Prioritization of biocidal substances for an environmental monitoring

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Structure

- **Objective of the prioritization**
  Success control of biocide regulation
- **Prioritization of biocides**
  Proposal for a pragmatic approach
- **Plausibility of results of the prioritization**
  Comparison with other concepts and monitoring data
- **Conclusions**

Source: www.umweltbundesamt.at/umweltsituation/chemikalien/

Motivation and background

- The European Biocidal Product Directive (BPD) 98/8/EC causes a change of the use of biocides in EU member states

- ~ 960 existing biocides in 2002, but only
  ~ 360 biocides are assessed in a review program;
  ~ 60 biocides already approved for Annex I / Ia

- For several biocides of the review program the placing on the market has already stopped because of non-inclusion decisions

- Use of other biocides may be restricted by risk mitigation schemes

Motivation and background

- **Expected consequence of changes caused by the BPD:**
  a decrease of discharges of affected biocides into the environment

- **This hypothesis may be proven by an environmental monitoring**

- **Obstacles:**
  - **concurrent use of biocidal compounds as, e.g., plant protection products (PPP) -**
    currently monitoring for BPD efficacy has to focus on compounds used solely as biocides

  - **coverage of relevant transformation products formed**

Prioritization of biocides for environmental monitoring

Prioritization concept - the suggested procedure has 3 steps:

- **Assessment of the emission relevance of biocides**
  - mainly based on use for biocides product types – PT -
- **Assessment of their ecotoxicological effect relevance**
  - e.g., by considering predicted no effect concentrations – PNECs -
- **Identification of the relevant environmental matrices for the highest scored biocides**
  - based on emission relevance and partition properties -

Source: www.biozide.at

Prioritization of biocides for environmental monitoring

- Prioritization was tested with data from ~ 80 biocides
- The data were retrieved mainly from EU Doc I assessment reports (available at circabc.europa.eu); triclosan data are from literature
- Missing data were estimated by QSAR (EPI suite, US EPA)
- Data from transformation products are also covered, if relevant
- Metal salts, alcohols and oxidizing compounds were excluded

Source: www.sabine-wils.eu/biozide.php

Monitoring of biocides

➢ Prioritization of biocides

Step 1:

Assessment of the emission relevance of biocides

(mainly based on use for biocides product types - PT)

Source: www.umweltbundesamt.at/umweltsituation/chemikalien/

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:
COWI A/S (2009), Kongens Lyngby, Denmark.
http://ec.europa.eu/environment/biocides/pdf/report_use.pdf

Product type (according to BPD)	Estimated tonnage (annual)	Environmental exposure, direct	Environmental exposure via STPs
1: Human hygiene biocidal products	XXX	-/X	XX
2: Private area and public health area biocidal products	XXX	X	XXX
3: Veterinary and hygiene biocidal products	XXX	X	XX
4: Food and feed area disinfectants	XXX	-	XXX
5: Drinking water disinfectants	XXX	X	X
6: In-can preservatives	XX	X	X
7: Film preservatives	XX	XX	X
8: Wood preservatives	XXX	XX/XXX	-
9: Fibre, leather, rubber, and polymerised materials preservatives	XX	-	X
10: Masonry preservatives	XXX	XX	-
11: Preservatives for liquid cooling and processing systems	XXX	XX	XX
12: Slimicides	XX	XX	XX
13: Metalworking fluid preservatives	XX	-	X
14: Rodenticides	-	XX	X
15: Avicides	-	XX	-
16: Molluscicides	-	XXX	-
17: Piscicides	-	XXX	-
18: Insecticides and products to control other arthropods	XX	XXX	-
19: Repellents and attractants	XX	XX	-
20: Preservatives for food and feedstock	X	-	-
21: Antifouling products	X	XXX	-/X
22: Embalming and taxidermist fluids	-	-	-
23: Control of other vertebrates	-	XX	-

Assessment of the emission relevance

- **Emission relevant product types (PTs)**

  ***PT 1, 2, 3, 4, 7, 8, 10, 11, 12, 14, 15, 16, 17, 18, 19, 21, 23:* each PT - score 1**

- **Number of products with the respective active ingredient in the biocide register at Federal Institute for Occupational Safety and Health (BAuA)**

up to 10 products	score 0	11 - 100 products	score 1
101 - 1000 products	score 2	> 1000 products	score 3

- **Production and/or import volumes (ESIS data base esis.jrc.ec.europa.eu)**

< 10 t/a	score 0	10 - 1000 t/a (LPV)	score 1
> 1000 t/a (HPV)	score 2	no data	score 1

- **Concurrent use of a substance also in plant protection products (BVL 2010)**

no authorization or authorization ended before the year 2002	score 0
authorization in the period 2002 - 2009	score 1
current authorization	score 2

- **Concurrent use in pharmaceuticals (DIMDI / AMIS data base)**

no marketable product	score 0
at least one marketable product	score 2
no data	score 1

➢ Prioritization of biocides

Step 2:

Assessment of the ecotoxicological effect relevance

Source: www.umweltbundesamt.at/umweltsituation/chemikalien/

Assessment of potential ecotoxicological effects

- **PNEC derived for aquatic organisms**

  PNEC < 0.01 µg/L: score 4 **PNEC 0.01 - 0.1 µg/L: score 3**
  PNEC > 0.1 - 1 µg/L: score 2 **PNEC > 1 - 10 µg/L: score 1**
  PNEC > 10 µg/L: score 0

- **Results of PEC/PNEC-assessment in the EU Doc I assessment report**
  (predicted environmental concentration / predicted no effect concentration)

  PEC/PNEC > 1 for several scenarios: score 2
  PEC/PNEC > 1 for a single scenario: score 1
  PEC/PNEC ≤ 1 for all scenarios: score 0
  no data: score 1

- **T-classification**

  T+: score 2 **neither T+ nor T: score 0**
  T: score 1 **no data: score 1**

- **Bioconcentration factor (BCF) fish**

  BCF ≤ 100: score 0 **BCF > 100 - 2000: score 1**
  BCF > 2000 - 5000: score 2 **BCF > 5000: score 3**

Prioritization of biocides

Step 3:

Identification of the relevant environmental matrices for the highest scored biocides

Source: www.umweltbundesamt.at/umweltsituation/chemikalien/

Identification of relevant environmental matrices

Relevant for monitoring in water?
relevant for all biocides with a score > 8 from the first two steps (emissions/effects) that are potentially released into waters

Direct releases into waters expected because applied for the following PTs (based on the assessment by COWI 2009):
PT 7, 8, 10, 11, 12, 14, 16, 18, 21

- for each relevant PT score 1 (max. score 5)

Indirect releases into waters via sewage treatment plants expected because applied for the following PTs (based on COWI 2009):
PT 1, 2, 3, 4, 5, 6, 7, 9, 11, 12, 13, 14, 19, 21

- for each relevant PT score 1 (max. score 5)

Ranking criterion for compounds: sum of all scores (from emission, effects, and relevance for water monitoring assessments)

Biocides (no current PPP) - relevant for monitoring in water

substance	CAS no.	PPP registration until	PT	PNEC water µg/L	BCF fish	SCORE emission	SCORE effects	SCORE relevance water	SCORE OVERALL
Methyltriclosan	4640-01-1	0	1,2,7,9	0.015	3600	8	5	5	18
Triclosan	3380-34-5	0	1,2,7,9	0.05	1500	8	4	5	17
Hydrogen cyanide	74-90-8	2001	8, 14, 18	0.8	3	7	5	4	16
Flufenoxuron	101463-69-8	0	8, 18	0.00065	25000	5	9	2	16
4,5-Dichloro-2-octyl-2H-isothiazol-3-one (DCOIT)	64359-81-5	0	8, 21	0.034	13	6	6	3	15
Flocoumafen	90035-08-8	2003	14	0.07	36134	3	9	2	14
Difethialone	104653-34-1	2004	14	0.0044	40000	4	8	2	14
Cyfluthrin	68359-37-5	2009	18	0.001	854	5	8	1	14
Didecylmethylpoly(oxyethyl)ammonium Propionate (Bardap 26)	94667-33-1	0	2, 4, 8	1	81	7	3	3	13
Cybutryne (Irgarol)	28159-98-0	0	21	0.0058	250	4	7	2	13
Creosote	8001-58-9	0	8	0.1	5000	6	6	1	13
Dichlofluanid	1085-98-9	2003	8	0.053	72	6	6	1	13
d-Phenothrin	188023-86-1	0	3, 18	0.047	1213	4	6	2	12
3-Iodo-2-propynyl butyl carbamate (IPBC)	55406-53-6	0	6, 8	0.5	19	6	4	2	12
Chrysanthemum cinerariaefolium, Extract	8003-34-7	0	18	0.086	502	5	6	1	12
Transfluthrin	118712-89-3	0	18	0.0007	1861	4	7	1	12
Pyriproxyfen	95737-68-1	0	18	0.0005	581	3	7	1	11
Fipronil	120068-37-3	0	18	0.012	321	5	5	1	11
methylisothiocyanate (MITC)	556-61-6	2004	8	0.1	3	5	5	1	11
Naled	300-76-5	1976	18	0.0098	25	2	7	1	10
Margosa extract	84696-25-3	0	18	10	3	4	5	1	10
N,N-Dimethyl-N'-phenylsulfamide (DMSA)	4710-17-2	2003	8	200	3	6	3	1	10
Methyl nonyl ketone	112-12-9	0	19	0.23	979	5	3	1	9
Bendiocarb	22781-23-3	2003	18	0.088	6	3	5	1	9
Dazomet	533-74-4	2004	8		2	5	3	1	9

Ready biodegradability was not considered here to cover also substances which may be pseudo-persistent due to constant releases

Identification of relevant environmental compartments

Relevant for monitoring in aquatic biota?
relevant for all biocides with a score > 8 from the first two steps (emissions/effects) that are potentially released into waters

Direct releases into waters: for each relevant PT 1 score (max. score 5)

Indirect releases into waters: for each relevant PT 1 score (max. score 5)

BCF > 100

Biodegradability

readily biodegradable:	score 0
not readily biodegradable:	score 1
no data / not applicable:	score 1

Persistence assessment

P-criterion met:	score 1
vP-criterion met:	score 2
P-criterion not met:	score 0
no data / not applicable:	score 1

Ranking criterion for compounds: sum of all scores (from emission, effects and relevance for aquatic biota monitoring assessments)

Biocides (no current PPP) - relevant for monitoring in aquatic biota

		PPP		PNEC		SCORE	SCORE	SCORE	SCORE	SCORE
substance	CAS no.	registration until	PT	water µg/L	BCF fish	emission	effects	relevance water	biodegrad. / persistence	relevance biota monitoring
Methyltriclosan	4640-01-1	0	1,2,7,9	0.015	3600	8	5	5	2	20
Triclosan	3380-34-5	0	1,2,7,9	0.05	1500	8	4	5	2	19
Flufenoxuron	101463-69-8	0	8, 18	0.00065	25000	5	9	2	3	19
Flocoumafen	90035-08-8	2003	14	0.07	36134	3	9	2	3	17
Difethialone	104653-34-1	2004	14	0.0044	40000	4	8	2	3	17
Cyfluthrin	68359-37-5	2009	18	0.001	854	5	8	1	2	16
Creosote	8001-58-9	0	8	0.1	5000	6	6	1	2	15
Cybutryne (Irgarol)	28159-98-0	0	21	0.0058	250	4	7	2	2	15
Transfluthrin	118712-89-3	0	18	0.0007	1861	4	7	1	2	14
d-Phenothrin	188023-86-1	0	3, 18	0.047	1213	4	6	2	2	14
Chrysanthemum cinerariaefolium, Extract	8003-34-7	0	18	0.086	502	5	6	1	1	13
Fipronil	120068-37-3	0	18	0.012	321	5	5	1	2	13
Pyriproxyfen	95737-68-1	0	18	0.0005	581	3	7	1	1	12
Methyl nonyl ketone	112-12-9	0	19	0.23	979	5	3	1	1	10

Readily biodegradable biocides are here not considered

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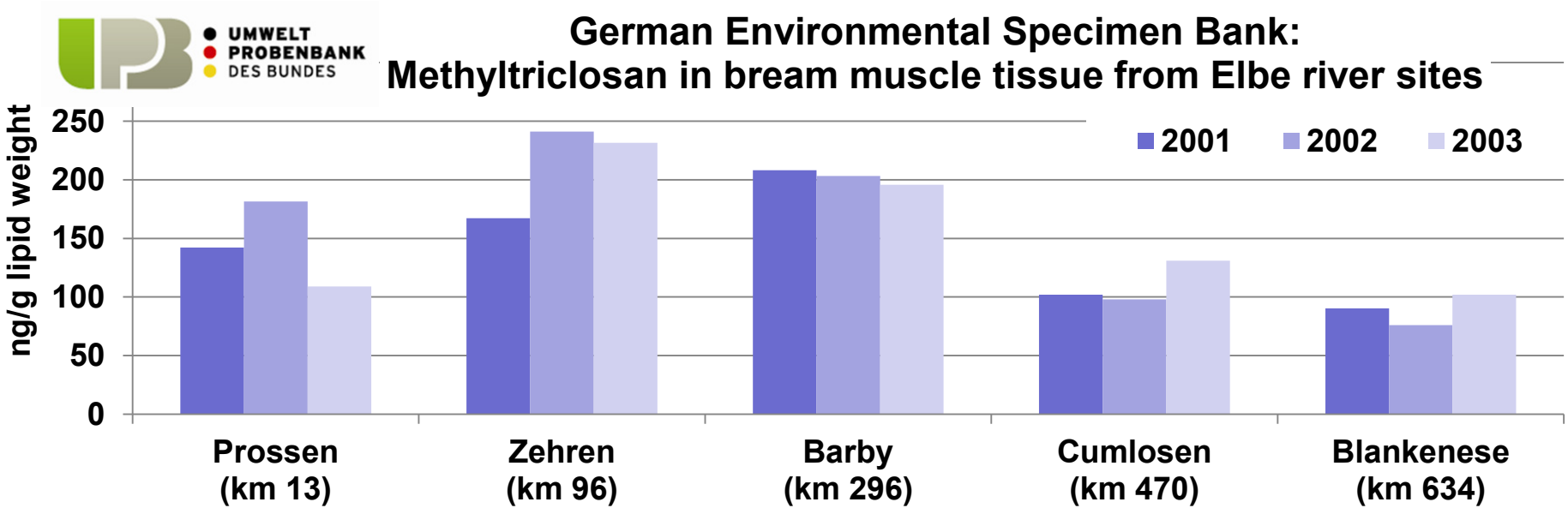
Discussion of the plausibility of the suggested scheme

Matching with monitoring data from the survey or literature reports

- **Triclosan is detected frequently in surface waters (von der Ohe et al. ESPR 2012) and also ranked high in the here generated list of prioritized compounds for the water compartment**
- **High scores for monitoring in biota received, e.g., flocoumafen (rodenticide, PBT classified) and methyltriclosan (triclosan transformation product). The latter result is also consistent with methyltriclosan fish monitoring data (Böhmer et al. OHC 2004):**



Discussion of the plausibility of the suggested scheme

Comparison with other prioritization approaches

- Bürgi et al. (UWSF 2009) identified ~ 20 candidate compounds for a biocide monitoring in surface waters including cybutryne/ Irgarol, dichlofluanid, IPBC, DCOIT which are also covered in our list; propiconazole, DEET were also identified, but not prioritized here
- Götz et al. (ESPR 2010) prioritized micro-contaminants for surface waters monitoring including triclosan and cybutryne/Irgarol which are also covered in our list
- Daginnus et al. (IJERPH 2011) identified compounds with a risk quotient PEC/PNEC > 1 for a monitoring in surface waters including the biocides dichlofluanid and terbutryne; dichlofluanid is also covered in the list generated here while terbutryne was not part of the test data set

Conclusions

- The suggested prioritization scheme allows the selection of biocides for an environmental monitoring. Necessary data are retrievable from the biocide EU Doc I assessment reports, from literature or by QSAR estimations
- So far the prioritization results seem to be consistent with other prioritization approaches and available monitoring data
- The prioritization scheme may be applied within a monitoring concept to follow changes induced by the BPD; however, the data base has to be broadened to cover all authorized biocides and all compounds currently under review for the BPD
- The prioritization scheme can also be adapted to other compartments: e.g., sediment, ground water, soil, sewage sludge, air
- To allow an assessment of the influence of BPD implementation the monitoring currently has to focus on compounds which are solely used as biocides (and not e.g. as plant protection products) to allow changes to be assigned unambiguously to biocide use

Acknowledgement

This study was funded by the Umweltbundesamt under contract no. FKZ 360 04 036 / UBA IV 1.2 – 81043/22

A German language report with English summary is available on request

Outlook

A new project funded by the Umweltbundesamt started in August 2012 (contract no. FKZ 3712 67 403):

Development of cornerstones for a monitoring program for the assessment of biocide emissions into the environment

Main work packages of the new project (2012 - 2015):

- **Compilation of biocide monitoring data from European countries**
- **Optimization and validation of the prioritization approach for biocides monitoring**
- **Planning and realization of a measurement program for selected biocides in, e.g., water, suspended particulate matter, sewage sludge: triclosan / methyltriclosan; irgarol and azole fungicides; rodenticides**

Outlook

This workshop co-organized by Umweltbundesamt and NORMAN shall serve as a kick-off to foster cooperation on biocide monitoring

- **exchange of knowledge and experiences between European countries**
- **joint activities on biocide monitoring including prioritization, sampling and analytical methods development and**
- **establishment of a common data base and data exchange structures (e.g., organized by NORMAN)**