

Results from the prioritisation of biocides for environmental monitoring in Germany



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Overview

- **Introduction**
why monitoring biocides?
- **Prioritisation of biocides**
what aspects are considered?
- **Plausibility of results of the prioritisation approach**
are the results from the prioritisation approach consistent with the existing monitoring data?
- **Conclusions**



Why is a specific biocides monitoring necessary?

To assess

- whether the **environmental impact of biocides** is changing as consequence of the EU biocide regulations
- whether environmental concentrations of **non-approved biocides** are decreasing
- whether levels of other/new biocides are increasing due to **substitutions** of non-approved compounds
- whether environmental concentrations of biocides are **exceeding no-effect concentrations**

Number	Product-type	Description
Main group 3: Pest control		
PT 14	Rodenticides	Used for the control of mice, rats or other rodents, by means other than repulsion or attraction.
PT 15	Avicides	Used for the control of birds, by means other than repulsion or attraction.
PT 16	Molluscicides, vermicides and products to control other invertebrates	Used for the control of molluscs, worms and invertebrates not covered by other product types, by means other than repulsion or attraction.
PT 17	Piscicides	Used for the control of fish, by means other than repulsion or attraction.
PT 18	Insecticides, acaricides and products to control other arthropods	Used for the control of arthropods (e.g. insects, arachnids and crustaceans), by means other than repulsion or attraction.

EU biocide regulations

- The number of biocides in Europe is decreasing due to the implemented biocide regulations, effective since 2013: EU Biocidal Products Regulation No. 528/2012 (BPR)
- About 360 biocides are assessed in a review program since 1998, about 150 are still under review - at least for the use in one or more biocide product types
- about 120 biocides are already on the list of approved biocides

Last updated 01-June-2015. Database contains 685 active substance-product type combinations for which approval has been sought.

EC Number	<input type="text"/>	CAS Number	<input type="text"/>
Substance Name	<input type="text"/>	Evaluating Competent Authority	<input type="text"/>
Type	<input type="text"/>	Legal Act	<input type="text"/>
Approval Status	<input type="text" value="Approved"/>	Date of Approval (min)	<input type="text"/>
Date of Approval (min)	<input type="text"/>	Date of Approval (max)	<input type="text"/>
Expiry Date (min)	<input type="text"/>	Expiry Date (max)	<input type="text"/>
Biocide ID	<input type="text"/>	Biocide Asset Number	<input type="text"/>

I have read and I accept the legal notice

<http://echa.europa.eu/web/guest/information-on-chemicals/biocidal-active-substances>

Showing 1 - 50 of 121 results.

Items per Page 50 Page 1 of 3 First Previous Next Last

Substance Name	EC Number	CAS Number	Type	Legal Act	Date of Approval	Expiry Date	Evaluating Competent Authority	Approval Status	Data	Related Authorised Products
(E)-1-(2-Chloro-1,3-thiazol-5-ylmethyl)-3- methyl-2-nitroguanidine (Clothianidin)	433-460-1	210880-92-5	8 - Wood preservatives	Directive 2008/15/EC	01/02/2010	01/02/2020	DE	Approved		
(RS)- α -cyano-3phenoxybenzyl-(1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (Cypermethrin)	257-842-9	52315-07-8	8 - Wood preservatives	Regulation (EU) 945/2013	01/06/2015	01/06/2025	BE	Approved		

Availability of EU biocides assessment reports

<http://echa.europa.eu/web/guest/information-on-chemicals/biocidal-active-substances>

4,5-Dichloro-2-octylisothiazol-3(2H)-one (4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT))

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Substance Identification

Name:	4,5-Dichloro-2-octylisothiazol-3(2H)-one (4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT))
IUPAC Name:	
EC Number:	264-843-8
CAS Number:	64359-81-5
Product Type:	8 - Wood preservatives

Administrative Data

Legislative act:	Directive 2011/66/EU
Date of approval:	01 Jul 2013
Expiry Date:	01 Jul 2023
Rapporteur Member State:	NO
Approval ID:	0022-08
Approval Status:	Approved
Asset No:	EU-0005365-0000

Assessment Report

[Assessment report](#)

Study Summaries (Doc IIIa)

[Data_001.pdf](#)

[Data_002.pdf](#)

Covered substances

- Not all biocides are covered by the proposed prioritisation approach:
 - no metal salts
 - no “readily biodegradable” compounds
 - no microorganisms or biological materials
- Compounds covered are organic compounds of synthetic or natural origin for which EU assessment reports are available
 - transformation products are covered if relevant and data are provided
 - about 100 biocides plus about 70 transformation products were evaluated
 - In some cases data were estimated (EPI suite, US EPA 2012)

Assessment Report



Propiconazole
Product-type 8
(Wood preservatives)

29 November 2007

Annex I - Finland

Scheme for the prioritisation of biocides for environmental monitoring

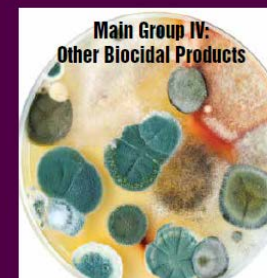
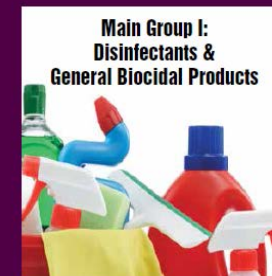
Assessment of each biocide regarding the

- **emission** relevance
- relevance for causing **effects**
- relevance for the **occurrence in environmental media** (waters / STPs / soils / air)

Compartment-specific prioritisation

- the scores from each step are multiplied and **relevant compounds are prioritised according to the total score**
- **filters are set considering the partitioning of compounds** in the respective compartment (e.g., persistence, bioaccumulation, sorption)

Biocide Standards Reference Guide



Overview on environmental relevance of biocidal product types (PTs)

XXX = major/high impact;
 XX = significant impact;
 X = moderate impact;
 - = minor/low impact

STP = Sewage Treatment Plant

Source:
 based on COWI A/S (2009), Kongens Lyngby, Denmark
 shaded fields: assessment changed based on expert judgement

Product type	Tonnage (annual)	Direct environmental exposure	Indirect environmental exposure via STPs
Main Group 1: Disinfectants			
1: Human hygiene	XXX	(-)	XX
2: Disinfectants and algaecides not intended for direct application to humans or animals	XXX	X	XXX
3: Veterinary and hygiene	XXX	X	XX
4: Food and feed area	XXX	(-)	XXX
5: Drinking water	XXX	X	X
Main group 2: Preservatives			
6: Preservatives for products during storage	XX	X	X
7: Film preservatives	XX	XX	XX
8: Wood preservatives	XXX	XX/XXX	X
9: Fibre, leather, rubber, and polymerised materials preservatives	XX	X	X
10: Construction material preservatives	XXX	XX	XX
11: Preservatives for liquid cooling and processing systems	XXX	XX	XX
12: Slimicides	XX	XX	XX
13: Working or cutting fluid preservatives	XX	(-)	X
Main Group 3: Pest control			
14: Rodenticides	X	XX	X
15: Avicides §	(-)	XX	(-)
16: Molluscicides, vermicides and products to control other invertebrates #	(-)	XXX	(-)
17: Piscicides §	(-)	XXX	(-)
18: Insecticides, acaricides and products to control other arthropods	XXX	XXX	XXX
19: Repellents and attractants	XX	XX	XX
20: Control of other vertebrates §	(-)	XX	(-)
Main Group 4: Other biocidal products			
21: Antifouling products	X	XXX	(-)/X
22: Embalming and taxidermist fluids	X	X	X

no biocide in the review program for this PT. § no authorization in Germany for this PT.

Assessment of emission relevance

- **Use in emission relevant product types (PT) #**
PT 1, 2, 3, 4, 7, 8, 10, 11, 12, 14, 16, 18, 19, 21:
each PT score 1 (maximum 3 scores)
- **Number of products registered in Germany**
(BAuA, Register of notified biocidal products)
up to 10 products: score 0 **11-100 products: score 1**
101 - 1000 products: score 2 **> 1000 products: score 3**
- **Production/import volumes (ESIS data base)**
< 10 t/a: score 0 **default (if no data): score 1**
10 - 1000 t/a (low production volume, LPV): score 2
> 1000 t/a (high production volume, HPV): score 3

based on COWI A/S (2009), Kongens Lyngby,
Denmark; modified based on expert judgement

Assessment of effect relevance (based on assessment reports)

■ PNEC for aquatic organism

PNEC < 0.01 µg/L: score 4

> 0,1 - 1 µg/L: score 2

> 10 µg/L: score 0

0.01 – 0.1 µg/L: score 3

> 1 - 10 µg/L: score 1

default (if no data) : score 1

■ PEC/PNEC comparison for relevant scenarios

PEC/PNEC > 1 for more than one scenario: score 2

PEC/PNEC > 1 for one scenario: score 1

PEC/PNEC < 1 for all scenarios: score 0

default-Wert (no data): score 1

■ Classification in GHS / C&L#

acute tox. 1 or 2 (T+): score 3

no acute tox. (not T/T+): score 0

acute tox. 3 (T): score 2

default: score 1

■ Fish bioaccumulation (bioconcentration factor, BCF)

BCF < 100: score 0

BCF > 2000: score 2

BCF > 100 - 2000: score 1

BCF > 5000: score 3

Assessment of **relevance for the occurrence in the environment**

- **Compartment-specific consideration of the emission relevance of the different product types (PT) (modified from COWI 2009)**
 - surface water: PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21; plus indirect inputs from sewage treatment plants: additionally PT 1, 2, 3, 4**
 - sewage treatment plants: PT 1, 2, 3, 4, 7, 10, 11, 12, 18 19**
 - soil: PT 7, 8, 10, 14, 18, 19; plus indirect inputs: from sewage sludge, additionally PT 1, 2, 3, 4, 11, 12; from liquid manure: additionally PT 3**
 - atmosphere: PT 8, 11, 14, 18**

**For each product type considered (approved or under review):
score 1 (maximum 3 scores)**
- **Consideration of biodegradability and persistence**
 - readily biodegradable: score 0; not readily biodegradable: score 2;**
 - default (no data/not applicable): score 1;**
 - P-criterion according to REACh Annex XIII met: score 2;**
 - vP-criterion met: score 3; P-criterion not met: score 0;**
 - default (no data/not applicable): score 1**

Total score biodegradability/persistence: sum of both criteria

Results from the prioritisation approach

Prioritisation of biocides for the **monitoring in water / water phase**

- filters: $K_{oc} < 100,000$; biodegradability/persistence score ≥ 2

Ranking WATER							
substance	CAS no.	PPP status authorized (Germany)	PT	SCORE Emission relevance	SCORE Effects relevance	SCORE Water relevance	SCORE product
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	no	7, 8, 9, 10, 11, 21	7	9	6	378
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	no	2, 6, 9, 11, 12, 13	8	7	5	280
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	no	6, 7, 8, 9, 10, 12, 13	8	5	6	240
Dichlofluanid	1085-98-9	2003	7, 8, 21	8	6	4	192
Tolyfluanid	731-27-1	2010	7, 8, 21	6	7	4	168
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	no	7, 8, 9, 10, 11, 21	7	5	6	210
(DCOIT-TP) 2-chloro-2-(n-octyl-carbamoyl)-1-ethene sulfonic acid	-	no	7, 8, 9, 10, 11, 21	7	4	6	168
NNOA (DCOIT-TP EW) N-(n-octyl) oxamic acid	-	no	7, 8, 9, 10, 11, 21	7	4	6	168
NNOA (DCOIT-TP) N-(n-octyl) acetamide	-	no	7, 8, 9, 10, 11, 21	7	4	6	168
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	6	9	3	162

No current PPP in the top 10 ranked compounds

Results from the prioritisation approach

Prioritisation of biocides for the monitoring in water / suspended particulate matter (SPM) or sediments

- filters: $K_{oc} > 10,000$; biodegradability/persistence score ≥ 2
incl. currently approved PPP / PPP transformation products

Ranking SPM / sediments		PPP status		SCORE	SCORE	SCORE	SCORE
substance	CAS	authorized (Germany)	PT	Emission relevance	Effects relevance	Water relevance	product
Didecylmethylpoly(oxyethyl)ammonium Propionate DMPAP (Bardap 26)	94667-33-1	no	2, 4, 8, 9, 10, 11, 12	6	5	6	180
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	6	9	3	162
Cypermethrin	52315-07-8	>2013	8, 18	6	9	3	162
Pyrethrins	8003-34-7	>2013	18, 19	4	8	4	128
Etofenprox	80844-07-1	>2013	8, 18	4	8	3	96
α -CO (Etofenprox TP W)	-	>2013	8, 18	4	8	3	96
4'-OH (Etofenprox TP Sed)	-	>2013	8, 18	4	7	3	84
Chlorfenapyr	122453-73-0	no	8, 18	3	9	3	81
Spinosad	168316-95-8	>2013	3, 18	4	6	3	72
Deltamethrin	52918-63-5	>2013	18	3	9	2	54

Results from the prioritisation approach

Prioritisation of biocides for the monitoring in water / suspended particulate matter (SPM) or sediments

- filters: $K_{oc} > 10,000$; biodegradability/persistence score ≥ 2 ; no currently approved PPP

Ranking SPM / sediments		PPP status		SCORE	SCORE	SCORE	SCORE
substance	CAS no.	authorized (Germany)	PT	Emission relevance	Effects relevance	Water relevance	product
Didecylmethylpoly(oxyethyl)ammonium Propionate DMPAP (Bardap 26)	94667-33-1	no	2, 4, 8, 9, 10, 11, 12	6	5	6	180
Permethrin (cis/trans ratio of 25:75)	52645-53-1	2001	8, 9, 18	6	9	3	162
Chlorfenapyr	122453-73-0	no	8, 18	3	9	3	81
Chrysanthemum cinerariaefolium, Extract	8003-34-7 / 89997-63-7	no	18	3	8	2	48
Transfluthrin	118712-89-3	no	18	4	6	2	48
(AEM 5772 TP) 3-(trihydroxysilyl) propyl dimethyloctadecyl ammonium chloride	199111-50-7	no	2, 7, 9	3	5	3	45
Flufenoxuron	101463-69-8	no	8	4	11	1	44
d-Phenothrin ((1R)-trans phenothrin)	26046-85-5	no	18	3	7	2	42
Creosote	8001-58-9	no	8	5	8	1	40
Cyfluthrin	68359-37-5	2009	18	2	10	2	40

Results from the prioritisation approach

Prioritisation of biocides for the monitoring in sewage treatment plant (STP) effluents

■ no filters

Ranking sewage treatment plant effluents		PPP status		SCORE	SCORE	SCORE	SCORE
substance	CAS	authorized (Germany)	PT	Emission relevance	Effects relevance	STP relevance	product
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	no	7, 8, 9, 10, 11, 21	7	9	3	189
1,2-Benzisothiazolin-3(2H)-one (BIT)	2634-33-5	no	2, 6, 9, 11, 12, 13	8	7	3	168
Alkyldimethylbenzylammonium Chloride (ADBAC; Quaternary ammonium compounds, benzyl-(C12-16)-alkyldimethyl, chlorides)	68424-85-1	no	1, 2, 3, 4, 6, 8, 10, 11, 12, 13	8	6	3	144
N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (Lonzabac 12)	2372-82-9	no	2, 3, 4, 6, 8, 11, 12, 13	7	6	3	126
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	no	6, 7, 8, 9, 10, 12, 13	8	5	3	120
Didecyldimethylammonium chloride (DDAC)	7173-51-5	no	1, 2, 3, 4, 6, 8, 10, 11, 12	8	5	3	120
NNOMA (DCOIT-TP) N-(n-octyl) malonamic acid	-	no	7, 8, 9, 10, 11, 21	7	5	3	105
Didecylmethylpoly(oxyethyl)ammonium Propionate DMPAP (Bardap 26)	94667-33-1	no	2, 4, 8, 9, 10, 11, 12	6	5	3	90
DCPP (5-Chloro-2-(4-chlorophenoxy)-phenol)	3380-30-1	no	1, 2, 4	5	6	3	90
NNOA (DCOIT-TP) N-(n-octyl) acetamide	-	no	7, 8, 9, 10, 11, 21	7	4	3	84

No current PPP in the top 10 ranked compounds

Example for the sensitivity of the prioritisation approach

Compartment-specific lists of compounds are sensitive to changes of usage of covered biocides in different biocide product types

Example: highest ranked compounds for monitoring in aquatic biota before and after changes of Triclosan product type approval in 2014 (phase-out of usage in PT 2, 7, 9 in April 2015)

Ranking AQUATIC BIOTA	CAS	PPP status authorized (Germany)	PT	SCORE Emission relevance	SCORE Effects relevance	SCORE Water relevance	SCORE product
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)							378
Permethrin (cis/trans ratio of 25:75)							162
Chlorfenapyr							81
Methyl-DCPP (DCPP TP)							75
Triclosan							50
Ranking AQUATIC BIOTA							SCORE Mon. water
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)							378
Triclosan							280
Methyltriclosan (Triclosan TP)							224
Permethrin (cis/trans ratio of 25:75)	52043-53-1	2001	0, 9, 10	0	9	3	162
Chlorfenapyr	122453-73-0	no	8, 18	3	9	3	81

Assessment report:
Bioconcentration of DCOITbased on analysis of total 14C-residues **steady-state BCF** for bluegill sunfish (whole body) is estimated to be **750** ($K_{uptake}/K_{depuration}$). **Only 1%** of the detected radioactivity in fish was DCOITmetabolites of the active compound seem to be incorporated into **protein of the fish** via amino acid adducts...

Filters: BCF > 100,
not readily biodegradable

Comparison with available biocide monitoring data

Compartment-specific list of compounds (only biocide transformation products already covered in monitoring, **without current PPP**):

green: covered in monitoring programmes, e.g., German federal states NORMAN EMPODAT, literature; **red**: detected above limit of quantification

- | | | |
|--|---|---|
| <p>■ surface waters:</p> <p>DCOIT,
BIT,
IPBC,
Dichlofluanid,
Tolyfluanid,
Permethrin,
hydrogen cyanide,
decanoic acid,
methylisothiocyanate (MITC),
5-chloro-2-methyl-4-isothiazolin-3-one (C(M)IT),
N,N-Dimethyl-N'-phenylsulfamide (DMSA)</p> | <p>■ suspended particulate matter / sediments:</p> <p>DMPAP (Bardap 26),
Permethrin,
Chlorfenapyr,
Chrysanthemum extract,
Transfluthrin,
Flufenoxuron,
d-Phenothrin,
Creosote,
Cyfluthrin,
Pyriproxyfen,
Hexaflumuron,
Triflumuron</p> | <p>■ sewage treatment plant (STP) effluents:</p> <p>DCOIT, BIT,
Alkyldimethylbenzylammonium chloride (ADBAC),
N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (Lonzabac 12), IPBC,</p> <p>limit of quantification not always appropriate: in some cases the LOQ is higher than the PNEC!
examples: permethrin, cyfluthrin
(Bardap 26),
DCPP (5-Chloro-2-(4-chlorophenoxy)-phenol),
decanoic acid, Methyl-DCPP,
Pyrethrins, C(M)IT</p> |
|--|---|---|

Conclusions (1)

- The proposed approach allows a **compartment-specific prioritisation of biocides** for an environmental monitoring
- Data used for the prioritisation are retrieved mainly from the **EU biocide assessment reports** (only in some cases additional QSAR estimations)
- **Compartment-specific lists were generated for all relevant media:** surface water, sediments, aquatic biota, sewage treatment plant effluents, sewage sludge, terrestrial biota, soil, ground water, air
- The prioritisation approach currently **covers only those biocides which are already approved or for which at least assessment reports are available**; it should be adapted after finalisation of the assessment of all existing biocides that are in the review programme and should consider also new biocides

Conclusions (2)

- Major purpose of the intended biocide monitoring is to **follow changes of environmental concentrations of biocides induced by regulatory measures**, e.g., phase-out after non-approval decisions
- **Obstacle: many biocides are also approved under other regulations**, e.g., as plant protection product, veterinary pharmaceutical, or industrial chemical (REACH)
- Only for **compounds solely used as biocides** changes of environmental levels may be correlated explicitly to changes of the approval status
- For some biocides **improvements of analytical methods** are required: **methods are not always sufficient sensitive** to allow the checking of possible exceedances of effect levels (PNECs)

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