufacturers are using a different synthetic route, avoiding use of TMCS.

Site-specific information about the processes (e.g. emission rates and number of days' operation) was obtained from industry sources, the identities of which have not been given for reasons of commercial sensitivity. Where an emission rate of zero for a route has been accepted, it is because information provided (relating to control measures for example) clearly established that emissions are unlikely to occur. These assertions have been based on information about specific procedures.



* as HMDS or trimethylsilanol
underline = potential emission to air and/or water

II.1. Production and import

Excluding by-product, the total production of HMDS in the European Union was 4825 tonnes in 2000. The contributors to the total tonnage are broken down in Table II-1.

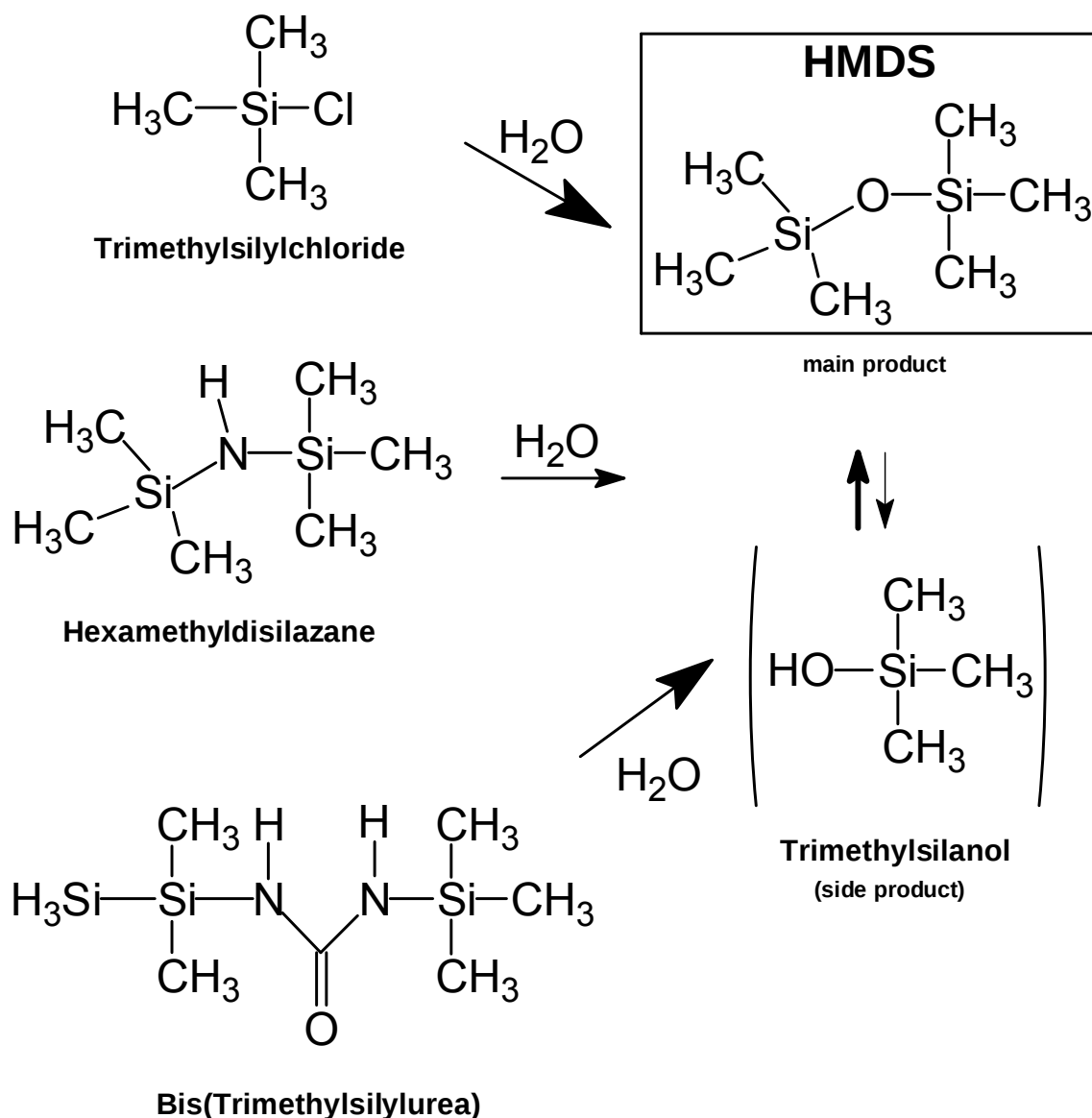
Producer 1 also imports 102 t per year and exports 892 t, and Producer 4 exports 10 t, leaving a total EU tonnage of 4025 t. The total EU tonnage is somewhat higher since there is also generation of HMDS as a by-product in other syntheses (see II.2). Producer 2 is a CES (Centre Européen des Silicones) member company that is not currently producing although there are other processes generating HMDS at that site.

Table II-1. Summary of production tonnage

Code	Ref	Tonnage
Producer 1	1	1803
Producer 3	3	912
Producer 4	4	1320
Producer 5	5	215
Producer 6	6	575

II.2. Generation of HMDS from other silicon-containing substances

A key feature of the life cycle of HMDS is that it is a by-product from the use of several other silicon-containing intermediates. These are trimethylsilylchloride (TMCS), hexamethyldisilazane (HMDZ), trimethylsilanol and bis(trimethylsilyl)urea (TMSU). The scheme below sets out the reaction pathways relevant to the present study. The main uses of those substances are in penicillin manufacture (HMDZ and TMCS), other pharmaceutical manufacture (HMDZ, TMCS and TMSU), production of silicone rubbers (HMDZ) and use as an end-blocker (trimethylsilanol).



All of these substances are known to hydrolyse effectively instantly to HMDS under most emissions conditions, although under dilute conditions, trimethylsilanol can be produced.

Trimethylsilanol can also be used as an intermediate. Synthesis processes during which HMDS is generated as a by-product are summarised in Appendix 6.

The companies/sites upon whose operating practices the site-specific exposure scenarios are based are given code names. These are simplistic and exist simply to indicate the general route of manufacture in the exposure scenario in EUSES. The code names are summarised in Appendix 4. A similar set of code names exists to describe the applications of HMDS.

II.3. Reprocessing of HMDS by-product to hexamethyldisilazane, trimethylsilylurea and trimethylchlorosilane (trimethylsilylchloride – TMCS)

Specialised companies reprocess waste from pharmaceutical use of HMDS precursors. HMDS is converted to HMDZ, trimethylsilylurea or trimethylchlorosilane, which thus form part of the production chain of those substances. The total reprocessing of HMDS was estimated from the information supplied to be 4500 tonnes in 2000. The contributors to the total tonnage are broken down in Table II-2.

Table II-2. Estimated total reprocessing of HMDS

Total HMDS (tonnes)	Code	Tonnage (t)
4500	By-product 3	1500
	By-product 1	2000
	By-product 2	1000

II.4. Uses of HMDS

The applications within which the total HMDS production and import year 2000 tonnage of 4025 tonnes was used are broken down in Appendix 7. Specific information obtained is detailed in tables A2.11 to A2.15 in Appendix 5.

II.5. Overall mass balance

The information from the producer companies and from users has allowed a picture of the use pattern in 2000 to be developed; overall, the tonnage can be tracked to an acceptable level. This is described in Appendix 8. The slight discrepancy between the mass created as by-product and reprocessed (see Appendix 8) probably due to the trend to phase out the use of HMDS for penicillin manufacture in particular (and thus reprocessing). There may have been also some overestimation of the fraction of HMDS present in the waste, leading to an overestimation of the tonnage used.

III. Concentrations in the environment

III.1. Exposure assessment

For the exposure assessment, releases to the environment are derived mainly based on site-specific information on emissions.

According to the TGD the local environment is considered to be the environment near to a site of release. The regional inland environment is taken to represent a highly industrialised area (size is 200 km by 200 km with 20 million inhabitants) and it is assumed that 10% of the European production or use takes place in this area. Summed over all the life cycle stages and all different use patterns, the most significant region of Europe on the basis of total emission levels was region 3.

The continental environment is the size of the EU and is generally used to obtain “background” concentrations of the substance.

A regional scenario for the marine environment has been developed. The size of the coastal compartment is 40 km long, 10km wide and 10 m deep.

Most of the information reported in each following subsections are fully described in Appendix 5.

III.1.1. Release from production

Site specific emissions data from production are available to air and water and supported in part. All five producers give information on emissions to surface water and quantitative emissions to air. Two producers have also information about solid wastes. Emissions and release data are summarised in Table A2.1 in Appendix 5 and in Appendix 6. The process of production takes place in closed system for all five producers and except for one producer wastewater is treated in a waste water treatment plant.

For reasons of simplicity and according to the information obtained from one producer, emissions of HMDS from import are consolidated into site losses from production.

III.1.2. Release from the generation of HMDS from other silicon-containing substances

Emissions for each synthesis process are summarised in Tables A2.2 to A2.9 in Appendix 5. The information in Table A2.5 in Appendix 5 have partly been derived from producers, and partly corroborated by the users. Users in the pharmaceutical sector have not been uniformly responsive. Locating personnel with the best information has not been easy, and sometimes, apparent contradictions were found. Research into the sales and life cycle of TMCS and HMDZ might assist.

One penicillin manufacturer (using TMCS) has given a site effluent concentration. One pharmaceutical manufacturer (using HMDZ) has given non-quantitative information on the process and wastewater treatment. One pharmaceutical manufacturer (using TMCS) sent HMDS for reprocessing but is no longer

operational. Five sites emitting HMDS from treatment of silica with hexamethyldisilazane in production of silicone rubbers give information about losses to air.

In the manufacture of penicillin, TMCS or HMDZ is used to produce the silylated urea, which is reacted to an intermediate; the trimethyl silyl group is then split off to form HMDS and the required end product. These three reactions are not 100% efficient, and silicon-containing wastes are generated and separated at each stage. In common with most pharmaceutical wastes, they are thought to be incinerated.

Emissions of HMDS accompanying use of trimethylsilanol as end blocker was not implemented in EUSES because losses were consolidated into site losses for the single site performing this process.

III.1.3. Release from reprocessing of HMDS by-product

Most of the processes of reprocessing of HMDS are carried in closed systems. Hence, emissions to the different compartments are set to zero. There are however some information regarding releases for the industries that are reported in Table A2.10 in Appendix 5.

III.1.4. Release from uses

Emissions associated with the different uses are summarised in Tables A2.11 to A2.15 in Appendix 5.

a) Releases from use as an intermediate in synthesis of other substances

Size of the site losses are described throughout the document and Table A2.11 in Appendix 5 lists some minor releases to water and the presence of a WWTP. However, no data on volume or concentration of HMDS in effluent is available. There is only an indication of concentration in river close to discharge point that gives a concentration below limit of detection (0,05 µg/l).

b) Releases from use in personal care products

Emissions associated with use in personal care products are summarised in Tables A2.12 to A2.14 in Appendix 5 and in Appendix 6.

The research has determined that the distributors do not repackage the substance, and therefore it is considered that no significant losses occur at the facilities of the distributors, and they are not considered further. However, the distributors have not been fully open with information about the number and location of their clients, and the majority of the minor formulators contacted have not responded despite repeated efforts from the authors. Therefore the picture in this sector is one in which defaults have had to be used in part. An approach to a major trade association yielded no response. Clearly, more information about this sector is desirable. The entire tonnage has been put into the private use stage using defaults.

c) Release from landfill sites

The importance of this source of HMDS, which is not known at present, has not been fully delineated. It is known that concentrations of trimethylsilanol/HMDS can be in the range 1 – 2 mg/m³. Typical gas production rates are 50 000 m³/d, i.e. 0,05 to 0,1 kg/d at a site (see section A2.5 in Appendix 5 for reference material). These losses are best considered as regional ones. Estimating that there may be 100 such sites in a region, the regional emission would be up to 10 kg/d. This emission is expected to be similar in each region.

d) Summary of release estimates

The release factors (default and site specific) are summarised in Appendix 10. From this table, it can be seen that the actual distribution of sites tend to be more concentrated than the defaults usually applied (E.U., 2003). However, the exposure model is still useful since the present data represent a reasonable worst case.

Regarding the defaults for release factors, it can be seen that where monitoring data exist the emission rates are lower than predicted. A comparison of daily local loss rates and defaults was also made and is reported in Appendix 10.

Information from production, use and emissions of HMDS during the different life cycle stages is summarised in Appendix 10. The defaults are those used in the EUSES model.

III.2. Aquatic compartment

III.2.1. Inland environment

The available site-specific information has been used to create exposure scenarios in EUSES 2.0, from which PECs have been developed. Based on the known site distribution and on emission levels, the PEC for local and regional air, water and soil were estimated. Beside these calculated concentrations, the available measured environmental concentrations are also reported.

a) *Calculation of PEC_{local}*

The main region is region 3 and it should be noted that because the main region was selected based on the emissions over all applications and use patterns of HMDS, it should not be assumed that there are not significant emissions in the other regions for individual uses. Therefore, PEC values for each local loss are presented also region by region.

EUSES 2.0 estimates PECs for surface water for each use assuming that the amount of substance released by site is released to waste water that enters a waste water treatment plant. Specificity of each WWTP has been included on a site-specific base in EUSES 2.0. It is assumed that no biodegradation occurs. The final assumption in calculation of the PEC for water is that the effluent from the sewage treatment plant is diluted by a factor of 10 (default value) for chemical industries on entering the surface water.

PEC_{local} for effluent STP, water and sediment for each application in region 3 are presented in Appendix 11. When this was possible a site specific scenario has been used. PECs for the sediment compartment were calculated by EUSES 2.0 using the partitioning coefficient method.

There are in addition releases in geographical locations outside the main region that must be considered. These values were obtained by running EUSES 2.0 separately for each region. The same basic approach was followed except that, to save time, the regional releases were also calculated and entered into EUSES 2.0 manually.

These runs give rise to PEC values as shown in Appendix 11. The term production here encompasses intended production and by-product HMDS generated from other intermediates.

b) *Calculation of $PEC_{regional}$ and $PEC_{continental}$*

$PEC_{regional}$ and $PEC_{continental}$ were calculated by the EUSES 2.0 model and are reported in Table III-1.

Table III-1. Estimated regional concentrations

	PEC_{water} (µg/l)	PEC_{sed} (mg/kgwwt)
Region 3	2,74E-02	1,48E-03

c) *Monitoring in the freshwater environment.*

Levels of HMDS in municipal wastewater and downstream river sediments are available (Degussa, 2001b). Dates of sampling are not provided, however all the values are on the basis of analysis performed over the last two years. Samples were collected mainly by CES member companies. Details of the studies are presented in Appendix 13.

Influent and effluent from two wastewater treatment plants were sampled in the United Kingdom. The concentration of HMDS in influent was 0,16 and 0,5 µg/l respectively. Effluent concentrations at both plants were less than 0,02 µg/l which is the level of detection. The sites were not located near any major facility. Therefore, they only represent the local private use.

Recent results (CES, 2002) from a manufacturing plant using HMDS in the production of personal care products are also available on concentrations in inflow and outflow of the waste water treatment plant plus the receiving water. Triplicate samples of each were done. The influent and effluent concentrations were 0,6 - 0,7 µg/l and not detectable (<0,1 µg/l) respectively. The concentration in the receiving water was also not detectable (<0,1 µg/l). In addition, no HMDS was detected in the WWTP sludge (<10 µg/kg dwt).

Another study measured the maximum concentration of HMDS in effluent from waste water treatment plants receiving waste from three silicone manufacturers as 0,6 µg/l. At a fourth site, where there was no on-site treatment of effluent, the concentration of HMDS in the outfall was 1,4 µg/l. In the three cases where there was discharge into a major river, the concentrations were found to fall to below the detection limit (>0,02 µg/l) within a short distance downstream of the discharge point.

A study reports concentrations of HMDS in the influent of three municipal WWTPs in Germany. The highest level of HMDS measured is of 0,05 µg/l. For reason of confidentiality no more information is available on this study.

Analysis of wastewater from penicillin manufacture which showed no HMDS are also available. The only silicone product detected was trimethylsilanol at a concentration of 0,04 mg/l or less.

The analytical results from the first two studies report similar results. The estimated values given by EUSES maybe overestimate the different concentrations. However the measured concentration reported in the third

study in the effluent is not really different from the estimated value. Therefore, the PEC values estimated by the EUSES model will be used in the risk assessment.

Concentrations of HMDS in sediment were also measured in different locations. Eight sediment samples were collected along the river Rhine equidistant from Karlsruhe to Rotterdam. The concentration of HMDS, measured by GC/MS was below the level of detection (1 µg/kg dwt) in all samples.

River sediments were also collected 3,5 km downstream from one of the WWTP in UK quoted before. The concentration of HMDS was also below the level of detection (1 µg/kg dwt).

III.2.2. Marine environment

a) Calculation of PEC_{local}

None of the sites dealing with HMDS are located or discharged directly to the sea. Local PEC calculations were nevertheless performed by taking into account the worst case scenario developed in the TGD and in EUSES 2.0 (no STP and a dilution factor of 100). The local PEC are reported in Appendix 11.

b) Calculation of $PEC_{regional}$ and $PEC_{continental}$

As for the inland environment, a regional scenario for the marine environment has been developed specifically for the coastal environment and is described before. It takes into account direct input from the regional river water but also direct emissions from the inland sources and direct emissions into the sea compartment if relevant. This scenario can be modelled with the multimedia fate model recently developed by the RIVM and that was implemented in the last version of EUSES, EUSES 2.0 (European Chemical Bureau, 1997).

Regional PECs for the marine environment (water and sediment) in the main region are reported below in Table III-2.

Table III-2. Regional exposure concentration in the coastal sea environment

	PEC _{marine water} (mg/l)	PEC _{marine sed} (mg/kg ww)
Region 3 (dilution factor)	2,34E-06	1,06E-04

c) Monitoring in the marine environment

Levels of HMDS in the marine environment are available only for the sediment compartment. HMDS was not detected (detection limit < 0,02µg/l) in samples of marine water as it is detailed in Appendix 13.

Regarding the sediment, a study from (Degussa, 2001a) is available in a marine location in the United Kingdom. Six sediment samples were collected by the Environment Agency in UK in the sediment of a bay. Two of them contained measurable quantities of HMDS at 20 µg/kg dwt and 7 µg/kg dwt. HMDS was not detected in the associated water. The others were <3 µg/kg dwt. Using the conversion factor between dry weight and wet weight given in EUSES the concentrations are 7,7 µg/kg ww and 2,7 µg/kg ww, and <1,2 µg/kg ww respectively. This bay is receiving water from a large urban city area, and possibly from a production site, although this is about 20 km away. It is not realistic to model these data on a site-specific basis, since this would require a very detailed knowledge of

- The population associated with the discharges to water, for private use;
- The presence of any downstream users of HMDS in the area;
- The volume of sediment in the bay;
- The tidal pattern in the bay.

The measurements are consistent with this site being considered as local not as regional background.

Another study reports marine sediment concentrations in samples from two areas previously used for sewage sludge disposal off the coast of Scotland (LAS St. Abbs and Bell Rock). The samples were analysed by GC/MS in addition to two respective control samples. The concentration of HMDS in the sampled sediment was below the detection limit of 1 µg/kg in all samples.

Six marine estuarine sediment were also sampled in the United Kingdom in 2001 and the concentrations of HMDS measured were also below the detection limit of 1 µg/kg dwt in all samples. The associated water was analysed but the concentration was below the detection limit (1 µg/l).

All these results are consistent with the estimated regional concentration of 0,073 µg/kg ww in the marine sediment.

III.2.3. Terrestrial compartment

a) Local, regional and continental estimated concentrations in soil

Predicted concentrations of HMDS in soil have been calculated using EUSES 2.0 for the local (all regions), regional and continental scenarios. The estimated concentrations are reported in Appendix 11. The concentrations were determined using the partitioning coefficient between soil and water.

b) Levels in soil

There is no available measured concentrations of HMDS in soil.

III.2.4. Atmosphere

a) Local, regional and continental estimated concentrations in air

Predicted concentrations of HMDS in air have been calculated using EUSES 2.0 for the local (all regions), regional and continental scenarios. The estimated concentrations are reported in Appendix 11.

b) Monitoring in the atmosphere

A study from (Degussa, 2001a) reports concentrations of HMDS in air from eleven locations undertaken between January and May 2001. Results are reported in Table III-3. A brief review of a CES report, which is available under separate cover, is available in Appendix 13 for more details on the sampling and analytical method used.

Table III-3. Measured levels of HMDS in different locations

Location of sampling	No. of samples	Highest level of HMDS	Further information
Around residential buildings	18	0,3 µg/m ³	-
City areas	18	ND (<0,1 µg/m ³)	-
Rural areas	6	ND (<0,1 µg/m ³)	-
In vicinity of silicone-handling plants	58	50,4 µg/m ³	median value of 0,1 µg/m ³ ; and 90% of these samples were <7 µg/m ³

These data are useful to compare with the local PEC_{air} values reported in Appendix 11. In general the measurements are of a similar order of magnitude or higher than the EUSES 2.0 local outputs, and therefore there is no cause for any concern regarding the models. The monitoring data at a wider level are generally supportive of the model results, but there are not sufficient data to make the use of the EUSES 2.0 based model unnecessary, or to amend it in any way.

Another study reports concentrations of HMDS in the air measured in 2000 from a forest area in the United Kingdom. Six samples were taken and no HMDS was measured.

III.2.5. Secondary poisoning

Predicted concentrations in fish have been calculated both in the inland and the marine environment by the EUSES 2.0 model. PEC values are reported in Appendix 11.

The concentrations in fish are calculated from the concentration in the surface water and the measured BCF (1300 in fish) according to the equations for predators (fresh and marine water) and top-predators (marine water) reported in the TGD. As there is no direct release in the marine compartment we can expect that preys of marine predators and top-predators are only exposed to regional concentrations. Calculated made by EUSES 2.0 for the marine that takes into account local concentrations are nevertheless also reported in Appendix 11.

Freshwater predators

$$PEC_{oral, predator} = (0,5 PEC_{local} + 0,5 PEC_{regional}) \cdot BCF_{fish} \cdot BMF$$

Marine predators and top-predators

$$PEC_{oral, predator} = PEC_{regional} \cdot BCF_{fish} \cdot BMF$$

PEC_{oral, predator}: concentration in the food of the predator (mg.kg⁻¹)

PEC_{oral top-predator}: concentration in the food of the top-predator (mg.kg⁻¹)

PEC_{local}: annual average predicted local environmental concentration (mg.l⁻¹)

PEC_{regional}: predicted regional (fresh or marine waters) environmental concentration (mg.l⁻¹)

BCF_{fish}: bioconcentration factor (1300 l.kg⁻¹)

BMF: biomagnification factor (1)

The calculated concentration in the food of predators and top-predators in the marine environment is of 3,04 µg.kg⁻¹ (this value was obtained with a marine regional concentration of 2,34.10⁻⁶ mg/l).

IV. Effects assessment

IV.1. Aquatic compartment

IV.1.1. Water column

Chronic values are available on freshwater organisms for only two trophic levels (algae and crustacean). The long-term values obtained with fish will not be considered for the determination of the PNEC as the duration of the studies (14 days and 9 days) is short and almost only mortality was recorded. There are no observed effect concentrations (NOEC) for *Daphnia magna* and EC10 for *Selenastrum capricornutum*. The most sensitive chronic value is reported for *Daphnia magna* in a 21 days study. The obtained NOEC value is 0,08 mg/l, expressed as measured concentrations. An assessment factor of 50 is applied on the NOEC (21 days) obtained with *Daphnia magna*, which gives:

$$\text{PNEC}_{\text{fresh water}} = 0,08/50 = 0,0016 \text{ mg/l}$$

$$\text{PNEC}_{\text{fresh water}} = 1,6 \text{ µg/l}$$

Regarding the PNEC for the marine compartment, only ecotoxicological results on freshwater organisms are available. Hence, according to the TGD (E.U., 2003) an assessment factor of 500 is applied to the NOEC value, which gives:

$$\text{PNEC}_{\text{marine water}} = 0,16 \text{ µg/l}$$

There is also toxicity data available for micro-organisms in domestic sewage sludge. No effect on the respiration rate was observed at the concentrations tested which gives an EC50 >100 mg/l. As no effects were observed the value of 100 mg/l can be considered as a NOEC. An assessment factor of 10 can be applied to this value which gives a PNEC for the micro-organisms of 10 mg/l.

$$\text{PNEC}_{\text{micro-organisms}} = 10 \text{ mg/l}$$

IV.1.2. Sediment

There are no studies available on sediment-dwelling organisms. In the absence of any ecotoxicological data, the PNEC may be calculated using the equilibrium partitioning method from the PNEC for aquatic organisms and the suspended matter-water partition coefficient.

The suspended matter-water partition coefficient can be calculated from the following equation:

$$K_{\text{susp-water}} = F_{\text{water}_{\text{susp}}} + F_{\text{solid}_{\text{susp}}} \cdot \frac{Kp_{\text{susp}}}{1000} \cdot RHO_{\text{solid}}$$

with $K_{\text{susp-water}}$: partition coefficient suspended matter-water (m³.m⁻³)

$F_{\text{water}_{\text{susp}}}$: volume fraction water in suspended matter (0,9 m_{water}³.m_{sed}⁻³)

$F_{\text{solid}_{\text{susp}}}$: volume fraction solids in suspended matter (0,1 m_{solid}³.m_{sed}⁻³)

Kp_{susp} : $F_{\text{oc}_{\text{susp}}} \cdot K_{\text{oc}}$

Kp_{susp} : partition coefficient solid-water in suspended matter (158,5 l/kg)

$F_{\text{oc}_{\text{susp}}}$: weight fraction of organic carbon in suspended matter (0,1 kg_{oc}.kg_{solid}⁻¹)

K_{oc} : partition coefficient organic carbon-water (1585 l/kg)

RHO_{solid} : density of the solid phase (2500 kg_{solid}.m_{solid}⁻³)

Then $K_{\text{susp-water}} = 0,9 + 0,1 \times (0,1 \times 1585)/1000 \times 2500 = 40,5 \text{ m}^3 \cdot \text{m}^{-3}$

$$\text{And } PNEC_{\text{sed}} = \frac{K_{\text{susp-water}}}{RHO_{\text{susp}}} \times PNEC_{\text{water}} \times 1000$$

With RHO_{susp} : bulk density of suspended matter ($1150 \text{ kg} \cdot \text{m}^{-3}$)

$$PNEC_{\text{freshwater sed}} = (40,5/1150) \times 1,6 \cdot 10^{-3} \times 1000 = 0,056 \text{ mg/kg wet weight}$$

$$PNEC_{\text{marine sed}} = (40,5/1150) \times 0,16 \cdot 10^{-3} \times 1000 = 0,0056 \text{ mg/kg wet weight}$$

IV.2. Terrestrial compartment

There are no studies available on soil organisms. In the absence of any ecotoxicological data, the PNEC may be calculated using the equilibrium partitioning method from the PNEC for aquatic organisms and the soil-water partition coefficient.

The soil-water partition coefficient can be calculated from the following equation:

$$K_{\text{soil-water}} = Fair_{\text{soil}} \cdot K_{\text{air-water}} + Fwater_{\text{soil}} + Fsolid_{\text{soil}} \cdot \frac{Kp_{\text{soil}}}{1000} \cdot RHO_{\text{solid}}$$

with $K_{\text{soil-water}}$: partition coefficient soil water ($\text{m}^3 \cdot \text{m}^{-3}$)

$Fwater_{\text{soil}}$: volume fraction water in sediment ($0,2 \text{ m}_{\text{water}}^3 \cdot \text{m}_{\text{soil}}^{-3}$)

$Fair_{\text{soil}}$: fraction air in soil ($0,2 \text{ m}_{\text{water}}^3 \cdot \text{m}_{\text{soil}}^{-3}$)

$K_{\text{air-water}}$: partition coefficient air water ($2,4 \text{ m}^3 \cdot \text{m}^{-3}$)

$Fsolid_{\text{soil}}$: volume fraction solids in sediment ($0,6 \text{ m}_{\text{solid}}^3 \cdot \text{m}_{\text{soil}}^{-3}$)

$$Kp_{\text{soil}} = Foc_{\text{soil}} \cdot Koc$$

Kp_{soil} : partition coefficient solid-water in sediment ($31,7 \text{ l/kg}$)

Foc_{soil} : weight fraction of organic carbon in sediment ($0,02 \text{ kg}_{\text{oc}} \cdot \text{kg}_{\text{solid}}^{-1}$)

Koc : partition coefficient organic carbon-water (1585 l/kg)

RHO_{solid} : density of the solid phase ($2500 \text{ kg}_{\text{solid}} \cdot \text{m}_{\text{solid}}^{-3}$)

Then $K_{\text{soil-water}} = 48,2 \text{ m}^3 \cdot \text{m}^{-3}$

$$\text{And } PNEC_{\text{soil}} = \frac{K_{\text{soil-water}}}{RHO_{\text{soil}}} \times PNEC_{\text{water}} \times 1000$$

With RHO_{soil} : bulk density of wet soil ($1700 \text{ kg} \cdot \text{m}^{-3}$)

$$PNEC_{\text{soil}} = (48,2/1700) \times 1,6 \cdot 10^{-3} \times 1000 = 0,045 \text{ mg/kg wet weight}$$

IV.3. Atmosphere

The effects assessment of chemicals in water and soil cannot be applied yet in the same manner to the atmosphere. Hence, no PNEC for the air compartment will be estimated and only a qualitative risk assessment will be done. Only abiotic effects could be estimated as no toxicological results are available on animal or plant species. There is no evidence of an influence of HMDS on global warming or ozone depletion/formation in the stratosphere. The atmospheric lifetime of HMDS is less than one year (12 days).

IV.4. Secondary poisoning

The log Kow value of 4,2 and the BCF value of 1300 in fish indicate a potential for bioaccumulation of HMDS in aquatic organisms.

IV.4.1. Oral toxicity

IUCLID (2002) reports several studies on chronic oral toxicity. One study reports a NOAEL of 8 mg/kg body weight in rat after an exposure period of 28 days to contaminated food. The test follows the OECD guideline 407 (Repeated Dose Oral Toxicity – Rodent: 28 days or 14 d study). The doses tested were 8, 40, 160 and 640 mg/kg body weight. No mortality or clinical signs were reported in any dose group but an increase of eosinophilic bodies in the kidney only of males rats were noticed at 40 mg/kg and above. This seems to be a

specific effect to rat. Actually several studies have shown this kind of nephrotoxicity with other substances such as limonene (an hydrocarbon monoterpene). The toxicity observed in male rats is due to the presence in the male rats urine of a naturally low molecular protein, the alpha 2μ-globulin. This protein is found in abundance only in adult male rats and is not synthesised by any other species (Friedli, 1992); (IARC, 1999). Therefore, this test results will not be used for the risk assessment as this is not relevant for other species. Other studies report NOAEL values much higher than this latter (around 1000 – 1500 mg/kg food). A 28 days oral toxicity studies on male and female rats was performed by Isquith *et al.* (1988). The doses tested were 1000 and 1500 mg/kg/day. No effects were observed at both doses and in groups control. Hence a NOAEL of 1500 mg/kg/day was determined. A conversion factor of 10 is applied to this value to express the value as a concentration in food. The final value is $NOEC_{mammal} = 15 \text{ g/kg food}$.

IV.4.2. PNEC for secondary poisoning

Only one result on oral toxicity study on mammals is available. Hence the $NOEC(28d) = 15 \text{ g/kg food}$ will be used in the determination of the $PNEC_{oral}$. An assessment factor of 300 is applied to this value as recommended by the TGD (E.U., 2003).

$$PNEC_{oral} = 50 \text{ mg/kg food.}$$

V. Risk assessment

V.1. Aquatic compartment

V.1.1. Inland environment

a) Water

The $EC_{water}/PNEC_{water}$ ratios reported in Appendix 12 don't indicate a significant risk to freshwater organisms from almost all the local sources. However the risk ratios are relatively high for a few specific sites. These sites can be separated into different groups: use of HMDS in personal care products such as solvent or cosmetic formulation, penicillin manufactures and the generation of HMDS as a by-product during synthesis of other substances.

In the first case, most of the time there were not on-site data, therefore the exposure assessment is only based on defaults values. In order to know precisely the risk for the freshwater compartment, the PEC should be refined in the light of on site data from these specific uses. Moreover monitoring data from a manufacturing plant using HMDS in the production of personal care products showed no HMDS in the receiving water (detection limit $< 0,1 \mu\text{g/l}$). The calculation made on this site with the available data show no significant risk for the aquatic organisms.

For penicillin manufactures and by-products, the assessment is based on the tonnage of precursors used in the synthesis. As explained before the HMDS is only formed, in these manufactures, as an intermediate of synthesis. Therefore the scenarios used are worst case scenarios which may overestimate the exposure concentration in the environment. Moreover, regular analysis of wastewater from penicillin manufactures showed no HMDS (the only silicone product detected was trimethylsilanol).

In conclusion the risk to freshwater organisms due to production and use of HMDS doesn't seem to be of a great concern particularly with regard to the high volatility of this compound. However the high PEC/PNEC ratios identified in several sites, mainly from penicillin and pharmaceuticals plants, due to a lack of knowledge on these sites should be further studied in order to refine the PEC values.

b) Sediment

The PEC and the PNEC for the sediment compartment were calculated from the sediment-water partition coefficient. Therefore, the risk calculation for the sediment compartment is the same as the one for the water column.

V.1.2. Microorganisms in the STP

The PEC/PNEC ratios are reported in Appendix 12. As all ratios are below 1, there is at present no risk for microorganisms in STP due to HMDS.

V.1.3. Marine environment

a) Water

The regional $PEC_{marine\ water}/PNEC_{marine\ water}$ ratio is reported in Table V-1. In addition to the calculations made at the regional level. Local PEC/PNEC ratios were also calculated in order to be protective of the environment (Appendix 12). It is assumed in the TGD that the dilution in marine water is higher than in

freshwater by a factor of 10 and that there is no use of STP. Local risk ratios are almost all above 1 by using the TGD worst case described before, however we have to underline the fact that all these sites are not located on the sea and are based in the freshwater risk assessment on realistic data that indicate that most of the time the industrial sites have a WWTP.

Local PEC/PNEC ratios are between 1 and 10 for HMDS use in personal care (formulation and private use) and in penicillin manufacture and by-product. In these cases, most of the time default TGD values were used as no information on site were available or when information on sites releasing substance in freshwater were used there was use of a WWTP. Therefore the PEC/PNEC ratios may be overestimated.

Local PEC/PNEC ratios are between 10-100 for one producer, in the formulation of HMDS in solvent and in penicillin manufacture. Specific on site information is available on the site of production of the substance located in the inland environment. HMDS is used there as an intermediate and there is a WWTP. Therefore the PEC/PNEC ratio for the marine environment may be overestimated and is not representative right now of a real situation. For the step of solvent formulation and the penicillin manufacture TGD default values were used and therefore the risk ratios may be overestimated.

Local PEC/PNEC ratios are above 100 only in penicillin manufacture and where HMDS is used as an intermediate or is generated as a by-product. In these different situations most of the time only default values were available and therefore the risk ratios may be overestimated.

In view of the reported ratios at the regional scale there is at present no risk for organisms living in the marine environment due to HMDS.

Table V-1. PEC/PNEC ratio for the marine water compartment

	PEC _{marine water} (µg/l)	PEC/PNEC ratio
Region 3	1,53E-06	9,56E-04

In conclusion there seems to be no risk for the marine environment at the regional scale. The calculation of the risk ratios at the local scale indicate risks for the organisms living in the marine waters. However for the moment the scenarios developed are hypothetical as none of the sites are located on the coasts. In case the HMDS industry decides to implement such sites on the coast a in depth risk assessment should be realised.

b) *Sediment*

PEC/PNEC ratios for the marine sediment are the same as those for the marine water column as it is explained in the inland environment section.

V.1.4. Terrestrial environment

The PEC/PNEC ratios for the terrestrial compartment are reported in Appendix 11. The PEC/PNEC ratios above one are almost the same as those reported for the water compartment (which is not surprising as the calculations made by EUSES 2.0 used the partition coefficient methodology). Therefore the conclusions are the same than those for the water compartment.

V.1.5. Atmosphere

HMDS has an atmospheric half-life of 12 days. In the POPs convention it is stated that substances that have an atmospheric half-life of two days or more still remain in air after 8-10 days and that during that time the substance may be transported several thousand kilometres. Therefore there is the possibility of long-range transport. However it is also clearly stated that the best way to establish whether or not long-range transport occurs is through direct measurements in, e.g. monitoring programs. There is really few data on presence of HMDS in water and/or biota. Moreover this substance is really volatile (vapour pressure of 6375 Pa), therefore it is a gas at normal temperature and then the possibility of deposition in remote areas of HMDS is really low.

V.1.6. Secondary poisoning

a) *Inland environment*

The PEC_{oral}/PNEC_{oral} ratios are reported in Appendix 12. There seems to be no risk of secondary poisoning in the freshwater environment due to HMDS.

b) *Marine environment*

If we consider that the preys of predators and top-predators are only exposed to regional concentration, the risk ratio is 6,04E-05 and therefore there seems to be no risk of secondary poisoning. If we consider risk

ratios taking into account local concentrations only one is around one (1,08) and the scenario is only based on default values where HMDS is generated as a by-product.

Therefore, at present there seems to be no risk of secondary poisoning in the marine environment due to HMDS.

VI. Desired reduction and identification of possible measures

VI.1. Achieving the desired reduction

VI.1.1. OSPAR Targets

In 2000, HMDS (Hexamethyldisiloxane) was included in the OSPAR list of chemicals for priority action. The OSPAR objective with regard to hazardous substances is to continuously reduce discharges, emissions and losses with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances. Every endeavour will be made to move towards the target of cessation discharges, emissions and losses of hazardous substances by the year 2020 (OSPAR, 1998).

At OSPAR 2002, the guidance on the role of marine risk assessment, which gives, in particular advice on the urgency of taking measures based particularly on the PEC/PNEC ratios and the PBT properties of the chemicals (cf. Annex 6 of OSPAR 2002 Summary Record) was adopted by OSPAR. We have attempted to apply this guidance to the document and reached the following conclusions. However, these conclusions are considered to be provisional, and could change in the light of further information.

HMDS cannot be considered a PBT chemical as defined in the TGD (E.U., 2003). Moreover this is a highly volatile substance (vapour pressure of 6375 Pa) which explains why there are so few and such low monitoring data of this chemical in the environmental compartments.

The risk assessment shows at present no risk for the marine environment at the regional scale.

On the local scale, more information is nevertheless needed for some specific uses in order to refine the exposure values especially for penicillin and pharmaceuticals manufactures where only default values were used.

None of the sites dealing with HMDS are located on the coasts. Therefore the local assessments realised for the marine environment are just hypothetical situations. However PEC/PNEC ratios higher than 100 have been calculated and therefore special care should be taken in the future when implementing a new site dealing with HMDS.

In conclusion, at present there is no need for reduction or measures on the production and use of HMDS. However for some specific uses (penicillin manufactures and pharmaceuticals manufactures) there is a need to refine the exposure data with a best understanding of the processes used.

VI.1.2. OSPAR's role in achieving the desired targets

The results of the risk assessment of the HMDS indicates that there is at present no risk for the marine environment.

No sites of production or processing of the HMDS are located on the coasts at the moment. However the calculated local PEC/PNEC ratios according to EUSES 2.0 indicate that there might be a risk due to releases of HMDS through specific local situations and processes. Therefore OSPAR Contracting Parties should be aware of that and give a special attention in the future on the implementation of new manufactures on the coasts.

VI.2. Identification of possible measures

VI.2.1. Review of existing OSPAR, EU and National Measures

No measures have been taken to date in any of these forums.

VI.2.2. Choice for actions

a) General considerations

The initial results of the risk assessment indicate that there should be concern over some specific uses of HMDS in the freshwater environment. At the regional scale there is no risk at present for the marine environment.

It should be noted that the PEC/PNEC ratios need to be refined and especially the PEC values in penicillin and pharmaceuticals manufactures for fresh and marine water compartments where only default values were available.

Special care should be taken in future in developing new manufacturing installations for HMDS near the coast, since calculated local PEC/PNEC ratios can be really high in such conditions.

b) *Action in the EC*

Contracting Parties which are also EU Member States should support the ongoing development of the Risk Assessment Review and provide new information, if available, on exposure and discharges, emissions and losses, which would enable the PEC/PNEC ratios to be refined.

To support this process and ensure that the information available in this background document and the conclusions reached by OSPAR are generally taken into account in the approach of the European Community, OSPAR should communicate this document to the European Commission.

c) *Action in OSPAR*

OSPAR should re-evaluate the risks posed by HMDS releases when further information has been collected. Any associated measures which might be justified in the light of new findings should be addressed through the background document review process.

VI.2.3. Action in other forums

To ensure that the information in this background document can be considered in the context of other international agreements which deal with hazardous substances, and with which Contracting Parties are associated, OSPAR should send copies of this background document to the appropriate bodies dealing with those agreements and invite Contracting Parties who are parties both to OSPAR and those other agreements to promote action to take account of this background document by those other international bodies in a consistent manner.

VII. References

- Annelin R.B. (1990a) - An attempt to access the lethal body burden of Me₃SiOSiMe₃ to Rainbow trout. Dow Corning Corporation. Internal report. 1990-I0000-35837.
- Annelin R.B. (1990b) - A fourteen day aquatic toxicity test of hexamethyl disiloxane in fathead minnow under flow-through saturated conditions. Dow Corning Corporation. internal report. 1990-I0000-35678.
- Atkinson R. (1991) - Kinetics of the gas-phase reactions of a series of organosilicon compounds with OH and NO₃ radicals and O₃ at 297.2 K. *Environmental Science Technol*, 25, 863-866.
- Atkinson R., Tuazon E.C., Kwok E.S.C., Arey J., Aschmann S.M. and Bridier I. (1995) - *J. Chem. Soc. Faraday Trans.*, 31, 3033.
- Böhmer H. (2002) - Photolytic degradation of HMDS in drinking water - preliminary test. A1 02055748.
- Bruggeman W.A., Weber-Fung D., Opperhuizen A., van der Steen J., Wijnbenga A. and Hutzinger O. (1984) - Absorption and retention of polydimethylsiloxanes (silicones) in fish : preliminary experiments. *Toxicological and environmental chemistry*, 7, 287-296.
- CES (2002) -. Centre Européen des Silicones. Internal report.
- Corning D. (1985) -. Dow Corning Corporation. Internal Technical Report.
- David M.D., Fendinger N.J. and Hand V.C. (2000) - Determination of Henry's law constants for organosilicones in actual and simulated wastewater. *Environmental Science Technol*, 34, 21, 4554-4559.
- Degussa (2001a) -.
- Degussa (2001b) -.
- E.U. (2003) - Technical guidance document in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) No 1488/94 on risk assessment for existing substances and Commission Directive (EC) 98/8 on biocides.
- European Chemical Bureau (1997) EUSES, the European Union System for the Evaluation of Substances.
- Flaningham O.L. (1986) - Vapour pressure of polydimethylsiloxane oligomers. *J. Chem.Eng. Data*, 31, 266-272.

- Friedli G.-L. (1992) Structure/activity comparison in the ability of some terpenoid food flavours to cause peroxisome proliferation. *M.Sc, University of Surrey*.
- Frye C.L. (1988) - The environmental fate and ecological impact of organosilicon materials: a review. *The Science of the total environment*, 73, 17-22.
- Grau R. (1991) - Hexamethyldisiloxane (M2), acute toxicity to rainbow trout in a flow-through test. Bayer AG. internal report. FF-313 study E2810536-5.
- Hooftman R.N., Rooseboom-Reimers A. and Henzen L. (2003) - Semi-static reproduction test with hexamethyldisiloxane and *Daphnia magna* (OECD Guideline No.211). TNO. Zeist. 01-2434/01.
- IARC (1999) - Species differences in thyroid, kidney and urinary carcinogenesis. IARC Scientific Publications No. 147.
- IUCLID (2002) - International Uniform Chemical Information Database.
- Kochetkov A., Smith J.S., Ravikrishna R., Valsaraj K.T. and Thibodeaux L.J. (2001) - Air-water partition constants for volatile methyl siloxanes. *Environmental Toxicology and Chemistry*, 20, 10, 2184-2188.
- Kohn D.Y. (2001) - Physical properties determination of Silanes. Chilworth technology. Reston. R/3116RP/0201/DYK.
- Markgraf S.J. and Wells J.R. (1997) - The hydroxyl radical reaction rate constants and atmospheric reaction products of three siloxanes. *Int. J. Chem. Kinet.*, 29, 6, 445-451.
- Mayer P., Oldersma H. and Schoonmade J.A. (2001) - Screening the effect of hexamethyldisiloxane on the respiration of activated sludge (OECD Guideline 209). TNO, Department of Environmental Toxicology. Delft, The Netherlands. TNO Chemistry. 01-2434/03.
- Mazzoni and al (1997) Ecologically relevant properties of selected organosilicon materials. vol 3 part H, *In: The handbook of environmental chemistry.*, O. Hutzinger Eds, 66.
- OECD (1984a) - Activated sludge. Respiration Inhibition Test. OECD Guideline for testing chemicals. OECD. PARIS.
- OECD (1984b) - Alga, Growth Inhibition Test, Guideline for Testing of Chemicals No. 201. OECD. Paris.
- OECD (1992) - Fish Acute toxicity test, Guideline for Testing of Chemicals No. 203. OECD. PARIS.
- OECD (1998) - *Daphnia* sp., reproduction test, Guideline for Testing of Chemicals No. 211. OECD. PARIS.
- Oldersma H., Hantsveit A.O. and Rooseboom-Reimers A. (2003) - Determination of the effect of hexamethyldisiloxane on the growth of the freshwater green alga *Selenastrum capricornutum*. TNO. Zeist, NL. 01-2434/02.
- OSPAR (1998) - OSPAR strategy with regard to hazardous substances. OSPAR. Summary record OSPAR 98/14/1, Annex 34.
- Sommerlade R., Parlar H., Wrobel D. and Kochs R. (1993) - Product analysis and kinetics of the gas-phase reactions of selected organosilicon compounds with OH radicals using a smog chamber-mass spectrometer system. *Environmental Science Technol*, 27, 2435-2440.
- Stevens C. and Annelin R.B. (1997) Ecotoxicity testing challenges of organosilicon materials. vol 3 part H, *In: The Handbook of environmental chemistry*, O. Hutzinger Eds.
- US-EPA (1996) - Ecological effects tests guidelines - Algal toxicity, Tiers 1 and 2, Public draft. US-EPA. Washington. OPPTS 850.5400.
- Varaprath S., Frye C.L. and Hamelink J. (1996) - Aqueous solubility of permethylsiloxanes (silicones). *Environmental Toxicology and Chemistry*, 15, 8, 1263-1265.
- Xu S., Lehmann R.G., Miller J.R. and Chandra G. (1998) - Degradation of polydimethylsiloxanes (silicones) as influenced by clay minerals. *Environmental Science Technol*, 32, 1199-1206.

Appendix 1: Complementary information on some physico-chemical properties studies

1. Air-water partition constant (Kochetkov *et al.*, 2001)

In Kochetkov *et al.* (2001) two methods of determination of the dimensionless form of the Henry's law constant (H_c) for HMDS are proposed: a static head space (HS) method and a newly developed vapour entry loop method (VEL). The air-water partition constant was determined for six volatile methyl siloxanes (three cyclic and three linear of which the HMDS).

The VEL method has been developed to suppress the formation of a colloidal emulsion that is sometimes observed when silicones are in contact with aqueous solution. This is the case in the HS method.

In the HS method, saturated aqueous solution are prepared and shaken gently and continuously for 2 days. After the settlement of the solution (4d), the solution is filtered (0,45 μm) to eliminate colloidal suspensions. The solution in sealed bottles is then shaken a second time and allowed to stand for 48 h at 28°C. After equilibration, samples of water and of the head space are withdrawn with a syringe and injected into the gas chromatograph (4 to 5 replicate injections).

In the VEL method, a system of valves and pump avoids colloidal formation. This system includes three steps. The first one allows reaching the equilibrium of the siloxane pure vapour between two reservoirs. Samples of vapour are made until the concentration of vapour is constant. The pump is then shut off and a part of the vapour is replaced by water (second step). In the third step, the pump is restarted and the circulation continues for 48 h. Samples of vapour and water are then made and injected into the gas chromatograph (4 to 5 samples for the vapour and 2 for the water).

A standard (benzene) has been used in both methods to validate the new one. The results obtained in both cases with benzene are close (0,24 and 0,19) and are also similar to other previous studies on benzene.

The determined constant values for HMDS are $1,3 \pm 0,2$ for the head space method and $2,4 \pm 0,2$ for the VEL method.

2. Photochemical reactions in the atmosphere

Due to a high Henry's law constant, HMDS released to water is expected to rapidly volatilise to the atmosphere. The most effective elimination process in the troposphere results from reaction with photochemically generated species like OH radicals, ozone and nitrate radicals. The specific first order degradation rate constant of the HMDS with OH-radicals (k_{OH}) was determined by Markgraf & Wells (1997). Hexamethyldisiloxane and OH radicals was put together in an irradiated reaction chamber. OH radicals were generated from the photolysis of methyl nitrite (CH_3ONO) in the presence of nitric oxide in air. Reference compounds (cyclohexane and hexane) were employed to determine the OH rate constants according to the following equation:

$$\ln\left(\frac{[\text{HMDS}]_0}{[\text{HMDS}]_t}\right) = \frac{k_S}{k_R} \ln\left(\frac{[R]_0}{[R]_t}\right)$$

$[\text{HMDS}]_0$, $[\text{HMDS}]_t$, $[R]_0$ and $[R]_t$ are the concentrations of HMDS and of the reference product at the beginning of the reaction and at time t .

k_S and k_R are the OH rate constant respectively of the HMDS and the reference product.

The typical concentrations of the pertinent species in the test chamber (100 litre) were 0,5-1 ppm hexamethyldisiloxane, 1,5-2,0 ppm reference, 9,0 ppm CH_3ONO and 2,3 ppm NO in air. The mixtures stood for 30 to 60 minutes before background samples were collected.

All samples were quantitatively monitored using a gas chromatograph (GC) with a flame ionization detector (FID). Typically five experimental runs were conducted.

The results showed no detectable loss of the test substance or the reference products over the experiment. The slope of the linear least-squares analysis with 95% confidence analysis is $0,231 \pm 0,008$. The OH rate constant for hexane is $5,61 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which yields to a k_{OH} value for HMDS of $1,32 \pm 0,05 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is in agreement with previous values measured by Atkinson (1991) and Sommerlade *et al.* (1993), of respectively $1,38 \pm 0,05 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $1,19 \pm 0,30 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

A pseudo-first order rate constant for degradation in air of the hexamethyldisiloxane can then be determined with an average estimated concentration of OH-radicals in atmosphere of $5 \cdot 10^5 \text{ molecules.cm}^{-3}$.

$$k_{deg_{air}} = k_{OH} \cdot OHCONC_{air} \cdot 24 \cdot 3600 = 0,057 \text{ d}^{-1}$$

An estimated half-life in the atmosphere of 12 days is expected for the HMDS.

The main degradation product observed in the experiment of Markgraf & Wells (1997) in the atmosphere is pentamethyldisiloxanol (MDOH), but experiments made by Atkinson *et al.* (1995) conclude that MDOH is a “second generation” product of water reacting with a siloxane ester product.

Appendix 2: Toxicological properties of HMDS (Centre Européen des Silicones)

8 October 2003 **DRAFT**

Advanced Research on Hexamethyldisiloxane (HMDS)

Resumé

Silicone manufacturers have conducted wide-ranging, advanced health effect studies on hexamethyldisiloxane (HMDS) as part of the industry's international commitment to Responsible Care®. Six commonly used siloxanes, including HMDS, have been the focus of more than 100 studies conducted to date through the Siloxane Research Program. HMDS displays very low acute toxicity. In subacute/subchronic inhalation studies, the No Observed Adverse Effect Level (NOAEL) is >1000 ppm in female rats and 200 ppm in male rats. Effects Observed in subacute/subchronic studies in male rats at higher concentrations were found to be species-specific and not relevant to humans. For these reasons, CES continues to be confident that use of, and exposure to, HMDS does not present any concerns for human health.

Background

HMDS was subjected to a two-year combined chronic/carcinogenicity whole-body vapour inhalation study. Prior to this 2-year study, data generated on HMDS indicated that this material is non-genotoxic and is of a very low acute oral, inhalation, and dermal toxicity. A sub-acute oral gavage study and subacute/subchronic inhalation studies in rats both showed protein droplets in the kidneys of male rats receiving 1500 mg/kg body weight in the gavage study and exposed to 500 and 1000 ppm in the inhalation study. In a 90-day whole body inhalation study, the kidneys of male rats showed tubular degeneration, hyaline and granular casts, tubular and papillary mineralization and fibrosis. Most effects in this study were confined to dose levels of 1500 ppm or greater. The findings in the kidneys in these studies are consistent with an α 2u-globulin-mediated mode of action, which is not relevant to humans.

Findings of the Two-Year Combined Chronic/Carcinogenicity Study

In a two-year life-span study, rats (Fischer 344) were exposed to 0, 100, 400, 1600, or 5000 ppm of HMDS, 6 hours/day, 5 days/week for up to two years. The results of the two-year combined chronic/oncogenicity inhalation study in F344 rats showed an apparent dose related increase in Leydig cell tumours in the testes of male rats after one year of exposure and an increase in testicular weights in a dose related manner in all exposure groups following two years of exposure. There was nearly a 100% incidence of Leydig cell tumours in the male rats in all dose groups including controls at two years. This is an expected observation in this strain of male rats at this time point.

The early onset of Leydig cell tumours in male rats is of little relevance to humans based on the following information:

- The strain of animal used in the experiments is much more sensitive to the development of Leydig cell tumours than human males. The development of such effects in humans is extremely rare. At the end of the two-year study period, all the male rats, including those that were not exposed to HMDS, showed high levels of Leydig cell abnormalities. The increase in the testicular weight is attributed to the presence of Leydig cell tumours. No effects were seen in female rats.
- Other studies have shown that a number of chemicals that cause adverse changes in Leydig cells in Fischer rats do not have this effect on people. Decisions by international scientific institutions, including the International Agency for Research on Cancer (IARC), support this lack of relevance.

An increase in kidney tumours in male rats exposed to 1600 and 5000 ppm HMDS was also observed following two years of exposure. Recently completed mechanistic work confirms that the kidney tumours are mediated through α 2u-globulin. Alpha 2u-globulin mediated nephropathy is a male rat specific effect that is not observed in other species of animals, including humans. Furthermore, α 2u-globulin mediated kidney tumours are of no relevance to humans as set forth by IARC. The use of data related to kidney nephropathy is therefore not relevant to hazard definition and risk assessment of HMDS for man or secondary poisoning in other species.

Impact of these Findings

Based on the information presented above, the conclusion is that the observed effects in the two-year combined chronic/carcinogenicity study are rat-specific and are not relevant to humans.

Regulatory assessment

Toxicologists and regulatory specialists have reviewed these studies. They have concluded that, in accordance with the European Guidelines on Hazard Classification and Labelling, the data do not meet the specific criteria for classification of HMDS as a hazardous substance.

Conclusions

Silicone manufacturers are confident that the production and use of HMDS does not adversely affect human health. We will share any new information with customers and other relevant parties in line with our commitment to Responsible Care®.

If you have questions or would like to obtain additional information please contact M. De Poortere, Secretary General CES, at:

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Appendix 3: HMDS factsheet

	NAME	Disiloxane, hexamethyl-		VERSION: 2002-04-15
	IDENTIFICATION			
1.1	CasNo	107460		
1.2	EINECS/ELINCS	203-492-7		
1.3	Synonym	hexamethyldisiloxane [HMDS]		
1.4	Group/Function	Siloxane		
1.5	Initial selection	PBT NSDB(III),		
1.6	Prioritised for action	Date: OSPAR 2000; Lead Country: France; Background document: OSPAR 2004		
	Parameter	Value	Source/Reference	Remarks
	PHYSICAL/CHEMICAL PROPERTIES			
2.1	Molecular weight, g/mole	162,38	QSAR-DK:	
2.2	Water solubility, mg/l	288E-02	QSAR-DK: EPIWIN 3.02	
		930E-03	Varaprath et al., 1993. Dow Corning Internal technical report	
2.3	Vapour pressure, Pa	521E+01	QSAR-DK: EPISUITE program MpBpVp v1.40	
		638E+01	Kohn, D.Y. (2001) Physical properties determinations of silanes. Reston, Chilworth technology.	
	ABIOTIC/BIOTIC DEGRADATION PROPERTIES			
3.1	Abiotic OH-oxidation $t_{1/2}$ d	119E-01	QSAR-DK: EPIWIN 3.02	
3.2	Photolysis $t_{1/2}$ d			
3.3	Ready Biodegradability			based on chemical structure no aerobic biodegradation is expected.
3.4	Half-life			
3.5	Inherent Biodegradability	19,99	European Commission, ECB, Existing chemicals, TP 280, I-21020 ISPRA	not inherently biodegradable (<20%)
3.6	Biodeg-QSAR	0,6702	QSAR-DK: BIOWIN1	readily biodegradable (>70%)
3.6		2,8403	QSAR-DK: BIOWIN3	
3.6			QSAR-DK: Interpretation of BIOWIN1 and BIOWIN3	readily biodegradable (>70 %)
3.6		0,2315	QSAR-DK: Environ.Tox.Chem. 18(8): 1763-1768. Environ.Tox.Chem. 19(10): 2478-2485. (Syracuse version of H. Loonen's Simca Fragment linear MITI model.)	not readily biodegradable (20-50%)
3.6		0,1145	QSAR-DK: Environ.Tox.Chem. 18(8): 1763-1768. Environ.Tox.Chem. 19(10): 2478-2485. (Syracuse version of H. Loonen's Simca Fragment non-linear MITI model)	not readily biodegradable (20-50%)

	BIOACCUMULATION/BIOCONCENTRATION			
4.1	logKow	5	QSAR-DK: EPIWIN 3.02	High potential for bioaccumulation
4.1		4	Bruggeman et al. (1984) Toxicol. Env. Chem. 7(4): 287-296	High potential for bioaccumulation
4.2	Bcf	339	QSAR-DK: EPIWIN 3.02	low bioconcentration factor
4.2		1300	Annelin & Hamelink (1990). A fourteen day aquatic toxicity test of HMDS in fathead minnows under flow-through saturated conditions. Dow Corning internal report	High bioconcentration factor
	AQUATIC TOXIC PROPERTIES			
5.1	Acute toxicity algae IC50, mg/l	>0,55	Oldersma et al. (2003)TNO report	
5.2	Acute toxicity daphnia EC50, mg/l	314	European Commission, ECB, Existing chemicals, TP 280, I-21020 ISPRA	Low toxicity (100-1000 mg/l)
5.3	Acute toxicity fish LC50, mg/l	3,02	European Commission, ECB, Existing chemicals, TP 280, I-21020 ISPRA	Toxic (1-10 mg/l)
		0,46	Grau (1991) Internal report Bayer AG	
5.4	Chronic toxicity daphnia NOEC, mg/l	0,08	Hooftman et al.(2003) TNO report	
5.5	Chronic toxicity fish NOEC, mg/l	0,082	European Commission, ECB, Existing chemicals, TP 280, I-21020 ISPRA	Very toxic (0,01-0,1 mg/l)
		0,93	Annelin & Hamelink (1990). A fourteen day aquatic toxicity test of HMDS in fathead minnows under flow-through saturated conditions. Dow Corning internal report	
5.6	Aquatox-QSAR	0,3906	QSAR-DK: Fish NOEC, Lethal Body Burden NOEC mg/l (A:C ratio 10:1) for fish based on EPIWIN 3.02 BCF	toxic (01-1 mg/l)
5.7	Aquatic toxicity - other species			
	Chronic toxicity algae NOEC, mg/l	0,01	Oldersma et al. (2003) TNO report	
	HUMAN TOXIC PROPERTIES			
6.1	Acute toxicity			
6.2	Carcinogenicity			
6.3	Chronic toxicity			
6.4	Mutagenicity			
6.5	Reprotoxicity			
	EXPOSURE			
7.1	Production Volume	LPVC	IUCLID:	10-1000
7.2	Use/Industry Category	Chemical industry: used in synthesis, personal and domestic, polymers industry, cosmetics, intermediates, other, pharmaceuticals, basic industry, basic chemicals, solvents		Source: IUCLID
7.3	Use in articles			
7.4	Environm.Occur. Measured			(Compartment)
7.5	Environm.Occur. Modelled			(Compartment)
8	EU-LEGISLATION			
8.1	Dir 67/548/EEC (Classification)		:Annex1, Dir 67/548/EEC	

8.2	<i>Reg 793/93/EEC (Existing substances)</i>			
8.3	<i>Dir 2000/60/EEC (WFD)</i>			
8.4	<i>Dir 76/769/EEC (M&U)</i>			
8.5	<i>Dir 76/464/EEC (water)</i>			
8.6	<i>Dir 91/414/EEC (ppp)</i>			
8.7	<i>Dir 98/8/EEC (biocid)</i>			
9	ADDITIONAL INFORMATION			
9.1	<i>Hazard assessment-OECD</i>			
9.2	<i>Other risk assessments</i>			

Appendix 4: Table of site references

The table A2.1 below is designed to provide a summary of the locations of sites identified in this document.

Table A2.1 Summary of sites, their codes and location codes

Code	Ref	Site number	Region number
Producer 1	1	1	1
Producer 2	2	2	2
Producer 3	3	3	3
Producer 4	4	4	3
Producer 5	5	5	4
Producer 6	6	6	5
Penicillin manufacturer 1	8	7	6
Penicillin manufacturer 2	9	8	6
Penicillin manufacturer 3	10	9	2
Penicillin manufacturer 4	11	10	6
Penicillin manufacturer 5	12	11	4
Penicillin manufacturer 6	13	12	6
Penicillin manufacturer 7	14	13	7
Penicillin manufacturer 8	15	14	7
Penicillin manufacturer 9	16	19	6
By-product 1	17	15	1
By-product 2	18	16	4
By-product 3	19	4	3
HMDZ by-product 1	21	17	3
HMDZ by-product 2	22	3	3
HMDZ by-product 3	23	4	3
HMDZ by-product 4	24	5	4
HMDZ by-product 5	25	6	5
HMDZ by-product 6	26	18	3
HMDZ by-product 7	27	7	6
HMDZ by-product 8	28	10	6
TMCS by-product 1	30	9	2
TMCS by-product 2	31	10	6
TMCS by-product 3	32	16	4
TMCS by-product 4	33	18	3
bis(Trimethylsilyl)urea use	35	9	2
Trimethylsilanol as end blocker	37	2	2
Personal care unspecified formulation	39		
Personal care private use	39a		
Personal care 1	40	21	7
Personal care 2	40b	25	1
Personal care 3	40d	26	2
Personal care 4	40e	27	5
Personal care 5 formulation	40f	24	1
Personal care 5 private use	40f		
Solvent unspecified formulation	42		

Code	Ref	Site number	Region number
Solvent unspecified processing	42a		
Solvent 2	44	22	3
Intermediate unspecified	45		
Intermediate 1	46	23	3
Landfill gas	48		

Appendix 5: Details of information regarding tonnage and emissions from individual sites

A2.1 Production and import

The contributors to the total tonnage are broken down in the document in Table II-1 and emissions are shown in Table A2.1 below.

Table A2.1. Emissions of HMDS from import

Code	Ref	Information
Nature of process		
Producer 1	1	Consolidated into site losses

For reasons of simplicity, production, import and export from this life cycle stage were consolidated with 'production' tonnage (a by-product) in penicillin manufacture and as a by-product of hexamethyldisilazane and TMCS. The summary figure of 6349 tonnes per year in the EU was used as the total tonnage.

EUSES

use 1 – production – 4835 t

use 2 – penicillin manufacture – 1471 t

use 4 – HMDZ by-product – 370 t precursor – but we know 40 t HMDS emitted therefore this figure is used.

use 5 – TMCS by-product – 1030 t precursor – but we know 3 t HMDS emitted therefore this figure is used.

Total HMDS: 6349 t

Site-specific exposure assessment

See tables A2.1 and A2.2.

For production (use 1) the main region included two sites (Producers 3 and 4).

Production of HMDS for the life cycle stage represented above was implemented in EUSES as follows:

- The local (i.e. major) site was Producer 3, because its total level of loss was the higher, although the tonnage handled was lower than Producer 4. The regional emission therefore comprises the sum of the losses from Producers 3 and 4, evaluated over 365 days to give emissions to air and waste-water in kg/day. The regional emissions for this use pattern are shown below. Site-specific information available from the main site included the dilution at the wastewater treatment plant.

Regional emission, use 1 – sum of losses from Producers 3 and 4

$0 + 0 = 0$ kg/d to air

$(1,4 \text{ kg/d on 300 days}) + 0 = 1,15$ kg/d to waste water over 365 days

- The remaining sites (Producers 1, 2, 5 and 6) were sited in separate regions outside the overall main region, therefore these are counted in EUSES as sources of emission on a continental scale. The continental emission comprises the sum of the losses from these four producers, divided by 365 days to give emissions to air and waste-water in kg/day.

Continental emission, use 1

$(6,77 + 0 + 0 + 50 \text{ kg/d on 300 days}) = 46,66$ kg/d to air over 365 days

$(0,09 + 17,20 \text{ kg/d on 300 days}) = 14,21$ kg/d to waste water over 365 days

Table A2.2. Emissions of HMDS from production

Code	Ref	Information
Nature of process		
Producer 1	1	Closed system.
Producer 3	3	Closed system.
Producer 4	4	Closed system.
Producer 5	5	Closed system.
Producer 6	6	Closed system.
Emission to WWTP		
Producer 1	1	Concentration in effluent prior to WWTP = 1 ppm approx. 90%-ile amount in effluent is 88,7 g/d. Average flow from WWTP = 5784 m ³ /day. Mean flow in river is 3600 m ³ /hour. Sludge incinerated.
Producer 3	3	Waste water is treated at WWTP. Concentration of HMDS in effluent from site WWTP is below limit of detection of 10 µg/l. Total discharge from WWTP is 50 x 10 ⁶ m ³ per annum and average flow in receiving river is 2000 m ³ per second (average), 1000 m ³ per second (minimum). Sludge incinerated.
Producer 4	4	Effluents treated at on-site WWTP and then discharged to surface water. Flow rate from WWTP = 0,25 m ³ /s. Flow rate in receiving river = 50 m ³ /s. Sludge is incinerated and no biogas is produced.
Producer 5	5	Effluents treated at on-site WWTP and then discharged to surface water. Sludge is incinerated and no biogas is produced.
Producer 6	6	None. Effluent is discharged directly via two discharges N and S. N – Concentration = 2,7 ppm, Flow rate = 0,06 m ³ /s. S – Concentration = 0,22 ppm, Flow rate = 0,17 m ³ /s. Flow rate in river = 8000 m ³ /s.
Emission as part of solid waste		
Producer 1	1	Sludge from WWTP primary treatment sent for landfill. Sludge from secondary treatment used as fertiliser by direct spraying. HMDS concentration in sludge not given.
Producer 3	3	None. Sludge and biogas from WWTP is incinerated.
Producer 4	4	None
Producer 5	5	None
Producer 6	6	None

Code	Ref	Information
Emission to air		
Producer 1	1	2,03 t
Producer 2	2	0,090 t in 1997/98.
Producer 3	3	No emissions from production since production and internal use is in the same building having one offgas exhaust. Offgas from this source is incinerated and the exhaust contains no HMDS.
Producer 4	4	37 t consolidated site loss: evaluated in HMDZ by-product step. For production, taken to be 0. 14 t are due to hydrophobing of silica; see also Table A2.9.
Producer 5	5	0,5 t
Producer 6	6	15 t
Days per year		
Producer 1	1	Not given
Producer 3	3	365 days
Producer 4	4	Not given
Producer 5	5	Not given
Producer 6	6	Not given

The site-specific information on the waste water treatment plant was removed.

A2.2. Generation as a by-product of synthesis of other substances

Synthesis processes during which HMDS is produced as a by-product are summarised in Appendix 6 and emissions for each synthesis process are summarised in Tables A2.3 to A2.5. The tonnage data listed in Appendix 6 are based on data from a single supplier.

Table A2.3. Summary of potential for HMDS production as a by-product of synthesising other substances

Total precursor (tonnes)	Tonnage (% of total) and origin			
		Code	Ref	
1471 EUSES use 2	Hexamethyldisilazane use in penicillin manufacture: 200	Penicillin manufacture 8	15	200 t of HMDZ
	Trimethylchlorosilane use in penicillin manufacture: 491	Penicillin manufacture 8	15	10 of TMCS
		Penicillin manufacture 2	9	80 of TMCS
		Penicillin manufacture 5	12	300 of TMCS
		Penicillin manufacture 6	13	100 of TMCS
		Penicillin manufacture 7	14	1 of TMCS
	Hexamethyldisilazane use in other pharmaceutical manufacture: 330	HMDZ by-product 7	27	250 t of HMDZ
		HMDZ by-product 8	28	80 t of HMDZ
		HMDZ by-product 4	24	0,5 t of HMDZ
	Trimethylchlorosilane use in pharmaceutical manufacture: 2010	TMCS by-product 1	30	900 t of TMCS
		TMCS by-product 2	31	80 t of TMCS
		TMCS by-product 3	32	500 t of TMCS
		TMCS by-product 4	33	530 t of TMCS
	bis(Trimethylsilyl)urea use in pharmaceutical production:	bis(Trimethylsilyl)urea use	37	Emissions consolidated with ref. 30 (see line above)
EUSES use 4	Hexamethyldisilazane (HMDZ) use in production of silicone rubbers: 40	HMDZ by-product 1	21	?
		HMDZ by-product 2	22	0,87 t of HMDS
		HMDZ by-product 3	23	14 t of HMDS
		HMDZ by-product 5	25	12 t of HMDS
		HMDZ by-product 6	26	0 t of HMDS
	Use of trimethylsilanol as end blocker	Trimethylsilanol as end blocker	37	Consolidated into site losses

Table A2.4. Emissions of HMDS from hexamethyldisilazane use in penicillin manufacture

Code	Ref	Information
Nature of processes		
Penicillin manufacture 8	15	Not given
Emission to WWTP		
Penicillin manufacture 8	15	Not given
Emission to industrial soil		
Penicillin manufacture 8	15	Not given
Emission to air		
Penicillin manufacture 8	15	Not given
Days per year		
Penicillin manufacture 8	15	Not given

Table A2.5. Emissions of HMDS from trimethylchlorosilane use in penicillin manufacture

Code	Ref	Information
Nature of processes		
Penicillin manufacture 8	15	Not given
Penicillin manufacture 2	9	Not given
Penicillin manufacture 5	12	Not given
Penicillin manufacture 6	13	Not given
Penicillin manufacture 7	14	Not given
Emission to WWTP		
Penicillin manufacture 8	15	Not given
Penicillin manufacture 2	9	Treated at on-site WWTP. Effluent concentration <1 mg/l
Penicillin manufacture 5		
Penicillin manufacture 6	12	Not given
Penicillin manufacture 7	13	Not given
	14	Not given
Emission to industrial soil		
Penicillin manufacture 8	15	Not given
Penicillin manufacture 2	9	Not given
Penicillin manufacture 5	12	Not given
Penicillin manufacture 6	13	Not given
Penicillin manufacture 7	14	Not given
Emission to air		
Penicillin manufacture 8	15	Not given
Penicillin manufacture 2	9	Not given
Penicillin manufacture 5	12	Not given
Penicillin manufacture 6	13	Not given
Penicillin manufacture 7	14	Not given
Days per year		
Penicillin manufacture 8	15	Not given
Penicillin manufacture 2	9	Not given
Penicillin manufacture 5	12	Not given
Penicillin manufacture 6	13	Not given
Penicillin manufacture 7	14	Not given

A2.2.1. HMDS from trimethylchlorosilane and hexamethyldisilazane use in penicillin manufacture

Site-specific exposure assessment

See Appendix 6 and A2.3 – A2.5

Production of HMDS for this use pattern (use 2) was implemented in EUSES as follows:

For this use pattern, there are no sites in the main region. The local and regional emissions are set to zero in EUSES; the emissions for Penicillin manufacturers 1-9 are summed to give the continental emission, i.e. the sum of the local losses from these nine penicillin manufacturers, evaluated over 365 days, to give emissions to air and waste-water in kg/day. Local emissions from the sites are a mixture of site-specific losses and defaults, since the data available was incomplete and a true picture of the level of emission control could not be gained.

Default losses

Fraction to air = 0,05 (see below)

Fraction to waste water = 0,003

Fraction to industrial soil = 0,0001 (see below)

300 days

On the basis of the available evidence from other sites at which HMDS is processed, it was considered that an emission rate of 5% to air was too high, as systems were likely to be in place to minimise emissions. A rate of 0,001 was used in the calculations to reflect likely custom and practice. For a substance as volatile as HMDS, it is reasonable to assume that any emission to industrial soil will ultimately go to air. Therefore emission to industrial soil is set at 0.

For Penicillin manufacturer 2 the only information given was an effluent concentration. The scenario was developed by estimation that the site effluent would be approximately 200 m³/d, leading to a local emission rate of 2 kg/d from that site.

Continental emission, use 2

2,58 kg/d to air over 365 days

7,89 kg/d to waste water over 365 days

Exposure assessment with default distribution

Local rates of loss were maintained as they are considered representative of the likely custom and practice. The regional tonnage was allowed to revert to the default (10% of the total) and the fraction of the main local source also allowed to revert to the default.

Table A2.6. Emissions of HMDS from hexamethyldisilazane use in other pharmaceutical manufacture

Code	Ref	Information
Nature of processes		
HMDZ by-product 7	27	HMDS remains in solvent phase and is sent for recycling to HMDZ. Transfer is in tanks with 'closed cycle' and transfer within reprocessing plant is through dedicated pipelines.
HMDZ by-product 8	28	Not given
HMDZ by-product 5	25	Not given
Emission to WWTP		
HMDZ by-product 7	27	Not given but waste water is sent to WWTP
HMDZ by-product 8	28	Not given
HMDZ by-product 5	25	Not given
Emission to industrial soil		
HMDZ by-product 7	27	Not given
HMDZ by-product 8	28	Not given
HMDZ by-product 5	25	Not given
Emission to air		
HMDZ by-product 7	27	Insignificant?
HMDZ by-product 8	28	Not given
HMDZ by-product 5	25	Not given
Days per year		
HMDZ by-product 7	27	Not given
HMDZ by-product 8	28	Not given
HMDZ by-product 5	25	Not given

A2.2.2. HMDS from hexamethyldisilazane use in other pharmaceutical manufacture and from treatment of silica with hexamethyldisilazane in production of silicone rubbers

Site-specific exposure assessment

See Appendix 6 and A2.6.

This source of HMDS is set up in EUSES as use 4. Production of HMDS for this stage was implemented in EUSES as follows.

There are four sites in the main region. The local (i.e. major) site is HMDZ by-product 3, because the tonnage handled was the highest in the region. The regional emission therefore comprises the sum of the losses from HMDZ by-product 1-3 and 6, evaluated over 365 days to give emissions to air and waste-water in kg/day. The regional emissions for this use pattern are shown below.

Regional emission, use 4 – HMDZ by-product 1 + 2 + 3 + 6 over the year

$(43,3 + 46,67 + 0) \text{ kg/d on 300 days} + 2,4 \text{ kg/d on 365 days} = 76,35 \text{ kg/d to air over 365 days}$

$0 + 0 + 0 + 0 = 0 \text{ kg/d to waste water}$

The remaining sites (HMDZ by-product 4, 5 and 7) were sited in separate regions outside the overall main region, therefore these are counted in EUSES as sources of emission on a continental scale. The continental emission comprises the sum of the losses from these three sites, divided by 365 days to give emissions to air and waste-water in kg/day.

Continental emission, use 4

$(1,60 + 40 + 0 \text{ kg/d on 300 days}) = 34,2 \text{ kg/d to air over 365 days}$

$0 + 0 + 0 = 0 \text{ kg/d to waste water}$

Exposure assessment with default distribution

Local rates of loss were maintained as they are considered representative of the likely custom and practice. The regional tonnage was allowed to revert to the default (10% of the total) and the fraction of the main local source also allowed to revert to the default.

Table A2.7. Emissions of HMDS from trimethylchlorosilane use in pharmaceutical production

Code	Ref	Information
Nature of processes		
TMCS by-product 1	30	Closed systems; sent for reprocessing. The plant is now no longer operational in respect of this use
TMCS by-product 2	31	Not given
TMCS by-product 3	32	Not given
TMCS by-product 4	33	Not given
TMCS by-product 5	34	Not given
TMCS by-product 6	35	Not given
Emission to WWTP		
TMCS by-product 1	30	Zero
TMCS by-product 2	31	Not given
TMCS by-product 3	32	Not given
TMCS by-product 4	33	Not given
TMCS by-product 5	34	Not given
TMCS by-product 6	35	Not given
Emission to industrial soil		
TMCS by-product 1	30	Zero
TMCS by-product 2	31	Not given
TMCS by-product 3	32	Not given
TMCS by-product 4	33	Not given
TMCS by-product 5	34	Not given
TMCS by-product 6	35	Not given
Emission to air		
TMCS by-product 1	30	Zero
TMCS by-product 2	31	Not given
TMCS by-product 3	32	Not given
TMCS by-product 4	33	Not given
TMCS by-product 5	34	Not given
TMCS by-product 6	35	Not given
Days per year		
TMCS by-product 1	30	Not given
TMCS by-product 2	31	Not given
TMCS by-product 3	32	Not given
TMCS by-product 4	33	Not given
TMCS by-product 5	34	Not given
TMCS by-product 6	35	Not given

A2.2.3. HMDS from trimethylchlorosilane, hexamethyldisilazane and bis(trimethylsilyl)urea use in pharmaceutical production

Site-specific exposure assessment

See Appendix 6 and A2.7.

Production of HMDS for use 5 represented above was implemented in EUSES as follows:

Two sites (TMCS by-product 4 and 5) were in the main region. Losses from TMCS by-product 5 are consolidated in the emissions from another stage which takes place at the same site (Producer 3). The regional emission therefore comprises the losses from TMCS by-product 4, evaluated over 365 days to give emissions to air and waste-water in kg/day. The regional emissions for this use pattern are shown below. The tonnage at the site is unknown, but it is known that emission levels are 0 – therefore for simplicity, EUSES is set up as if TMCS by-product 4 site did not exist, i.e. as if there were no site in the main region.

The remaining sites (TMCS by-product 1-3 and 6, HMDZ by-product 8 and bis(trimethylsilyl)urea use) were sited in separate regions outside the overall main region, therefore these are counted in EUSES as sources of emission on a continental scale. The continental emission comprises the sum of the losses from these producers, evaluated over 365 days to give emissions to air and waste-water in kg/day. Tonnages of precursor are known, however tonnages of HMDS are not, but it is known that total losses account for 3 t HMDS per year.

Continental emission, use 5

3000 kg over 365 days = 8,22 kg/d to air

0 kg/d to waste water

Exposure assessment with default distribution

Local rates of loss were maintained as they are considered representative of the likely custom and practice. The regional tonnage was allowed to revert to the default (10% of the total) and the fraction of the main local source also allowed to revert to the default.

Table A2.8. Emissions of HMDS from bis(trimethylsilyl)urea use in pharmaceutical production

Code	Ref	Information
Nature of process		
bis(bis(Trimethylsilyl))urea use	37	Hydrolysis of bis(trimethylsilyl)urea
Emission to WWTP		
bis(Trimethylsilyl)urea use	37	Not given
Emission to industrial soil		
bis(Trimethylsilyl)urea use	37	Not given
Emission to air		
bis(Trimethylsilyl)urea use	37	Not given
Days per year		
bis(Trimethylsilyl)urea use	37	Not given

Table A2.9. Emissions of HMDS from treatment of silica with hexamethyldisilazane in production of silicone rubbers

Code	Ref	Information
Nature of process		
HMDZ by-product 1	21	Closed system
HMDZ by-product 2	22	Closed system
HMDZ by-product 3	23	Closed system
HMDZ by-product 4	24	Closed system
HMDZ by-product 5	25	Closed system
HMDZ by-product 6	26	Closed system
Emission to WWTP		
HMDZ by-product 1	21	None; all emissions to air
HMDZ by-product 2	22	(Consolidated site loss: see also Producer 3)
HMDZ by-product 3	23	(Consolidated site loss: see also Producer 4)
HMDZ by-product 5	25	None; all emissions to air
HMDZ by-product 6	26	None; wastes incinerated.
Emission to industrial soil		
HMDZ by-product 1	21	None; all emissions to air.
HMDZ by-product 2	22	None
HMDZ by-product 3	23	(Consolidated site loss: see also Producer 4)
HMDZ by-product 5	25	None; all emissions to air
HMDZ by-product 6	26	None; wastes incinerated.
Emission to air		
HMDZ by-product 1	21	5 t produced = 16,7 kg/d to air; estimate based on limited measurements
HMDZ by-product 2	22	0,87 t
HMDZ by-product 3	23	14t (Consolidated site loss: see also Producer 4)
HMDZ by-product 5	25	Consolidated site loss: see Producer 6
HMDZ by-product 6	26	None; wastes incinerated.
Days per year		
HMDZ by-product 1	21	Taken as 300 days
HMDZ by-product 2	22	365 days
HMDZ by-product 3	23	(Consolidated site loss: see also Producer 4)
HMDZ by-product 5	25	Not given.
HMDZ by-product 6	26	None; wastes incinerated.

Table A2.10. Emissions of HMDS from use of trimethylsilanol as end blocker

Code	Ref	Information
Nature of process		
Trimethylsilanol as end blocker	39	Not given
Emission to WWTP		
Trimethylsilanol as end blocker	39	Not given
Emission to industrial soil		
Trimethylsilanol as end blocker	39	Not given
Emission to air		
Trimethylsilanol as end blocker	39	Not given
Days per year		
Trimethylsilanol as end blocker	39	Not given

Emissions of HMDS accompanying this use was not implemented in EUSES because losses were consolidated into site losses for the single site performing this process.

A2.3 Reprocessing of HMDS by-product to hexamethyldisilazane, trimethylsilyurea and trimethylchlorosilane

The total reprocessing of HMDS was 4500 tonnes in 2000. The contributors to the total tonnage are broken down in Table II-2 and emissions are shown in Table A2.11.

Site-specific exposure assessment

See Table II-2 and A2.11

Emission of HMDS for this process (use 3) was implemented in EUSES as follows:

By-product 3 is situated in the main region, but it has no emissions to air or waste water. Therefore although it is the local (i.e. major) site, local and regional emissions total 0.

The remaining sites (By-product 1 and 2) are situated in separate regions outside the overall main region, therefore these are counted in EUSES as sources of emission on a continental scale. The continental emission comprises the sum of the losses from these sites, evaluated over 365 days to give emissions to air and waste-water in kg/day.

Continental emission, use 3

$0 + 0 + 16\,200 \text{ kg over } 365 \text{ days} = 44,38 \text{ kg/d to air}$

$0 + 0 + 1 \text{ kg/d on } 300 \text{ days} = 0,82 \text{ kg/d to waste water over } 365 \text{ days}$

Exposure assessment with default distribution

Local rates of loss were maintained as they are considered representative of the likely custom and practice. The regional tonnage was allowed to revert to the default (10% of the total). The rates of emission were calculated based on known rates of loss from the largest site. The fraction of the main local source was not simply set to the default since the A/B tables do not recognise a recovery stage for the industry category/use category. Instead, the fraction of the main source and number of days were set as 1 and 300 respectively.

Table A2.11. Emissions of HMDS from Reprocessing of HMDS

Code	Ref	Information
Nature of processes		
By-product 3	19	HMDS is converted to HMDZ, trimethylsilyurea or trimethylchlorosilane.
By-product 1	17	Recycling is a closed loop process. Transfer is in tanks with 'closed cycle' and transfer within reprocessing plant is through dedicated pipelines.
By-product 1	17	Recycling is carried out using dedicated batch equipment.
		Dedicated tankers not always used to transport HMDS to recycling plant. Non-dedicated tankers are later washed out at a local tanker washing facility with wash water going to local sewer. Estimated loss per wash cycle is < 1 kg with majority going ultimately to air.
By-product 2	18	Reprocessing using enclosed systems. Zero discharges verified by local authority.
Emission to WWTP		
By-product 3	19	None: site WWTP sludge incinerated
By-product 1	17	<0,3 t (Some further releases possible from tanker washing; see above)
By-product 2	18	None
Emission to industrial soil		
By-product 3	19	None: site WWTP sludge incinerated
By-product 1	17	None
By-product 2	18	?
Emission to air		
By-product 3	19	None: site WWTP sludge incinerated, no biogas
By-product 1	17	16,2 t (Including releases from tanker washing; see above). Not known if biogas from WWTP is incinerated.
By-product 2	18	None
Days per year		
By-product 3	19	Not given
By-product 1	17	Not given
By-product 2	18	?

A2.4 Uses of HMDS

The applications within which the total HMDS production and import year 2000 tonnage of 4045 tonnes was used are broken down in Appendix 7. Emissions associated with use are summarised in Tables A2.12 to A2.16.

Site-specific exposure assessment

See table A2.12.

This application (Use 8) is set up in EUSES as follows:

Site Intermediate 1 is situated in the main region, and therefore local emissions are those from this site. It is assumed that 1 t is processed per day, because 180 days' processing per year is reasonable. It is assumed that losses to waste water from the site are effectively zero. Losses to air are unknown and so the default rate of loss is used.

It is known that a further 270 tpa are used for this application at unknown sites; therefore the 10% rule is applied and default rates of loss are used to characterise emissions on this tonnage ('Intermediate', ref. 47). This means that the regional emission comprises losses from the main site and also the regional losses from the remaining tonnage.

Default losses

Fraction to air = 0,05

Fraction to waste water = 0,00001

Regional emission, use 8 – default losses from 27 tpa plus the local loss, over 365 days

28,4 kg/d to air

0 + 0,00074 kg/d to waste water

Continental emission, use 8 – default losses from 243 tpa, over 365 days

33,3 kg/d to air

0,0067 kg/d to waste water

Exposure assessment with default distribution

Local rates of loss were maintained as they are considered representative of the likely custom and practice. The regional tonnage was allowed to revert to the default (10% of the total) and the fraction of the main local source also allowed to revert to the default.

Table A2.12. Emissions from use as intermediate in synthesis of other substances

Processing as an intermediate by manufacturers is not listed because the emissions are all included under production. Ref. 47 can not be characterised on a site-specific basis as the information has not been made available; this is a generic 'stage' simply to balance the mass.

Code	Ref	Information
Nature of processes		
Intermediate	47	Synthesis of substances using HMDS by users other than the manufacturers. Total 270 tpa
Intermediate 1	48	180 tpa; Conversion to oligomers. Concentrations in downstream formulations <10%.
Emission to WWTP		
Intermediate 1	48	Minor fraction of emissions are to water. HMDS concentration data for effluent discharged directly from site not currently available but expected in next couple of weeks. No data on volume discharged and flow-rate in receiving water. Collected waste water is sent to regional WWTP that treats most municipal and industrial waste water in the local area. Effluent from WWTP discharged to large river. No data for volume and HMDS concentration in effluent from WWTP site but concentration in river close to discharge point was below limit of detection (0,05 µg/l). No data for flow rate for river. Biogas and sludge from WWTP is incinerated.
Emission to solid waste		
Intermediate 1	48	None
Emission to air		
Intermediate 1	48	Major part of gaseous emissions incinerated. Biogas and sludge from WWTP is incinerated.
Days per year		
Intermediate 1	48	Not given

Table A2.13. Emissions from use in personal care products

Code	Ref	Information
Nature of processes		
Personal Care generic	41	Assume concentration in downstream formulations to be 10%
Personal Care 1	42	(88 tpa) use typically 10, up to 90%
Personal Care 5	45	2 t used in aerosols, at 7%
Emission to WWTP at point of formulation		
Personal Care 1	42	<200 mg/l in site effluent
Personal Care 5	45	0
Emission to industrial soil at point of formulation		
Personal Care 1	42	?
Personal Care 5	45	?
Emission to air at point of formulation		
Personal Care 1	42	0
Personal Care 5	45	?
Days per year		
Personal Care 1	42	?
Personal Care 5	45	?

Site-specific exposure assessment

See table A2.13.

Tables A2.14 and A2.15 are included for completeness, on the basis of known sales and uses in the past. A survey of downstream users provided no specific information to place into these categories.

This application (use 6) is set up in EUSES as follows:

It is believed that 130 tpa are used privately in the EU for personal care. It is known that 90 t are formulated at two sites, neither of which are in the main region. The remaining 40 t are treated as 'generic personal care'. The 10% rule is applied (therefore there are 4 tpa formulated in the region). The 10% rule is applied to the private use of the entire formulated tonnage.

Defaults for formulation step

Fraction to air = 0,025

Fraction to waste water = 0,02

Assume 0 to industrial soil

300 days formulation per year

Formulation - Regional emissions – based on 365 days per year

The main region has 4 tpa to which default rates of loss are applied

0,274 kg/d to air

0,219 kg/d to waste water

Formulation - Continental emissions – based on 365 days per year

The remaining 126 t are formulated in the continent. It is known that there are no losses to air from site Personal Care 1, but default losses to waste water are used. Default rates of loss to both air and waste water apply to the remaining continental tonnage (Personal care generic, ref. 41).

2,6 kg/d to air

6,9 kg/d to waste water

Defaults for Private Use

Fraction to air = 0,45

Fraction to waste water = 0,45

Fraction of the main local source = 0,002

Private use – regional emissions

The 10% rule applies to the whole tonnage for private use, so there are 12,4 t in the main region once the losses from the formulation have been accounted for. Applying the rates of loss above, over 365 days:

15,3 kg/d to air

15,3 kg/d to waste water

Private use – Continental emissions

The remaining 111,6 t are used on the continental scale.

138 kg/d to air

138 kg/d to waste water

Exposure assessment with default distribution

Local rates of loss were maintained as they are considered representative of the likely custom and practice for formulation and private use. The regional tonnage was allowed to revert to the default (10% of the total) and the fraction of the main local source also allowed to revert to the default for formulation. The TGD does not recognise a private use stage for this IC/UC combination and values equivalent to a typical default for private use were entered.

Table A2.14. Emissions from use in household care products

Information
Nature of processes
Assume concentration in downstream formulations to be 10%
Industry category(s)
?
Emission to WWTP
?
Emission to industrial soil
?
Emission to air
?
Days per year
?

Table A2.15. Emissions from use in products used for non-specified applications

Information
Nature of processes
Assume concentration in downstream formulations to be 10%
Industry category(s)
?
Emission to WWTP
?
Emission to industrial soil
?
Emission to air
?
Days per year
?

Table A2.16. Emissions from use in products used as solvents

Code	Ref	Information
Nature of processes		
Solvent generic	44	?
Solvent 2	46	20 t used in paper deacidification products
Industry category(s)		
Solvent generic	44	?
Emission to WWTP		
Solvent 2	46	0 for formulation stage (treated at on-site WWTP, from which sludge is brought to an authorised recultivator)
Emission to industrial soil		
Solvent generic	44	?
Solvent 2	46	0 for formulation stage (treated at on-site WWTP, from which sludge is brought to an authorised recultivator)
Emission to air		
Solvent 2	46	0 for formulation stage (site gaseous emissions are scrubbed; airstream concentration < limit of detection)
Days per year		
Solvent generic	44	?

Site-specific exposure assessment

See table A2.16.

Use as a solvent (use 7) is set up in EUSES as follows:

It is believed that a total of 30 t HMDS are used as a solvent over the EU. It is known that 20 t are formulated at one site, in the main region, from which there are no emissions to air or water. The remaining 10 t are considered within a generic solvent scenario. The 10% rule is applied to formulation of this 10 t, and the 10% rule applies to the full 30 t for the processing step. It is not considered likely that HMDS solvents will be used privately.

Therefore formulation and processing are the only life cycle stages set up in EUSES.

Defaults for formulation stage

Fraction to air = 0,025

Fraction to waste water = 0,02

300 days per year

Formulation – regional emissions – main site plus 10% of the remaining 10 t, over 365 days

0,068 kg/d to air

0,055 kg/d to waste water

Formulation – continental emissions

0,616 kg/d to air

0,493 kg/d to waste water

Defaults for processing

Fraction to air = 0,95

Fraction to waste water = 0,05

10 days processing per year

Processing – regional emissions

7,46 kg/d to air
0,393 kg/d to waste water

Processing – continental emissions

67,2 kg/d to air
3,54 kg/d to waste water

Exposure assessment with default distribution

Local rates of loss were maintained as they are considered representative of the likely custom and practice. The regional tonnage was allowed to revert to the default (10% of the total) and the fraction of the main local source also allowed to revert to the default.

A2.5 Emissions of HMDS from landfill sites

The importance of this source of HMDS has not been fully delineated.

Ref. 20: Schweigkofler and Niessner (1999): Using GC-MS, HMDS was monitored at 2 domestic waste landfill sites and 2 wastewater treatment plants (WWTPs). Results are as follows (concentrations are in mg/m³); for comparison the values for xylene have also been included:

	Landfill site A ^a	Landfill site B ^b	WWTP A ^b	WWTP B ^c
HMDS	1,04-1,31	0,38-0,77	0,05	0,01
Xylene	54,1-74,1	40,3-54,9	0,7-0,8	0,4-0,5

Key: (^a) Site was sampled 3 times

(^b) Site was sampled twice

(^c) Site was sampled once

Fascuabu and Roveretto (1998): Using HRGC-MS, biogas from a number (number not specified) municipal landfill sites was measured. The average concentration was 1,7 mg/m³, the minimum was 0,15 mg/m³ and the maximum concentration was 12,6 mg/m³. No other details were provided.

New Reference: M. Schweigkofler and R.Niessner (2001) Removal of siloxanes in biogases (J. Haz. Mats. 183-196) HMDS at a landfill site was between 0,7-0,9 mg/m³ as compared to two WWTPs, where concentrations were <0,05. Analysis was again by GC-MS.

Therefore it is known that concentrations of trimethylsilanol/HMDS are usually in the range 1 – 2 mg/m³; typical gas production rates are 50 000 m³/d, i.e. 0,05 to 0,1 kg/d at a site.

These losses are best considered as regional ones. Estimating that there may be 100 such sites in a region, the regional emission would be up to 10 kg/d. This emission is expected to be similar in each region.

The source of the HMDS is not known at present.

Exposure assessment

Landfill emissions of HMDS (use 9) is set up in EUSES as a total of 100 kg per day over the EU. It is a source of HMDS but not a recognised production step for EUSES, so the tonnage produced in this way is set to 0 so that the true production levels are not affected.

The application of the 10% rule means that the regional emission is 10 kg/d over 365 days, and the total continental emission is 90 kg/d over the year. This emission scenario is neither site-specific nor default.

Appendix 6: Summary of potential for HMDS production as a by-product of synthesising other substances

Total precursor (tonnes)	Tonnage and origin		
		Code	
1471 t	Hexamethyldisilazane use in penicillin manufacture: 200 t	Penicillin manufacture 8	200 t of HMDZ
	Trimethylchlorosilane use in penicillin manufacture: 741 t	Penicillin manufacture 8	10 t of TMCS
		Penicillin manufacture 2	330 t of TMCS
		Penicillin manufacture 5	300 t of TMCS
		Penicillin manufacture 6	100 t of TMCS
		Penicillin manufacture 7	1 t of TMCS
	Hexamethyldisilazane use in other pharmaceutical manufacture: 330 t	HMDZ by-product 7 HMDZ by-product 8 HMDZ by-product 4	250 t of HMDZ 80 t of HMDZ 0,5 t of HMDZ
	Trimethylchlorosilane use in pharmaceutical manufacture: 2010 t	TMCS by-product 1 TMCS by-product 2 TMCS by-product 3 TMCS by-product 4	900 t of TMCS 80 t of TMCS 500 t of TMCS 530 t of TMCS
	bis(Trimethylsilyl)urea use in pharmaceutical production:	bis(Trimethylsilyl)urea use	-
32 t	Hexamethyldisilazane (HMDZ) use in production of silicone rubbers: 32 t	HMDZ by-product 1	
		HMDZ by-product 2	5 t of HMDS formed
		HMDZ by-product 3	0,87 t of HMDS formed
		HMDZ by-product 5	14 t of HMDS formed
		HMDZ by-product 6	12 t of HMDS formed
	Use of trimethylsilanol as end blocker	Trimethylsilanol as end blocker	0 t of HMDS formed
			No information

Appendix 7: Applications within which total HMDS production and import tonnage are used

Applications	Tonnage (tonnes)	Remarks
<i>Internal intermediate: 3391 t</i>	Producer 1: 855,1 Producer 3: 723 Producer 4: 1200 Producer 5: 215 Producer 6: 398	HMDS used at the site of manufacture.
<i>External sales by producers: 655 t</i>	Producer 1: 157,7 Producer 3: 190 Producer 4: 113 Producer 5: 18 Producer 6: 177	The tonnage reported in are totals that are split into various uses, summarised in Appendix 7.

Appendix 8: Balance of HMDS

Balance of HMDS produced directly/imported and subsequent use

	Producer 1	Producer 3	Producer 4	Producer 5	Producer 6	Total
Tonnage produced*	1013 t*	912	1320*	215	575	4025
Used internally as intermediate	855 t	723 t	1200 t	215 t	398 t	3391 (84%)
Sold on						
Personal care	58	0	72	0	104?	234?
Household care	3	0	0	0	?	?
Intermediate	65	190	36	0	0?	291
Solvent	32	0	12?	0	76?	120?
	158 t	190 t	120 t	0	177 t	645 t
Known customers – household/personal care		Known customers – solvents		Known customers – intermediate		Total known used
Personal care 1	88	Solvent 2	20	Intermediate 1	180	
Personal care 2	3					
Personal care 3	50	Other	?	Other	111	
Personal care 4	50					
Personal care 5	2					
Subtotal:	193 t	Subtotal:	20 t	Subtotal:	291 t	504 t
Unspecified personal care	Estimate 41	Unspecified solvent	Estimate 100?*	Unspecified intermediate	0	141 t
Total:	234 t	Total:	120 t	Total:	291 t	645 t

? in the table implies calculation has been used to balance the amounts.

The two estimates have been made by the authors on the basis of the overall information obtained.

* export accounted for

** 218 t in 1999

Balance of HMDS produced indirectly/reprocessed

From TMCS/TMSU		From HMDZ		From TMCS other		
Penicillin manufacture 1	500			TMCS by-product 1	900	
Penicillin manufacture 2	330			TMCS by-product 2	130	
Penicillin manufacture 3	0			TMCS by-product 3	0	
Penicillin manufacture 4	0			TMCS by-product 4	530	
Penicillin manufacture 5	1100					
Penicillin manufacture 6	0					
Penicillin manufacture 7	1	HMDZ by-product 7	250			
Penicillin manufacture 8	210	HMDZ by-product 8	80			
Penicillin manufacture 9	0					
Subtotal:	2141	Subtotal:	330	Subtotal:	1560	4031
Reprocessing						Totals
By-product 1	2000 t	By-product 2	1000	By-product 3	1500 t	4500

Appendix 9: Summary table of emissions data

REF	IDENTITY AND LOCATION			LIFE CYCLE						VOLUME	RELEASE DATA with summary of the justification
	Company	Region	Site n°	Production	Formulation	Processing	Private use	Recovery	Comment	2000	
	Code	Code								Use pattern	Releases
1	Producer 1	1	1	X		(X)			Proc = use as intermediate; single site info on losses	1803 t produced; 102 t imported; 855,1 t used, 892 t exported; 157 t sold on	0,089 kg/d to water, mean effluent flow 5784 m3/d; 1/3 of estimated mean river flow = 28 800 m3/d; sludge from first stage incinerated, second spread. 6,77 kg/d to air. Analytical support.
2	Producer 2	2	2	X						Not an HMDS production site	1,5 kg/d to air (estimate in part)
3	Producer 3	3	3	X		(X)			Proc = use as intermediate	912 t produced 722 t as in-house intermediate, 190 t as intermediate sold on	<1,4 kg/d to water 137 000 m3/d into river 8,64e7 m3/d low flow; 0 to air from production. Off gases and sludge from on site WWTP incinerated. Analytical support.
4	Producer 4	3	4	X		(X)			Proc = use as intermediate	1320 t produced, ca 1200 t intermediate, 120 t sold on, 10 t exported	On site wwtp sludge incinerated, no biogas. 0 to air from production
5	Producer 5	4	5	X		(X)			Proc = use as intermediate	215 t produced and used as intermediate	On site wwtp sludge incinerated, no biogas. 0 to air from production
6	Producer 6	5	6	X		(X)			Proc = use as intermediate	575 t produced 398 t used internally, 177 t sold	3 t to air = 10 kg/d from this process, 15 t total = 50 kg/d (obtained by mass balance); 17,2 kg/d to water (measured), 6,9e8 m3/d, no WWTP
8	Penicillin man're 1	6	7	X					TM silyl urea or chloride, HMDZ	500 t of precursor	Closed systems, losses = 0
9	Penicillin man're 2	6	8	X					No specific loss information	330 t of precursor	Zero to air; estimate <0,1 mg/l to water diluted by 10 into surface water, volumes not known.
10	Penicillin man're 3	2	9	X					TM silyl urea or chloride	0	No longer used for penicillin.
11	Penicillin man're 4	6	10	X					TM silyl urea or chloride	0	No longer used

REF	IDENTITY AND LOCATION			LIFE CYCLE						VOLUME	RELEASE DATA with summary of the justification
	Company	Region	Site n°	Production	Formulation	Processing	Private use	Recovery	Comment	2000	
	Code	Code								Use pattern	
12	Penicillin man're 5	4	11	X					Various precursors including TMCS	1100 t of precursor	<0,1% (partially supported statement); gaseous waste incinerated.
13	Penicillin man're 6	6	12	X						100 t of precursor according to supplier; now no longer in use for any process.	Zero since now not used
14	Penicillin man're 7	7	13	X					No specific loss information	1 t of precursor	No info on losses; assume 10 d 'production' and default releases for IC3/UC32
15	Penicillin man're 8	7	14	X					No specific loss information	210 t of precursors	No info on losses; assume 210 d 'production' and default releases for IC3/UC33
16	Penicillin man're 9	6	19	X					No specific loss information	Believed to be relatively minor	No info on losses
17	By-product 1	1	15					X		2000 t	16 200 kg/y to air, based on 4 measurements/y. Site effluent <1mg/l daily composite sample, wwtp flow 10 000 m3/d, river flow 6 x 10e6 m3/d
18	By-product 2	4	16					X		1000 t	No losses to air or water based on procedures disclosed
19	By-product 3	3	4					X	Site loss could consolidate above	1500 t	Losses consolidated into total site losses of 37 t to air
21	HMDZ by-product 1	3	17	X					Liquid waste sent for recycling (8 t)	5 t (estimate obtained by mass balance)	5 t produced = 16,7 kg/d to air; estimate based on limited measurements
22	HMDZ by-product 2	3	3	X					Loss to air from this process only	0,87 t generated as waste to air	0,87 t produced 2,9 kg/d to air over 300 days; site loss (not included above). Limited analytical support for air loss (annual measurement)
23	HMDZ by-product 3	3	4	(X)					Site loss could consolidate above	14 t from this process consolidated into site loss.	14 t to air, 46,7 kg/d; site loss (not included above).

REF	IDENTITY AND LOCATION			LIFE CYCLE						VOLUME	RELEASE DATA with summary of the justification
	Company	Region	Site n°	Production	Formulation	Processing	Private use	Recovery	Comment	2000	
	Code	Code								Use pattern	Releases
24	HMDZ by-product 4	4	5	(X)					Site loss could consolidate above	0,5 t	0,5 t to air; 1,6 kg/d
25	HMDZ by-product 5	5	6	(X)					Site loss could consolidate above	12 t	Losses consolidated into total site losses
27	HMDZ by-product 7	6	7	(X)					Site loss could consolidate above	250 t	Losses consolidated into total site losses
28	HMDZ by-product 8	6	10	X						80 t of precursor	No info on losses; assume 210 d 'production' and default releases for IC3/UC33
30	TMCS by-product 1	2	9	(X)					Site loss could consolidate above	900 t	Closed systems, losses = 0. Sent for reprocessing. Some losses as the silanol.
31	TMCS by-product 2	6	10	(X)					Site loss could consolidate above	130 t of precursor	Losses consolidated into total site losses
32	TMCS by-product 3	4	16	(X)					Site loss could consolidate above	? - but not significant	Losses consolidated into total site losses
33	TMCS by-product 4	3	18	(X)						530 t	Zero losses, due to use of incineration
35	bis(Trimethylsilyl) urea use	2	9	(X)					Site loss could consolidate above	? - but not significant	Losses consolidated into total site losses
37	Trimethylsilanol as end blocker	2	2	(X)					Site loss - consolidated above		Losses consolidated into total site losses
39	Personal care	-	-		X				Typically 10% in formulations	41 t assume 40% in main region	Use default model applied to 40% in the region; fmls = 0,6, 96 days
39a	Personal care	-	-				X			Total 232 t assume 10% in the region	Use default model for IC5/UC9; fmls = 0,002, 365 days

REF	IDENTITY AND LOCATION			LIFE CYCLE						VOLUME	RELEASE DATA with summary of the justification
	Company	Region	Site n°	Production	Formulation	Processing	Private use	Recovery	Comment	2000	
	Code	Code								Use pattern	Releases
40	Personal care 1	7	21		X				Typically 10% in formulations, up to 90%	88 t	0 to air; amount in effluent is estimated as 4,4 t/y (14,7 kg/d) (5%) , wwtp treats 4e7 m3/y = 110 000 m3/d; no info on receiving water.
40b	Personal care 2	1	25		X					3 t	<0,1% loss estimate only
40d	Personal care 3	2	26		X				Single company not identified by the research	50 t	No info on losses; use default, 150 days
40e	Personal care 4	5	27		X				Single company not identified by the research	50 t	Influent and effluent concentrations were respectively of 0,6 to 0,7 µg/l and not detectable (<0,1 µg/l). Concentration in receiving water was also non detectable. No HMDS was detected in the WWTP sludge (<10 µg/kg dwt).
40f	Personal care 5	1	24		X					2 t in aerosol at 7% in formulation	No info on losses to air; use default, zero to water. 40 days
40f	Personal care 5	1	-				X			Assume all in Region	Assume that 100% of the contents of aerosols released to air over 365 days.
42	Solvent	-	-		X					100 t, assume 10% in the region	Use default fmls = 1, 300 d; IC15/UC48; 0,1 in formn
42a	Solvent	-	-			X				120 t assume 10% in the region	Use default fmls = 0,8, 32 d. IC15/UC48
44	Solvent 2	3	22		X					20 t in paper deacidification products	Zero losses at point of formulation
45	Intermediate	-	-			X				111 t assume 40% in the region	Use default fmls = 0,8, 32 d. IC11/UC33
46	Intermediate 1	3	23			X				180 t	Emissions to air incinerated. WWTP gas /sludge incinerated; conc in Rhine < 5e-3 mg/l, <4,3 kg/d.
48	None - landfill gas	-	-	X						assume 10% in the region	To air.

Appendix 10: Summary of releases estimates

Default versus site-specific distribution and release factors

	Fraction of tonnage in main region for this application		Fraction of main local source		Release fractions air, water		
	Site-specific	Default	Site-specific	Default	Site-specific	Default	
Production	0,463	0,1	1	1	0 0	0,001 0,003	air water
Penicillin manufacture	0	0,1	NA	1	-	-	-
By-product reprocessing	0,333	0,1	1	- ¹	0 0	(0,0001 0,003)	air water
HMDZ by-product	0,7	0,1	0,5	1	N/A ²	-	
TMCS by-product	0	0,1	NA	1	N/A N/A ³	0,001 0,003	air water
Personal care							
- Formulation	0,03	0,1	1	1	-	0,025 0,02	air water
- Private use	0,1	0,1	0,002 (IC5, UC9)	*		0 0,99	air water
Solvent							
- Formulation	-	0,1	0,33	1	-	0,025 0,02	air water
- Processing			0,8	0,8		0,50 0,01	air water
Intermediate	0,77	0,1	0,87	0,35	-	0,025 0,00001	air water
Landfill gas	0,1	0,1	NA	N/A	-	-	-

¹ The TGD does not envisage these life-cycle stages for the industry category/use category used and hence default values do not exist.

² Tonnage of HMDZ not known.

³ Tonnage of TMCS not known.

Comparison of the daily local loss rates with the defaults for Region 3

		Emission to air (kg/d)		Emission to water (kg/d)	
		Measured	Default	Measured	Default
1	Production and import				
	Producer 3 - 912 t	0	3,04	0	9,12
	Producer 4 - 1320 t	0	4,43	0	13,3
2	Generation as a by-product		N/A ¹		N/A ⁴
	HMDZ by-product 1	16,7		0	
	HMDZ by-product 2	2,9		0	
	HMDZ by-product 3	123,3		0	
3	Reprocessing of by-product				
	1500 t	0	0,5	0	15
4	Use of the substance				
	Personal care				
	40% of EU for Formulation ² - 16 t	-	1,33	-	1,07
	10% of EU for Use - 23 t	-	0	-	0,12
	Solvent				
	10% of EU Formulation - 10 t	-	0,83	-	0,67
	10% of EU for Use - 12 t	-	150	-	0,03
	Intermediate				
	Intermediate 1 - 180 t	0	30	<4,3	0
	Processing - 44 t	-	50	-	0

¹ N/A because total use of HMDZ/TMCS at HMDS producer sites is not presently available.

² Data are not available for all sites.

Summary of the life cycle stages of HMDS production and use

		Total tonnage (t)	Industry Category	Use Category	Regional tonnage fraction		These fractions are all of the amount in the region							
							Fraction of main local source		Emission to air (fraction)		Emission to water (fraction)		Emission to industrial soil (fraction)	
					Region 3	Default	Region 3	Default	Region 3	Default	Region 3	Default	Region 3	Default
1	Production and import	4835*	11 Polymers	33 Intermediates	0,46	0,1	1	1	0	0,001	0	0,003	0	0,0001
2	Generation as a by-product		3 Chemicals used in synthesis	33 Intermediates	0,33	0,1	-	1	-	0,0001	-	0,003	-	0,0001
3	Reprocessing of by-product	4500	3 Chemicals used in synthesis	33 Intermediates	0,33	0,1	1		0	0,0001	0	0,003	0	0,0001
4	Use of the substance													
	Personal care	234	5 Personal domestic	15 Cosmetics										
	Formulation				0,03	0,1		1	(0,025)	0,025	(0,02)	0,021	0	0,0001
	Private Use				0,1	0,1	0,002	0,002	(0)	(0,99)	(0)	0,99	0	0
	Solvent	120	15 Other	48 solvents										
	Formulation				0,7	0,1	0,33	1	(0,025)	0,025	(0,025)	0,01	0	0,0001
	Use				0,1	0,1	0,8	0,8	(0,50)	0,50	(0,01)	0,01	0	0,0005
	Intermediate	291	11 Polymers	33 Intermediates					0 from main site	0,05	0,0072 from main site	1e-5	0	0,0001
	Processing				0,77	0,1	0,87	0,35						
5	Release from landfill gas (regional)	-			0,1	0,1	-	-	-	-	-	-	-	-

* 892 t exported, 3590 t used at site of production.

Appendix 11: Predicted exposure concentrations (PECs) in the different relevant environmental compartments.

Local estimated PECs in the effluent of the WWTP, in surface water and in sediments of the freshwater compartment in Region 3

	Local - region 3		
	Effluent STP (mg/l)	Surface water (mg/l)	Sediment (mg/kgwwt)
Application			
<i>Producer 4</i>	0	2,74E-05	9,65E-04
<i>Producer 3</i>	0	4,36E-05	1,53E-03
<i>HMDZ by-product</i>	0	2,74E-05	9,65E-04
<i>Personal care</i> <i>- Formulation</i>	1,22E-03	1,49E-04	5,26E-03
<i>- Private use</i>	3,21E-03	3,47E-04	1,22E-02
<i>Solvent</i> <i>- Formulation</i>	1,7E-02	1,72E-03	6,06E-02
<i>- Industrial use</i>	6,08E-04	8,80E-05	3,10E-03
<i>Intermediate</i>	2,61E-04	5,35E-05	1,88E-03
<i>Intermediate</i>	-	7,73E-05	2,72E-03
<i>Landfill sites</i>	-	2,74E-05	9,65E-04

Freshwater compartment in other EU regions

Region		Life Cycle Stage	Effluent STP (mg/l)	Surface water (mg/l)	Sediment (mg/kgwwt)
1	By-product 1	<i>Production</i>	5,09E-03	4,39E-05	1,55E-03
	Producer 1	<i>Production</i>	7,93E-04	1,68E-04	5,91E-03
	Personal care 2	<i>Formulation</i>	2,55E-04	6,09E-05	2,14E-03
	Personal care 5	<i>formulation</i>	0	3,55E-06	1,25E-03
		<i>Private use</i>	0	3,55E-06	1,25E-03
2	TMCS by-product	<i>Production</i>	0	3,67E-05	1,29E-03
	Personal care 3	<i>Formulation</i>	3,95E-03	4,31E-04	1,52E-02
4	Producer 5	<i>Production</i>	0	3,52E-05	1,24E-03
	By-product 2	<i>Industrial use</i>	0	3,52E-05	1,24E-03
	Penicillin manufacture 3	<i>Formulation</i>	9,65E-02	9,66E-03	3,4E-01
5	Producer 6	<i>Production</i>	0	8,46E-06	2,98E-03
	Personal care 4	<i>Formulation</i>	3,68E-05	6,34E-05	2,23E-03
6	HMDZ by-product 8	<i>Production</i>	5,26E-01	5,26E-02	1,85
	Penicillin manufacture 9	<i>Production</i>	5,26E-03	5,67E-04	2E-02
7	Penicillin manufacture 8	<i>Production</i>	4,06E-01	4,60E-02	4,6E-02
	Penicillin manufacture 7	<i>Production</i>	5,26E-02	5,30E-03	0,187
	Personal care 1	<i>Formulation</i>	7,03E-03	7,50E-04	2,64E-02

Local estimated PECs in surface water and in sediments of the marine compartment

	Life cycle stages	Local PEC _{marine water} (mg/l)	Local PEC _{marine sediment} (mg/kgwwt)
REGION 3			
Producer 4	<i>Production</i>	2,34E-06	8,22E-05
Producer 3	<i>Production</i>	6,99E-03	2,46E-01
HMDZ by-product	<i>(Production)</i>	2,34E-06	8,22E-05
Personal care	<i>Formulation</i>	2,42E-04	8,51E-03
	<i>Private use</i>	6,30E-04	0,0222
Solvent	<i>Formulation</i>	3,33E-03	0,117
	<i>Industrial use</i>	1,21E-04	4,28E-03
Intermediate	<i>(Production)</i>	5,35E-05	1,89E-03
Intermediate	<i>(Production)</i>	0,0216	0,759
landfill sites		2,34E-06	8,22E-05
REGION 1			
By-product 1	<i>Production</i>	1,00E-03	3,52E-02
Producer 1	<i>Production</i>	1,58E-04	5,58E-03
Personal care 2	<i>Formulation</i>	5,29E-05	1,86E-03
Personal care 5	<i>Private use</i>	3,04E-06	1,07E-04
	<i>Production</i>	3,04E-06	1,07E-04
REGION 2			
TMCS by-product	<i>Production</i>	3,14E-06	1,11E-04
Personal care	<i>Formulation</i>	7,51E-04	0,0265
REGION 4			
Producer 5	<i>Production</i>	3,02E-06	1,06E-04
By-product 2	<i>Industrial use</i>	3,02E-06	1,06E-04
Penicillin manufacture 3	<i>Production</i>	0,0183	0,644
REGION 5			
Producer 6	<i>Production</i>	8,58E-02	3,02
Personal care 4	<i>Formulation</i>	1,21E-05	4,26E-04
REGION 6			
HMDZ by-product 8	<i>Production</i>	0,0998	3,51
Penicillin manufacture 9	<i>Production</i>	1,00E-03	0,0353
REGION 7			
Penicillin manufacture 8	<i>Production</i>	0,0872	3,07
Penicillin manufacture 7	<i>Production</i>	9,98E-03	0,351
Personal care 1	<i>Formulation</i>	1,33E-03	0,047

Local and regional estimated PECs in soil

	Life cycle stages	Local PEC _{soil} (mg/kgwwt)
REGION 3		
Producer 4	<i>Production</i>	6,61E-10
Producer 3	<i>Production</i>	1,77E-05
HMDZ by-product	<i>(Production)</i>	1,02E-04
Personal care	<i>formulation</i>	7,16E-02
	<i>Private use</i>	8,45E-03
Solvent	<i>formulation</i>	4,48E-02
	<i>Industrial use</i>	1,70E-03
Intermediate	<i>(Production)</i>	7,07E-04
Intermediate	<i>(Production)</i>	6,61E-10
Landfill sites		3,71E-05
Regional		4,3-04
REGION 1		
By-product 1	<i>Production</i>	6,74E-02
Producer 1	<i>Production</i>	4,17E-05
Personal care 2	<i>Formulation</i>	6,68E-04
Personal care 5	<i>Private use</i>	1,02E-06
	<i>Production</i>	3,88E-05
REGION 2		
TMCS by-product	<i>Production</i>	1,18E-05
Personal care	<i>Formulation</i>	1,13E-02
REGION 4		
Producer 5	<i>Production</i>	1,26E-05
By-product 2	<i>Industrial use</i>	5,87E-10
Penicillin manufacture 3	<i>Production</i>	2,77E-01
REGION 5		
Producer 6	<i>Production</i>	3,95E-04
Personal care 4	<i>Formulation</i>	2,15E-04
REGION 6		
HMDZ by-product 8	<i>Production</i>	1,51
Penicillin manufacture 9	<i>Production</i>	1,51E-02
REGION 7		
Penicillin manufacture 8	<i>Production</i>	1,32
Penicillin manufacture 7	<i>Production</i>	1,51E-01
Personal care 1	<i>Formulation</i>	2,02E-02
REGIONAL		4,30E-04
CONTINENTAL		3,84E-05

Local and regional estimated PECs in air

	Life cycle stages	Local PEC _{air} (mg/m ³)
REGION 3		
Producer 4	<i>Production</i>	2,82E-06
Producer 3	<i>Production</i>	6,66E-04
HMDZ by-product	<i>(Production)</i>	3,81E-03
Personal care	<i>formulation</i>	1,19E-05
	<i>Private use</i>	3,19E-05
Solvent	<i>formulation</i>	1,93E-04
	<i>Industrial use</i>	3,49E-09
Intermediate	<i>(Production)</i>	5,89E-04
Intermediate	<i>(Production)</i>	2,82E-06
Landfill sites		1,39E-03
REGION 1		
By-product 1	<i>Production</i>	1,23E-02
Producer 1	<i>Production</i>	1,55E-03
Personal care 2	<i>Formulation</i>	5,26E-06
Personal care 5	<i>Private use</i>	4,14E-05
	<i>Production</i>	1,46E-03
REGION 2		
TMCS by-product	<i>Production</i>	3,45E-04
Personal care	<i>Formulation</i>	3,10E-05
REGION 4		
Producer 5	<i>Production</i>	3,68E-04
By-product 2	<i>Industrial use</i>	2,51E-06
Penicillin manufacture 3	<i>Production</i>	6,96E-04
REGION 5		
Producer 6	<i>Production</i>	1,14E-02
Personal care 4	<i>Formulation</i>	1,91E-03
REGION 6		
HMDZ by-product 8	<i>Production</i>	3,79E-03
Penicillin manufacture 9	<i>Production</i>	1,54E-05
REGION 7		
Penicillin manufacture 8	<i>Production</i>	2,32E-03
Penicillin manufacture 7	<i>Production</i>	1,56E-05
Personal care 1	<i>Formulation</i>	2,78E-03
REGIONAL		2,82E-06
CONTINENTAL		9,82E-07

Local and regional estimated PECs in freshwater and marine fish and top – predator according to EUSES 2.0

	Life cycle stages	PEC freshwater fish (mg/kg ww)	PEC marine fish (mg/kg ww)	PEC top predator (mg/kg ww)
REGION 3				
Producer 4	<i>Production</i>	3,56E-02	3,04E-03	3,04E-03
Producer 3	<i>Production</i>	4,42E-02	3,73	7,49E-01
HMDZ by-product	<i>(Production)</i>	3,56E-02	3,04E-03	3,04E-03
Personal care	<i>formulation</i>	1,01E-01	1,31E-01	2,86E-02
	<i>Private use</i>	2,43E-01	4,11E-01	8,46E-02
Solvent	<i>formulation</i>	9,41E-01	1,78	3,58E-01
	<i>Industrial use</i>	3,91E-02	9,82E-03	4,39E-03
Intermediate	<i>(Production)</i>	3,63E-02	4,40E-03	3,31E-03
Intermediate	<i>(Production)</i>	6,23E-02	11,5	2,31
Landfill site		0,0356	3,04E-04	3,04E-04
REGION 1				
By-product 1	<i>Production</i>	5,07E-02	5,37E-01	1,11E-01
Producer 1	<i>Production</i>	1,17E-01	8,69E-02	2,05E-02
Personal care 2	<i>Formulation</i>	5,97E-02	3,06E-02	9,28E-03
Personal care 5	<i>Private use</i>	4,61E-02	3,95E-03	3,95E-03
	<i>Production</i>	4,61E-02	3,95E-03	3,95E-03
REGION 2				
TMCS by-product	<i>Production</i>	4,77E-02	4,09E-03	4,09E-03
Personal care	<i>Formulation</i>	2,58E-01	4,04E-01	8,4E-02
REGION 4				
Producer 5	<i>Production</i>	4,58E-02	3,92E-03	3,92E-03
By-product 2	<i>Industrial use</i>	4,58E-02	3,92E-03	3,92E-03
Penicillin manufacture 3	<i>Production</i>	5,19	9,78	1,96
REGION 5				
Producer 6	<i>Production</i>	9,09E-02	45,8	9,17
Personal care 4	<i>Formulation</i>	7,96E-02	1,04E-02	7,41E-03
REGION 6				
HMDZ by-product 8	<i>Production</i>	28,1	53,3	10,7
Penicillin manufacture 9	<i>Production</i>	1,48E-01	1,82E-01	4,02E-02
REGION 7				
Penicillin manufacture 8	<i>Production</i>	32,6	32,6	6,53
Penicillin manufacture 7	<i>Production</i>	1,83E-01	1,83E-01	4,09E-02
Personal care 1	<i>Formulation</i>	7,16E-01	7,16E-01	1,47E-02

Appendix 12: Risk characterisation for the different relevant environmental compartments

Local PEC/PNEC ratios for the freshwater compartment and for microorganisms in STP

	Life cycle stages	PEC/PNEC ratio (water)	PEC/PNEC ratio (STP)
REGION 3			
Producer 4	<i>Production</i>	1,71E-02	0
Producer 3	<i>Production</i>	2,73E-02	0
HMDZ by-product	<i>(Production)</i>	1,71E-02	0
Personal care	<i>Formulation</i>	9,31E-02	1,22E-04
	<i>Private use</i>	2,17E-01	3,21E-04
Solvent	<i>Formulation</i>	1,08	1,70E-03
	<i>Industrial use</i>	5,50E-02	6,08E-05
Intermediate	<i>(Production)</i>	3,34E-02	2,61E-05
Intermediate	<i>(Production)</i>	4,83E-02	-
Landfill sites		1,71E-02	-
REGION 1			
By-product 1	<i>Production</i>	2,74E-02	5,09E-04
Producer 1	<i>Production</i>	1,05E-01	7,93E-05
Personal care 2	<i>Formulation</i>	3,81E-02	2,55E-05
Personal care 5	<i>Private use</i>	2,22E-03	0
	<i>Production</i>	2,22E-03	0
REGION 2			
TMCS by-product	<i>Production</i>	2,29E-02	0
Personal care	<i>Formulation</i>	2,69E-01	3,95E-04
REGION 4			
Producer 5	<i>Production</i>	2,20E-02	0
By-product 2	<i>Industrial use</i>	2,20E-02	0
Penicillin manufacture 3	<i>Production</i>	6,04	9,65E-03
REGION 5			
Producer 6	<i>Production</i>	5,29E-03	0
Personal care 4	<i>Formulation</i>	3,96E-02	1,76E-02
REGION 6			
HMDZ by-product 8	<i>Production</i>	32,9	5,26E-02
Penicillin manufacture 9	<i>Production</i>	3,54E-01	5,26E-04
REGION 7			
Penicillin manufacture 8	<i>Production</i>	28,8	4,60E-02
Penicillin manufacture 7	<i>Production</i>	33,1	5,26E-03
Personal care 1	<i>Formulation</i>	4,69E-01	7,03E-04

Local PEC/PNEC ratios for the marine compartment

	Life cycle stages	PEC/PNEC ratios
REGION 3		
Producer 4	<i>Production</i>	1,46E-02
Producer 3	<i>Production</i>	43,7
HMDZ by-product	<i>(Production)</i>	1,46E-02
Personal care	<i>Formulation</i>	1,51
	<i>Private use</i>	3,94
Solvent	<i>Formulation</i>	20,8
	<i>Industrial use</i>	7,56E-01
Intermediate	<i>(Production)</i>	3,34E-01
Intermediate	<i>(Production)</i>	135,
Landfill sites		1,46E-02
REGION 1		
By-product 1	<i>Production</i>	6,25
Producer 1	<i>Production</i>	9,88E-01
Personal care 2	<i>Formulation</i>	3,31E-01
Personal care 5	<i>Private use</i>	1,90E-02
	<i>Production</i>	1,90E-02
REGION 2		
TMCS by-product	<i>Production</i>	1,96E-02
Personal care	<i>Formulation</i>	4,69
REGION 4		
Producer 5	<i>Production</i>	1,89E-02
By-product 2	<i>Industrial use</i>	1,89E-02
Penicillin manufacture 3	<i>Production</i>	114
REGION 5		
Producer 6	<i>Production</i>	536
Personal care 4	<i>Formulation</i>	7,56E-02
REGION 6		
HMDZ by-product 8	<i>Production</i>	624
Penicillin manufacture 9	<i>Production</i>	6,25
REGION 7		
Penicillin manufacture 8	<i>Production</i>	545
Penicillin manufacture 7	<i>Production</i>	62,4
Personal care 1	<i>Formulation</i>	8,31

Local PEC/PNEC ratios for terrestrial compartment

	Life cycle stages	PEC/PNEC ratios
REGION 3		
Producer 4	<i>Production</i>	1,47E-08
Producer 3	<i>Production</i>	3,93E-04
HMDZ by-product	<i>(Production)</i>	2,27E-03
Personal care	<i>Formulation</i>	1,59
	<i>Private use</i>	1,88E-01
Solvent	<i>Formulation</i>	9,96E-01
	<i>Industrial use</i>	3,78E-02
Intermediate	<i>(Production)</i>	1,57E-02
Intermediate	<i>(Production)</i>	1,47E-08
Landfill sites		8,24E-04
REGION 1		
By-product 1	<i>Production</i>	1,5
Producer 1	<i>Production</i>	9,27E-04
Personal care 2	<i>Formulation</i>	1,48E-02
Personal care 5	<i>Private use</i>	2,27E-05
	<i>Production</i>	8,62E-04
REGION 2		
TMCS by-product	<i>Production</i>	2,62E-04
Personal care	<i>Formulation</i>	2,51E-01
REGION 4		
Producer 5	<i>Production</i>	2,80E-04
By-product 2	<i>Industrial use</i>	1,30E-08
Penicillin manufacture 3	<i>Production</i>	6,16
REGION 5		
Producer 6	<i>Production</i>	8,78E-03
Personal care 4	<i>Formulation</i>	4,78E-03
REGION 6		
HMDZ by-product 8	<i>Production</i>	33,6
Penicillin manufacture 9	<i>Production</i>	3,36E-01
REGION 7		
Penicillin manufacture 8	<i>Production</i>	29,3
Penicillin manufacture 7	<i>Production</i>	3,36
Personal care 1	<i>Formulation</i>	4,49E-01

Local PEC/PNEC ratios for secondary poisoning

	Life cycle stages	PEC/PNEC freshwater fish (mg/kg ww)	PEC/PNEC marine fish (mg/kg ww)	PEC/PNEC top predator (mg/kg ww)
REGION 3				
Producer 4	Production	7,12E-04	6,08E-05	6,08E-05
Producer 3	Production	8,84E-04	7,46E-02	1,50E-02
HMDZ by-product	(Production)	7,12E-04	6,08E-05	6,08E-05
Personal care	Formulation	2,02E-03	2,62E-03	5,72E-04
	Private use	4,86E-03	8,22E-03	1,69E-03
Solvent	Formulation	1,88E-02	3,56E-02	7,16E-03
	Industrial use	7,82E-04	1,96E-04	8,78E-05
Intermediate	(Production)	7,26E-04	8,80E-05	6,62E-05
Intermediate	(Production)	1,25E-03	2,30E-01	4,62E-02
Landfill sites		7,12E-04	6,08E-05	6,08E-05
Regional		-	6,14E-05	
REGION 1				
By-product 1	Production	1,01E-03	1,07E-02	2,22E-03
Producer 1	Production	2,34E-03	1,74E-03	4,10E-04
Personal care 2	Formulation	1,19E-03	6,12E-04	1,86E-04
Personal care 5	Private use	9,22E-04	7,90E-05	7,90E-05
	Production	9,22E-04	7,90E-05	7,90E-05
REGION 2				
TMCS by-product	Production	9,54E-04	8,18E-05	8,18E-05
Personal care	Formulation	5,16E-03	8,08E-03	1,68E-03
REGION 4				
Producer 5	Production	9,16E-04	7,84E-05	7,84E-05
By-product 2	Industrial use	9,16E-04	7,84E-05	7,84E-05
Penicillin manufacture 3	Production	1,04E-01	1,96E-01	3,92E-02
REGION 5				
Producer 6	Production	1,82E-03	9,16E-01	1,83E-01
Personal care 4	Formulation	1,59E-03	2,08E-04	1,48E-04
REGION 6				
HMDZ by-product 8	Production	5,62E-01	1,07	2,14E-01
Penicillin manufacture 9	Production	2,96E-03	3,64E-03	8,04E-04
REGION 7				
Penicillin manufacture 8	Production	3,44E-01	6,52E-01	1,31E-01
Penicillin manufacture 7	Production	3,12E-03	3,66E-03	8,18E-04
Personal care 1	Formulation	8,74E-03	1,43E-02	2,94E-03

Appendix 13: Summary of monitoring reports provided by CES

1. Presence of HMDS in ambient air samples

Report from Degussa, Goldschmidt AG., October 9th 2001

Sampling and analytical method

Sampling tubes filled with TENAX adsorption material; following thermal desorption at 280°C, then analysed by GC/MS coupling.

Long-term tests showed that sample tubes stored individually in glass containers with screw-caps are stable at room temperature for at least four weeks.

Samples collected by pumping a total of 2 l (error 1.9 – 2.1 l based on specification of pump) of air through the tube over a 20-minute period. Three consecutive samples collected allowed the determination of a one-hour average.

The tubes were then desorbed at 280°C flushing with pre-cleaned helium.

For calibration, a solution of HMDS, ethylbenzene, m- and o-xylene in toluene was prepared. The detection limit is 0,1 micrograms/cubic metre.

Validation

Storage stability was verified by an average recovery of 91% over 14 days, for four samples spiked with 5 – 10 ng HMDS.

A calibration plot of peak area by spike concentration gave excellent linearity with $R^2 = 0,999$. Recovery of HMDS from the tubes was tested by spiking the tubes, drawing 2 l purified nitrogen, and analysing as before. A recovery level of 71 – 76% was obtained.

Samples taken and results

Sampling was undertaken at between January and May 2001, at eleven locations, by four companies.

Location of sampling	No. of samples	Highest level of HMDS	Further information
Around residential buildings	18	0,3 µg/m ³	
City areas	18	ND (<0,1 µg/m ³)	
Rural areas	6	ND (<0,1 µg/m ³)	
In vicinity of silicone-handling plants	58	50,4 µg/m ³	median value of 0,1 µg/m ³ ; and 90% of these samples were <7 µg/m ³

2. Monitoring of HMDS in the aquatic environment

Degussa, Goldschmidt AG, no date

Sampling and analytical method

100 ml water samples were taken in flasks containing NaCl, and sealed until time of analysis. A pentane extraction in the sample flask (by replacing 5 ml aqueous sample with 5 ml pentane, containing a known amount of toluene-d8) removed the non-polar components into the solvent phase. The pentane phase is analysed, by GC/MS. A detection limit of 0,02 µg /l applies.

It is noted that traces of silylating agents (e.g. MSTFA), used routinely in the GC laboratory, are able to form HMDS in the presence of water and hence that the values reported may be too high. No further discussion of this issue is set out.

250 ml – 1 l samples of sediment were collected. Samples were analysed in 25 g portions. 50 ml acetone was added with stirring and cooling, followed by addition of 50 ml pentane. 25 ml water was added and the organic phase separated. The pentane phase is analysed by GC/MS, applying a correction for the dry matter content. The detection limit is 1 µg /kg with a quantification limit estimated as 3 microgram/kg.

Samples taken and results

Dates of sampling are not provided, although all the values are on the basis of analysis performed 'over the last two years'. Marine water and sediment samples were collected by the Environment Agency; others were collected by experienced personnel, mainly from CES member companies.

Water was sampled in rivers, and upstream and downstream of municipal and industrial wastewater treatment works.

Location of sampling	No. of samples	Highest level of HMDS	Further information
Marine: mouth of River Mersey, UK	6	ND (<0,02 µg /l)	
Marine: Cardiff Bay, UK	6	ND (<0,04 µg /l)	Higher limit of detection due to higher blank values of the solvent used.
Three municipal WWTPs in Germany	3 reported	0,05 µg /l (influent)	Results summarised in the report for reasons of confidentiality
Two WWTPs in UK	2 influent 2 effluent	0,5 ND (<0,02 µg /l)	In both cases HMDS was quantifiable in influent, ND in effluent. Municipal/industrial not stated.
Four silicones industry industrial WWTPs	7	1,4 µg /l in effluent	Levels confirmed to fall to ND a short distance downstream in three cases.

Sampling of sediment was undertaken in riverine and marine (estuarine) environments.

Location of sampling	No. of samples	Highest level of HMDS	Further information
3,5 km downstream from a municipal WWTP in the UK	3	ND	River flow velocity 0,05 – 0,9 f/s
various locations on the River Rhine in Germany and the Netherlands	8	ND (seven)	
Marine: mouth of River Mersey, UK	6	ND	
Marine: Cardiff Bay, UK	6	20 micrograms/kg	Detected in all six samples but not quantifiable (<3 micrograms/kg) in four
Marine: open sea (Las St. Abbs, Bell Rock)	3 6	ND ND	Various depths of sediment sampled.

Validation

No detail of validation of the analytical method is presented in the report. No information on storage or recovery levels.