

SUBSTANCE EVALUATION REPORT

Public Name: 1,1,1,3,3,3-hexamethyldisilazane (HMDZ)

EC Number(s): 213-668-5

CAS Number(s): 999-97-3

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Year of evaluation (as given in the CoRAP): 2014

VERSION NUMBER: 2

DATE: 31 August 2015

Conclusions of the most recent evaluation step*	Tick relevant box(es)
Concern not clarified; Need to request further information from the Registrant(s) with the draft decision	
Concern clarified; No need of further risk management measures	X
Concern clarified; Need for risk management measures; RMO analysis to be performed	

**Include details in the executive summary.*

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Executive summary

Grounds for concern

- Initial grounds for concern of 1,1,1,3,3,3-hexamethyldisilazane (HMDZ), were related to exposure, high RCR (terrestrial compartment) and aggregated tonnage. To remove uncertainties on these concerns, HMDZ was included in the Community rolling action plan (CoRAP) to be evaluated in 2014.
- Based on these initial concerns justification for release factors from different uses was also needed and requested.
- In the course of the evaluation, the evaluating MSCA also checked additional issues that could result in the identification of potential RCRs above 1, or other endpoints of concern for other environmental compartments.

Procedure

- The initial assessment was based on the information submitted by registrants in the registration dossier. Due to confidentiality reasons, no specific information was available regarding volume (manufacture/imported/used) within the CSR of the joint submission registration dossier. Therefore, a worst case generic scenario was applied for this risk assessment.
- After the initial examination of the information included in the registration dossier some concerns were raised. Briefly,
 - o In contact with water, HMDZ reacts very rapidly (half-life \ll 1 minute at 25°C and pH 4, 7 and 9) to produce trimethylsilanol (TMS) and ammonia. For the calculation of the PNEC_{marine} a higher pH of 8 has been taken into account for the calculation of the total loading of the ratio ammonia/ammonium. This recalculation resulted in an additional factor of x10 for the ammonia/ammonium loading of the marine compartment, in contrast to the ratio at pH of 7.
 - o For the PNEC_{aq} of TMS an assessment factor of 1000 has been used for the intermittent releases.
 - o Uncertainties regarding the ES1 scenario, which was initially considered only as a “Production” scenario, were clarified by registrants. It was clarified that both, manufacture and on-site use as intermediate and processing aid in polymerization process must be included within this scenario. Based on this information a higher tonnage was considered in the assessment for this scenario (ES1), being the final volume of use in agreement with the aggregated produced/imported volume indicated by registrants.
 - o Specific emission dilution factors have also been applied for the several sites of concern, otherwise, default dilution factors have been used in the assessment,
 - o Abatement and risk management measures have also been applied when indicated for the different use scenarios, otherwise USES default emission factors have been used,

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- As no information is included regarding the scenario ES5, estimation has been carried out assuming a worst case volume of industrial use. RCRs below 1 have been obtained for this scenario.
 - A declaration that the risk management measures are implemented and communicated is also included by the registrants.
- Comments were sent to registrants in June 2014, in order to get additional information and clarifications on the exposure assessment.
 - After several e-mail exchanges, clarifications were provided by registrants by August 2014, including an update of the registration dossier.
 - Data and assessment estimations have been checked and recalculated by the eMSCA based on the registrants' CSR and the additional information provided after requestion.
 - Any relevant information for the environmental exposure has been considered for the assessment and to remove those identified grounds of concerns for the environment.
 - Enough and relevant information was provided in the registration dossier for the hazard and effects assessment.

Conclusions

- The eMSCA has carried out an environmental assessment for the substance. The outcome of the assessment results in RCRs below 1 and therefore, no additional information is considered to be needed. No other environmental concerns have been identified during the assessment.

Statement of reasons

- Initial environmental grounds of concern regarding its inclusion in the CoRAP-2014 process have been clarified and no new environmental concerns have been identified, therefore, no additional information nor risk management measures are considered to be needed.

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1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

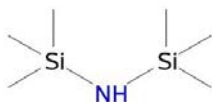
1.1 Name and other identifiers of the substance

Following identifiers are considered for 1,1,1,3,3,3-hexamethyldisilazane (HMDZ).

Table 1: Substance identity

Public Name:	1,1,1,3,3,3-Hexamethyldisilazane
EC number:	213-668-5
EC name:	1,1,1,3,3,3-Hexamethyldisilazane
CAS number (in the EC inventory):	
CAS number:	999-97-3
CAS name:	
IUPAC name:	Dimethyl-(trimethylsilylamino)silyl]methane
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	C ₆ H ₁₉ NSi ₂
Molecular weight range:	161.4 g/mol
Synonyms:	HMDZ

Structural formula:



1.2 Composition of the substance

1,1,1,3,3,3-Hexamethyldisilazane is a monoconstituent substance with typically a high purity.

The potential PBT characteristics of constituents and impurities have been screened by the eMSCA. According to the initial screening impurities do not have PBT characteristics. Additionally, their concentration are below 0.1% or around this percentage.

No additives are present.

1.3 Physico-chemical properties

A summary of the relevant physicochemical properties are included in

Table 2. Additional information and rationale for the selection of values is included in the CSR dossier (2014) of the registrants or the ECHA (2015) dissemination website. These values have been used by the eMSCA in this assessment.

As the substance hydrolyses very rapidly in contact with water to form trimethylsilanol (TMS) and ammonia, the physicochemical characteristics of the hydrolysis products are also relevant for the assessment.

Table 2: Overview of physicochemical properties

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Property	Value	Remarks
Physical state at 20°C and 101.3 kPa	Liquid at standard temperature and pressure.	Value used for CSA: liquid at 20°C and 101.3 kPa
Vapour pressure	Vapour pressure (HMDZ): 2400 Pa at 25°C Vapour pressure (TMS): 1300 Pa at 20°C (EU Method A.4) Vapour pressure (ammonia): 861100 Pa at 20°C	Value used for CSA: 2400 Pa at 25°C A vapour pressure value of 1300 Pa at 20°C Pa at 25°C were determined for TMS. Ammonia has a vapour pressure of 861100 Pa at 20°C (OECD SIDS (2007)).
Water solubility	Water solubility (HMDZ): Not Relevant due to hydrolysis Water solubility (TMS): 20000 mg/l at 20°C (EU Method A.6;OECD 105); Water solubility (ammonia): 510000-531000 mg/l at 20°C.	The requirement to test the substance for water solubility is waived on the basis that it hydrolyses very rapidly. A water solubility value of 20000 ± 700 mg/l at 20°C was determined for TMS. Ammonia has a measured water solubility of 510,000 - 531000 mg/l at 20°C (OECD SIDS (2007)).
Partition coefficient n-octanol/water (log value)	Log K _{ow} (HMDZ): Not relevant due to hydrolysis Log K _{ow} (TMS): 1.19 at 20°C (OECD 107) Log K _{ow} (ammonia): not relevant	An estimated log Low of 2.62 is considered for potential modellizations. The log K _{ow} of TMS, was determined to be 1.19 at 20°C. Log K _{ow} is not applicable for the other hydrolysis product, ammonia, as it is inorganic.
Dissociation constant	Dissociation constant (HMDZ and TMS): Not relevant. Dissociation constant (ammonium ion): 9.25	TMS is not expected to undergo significant dissociation within an environmental relevant range.. The pK _a of the ammonium ion, NH ₄ ⁺ , is given in a reliable handbook as 9.25 (Haynes W. M, Lide D.R. 2010).

Relevant physicochemical properties for the assessment

As it has been said, in contact with water, HMDZ reacts very rapidly (half-life <<1 minute at 25°C and pH 4, 7 and 9) to produce trimethylsilanol (TMS) and ammonia according to the following equation:



Therefore, requirements for testing of water-based physicochemical properties for HMDZ are waived on the basis of instability in water. Following properties of the HMDZ hydrolysis products, TMS and ammonia are considered relevant for the assessment instead.

Parameter	HMDZ	TMS	Ammonium
CAS N°	999-97-3	1066-40-6	7664-41-7
EC N°	213-668-5	213-914-1	231-635-3
MW	161.4	90.20	17.03
Water solubility (g/L)	-	20	510-530
Log K _{ow}	-	1.19	-
pK _a (25°C)	-	11	9.25
VP (kPa)	2.4 (25°C)	1.3 (20°C) 1.9 (25°C)	861 (20°C)

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In general, as pH increases, the fraction of the total ammonia which is unionised increases. The concentration of unionised ammonia will be lower at higher ionic strengths of very hard fresh water or salt water environments. This effect can be significant in estuarine and marine waters. At pH 8.5 (considered for marine compartment), the proportion of unionised ammonia is approximately 10 times higher than at pH 7.5 (considered for the fresh water compartment). Moreover, the pKa is reciprocally related to temperature. For every 9°C increase in temperature, the proportion of unionised ammonia approximately doubles (EA 2007). This effect is taken into account for the exposure assessment.

2 MANUFACTURE AND USES

2.1 Quantities

The aggregated tonnage band registered for HMDS is 1000 – 10 000 tonnes/year.

Table 3: Aggregated tonnage (per year)

1 – 10 t	10 – 100 t	100 – 1000 t	<u>1000- 10,000 t</u>	10,000-50,000 t
50,000 – 100,000 t	100,000 – 500,000 t	500,000 – 1000,000 t	> 1000,000 t	Confidential

2.1.1 Manufacturing processes

After the evaluation of the information provided in the CSR by the eMSCA, this information considered not to be relevant for this assessment. Therefore, to avoid potential conflicts of confidentiality the information on manufacturing process is not included in this report.

As a summary, the available information from manufacturing sites indicate that there is no solid waste or non-aqueous waste containing the registered substance or its hydrolysis product during manufacturing.

Contaminated aqueous streams containing the registered substance, e.g. from cleaning operations, are assessed as emissions to waste water in the environmental exposure assessment (Section 9).

2.2 Identified uses

There are five identified uses registered for HMDZ, in agreement with the information publicly available at the ECHA dissemination website:

- I. Use as a processing aid in polymerisation processes (ES1),
- II. Use as an intermediate in the production of other organic chemicals (ES2),
- III. Use as a non-metal surface treatment agent (ES3),
- IV. Use in the electronics industry for semiconductor manufacture (ES4) and,
- V. Use as a laboratory chemical/reagent – as a small-scale derivatising agent in analytical laboratories (ES5)

Products for end use as surface treatment agents may be formulated either at the point of use or in a separate industrial process.

The uses are summarised in terms of the appropriate REACH descriptor codes in Table 4 (ECHA, 2010a), and are described in more detail in the following sections.

Table 4. Description of identified uses.

Identified use (exposure scenario)	Sectors of end-use (SU)	Chemical Product Category (PC)	Process Category (PROC)	Environmental Release Category (ERC)
Processing aid in polymerisation processes (ES1 ¹)	8, 9	20	1, 2, 3, 8b, 9	6b
Intermediate (ES2)	8, 9	19	1, 2, 3, 8b	6a, 6d
Non-metal surface treatment agent (ES3)	8, 9, 11, 12, 13	15	1, 2, 3, 5, 8a, 8b, 9	6a, 6b, 6d
Semiconductor manufacture (ES4)	16	33	1, 8b, 13 ²	6a, 6b
Laboratory chemical/reagent (ES5)	9, 24, Other	21	5	7

Sectors of End-Use (SU):

SU 8: Manufacture of bulk, large scale chemicals (including petroleum products)

SU 9: Manufacture of fine chemicals

SU 11: Manufacture of rubber products

SU 12: Manufacture of plastics products, including compounding and conversion

SU 13: Manufacture of other non-metallic mineral products, e.g. plasters, cement

SU 16: Manufacture of computer, electronic and optical products, electrical equipment

SU 24: Scientific research and development

Other: NACE Code M71.2: Technical testing and analysis

Chemical Product Category (PC)

PC 15: Non-metal-surface treatment products

PC 19: Intermediate

PC 20: Products such as ph-regulators, flocculants, precipitants, neutralisation agents

PC 21: Laboratory chemicals

PC 33: Semiconductors

Process Category (PC)

PROC 1: Use in closed process, no likelihood of exposure

PROC 2: Use in closed, continuous process with occasional controlled exposure

PROC 3: Use in closed batch process (synthesis or formulation)

¹ Use as a processing aid in polymerisation processes is covered under the exposure scenario for manufacture and on-site use (ES1).

² This relates to the spin coating process in semiconductor manufacturing which takes place under strictly controlled conditions that are equivalent to PROC 1.

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PROC 5: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact)

PROC 8a: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities

PROC 8b: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities

PROC 9: Transfer of substance or preparation into small containers (dedicated filling line, including weighing)

PROC 13: Treatment of articles by dipping and pouring

Environmental Release Category (ERC)

ERC 6a: Industrial use resulting in manufacture of another substance (use of intermediates)

ERC 6b: Industrial use of reactive processing aids

ERC 6d: Industrial use of process regulators for polymerisation processes in production of resins, rubbers, polymers

ERC 7: Industrial use of substances in closed systems

2.2.1. Use of HMDZ as a chemical intermediate (ES2)

According to registrants' clarifications and information included in the CSR, given the hazardous nature of HMDZ, high level of containment, in line with industry best practice, are in place at the point of use. Local exhaust ventilation and other risk reduction measures typical of the chemical industry are used. Any residue or waste substance will be treated as hazardous waste, typically for incineration.

No specific information is available on waste generated from the use of the substance as a chemical intermediate. The EU BREF for Organic Fine Chemicals, which is considered relevant for the use of the substance as a chemical intermediate, shows that there is a possibility to generate non-recyclable waste in high ratio in this industry (EC, 2006). Spent solvents are burned in an incinerator to prevent transportation to waste disposal.

The registered substance, however, reacts very rapidly and is not expected to be in waste. The waste life cycle stage is, therefore, only assessed as a worst case because of the generation of trimethylsilanol and ammonia from HMDZ.

2.2.2 Use of HMDZ as processing aid in polymermerisation processes (ES1)

HMDZ is used in polymerisation processes for end capping and as a processing aid for deactivating the catalyst used during polymerisation. Hence, it is essentially similar to use of an intermediate described above in terms of operating conditions and potential for exposure. This process takes place at the manufacturing site and is assessed as part of the manufacturing exposure scenario. Based on available information, typical solid or non-aqueous waste that may contain the substance are indicated to be either recycled within the process or disposed of via incineration.

Contaminated aqueous streams containing the registered substance, e.g. from cleaning operations, are assessed as emissions to waste water in the environmental exposure assessment (Section 9).

2.2.3 Use of HMDZ as a non-metal surface treatment agent (ES3)

The worst case use of the substance in this application as described in Section 2.2.2, is similar to the use of coupling agents in for plastics.

Although residues of additives in delivery containers typically join the general waste stream and are most likely disposed of to landfill; it is indicated in the CSR that any waste known to constitute any form of hazard are handled and disposed off in an appropriate manner.

Given the hazardous nature of HMDZ, any residue or waste substance will be treated as hazardous waste, typically for incineration. The registered substance, however, reacts very rapidly and is not expected to be in waste. The waste life cycle stage is, therefore, only assessed as a worst case because of the generation of TMS and ammonia from HMDZ.

2.2.4 Use of HMDZ in semiconductor manufacture (ES4)

According to registrants information operational conditions are highly controlled; processes take place in a high integrity contained system where little potential exists for exposures (PROC 1). The substance is used in a vapour form and reacts completely on use. Therefore, it is no expected relevant waste stream to treat from the use of the substance in this application.

2.2.5 Use of HMDZ as a laboratory reagent (ES5)

A small-scale use of HMDZ is used as a reagent in analytical chemistry laboratories.

HMDZ is supplied in small quantities (up to around 250 ml) in amber glass bottles for this application. In addition, it can be assumed that any small quantities of waste or unused HMDZ are treated as hazardous waste and disposed of accordingly. These are however not considered significant given the very small volume of the registered substance used in this application. A worst case assumption volume has been applied for the assessment.

3 CLASSIFICATION AND LABELLING

3.1 Harmonised Classification in Annex VI of the CLP Regulation

No agreed/harmonised classification is reported as included in Annex VI of the CLP Regulation ((EC) No 1272/2008).

3.2 Self classification

-

3.3 Proposed classification

The CL-Inventory present the following notified classification and labelling according to CLP criteria.

Classification according to CLP

Labelling

Signal word: Danger

Hazard statements:

H225: Highly flammable liquid and vapour.

H302: Harmful if swallowed.

H311: Toxic in contact with skin.

H314: Causes severe skin burns and eye damage

H332: Harmful if inhaled.

H412: Harmful to aquatic life with long lasting effects.

Precautionary statements:

P210: Keep away from heat/sparks/open flames/... /hot surfaces.... No smoking.

P233: Keep container tightly closed.

P273: Avoid release to the environment.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

P303+P361+P353: IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower.

P305+P351+P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P310: Immediately call a POISON CENTER or doctor/physician.

P370+P378: In case of fire: Use... for extinction.

P403+P235: Store in a well-ventilated place. Keep cool.

P501: Dispose of contents/container to...

Classification according to DSD /DPD

Indication of danger:

F - highly flammable

Xn - harmful

R-phrases:

R11 - Highly flammable

R20/21/22 - Harmful by inhalation, in contact with skin and if swallowed

R52/53 - Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment

S-phrases:

S7 - keep container tightly closed

S36/37 - wear suitable protective clothing and gloves

S61 - avoid release to the environment. Refer to special instructions/safety data sheets

4 ENVIRONMENTAL FATE PROPERTIES

Only relevant information on fate properties, agreed by the eMSCA and relevant for this assessment, has been compiled in this report. Additional studies and information on HMDZ can be found on the ECHA dissemination website.

4.1 Degradation

4.1.1 Abiotic degradation

4.1.1.1 Hydrolysis

HMDS is known to undergo rapid hydrolysis in the presence of water. A half-life (DT50) of < 0.04 min at 1.5°C has been determined (OECD Guideline 111). This value represents an estimated upper limit of the hydrolysis half-life cited in the CSR (2014). It refers to disappearance of the test material (based on ammonium ion concentration). This information is in agreement with other material safety datasheets and reports (CAN, 2013).

As it has been said, the hydrolysis products for HMDS are trimethylsilanol and ammonia.

Ammonia (NH₃) exists in solution in equilibrium with the ammonium ion, (NH₄⁺). Under normal environmental conditions (pH of 7), ammonium ions (NH₄⁺) predominate in a ratio of c.a. 178-181.

$$\text{pOH} = \text{pKb}_{\text{NH}_3} + \log (\text{NH}_3/\text{NH}_4^+)$$

The following information is taken into account for any hazard / risk / persistency assessment:
Hydrolysis: Half-life << 1 min at 25°C and pH 4, 7 and 9 (OECD 111)

4.1.1.2 Phototransformation/photolysis

4.1.1.2.1 Phototransformation in air

No measured data are available for HMDZ.

HMDZ and its silanol hydrolysis product trimethylsilanol contain no chromophores that would absorb visible or UV radiation, so direct photolysis is not likely to be significant. Indirect photolysis resulting from gas-phase reaction with photochemically-produced hydroxyl radicals may occur.

The AOPWIN program (v1.92; EPA 2010) has been used to obtain values of the rate constant k OH for reaction of HMDZ and TMS with hydroxyl radicals. This prediction method has not been validated to assess applicability to organosilicon substances; therefore, there is uncertainty associated with the calculated values obtained. The outcome indicates a half-life of 12 days.

The other hydrolysis product of HMDZ is ammonia. Ammonia may react with ozone, hydroxyl radicals, and atomic oxygen in air (OECD, 2007 citing NRC, 1979; Verschueren, 1996;

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Environment Canada, 2001). The primary reaction of ammonia is with hydroxyl radicals and is the rate-determining step in the atmospheric oxidation of ammonia. The rate constant is $1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 25°C (OECD, 2007 citing Stuhl, 1973; Diau et al., 1990) with a corresponding lifetime of 34 days (OECD, 2007 citing Diau et al., 1990; Renard et al., 2004).

Measured data are provided in the CSR (2014) for TMS and other organosilanes. The measured data for TMS is in good agreement with the data predicted by the eMSCA. A summary of the results for the compounds involved in the assessment are given in the table below:

Table 5. Results of photodegradation in air calculations

Parameter	HMDZ*	TMS	NH3
$k_{\text{OH}}(\text{cm}^3/\text{molecule}\cdot\text{sec})$	0.90×10^{-12}	3.9×10^{-12}	1.5×10^{-13}
$k_{\text{deg}_{\text{air}}}$	0.039	0.17	-
DT50 (days)	12-18	2.8-4.1	34

4.1.1.2.2 Phototransformation in water

No data are available for phototransformation in water, but it is not expected to be a significant removal process for the parent substance or the silanol hydrolysis product.

4.1.1.2.3 Phototransformation in soil

No data are available for phototransformation in soil, but it is not expected to be a significant removal process for the parent substance or the silanol hydrolysis product.

4.1.2 Biodegradation

4.1.2.1 Biodegradation in water

4.1.2.1.1 Estimated data

4.1.2.1.2 Screening tests

A study on biodegradation in water (screening tests) indicates that HMDZ is not Ready biodegradable. This result is expected and in agreement with the rapid hydrolysis of the substance in contact with water.

4.1.2.1.3 Simulation tests (water and sediments)

4.1.2.1.4 Summary and discussion of biodegradation in water and sediment

No Ready Biodegradability is assumed and expected for HMDZ. This information is taken into account for any hazard / risk / persistency assessment.

4.1.2.2 Biodegradation in soil

Testing is not considered necessary for the assessment based on its physical and chemical properties and the expected lack of biodegradation.

4.1.3 Summary and discussion on degradation

The substance does not fulfil the criteria for Ready biodegradability. No degradation, but hydrolysis into TMS and ammonia is expected in contact with water. A DT50 of 0.46 min (12°C) has been calculated and used for the environmental assessment. In **Table 6** are summarized the expected degradation rates on different environmental compartments.

Table 6. Summary of degradation rates

Degradation rate in water:	Hydrolysis half-life: <<1 min at pH 7 and 25°C, for removal of parent (measured). No significant biodegradation expected.
Degradation rate in sediment:	No significant biodegradation expected.
Degradation rate in soil:	No significant biodegradation expected.
Degradation rate in air:	Half-life for reaction with hydroxyl radicals in air: 18 days for parent; 4.1 days for silanol hydrolysis product (predicted).

4.2 Environmental distribution

4.2.1 Adsorption/desorption

Data waived by registrants because the substance hydrolyses very rapidly to TMS and ammonia.

Considering the hydrolysis products:

- Regarding TMS, it has a low log K_{ow} value (<3) and thus has low potential for adsorption.

- Regarding ammonia, based on its solubility, ammonia (unionised) is not expected to adsorb to soil particulate matter, suspended solids or sediment (Environment Agency, 2007). Sufficient information is available in the public domain about the behaviour of ammonia in soil. In accordance with Column 2 of REACH Annex IX, the adsorption/desorption study does not need to be conducted.

For environmental exposure assessment, adsorption is predicted for the hydrolysis products, TMS and ammonia, using the EU TGD (Technical Guidance Document) ‘non-hydrophobics’ log K_{ow} prediction method (EC, 2003a), also referred to in REACH Guidance R7a (ECHA, 2014).

The following information is taken into account for any environmental exposure assessment:

Adsorption/desorption: Predicted Log K_{oc} of TMS= 1.6; Predicted Log K_{oc} of ammonia = 1.1.

Log K _{oc} TMS	Log K _{oc} ammonia
1.6	1.1

4.2.2 Volatilisation

The transfer of a substance from the water phase to the gas phase can be estimated by means of the Henry’s Law Constant (HLC). No measured value for this parameter is available. The HLC has been estimated from the ratio of the vapour pressure (VP) to the water solubility (WS).

Volatilisation from water is not relevant for the parent substance due to its very rapid hydrolysis in contact with water to TMS and ammonia.

Volatilization TMS	Volatilization ammonia
The calculated HLC value at environmental temperature (12°C) is low, 3.7 Pa m ³ mol ⁻¹ (EUSES 2.1.2).	The calculated HLC value at environmental temperature (12°C) is moderate, 17 Pa m ³ mol ⁻¹ (EUSES 2.1.2).

4.2.3 Distribution modelling

The distribution in a sewage treatment plant (STP) has been estimated using the SimpleTreat model (implemented in EUSES 2.1.2), see table below. Due to the rapid hydrolysis of the parent substance to TMS and ammonia, the distribution calculation is done for the hydrolysis products.

Table 7. Distribution modelling for STP

	TMS	ammonia
Fraction of emission directed to air by STP (%)	6.5	23.2
Fraction of emission directed to water by STP (%)	93	76.7
Fraction of emission directed to sludge by STP (%)	0.534	0.163
Fraction of the emission degraded in STP (%)	0	0

As it has been said, HMDZ hydrolyses very rapidly in contact with water to TMS and ammonia.

- TMS is not expected to undergo any significant biodegradation, has moderate Henry's Law constant and low log Kow /log Koc. Water and air are the main compartments to which it is expected to partition in a sewage treatment plant.
- The physicochemical properties of ammonia presented in Section 1.3 (Physico-chemical properties) of the CSR (2014) are used in EUSES 2.1.2; its conversion to nitrite and nitrate is not taken into account as a worst case.

The distribution of ammonia/ammonium is discussed further below.

Ammonia (unionised) is lost from water by volatilisation. Based on its solubility, ammonia (unionised) is not expected to adsorb to soil particulate matter, suspended solids or sediment. (EA, 2007).

In general, natural ammonia levels in soil are very low (<1 mg/kg) due to the rapid conversion of ammonium to nitrite by Nitrosomonas species and then to nitrate by Nitrobacter species in the temperature range 0–35°C (Henry 1995, cited in Environment Canada, Health Canada, 2001).

4.2.4 Summary and discussion of environmental distribution

HMDZ hydrolyses very rapidly to TMS and ammonia. TMS has a log Kow of 1.2 and therefore an expected low potential for adsorption. Regarding ammonia, based on its solubility it is neither expected to be adsorbed to soil particulate matter, suspended solids or sediment.

The atmospheric compartment is not expected to be the sink for TMS nor ammonia due to its low potential for volatilization.

Taking into account the low log Kow of TMS and the high water solubility, the aquatic compartment is expected to be the main environmental receptor.

4.3 Bioaccumulation

4.3.1 Aquatic bioaccumulation

No data available.

The substance hydrolyses very rapidly to TMS and ammonia. TMS and ammonia have low log Kow values of 1.2 and 0.23, respectively, and thus, they are expected to have low potential for bioaccumulation.

4.3.2 Terrestrial bioaccumulation

The substance hydrolyses very rapidly to TMS and ammonia. TMS and ammonia have low log Kow values of 1.2 and 0.23, respectively, and thus have low potential for bioaccumulation.

In the soil compartment, ammonia enters the nitrogen cycle and is not expected to bioaccumulate.

Although ammonia is assimilated by aquatic plants for use as a nitrogen source, its bioaccumulation in biota is not important. (EA, 2007).

The following information is taken into account for any hazard / risk / bioaccumulation assessment:
Bioaccumulation: terrestrial: Low potential for bioaccumulation.

4.3.3 Summary and discussion of bioaccumulation

The substance hydrolyses very rapidly to TMS and ammonia. TMS and ammonia have low log Kow values of 1.2 and 0.23, respectively, and thus, have low potential for bioaccumulation.

4.4 Secondary poisoning

Based on the available information, there is no indication of a bioaccumulation potential in the food chain and, hence, secondary poisoning is not considered relevant.

5 HUMAN HEALTH HAZARD ASSESSMENT

No relevant for this assessment. Nevertheless, those endpoints that could be relevant for the PB(T) criteria have been reviewed.

There is no information suggesting that HMDZ should be classified as CMR or any other property relevant for T classification such as endocrine disruption.

**6 HUMAN HEALTH HAZARD ASSESSMENT OF PHYSICO
CHEMICAL PROPERTIES**

Not relevant for this assessment.

7 ENVIRONMENTAL HAZARD ASSESSMENT

Only relevant information for the environmental hazard assessment, agreed by the eMSCA and relevant for this assessment has been compiled in this report. Additional studies on HMDZ can be found on bibliography or at the ECHA (2015) dissemination website.

As a most relevant characteristic of HMDZ for the environmental risk assessment, it is considered that the rapid hydrolysis half-life of HMDZ is $\ll 1$ min at pH 7, 25°C to TMS and ammonia. As DT50 <12 hours, the environmental effects are likely to be attributed to the hydrolysis product rather than to the parent itself (ECHA 2012, Section R.16.5.4.1.). Therefore, this environmental hazard assessment, including sediment and soil compartments, is based on the properties of the hydrolysis product, in accordance with REACH guidance.

Data for TMS and ammonia are considered in this assessment and PNECs calculations are based on data of these hydrolysis products.

Considerations regarding the hydrolysis products

In the following paragraphs, the approach that has been taken for the environmental assessment of hydrolysis products of HMDZ is outlined, taking into account structure, hydrolysis rate and physicochemical properties of the HMDZ and its hydrolysis products (**Table 8**). Briefly,

- TMS is a monosilanol containing three methyl groups and is not subject to further hydrolysis. The aquatic data available for this substance indicates that it is of low short-term toxicity to aquatic organisms, with L(E)C 50 values in the range 124 to >750 mg/l.
- Ammonia is a known toxicant for aquatic organisms, in particular to fish and invertebrates. This compound drives the aquatic toxicity of the substance and is assessed separately to the silanol hydrolysis product. Further details on the assessment of the substance are presented in the toxicity test results section that follows.

Relevant ecotoxicological information for this assessment has been compiled in this report regarding HMDZ, TMS and ammonia. Additional information can be found on bibliography or ECHA website.

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Table 8. Summary of physico-chemical and ecotoxicological properties of the registered and surrogate substances.

Chemical Name CAS N°	HMDZ 999-97-3	TMS 1066-40-6	Ammonia 7664-41-7	Refs
SMILES	C[Si](C)(C)N[Si](C)(C)C	C[Si](C)(C)O	N	
Si hydrolysis product	TMS and Ammonia	n/a	n/a	
Molecular weight	161.4	90.2	17.03	
log Kow	n/a	1.2	0.23	
Water solubility	n/a	20000 mg/l but concentration dissolved in water may be limited above approximately 1000 mg/l by condensation reactions	531000 mg/l	
Vapour pressure	2400 Pa (25°C)	1900 Pa (25°C)	861100 Pa (20°C)	
Hydrolysis t 1/2 at pH 4, 7, 9 at 25°C	<<1 min at 25°C	n/a	n/a	
Short-term toxicity to fish (96h-LC50)	96h-LC50 88 mg/l (1)	96h-LC50 271 mg/l (2)	96h-LC50 0.083 mg/l (3)	1. Hulls, 1994a, cited in CSR 2. Cited in SIDS 2014 3. Rice and Baley, 1980
Short-term toxicity to aquatic invertebrates (EC50)	48h-EC50 80 mg/l (4)	48h-EC50 124 mg/l (5)	96h-LC50 0.16 mg/l (6)	4. Hulss, 1994b, cited in CSR 5. WLI, 2004b 6. Cited in CSR
Algal inhibition (ErC 50 and NOEC)	72h-EC 50 : 50 mg/l (7) and 72h-NOEC: 7.5 mg/l (7)	72h-EC 50 : >750 mg/l (8) and 72h-NOEC:50 mg/l (8)	5d-EC 50 2.0 mg/l (9) 14d-NOEC 1.5 mg/l (10)	7. Hulls, 1994 c, cited in CSR 8. WLI 2004c 9. EA, 2007 10. EA, 2007
Long-term toxicity to fish (NOEC)	n/a	n/a	73d-NOEC 0.011 mg (11) NH3/l	11. EA, 2007
Long-term toxicity to aquatic invertebrates (NOEC)	n/a	n/a	29d-NOEC 0.066 mg NH3/l (12)	12. EA, 2007
Long-term sediment toxicity (NOEC)	n/a	n/a	n/a	
Long-term terrestrial toxicity (NOEC)	n/a	n/a	n/a	

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In order to derive the PNEC for the HMDZ, the lowest reliable results of the studies for TMS and ammonia (NH₃) have been converted into the equivalent amount of HMDZ that would generate that amount of TMS or NH₃ upon full hydrolysis (Table 9). For ammonia, the L(E)C50 results from the short-term tests were 0.083, 0.16 and 2.0 mg unionised NH₃/l for fish, invertebrates and algae, respectively. Taking into account the mean pH experienced in the short-term tests with HMDZ (to give the fraction of the total ammonia ionised) and the MW of HMDZ and ammonia, the amount of HMDZ that would produce an equivalent amount of unionised NH₃ to the L(E)C50 values seen in the ammonia short-term tests was calculated. The calculated numbers for NH₃ can therefore be interpreted as being the L(E)C50s that would be expected for HMDZ based on the data for ammonia. The fact that the actual L(E)C50s are equivalent to or lower than these calculated numbers indicates that HMDZ is not more toxic than would be expected based on its capacity to generate NH₃.

Table 9. Comparison of short-term test results (L(E)C 50 s) for HMDZ and its hydrolysis products.

Test Organism	Test pH (in test with HMDZ)	HMDZ mg/l	TMS mg/l as HMDZ (derived from the short-term toxicity (L(E)C50) results from the tests with TMS)	Unionised Ammonia (NH ₃) mg/l as HMDZ (derived from the short-term toxicity (L(E)C50) results from the tests with ammonia)
Fish	7.8 - 8.7 (8.25)	88	242	8.6
Aquatic Invertebrates	6.6 - 8.5 (7.55)	80	111	77
Alga	8.9 – 9.25 (9.1)	50	7671	46

Additional information about the aquatic ecotoxicity of ammonia

Ammonia is known to be toxic to the aquatic environment and has been reviewed by a number of different regulatory programmes such as the SIAR for the Ammonia category (OECD, 2007; the Canadian Environmental Protection Act, 1999, Priority Substance List Assessment Report, Ammonia in the Aquatic Environment, and the UK Environment Agency (EA, 2007) which takes a thorough look at the data.

Ammonium salts dissociate in water to give ammonia/ammonium ion and, therefore, data for these salts may be used to assess the toxicity of ammonia. The ammonia/ammonium ion in aqueous solution exists in equilibrium between NH₃ and NH₄⁺, depending on the pH. The unionised species is by far the most toxic; the ammonium ion is assumed to be essentially non-toxic. Therefore, toxicity due to ammonia increases with increasing pH according to the following equation (Emerson, 1975):

$$\text{Fraction unionised} = 1/(10^{\text{pKa-pH}} + 1)$$

At pH 8.5, the proportion of unionised ammonia is approximately 10 times that at pH 7.5. For every 9°C increase in temperature, the proportion of unionised ammonia approximately doubles (EA, 2007).

7.1 Aquatic compartment (including sediment)

Reliable short-term toxicity test results are available for freshwater fish (*Brachydanio rerio*), invertebrates (*Daphnia magna*) and algae (*Scenedesmus subspicatus*).

Testing for long-term toxicity to aquatic organisms is not considered necessary because:

- The substance is used under highly controlled conditions and, therefore, exposure of the aquatic environment is low (see Section 9 for further details).
- Risk characterisation ratios (RCR) based on existing data are $\ll 1$.
- The silanol hydrolysis product, trimethylsilanol, is not acutely toxic to aquatic organisms at loading rates of 100 mg/l.

Chronic data are available for the other hydrolysis product, ammonia.

7.1.1 Toxicity data

The eMSCA has taken into consideration and agree with the information provided by the registrants in the CSR regarding the effects assessment. Only relevant information selected for the PNEC derivation has been included in this assessment.

7.1.1.1 Fish

7.1.1.1.1 Short-term toxicity to fish

HMDZ: A reliable acute toxicity test result for HMDZ is available for freshwater fish (*Brachydanio rerio*): 96h-LC50 of 88 mg/l. It is likely that the test organisms were exposed to the hydrolysis products of the substance Hüll, (1994a).

TMS: A short-term aquatic toxicity test result is available for the test substance silanol hydrolysis product, TMS (CAS 1066-40-6). A 96-hour LC 50 value of 271 mg/l (measured concentration) has been determined for the effects of TMS on mortality of *Oncorhynchus mykiss*.

Ammonia: A short-term test results are available for ammonia sourced from the Environment Agency Proposed EQS for Water Framework Directive Annex VIII Substances: Ammonia (unionised) 2007. The most sensitive species to ammonia was found to be fish (*Oncorhynchus gorbusha* – pink salmon), with an 96h-LC50 of 0.083 mg unionised NH₃ /L (Rice and Bailey, 1980).

The following information is taken into account for acute fish toxicity for the derivation of PNECs:

- For TMS: a 96-hour LC50 value of 271 mg/l (measured concentration) on *Oncorhynchus mykiss* has been used for the estimations.
- For unionised NH₃: a 96-hour LC50 value of 0.083 mg/l unionised NH₃ (measured concentration) on *Oncorhynchus gorbusha* for the estimations.

7.1.1.1.2 Long-term toxicity to fish

No data is available for HMDZ and long-term toxicity testing on fish.

TMS Long-Term Toxicity to Fish:

Considering a factor of x10 between acute and chronic toxicity, a tentative long-term toxicity of 27.1 mg/L could be assumed for TMS based on the acute data on fish.

The ECOSAR 1.1 estimations result in a chronic value of 38.87 mg/L on fish which is in the same order of magnitude that the estimated by applying the assessment factor on the acute value. This value which is similar and in the same order of magnitude that the estimated by applying the assessment factor supports that ammonium is the most toxic hydrolysis product.

Ammonia Long-Term Toxicity to Fish:

Reliable long-term data are available sourced from the Environment Agency Proposed EQS for Water Framework Directive Annex VIII Substances: Ammonia (unionised) (EA, 2007).

The lowest credible concentration of unionised ammonia at which long-term effects were found is 0.022 mg/l of nitrogen present as NH₃ (0.027 mg NH₃ /l) when a cumulative mortality of 71 per cent was observed for eggs, larvae and fry of rainbow trout (*Oncorhynchus mykiss*) over 73 days exposure (Solbe et al., 1989). No NOEC value was derived in the study since effects were observed at the lowest exposure concentration. However, data on the concentration–response curve for similar effects in other fish have been evaluated, and these indicate 2–3 times difference in exposure concentration for a 50 per cent reduction in survival (from the controls) in such an early life stage test (EA 2007). A factor of 2 is applied to the LOEC result to estimate a NOEC, giving a long-term toxicity to fish result of 0.014 mg NH₃ /l.

The following information is taken into account for chronic fish toxicity for the derivation of PNECs:

- For TMS: No data available, although an estimated long-term toxicity of 27.1 mg/L should be taken into account for TMS based on the acute data on fish as an indication of low long-term toxicity.
- For ammonium: A 73-day NOEC value of 0.011 mg NH₃ /l (measured concentration) has been determined for the effects of ammonia on mortality of *Oncorhynchus mykiss*.

7.1.1.2 Aquatic invertebrates

7.1.1.2.1 Short-term toxicity to aquatic invertebrates

HMDZ: An acute toxicity test result for hexamethyldisilazane is selected for invertebrates (*Daphnia magna*): 48h-EC₅₀ 80 mg/l. It is likely that the test organisms were predominantly exposed to the hydrolysis products of the substance (Hüls, 1994b).

TMS: A short-term aquatic toxicity tests results is selected for the test substance hydrolysis

product, trimethylsilanol (CAS 1066-40-6). A 48h-EC₅₀ value of 124 mg/l (nominal concentration) has been determined for the effects of trimethylsilanol on mortality and mobility of *Daphnia magna* (Wildlife International, Ltd., 2004b).

Ammonia: A short-term test results is selected for ammonia sourced from the Environment Agency Proposed EQS for Water Framework Directive Annex VIII Substances: Ammonia (unionised) 2007. A 96h-LC₅₀ of 0.16 mg unionised mg NH₃/l has been reported for short-term toxicity of ammonia to aquatic invertebrates.

The following information is taken into account for short-term toxicity to aquatic invertebrates for the derivation of PNEC:

- For TMS: A 48h-EC₅₀ value of 124 mg/l (measured concentration) has been determined for the effects on mortality and mobility of *Daphnia magna*.
- For ammonia: A 96h-LC₅₀ of 0.16 mg unionised NH₃/l has been reported for the effects of ammonia on mortality of *Hyalella azteca*.

7.1.1.2.2 Long-term toxicity to aquatic invertebrates

TMS long-Term Toxicity to aquatic invertebrates:

No long-term toxicity is available for TMS. But,

- Considering a factor of x10 between acute and chronic toxicity, a tentative long-term toxicity of 12.4 mg/L could be assumed for TMS based on the acute data on daphnia magna.
- The ECOSAR 1.1 estimations result in a chronic value of 17.91 mg/L on daphnid. This value which is similar and in the same order of magnitude that the estimated by applying the assessment factor supports the fact that ammonium is the most toxic hydrolysis product.
- Data for long-term toxicity to aquatic invertebrates are available for two read across substances (mentioned by the registrants in PFA 2013y). The data present NOEC values of 32 mg/l and ≥100 mg/l for substances having hydrolysis products with log K_{ow} values of -1.9 and 0.9 respectively.

Ammonia long-Term Toxicity to aquatic invertebrates:

Long-term data are available sourced from the UK Environment Agency Proposed EQS for Water Framework Directive Annex VIII Substances: Ammonia (unionised) (EA, 2007). A 29d-NOEC of 0.066 mg NH₃ /l has been reported for toxicity of ammonia to the aquatic invertebrate *Deleatidium sp.* (Champ et al., 1977 cited in the CSR and referred in the ECHA dissemination website).

The following information is taken into account for long-term toxicity to aquatic invertebrates for the derivation of PNECs:

- For TMS: The estimated long-term toxicity of 12.4 mg/L could be assumed for TMS will be taken account as an indication of low long-term toxicity of TMS.
- For ammonium: A 29d-NOEC of 0.066 mg NH₃/l has been reported for toxicity of ammonia to the aquatic invertebrate *Deleatidium sp.*

7.1.1.3 Algae and aquatic plants

MHDZ: Acute toxicity test result for HMDZ is available for algae (*Scenedesmus subspicatus*). A 72 h EC₅₀ value of 50 mg/l and a NOEC of 7.5 mg/l was determined in the algal test (Hülls, 1994c cited in the CSR and referred in the ECHA dissemination website). It is likely that the test organisms were predominantly exposed to the hydrolysis products of the substance.

TMS: Short-term aquatic toxicity tests results are available for TMS. A 72 EC 50 value of >1053 mg/l and NOEC of 70 mg/l (initial measured concentration) have been determined for the effects of trimethylsilanol on growth rate of *Selenastrum capricornutum* (new name: *Pseudokirchnerella subcapitata*). The same algal test results expressed in terms of mean measured concentrations were >750 mg/l and 50 mg/l respectively.

Ammonium: Reliable short-term test results are available for ammonia sourced from the Environment Agency Proposed EQS for Water Framework Directive Annex VIII Substances: Ammonia (unionised) (EA, 2007). A 5d-EC₅₀ of 2.0 mg NH₃ /l, and a 14 day LOEC of 3.0 mg NH₃ /l has been reported for toxicity of ammonia to algae. This LOEC results in a 14d-NOEC of 1.5 mgNH₃/L.

The following information is taken into account for effects on algae / cyanobacteria for the derivation of PNECs:

- For TMS: A 72-hour EC 50 value of >750 mg/l and NOEC of 70 mg/l (initial measured concentration) have been determined for the effects of TMS on growth rate of *Selenastrum capricornutum* (new name: *Pseudokirchnerella subcapitata*). The same algal test results expressed in terms of mean measured concentrations were >750 mg/l and 50 mg/l respectively.
- For ammonium: A 5-day EC 50 of 2.0 mg NH₃ /l, and a 14 day NOEC of 1.5 mg NH₃/l has been reported for the effects of ammonia on abundance of *Chlorella vulgaris*.

7.1.1.4 Sediment organisms

No data is available on long-term toxicity testing on sediment organisms.

7.1.1.5 Other aquatic organisms

7.1.2 Calculation of Predicted No Effect Concentration (PNEC)

As it has been said, HMDZ hydrolyses very rapidly to TMS and ammonia; therefore PNECs are derived for each hydrolysis product.

- From acute data for the silanol hydrolysis product, TMS and,
- From the chronic data for ammonium compounds.

Given the rapid hydrolysis of hexamethyldisilazane, it is appropriate to carry out risk characterisation on the basis of the properties of the two hydrolysis products. Therefore, the PNECs based on data for TMS and ammonia are used. In **Table 10** is included a summary of the aquatic ecotoxicity data selected for the derivation of the PNECs for the aquatic compartment.

Table 10. Summary of the acute and chronic values considered for the PNEC calculations.

	HMDZ		TMS		Ammonia	
	Acute	Long-term	Acute	Long-term	Acute	Long-term
96h-LC50 (mg/L) Fish	88	waived	271	waived	0.083	73d-LOEC = 0.011
48h-EC50 (mg/L) Aq. Invert	80	waived	124	waived	0.16	29d-NOEC = 0.066
ECr50 (mg/L)	50		>750		2	
NOEC (mg/L) Algae		7.5		70		NOEC = 1.5

PNEC_{aq} calculation for Trimethylsilanol (TMS)

According to the above data, the generic assessment factor of 1000 is applied for PNEC calculation of TMS. The lowest L(E)C 50 value for trimethylsilanol is 124 mg/l for invertebrates. Therefore, PNEC_{aq} is 124/1000 = 0.124 mg/l.

PNEC_{aq} calculation for ammonia

The PNEC freshwater from long-term data, can be derived based on the 73-day LOEC of 0.022 mg/l of nitrogen present as NH₃ to which a factor of 2 is applied to estimate a NOEC and an assessment factor of 10 to extrapolate to a PNEC freshwater of 1.1 µg l⁻¹ unionised ammonia. Assuming a pH 7.0, the ratio of NH₃ to NH₄⁺ in solution is 1:181. This means that a PNEC of 0.0011 mg NH₃/l is equivalent to 0.20 mg ammonia/ammonium/l. This is equivalent to 1.82 mg/l of HMDZ. In reality, the PNEC in terms of total loading would vary significantly according to test conditions.

Using the PNEC freshwater result of 0.0011 mg NH₃/l and applying an additional assessment factor of 10, this results in a PNEC_{aq} (marine water) of 0.00011 mg NH₃/l.

Assuming that the contribution of NH₄⁺ to toxicity may be considered negligible, the PNEC in terms of ammonia/ammonium total loading may be calculated.

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Due to the increased pH of saltwater, a pH of 8 has been assumed and the ratio of NH_3 to NH_4^+ in solution is 1:18.1. This means a PNEC aqua (marine water) of 0.00011 mg NH_3 /l is equivalent to 0.0020 mg ammonia/ammonium/l.

No suitable data for the toxicity of the substance or its silanol hydrolysis product to marine organisms has been identified. Therefore, PNEC aquatic-marine is derived from PNEC aquatic-freshwater by application of an additional assessment factor of 10.

7.1.2.1 PNEC water

Table 11. PNECs for the aquatic compartment: TMS

Compartment	PNECs	Remarks/Justification
Freshwater	PNECaq: 0.124 mg/l	The PNEC is 0.124 mg/l, based on the lowest EC50 value for Daphnia of 124 mg/l.
Marine water	PNEC aqua (marine water) : 0.0124 mg/l	By application of an additional assessment factor of 10.
Intermittent releases to water	PNECaq (intermittent releases) : 1.24 mg/l	An assessment factor of 100 is applied to the lowest E(L)C 50 of three short-term tests from three trophic levels. In this case the lowest EC50 value is 124 mg/l for Daphnia = 124/100 = 1.24 mg/l PNEC for TMS.

Table 12. PNECs for the aquatic compartment: Ammonia

Compartment	PNECs	Remarks/Justification
Freshwater	PNEC aqua (freshwater) : 0.2 mg/l	For ammonia, the long-term PNEC freshwater can be derived for the 73-day LOEC for rainbow trout (<i>Oncorhynchus mykiss</i>) of 0.022 mg NH_3 /l to which a factor of 2 is applied to estimate a NOEC and an assessment factor of 10 to extrapolate to a long-term PNEC freshwater of 0.0011 mg NH_3 /l unionised ammonia. Assuming that the contribution of NH_4^+ to toxicity may be considered negligible, the PNEC in terms of ammonia/ammonium total loading may be calculated. Assuming a pH 7.0, the ratio of NH_3 to NH_4^+ in solution is 1:181. This means that a PNEC of 0.0011 mg NH_3 /l is equivalent to 0.20 mg ammonia/ammonium/l.
Marine water	PNEC aqua (marine water): 0.002 mg/l	For ammonia, using the PNEC freshwater result of 0.0011 mg NH_3 /L and applying an additional assessment factor of 10, this results in a PNEC aqua (marine water) of 0.00014 mg NH_3 /l. Assuming that the contribution of NH_4^+ to toxicity may be considered negligible, the PNEC in terms of ammonia/ammonium total loading may be calculated. Due to the increased pH of saltwater, a pH of 8 has been assumed and the ratio of NH_3 to NH_4^+ in solution is 1:18.1. This means a PNEC aqua (marine water) of 0.00011 mg NH_3 /l is equivalent to 0.0020 mg ammonia/ammonium/l.
Intermittent releases to water	PNEC aqua (intermittent releases) : 0.151 mg/l	For ammonia, test results are sourced from the SIAR for the Ammonia category (OECD, 2007; sponsored by USA, shared partnership with European Fertilizers Manufacturing Association (EFMA-Europe) and The Fertilizer Institute (TFI-US)). An assessment factor of 100 is applied to the lowest reliable E(L)C50 of three short-term tests from three trophic levels. In this case the lowest E(L)C50 value for ammonia is 0.083 mg unionised NH_3 /l for fish. = 0.083/100 = 0.00083 PNEC unionised ammonia.

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		Assuming that the contribution of NH ₄ ⁺ to toxicity may be considered negligible, the PNEC in terms of ammonia/ammonium total loading may be calculated. Assuming a pH 7.0, the ratio of NH ₃ to NH ₄ ⁺ in solution is 1:181. This means that a PNEC of 0.00083 mg NH ₃ /l is equivalent to 0.151 mg ammonia/ammonium/l.
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7.1.2.2 PNEC sediment

Table 13. PNECs for the sediment compartment: TMS

Compartment	PNECs	Remarks/Justification
Sediments (freshwater)	PNEC sediment (freshwater) : 0.216 mg/kg sediment ww	Extrapolation method: partition coefficient $PNEC_{sediment} = K_{susp-water} / RHO_{susp} * PNEC_{freshwater} * 1000$ therefore $PNEC_{sediment} = 1.99/1150 * 0.124 * 1000 = 0.216$ mg/kg wwt.
Sediments (marine water)	PNEC sediment (marine water): 0.021 mg/kg sediment ww	Extrapolation method: partition coefficient $PNEC_{sediment\ marine} = K_{susp-water} / RHO_{susp} * PNEC_{saltwater} * 1000$ therefore $PNEC_{sediment\ marine} = 1.99/1150 * 0.0124 * 1000 =$ PNEC _{sediment marine} for the hydrolysis product trimethylsilanol = 0.021 mg/kg wwt.

Table 14. PNECs for the sediment compartment: Ammonia

Compartment	PNECs	Remarks/Justification
Sediments (freshwater)	PNEC sediment (freshwater) : 0.452 mg/kg sediment ww	PNEC sediment for ammonia has been calculated using the Equilibrium Partitioning Method (EPM) approach. Given the chemical structure of ammonia, the octanol–water partition coefficient (log K _{ow}) is likely to be low. This is confirmed by the predicted log K _{ow} value of 0.23. Sediments are not likely to be exposed to ammonia, as hydrolysis product of HMDZ, nor be accumulated in sediments. (EA 2007). Therefore, the derivation of sediment PNECs for the protection of benthic organisms is considered not to be necessary
Sediments (marine water)	PNEC sediment (marine water): 0.0452 mg/kg sediment ww	PNEC _{sediment marine} for ammonia has been calculated using the EPM approach.

7.2 Terrestrial compartment

No data is available for HMDZ on soil dwelling organisms. But, when considering the assessment it should also be taken into account:

- Fraction of emission directed to sludge by STP is 0.53% and 0.163% for TMS and ammonium, respectively; therefore, it does not seem likely that soil would be exposed by sludge application.
- Due to the low K_{ow} of 2.62 and 1.2 for TMS and ammonium, it is not expected a high potential to adsorb to the soil.

Toxicity of TMS:

According to the report PFA (2013y) (included in the IUCLID registration dossier), soil data are available for the silanol hydrolysis products of three substances in the sub-group of silanol substances having log K_{ow} values ≤ 1 . Data represent several short-term exposure studies with plants and one short-term study with the earthworm *Eisenia foetida*, showing no toxicity at the highest concentrations tested (L(E)C₅₀ values between >100 and >1000 mg/kg dwt).

Toxicity of Ammonia:

The following results for terrestrial toxicity of ammonia are sourced from the OECD HPV Chemical Programme, (OECD, 2007). The effects of ammonia gas was tested on terrestrial plant species resulting in a 4h-LOECs for damage to leaf area ranged from 3 ppm to 40 ppm.

7.2.1 Toxicity test results

7.2.1.1 Toxicity to soil macro organisms

No toxicity data is available on soil macro organisms.

7.2.1.2 Toxicity to terrestrial plants

No toxicity data is available on terrestrial plants

7.2.1.3 Toxicity to soil micro-organisms

No toxicity data is available on soil micro-organisms.

7.2.1.4 Toxicity to other terrestrial organisms

No data on other terrestrial organisms are available.

7.2.2 Calculation of Predicted No Effect Concentration (PNEC soil)

Table 15. PNEC for the soil compartment: TMS

Compartment	PNECs	Remarks/Justification
Soil	PNEC soil: 0.19 mg/kg soil dw	Extrapolation method: partition coefficient A PNEC soil for trimethylsilanol of 0.22 mg/kg wwt, equivalent to 0.25 mg/kg dwt has been calculated using the equilibrium partitioning method. No toxicity data are currently available for soil-dwelling organisms, therefore it is not possible to determine a PNECsoil based on measured data. PNECsoil can be calculated by the equilibrium partitioning method using the following equation: $PNEC_{soil} = K_{soil-water}/RHO_{soil} * PNEC_{water} * 1000$ For trimethylsilanol this is: $PNEC_{soil} = 1.51/1700 * 0.124 * 1000 = 0.19$ mg/kg wwt. Hence PNECsoil 0.19 mg/kg wwt will be used for risk characterisation.

Table 16. PNEC for the soil compartment: Ammonia

Compartment	PNECs	Remarks/Justification
Soil	PNEC soil: 0.233 mg/kg soil dw	PNEC soil for ammonia has not been calculated. Based on its solubility, ammonia is not expected to adsorb to soil particulate matter, suspended solids or sediment to an appreciable degree. In addition, bioaccumulation of ammonia in biota is not considered of importance in the environment as it does not accumulate in lipid-rich tissues in the same manner as organic chemicals, even though levels of ammonia in the blood of exposed animals may increase.

7.3 Atmospheric compartment

The predicted environmental concentration of HMDZ (in terms of its hydrolysis products) in air from direct releases and releases from waste water treatment plants for the uses assessed is low.

The silanol hydrolysis product has low volatility from water (calculated Henry's Law Constant $3.7 \text{ Pa m}^3 \text{ mol}^{-1}$ at environmental temperature, see Section 4.2.2) and releases to air are likely to be low.

In addition, there is no indication that either TMS or ammonia would have abiotic effects on the atmosphere. Therefore, further consideration of the effect of this substance on the atmosphere is considered not to be necessary.

7.4 Endocrine disrupting properties

Considering the substance and its hydrolysis products, endocrine disrupting properties are not relevant for this assessment.

7.5 Microbiological activity in sewage treatment systems

7.5.1 Toxicity to aquatic micro-organisms

The results on aquatic micro-organisms are summarised in the following table:

Table 17. Results on aquatic micro-organisms.

Method				Results	Remarks	Reference
Method equivalent or similar to OECD Guideline 209 (Activated Sludge, Respiration Test)	Results	Remarks	Reference	EC 50 : 6670 mg/l test mat. (nominal) based on: respiration rate	2 (reliable with restrictions) key study Test material: TMS	Muller (1992) cited in the CSR (2014)

Discussion

There are no reliable microorganism toxicity data available for HMDZ. Therefore data for the silanol hydrolysis product, TMS, have been read across.

TMS: In a study with trimethylsilanol, an EC50 value of 6670 mg/l (nominal) for toxicity to microorganisms (respiration rate) was determined in a study conducted according to an appropriate OECD 209 method but full details are not available (Muller (1992) (cited in the CSR (2014) and referred in the ECHA dissemination website).

Ammonia: Typical levels of free ammonia in municipal sewage treatment plants range from approximately 12-50 mg/l in the sewage treatment plant collection system (Lehr 2005). For the registration substance, the predicted environmental concentrations of the hydrolysis product ammonia in a sewage treatment plant are negligible compared to this typical level. A tentative PNECs for STP have been estimated.

The following information is taken into account for effects on aquatic micro-organisms for the derivation of PNEC:

- Toxicity to microorganisms: EC50 6670 mg/l (nominal) (respiration rate) read-across from the silanol hydrolysis product trimethylsilanol.

7.5.2 PNEC for sewage treatment plant

Table 18. PNEC for the Sewage Treatment Plant: TMS

Compartment	PNECs	Remarks/Justification
Sewage treatment plant	PNEC STP: >10 mg/l	For trimethylsilanol, an EC 50 of >6670 mg/l has been determined in an ASRI test according to OECD 209. Such a high loading rate corresponds to unrealistic kg/d releases. Therefore, the value is capped at >1000 mg/l. An assessment factor of 100 is applied to give a PNEC of >10 mg/l.

Table 19. PNEC for the Sewage Treatment Plant: Ammonia

Compartment	PNECs	Remarks/Justification
Sewage treatment plant	PNEC STP: 5 mg/L	

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

7.6.1 Toxicity to birds

No relevant for this assesment.

7.6.2 Toxicity to mammals

There are no data for toxicity to mammals via the food chain. Studies of mammalian toxicity are discussed in Section 5 of the CSR. This information has been reviewed by the eMSCA and considered not to be relevant for this assessment.

7.6.3 Calculation of PNECoral (secondary poisoning)

Table 20. PNEC for secondary poisoning: TMS and Ammonia

Compartment	PNECs	Remarks/Justification
Secondary poisoning	No potential for bioaccumulation	Bioaccumulation is not of concern for this substance; therefore, PNEC oral is not required.

7.7 Conclusion on the environmental hazard assessment and on classification and labelling

Reliable acute toxicity tests results are available for freshwater fish (*Brachydanio rerio*), invertebrates (*Daphnia magna*) and algae (*Scenedesmus subspicatus*). LC 50 or EC 50 values for the three organisms were all between 10 and 100 mg/l. No chronic studies are available for fish or invertebrates. The substance hydrolyses rapidly, however, the hydrolysis product TMS may persist in the environment.

Therefore, the proposed classification and labelling is as follows:

According to Regulation (EC) No 1272/2008:

Aquatic Acute: Not classified.

Aquatic Chronic: Category 3

According to Directive 67/548/EEC:

R52-53 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

8 PBT AND VPVB ASSESSMENT

8.1 Assessment of PBT/vPvB properties – Comparison with the criteria of Annex XIII

The substance hydrolyses very rapidly in contact with water, and therefore the substance does not meet the criteria for PBT or vPvB. The hydrolysis products have been assessed for PBT characteristics.

8.1.1 Persistence assessment

TMS is not readily biodegradable, and therefore, this hydrolysis product meets the criteria for persistence (P).

Conclusion: based on TMS, the substance can be concluded as vP (and P).

8.1.2 Bioaccumulation assessment

TMS has a low log Kow of 2.62 which is lower than the cut-off criteria (4.5) and, therefore, does not meet the screening criteria for bioaccumulation.

Ammonia is inorganic and the PBT/vPvB criteria are not applicable; it enters the nitrogen cycle and is not expected to bioaccumulate.

Conclusion: based on both hydrolysis products, HMDZ can be concluded as not B/vB.

8.1.3 Toxicity assessment

TMS has resulted in low toxicity to the aquatic organisms and no CMR properties or other T characteristic.

Ammonia would be borderline regarding long-term effects on fish (NOEC of 0.011 mg&L. But this is an inorganic substance and the PBT/vPvB criteria are not applicable.

Conclusion: based on both hydrolysis products, HMDZ can be concluded as not T.

8.1.4 Summary and overall conclusions on PBT and vPvB Properties

Based on the assessment described in the subsections above the submission substance is not a PBT / vPvB substance.

9 EXPOSURE ASSESSMENT

9.0 Overview

Exposure scenarios are presented for the manufacture of 1,1,1,3,3,3-hexamethyldisilazane (HMDZ) and the five identified uses described in Section 2.:

Use as a processing aid in polymerisation processes is covered under the exposure scenario for manufacture and on-site use.

The uses and relevant descriptor codes for each identified use are summarised in **Table 21**.

Exposure Scenario 1 describes the manufacture of HMDZ and its on-site uses including use as a processing aid in polymerisation processes.

Exposure Scenario 2 describes the use of HMDZ as a chemical intermediate.

Exposure Scenario 3 describes the use of HMDZ as a non-metal surface treatment agent.

Exposure Scenario 4 describes the use of HMDZ in the manufacture of semiconductors.

Exposure Scenario 5 describes the use of HMDZ as a laboratory reagent.

In all cases, the exposure scenarios are based on information in the public domain (ECHA website) and provided by the producer companies. To the best of our knowledge, due to the lack of specific information on volume corresponding to each registrant or site-plant, it has been assumed, as a worst case, that the ESs described cover several identified uses which take place systematically at the same place. This assumption will consider the total aggregated volume for each scenario. Therefore one worst-case release factor will be applied as a base for the assessment.

The exposure scenario is written on behalf of several registrants, and is written in generic terms not site-specific ones. Practices at individual sites will equal under the conditions described in respect of environmental safety.

Data are available for the site specific flow rates of effluent and of receiving water (see appendix I). According to the information provided and the RCRs for the environmental compartments no more specific information is considered to be needed.

All the intended uses are industrial only. There are no downstream uses that would result in exposure of consumers. As HMDZ is extremely reactive and no residual unreacted starting material is present in the end products.

Industrial use of the substance is carried out under highly controlled conditions; this is discussed in detail in Fisk et al. (2010) (cited in CSR and referred in ECHA dissemination website). The manufacture and industrial uses of the substance are also such that there is no direct release to soil. Nevertheless, default estimations have also been calculated for the soil compartment.

It is considered appropriate to carry out environmental exposure assessment and risk characterisation based on the properties of the two hydrolysis products of HMDZ. Based on this

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assumption, all release amounts for environmental exposure calculations are therefore corrected for the molecular weight of:

(i) two moles the silanol hydrolysis product (90.2 g/mol) compared to the parent (161.4 g/mol). This gives a correction factor of $(2 \times 90.2)/161.4 = 1.12$

(ii) 1 mole the ammonia hydrolysis product (17.03 g/mol) compared to the parent (161.4 g/mol). This gives a correction factor of $17.03/161.4 = 0.11$.

Therefore, all predicted environmental concentrations (PECs) have been calculated on the basis of the physicochemical properties of the hydrolysis products: TMS and ammonia.

The rapid hydrolysis of HMDZ and the low log K_{ow} ($\ll 3$ (predicted value (EPA, 2010))) for the hydrolysis products indicate that bioaccumulation is not a concern. Also as mentioned in Section 4, ammonia enters the nitrogen cycle and is not expected to bioaccumulate. Therefore, the assessment of secondary poisoning for the two hydrolysis product is not considered further.

Table 21. Overview on exposure scenarios and coverage of substance life cycle.

ES number	Volume (tonnes*)	Manufacture	Identified uses			Resulting life cycle stage		Sector of Use		Chemical Product Category (PC)	Process category (PROC)	Environmental Release Category (ERC)
			Formulation	Ind. Use	Consumer use	Service life (for articles)	Waste stage	Main user group (SU)	Sector of end uses (SU)			
ES 1	4000	X		X				SU3	SU8	PC19 PC20	PROC1 PROC2 PROC3 PROC9 PROC8b	ERC1 ERC6A ERC6B
ES 2	200			X				SU3	SU9	PC19	PROC1 PROC2 PROC3 PROC8b	ERC6A
ES 3	60		X	X				SU3	SU8 SU9 SU11 SU12 SU13	PC15	PROC1 PROC2 PROC3 PROC5 PROC8a PROC8b	ERC6B, ERC6D
ES 4	3			X				SU3	SU16	PC33	PROC1 PROC8b PROC13 ³	ERC6B
ES 5	0.1			X				SU3	SU24	PC21	PROC15	-

* Local tonnage assessed for each ES (see relevant ES).

³ This relates to the spin coating process in semiconductor manufacturing which takes place under strictly controlled conditions that are equivalent to PROC 1. Hence PROC13 has been mentioned for completeness only, but it is not assessed further for ES4.

9.0.1 ES1: Manufacture and on-site use of HMDZ

The exposure scenario is written on behalf of several registrants, and is written in generic terms not site-specific ones. Practices at individual sites will equal under the conditions described in respect of environmental safety.

This exposure scenario covers the manufacture of HMDZ. It also covers use as an intermediate and as a processing aid in polymerisation processes by manufacturers and importers of the substance. Use as an intermediate by downstream users is covered by Exposure Scenario 2. Manufacture and use as a chemical intermediate could take place in closed continuous processes or in a closed batch processes.

Transfer of the substance (e.g. from vessels/tankers) takes place at dedicated facilities. The substance is also transferred into small containers for shipping, using a dedicated filling line.

Table 22. Duration, frequency and amount (ES1)

Information type	Generic scenario	Explanation
Used amount of substance per day	13000 kg/d	This is based on a generic worst case production volume estimate from confidential production site information
Annual amount used per site	4000 tonnes/year	This is based on a generic worst case production volume estimate from confidential production site information.
Emission days per site	300 d/y	REACH default number of days

Environmental surroundings characteristics

Environmental surrounding characteristics are considered for both fresh water and marine water as follows:

Fresh water flow rate: 1170000 m³/d (worst case based on site-specific effluent flow rate (1300 m³/d) information for all relevant EU HMDZ production sites and dilution of 900 considered for receiving water.

Marine water flow rate: A default dilution factor for discharges to a coastal zone (marine environment) of 100 is assumed to be representative for a realistic worst case.

Other operational conditions of use

The level of handling and control in place during the production of HMDZ is high. Therefore, default factors for releases to air (0.025) and water (0.003) during production are conservative and does not seem to be appropriate to be applied to HMDZ. Following estimations of losses has been considered in the assessment according to potential process in which losses can be produced and registrants information:

- **Losses from reaction vessels**

Manufacture of HMDZ can take place in closed continuous processes or a closed batch process; where minimal losses may occur, for example, during sampling. These losses are considered to be negligible compared to those listed below.

- **Losses from purification**

Information from registrants from manufacturing site questionnaires shows that crude HMDZ is purified by distillation. The distillation process for HMDZ is assumed to be similar to that of chlorosilanes, which involves two stages, with primary and secondary condensers both having efficiency of 99%. The estimated fugitive release from the distillation condensers of a daily tonnage production of 13 tonnes of HMDZ is:

$$0.01 \times 13000 \text{ kg/d} \times 0.01 = 1.3 \text{ kg/d}$$

Although fugitive releases are sent to incinerators at some sites, use of scrubber (with 99% efficiency is assumed). Therefore, the loss of HMDZ from purification process is as follows:

$$\text{Release to water: } 1.3 \text{ kg/d} \times 0.99 = 1.29 \text{ kg/day}$$

- **Releases from container loading and cleaning operations**

Fugitive release of HMDZ to the atmosphere can occur during loading, filling and cleaning activities. However, these activities are expected to be limited during the production year.

As indicated by registrants, cleaning operations for reaction vessels are infrequent (limited to a few days per production year), because mainly dedicated equipment is used. All equipment is purged with nitrogen to reduce releases. Any waste water from cleaning operations is typically collected and incinerated. Thus, releases from cleaning operations are assumed negligible and are not considered further.

HMDZ is sold in small containers; filling takes place via a dedicated filling line. A worst-case for the amount moved off-site is 1500 tpa. The calculation below is based on a 150 kg drum, although much of the product is shipped in smaller quantities.

The EA ESD for transport and storage gives the following equations for calculating emissions from filling of drums:

$$E = (V * x * VP) / (R * T * 1000) * MW / 1000$$

E is the emission per drum filled

V is the volume of substance – 150 kg / 0.77 g/cm³ (eq 0.77 kg/l) = 195 litres

x is the mole fraction of the chemical in the liquid = 1 for pure substance

R is the ideal gas constant = 8.314 J / K / mol

T is temperature = 298 K

VP is the vapour pressure = 2400 Pa at 25°C

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MW is the molecular weight = 161.4 g/mol
Conversion factor between m³ and l is 1000
Conversion factor between kg and g is 1000

$$E = (195 * 1 * 2400) / (8.314 * 298 * 1000) * 161.4 / 1000 = 0.03 \text{ kg/event}$$

The number of drums is 1500 tpa / 150 kg = 10000 drums/year.

Therefore, the total loss is 0.03 * 10000 = 300 kg/year.
Assuming 300 days per year, the daily loss is 1 kg/day.

Although fugitive releases are typically extracted and sent to incinerators, use of scrubber (with 99% efficiency) is assumed as a worst case. Therefore, the loss of HMDZ from loading and cleaning operations is as follows:

Release to water: 1 kg/d x 0.99 = 0.99 kg/day

- **Loss from minor spillages during routine activities**

From knowledge of the silicone industry and scale of operation, it can be assumed that minor spillages from routine activities, e.g. run-off of HMDZ from the purification distillation column and filling, occur. Spills are properly cleaned up or washed in line with industry best practise, typically via incineration. Spills may, occasionally, also be washed to and treated in waste water treatment plants. Hence, it is conservatively assumed that only 0.005 kg/d of the spillages end up in the waste water stream.

Therefore, 0.005 kg/d of HMDZ is assumed to be lost to waste water from minor spillages during routine activities.

- **Releases from HMDZ contaminated by-product**

Ammonium chloride (NH₄Cl) by-product from the production of HMDZ can be contaminated with an average concentration of 330 ppm of HMDZ. Some of the NH₄Cl is lost and/or released to waste water. Site specific information shows a release of up to 1.9 kg/day of HMDZ to waste water, from NH₄Cl lost.

- **Releases from storage tanks**

Given the daily production tonnage of 13 tonnes, it is considered that storage tanks of 50 m³ capacity are present, which are only completely emptied twice per year.

Loss of liquids can also occur from overflow and leakage, although a large number of tanks will have a secondary containment system that will collect such emissions for disposal (OECD, 2009).

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Total releases

The total releases per day of HMDZ to waste water and to air are estimated to be:

Water: 4.19 kg/day

This is made up of releases from filling, purification, loss from minor spillages and releases from NH₄Cl contaminated with HMDZ (0.99 + 1.29 + 0.005 + 1.9). This is 0.032% of the 13 tonnes per day covered by this scenario.

In terms of the hydrolysis products, the total release to water is:

TMS: $1.12 \times 4.19 \text{ kg/d} = 4.7 \text{ kg/d}$

Ammonia: $0.11 \times 4.19 \text{ kg/d} = 0.46 \text{ kg/d}$

Table 23. Technical fate of substance and losses from process/use to waste, waste water (ES1)

Information type	Generic scenario	Explanation
Fraction of applied amount lost from process/use to waste water	0.00032 kg/kg	See text

Table 24 summarises the risk management measures in place during production of HMDZ (CSR, 2014).

Table 24. Risk management measures for industrial site (Environment) (ES1)

Information type	Data field	Explanation
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water	No measured data	Neutralisation
Resulting fraction of initially applied amount in waste water released from site to the external sewage system	No analytical data	pH control of effluents, specified in site consent requirements, mean that residual ammonia and HMDZ are not present in the treated waste water.
Air emission abatement	Incineration – 99 % efficient Scrubber – 99 % efficient	Scrubbers, condensers, incineration, energy recovery
Resulting fraction of applied amount in waste gas released to environment	1.0E-02 kg/kg	This is the fraction released from emission control devices only (i.e the efficiency of the air emission abatement equipment). Releases from other sources also accounted for in the final release estimate. See text
Onsite waste treatment	Yes	Secondary biological treatment
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues from onsite waste water and waste gas treatment.	No measured data	
Municipal or other type of external waste water treatment	Yes	Generic environmental surrounding characteristics considered covers both on-site waste water and municipal or

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		external waste water treatment.
Effluent (of the waste water treatment plant) discharge rate	1300 m ³ /d – Discharged to fresh water 3100 m ³ /d – Discharged to marine water	Generic worst case flow rate of waste water treatment plant based on information from EU production sites (see appendix I).
Recovery of sludge for agriculture or horticulture	No	Biosludge ultimately sent to landfill or incinerated

Environmental exposure

Production of HMDZ is highly regulated and controlled and designed to ensure process containment under normal operating conditions. But measured environmental release data are not readily available.

Therefore, predicted environmental release estimates have been used for releases during manufacture and on-site use. The releases have been estimated using the above exposure scenario and Predicted Environmental Concentrations (PECs) for the hydrolysis products (TMS and ammonia) reported in **Table 25** and **Table 26** have been determined using EUSES 2.1.2. The EUSES program implements the environmental exposure models described in REACH Technical Guidance Chapter R16. Default model parameters have been used with the following exceptions:

Generic worst case daily flow rate to WWTP – 1300 m³/d (discharged to fresh water (see appendix I for production site specific information))

Dilution factor (fresh water) - 900

Dilution factor (marine water) - 100

The basis of local and regional production tonnages is to consider the sizes of the largest sites in the EU relative to the total tonnage as follows:

Regional Tonnage: 4000 Tonnes

Fraction of main local source: 1

Local tonnage: 13 Tonnes per day

Number of days: 300 (consistent with the default)

The contribution of local releases to the regional concentration has been considered using the appropriate calculation in EUSES 2.1.2.

Table 25. ES 1 - Predicted Environmental Concentrations (PEC) for TMS (ES1)

Protection target	Local PEC	Explanation / Justification
Fresh Water	3.8E-03 mg/L	Local PEC in surface water during emission episode (dissolved)
Fresh Water sediment	6.6E-03 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
Marine Water	1.3E-03 mg/L	Local PEC in seawater during emission episode (dissolved)
Marine sediment	2.3E-03 mg/kgwwt	Local PEC in marine sediment during emission

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Protection target	Local PEC	Explanation / Justification
		episode
Agricultural soil	1.0E-01 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
Sewage Treatment Plant	3.4E+00 mg/L	PEC for micro-organisms in the STP

Table 26. ES 1 - Predicted Environmental Concentrations (PEC) for ammonia (ES1)

Protection target	Local PEC	Explanation / Justification
Fresh Water	3.0E-04 mg/L	Local PEC in surface water during emission episode (dissolved)
Fresh Water sediment	3.3E-04 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
Marine Water	2.7E-04 mg/L	Local PEC in seawater during emission episode (dissolved)
Marine sediment	2.9E-04 mg/kgwwt	Local PEC in marine sediment during emission episode
Agricultural soil	2.1E-03 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
Sewage Treatment Plant	2.7E-01 mg/L	PEC for micro-organisms in the STP

9.0.2 ES2: Use of HMDZ as a chemical intermediate

This scenario covers the use of HMDZ as a chemical intermediate in the synthesis of organic fine chemicals and pharmaceutical ingredients. These processes take place at both, the production site and downstream customers' sites. Use as an intermediate at a production site is considered as equivalent to production and is covered in ES1.

Synthesis may take place in batch or continuous processes, but due to the flammable and corrosive nature of HMDZ, processes are usually closed.

Table 27. Duration, frequency and amount (ES2)

Information type	Generic scenario	Explanation
Used amount of substance per day	2 tonnes /day	Generic information
Annual amount used per site	200 tonnes	Generic information
Emission days per site	100 d/y	Generic information

Environmental surroundings characteristics

Dilution factor: 40 (default for large industrial site).

Dilution in marine water: 100

Releases to water

The REACH ERC 6A (Industrial use of intermediates) default release estimates to waste water is 2%. This gives a daily release of 40 kg/d (2000 kg/d x 0.02) to water. The default ERC release value is considered to be very high for the use of the substance as a chemical intermediate, and releases of the substance at such a level to water, with the generation of TMS and ammonia, would be in contravention of national and local regulations.

A more realistic release to waste water can be justified based on the following considerations:

- 1) Realistic losses to waste water from the processing of HMDZ at a typical industrial site are expected to come from minor routine or occasional spillages and washing of waste gas in scrubbers. Given the high reactivity of HMDZ (hydrolysis half-life at pH 7 and 1.5°C: ≤ 0.5 min), the presence of water is carefully excluded from all processes to prevent undesirable hydrolysis.
- 2) Industrial sites have clean up processes or facilities such as settling tanks for waste water generated on-site.

In the absence of more specific/detailed site information for the processing of HMDZ as a chemical intermediate and based on the high reactivity of the substance and justifications above, it is reasonable to assume, as a worst case:

- that 95% of HMDZ reacts on use

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- the 'unreacted' substance (5%) is passed through a 90% efficient incinerator and then washed out in a scrubber. This gives the release estimate to waste water of 0.005 (0.05 x 0.1) and a daily release of the substance as:

$$2000 \text{ kg/d} \times 0.005 = 10 \text{ kg/d}$$

In terms of the hydrolysis products, the release to water is:

$$\text{TMS: } 1.12 \times 10 \text{ kg/d} = 11.2 \text{ kg/d}$$

$$\text{Ammonia: } 0.11 \times 10 \text{ kg/d} = 1.1 \text{ kg/d}$$

It can be assumed that this process will be taking place at a large industrial site located near a large urban area and, therefore, waste water will pass to a larger-than-default WWTP. A flow rate of 10,000 m³/day is used, in line with the EU Emission Scenario Document for chemical intermediates, a document which was based on extensive research into the chemical industry.

Table 28. Technical fate of substance and losses from process/use to waste, waste water and air (ES2)

Information type	Generic scenario	Explanation
Fraction of applied amount lost from process/use to waste water	0.005 kg/kg	See text

Table 29 summarises the risk management measures in place during use of HMDZ as a chemical intermediate.

Table 29. Risk management measures for industrial site (Environment) (ES2)

Information type	Data field	Explanation
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water	-	-
Resulting fraction of initially applied amount in waste water released from site to the external sewage system	0.005	-
Air emission abatement	Yes	Incinerators, scrubbers, condensers
Resulting fraction of applied amount in waste gas released to environment	0.001	See text
Onsite waste treatment	Yes	Waste water treatment could be on-site or communal (collection of industries) or municipal facility
Municipal or other type of external waste water treatment	Yes	Waste water treatment could be on-site or communal (collection of industries) or municipal facility
Effluent (of the waste water treatment plant) discharge rate	1 * 10 ⁷ l/d	Default for a large industrial site (based on the EU ESD for chemical intermediates)
Recovery of sludge for agriculture or horticulture	Yes	Worst-case assumption as no specific information available.

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No specific information is available on the amount of waste generated for the use of the substance in this application. The default fractions of amount ending up in waste, according to the used ending in the REACH Guidance Chapter R.18 (ECHA, 2010c), is therefore specified for HMDZ in waste from this application, as a worst case.

Fraction of amount used ending up as waste: 5% (Hazardous waste from use as intermediate)

According to registrants information, the suitable disposal keep any waste containing the substance or its hydrolysis products separate and dispose of hazardous waste by incineration operated according to Council Directive 2008/98/EC on waste, Directive 2000/76/EC on the incineration of waste and the Reference Document on the Best Available Techniques for Waste Incineration (EC, 2006).

Release rate to water for incineration: 0.0001

Daily release to water from incineration: $2000 \text{ kg/d} \times 0.5 \times 0.0001 = 0.1 \text{ kg/d}$

The processes described for use of the pure substance (and the related conditions of use) as a chemical intermediate would also cover the type of processes (by PROC) and conditions of use during incineration of waste containing the hydrolysis products of the substance.

Environmental exposure

Predicted Environmental Concentrations for the hydrolysis products (TMS and ammonia) reported in **Table 30** and **Table 31** have been determined using EUSES 2.1.2.

Local and regional tonnages used for environmental release assessment are as follows:

Regional Tonnage: 200 Tonnes per year

Fraction of main local source: 1

Local tonnage: 200 tonnes per year

Number of days: 100 days/year

Table 30. ES 2 - Predicted Environmental Concentrations (PEC) for TMS (ES2)

Protection target	Local PEC	Explanation / Justification
Fresh Water	2.6E-02 mg/L	Local PEC in surface water during emission episode (dissolved)
Fresh Water sediment	4.5E-02 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
Marine Water	1.1E-02 mg/L	Local PEC in seawater during emission episode (dissolved)
Marine sediment	1.9E-02 mg/kgwwt	Local PEC in marine sediment during emission episode
Agricultural soil	3.1E-02 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
Sewage Treatment Plant	1.0E+00 mg/L	PEC for micro-organisms in the STP

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Table 31. ES 2 - Predicted Environmental Concentrations (PEC) for ammonia (ES2)

Protection target	Local PEC	Explanation / Justification
Fresh Water	2.1E-03 mg/L	Local PEC in surface water during emission episode (dissolved)
Fresh Water sediment	2.3E-03 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
Marine Water	1.1E-03 mg/L	Local PEC in seawater during emission episode (dissolved)
Marine sediment	1.2E-03 mg/kgwwt	Local PEC in marine sediment during emission episode
Agricultural soil	6.5E-04 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
Sewage Treatment Plant	8.4E-02 mg/L	PEC for micro-organisms in the STP

9.0.3 ES 3: Use of HMDZ as a surface treatment agent

According to registrants' information, this scenario covers the use of HMDZ in the production of surface-treated silica or other minerals using a direct pre-treatment process. Direct pre-treatment occurs in industrial facilities in enclosed vessels in a continuous process which is integrated with silica production. The process is either fully closed or closed with occasional controlled exposure. This exposure scenario also covers the formulation of products containing up to 5% HMDZ for use in non-metal surface treatment.

Formulation takes place in batch processes which may either be closed, or multistage.

Table 32. Duration, frequency and amount (ES3)

Information type	Generic scenario	Explanation
Used amount of substance per day	1.2 tonnes per day	Generic information
Annual amount used per site	60 tonnes	Generic information
Emission days per site	50 days	Generic information

Environmental surroundings characteristics

Default sized WWTP and receiving water flow rates are used as follows:

Effluent discharge rate of STP = 2,000 m³/d.

Dilution factor at the point of complete mixing:

Dilution in Fresh water = 10

Dilution in marine water = 100

No measured data are available for releases of HMDZ to waste water from use as a surface treatment agent. Given the highly controlled nature of the processes, losses to water from direct pre-treatment are considered equivalent/similar to those resulting from use as a chemical intermediate, described in Section 9.0.2, and are not discussed further here.

For use of HMDZ *in situ* treatment during polymer manufacture, it is assumed that processes are carried out according to typical practice in the plastics and rubber industries. Accordingly, release estimations can be made on the basis of the OECD Emission Scenario Document on Plastic Additives (OECD, 2009). The substance category for 'coupling agents' is considered to be the most appropriate for this use. Although the ESD states that normal practice would be to pre-treat the filler in a separate facility, other sources (e.g. Gelest, 2009 cited in CSR) report use *in situ*.

Addition levels are of the order 0.2 to 1.0% by weight of the silazane in the total mix. There is potential for release to the environment from raw materials handling and compounding (mixing with other ingredients). There is no release from conversion (formation of final articles) of the polymers as the reagents are consumed during the process (OECD, 2009).

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During compounding, all releases are initially to air, but the ESD assumes subsequent condensation onto surfaces that ultimately results in release to waste water during cleaning processes, so the initial releases are split 50:50 to air and water.

For a high volatility substance, releases during compounding are reported as:

F compounding , water = 0.025%

F compounding , air = 0.025%

Releases to air due to handling losses are not considered for coupling agents in the ESD, and releases to water are estimated as 0.01%.

Releases to waste water

The total release to waste water is 0.035% based on the sum of losses from handling (0.01%) and compounding (0.025%).

The daily release of the parent substance to water is:

$0.00035 \times 1200 \text{ kg/d} = 0.42 \text{ kg/d}$

In terms of the hydrolysis products, the release to water is:

Trimethylsilanol: $1.12 \times 0.42 \text{ kg/d} = 0.47 \text{ kg/d}$

Ammonia: $0.11 \times 0.42 \text{ kg/d} = 0.046 \text{ kg/d}$

Table 33. Technical fate of substance and losses from process/use to waste, waste water and air (ES3)

Information type	Generic scenario	Explanation
Fraction of applied amount lost from process/use to waste water	0.00035 kg/kg	See text

Table 34 summarises the risk management measures in place during use of HMDZ as a surface treatment agent.

Table 34. Risk management measures for industrial site (Environment) (ES3)

Information type	Data field	Explanation
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water	-	-
Resulting fraction of initially applied amount in waste water released from site to the external sewage system	0.00035	See text
Air emission abatement	Yes	Incinerators and scrubbers
Resulting fraction of applied amount in waste gas released to environment	0.00025	See text
Onsite waste treatment	Yes	Secondary biological treatment
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues	No measured data	

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from onsite waste water and waste gas treatment.		
Municipal or other type of external waste water treatment	Yes	Waste water treatment could be on-site or communal (collection of industries) or municipal facility
Effluent (of the waste water treatment plant) discharge rate	$2 * 10^6 \text{ l d}^{-1}$	Default used as no specific information is available.
Recovery of sludge for agriculture or horticulture	Yes	Worst-case assumption as no specific information available.

No specific information is available on the amount of waste generated for the use of the substance in this application. Therefore, default fractions of amount ending up in waste, according to the used ending in the REACH Guidance Chapter R.18 (ECHA, 2010), is therefore specified for HMDZ in waste from this application, as a worst case.

Fraction of amount used ending up as waste: 2.5% (Hazardous waste from formulation)

Suitable disposal: Keep any waste containing the substance or its hydrolysis products separate and dispose of hazardous waste by incineration operated according to Council Directive 2008/98/EC on waste, Directive 2000/76/EC on the incineration of waste and the Reference Document on the Best Available Techniques for Waste Incineration (EC, 2006).

Release rate to water for incineration: 0.0001

Daily release to water from incineration: $1200 \text{ kg/d} \times 0.025 \times 0.0001 = 0.003 \text{ kg/d}$

The processes described for use of the pure substance (and the related conditions of use) as a surface treatment agent would also cover the type of processes (by PROC) and conditions of use during incineration of waste containing the hydrolysis products of the substance.

Environmental exposure

Industrial use of a reactive organosilicon substance such as HMDZ is highly regulated and controlled and designed to ensure process containment under normal operating conditions (CES, 2003).

Releases have been estimated using the exposure scenario for use as a surface treatment agent and waste lifecycle stage. The estimated releases from the waste lifecycle stage are negligible and are therefore not added to those from use as a surface treatment for predicting environmental concentrations.

Predicted Environmental Concentrations, for the hydrolysis products (TMS and ammonia) are reported in **Table 35** and **Table 36**, have been determined using EUSES 2.1.2.

Local and regional tonnages used for environmental release assessment are as follows:

Regional Tonnage: 60 tonnes per annum

Fraction of main local source: 1

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Local tonnage: 60 tonnes per year

Number of days: 50 days/year

Table 35. ES 3 - Predicted Environmental Concentrations (PEC) for trimethylsilanol (ES3)

Protection target	Local PEC	Explanation / Justification
Fresh Water	2.2E-02 mg/L	Local PEC in surface water during emission episode (dissolved)
Fresh Water sediment	3.8E-02 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
Marine Water	2.4E-03 mg/L	Local PEC in seawater during emission episode (dissolved)
Marine sediment	4.1E-03 mg/kgwwt	Local PEC in marine sediment during emission episode
Agricultural soil	6.6E-03 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
Sewage Treatment Plant	2.2E-01 mg/L	PEC for micro-organisms in the STP

Table 36. ES 3 - Predicted Environmental Concentrations (PEC) for ammonia (ES3)

Protection target	Local PEC	Explanation / Justification
Fresh Water	1.8E-03 mg/L	Local PEC in surface water during emission episode (dissolved)
Fresh Water sediment	1.9E-03 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
Marine Water	2.3E-04 mg/L	Local PEC in seawater during emission episode (dissolved)
Marine sediment	2.5E-04 mg/kgwwt	Local PEC in marine sediment during emission episode
Agricultural soil	1.3E-04 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
Sewage Treatment Plant	1.8E-02 mg/L	PEC for micro-organisms in the STP

9.0.4 ES 4: Use of HMDZ in the manufacture of semiconductors

This scenario covers the use of HMDZ in the semiconductor and electronics industry. This is essentially a surface treatment application. Processes are fully closed and there is no opportunity for direct handling or exposure to the substance. This is treated as equivalent to PROC1 in the ECETOC TRA model. Transfer of the substance (e.g. from vessels/tankers) takes place at dedicated facilities.

Many small electronic component manufacturers do not have on-site waste water treatment facilities and instead rely on controlling quantities of waste water effluent discharged directly into municipal sewers to meet standards locally agreed discharge consent limits (most frequently in terms of pH, total organic carbon and certain metals). Larger sites subject to IPPC need to describe the chemical contaminants in waste water and work to more controlled (perhaps substance-specific) limits (EA, 2007).

No specific information is available on the tonnage of HMDZ used in the electronics industry; therefore, a reasonable worst-case estimate is used. Based on the typical supply of chemicals in small containers (such as 4-litre bottles, 10-litre pack bottles and/or 25 kg containers) in the electronics industry, amount of HMDZ used is assumed as follows:

Volume used in EU for this application: 50 tonnes

Regional Tonnage: 5 tonnes (applying 10% rule)

Fractional of main local source: 0.6 (Single large site/user)

Local amount used: 10 kg/day

Number of days: 300 days

It is assumed that formulation (if necessary) and use occur at the electronics facility.

9.0.4.1.2 Operational conditions related to frequency, duration and amount of use

Table 37. Duration, frequency and amount (ES4)

Information type	Generic scenario	Explanation
Used amount of substance per day	10 kg/day	Generic information
Annual amount used per site	3 tonnes	Generic information
Emission days per site	300 d/y	Generic information

Environmental surroundings characteristics

Electronics facilities are not part of chemical industry production areas, and therefore default sized WWTP and receiving water flow rates are used as follows:

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Effluent discharge rate of STP = 2,000 m³/d.

Dilution factor at the point of complete mixing dilution = 10.

Releases to waste water

The release of the substance to water from this use comes from treatment of waste gas in wet scrubber (90% efficiency). Therefore, the release estimate to waste water is 0.045 (0.05 x 0.9) and the daily release of the substance to waste water is:

$$10 \text{ kg/d} \times 0.045 = 0.45 \text{ kg/d}$$

Due to the extremely rapid hydrolysis of HMDZ, ultimate releases to air or waste water treatment systems would be of ammonia and trimethylsilanol.

In terms of the hydrolysis products, the release to air is:

$$\text{TMS: } 1.12 \times 0.45 \text{ kg/d} = 0.5 \text{ kg/d}$$

$$\text{Ammonia: } 0.11 \times 0.05 \text{ kg/d} = 0.05 \text{ kg/d}$$

Table 38. Technical fate of substance and losses from process/use to waste, waste water and air (ES4)

Information type	Generic scenario	Explanation
Fraction of applied amount lost from process/use to waste water	0.045 kg/kg	See text

Table 39 summarises the risk management measures in place during the use of HMDZ in the electronics industry.

Table 39. Risk management measures for industrial site (Environment) (ES4)

Information type	Data field	Explanation
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water	-	-
Resulting fraction of initially applied amount in waste water released from site to the external sewage system	0.045	See text
Air emission abatement	Yes	Incinerators and scrubbers
Resulting fraction of applied amount in waste gas released to environment	0.005	See text
Onsite waste treatment	n/a	n/a
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues from onsite waste water and waste gas treatment.	No measured data	

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Municipal or other type of external waste water treatment	Yes	Many small electronic component manufacturers do not have on-site waste water treatment facilities and instead rely on controlling quantities of waste water effluent discharged directly into municipal sewers to meet standards locally agreed discharge consent limits. This is considered as a worst case scenario.
Effluent (of the waste water treatment plant) discharge rate	2E+06 l/d	Effluent (of the waste water treatment plant) discharge rate
Recovery of sludge for agriculture or horticulture	Yes	Worst-case assumption as no specific information available.

Environmental exposure

Predicted environmental release estimates have been used for releases during use of HMDZ in the electronics industry. The releases have been estimated using the exposure scenario and Predicted Environmental Concentrations for the hydrolysis products (TMS and ammonia) reported in **Table 40** and **Table 41** have been determined using EUSES 2.1.2.

Local and regional tonnages used for environmental release assessment are as follows:

Regional Tonnage: 5 tonnes per year

Fraction of main local source: 0.6

Local tonnage: 3 tonnes per year

Number of days: 300 days/year

Daily local tonnage: 10 kg/day

Table 40. ES 4 - Predicted Environmental Concentrations (PEC) for trimethylsilanol (ES4)

Protection target	Local PEC	Explanation / Justification
Fresh Water	2.3E-02 mg/L	Local PEC in surface water during emission episode (dissolved)
Fresh Water sediment	4.1E-02 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
Marine Water	2.5E-03 mg/L	Local PEC in seawater during emission episode (dissolved)
Marine sediment	4.4E-03 mg/kgwwt	Local PEC in marine sediment during emission episode
Agricultural soil	7E-03 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
Sewage Treatment Plant	2.1E-01 mg/L	PEC for micro-organisms in the STP

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Table 41. ES 4 - Predicted Environmental Concentrations (PEC) for ammonia (ES4)

Protection target	Local PEC	Explanation / Justification
Fresh Water	1.9E-03 mg/L	Local PEC in surface water during emission episode (dissolved)
Fresh Water sediment	2.1E-03 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
Marine Water	2.5E-04 mg/L	Local PEC in seawater during emission episode (dissolved)
Marine sediment	2.7E-04 mg/kgwwt	Local PEC in marine sediment during emission episode
Agricultural soil	1.5E-04 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
Sewage Treatment Plant	1.9E-02 mg/L	PEC for micro-organisms in the STP

9.0.5 ES 5: Use of HMDZ as a laboratory chemical

This scenario covers the use of HMDZ as a laboratory chemical/reagent for silanizing glassware or derivatisation reactions. All applications involve the use of very small quantities of material and all procedures are carried out in a fume cupboard.

There is no intentional release of HMDZ to waste water and any fugitive releases to air will be of negligible volume. Registrants indicate that on-site risk management measures of treatment preclude the discharge of waste to the aquatic compartment. Wastewater should be collected and disposed of in line with best practices, e.g. incineration.

Table 42. Operational conditions related to frequency, duration and amount of use (ES5)

Information type	Generic scenario	Explanation
Used amount of substance per day	<10 grams	See text
Annual amount used per site	0.1 Tonnes	Generic worst case
Emission days per site	1	EUSES default values

Table 43. Technical fate of substance and losses from process/use to waste, waste water and air (ES5)

Information type	Data field	Explanation
Fraction of applied amount lost from process/use to waste water	-	Not applicable

Table 44 summarises the risk management measures in place during use of HMDZ as a laboratory reagent.

Table 44. Risk management measures for industrial site (Environment) (ES5)

Information type	Data field	Explanation
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water		Not applicable
Resulting fraction of initially applied amount in waste water released from site to the external sewage system		Not applicable
Air emission abatement		Not applicable
Resulting fraction of applied amount in waste gas released to environment		Not applicable
Onsite waste treatment	No discharge of to waste water	Waste water should be collected and disposed of in line with best practice e.g. incineration
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues from onsite waste water and waste		Not applicable

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gas treatment.		
Municipal or other type of external waste water treatment		Not applicable
Effluent (of the waste water treatment plant) discharge rate		Not applicable
Recovery of sludge for agriculture or horticulture		Not applicable

It can be assumed that any small quantities of waste or unused HMDZ in this application are treated as hazardous waste and disposed of accordingly. These are however not considered significant given the very small volume of the registered substance used in this application.

9.1 Environmental exposure assessment

As it has been previously indicated, the exposure scenarios are based on information in the public domain (ECHA website) or provided by the producer companies. Due to the lack of specific information on volume corresponding to each registrant or site-plant, it has been assumed, as a worst case, that the ESs described cover several identified uses which take place systematically at the same place. This assumption will consider the total aggregated volume for each scenario. Therefore a worst-case release factor will be applied as a base for the aggregated assessment.

The exposure scenario is written on behalf of several registrants, and is written in generic terms not site-specific ones. Practices at individual sites will equal or exceed the conditions described in respect of worker and environmental safety.

9.1.1 Aquatic compartment (incl. sediment)

9.1.1.1 Overview of uses and exposure scenarios

In Table 45 and Table 46 are summarised the PECs for the aquatic compartment, estimated for TMS and ammonia, respectively.

Table 45. Predicted Environmental Concentrations (PEC) of TMS for the aquatic compartment.

Scenario	Protection target	Local PEC	Explanation / Justification
ES1	Fresh Water	3.8E-03 mg/L	Local PEC in surface water during emission episode (dissolved)
	Fresh Water sediment	6.6E-03 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	1.3E-03 mg/L	Local PEC in seawater during emission episode (dissolved)
	Marine sediment	2.3E-03 mg/kgwwt	Local PEC in marine sediment during emission episode
ES2	Fresh Water	2.6E-02 mg/L	Local PEC in surface water during emission episode (dissolved)
	Fresh Water sediment	4.5E-02 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	1.1E-02 mg/L	Local PEC in seawater during emission episode (dissolved)
	Marine sediment	1.9E-02 mg/kgwwt	Local PEC in marine sediment during emission episode
ES3	Fresh Water	2.2E-02 mg/L	Local PEC in surface water during emission episode

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Scenario	Protection target	Local PEC	Explanation / Justification
			(dissolved)
	Fresh Water sediment	3.8E-02 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	2.4E-03 mg/L	Local PEC in seawater during emission episode (dissolved)
	Marine sediment	4.1E-03 mg/kgwwt	Local PEC in marine sediment during emission episode
ES4	Fresh Water	2.3E-02 mg/L	Local PEC in surface water during emission episode (dissolved)
	Fresh Water sediment	4.1E-02 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	2.5E-03 mg/L	Local PEC in seawater during emission episode (dissolved)
	Marine sediment	4.4E-03 mg/kgwwt	Local PEC in marine sediment during emission episode
ES5	Fresh Water	7.12E-6 mg/L	Local PEC in surface water during emission episode (dissolved)
	Fresh Water sediment	3.09E-3 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	5.13E-5 mg/L	Local PEC in seawater during emission episode (dissolved)
	Marine sediment	3.09E-4 mg/kgwwt	Local PEC in marine sediment during emission episode

Table 46. Predicted Environmental Concentrations (PEC) of ammonia for the aquatic compartment

Scenario	Protection target	Local PEC	Explanation / Justification
ES1	Fresh Water	3.0E-04 mg/L	Local PEC in surface water during emission episode (dissolved)
	Fresh Water sediment	3.3E-04 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	2.7E-04 mg/L	Local PEC in seawater during emission episode (dissolved)
	Marine sediment	2.9E-04 mg/kgwwt	Local PEC in marine sediment during emission episode
ES2	Fresh Water	2.1E-03 mg/L	Local PEC in surface water during emission episode (dissolved)
	Fresh Water sediment	2.3E-03 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	1.1E-03 mg/L	Local PEC in seawater during emission episode (dissolved)
	Marine sediment	1.2E-03 mg/kgwwt	Local PEC in marine sediment during emission episode
ES3	Fresh Water	1.8E-03 mg/L	Local PEC in surface water during emission episode (dissolved)
	Fresh Water sediment	1.9E-03 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	2.3E-04 mg/L	Local PEC in seawater during emission episode (dissolved)
	Marine sediment	2.5E-04 mg/kgwwt	Local PEC in marine sediment during emission episode
ES4	Fresh Water	1.9E-03 mg/L	Local PEC in surface water during emission episode (dissolved)
	Fresh Water sediment	2.1E-03 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	2.5E-04 mg/L	Local PEC in seawater during emission episode (dissolved)

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Scenario	Protection target	Local PEC	Explanation / Justification
	Marine sediment	2.7E-04 mg/kgwwt	Local PEC in marine sediment during emission episode
ES5	Fresh Water	7.00E-7 mg/L	Local PEC in surface water during emission episode (dissolved)
	Fresh Water sediment	3.04E-4 mg/kgwwt	Local PEC in fresh-water sediment during emission episode
	Marine Water	5.04E-6 mg/L	Local PEC in marine sediment during emission episode
	Marine sediment	3.04E-5 mg/kgwwt	Local PEC in surface water during emission episode (dissolved)

In Table 47 and Table 48 are summarised the PECs for the aquatic compartment, estimated for TMS and ammonia, respectively.

Table 47. Predicted Environmental Concentrations (PEC) for TMS and STP

Scenario	Protection target	Local PEC	Explanation / Justification
ES1	Sewage Treatment Plant	3.4E+00 mg/L	PEC for micro-organisms in the STP
ES2	Sewage Treatment Plant	1.0E+00 mg/L	PEC for micro-organisms in the STP
ES3	Sewage Treatment Plant	2.2E-01 mg/L	PEC for micro-organisms in the STP
ES4	Sewage Treatment Plant	2.1E-01 mg/L	PEC for micro-organisms in the STP
ES5	Sewage Treatment Plant	5.6E-3 mg/L	PEC for micro-organisms in the STP

Table 48. Predicted Environmental Concentrations (PEC) for ammonia and the STP

Scenario	Protection target	Local PEC	Explanation / Justification
ES1	Sewage Treatment Plant	2.7E-01 mg/L	PEC for micro-organisms in the STP
ES2	Sewage Treatment Plant	8.4E-02 mg/L	PEC for micro-organisms in the STP
ES3	Sewage Treatment Plant	1.8E-02 mg/L	PEC for micro-organisms in the STP
ES4	Sewage Treatment Plant	1.9E-02 mg/L	PEC for micro-organisms in the STP
ES5	Sewage Treatment Plant	5.50E-4 mg/L	PEC for micro-organisms in the STP

9.1.2 Terrestrial compartment

9.1.2.1 Overview of uses and exposure scenarios

In Table 49 and Table 50 are summarised the PECs for the terrestrial compartment, estimated for TMS and ammonia, respectively.

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Table 49. Predicted Environmental Concentrations (PEC) of TMS for the terrestrial compartment.

Scenario	Protection target	Local PEC	Explanation / Justification
ES1	Agricultural soil	1.0E-01 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
ES2	Agricultural soil	3.1E-02 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
ES3	Agricultural soil	6.6E-03 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
ES4	Agricultural soil	7E-03 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
ES5	Agricultural soil	2.07E-3 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days

Table 50. Predicted Environmental Concentrations (PEC) of ammonia for the terrestrial compartment.

Scenario	Protection target	Local PEC	Explanation / Justification
ES1	Agricultural soil	2.1E-03 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
ES2	Agricultural soil	6.5E-04 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
ES3	Agricultural soil	1.3E-04 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
ES4	Agricultural soil	1.5E-04 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days
ES5	Agricultural soil	2.04E-4 mg/kgwwt	Local PEC in agric. soil (total) averaged over 30 days

10 RISK CHARACTERISATION

In **Table 51**, **Table 52** and **Table 53** are presented the RCRs for the different environmental compartments and the scenarios referred. In all cases, RCRs are calculated taking into account the expected moles of TMS and ammonia formed after the hydrolysis of HMDZ.

Table 51. RCRs calculated for the different scenarios and the aquatic compartment.

Scenario	Protection target	PEC/PNEC - TMS	PEC/PNEC ammonia
ES1	Fresh Water	0.3E-2	1.5E-2
	Fresh Water sediment	3,06E-02	7,30E-04
	Marine Water	1,05E-01	1,35E-02
	Marine sediment	1,10E-01	6,42E-03
ES2	Fresh Water	2,10E-01	1,05E-02
	Fresh Water sediment	2,08E-01	5,09E-03
	Marine Water	8,87E-01	5,50E-02
	Marine sediment	9,05E-01	2,65E-02
ES3	Fresh Water	1,77E-01	9,00E-03
	Fresh Water sediment	1,76E-01	4,20E-03
	Marine Water	1,94E-01	1,15E-02
	Marine sediment	1,95E-01	5,53E-03
ES4	Fresh Water	1,85E-01	9,50E-03
	Fresh Water sediment	1,90E-01	4,65E-03
	Marine Water	2,02E-01	1,25E-02
	Marine sediment	2,10E-01	5,97E-03
ES5	Fresh Water	5,74E-05	3,50E-06
	Fresh Water sediment	1,43E-02	6,73E-04
	Marine Water	4,14E-03	2,52E-04
	Marine sediment	1,47E-02	6,73E-04

Typical levels of free ammonia in municipal STPs collection system range from ca. 12-50 mg/l. The PECs of ammonia in STP for all the exposure scenarios assessed are small compared to the typical level of ammonia in the STP.

Table 52. RCRs calculated for the different scenarios and the STPs.

Scenario	Protection target	PEC/PNEC – TMS	PEC/PNEC - ammonia
ES1	Sewage Treatment Plant	3.4E-1	5,40E-02
ES2	Sewage Treatment Plant	1,00E-01	1,68E-02
ES3	Sewage Treatment Plant	2,20E-02	3,60E-03
ES4	Sewage Treatment Plant	2,10E-02	3,80E-03

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Scenario	Protection target	PEC/PNEC – TMS	PEC/PNEC - ammonia
ES5	Sewage Treatment Plant	5,60E-04	1,10E-04

Table 53. RCRs calculated for the different scenarios and the terrestrial compartment.

Scenario	Protection target	PEC/PNEC - TMS	PEC/PNEC - ammonia
ES1	Agricultural soil	5,26E-01	9,01E-03
ES2	Agricultural soil	1,63E-01	2,79E-03
ES3	Agricultural soil	3,47E-02	5,58E-04
ES4	Agricultural soil	3,68E-02	6,44E-04
ES5	Agricultural soil	1,09E-02	8,76E-04

According to the results of the current environmental assessment, no follow-up action at EU level is considered to be needed at this time.

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