Survey of biocide environmental monitoring data in Germany

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Structure

- **Survey of biocides monitoring in Germany**
  Questionnaire evaluation
- **Literature evaluation**
  Compilation of monitoring data
- **Evaluation of data from the survey and literature**
  Substances and matrices
- **Conclusions**

Source: ec.europa.eu/environment/biocides/index.htm

Status of biocides monitoring in Germany

- **Survey of biocides monitoring in Germany**

  Questionnaire evaluation

Source: ec.europa.eu/environment/biocides/index.htm

Status of biocides monitoring in Germany

- **In autumn 2011 a questionnaire was sent to ~ 75 persons and/or organizations in Germany;**
- **Additionally 8 departments of the Federal Environment Agency involved in monitoring activities were contacted**
- **~ 25 organizations responded and provided information from monitoring and projects (in some cases also reports and data files)**

Questionnaire Biocide Monitoring

1. Does your institution perform a **routinely biocide monitoring** or exist any **experience from projects**?
2. When did the monitoring start and what **period** is **covered**?
3. Which matrices are sampled?

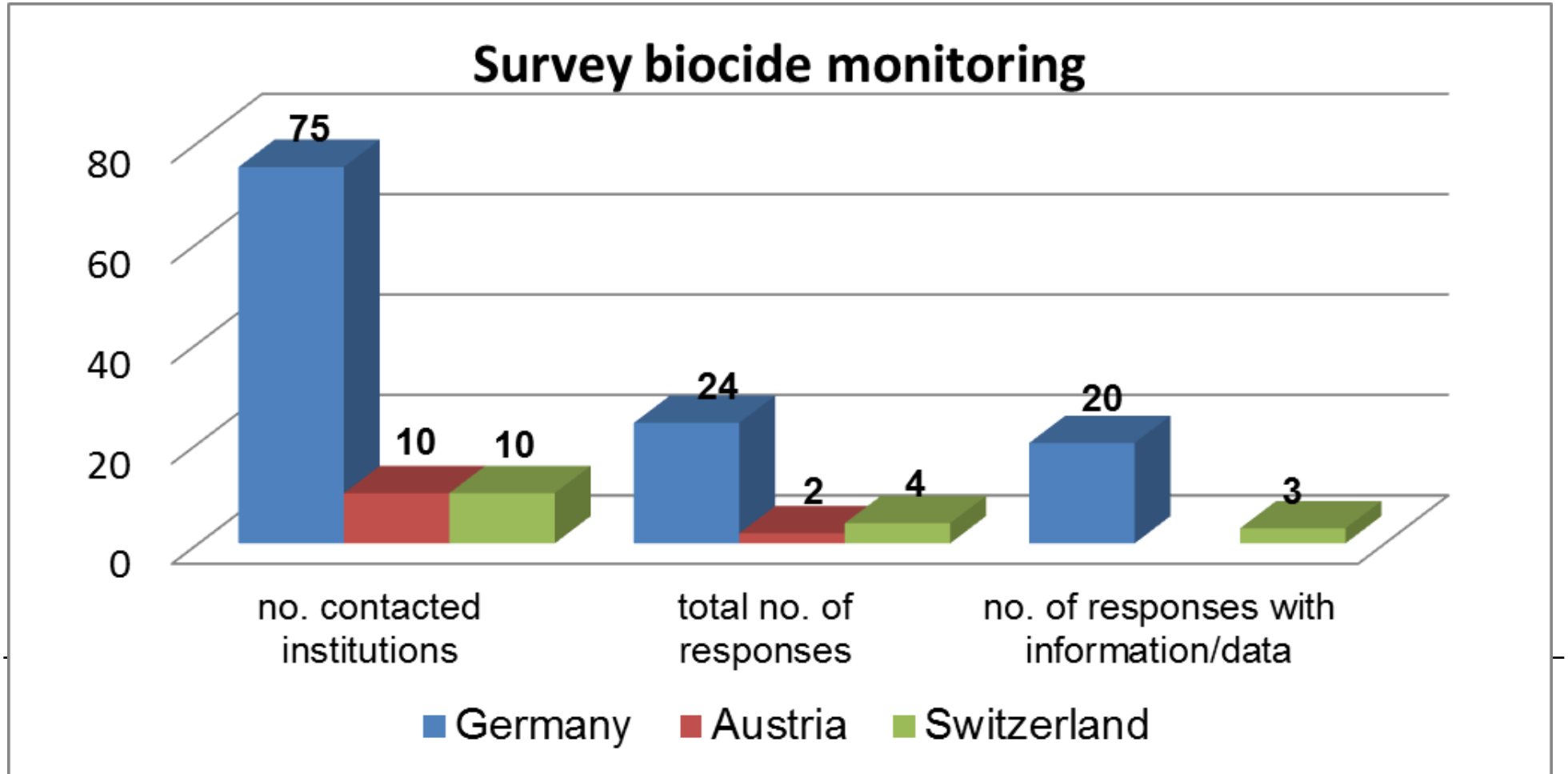
Matrix	**YES** (mark X)	**period (continued?)**	**substances covered**
surface waters			
suspended particulate matter (SPM)			
sediments			
aquatic organisms			
passive sampling devices (PSD)			
ground water			
Waste water (effluents of WWTP)			
sewage sludge			
manure			
soil			
terrestrial organisms			
air			
other matrices			

4. Which aspects were considered for the **selection of sampling sites**?
5. **How many sites** are sampled?
6. Are **data published** or available on request?

.....

Status of biocides monitoring in Germany

- **Response in Germany by about 1/3 of contacted institutions**
- **Some institutions in Austria and Switzerland were contacted, too**
- **Comprehensive data from Switzerland (not covered in this presentation, see other contributions to this workshop)**



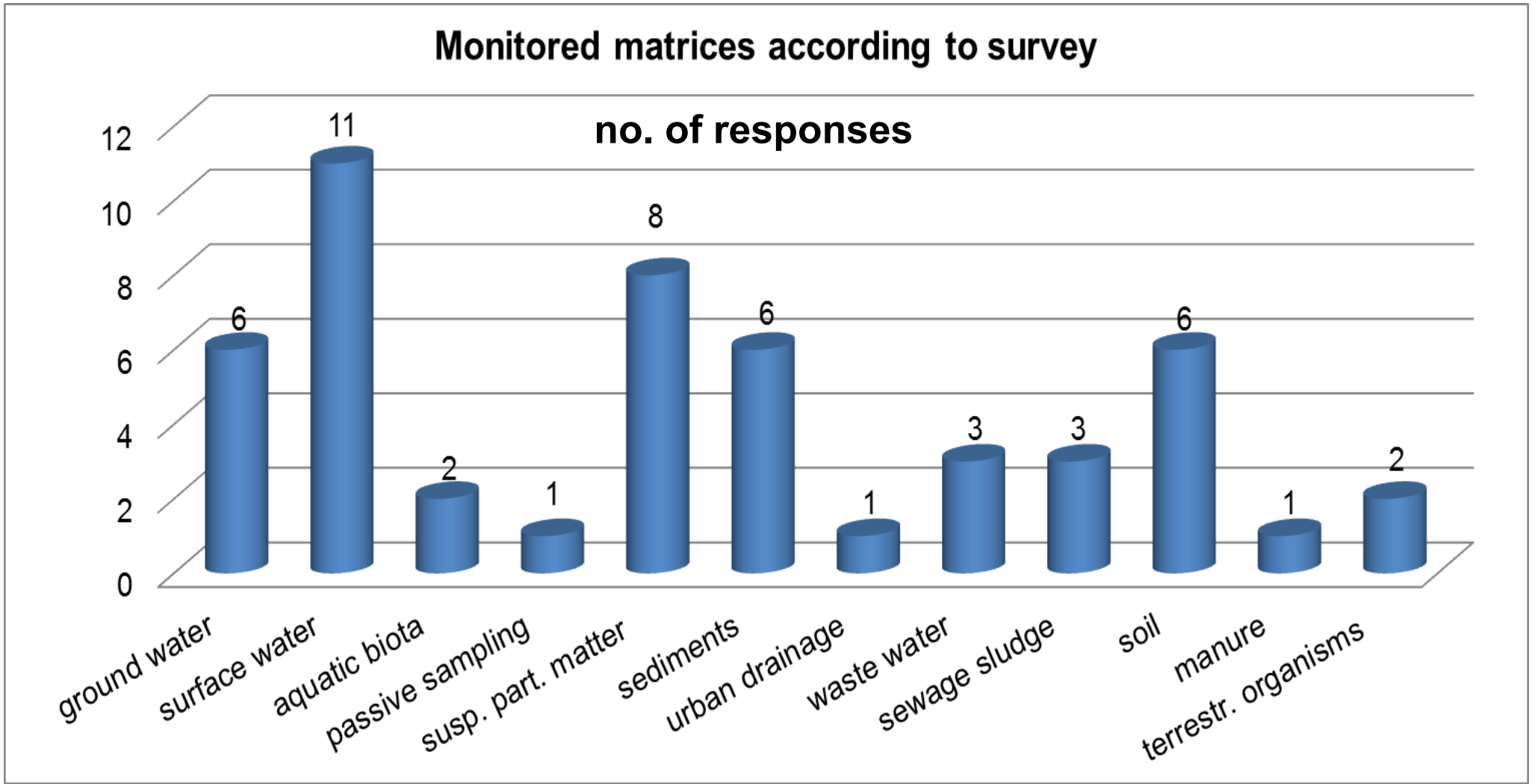
Status of biocides monitoring in Germany

- With the questionnaire a list of about 100 biocides were provided for which the addresses could tick whether these were monitored
- List comprised biocides monitored due to obligations (e.g., WFD) and compounds often used in biocidal products
- Further included: biocides also used as plant protection products (PPP)

List of potentially relevant biocides	CAS no.
German Surface Water Ordinance Annex 5	
Chlortoluron	15545-48-9
Dimethoate	60-51-5
Fenitrothion	122-14-5
Malathion	121-75-5
Phoxim	14816-18-3
Prometryn	7287-19-6
Propiconazole	60207-90-1
Terbuthylazine	5915-41-3
German Surface Water Ordinance Annex 7 / priority substances WFD	
Chlorpyrifos	2921-88-2
Diuron	330-54-1
Isoproturon	34123-59-6
Naphthalin	91-20-3
Tributylzinnverbindungen (als Kation)	36643-28-4
Biocides often used in products (information from Umweltbundesamt)	
5-Chlor-2-methyl-2H-isothiazol-3-on / 2-Methyl-2H-isothiazol-3-on	2682-20-4
Didecyldimethylammoniumchlorid	7173-51-5
2-Octyl-2H-isothiazol-3-on	26530-20-1
Quaternäre Ammoniumverbindungen, Benzyl-C12-16-alkyldimethylchloride	68424-85-1
Bronopol	52-51-7
3-Iod-2-propinylbutylcarbamat (IPBC)	55406-53-6
1,2-Benzisothiazol-3(2H)-on	2634-33-5

Status of biocides monitoring in Germany

- Most biocide investigations cover the aquatic environment
- Long-term monitoring of biocides is conducted mainly in surface water
- Only in some cases biota samples were investigated



Biocides in surface waters – response from 11 organizations

biocide (not PPP)
biocide, PPP until recently
biocide and PPP

		CAS no	LUNG	LUWG	LUBW	Berlin	LHW	LUG	NLWKN	LANUV	UBA	BfG	RWTH
1,2-Benzisothiazol-3(2H)-on		2634-33-5										X	
2-Octyl-2H-isothiazol-3-on		26530-20-1										X	
3-Iod-2-propinylbutyl-carbamat (IPBC)		55406-53-6										X	
4,5-Dichlor-2-octyl-2H-isothiazol-3-one		64359-81-5										X	
Acetamiprid		160430-64-8		X									
alpha-Cypermethrin		67375-30-8	X					X					
Bifenthrin		82657-04-3	X										
Biphenyl-2-ol		90-43-7			X								
Captan		133-06-2	X										
Carbendazim		10605-21-7	X	X								X	
Chlorpyrifos		2921-88-2	X	X	X	X	X	X	X	X			
Chlorthalonil		1897-45-6	X		X								
Chlortoluron		15545-48-9	X	X	X	X	X	X	X	X	X		
Clothianidin		210880-92-5		X									
Cyanamid		420-04-2										X	
Cyfluthrin		68359-37-5	X					X					
Cypermethrin		52315-07-8			X								
Cyproconazole		94361-06-5	X	X									
Deltamethrin		52918-63-5						X					
Dibutylzinnverbindungen (als Kation)		14488-53-0	X				X	X		X	X		
Dichlofluanid		1085-98-9								X			
Dimethoat		60-51-5	X	X	X	X	X	X	X	X	X		
Diuron		330-54-1	X	X	X	X	X	X	X	X	X	X	
Esfenvalerat		66230-04-4						X					
Etofenprox		80844-07-1	X					X					
Fenitrothion		122-14-5	X	X	X	X		X			X		
Fenoxycarb		72490-01-8	X	X									
Fenpropimorph		67564-91-4	X	X			X	X	X			X	
Flufenoxuron		101463-69-8	X										
Fluometuron		2164-17-2	X									X	

Biocides in surface waters – response from 11 organizations

biocide (not PPP)
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	CAS no	LUNG	LUWG	LUBW	Berlin	LHW	LUG	NLWKN	LANUV	UBA	BfG	RWTH
1,2-Benzisothiazol-3(2H)-on	2634-33-5										X	
2-Octyl-2H-isothiazol-3-on	26530-20-1										X	
3-Iod-2-propinylbutyl-carbamat (IPBC)	55406-53-6										X	
4,5-Dichlor-2-octyl-2H-isothiazol-3-one	64359-81-5										X	
Biphenyl-2-ol	90-43-7			X								
Chlorthalonil	1897-45-6	X		X								
Clothianidin	210880-92-5		X									
Cyanamid	420-04-2										X	
Cyfluthrin	68359-37-5	X					X					
Cypermethrin	52315-07-8			X								
Cyproconazole	94361-06-5	X	X									
Deltamethrin	52918-63-5						X					
Dibutylzinnverbindungen (als Kation)	14488-53-0	X				X	X		X	X		
Dichlofluanid	1085-98-9								X			
Diuron	330-54-1	X	X	X	X	X	X	X	X	X	X	
Fenitrothion	122-14-5	X	X	X	X		X			X		
Flufenoxuron	101463-69-8	X										
Fluometuron	2164-17-2	X									X	
Irgarol/Cybutryne	28159-98-0	X	X	X	X	X			X		X	
Malathion	121-75-5	X	X	X	X		X		X		X	
Monobutylzinnverbindungen (als Kation)	78763-54-9	X					X		X			
N,N-diethyl-m-toluamid (DEET)	134-62-3			X				X			X	
Naphthalin	91-20-3	X	X	X	X	X	X	X	X	X		
Phoxim	14816-18-3	X			X		X	X	X	X		
Terbutryn	886-50-0	X	X	X	X		X		X		X	
Tolylfluanid	731-27-1	X		X					X			
Tributylzinnverbindungen (als Kation)	36643-28-4	X			X	X	X	X	X			
Triclocarban	101-20-2										X	X
Triclosan	3380-34-5										X	

Biocides in sediment and/or SPM – response from 8 organizations

biocide (not PPP)
biocide, PPP until recently
biocide and PPP

		CAS no	LUWG	LUBW	Berlin	LUG	LANUV	UBA	BfG	RWTH
1,2-Benzisothiazol-3(2H)-one		2634-33-5							X	
2-Octyl-2H-isothiazol-3-one		26530-20-1							X	
3-Iod-2-propinylbutylcarbamat (IPBC)		55406-53-6							X	
4,5-Dichlor-2-octyl-2H-isothiazol-3-one		64359-81-5							X	
Carbendazim		10605-21-7							X	
Cyanamid		420-04-2							X	
Dibutylzinnverbindungen (als Kation)		14488-53-0	X	X	X	X	X	X	X	
Diuron		330-54-1					X		X	
Fenpropimorph		67564-91-4							X	
Fluometuron		2164-17-2							X	
Imazalil		35554-44-0							X	
Imidacloprid		138261-41-3							X	X
Indoxacarb		173584-44-6							X	
Irgarol/Cybutryne		28159-98-0							X	
Isoproturon		34123-59-6					X		X	
Malathion		121-75-5							X	
Monobutylzinnverbindungen (als Kation)		78763-54-9		X	X	X	X		X	
N,N-diethyl-m-toluamid (DEET)		134-62-3							X	
Naphthalin		91-20-3		X	X		X		X	
Prometryn		7287-19-6							X	
Propiconazol		60207-90-1							X	
Tebuconazol		107534-96-3							X	
Terbuthylazin		5915-41-3							X	
Terbutryn		886-50-0							X	
Thiabendazol		148-79-8							X	
Thiacloprid		111988-49-9							X	
Thiamethoxam		153719-23-4							X	
Tributylzinnverbindungen (als Kation)		36643-28-4		X	X	X	X	X	X	
Triclocarban		101-20-2							X	X
Triclosan		3380-34-5							X	

Biocides in sediment and/or SPM – response from 8 organizations

biocide (not PPP)
biocide, PPP until recently
biocide and PPP

Chemical		CAS no	LUWG	LUBW	Berlin	LUG	LANUV	UBA	BfG	RWTH
1,2-Benzisothiazol-3(2H)-one		2634-33-5							X	
2-Octyl-2H-isothiazol-3-one		26530-20-1							X	
3-Iod-2-propinylbutylcarbamat (IPBC)		55406-53-6							X	
4,5-Dichlor-2-octyl-2H-isothiazol-3-one		64359-81-5							X	
Cyanamid		420-04-2							X	
Dibutylzinnverbindungen (als Kation)		14488-53-0	X	X	X	X	X	X	X	
Diuron		330-54-1					X		X	
Fluometuron		2164-17-2							X	
Irgarol/Cybutryne		28159-98-0							X	
Malathion		121-75-5							X	
Monobutylzinnverbindungen (als Kation)		78763-54-9		X	X	X	X		X	
N,N-diethyl-m-toluamid (DEET)		134-62-3							X	
Naphthalin		91-20-3		X	X		X		X	
Terbutryn		886-50-0							X	
Tributylzinnverbindungen (als Kation)		36643-28-4		X	X	X	X	X	X	
Triclocarban		101-20-2							X	X
Triclosan		3380-34-5							X	

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Biocides in sewage sludge – response from 3 organizations

biocide (not PPP)
biocide, PPP until recently
biocide and PPP

Chemical	CAS no	BfG	RWTH	LUG
1,2-Benzisothiazol-3(2H)-one	2634-33-5	X		
2-Octyl-2H-isothiazol-3-one	26530-20-1	X		
3-Iod-2-propinylbutylcarbamat (IPBC)	55406-53-6	X		
4,5-Dichlor-2-octyl-2H-isothiazol-3-one	64359-81-5	X		
Carbendazim	10605-21-7	X		
Cyanamid	420-04-2	X		
Dibutyltin compounds (as cation)	14488-53-0			X
Diuron	330-54-1	X		
Fenpropimorph	67564-91-4	X		
Fluometuron	2164-17-2	X		
Imazalil	35554-44-0	X		
Imidacloprid	138261-41-3	X	X	
Indoxacarb	173584-44-6	X		
Irgarol/Cybutryne	28159-98-0	X		
Isoproturon	34123-59-6	X		
Malathion	121-75-5	X		
Monobutyltin compounds (as cation)	78763-54-9			X
N,N-diethyl-m-toluamid (DEET)	134-62-3	X		
Prometryn	7287-19-6	X		
Propiconazol	60207-90-1	X		
Tebuconazol	107534-96-3	X		
Terbuthylazin	5915-41-3	X		
Terbutryn	886-50-0	X		
Thiabendazol	148-79-8	X		
Thiacloprid	111988-49-9	X		
Thiamethoxam	153719-23-4	X		
Tributyltin compounds (as cation)	36643-28-4			X
Triclocarban	101-20-2	X	X	
Triclosan	3380-34-5	X		

Biocides in sewage sludge – response from 3 organizations

biocide (not PPP)
biocide, PPP until recently
biocide and PPP

Chemical	CAS no	BfG	RWTH	LUG
1,2-Benzisothiazol-3(2H)-one	2634-33-5	X		
2-Octyl-2H-isothiazol-3-one	26530-20-1	X		
3-Iod-2-propinylbutylcarbamat (IPBC)	55406-53-6	X		
4,5-Dichlor-2-octyl-2H-isothiazol-3-one	64359-81-5	X		
Cyanamid	420-04-2	X		
Dibutyltin compounds (as cation)	14488-53-0			X
Diuron	330-54-1	X		
Fluometuron	2164-17-2	X		
Irgarol/Cybutryne	28159-98-0	X		
Malathion	121-75-5	X		
Monobutyltin compounds (as cation)	78763-54-9			X
N,N-diethyl-m-toluamid (DEET)	134-62-3	X		
Terbutryn	886-50-0	X		
Tributyltin compounds (as cation)	36643-28-4			X
Triclocarban	101-20-2	X	X	
Triclosan	3380-34-5	X		

Status of biocides monitoring in Germany

- **Literature evaluation**

  Compilation of monitoring data

Source: ec.europa.eu/environment/biocides/index.htm

Literature search for biocide monitoring data from Germany

Information on monitoring data were already available from two studies:

- **Data compiled by Kahle and Nöh (2009), published as UBA-Texte 09/09 (German language)**
- **Gartiser et al. (2011), final report of an R&D-project funded by UBA**

Monitoring data from all retrieved monitoring studies were compiled

- **Due to limited project resources focus on detected compounds (therefore not representative), as basis for planning of future monitoring programs**
- **Aggregated monitoring data are summarized in a table in the final project report (status autumn 2011)**

Literature evaluation biocide monitoring data from Germany

Summary of literature search

- Data for about **60 biocides / metabolites / transformation products**
- About **35 papers and reports** (grey literature) were evaluated
- Data are **mainly from the period 1995-2010**, one retrospective study dating back to 1985

Stoff	CAS-Nr.	Wirkstoff-Status / PA	Matrix	Region	Zeit-raum	Angaben zu Konzentrationen		Quelle
Isoproturon§	34123-59-6	Review-Programm PA 7, 10	Oberflächen-wasser	Rheineinzugs-gebiet	2005-2007	An 3 Mess-stellen von 36 > Zielwert (> 0.1 µg/L)	0.11 - 0.31 µg/L	Umweltbundesamt 2010
Isoproturon§	34123-59-6	Review-Programm PA 7, 10	Oberflächen-wasser	Maaseinzugs-gebiet	2005-2007	An 1 Mess-stelle von 2 > Zielwert (> 0.1 µg/L)	0.16 µg/L	Umweltbundesamt 2010
Isoproturon§	34123-59-6	Review-Programm PA 7, 10	Oberflächen-wasser	Unterelbe	2000-2002	8,4 ng/L		Gerwinski 2002
Isoproturon§	34123-59-6	Review-Programm PA 7, 10	Oberflächen-wasser	Nord- und Ostsee	2000-2002	0,4 - 3,3 ng/L		Gerwinski 2002
Malathion§§	121-75-5	Nicht im Review-Programm	Oberflächen-wasser	Elbe, Ems, Weser, Aller	1994 - 2004	Max. Konz. 0,03 µg/L	1037 Messungen, 9 % > NG	Schäfer et al. 2011

Status of biocides monitoring in Germany

- **Evaluation of data from the survey and literature**

  Substances and matrices

Source: ec.europa.eu/environment/biocides/index.htm

Evaluation of reports from agencies (examples)

Detection of biocides in surface waters (> limit of quantification LOQ)

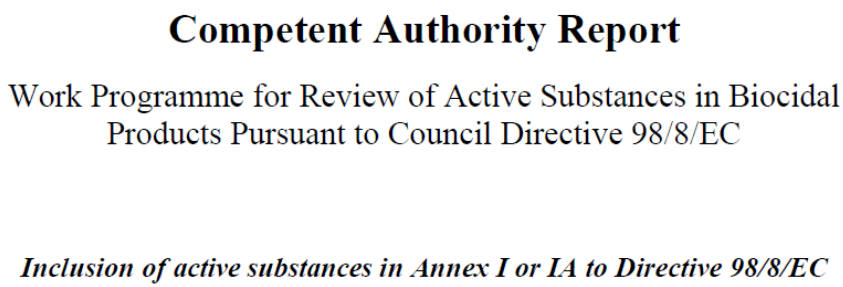
- **Federal Environment Agency (UBA) / Germany**
  - **In the period 2006 - 2008 exceedances of target value for drinking water production (0.1 µg/L) at some sites: chlortoluron, dimethoate, diuron, isoproturon, mecoprop, prometryne, simazine and terbuthylazine**
  - **In 2008 annual average concentrations of these compounds exceeded the WFD environmental quality standards (EQS) at some sampling sites: DDT, diuron, lindane, monolinuron and terbutryne**

- **LUWG / Rhineland-Palatinate**
  - **Data from the years 2008/2009 show values above LOQ for: chlortoluron, dimethoate, isoproturon, propiconazole, tebuconazole, terbuthylazine, terbutryne and others**

Status of biocides monitoring in Germany

Examples for biocide monitoring data for surface waters

- **clothianidin; fenpropimorph; imidacloprid; DEET; propiconazole; tebuconazole; thiabendazole; thiamethoxam were detected at concentrations below the predicted no effect concentrations (PNECs) (PNEC source: EU Doc I assessment reports)**
- **Substances with concentrations often above the PNECs were, e.g., triclosan (PNEC of 0.05 µg/L; Danish EPA 2003) and cybutryne (Irgarol; PNEC of 0.0058 µg/L; PNEC source: EU Doc I assessment report)**



Competent Authority Report

Work Programme for Review of Active Substances in Biocidal Products Pursuant to Council Directive 98/8/EC

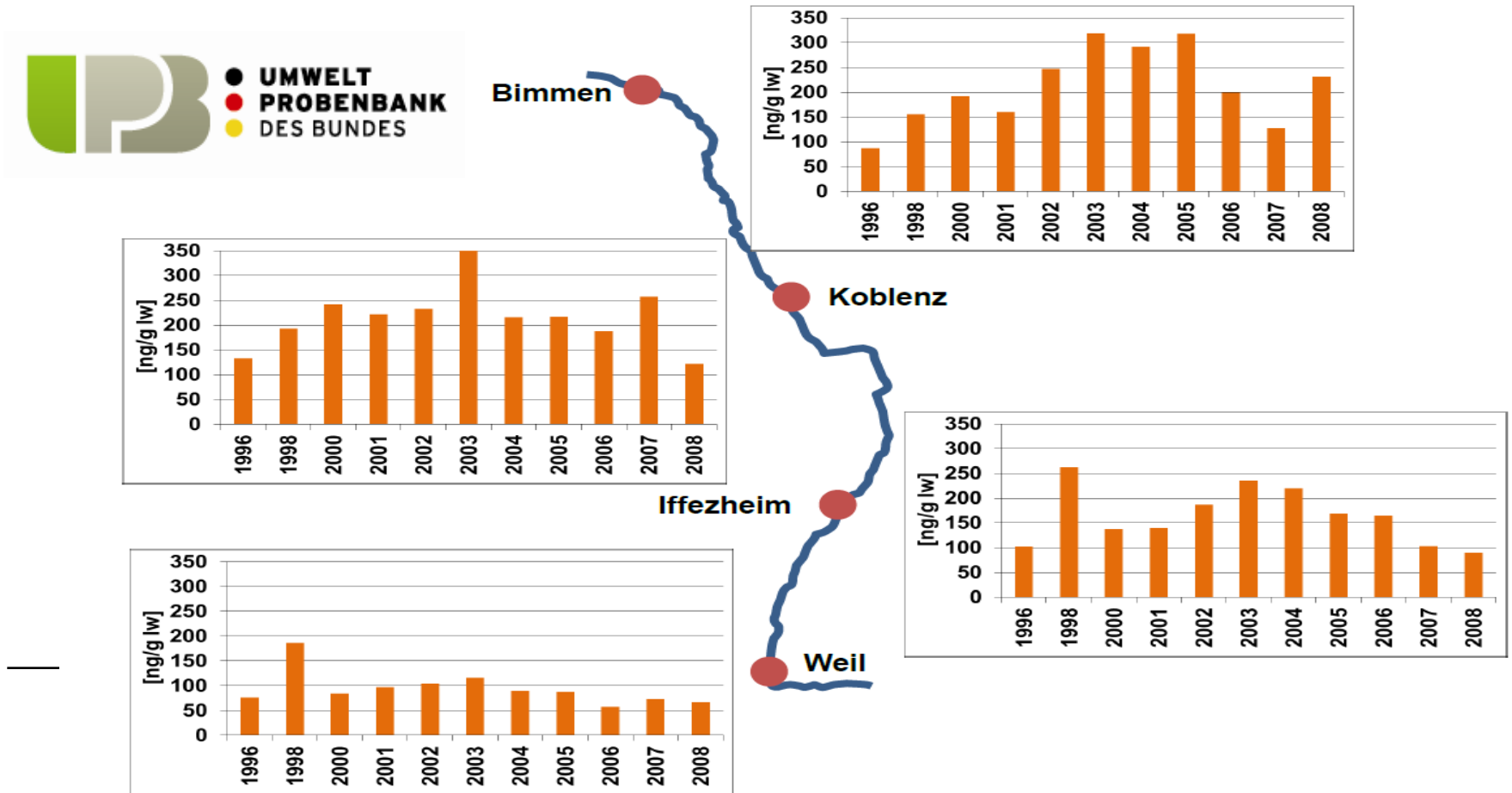
Inclusion of active substances in Annex I or IA to Directive 98/8/EC

DOCUMENT I

Example for biocide monitoring data for freshwater fish

One study covered triclosan and methyltriclosan (transformation product) - methyltriclosan levels exceeded those of triclosan and increased until about 2003-2005 (Böhmer et al. OHC 2004, Rüdel et al. 2012 submitted)

Methyltriclosan concentration time series for bream from German Rhine sites (muscle tissue, ng/g lipid weight)



Relevant matrices for monitoring (from survey and literature search)

Matrix	Relevant according to monitoring data	Detected biocides (> LOQ, examples)
surface water	XXX	carbendazim, diuron#, isoproturon, diazinon#, irgarol#, tebuconazole
susp. part. matter	X	TBT#
sediments	X	irgarol#, triclosan#, TBT#
aquatic organisms	X	triclosan# and methyltriclosan, clorophene#, TBT# and DBT/MBT
passiv sampling devices	-	pirimicarb§, tebuconazole§, diazinon#§§, diuron#§§, irgarol#§§, terbutryne#§§; triclosan#§§§
WWTP effluents	X	diuron#, thiabendazol, triclosan#
sewage sludge	X	clorophene#, imazalil
soil	X	diuron#, chlortoluron
terrestr. organisms	X	bromadiolone
ground water	XX	propiconazol, terbutryne#
atmosphere	-	-
manure	(X)	-
further matrices: compost, digestates	**(X)**	imazalil, thiabendazol, tebuconazole

X only single information/data, no systematic monitoring; XX data basis for several biocides; XXX broad data basis for many biocides, systematic monitoring

 # not (or no longer) used as PPP

Status of biocides monitoring in Germany

- **Conclusions**

Source: ec.europa.eu/environment/biocides/index.htm

Conclusions

- **In most programs no specific biocides monitoring is performed - biocides covered are mainly those which are also used as plant protection products (PPP)**

- **Monitoring covers mainly surface water (11 responses; up to 50 compounds investigated) - because of monitoring obligations by EU Water Framework Directive or German Surface Water Ordinance (OGewV)**

- **Other compartments are covered less intensively: sediments and suspended particulate matter > groundwater > soils > sewage sludge and sewage treatment plant effluents > biota**

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