SUBSTANCE EVALUATION REPORT

Public Name: HDI oligomers, isocyanurate

EC Number(s): 931-274-8

CAS Number(s): 28182-81-2

Submitting Member State Competent Authority: Chemicals Office of the Republic Slovenia, Ajdovščina 4, 1000 Ljubljana, Slovenia

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

VERSION NUMBER: 2 **DATE: 18 September 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	
Other: [*please specify*]	

DISCLAIMER

The Substance evaluation report has been prepared by the evaluating Member State as a part of the substance evaluation process under the REACH Regulation (EC) No 1907/2006. The information and views set out in this document are those of the author and do not necessarily reflect the position or opinion of the European Chemicals Agency or other Member States. The Agency does not guarantee the accuracy of the information included in the document. Neither the Agency nor the evaluating Member State nor any person acting on either of their behalves may be held liable for the use which may be made of the information contained therein. Statements made or information contained in the document are without prejudice to any further regulatory work that the Agency or Member States may initiate at a later stage.

Executive summary

Grounds for concern

The initial grounds for concerns from the justification document in the CoRAP 2014 were a suspected PBT/vPvB, potential for wide dispersive use from professional uses and high aggregated tonnage. Due to the fact that the molecular formula of this organic UVCB substance is not specified and the fact that substance is a complex mixture with variable composition which leads to difficulties in substance identification and wide variation in given phys-chem parameters the identity of the substance can be identified as a concern as well.

Substance has a low vapour pressure (2.46×10^{-3} Pa at 20 °C, 2.55×10^{-3} Pa at 25 °) and is hydrolytically unstable (half-life <12 hours). Partitioning coefficient log Pow for the main component was calculated as 9.81.
Calculated Log Koc values ranged from 4.28 to 24.25 (KOCWIN v 2.00, EPI suite™).

Persistency
Degradation of the registered substance was only 1% after 28 days in a ready biodegradation tests with adapted inoculum. Screening criteria for persistence were met. Substance could be potentially P/vP.

Bioaccumulation
Screening criteria for B (e.g. log Kow >4.5) were met and no data available to conclude on definitive criteria.

Toxicity
There were aquatic toxicity tests for fish, Daphnia and algae available. Neither definitive nor screening criteria for T appear to be met.

The substance evaluation shall clarify the following issues:

- UVCB substance identity
- Validation of log Pow on UVCB-substance
- The substance could be potentially vPvB

Procedure

The substance evaluation was based on information in the aggregated registration dossier (technical dossier, IUCLID), the Chemical Safety Report (CSR) but also other relevant literature and regulatory information were assessed. During the evaluation the representative of the Registrants has been contacted by the Slovene competent authority (CA) in order to discuss initial concerns. All additional explanations and information received were considered.

The evaluation as well as the documentation in the substance evaluation report focuses on the initial concerns. The evaluation was targeted on:

Information related to the PBT assessment:

The Slovene CA concluded that it is not necessary to request new data and therefore no draft decision was prepared. In addition the substance evaluation can be concluded with a report, based upon the following conclusions.

Conclusions

The clarification on the identity of the substance is considered adequate for an UVCB substance.

HDI oligomers, isocyanurate is not considered to be a PBT/vPVB substance as the parent compound is not P/vP. The main constituent HDI trimer does not meet criteria for T and also other constituents are unlikely to meet criteria for T. The relevant transformation products are the corresponding oligomeric and polymeric urea compounds. It is unlikely that the oligomeric urea compounds would meet the P/vP criterion and therefore it is appropriate to state that oligomeric urea does not meet the PBT/vPvB-criteria. Because of its high molecular weight one can state that polymeric urea shows no bioaccumulation potential and consequently does not meet the PBT/vPvB-criteria.

Based on the conclusions of the substance evaluation (SEv) no further risk management measures are needed.

CONTENTS

1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES 7

1.1 Name and other identifiers of the substance 7

1.2 Composition of the substance 9

1.3 Physico-chemical properties 10

2 MANUFACTURE AND USES 13

2.1 Quantities 13
2.1.1 Manufacturing processes 13

2.2 Identified uses 13
2.2.1 Uses by workers in industrial settings 13
2.2.2 Use by professional workers 14
2.2.3 Uses by consumers 16

2.3 Uses advised against 16
2.3.1 Uses by workers in industrial settings advised against 16
2.3.2 Use by professional workers advised against 16
2.3.3 Uses by consumers advised against 16

3 CLASSIFICATION AND LABELLING 16

3.1 Harmonised Classification in Annex VI of the CLP Regulation 16

3.2 Self classification 16

4 ENVIRONMENTAL FATE PROPERTIES 19
4.1.1 Abiotic degradation 19
4.1.2 Biodegradation 21

4.2 Environmental distribution 23
4.2.1 Adsorption/desorption 23
4.2.2 Volatilisation 24
4.2.3 Distribution modelling 24
4.2.4 Summary and discussion of environmental distribution 25

4.3 Bioaccumulation 25
4.3.1 Aquatic bioaccumulation 25
4.3.2 Terrestrial bioaccumulation 26
4.3.3 Summary and discussion of bioaccumulation 26

4.4 Secondary poisoning 26

5 HUMAN HEALTH HAZARD ASSESSMENT 26

6 HUMAN HEALTH HAZARD ASSESSMENT OF PHYSICO CHEMICAL PROPERTIES 26

7 ENVIRONMENTAL HAZARD ASSESSMENT 26

7.1 Aquatic compartment (including sediment) 26

7.1.1 Toxicity data 26
7.1.2 Calculation of Predicted No Effect Concentration (PNEC) 31

7.2 Terrestrial compartment 32
7.2.1 Toxicity test results 32
7.2.2 Calculation of Predicted No Effect Concentration (PNEC_soil) 34

7.3 Atmospheric compartment 34

7.4 Endocrine disrupting properties 34

7.5 Microbiological activity in sewage treatment systems 35
7.5.1 Toxicity to aquatic micro-organisms 35
7.5.2 PNEC for sewage treatment plant 35

7.6 Non compartment specific effects relevant for the food chain (secondary poisoning) 35
7.6.1 Toxicity to birds 35
7.6.2 Toxicity to mammals 35
7.6.3 Calculation of PNEC oral (secondary poisoning) 35

7.7 Conclusion on the environmental classification and labelling 35

8 PBT AND VPVB ASSESSMENT 36

8.1 Assessment of PBT/vPvB properties – Comparison with the criteria of Annex XIII 36
8.1.1 Persistence assessment 40
8.1.2 Bioaccumulation assessment 46
8.1.3 Toxicity assessment 50
8.1.4 Summary and overall conclusions on PBT and vPvB Properties 51

9 EXPOSURE ASSESSMENT 53

10 RISK CHARACTERISATION 54

10.1 Human Health 54

10.2 Environment 54
10.2.1 Risk characterisation for PBT 54
10.2.2 Aquatic compartment (incl. sediment) 54
10.2.3 Terrestrial compartment 54
10.2.4 Atmospheric compartment 54
10.2.5 Microbiological activity in sewage treatment systems 54

10.3 Overall risk characterisation 54

11 OTHER INFORMATION 55

12 REFERENCES 55

13 ABBREVIATIONS 57

1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

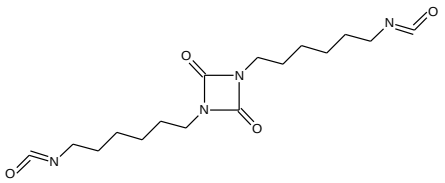
1.1 Name and other identifiers of the substance

Based on the available information, the substance is still identified as an UVCB substance, because the ratio between constituents is variable and poorly predictable. Otherwise, constituents can be qualitatively identified.

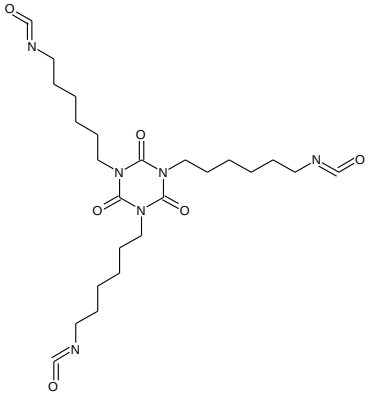
Table 1: Substance identity

Public Name:	HDI oligomers
EC number:	931-274-8
EC name:	HDI oligomers, isocyanurate
CAS number (in the EC inventory):	/
CAS number:	28182-81-2
CAS name:	Poly (hexamethylene) diisocyanate
IUPAC name:	HDI Oligomers, isocyanurate
Index number in Annex VI of the CLP Regulation	/
Molecular formula:	$(C_8H_{12}N_2O_2)_n$
Molecular weight range:	504-2185
Synonyms:	Poly (hexamethylene) diisocyanate HDI-based polyisocyanates

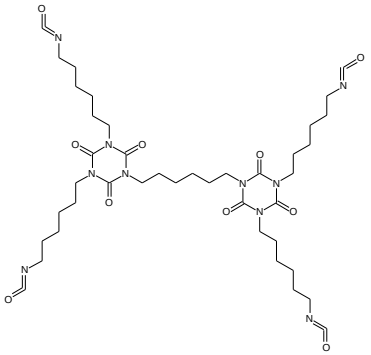
Structural formula: The substance is a UVCB. Representative structures are presented below:



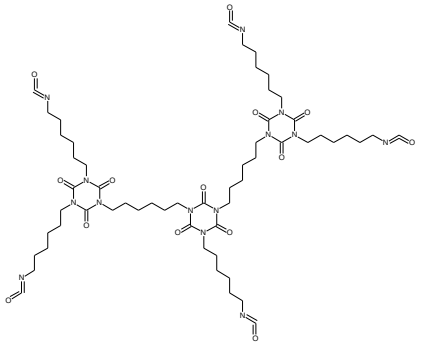
Structure 1 HDI dimer



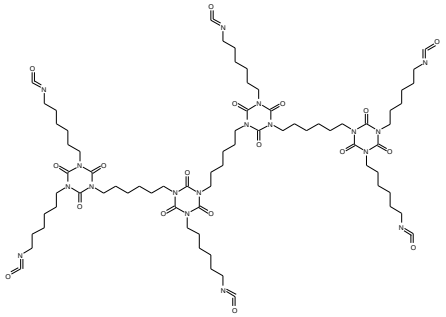
Structure 2 HDI trimer



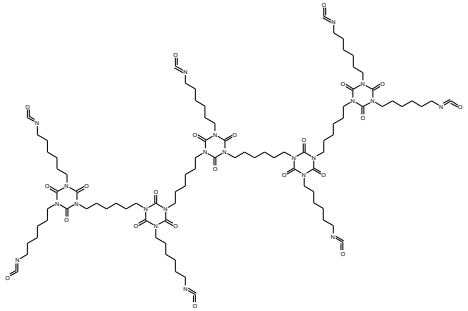
Structure 3



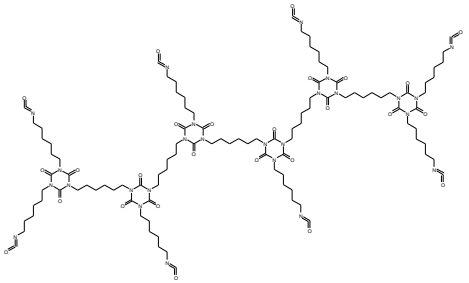
Structure 4



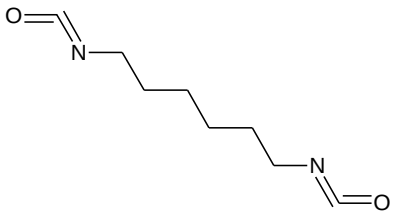
Structure 5



Structure 6



Structure 7



Sructure 8 HDI

1.2 Composition of the substance

Name: HDI Oligomers, isocyanurate

Description: UVCB

Degree of purity: Not relevant

Data (tables) on constituents and additives provided in Chemical Safety Report are included in Annex: Confidential information.

1.3 Physico-chemical properties

Table 5 : Overview of physicochemical properties

Property	Value	Remarks	Reference
Physical state at 20°C and 101.3 kPa	colourless, clear and visous organic liquid	liquid at 20°C and 101.3 kPa	Currenta, 2010
Melting/freezing point	The melting range lies between -51.3 and -28.4 °C	Guideline OECD 102	Laus, 2010
Boiling point	418 °C (calculated)	Guideline OECD 103: No boiling point could be determined because of decomposition of the test item, taking place at approx. 250 °C.	Laus, 2010
Relative density	1.17 g/cm³ at 20 °C and 1.09 g/cm³ at 23 °C	Guideline:- EU Method A 1.3- DIN EN 45001	Currenta 2009 Currenta 2008
Vapour pressure	2.46*10 E-03 Pa at 20 °C (calculated) 2.55*10 E-03Pa at 25 °C (calculated)	Guideline OECD 104 Value used for SEv: 0.00246 Pa at 20 °C	LAUS GmbH, 2010
Surface tension	-	Performing of a test is scientifically not necessary. The study does not need to be conducted based on structure. The surface activity is not expected or can be predicted, or is a desired property of the material, as well.	
Water solubility	-	In accordance with column 2 of REACH Annex VII, the study does not need to be conducted as the substance is hydrolytically unstable (half-life <12 hours).	
Partition coefficient n-octanol/water (log value)	The calculated partition coefficient (KOWWIN v 1.66) on the basis of the structural formula of the ideal HDI Trimer with 3 HDI units is 9.81. By calculation the log Pow value of 9.81 for the main constituent of HDI Trimer (HDI socyanurate, n = 3) was calculated according to KOWWIN	In accordance with column 2 of REACH Annex VII, an experimental test was not performed, as the substance decomposes in water within a few hours (half-time 7.7 hours).	Currenta, 2009

Property	Value	Remarks	Reference
	v.1.67.		
Flash point	228 °C	Guideline: DIN EN 22719	Currenta, 2008
Flammability	(a) No flammability in contact with water: The substance contains no metals or metalloids and therefore will not release flammable gases in contact with water. (b) Experience in production or handling;substance is known to be stable at room temperature.	Performing of a study according to EG A10 is technically not feasible, as the substance is a liquid.	
Explosive properties	.	Performing of a test is scientifically not necessary. According to United Nations (2003) (Annex 6, Table 6.1), the substance does not contain a chemical moiety suggesting a potential for explosivity.	
Self ignition temperature / Auto flammability	-	In accordance with column 2 of REACHAnnex VII, the study does not be conducted because HDI trimer has a flash point above 200 °C.	
Oxidising properties	-	Performing of a test is scientifically not necessary. According to United Nations (2003) (Annex 6, Table 6.1), the substance does not contain a chemical moiety suggesting an oxidising potential.	
Granulometry	.	In accordance with column 2 of REACH Annex VII, the study does not need to be conducted as the substance is marketed or used in a non solid or granular form.	
Stability in organic solvents and identity of relevant degradation products	In protic solvents like alcohols, isocyanates react rapidly. Stablility is expected with non-protic solvents like toluene,	Guideline: "in house" method "Determination of the NCO-content by dibutylamine titration"	Bayer, 2004 Bayer AG, 1999

Property	Value	Remarks	Reference
	acetone, dioxane etc. Isocyanates form urethanes in alcohol. The concentration of HDI trimer in an acetonitrile solution without addition of water was stable within 26 hours.		
Dissociation constant	-	In accordance with column 2 of REACH Annex IX, the study does not need to be conducted as HDI trimer is hydrolytically unstable (half-life 3 hours)	
Viscosity	dynamic viscosity: 3851.69 +/- 17.458 mPa*s	Guideline: OECD Test guideline 114	Laus GmbH, 2010
Reactivity towards container material	-		
Thermal stability	-		

2 MANUFACTURE AND USES

2.1 Quantities

Aggregated tonnage band per year: 10,000 - 100,000 tonnes

2.1.1 Manufacturing processes

Manufacture of the test material is not relevant and not covered in this report.

2.2 Identified uses

2.2.1 Uses by workers in industrial settings

Table 6: Uses by workers in industrial settings

IU No.	Identified Use (IU) name	Substance supplied to that use	Use descriptors
1	F-1: Industrial and professional use for formulation of preparations	As such In a mixture	**Environmental release category (ERC):** ERC 2: Formulation of preparations **Process category (PROC):** 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) PROC 4: Use in batch and other process (synthesis) where opportunity for exposure arises 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 15: Use as laboratory reagent **Technical function of the substance during formulation:** Binding agents

IU No.	Identified Use (IU) name	Substance supplied to that use	Use descriptors
2	IW-1: Industrial end use		**Environmental release category (ERC):** ERC 6a: Industrial use resulting in manufacture of another substance (use of intermediates) **Process category (PROC):** 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) PROC 4: Use in batch and other process (synthesis) where opportunity for exposure arises PROC 5: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact) PROC 7: Industrial spraying 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 10: Roller application or brushing PROC 13: Treatment of articles by dipping and pooring PROC 14: Production of preparations or articles by tabletting, compression, extrusion, pelletisation PROC 15: Use as laboratory reagent **Sector of end use:** SU 12: Manufacture of plastics products, including compounding and conversion SU 13: Manufacture of other non-metallic mineral products, e.g. plasters, cement SU 19: Building and construction work **Technical function of the substance during formulation:** Binding agents

2.2.2 Use by professional workers

Table 7: Use by professional workers

IU number	Identified Use (IU) name	Substance supplied to that use	Use descriptors

IU number	Identified Use (IU) name	Substance supplied to that use	Use descriptors
/	PW-1: Professional end use	As such In a mixture	**Environmental release category (ERC):** ERC 8f: Wide dispersive outdoor use resulting in inclusion into or onto a matrix ERC 8c: Wide dispersive indoor use resulting in inclusion into or onto a matrix **Process category (PROC):** PROC 3: Use in closed batch process (synthesis or formulation) PROC 4: Use in batch and other process (synthesis) where opportunity for exposure arises 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 10: Roller application or brushing PROC 11: Non industrial spraying PROC 13: Treatment of articles by dipping and pouring PROC 14: Production of preparations or articles by tabletting, compression, extrusion, pelletisation PROC 15: Use as laboratory reagent **Sector of end use:** SU 10: Formulation [mixing] of preparations and/or re-packaging (excluding alloys) SU 12: Manufacture of plastics products, including compounding and conversion SU 13: Manufacture of other non-metallic mineral products, e.g. plasters, cement SU 19: Building and construction work **Identifiers Use descriptors Other information** **Technical function of the substance during formulation:** Binding agents

2.2.3 Uses by consumers

Table 8: Uses by consumers

IU number	Identified Use (IU) name	Substance supplied to that use	Use descriptors
/	C-1: Do-It-Yourself application	/	/

Remarks: All consumer uses are strongly advised against by the registrants. The hazardous properties of the substance require safety measures which can, in principle, not be sufficiently ensured in the home worker sector.

2.3 Uses advised against

See Section 2.2.3. of this report.

2.3.1 Uses by workers in industrial settings advised against

None.

2.3.2 Use by professional workers advised against

None.

2.3.3 Uses by consumers advised against

All consumer uses are strongly advised against by the registrants.

3 CLASSIFICATION AND LABELLING

3.1 Harmonised Classification in Annex VI of the CLP Regulation

Substance has not yet been included in Annex VI of the CLP Regulation (EC) No 1272/2008.

3.2 Self classification

Self-classification reported by the registrant is as follows:

- For physical-chemical properties:

Endpoints	Classification / Reason for no classification
Explosives:	conclusive but not sufficient for classification
Flammable gases:	conclusive but not sufficient for classification

Flammable aerosols:	conclusive but not sufficient for classification
Oxidising gases:	conclusive but not sufficient for classification
Gases under pressure:	conclusive but not sufficient for classification
Flammable liquids:	conclusive but not sufficient for classification
Flammable solids:	conclusive but not sufficient for classification
Self-reacting substances and mixtures:	conclusive but not sufficient for classification
Pyrophoric liquids:	conclusive but not sufficient for classification
Pyrophoric solids:	conclusive but not sufficient for classification
Self-heating substances and mixtures:	conclusive but not sufficient for classification
Substances and mixtures which in contact with water emits flammable gases:	conclusive but not sufficient for classification
Oxidising liquids:	conclusive but not sufficient for classification
Oxidising solids:	conclusive but not sufficient for classification
Organic peroxides:	conclusive but not sufficient for classification
Corrosive to metals:	conclusive but not sufficient for classification

- **For health hazards:**

Endpoints	**Classification / Reason for no classification**
Acute toxicity - oral:	conclusive but not sufficient for classification
Acute toxicity - dermal:	conclusive but not sufficient for classification
Acute toxicity - inhalation:	Acute Tox. 4 (H332 Harmful if inhaled)
Skin corrosion/irritation:	conclusive but not sufficient for classification
Serious damage/eye irritation:	conclusive but not sufficient for classification
Respiration sensitization:	conclusive but not sufficient for classification
Skin sensitation:	Skin Sens. 1 (H317 May cause an allergic skin reaction)
Aspiration hazard:	conclusive but not sufficient for classification
Reproductive Toxicity:	conclusive but not sufficient for classification
Reproductive Toxicity: Effects on or via lactation:	conclusive but not sufficient for classification
Germ cell mutagenicity:	conclusive but not sufficient for classification
Carcinogenicity:	conclusive but not sufficient for classification
Specific target organ toxicity - single:	STOT Single Exp. 3 (H335 May cause respiratory irritation)
Specific target organ toxicity - repeated:	conclusive but not sufficient for classification

Specific concentration limits for health hazard:

Concentration (%)	**Classification**

/	/

- **For environmental hazards:**

Endpoints	Classification / Reason for no classification
Hazards to the aquatic environment (acute short-term):	conclusive but not sufficient for classification
Hazards to the aquatic environment (long-term):	conclusive but not sufficient for classification
Hazardous to the ozone layer	conclusive but not sufficient for classification

Labelling

Signal word: Warning

Hazard pictogram:

GHS07

Hazard statements:

H317: May cause an allergic skin reaction.
H332: Harmful if inhaled.
H335: May cause respiratory irritation.

Precautionary statements:

P260: Do not breathe dust/fume/gas/mist/vapours/spray.
P280: Wear protective gloves/protective clothing/eye protection/face protection.
P285: In case of inadequate ventilation wear respiratory protection.
P333+P313: If skin irritation or rash occurs: Get medical advice/attention.
P302+P352: IF ON SKIN: Wash with plenty of soap and water.
P304+P340: IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P403+P233: Store in a well-ventilated place. Keep container tightly closed.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 Degradation

4.1.1 Abiotic degradation

4.1.1.1 Hydrolysis

In a screening test at 50°C the HDI Trimer was found to hydrolyse by 84 – 89% within less than 1 hour at pH values of 4, 7, and 9 (Bayer Industry Services, 2007). Approximate mean half lives of 3 hours at 25°C were estimated at any pH and environmental relevant temperatures. A hydrolysis product based on the hydrolysis of the 3 Isocyanate groups to the corresponding amine functions has been proposed (BIS, 2007).

Based on the determination of the Isocyanate function, the half-time of HDI Trimer in the acetonitrile/water solution is approx. 7.7 hour at room temperature (23 °C) (Bayer AG, 1999). Hydrolysis products have not been elucidated. However similar substances containing several isocyanate groups like HDI, MDI are known to react rapidly with water forming insoluble oligomeric and polymeric ureas. The below mentioned corresponding triamine is only a theoretical worst-case assumption in order to have a basis for assessment but which in reality reflects only insignificant traces.

Table 9. Studies on hydrolysis

Method	Results	Remarks	Reference
OECD Guideline 111 (Hydrolysis as a function of pH)	Half-life (DT_{50}): t1/2 (pH 4): < 1 h at 50° C t1/2 (pH 7): < 1 h at 50° C t1/2 (pH 9): < 1 h at 50° C Type: estimated Transformation products: yes	2 (reliable with restrictions) key study experimental result Test material (EC name): HDI oligomers, isocyanurate	Bayer Industry Services (2007)
"in house" method "Determination of the NCO-content by dibutylamine titration". equivalent or similar to ASTM D4666-method (Standard Test Methods for Polyurethane Raw Materials Determination of the Isocyanate Content) The calculation of the NCO-content is based upon the consumption of di-n-butyl amine.	Half-life (DT_{50}): t1/2: ca. 7.7 h at 23° C	2 (reliable with restrictions) key study experimental result Test material (EC name): HDI oligomers, isocyanurate	Bayer AG (1999)

4.1.1.2 Phototransformation/photolysis

4.1.1.2.1 Phototransformation in air

The atmospheric oxidation rate constant of the main component HDI Trimer (Isocyanurat, n=3) is 37.5×10^{-12} cm^3/(molecule *s) and its atmospheric half-life is 10.3 h (Currenta, 2009a).
The atmospheric oxidation rate constant of the corresponding triamine of the main component HDI Trimer (Isocyanurat, n=3) is 129.1 × 10^{-12} cm^3/(molecule *s) and its atmospheric half-life is 3.0 h (Currenta, 2009b).

Table 10: Studies on phototransformation in air

Method	Results	Remarks	Reference
Calculated with AOP Program v1.92 of EPI-Suite Software. The Atmospheric Oxidation Program (AOPWIN) estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals. The rate constants are then used to calculate atmospheric half-lives for organic compounds based upon average atmospheric concentrations of hydroxyl radicals and ozone. Photochemical reaction with OH radicals - sensitiser for indirect photolysis: OH radicals Concentration of OH radicals: 0.5 E6 OH/cm³, 24 h/d	Half-life (DT_{50}): 10.3 h	2 (reliable with restrictions) key study estimated by calculation Test material: (CAS number): 3779-63-3	Currenta, 2009a
	Half-life (DT_{50}): 3 h	2 (reliable with restrictions) key study estimated by calculation Test material (Chemical name): corresponding triamine of the sym. HDI trimer(HDI Isocyanurate, n=3**)**	Currenta, 2009b

4.1.1.2.2 Phototransformation in water

Data on phototransformation in water are not available for the substance.

4.1.1.2.3 Phototransformation in soil

Data on phototransformation in soil are not available for the substance

4.1.2 Biodegradation

4.1.2.1 Biodegradation in water

4.1.2.1.1 Estimated data

Estimated data are not available for the substance.

4.1.2.1.2 Screening tests

Beside valid tests, there is a study according to a modified MITI-I where the substance was determined to be not readily biodegradable (Bayer AG, 1988). This study is not regarded as reliable: within 28 days only 48 % degradation of the reference substance (aniline) was observed.

Within 28 days, a degradation of 1 % was determined for HDI Trimer (Desmodur N 3600) in a 'Closed Bottle Test' (Bayer AG, 2001a). HDI Trimer is regarded as "not readily biodegradable".

In a 'Modified Manometric Respirometry Test' with adapted inoculum no degradation of HDI Trimer (Desmodur N 3600) could be obtained within 28 days (BayerAG, 2001b).

It can be concluded that screening criteria for persistence are met. There is a possible inhibition of the inoculum in the ready biodegradability tests (negative biodegradation values).

In a biodegradation test with adapted industrial bacteria it was shown that the substance is not degradable. This result is used for assessing the behaviour of the substance in STPs.

Table 11: An overview of screening tests for biodegradation in water

Method	Results	Remarks	Reference
Test type: ready biodegradability activated sludge, domestic, non-adapted OECD Guideline 301D (Ready Biodegradability: Closed bottle test)	under test conditions no biodegradation observed % degradation of test substance: 0 % after 14 d (O_2 consumption) 0 % after 14 d (O_2 consumption) 1% after 28 d (O_2 consumption)	2 (reliable with restrictions) key study experimental result Test material (EC name): HDI oligomers, isocyanurate	Bayer AG, 2001a

Method	Results	Remarks	Reference
Test type: inherent biodegradability activated sludge, industrial, adapted OECD Guideline 301 F (“Ready” Biodegradability: Manometric Respirometry Test)	under test conditions no biodegradation observed % degradation of test substance 1% after 8 d (BOD) 1% after 12 d (BOD) 1% after 20 d (BOD) 0% after 26 d (BOD) 0% after 28 d (BOD)	2 (reliable with restrictions) supporting study experimental result Test material (EC name): HDI oligomers, isocyanurate	Bayer AG, 2001b

4.1.2.1.3 Simulation tests (water and sediments)

No simulation tests on biodegradation are available for this substance. The test is considered scientifically unjustified. In test for ready biodegradation as well as in a test with adapted inoculum no signs for biodegradation were observed. Therefore, it is not expected that biodegradation will occur in a simulation test.

4.1.2.1.4 Summary and discussion of biodegradation in water and sediment

It can be concluded that screening criteria for persistence are met.

4.1.2.2 Biodegradation in soil

No data on biodegradation in soil are available for this substance. Because of the relatively rapid reaction of HDI Trimer with hydroxyl radicals in the atmosphere (Currenta, 2009), and the rapid hydrolysis in water (Bayer AG, 1999/BIS, 2007) significant concentrations of HDI Trimer would be not be expected to occur in soil with the exception of environmental spills for example. Hydrolysis of HDI Trimer is expected to occur much more rapidly than biodegradation. Therefore, the reaction with water is expected to be the only significant fate process of HDI Trimer in moist soil. Only small amounts of unreacted HDI Trimer may persist in soil, if encapsulated in water-insoluble polyurea crusts formed during hydrolysis. Therefore no data were submitted.

4.1.2.3 Summary of biodegradation

According to the available biodegradation results the main constituent HDI Trimer is not readily biodegradable.

Degradation rate in water:	Not readily biodegradable, hydrolysis: half live <1h
Degradation rate in sediment:	Not readily biodegradable
Degradation rate in soil:	Not readily biodegradable
Degradation rate in air:	Indirect photolysis: 37.5×10^{-12} cm^3/(molecule×s)

No information is available for the other constituents of the substance.

4.2 Environmental distribution

4.2.1 Adsorption/desorption

The main component HDI Trimer (Isocyanurat, n=3) of Desmodur N 3300 and Desmodur N 3600 is characterized by a Koc of 5.7×10^7 being calculated with PCKOCWIN v. 1.66 (Currenta, 2009a). According to the method of Gerstl (1999) the Koc of 2.1×10^7 accounts for the main component (Currenta, 2009a). No information is available for the other constituent of the substance.

Table 12: Studies on adsorption/desorption

Method	Results	Remarks	Reference
Study type: adsorption (soil)estimation Calculated using PCKOC Program v1.66 of EPI-Suite software as well as according to Sabljic (1995) and Gerstl (1990). The calculation of PCKOC program is based upon the molecule structure using the molecular connectivity method. The calculation according to Sabljic (1995, QASR Modelling of Soil Sorption. Improvements and Systematics of logKoc vs. logKow Correlations. Chemosphere, Vol. 31, pp. 4498-4514) is based on a statistical relationship between Koc and the octanol/water partition	Adsorption coefficient: Koc: ca. 21000000 - ca. 57000000 log Koc: ca. 7.3 - ca. 7.8	2 (reliable with restrictions) key study estimated by calculation Test material (CAS number): 3779-63-3	Currenta, 2009a
	Adsorption coefficient: Koc: ca. 27000 - ca. 610000 log Koc: ca. 4.4 - ca. 5.8	2 (reliable with restrictions) key study estimated by calculation Test material(Chemical name): corresponding triamine of the sym. HDI trimer (HDIIsocyanurate, n=3)	Currenta, 2009b

Method	Results	Remarks	Reference
coefficient. The calculation according to Gerstl (1990, Estimation of Organic Chemical Sorption by Soils, Journal of Contaminant Hydrology, 6, pp. 357-375) is based on a statistical relationships between Koc and the octanol/water partition coefficient.			

4.2.2 Volatilisation

With a vapour pressure of about 0.001 Pa volatilisation of the substance is unlikely. Henry´s law constant was estimated using HENRYWIN v. 1.30 to be 1.31 Pa × 10^{-12} Pa m^3/mol at a temperature of 25 °C. For the calculation the main constituent of HDI Trimer (Isocyanaurate, n=3) was chosen (Currenta, 2009c).

Table 13. Studies on volatilisation

Method	Results	Remarks	Reference
QSAR estimation with HENRYWIN v. 1.30	1.31 Pa × 10^{-12} Pa m^3/mol	2 (reliable with restrictions) key study estimated by calculation Test material (CAS number): 3779-63-3	Currenta, 2009c

4.2.3 Distribution modelling

HDI Trimer hydrolyses rapidly in the presence of water yielding a complex mixture of oligomeric and polymeric urea derivatives which are non-soluble in water. Due to the rapid hydrolysis of HDI Trimer, a transport of the substance between environmental compartments is unlikely. Consequently, a calculation of the distribution between the environmental compartments according to the Mackay fugacity model level 1 or 3 is not suitable. No information is provided for the other constituents of the substance.

However it is noted that an overall conclusion on environmental distribution depends on the conclusion of the PBT/vPvB assessment (see also Section 8.1.4 of this report).

4.2.4 Summary and discussion of environmental distribution

HDI Trimer hydrolyses rapidly in the presence of water yielding a complex mixture of oligomeric and polymeric urea derivatives which are non-soluble in water. Due to the rapid hydrolysis of HDI Trimer, a transport of the substance between environmental compartments is unlikely. Consequently, a calculation of the distribution between the environmental compartments according to the Mackay fugacity model level 1 or 3 is not suitable.

4.3 Bioaccumulation

4.3.1 Aquatic bioaccumulation

The direct and indirect exposure of the aquatic compartment to the main component HDI Trimer (Isocyanurat, n=3) is unlikely because Desmodur N 3300 hydrolysis completely in water within 3-7.7 hours. Therefore the BCF-values were calculated. Bioconcentration factors (BCF) of 3.16 and 367.7 L/kg for the main component HDI Trimer (Isocyanurat, n=3) of Desmodur N 3300 and Desmodur N 3600 and its corresponding triamine were obtained (Currenta, 2009a). Even the corresponding triamine of HDI Trimer (Isocyanurat, n=3) with a bioconcentration factor of 367.7 does not have high bioaccumulation potential (Currenta, 2009b). Only minor amounts (ca. 4%) of the hydrolysed substance are soluble in water indicating that bioaccumulation is not expected.

Table 14: Studies on adsorption/desorption

Method	Results	Remarks	Reference
none, estimated by calculation Details on estimation of bioconcentration: Basis for calculation of BCF - Estimation software: BCF Program v2.17 - Result based on calculated log Kow of: 9.81(Calculation by KOWWIN v1.67 © 2000 U.S. EPA Calculated with BCF Program v2.17, © 2000 U.S. EPA. The estimation methodology is based on the chemical structure of an organic compound and its log octanol-water partition	BCF: 3.162 (calculation)	2 (reliable with restrictions) key study estimated by calculation Test material (CAS number): 3779-63-3	Currenta, 2009a
	BCF: 367.7 (calculation)	2 (reliable with restrictions) key study estimated by calculation Test material (Chemical name): corresponding triamine of the sym. HDI trimer (HDI Isocyanurate, n=3)	Currenta, 2009b

Method	Results	Remarks	Reference
coefficient (Kow). Depending on chemical structure, structural correction factors are applied.			

No information is given for the other constituents of the substance.

4.3.2 Terrestrial bioaccumulation

No data on terrestrial bioaccumulation are available for this substance.

4.3.3 Summary and discussion of bioaccumulation

The Slovene CA evaluation of the data in relation to the B or vB criterion is presented in Section 8.1.2 of this report

4.4 Secondary poisoning

No risk assessment for secondary poisoning is provided for this substance.

The Slovene CA evaluation of the data in relation to the B or vB criterion is presented in Section 8.1.2. of this report.

5 HUMAN HEALTH HAZARD ASSESSMENT

Not evaluated.

6 HUMAN HEALTH HAZARD ASSESSMENT OF PHYSICO CHEMICAL PROPERTIES

Not evaluated.

7 ENVIRONMENTAL HAZARD ASSESSMENT

7.1 Aquatic compartment (including sediment)

7.1.1 Toxicity data

The available aquatic toxicity endpoints are calculated as water-accommodated fraction (WAF) in accordance with the guidance for determining aquatic toxicity of multi-component substances

which are only partly soluble in water in OECD (2000)[1], paragraph 3.13. The solubility of the substance was demonstrated to be loading dependent. Determining the toxicity based on WAF (cq. the toxicity for the fraction of multi-component substances that is dissolved and/or present as a stable emulsion in water) is deemed appropriate for the purpose of classification and labelling (see ECHA 2013[2], Section 4.1.4.3) and for PNEC derivation.

However, further testing is not considered necessary to conclude on PBT (vPvB) assessment.

7.1.1.1 Fish

7.1.1.1.1 Short-term toxicity to fish

Two acute toxicity studies were performed on HDI Trimer in accordance with the EU Method C.1 and under GLP. Considering the variable composition of the test substance, a Water Accommodated Fraction procedure was used (100 mg of the test substance was added to 1L of water). Fish (species: *Danio rerio*) were exposed to the WAF under static conditions (Bayer AG 2000a, Bayer AG 2001c). The endpoint is lethal loading rate. In both studies, the 96 -h LL0 was found to be higher than 100 mg/L (nominal concentration).

Disregarded study: For fish (*Danio rerio)* a LC_{50} of 8.9 mg/L (geom. mean.) after 96 h was obtained. The study was conducted according to the German standard method “UBA-Verfahrensvorschlag: Letale Wirkung beim Zebrabärbling (*Brachydanio rerio*), May 1984” (Bayer AG, 1988). This study is not regarded as being reliable. Even if the validity criteria are fulfilled according to the validity criteria of 1988 the study design does not meet the criteria of today standard methods. The stirring period of 60 seconds was regarded as too short for a complete hydrolysis of HDI Trimer.

The results of studies are summarised in the following table:

Table 15 : Overview of short-term effects on fish

Method	Results	Remarks	Reference
Brachydanio rerio (new name: Danio rerio) freshwater static OECD Guideline 203 (Fish, Acute Toxicity Test)	LL0 (96 h): ≥ 100 mg/L test mat. (nominal) based on: mortality	2 (reliable with restrictions) key study experimental result Test material (EC name): HDI oligomers, isocyanurate	Bayer AG (2001c)
Brachydanio rerio (new name: Danio rerio) freshwater	LL0 (96 h): ≥ 100 mg/L test mat. (nominal) based on: mortality	2 (reliable with restrictions) key study experimental result	Bayer AG (2000a)

[1] OECD (2000). Guidance document on aquatic toxicity testing of difficult substances and mixtures. OECD Series on Testing and Assessment Number 23, ENV/JM/MONO(2000)6..

[2] ECHA (2013). Guidance on the Application of the CLP criteria – Guidance to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures. Version 4.0, November 2013

Method	Results	Remarks	Reference
static OECD Guideline 203 (Fish, Acute Toxicity Test)		Test material (EC name): HDI oligomers, isocyanurate	

7.1.1.1.2 Long-term toxicity to fish

No data are available for this substance. The eMSCA does not see the need to request further information to conclude on PBT(vPvB) assessment. However, further testing is not considered necessary to conclude on PBT (vPvB) assessment.

7.1.1.2 Aquatic invertebrates

7.1.1.2.1 Short-term toxicity to aquatic invertebrates

The 48–hr acute toxicity of HDI Trimer to Daphnids (Daphnia magna) was studied under static conditions. The experiment was carried out in accordance with the EU Method C.2. The medium composition was compliant with the Guideline requirement. Considering the variable composition of the substance, a WAF procedure was used (ratio: 100 mg of the test item was added to 1 L of water). The results are expressed in terms of effective loadings (EL). Immobilization was observed daily. Mobility was recorded daily in control and treated groups. No immobiles were observed after 24h in any groups. After 48 hours, 4 of 20 daphnids were immobile (20%) in the 50 mg/L group and 7 daphnids in the 100 mg/L group (35%). In the test report, no EL_{50} was given, but an EL_{100} > 100mg/L. The EL_{50} was later (2010) extrapolated and calculated using TOXRAT (EL_{50}=127 mg/L). (Bayer AG, 2001d).

Disregarded study: For Daphnia magna STRAUS an EC_0 of ≥ 100 mg/L was obtained after 24 hours. The study was conducted according to the German standard method „UBA-Verfahrensvorschlag: Bestimmung der Schwimmunfähigkeit beim Wasserfloh (Daphnia magna), EC_0/EC_{50}/EC_{100}, 24 Std. statisches System“. The result relates to the nominal concentration. This study is not regarded as being reliable. Even if the validity criteria are fulfilled according to the validity criteria of 1989 the study design does not meet the criteria of today standard methods. According to international standard methods an exposure time of 48 hours follows the state-of-the-art of science (Bayer AG, 1989).

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

The acute toxicity to Daphnia magna STRAUS expressed in terms of effective loadings (EL_0, 48 h) lead to an EL_0 of ≥ 100 mg/L and 25 mg/L for HDI Trimer, respectively. After 48 hours the EL_{50} for HDI Trimer was 127 mg/L. The studies were conducted according to Directive 92/69/EEC, C2 (Bayer AG, 2001). The results relate to the nominal concentration.

The results of the study are summarised in the following table:

Table 16: Overview of short-term effects on aquatic invertebrates

Method	Results	Remarks	Reference

Method	Results	Remarks	Reference
Daphnia magna freshwater static OECD Guideline 202 (*Daphnia* sp. Acute Immobilisation Test)	EL_0 (48 h): 25 mg/L test mat. (nominal) based on: mobility EL_{20} (48 h): 50 mg/L test mat. (nominal) based on: mobility EL_{35} (48 h): 100 mg/L test mat. (nominal) based on: mobility EL_{50} (48 h): 127 mg/L test mat. (nominal) based on: mobility EL_0 (24 h): ≥ 100 mg/L test mat. (nominal) based on: mobility EL_{100} (24 h): > 100 mg/L test mat. (nominal) based on: mobility	2 (reliable with restrictions) key study experimental result Test material (EC name): HDI oligomers, isocyanurate	Bayer AG (2001d)
Daphnia magna freshwater static OECD Guideline 202 (Daphnia sp. Acute Immobilisation Test)	EL_0 (24 h): ≥ 100 mg/L test mat. (nominal) based on: mobility EL_0 (48 h): ≥ 100 mg/L test mat. (nominal) based on: mobility	2 (reliable with restrictions) key study experimental result Test material (EC name): HDI oligomers, isocyanurate	Bayer AG (2000b)

7.1.1.2.2 Long-term toxicity to aquatic invertebrates

No data are available for this substance. The eMSCA does not see the need to request further information to conclude on PBT(vPvB) assessment.

7.1.1.3 Algae and aquatic plants

The toxicity of HDI Trimer to algae (*Desmodesmus subspicatus*) was assessed performing a study according to the German standard: DIN 38 412, Part 9 (1989) "Zellvermehrungshemmtest: *Scenedesmus subspicatus* CHODAT (Grünalge)", which is in most parts equivalent to the OECD TG 201 (Bayer AG, 1989). The 72-h EC_{10} was 370 mg/l. The EC_{50} was > 1000 mg/L.

In a supporting study the toxicity of HDI Trimer to algae (*Desmodesmus subspicatus* CHODAT) was assessed performing a study according to the Directive 92/69/EEC, C.3: Algal inhibition test, which is in most parts equivalent to the OECD TG 201 (Bayer AG, 2001). No inhibition of the algal population as reduction in growth rate was observed after 72 h at a test concentration of 100 mg/L. The results are expressed in terms of nominal concentrations.

The results of the study are summarised in the following table:

Table 17: Overview of effects on algae and aquatic plants

Method	Results	Remarks	Reference
Selenastrum capricornutum (new name: Pseudokirchnerella subcapitata) (algae) freshwater static German standard: DIN 38 412, Part 9 (1989) "Zellvermehrungshemmtest: *Scenedesmus subspicatus* CHODAT (Grünalge)" Equivalent or similar to: OECD Guideline 201 (Alga, Growth Inhibition Test)	EC_{50} (72 h): > 1000 mg/L test mat. (nominal) based on: biomass (geom. mean) EC_{50} (72 h): > 1000 mg/L test mat. (nominal) based on: growth rate (geom. mean) EC_{10} (72 h): 110 mg/L test mat. (nominal) based on: biomass (geom. mean) EC_{10} (72 h): 370 mg/L test mat. (nominal) based on: growth rate (geom. mean)	2 (reliable with restrictions) key study experimental result Test material (EC name): HDI oligomers, isocyanurate	Bayer AG (1989)
Selenastrum capricornutum (new name: Pseudokirchnerella subcapitata) (algae) freshwater static OECD Guideline 201 (Alga, Growth Inhibition Test)	EC_0 (72 h): 100 mg/L test mat. (nominal) based on: growth rate EC_0 (72 h): 100 mg/L test mat. (nominal) based on: biomass	2 (reliable with restrictions) key study experimental result Test material (EC name): HDI oligomers, isocyanurate	Bayer AG (2001e)

7.1.1.4 Sediment organisms

No data on toxicity to sediment organisms are available for this substance. The eMSCA does not see the need to request further information to conclude on PBT(vPvB) assessment.

7.1.1.5 Other aquatic organisms

No data on the effect of the substance on other aquatic organisms are available.

7.1.2 Calculation of Predicted No Effect Concentration (PNEC)

7.1.2.1 PNEC water

The derivation of the PNEC water is reported below.

Table 18: PNEC aquatic

	Value	Assessment factor	Remarks/Justification
PNEC aqua – freshwater (mg/L)	0.127	1000	Short-term toxicity results are available from three species representing three trophic levels (fish, Daphnia and algae). An assessment factor of 1000 is applied using the lowest available effect concentration (EL_{50} mg/L: 127 mg/L) for Daphnia.
PNEC aqua - marine water (mg/L)	0.0127	10000	For the marine compartment no tests are available. For PNEC derivation, short-term toxicity results from three species representing three trophic levels (fish, aphnia and algae) for the freshwater compartment are taken into account. An assessment factor of 10000 is applied using the lowest available effect concentration, which was obtained for Daphnia.
PNEC aqua – intermittent releases (mg/L)	1.27	100	Short-term toxicity results are available from three species representing three trophic levels (fish, Daphnia and algae). The default assessment factor of 100 is applied using the lowest available effect concentration, which was obtained for Daphnia.

7.1.2.2 PNEC sediment

The derivation of the PNEC sediment is reported below.

Table 19: PNEC sediment

	Value	Assessment factor	Remarks/Justification
PNEC sediment (mg/kg d.w.)	266700	See equations below	extrapolation method The PNEC sediment was derived on the basis of aquatic toxicity data applying the Equilibrium Partitioning Theory (EPT) as no data is available covering sediment organisms. To derive the PNECsediment on the basis of EPT, the Koc, the Henry's Law Constant (HLC) as well as the PNECaqua are crucial. Following values have been used for the main component of HDI Trimer (Isocyanurat, n=3): Koc= 2.1×10^{7} (calc. acc. to EPIWIN) HLC= 1.31×10^{-12} Pa·m³/mole (calc. acc. to EPIWIN) PNECaqua= 0.127 mg/L Due to dissociating properties, the adsorption/desorption behaviour, expressed as Koc, is characterized by a range rather than a single value. Describing processes in the sediment, lowervalues are linked to a lower sorption potential, what in turn EC No: 931-274-8 HDI Oligomers, isocyanurate 2011-05-19 Endpoint Summary information 9 means higher concentrations in the pore water. As effects towards sediment organisms are assumed to be caused by the fraction dissolved in the pore water, lower Koc values are synonymous with a higher exposure of sediment organisms and were thus used to calculate the PNECsediment. The PNEC sediment concerning the wet weight is 57978 mg/kg Conversion factor for sediment concentrations (wwt to dwt): 4.6

7.2 Terrestrial compartment

7.2.1 Toxicity test results

Not relevant.

7.2.1.1 Toxicity to soil macro organisms

Toxicity to soil macro-organisms except arthropods

No data on toxicity to soil macro organisms are available for this substance. The eMSCA does not see the need to request further information to conclude on PBT(vPvB) assessment.

Toxicity to terrestrial arthropods

No data on toxicity to terrestrial arthropds are available for this substance. The eMSCA does not see the need to request further information to conclude on PBT(vPvB) assessment.

7.2.1.2 Toxicity to terrestrial plants

No data on toxicity to terrestrial plants are available for this substance. The eMSCA does not see the need to request further information to conclude on PBT(vPvB) assessment.

7.2.1.3 Toxicity to soil micro-organisms

No data on toxicity to soil macro organisms are available for this substance. The eMSCA does not see the need to request further information to conclude on PBT(vPvB) assessment.

7.2.1.4 Toxicity to other terrestrial organisms

No data on the toxicity of the substance to other terrestrial organisms are available.

7.2.2 Calculation of Predicted No Effect Concentration (PNEC_soil)

The derivation of the PNEC soil is reported below.

Table 20: PNEC soil

	Value	Assessment factor	Remarks/Justification
PNEC soil (mg/kg.w.)	53182	See equations below	The PNEC sediment was derived on the basis of aquatic toxicity data applying the Equilibrium Partitioning Theory (EPT) as no data is available covering soil organisms. To derive the PNECsoil on the basis of EPT, the Koc, the Henry's Law Constant (HLC) as well as the PNECaqua are crucial. Following values have been used for the main component of HDI Trimer (Isocyanurat, n=3): Koc= 2.1×10^{7} (calc. acc. to EPIWIN) HLC= 1.31×10^{-12} Pa·m³/mole (calc. acc. to EPIWIN) PNECaqua= 0.127 mg/L Due to dissociating properties, the adsorption/desorption behaviour, expressed as Koc, is characterized by a range rather than a single value. Describing processes in the soil, lower values are linked to a lower sorption potential, what in turn means higher concentrations in the pore water. As effects towards sediment organisms are assumed to be caused by the fraction dissolved in the pore water, lower Koc values are synonymous with a higher exposure of sediment organisms and were thus used to calculate the PNECsoil. The PNEC soil concerning the wet weight is 47064 mg/kg Conversion factor for soil concentrations (wwt to dwt): 1.13

7.3 Atmospheric compartment

No data on exposure of the atmospheric compartment are available for this substance.

7.4 Endocrine disrupting properties

Not evaluated.

7.5 Microbiological activity in sewage treatment systems

7.5.1 Toxicity to aquatic micro-organisms

An overview of study results is included in the Chemical Safety Report of the registrants.

7.5.2 PNEC for sewage treatment plant

For HDI Trimer a test with activated sludge with a duration time of 3 hours was performed using a method comparable to OECD 209. A 3h-EC50 value of 3828 mg/L was obtained (Bayer 1989).

Table 21: PNEC sewage treatment plant

	Value	Assessment factor	Remarks/Justification
PNEC $_{STP}$ (mg/L)	38.28	100	There is only one reliable toxicity test result to microorganisms available. In a respiration inhibition test conducted with activated sludge a 3 h-EC_{50} of 3828 mg/L obtained. This result is used for PNEC STP derivation. An assessment factor of 100 applied.

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

The CA evaluation of the data in relation to the B or vB criterion is presented in Section 8.1.2.

Further testing on secondary poisoning is not considered necessary to conclude on PBT (vPvB) assessment.

7.6.1 Toxicity to birds

No data on toxicity to birds are available for this substance. The eMSCA does not see the need to request further information to conclude on PBT(vPvB) assessment.

7.6.2 Toxicity to mammals

Not evaluated.

7.6.3 Calculation of PNEC oral (secondary poisoning)

As the main constituent of HDI trimer (HDI Isocyanurate, n=3) has only a moderate bioaccumulation potential, no risk characterisation for secondary poisoning is carried out.

7.7 Conclusion on the environmental classification and labelling

Based on the available environmental fate and ecotoxicological data for Daphnids, fish and algae, this substance has acute aquatic toxicity >100 mg/L in the most sensitive species, it is not readily biodegradable, and has a log Pow ranging from 6.62 to 42.91. The main constituents are rapidly hydrolysed. The isocyanate groups react with water yielding an amino function as an intermediate.

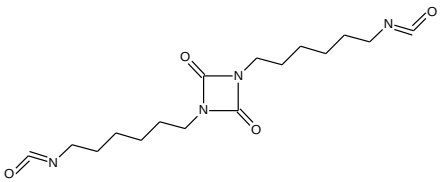
The amine groups rapidly react further with another isocyanate groups yielding the ureas. No studies are available for the ureas. Due to the inertness, low water solubility and high molecular weight, polymeric urea is considered to be not bioavailable and therefore non toxic.

8 PBT AND vPvB ASSESSMENT

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

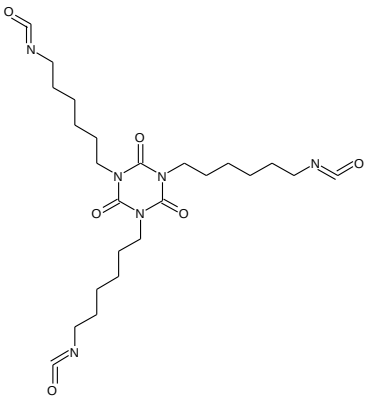
According to the guidance for the assessment of multi constituent substances in Section R.11.4.2.2 of the draft update of the ECHA PBT guidance document (ECHA, 2014) a PBT assessment has to be performed on the representative structures in an UVCB substance. The representative constituent structures were drawn with ACD/Chemsketch freeware. This enabled to search information on the exact structure via the internet. Key information on the constituent structures for the substance under evaluation is summarized below.

Constituent structure 1 (HDI dimer)



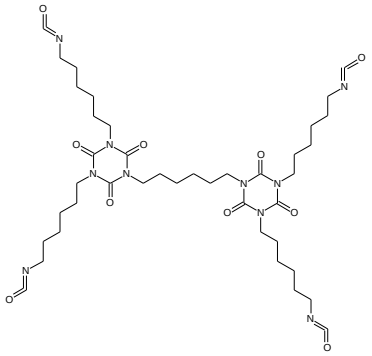
Molecular formula: $C_{16}H_{24}N_4O_4$
Molecular weight: 336.39
SMILES notation:
O=C1N(CCCCCC\N=C=O)C(=O)N1CCCCCC\N=C=O
IUPAC name: 1,3-bis(6-isocyanatohexyl)-1,3-diazetidine-2,4-dione
EINECS no: 245-699-5
CAS no: 23501-81-7
PubChem code: CID 90132
Log Kow 6.62 (BCFWIN version 1.68)
Log Koc 4.28 (KOCWIN v 2.00)
BCF 457 L/kg wet-wt (BCFBAF v 3.01)

Constituent structure 2 (HDI trimer)



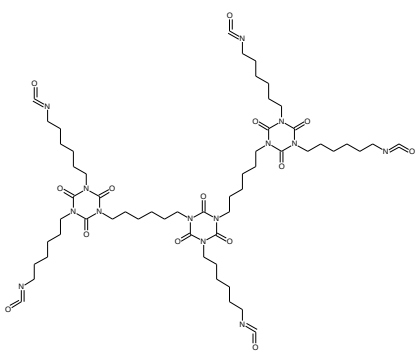
Molecular formula: $C_{24}H_{36}N_6O_6$
Molecular weight: 504.58
SMILES notation:
C(CCCN1C(=O)N(C(=O)N(C1=O)CCCCCCN=C=O)CCCCCCN=C=O)CCN=C=O
IUPAC name: -
EINECS no: 223-242-0
CAS no: 3779-63-3
Log Kow 9.81 (BCFWIN version 1.68)
Log Koc 6.27 (KOCWIN v 2.00)
BCF 140.8 L/kg wet-wt (BCFBAF v 3.01)

Constituent structure 3



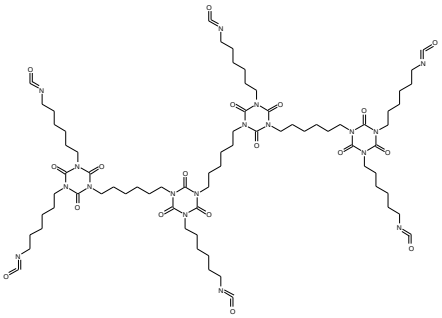
Molecular formula: $C_{40}H_{60}N_{10}O_{10}$
Molecular weight: 840.97
SMILES notation:
O=C2N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C(=O)N2CCCCCCN1C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C1=O
IUPAC name: -
EC no: -
CAS no: -
Log Kow 16.43 (BCFWIN version 1.68)
Log Koc 9.86 (KOCWIN v 2.00)
BCF 3.16 L/kg wet-wt (BCFBAF v 3.01)

Constituent structure 4



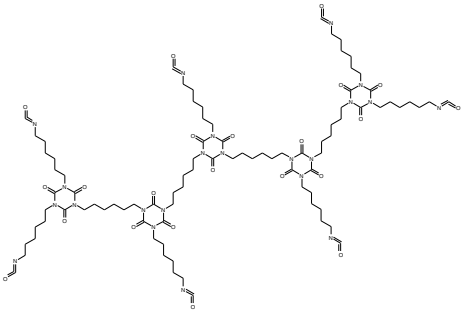
Molecular formula: $C_{56}H_{84}N_{14}O_{14}$
Molecular weight: 1177.35
SMILES notation:
O=C3N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C(=O)N3CCCCCCN2C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCCN1C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C1=O)C2=O
IUPAC name:-
EC no: -
CAS no: -
Log Kow 23.05 (BCFWIN version 1.68)
Lot Koc 13.46 (KOCWIN v 2.00)
BCF 3.16 L/kg wet-wt (BCFBAF v 3.01)

Constituent structure 5



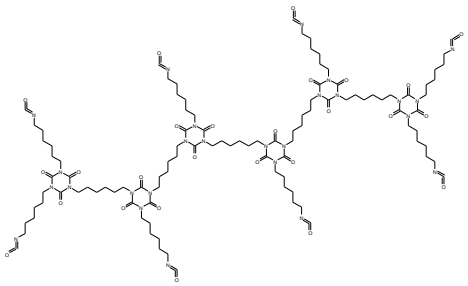
Molecular formula: $C_{72}H_{108}N_{18}O_{18}$
Molecular weight: 1513.74
SMILES notation:
O=C4N(CCCCCC\N=C=O)C(=O)N(CCCCCCN3C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCCN2C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCCN1C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C1=O)C2=O)C3=O)C(=O)N4CCCCCC\N=C=O
IUPAC name: -
EC no: -
CAS no: -
Log Kow 29.67 (BCFWIN version 1.68)
Log Koc 17.05 (KOCWIN v 2.00)
BCF 3.16 L/kg wet-wt (BCFBAF v 3.01)

Constituent structure 6



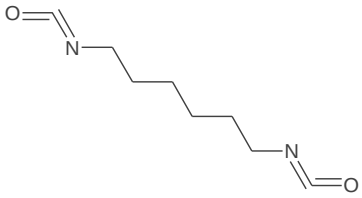
Molecular formula: $C_{88}H_{132}N_{22}O_{22}$
Molecular weight: 1850.12
SMILES notation:
O=C5N(CCCCCCN1C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C1=O)C(=O)N(CCCCCC\N=C=O)C(=O)N5CCCCCCN4C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCCN3C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCCN2C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C2=O)C3=O)C4=O
IUPAC name: -
EC no: -
CAS no: -
Log Kow 36.29 (BCFWIN version 1.68)
Log Koc 20.65 (KOCWIN v 2.00)
BCF 3.16 L/kg wet-wt (BCFBAF v 3.01)

Constituent structure 7



Molecular formula: $C_{104}H_{156}N_{26}O_{26}$
Molecular weight: 2186.51
SMILES notation:
O=C6N(CCCCCCN2C(=O)N(CCCCCCN1C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C1=O)C(=O)N(CCCCCC\N=C=O)C2=O)C(=O)N(CCCCCC\N=C=O)C(=O)N6CCCCCCN5C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCCN4C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCCN3C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C3=O)C4=O)C5=O
IUPAC name: -
EC no: -
CAS no: -
Log Kow 42.91 (BCFWIN version 1.68)
Log Koc 24.25 (KOCWIN v 2.00)
BCF 3.16 L/kg wet-wt (BCFBAF v 3.01)

Constituent structure 8 (HDI)



Molecular formula: $C_8H_{12}N_2O_2$
Molecular weight: 168.19
SMILES notation:
O=C=N\CCCCCC\N=C=O
IUPAC name: 1,6-hexamethylene diisocyanate
EC no: 212-485-8
CAS no: 822-06-0
Log Kow 42.91 (BCFWIN version 1.68)
Log Koc 24.25 (KOCWIN v 2.00)
BCF 3.16 L/kg wet-wt (BCFBAF v 3.01)

Where data on the representative structure were lacking, read-across from data on similar structures was attempted following an analogue approach as defined in OECD guidance on grouping of chemicals (2007).

8.1.1 Persistence assessment

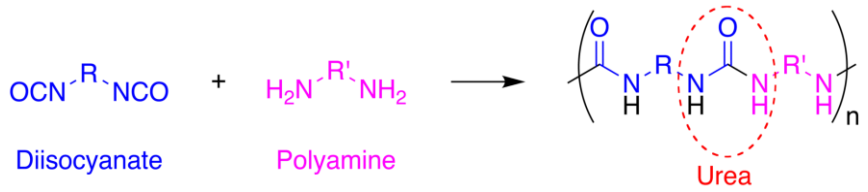
The main constituent of the substance under evaluation HDI trimer was not readily biodegradable. In the Chemical Safety Report the substance is identified as being potentially persistent, but only test results for HDI trimer are considered. According to the guidance for the assessment of multi constituent substances (R.11.4.2.2 Assessment of multi constituent substances) in the draft update of the ECHA PBT guidance document persistence assessment has to be performed on the representative structures in this UVCB substance that are present at ≥ 0.1% w/w.

In general, isocyanates are known to rapidly react with water to form carbon dioxide:

$$RNCO + H_2O \rightarrow RNH_2 + CO_2$$

In the presence of isocyanates amines will react further to form a complex mixture of polymeric ureas. Since the primary amino group is a much stronger nucleophile than water, the amino group will immediately react with another isocyanate group to yield an urea group. The rate constants for such a nucleophile addition reaction depend on several factors and reaction conditions:
• ± I and M- effects at the electrophile (here the –N=C=O group with its aliphatic chain)
• steric impact of the adjacent groups (here the $–CH_2$)
• the nucleophile power of the attacking nucleophile which correlates to some
extent to its basicity (this however is defined via Brönsted)
• the solvent, temperature etc…of the reaction medium
Applied to the reaction of HDI oligomers, isocyanurate with water, it clearly explains the resulting general reaction scheme:

$$R\text{-}N{=}C{=}O + H_2O \rightarrow [R\text{-}NH\text{-}COOH] \rightarrow R\text{-}NH_2 + CO_2$$



The reaction, i.e. the formation of urea from the isocyanate is exothermic with 47 kcal per mole of water reacted (Herrington 1998).

HDI oligomers, isocyanurate rapidly reacts with water with the formation of hard, crusty, insoluble and inert polyurea. This is due to the fact that as soon as the first primary amino group is generated from the first molecule HDI oligomers, isocyanurate and water, this primary amino group immediately reacts with another isocyanate group to form a urea group. This urea group has two secondary amido groups, which also can react with an isocyanate group with the formation of other, crosslinking groups. And, due to continued generation of primary amines from the isocyanate-water reaction, which is accompanied by CO_2 -formation, the build-up of a polymeric, highly cross-linked, insoluble polyurea is the final reaction product. Since the resulting initial hydrolysis product from the HDI oligomers, isocyanurate / water reaction is the primary amine with its much higher reactivity towards isocyanates, than that of water, the amino-isocyanate reaction becomes faster than the initial water-isocyanate reaction.

Based on read-accross, data from TDI (toluene diisocyanate) can be used to predict the behavior of HDI oligomers, isocyanurate. With reference to a number of experimental hydrolysis studies the behaviour of TDI is described in the industry risk assessment by D. Pemberton and B. Tury: “However, TDI is hydrophobic and of low solubility in water, and such fast reaction is only achieved by vigorous agitation of the mixture. Under conditions typical of environmental contact, with relatively poor dispersion of the denser diisocyanate, the reaction is heterogeneous (at the interface) and is slower. The reaction leads to the formation of a solid crust of polyureas encasing unreacted material. This crust restricts ingress of water and egress of amine, and thereby slows hydrolysis even further an enhances the amine reaction with isocyanate, leading to an even higher yield of polyureas.

These effects were clearly seen in studies of the heterogeneous reaction of TDI with water (Kitano et al., 1989, 19914; Yakabe et al., 1994a, Yakabe et al., 1999). The rate of reaction of 2,4-TDI was markedly dependent on stirring energy with half-lives at 27°C ranging from 30 sec with very efficient dispersion, to about an hour with moderate dispersion, and several days (dependent on surface area) when unstirred.”

Since both reactions, the hydrolysis of isocyanate (e.g. HDI oligomers, isocyanurate) and the formation of polyurea are exothermic, the resulting reaction heat cannot be released out of the encapsulating shell of polyurea and thus will further accelerate the hydrolysis of HDI oligomers, isocyanurate and the fast build-up of polyurea. Since the latter is being generated from the inside, the whole formation process can best be characterized with “self-annealing”.

Yakabe et al (1999) and Sendijarevic et al. (2004) have carried out two key studies on the hydrolysis of TDI and its subsequent formation of polyurea:

“The solid polymer obtained from stirring 2,4-TDI in water was insoluble in all solvents tested except DMF containing 10 mM LiCl, which dissolved part of it. Gel permeation chromatography of the DMF-LiCl-soluble portion of the polyurea showed that the molecular weight increased with reaction time over a period of several days, long after free TDI had reacted. The weight average molecular weight and number average molecular weight, determined by low angle laser light scattering coupled to the GPC, were approximately 5.6×10^3 and 1.2×10^3 respectively”.

As Yakabe et al (1999) have shown in their studies for TDI, primary amines can only be detected in the hydrolysis of polyfunctional isocyanates, at very low loadings of isocyanate (less than 10 mg/L or lower), if efficient stirring of isocyanate into water is applied! This observation clearly corresponds with the findings as mentioned above: Only in that case, where the formed intermediate TDA has no further free isocyanate left to react with, can TDA be detected at very low concentrations of ~ 4 mg/L. Since TDI has a very poor water solubility, and high stirring was applied all TDI was stirred away from the intermediately formed TDA.

These circumstances however do not apply to environmental conditions.

Even if higher TDI loadings (well above 10 mg/L and up to 10 000 mg/L) were applied without stirring, the maximum TDA concentration detected were always at this very low level of ~ 4 mg/L . With high stirring and high TDI loadings, a max. concentration of TDA detected was 28 mg/L, which correlates to a yield of < 1% of the high TDI Loading.

As HDI oligomers, isocyanurate have a similar isocyanate functionality, the results from TDI can be transferred to HDI oligomers, isocyanurate.

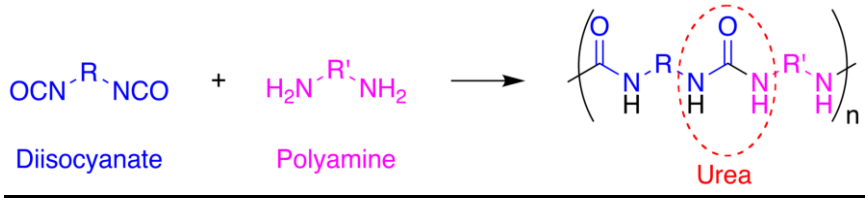
Constituent structure 1 (HDI dimer)

There are no experimental data for the degradation of hexamethylene diisocyanate dimer. Based on the lack of biodegration of the analogue structure HDI trimer in ready biodegradabilty tests, it can be expected that screening criteria for persistence would be met in ready biodegradabilty tests.

However, isocyanates such as hexamethylene diisocyanate dimer are reactive and rapidly react with water to form carbon dioxide:

$$RNCO + H_2O \rightarrow RNH_2 + CO_2$$

In the presence of isocyanides amines will react further to form a complex mixture of polymeric ureas. As explained above primary amines are not likely to be present at significant levels under environmental conditions.

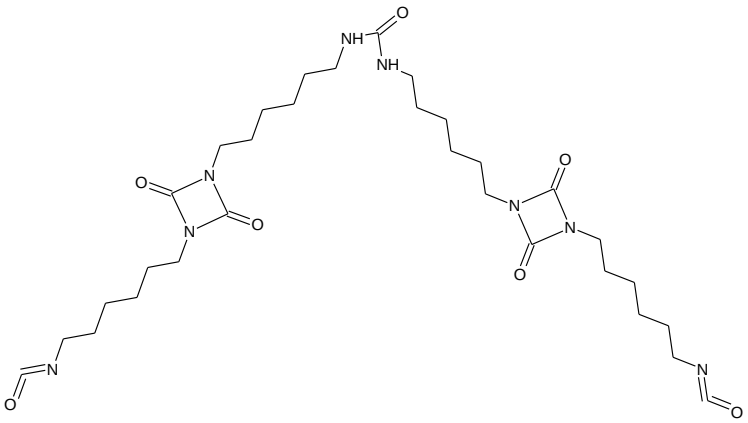


The reaction, i.e. the formation of urea from the isocyanate is exothermic with 47 kcal per mole of water reacted (Herrington 1998).

No experimental biodegradation studies are available for oligomeric and polymeric ureas. For this reason, QSAR estimations were performed using the simplest representatives of an urea formed from HDI dimer where one amino group, formed by hydrolysis of an isocyanate group, reacts with an isocyanate group from another molecule HDI dimer or from a molecule HDI trimer, respectively. It should be noted that given the low fraction HDI dimer in HDI oligomers, isocyanate the reaction with a molecule of the main constituent HDI trimer is likely to dominate.

The reaction with an isocyanate group from another molecule HDI dimer yields the following structure:

SMILES code:
O=C2N(CCCCCCC\N=C=O)C(=O)N2CCCCCCNC(=O)NCCCCCCN1C(=O)N(CCCCCC\N=C=O)C1=O



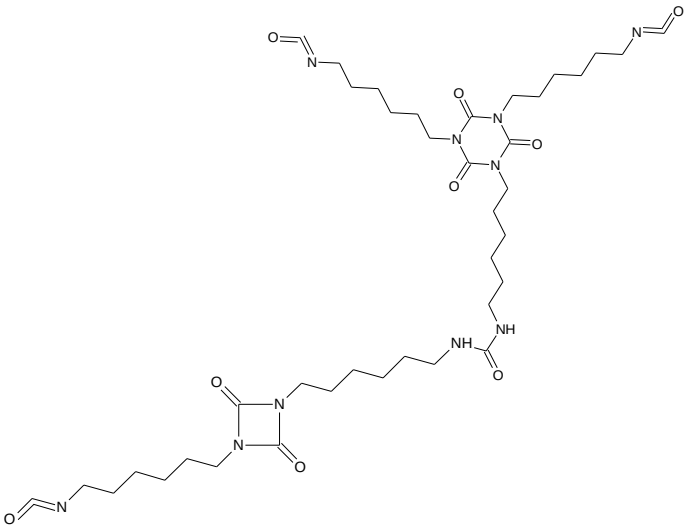
Molecular formula: $C_{32}H_{52}N_8O_7$
Molecular weight: 660.80

QSAR estimations were performed using the Biowin models 2, 3, 5 and 6 which are recommended in REACH guidance document R11 (2014). These models are available in the EPIWIN package version 4.1.1. The following results were obtained:

Biowin 2 (Non-Linear Model Prediction):	Does not biodegrade fast
Biowin 3 (Ultimate Biodegradation Timeframe):	Recalcitrant
Biowin5 (MITI Linear Model Prediction):	Not ready degradable
Biowin 6 (MITI Non-Linear Model Prediction):	Not ready degradable
Ready biodegradability prediction:	No

The reaction with an isocyanate group from a molecule HDI trimer yields the following structure:

Smiles code:
O=C2N(CCCCCC\N=C=O)C(=O)N2CCCCCCNC(=O)NCCCCCCN1C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C1=O



Molecular formula: $C_{39}H_{62}N_{10}O_9$
Molecular weight: 814.97

QSAR estimations were performed using the Biowin models 2, 3, 5 and 6 which are recommended in REACH guidance document R11 (2014). These models are available in the EPIWIN package version 4.1.1. The following results were obtained:

Biowin 2 (Non-Linear Model Prediction):	Does not biodegrade fast
Biowin 3 (Ultimate Biodegradation Timeframe):	Recalcitrant
Biowin5 (MITI Linear Model Prediction):	Not ready degradable
Biowin 6 (MITI Non-Linear Model Prediction):	Not ready degradable
Ready biodegradability prediction:	No

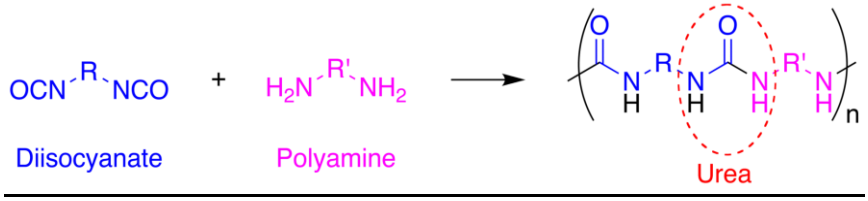
Conclusion is that both ureas are not biodegradable. In the presence of water further reaction to form persistent polyureas is however to be expected (see below).

Constituent structure 2
Within 28 days, a degradation of 1 % was determined for HDI Trimer (Desmodur N 3600) in a 'Closed Bottle Test' (Bayer AG, 2001). HDI Trimer is regarded as "not readily biodegradable". In a 'Modified Manometric Respirometry Test' with adapted inoculum no degradation of HDI Trimer (Desmodur N 3600) could be obtained within 28 days (Bayer AG, 2001). It can be concluded that screening criteria for persistence are met.

Isocyanates such as HDI trimer are reactive and rapidly react with water to form carbon dioxide:

$R\text{-}N{=}C{=}O + H_2O \rightarrow [R\text{-}NH\text{-}COOH] \rightarrow R\text{-}NH_2 + CO_2$

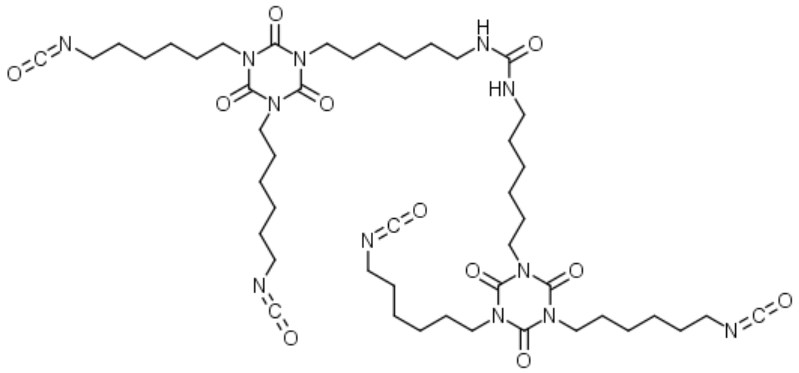
In the presence of isocyanides amines will react further to form a complex mixture of polymeric ureas according to the following general reaction for forming a polyurea chain.



No experimental biodegradation studies are available for oligomeric and polymeric ureas. For this reason, QSAR estimations were performed using the simplest representative of an urea formed from HDI oligomers, isocyanurate where one amino group, formed by hydrolysis of an isocyanate group, reacts with an isocyanate group from another molecule HDI oligomers, isocyanurate, yielding the substance as shown below:

Smiles code:
O=C1N(CCCCCCNC(=O)NCCCCCCN2C(=O)N(CCCCCCN=C(=O))C(=O)N(CCCCCC
N=C(=O))C2(=O))C(=O)N(CCCCCCN=C(=O))C(=O)N1CCCCCCN=C=O

Structural formula:



Molecular formula: $C_{47}H_{74}N_{12}O_{11}$
Molecular weight: 983.19

QSAR estimations were performed using the Biowin models 2, 3, 5 and 6 which are recommended in REACH guidance document R11 (2014). These models are available in the EPIWIN package version 4.1.1. The following results were obtained:

Biowin 2 (Non-Linear Model Prediction):	Does not biodegrade fast
Biowin 3 (Ultimate Biodegradation Timeframe):	Recalcitrant
Biowin5 (MITI Linear Model Prediction):	Not ready degradable
Biowin 6 (MITI Non-Linear Model Prediction):	Not ready degradable
Ready biodegradability prediction:	No

Conclusion is that the monourea is not biodegradable. In the presence of water further hydrolysis to form persistent polyureas is however to be expected.

The highly exothermic reactions of both, the hydrolysis of isocyanate to amine and the nucleophile addition of amine to isocyanate result in the formation of a thermodynamically favorable urea. HDI oligomers, isocyanurate would end up in a cross-linked polymeric urea. This reaction with a high free reaction enthalpy (47 kcal per mole water). Therefore it would require a very high activation energy in order to cleave back this polymer into its original monomers. In addition, as the formation of the polyurea is accompanied by the formation and release of CO_2, the entropic term for the polyurea formation significantly contributes to the overall thermodynamic stability of the resulting polymer. These explanations are supported by the experiments of Sendijarevic et al. (2004):

“We believe that the potential environmental impact of these polyureas based on TDI and PMDI can be best understood by looking at the time when a major fraction of the aromatic amines might potentially be released. Treating the laboratory hydrolyses as pseudo-first-order reactions predicts geological time scales: 300 000 years for 50% release of TDA or 12 000 000 years for 50% release of MDA.
Alternatively, assuming zero-order kinetics, the laboratory reaction rate extrapolates to 18 000 years for 50% release of TDA and 110 000 years for 50% release of MDA. Similar geological time scales are also expected for ureas formed by HDI oligomers, isocyanurate.
In the environment, the reaction system is obviously heterogeneous, for example, with the bulk of the polyurea on the bottom of a water body and some particles of polyurea floating. It is proposed that an assumption that the surface-to-volume ratio of large quantities of polyurea is comparable to that of the laboratory samples and that they would have a similar hydrolysis rate is a conservative one. These data indicate that polyureas formed in contact with water can be expected to be essentially unreactive in the environment for millennia."

"Hydrolysis of a urea group in a polyurea does not necessarily lead to diamine, of course. When considering the cleavage of any one group, only one adjacent to the polymer end will give diamine,

all others will produce two shorter-chain polyureas. Statistically it follows that the chance of diamine being produced will increase as the reaction proceeds and the overall chain-length decreases. Similarly, the production of triamine from a cross-linked polymer of HDI oligomers, isocyanurate based urea will depend on two specific links being broken from a multiplicity of possibilities, and initial formation will be even slower."

Conclusion is that the polymeric ureas are highly likely to fulfil criteria for persistence.

Constituent structure 3, 4, 5, 6 and 7
There are no experimental data for the degradation of constituent structures 3, 4, 5, 6, and 7. Based on the lack of biodegration of the analogue structure 2 (HDI trimer) in ready biodegradabilty tests, it can be expected that screening criteria for persistence would be met in ready biodegradabilty tests. No biodegradation is predicted by QSAR estimations using the Biowin models 2, 3, 5 and 6 which are recommended in REACH guidance document R11 (2014). However, as explained before isocyanates are reactive and rapidly react with water to form carbon dioxide and the resulting primary amines will react further to form a complex mixture of polymeric ureas. As explained above these polymeric ureas are highly likely to fulfil criteria for persistence.

Constituent structure 8 (HDI)
No experimental data for the degradation of constituent structure 8 (HDI) were found. Like other diisocyanates hexamethylene diisocyanate reacts readily with water to form amines. The resulting primary amines will react further to form a complex mixture of polymeric ureas. As explained above these polymeric ureas are highly likely to fulfil criteria for persistence.

8.1.2 Bioaccumulation assessment

In the Chemical Safety Report bioaccumulation was only assessed for the main constituent. According to the guidance for the assessment of multi constituent substances in the revised PBT guidance document a bioaccumulation assessment has to be performed on the representative structures in this UVCB substance that are present at ≥0.1% w/w.

Several methodologies were used to characterize or estimate the bioconcentration factor (BCF) of the constituent structures. These methods included:

(i) searches for empirical bioconcentration, bioaccumulation and K_{OW} data
(ii) estimation of the K_{OW} for the constituent structures
(iii) estimation of the BCF using the BCFWIN model

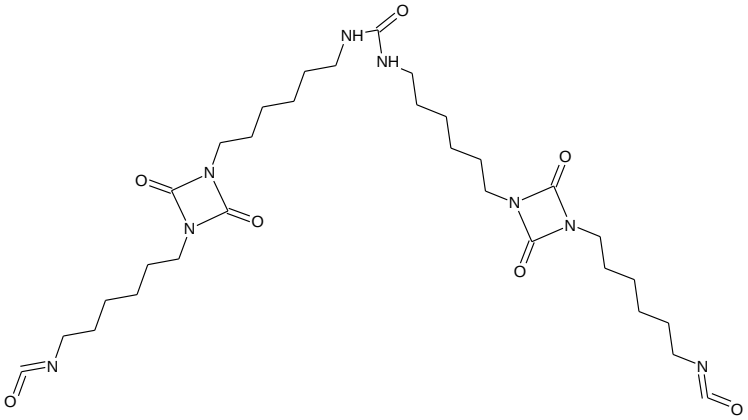
Constituent structure 1 (HDI dimer)
No empirical bioconcentration, bioaccumulation and K_{OW} data were found for constituent structure 1 (HDI dimer). The estimated log Kow is 6.62 (BCFWIN version 1.68), thus the screening criterion log Kow ≥4.5 is fulfilled. The estimated BCF is 457 L/kg wet-wt (BCFBAF v 3.01). Constituent structure 1 does not fulfil the criteria for either B or vB based on predicted BCF, but there is no supporting evidence from experimental data for analogue structures. However, because of the ready hydrolysis of HDI dimer in the environment it is neither possible nor very relevant to determine whether HDI dimer would meet the B-criterion (BCF > 2000 L/kg) in an experimental study.

The relevant transformation products resulting from hydrolysis are oligomeric and polymeric ureas. As explained above the oligomeric ureas are likely to further react to form a mixture of polymeric ureas and thus are not expected to be persistent. However, in the absence of analytical data to confirm the transient status of oligomeric ureas the bioaccumulation potential of the oligomeric ureas was also assessed. No experimental studies for bioaccumulation are available for the

corresponing oligomeric and polymeric ureas. For this reason, QSAR estimations were performed using the simplest representatives of an urea formed from HDI dimer where one amino group, formed by hydrolysis of an isocyanate group, reacts with an isocyanate group from another molecule HDI dimer or from a molecule HDI trimer, respectively.

The reaction with an isocyanate group from another molecule HDI dimer yields the following structure:

SMILES code:
O=C2N(CCCCCCC\N=C=O)C(=O)N2CCCCCCNC(=O)NCCCCCCN1C(=O)N(CCCCCC\N=C=O)C1=O



Molecular formula: $C_{32}H_{52}N_8O_7$
Molecular weight: 660.80

QSAR estimations were performed using the EPIWIN package version 4.1.1. The following results were obtained:
Log Kow: 11.53
BCF: 3.39 L/kg

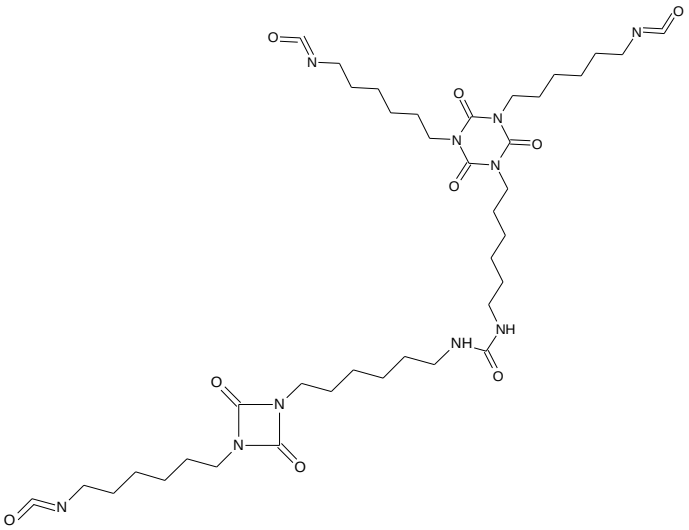
In a weight-of-evidence approach according to REACH guidance document R11 (2014), the bioaccumulation behavior of this model substance is assessed based on molecular weight and on log Kow.

According to REACH guidance document R11 (2014), “a molecular weight of 1100 g/mol is an indicator that the aquatic BCF is lower than 2000 L/kg. If the substance has a molecular weight higher than 700 g/Mol this is an indicator that the BCF is below 5000 L/kg ”.
The very first and smallest molecule obtained by reaction of 2 molecules of HDI dimer with water has a molecular weight of 661. The trigger value for B of 1100 is not reached. It should be noted that given the low fraction HDI dimer in HDI oligomers, isocyanate the reaction with another HDI molecule is not likely and formation of the corresponding urea is probably negligible. The reaction with a molecule of the main constituent HDI trimer will dominate.

A log Kow of 11.53 has been estimated using EPIWIN 4.1.1. This value exceeds the trigger value of 10. For this reason, the depicted structure is unlikely to be bioaccumulative (BCF <2000 L/kg). An estimated BCF of 3.39 L/kg supports this finding.

The reaction with an isocyanate group from a molecule HDI trimer yields the following structure:

Smiles code:
O=C2N(CCCCCC\N=C=O)C(=O)N2CCCCCCNC(=O)NCCCCCCN1C(=O)N(CCCCCC\N=C=O)C(=O)N(CCCCCC\N=C=O)C1=O



Molecular formula: $C_{39}H_{62}N_{10}O_9$
Molecular weight: 814.97

QSAR estimations were performed using the EPIWIN package version 4.1.1. The following results were obtained:
Log Kow: 14.24
BCF: 0.90 L/kg

In a weight-of-evidence approach according to REACH guidance document R11 (2014), the bioaccumulation behavior of this model substance is assessed based on molecular weight and on logKow.

According to REACH guidance document R11 (2014), “a molecular weight of 1100 g/mol is an indicator that the aquatic BCF is lower than 2000 L/kg. If the substance has a molecular weight higher than 700 g/mol this is an indicator that the BCF is below 5000 L/kg ”.
The molecule obtained by reaction of a molecule of HDI dimer with an isocyanate group from a molecule HDI trimer has a molecular weight of 815 g/mol. The trigger value for B of 1100 L/kg is not reached.

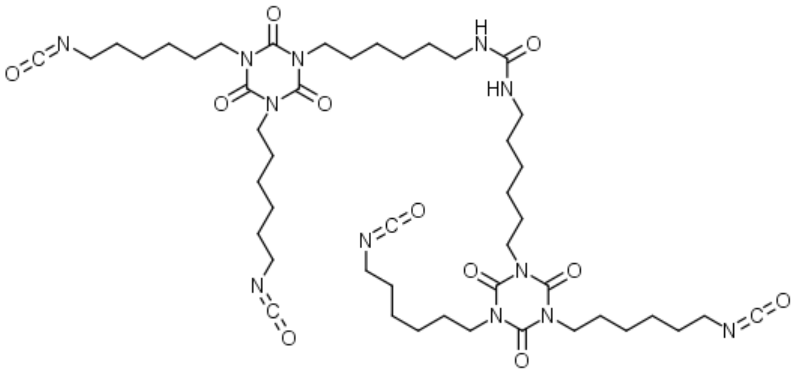
A log Kow of 14.24 has been estimated using EPIWIN 4.1.1.. This value exceeds by far the trigger value of 10. For this reason, the depicted structure is unlikely to be bioaccumulative (BCF <2000 L/kg). An estimated BCF of 0.90 L/kg supports this finding.

<u>Constituent structure 2 (HDI trimer)</u>
No empirical bioconcentration, bioaccumulation and K_{OW} data were found for constituent structure 2 (HDI trimer). The estimated log Kow is 9.81 (BCFWIN version 1.68), thus the screening criterion log Kow ≥4.5 is fulfilled. The estimated BCF is 140.8 L/kg wet-wt (BCFBAF v 3.01). Constituent structure 2 does not fulfil the criteria for either B or vB based on predicted BCF, but there is no supporting evidence from experimental data for analogue structures. However, because of the ready hydrolysis of HDI trimer in the environment it is neither possible nor very relevant to determine whether HDI trimer would meet the B-criterion (BCF > 2000 L/kg) in an experimental study.

The relevant transformation products resulting from hydrolysis are oligomeric and polymeric ureas. As explained above the oligomeric ureas are likely to further react to form a mixture of polymeric ureas and thus are not expected to be persistent. However, in the absence of analytical data to confirm the transient status of oligomeric ureas the bioaccumulation potential of the oligomeric

ureas was also assessed. No experimental studies for bioaccumulation are available for the corresponing oligomeric and polymeric ureas. For this reason, QSAR estimations were performed using the simplest representative of an urea formed from HDI oligomers, isocyanurate where one amino group, formed by hydrolysis of an isocyanate group, reacts with an isocyanate group from another molecule HDI oligomers, isocyanurate, yielding the substance shown below:

Smiles code: O=C1N(CCCCCCNC(=O)NCCCCCCN2C(=O)N(CCCCCCN=C(=O))C(=O)N(CCCCCC N=C(=O))C2(=O))C(=O)N(CCCCCCN=C(=O))C(=O)N1CCCCCCN=C=O



Molecular formula: $C_{47}H_{74}N_{12}O_{11}$
Molecular weight: 983.19

QSAR estimations were performed using the EPIWIN package version 4.1.1. The following results were obtained:
logKow: 17.4
BCF: 3.16 L/kg

In a weight-of-evidence approach according to REACH guidance document R11 (2014), the bioaccumulation behavior of this model substance is assessed based on molecular weight and on logKow.
a) According to REACH guidance document R11 (2014), “a molecular weight of 1100 g/mol is an indicator that the aquatic BCF is lower than 2000 L/kg. If the substance has a molecular weight higher than 700 g/Mol this is an indicator that the BCF is below 5000 L/kg ”.
The very first and smallest molecule obtained by reaction of 2 molecules of HDI oligomers, isocyanurate with water has a molecular weight of 983. This value indicates, that this molecule is not vB. The trigger value for B of 1100 is not reached but rather close. It should be mentioned that the model substance is only the first step in the hydrolysis of HDI oligomers, isocyanurate and in the formation of ureas. Already after the next reaction step, the oligomeric urea consists of 2 urea units and 3 HDI Trimer units (n=3, n is the number of HDI units), the molecular weight is far above 1100. Obviously, higher oligomers with n=5, 7 etc. react in the same manner but yielding much higher molecular masses.

b) According to REACH guidance document R11 (2014), “it is unlikely to have a BCF>2000 L/kg on the basis of the following information: octanol-water-partition coefficient as logKow > 10 (calculated value, preferably by several estimation programs, for substances for which LogKow can be calculated and the model is reliable)”.
As described above, a logKow of 17.4 has been estimated using EPIWIN 4.1.1.. This value exceeds by far the trigger value of 10. For this reason, the depicted structure is unlikely to be bioaccumulative (BCF <2000 L/kg). An estimated BCF of 3.16 L/kg support this finding.

<u>Constituent structures 3, 4, 5, 6 and 7</u>
No empirical bioconcentration, bioaccumulation and KOW data were found for constituent structures 3, 4, 5, 6 and 7. The estimated log Kow values range from 16.43 to 42.91 (BCFWIN

version 1.68), thus the screening criterion log Kow ≥4.5 is fulfilled. The estimated BCF ranges 11.69 L/kg wet-wt (BCFBAF v 3.01). Constituent structures 3, 4, 5, 6 and 7 do not fulfil the criteria for either B or vB based on predicted BCF, but there is no supporting evidence from experimental data for analogue structures. However, because of the ready hydrolysis of HDI oligomers in the environment it is neither possible nor very relevant to determine whether constituent structures 3, 4, 5, 6 and 7 would meet the B-criterion (BCF > 2000 L/kg) in an experimental study.

The relevant transformation products resulting from hydrolysis are oligomeric and polymeric ureas. As explained above the oligomeric ureas are likely to further react to form a mixture of polymeric ureas and thus are not expected to be persistent. However, in the absence of analytical data to confirm the transient status of oligomeric ureas the bioaccumulation potential of the oligomeric ureas was also assessed. Obviously, higher oligomers with n=5, 7 etc. react in the same manner as described above for HDI dimer and HDI trimer but yielding much higher molecular masses.

a) According to REACH guidance document R11 (2014), “a molecular weight of 1100 g/mol is an indicator that the aquatic BCF is lower than 2000 L/kg. If the substance has a molecular weight higher than 700 g/mol this is an indicator that the BCF is below 5000 L/kg ”. Also the smallest monoureas formed from constituent structures 3, 4, 5, 6 and 7 have a molecular mass above 1100 g/mol.

b) According to REACH guidance document R11 (2014), “it is unlikely to have a BCF>2000 L/kg on the basis of the following information: octanol-water-partition coefficient as logKow > 10 (calculated value, preferably by several estimation programs, for substances for which LogKow can be calculated and the model is reliable)”.
The log Kow values for larger monoureas formed as hydolysis products of constituent structures 3, 4, 5, 6 and 7 will be even higher than the value of 17.4 obtained above and thus exceed by far the trigger value of 10. For this reason, the hydrolysis products are unlikely to be bioaccumulative (BCF <2000 L/kg).

Constituent structure 8 (HDI)
No empirical bioconcentration, bioaccumulation and K_{OW} data were found for constituent structure 8 (HDI). The estimated log Kow is 3.20 (BCFWIN version 1.68), thus the screening criterion log Kow ≥4.5 is not fulfilled. The estimated BCF is 167.8 L/kg wet-wt (BCFBAF v 3.01). Constituent structure 8 does not fulfil the criteria for either B or vB based on predicted BCF, but there is no supporting evidence from experimental data for analogue structures. However, because of the ready hydrolysis of HDI in the environment it is neither possible nor very relevant to determine whether HDI would meet the B-criterion (BCF > 2000 L/kg) in an experimental study.

The relevant transformation products resulting from hydrolysis are oligomeric and polymeric ureas. As explained above the oligomeric ureas will further react to form a mixture of polymeric ureas and thus are not expected to be persistent. Also for the oligomeric urea, because of the ready hydrolysis in the environment it is neither possible nor very relevant to determine whether it would meet the B-criterion (BCF > 2000 L/kg) in an experimental study. The polymeric ureas are highly likely to fulfil criteria for persistence, but are not bioaccumulative.

8.1.3 Toxicity assessment

In the Chemical Safety Report toxicity was only assessed for the main constituent. According to the guidance for the assessment of multi constituent substances in the revised PBT guidance document a bioaccumulation assessment has to be performed on the representative structures in this UVCB substance that are present at ≥0.1% w/w. The eMSCA conclusion on toxicity reached in this report are based on the presented assessment of toxicity to the environment and the current non-classification of the substance for human health. Human health endpoints were not assessed. The results are evaluated below in conjunction with publicly available information on analogous substances.

Constituent structures 1, 3, 4, 5, 6, 7 and 8

No toxicity data or QSAR estimates of toxicity were found for these structures. Data are available for the analogue substance HDI Trimer suggesting a low toxicity. It is concluded that constituent structures are not likely to fulfil endpoint criteria for T. HDI oligomers, isocyanurate type hydrolyses to a mixture of oligomeric and polymeric ureas. It is formed by reaction of the substance with water. The isocyanate groups react with water yielding an amino function as an intermediate. The amine groups rapidly react further with another isocyanate groups yielding the ureas. No studies are available for the ureas. Due to the inertness, low water solubility and high molecular weight, the substance is considered to be not bioavailable and therefor non toxic.

Constituent structure 2

HDI Trimer (Desmodur N 3600) is not considered as T based on criteria laid down in Annex XIII of REACH Regulation.

HDI hydrolyses to a mixture of oligomeric and polymeric ureas. It is formed by reaction of the substance with water. The isocyanate groups react with water yielding an amino function as an intermediate. The amine groups rapidly react further with another isocyanate groups yielding the ureas. No studies are available for the ureas. Due to the inertness, low water solubility and high molecular weight, polymeric urea is considered to be not bioavailable and therefore non toxic.

8.1.4 Summary and overall conclusions on PBT and vPvB Properties

HDI oligomers, isocyanurate is not considered to be a PBT/vPVB substance as the parent compound is not P/vP. The main constituent HDI trimer does not meet environmental criteria for T and also other constituents are unlikely to meet environmental criteria for T. An overall eMSCA conclusion of the toxicity assessment cannot be drawn, because human health endpoints were not assessed.

The relevant transformation products are the corresponding oligomeric and polymeric urea compounds. It is unlikely that the oligomeric urea compounds would meet the P/vP criterion and therefore it is appropriate to state that oligomeric urea does not meet the PBT/vPvB-criteria. Because of its high molecular weight one can state that polymeric urea shows no bioaccumulation potential and consequently does not meet the PBT/vPvB-criteria. These conclusions are also consistent with conclusions reached in the PBT assessment of the structurally similar substance o-(p-isocyanatobenzyl)phenyl isocyanate (2,4-MDI) by Belgium.

An overview of the conclusions:

	P	vP	B	vB	T	Fulfilling the PBT /vPvB criteria
Constituent structure 1	No	No	No	No	No	**No**
Constituent structure 2	No	No	No	No	No	**No**
Constituent structure 3	No	No	No	No	No	**No**
Constituent structure 4	No	No	No	No	No	**No**
Constituent structure 5	No	No	No	No	No	**No**
Constituent structure 6	No	No	No	No	No	**No**
Constituent structure 7	No	No	No	No	No	**No**
Constituent structure 8	No	No	No	No	No	**No**
Hydrolysis products – oligomeric ureas	No	No	Potentially	No	No	**No**
Hydrolysis products – polymeric ureas	Yes	Yes	No	No	No	**No**
Evaluated substance						**No**

9 EXPOSURE ASSESSMENT

Not evaluated.

10 RISK CHARACTERISATION

10.1 Human Health

Not evaluated.

10.2 Environment

10.2.1 Risk characterisation for PBT

The substance under evaluation is not considered a PBT or vPvB substance, since none of the constituents fulfils endpoint criteria for B or vB.

10.2.2 Aquatic compartment (incl. sediment)

Not evaluated.

10.2.3 Terrestrial compartment

Not evaluated.

10.2.4 Atmospheric compartment

Not evaluated.

10.2.5 Microbiological activity in sewage treatment systems

Not evaluated.

10.3 Overall risk characterisation

Not evaluated.

11 OTHER INFORMATION

None.

12 REFERENCES

ACD Chemsketch for Academic and Personal use:
http://www.acdlabs.com/resources/freeware/chemsketch/

Bayer AG (1988). Prüfbericht 18 A/88. Bayer AG, Building 4242, 51368 Leverkusen (Germany). Testing laboratory: WV-LE Umweltschutz AWALU Mikrobiologie. Report no.: 18 A/88. Owner company: Bayer MaterialScience AG. Report date: 1988-07-26.

Bayer AG (1989). Prüfbericht 53 A/88. Bayer AG, Institut for Environmental Analysis, 5090 Leverkusen
Bayerwerk (Germany). Testing laboratory: WV-LE Umweltschutz Wasserbiologie. Report no.: 53 A/88. Owner company: Bayer MaterialScience AG. Report date: 1989-05-05.

Bayer AG (1999). NCO-Abnahme in Wasser. Bayer AG, Building Q 18, 51368 Leverkusen (Germany). Testing laboratory: ZF-Zentrale Analytik. Report no.: G 99/0179/01 LEV. Owner company: Bayer MaterialScience AG. Report date: 2000-02-04.

Bayer AG (2000a). Investigation of the ecological properties of Desmodur N 3300. Bayer AG, Institute of
Environmental Analysis, 51368 Leverkusen (Germany). Testing laboratory: WV-LE Institute of Environmental
Analysis. Report no.: 954 A/00. Owner company: Bayer MaterialScience AG. Report date: 2000-03-21.

Bayer AG (2000b). Investigation of the ecological properties of Desmodur N 3300. Bayer AG, Institute of
Environmental Analysis, 51368 Leverkusen (Germany). Testing laboratory: WV-LE Institute of Environmental
Analysis. Report no.: 954 A/00. Owner company: Bayer MaterialScience AG. Report date: 2000-04-10.

Bayer AG (2001a). Desmodur N 3600 - Biodegradation. Bayer AG, Institute for Environmental Analysis and Evaluation, building W 15, 51368 Leverkusen, Germany. Testing laboratory: WD-UWS. Report no.: 21258249. Owner company: Bayer MaterialScience AG. Report date: 2001-01-11.

Bayer AG (2001b). Desmodur N 3600 - Biodegradation. Bayer AG, Institute for Environmental Analysis and
Evaluation, building W 15, 51368 Leverkusen, Germany. Testing laboratory: WD-UWS. Report no.: 21258249. Owner company: Bayer MaterialScience AG. Report date: 2001-03-16.

Bayer AG (2001c). Akute Fischtoxizität - Desmodur N 3600. Bayer AG, Institute for Environmental Analysis
and Evaluation, building W 15, 51368 Leverkusen, Germany. Testing laboratory: WD-UWS. Report no.:
21258249. Owner company: Bayer MaterialScience AG. Report date: 2001-04-03.

Bayer AG (2001d). Desmodur N 3600 - Akute Daphnientoxizität. Bayer AG, Institute for Environmental
Analysis and Evaluation, building W 15, 51368 Leverkusen, Germany. Testing laboratory: WD-UWS. Report
no.: 21258249. Owner company: Bayer MaterialScience AG. Report date: 2001-01-30.

Bayer AG (2001e). Desmodur N 3600 - Algeninhibitionstest (Grünalge). Bayer AG, Institute for Environmental Analysis and Evaluation, building W 15, 51368 Leverkusen, Germany. Testing laboratory: WD-UWS. Report no.: 21258249. Owner company: Bayer MaterialScience AG. Report date: 2001-04-04.

Bayer Industry Services (2007). Determination of hydrolysis of HDI Trimer. Testing laboratory: Bayer Industry
Services, D-51368 Leverkusen, building Q18. Report no.: 2006/0114/02. Owner company: BASF AG, Bayer
MaterialScience AG, Degussa AG, Rhodia Operations. Report date: 2007-09-21.

Currenta GmbH & Co. OHG (1997). Prüfbericht (nach DIN EN 45001) der Proben N75M Z 4470 N 3300
Desmodur. Laboratorien für sicherheitstechnische Kenndaten und Messungen 51368 Leverkusen, Germany.
Testing laboratory: WD-SI VA 1. Report no.: 97/12490 PB - 97/12499 PB. Owner company: Bayer MaterialScience AG. Report date: 2008-09-04.

Currenta GmbH & Co. OHG (2009a). QSAR Estimations for the main component (sym. HDI Trimer) of
Desmodur N 3300 and Desmodur N 3600 (CAS:28182-81-2). Currenta GmbH & Co. OHG, 51368 Leverkusen (Germany). Testing laboratory: SER-ANT. Owner company: Bayer MaterialScience AG. Report date: 2009-07-09.

Currenta GmbH & Co. OHG (2009b). QSAR Estimations for the corresponding triamine of the main component (sym. HDI Trimer) of Desmodur N 3300 and Desmodur N 3600 (CAS:28182-81-2). Currenta GmbH & Co. OHG, 51368 Leverkusen (Germany). Testing laboratory: SER-ANT. Owner company: Bayer MaterialScience AG. Report date: 2009-07-09.

Currenta GmbH & Co. OHG (2009c). QSAR Estimations for the main component (sym. HDI Trimer) of
Desmodur N 3300 and Desmodur N 3600 (CAS:28182-81-2). Currenta GmbH & Co. OHG, 51368 Leverkusen (Germany). Testing laboratory: SER-ANT. Owner company: Bayer MaterialScience AG. Report date: 2007-07-09.

ECHA (2013). Guidance on the Application of the CLP criteria – Guidance to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures. Version 4.0, November 2013

ECHA (2014) Guidance on information requirements and chemical safety assessment – Chapter R.11: PBT and vPvB Assessment. Version 2.0, November 2014

Herrinton R; and Hock K; Flexible Polyurethane Foams, 2nd Ed., The Dow Chem Co (1998)

Kitano M., Ouchiyama, N., and Shimogawa, Y. (1989). Fate of TDI in water. Part 1: 2,4-TDI (T-100). Chemicals Inspection and Testing Institute, Japan. III Report No. 10691. Kitano, M., Shimogawa, Y., and Yakabe, Y. (1991).

Kitano M., Ouchiyama, N., and Shimogawa, Y. (1989). Study on the fate of 2,6-TDI (T-0) in water. Chemicals Inspection and Testing Institute, Japan. III Report No. 10911

OECD (2000). Guidance document on aquatic toxicity testing of difficult substances and mixtures. OECD Series on Testing and Assessment Number 23, ENV/JM/MONO(2000)6.
PubChem: http://pubchem.ncbi.nlm.nih.gov/

Sendijarevic, V., Sendijarevic, A., Sendijarevic, I., Bailey, R. E., Pemberton, D., and Reimann, K. A., Hydrolytic stability of toluene diisocyanate and polymeric methylenediphenyl diisocyanate based polyureas under environmental conditions. Environ.Sci.Technol., 38, (4), 1066-72 (2004).

TDI industry risk assessment, GIL report Number 2004/E, Gilbert International Limited, Bridgewater House, Whitworth Street, Manchester M1 6LT, UK, Tel UK + 44(0)161 236 3774 Fax: UK +44(0)161 236 7855 e-mail: Office@gilbertinternational.co.uk

Yakabe, Y., Henderson, K. M., Thompson, W. C., Pemberton, D., Tury, B., and Bailey, R.E. (1999). Fate of methylenediphenyl diisocyanate and toluene diisocyanate in the aquatic environment. Environ.Sci.Technol., 33, (15), 2579-83.

13 ABBREVIATIONS

AOPWIN	The Atmospheric Oxidation Program estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals.
BCF	Bioconcentration factor
BIOWIN	Estimates aerobic and anaerobic biodegradability of organic chemicals using 7 different models.
CA	Competent Authority
CAS	Chemical Abstracts Service
CSR	Chemical Safety Report
CLP	Classification, Labelling and Packaging (of hazardous chemicals)
DNEL	Derived No Effect Level
ECHA	European Chemicals Agency
EPA	Environmental Protection Agency
EPIWIN	The EPI (Estimation Programs Interface) Suite™ is a Windows®-based suite of physical/chemical property and environmental fate estimation programs developed by the EPA's Office of Pollution Prevention Toxics and

	Syracuse Research Corporation (SRC).
EPT	Equilibrium Partitioning Theory
ERC	Environmental Release Category
GHS	Globally Harmonized System (of Classification and Labelling of Chemicals)
HENRYWIN	Calculates the Henry's Law constant (air/water partition coefficient) using both the group contribution and the bond contribution methods.
HLC	Henry's Law Constant
IUCLID	International Uniform Chemical Information Database
IUPAC	International Union of Pure and Applied Chemistry
KOCWIN	The program estimates the organic carbon-normalized sorption coefficient for soil and sediment; i.e. K_{OC}. $K_{OC}$is estimated using two different models: the Sabljic molecular connectivity method with improved correction factors; and the traditional method based on log K_{OW}.
NOAEL	No Observable Adverse Effect Level
OECD	Organization for Economic Cooperation and Development
QSAR	Quantitative Structure-Activity Relationship
PBT	Persistent Bioaccumulative and Toxic
PNEC	Predicted No Effect Concentration
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RMO	Risk Management Options
SEv	Substance Evaluation
UVCB	Substances of Unknown or Variable composition, Complex reaction products or Biological materials.
vPvB	Very Persistent and Very Bioaccumulative
WAF	Water-accommodated fraction

Annex: Data (tables) on constituents and additives as provided in Chemical Safety Report. This annex is confidential and not included in the public version of this report..