How to implement a compartment-specific biocide monitoring under consideration of existing monitoring programmes

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Overview

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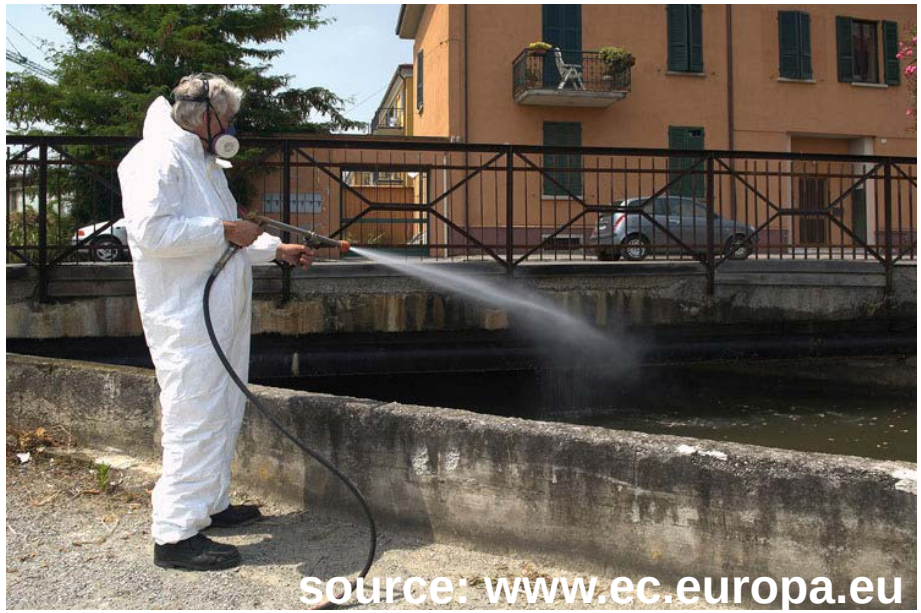
  Aims of a biocide monitoring

- **Current status of biocide monitoring in Germany**

  Are appropriate monitoring data already available?

- **Implementation of a biocide comprehensive monitoring programme**
  - **characterisation of monitoring approaches**
  - **examples for selected compartments**

- **Conclusions**



Aims of a biocide monitoring in Germany

- **The European Biocidal Product Directive (98/8/EC) and the Biocidal Product Regulation (No. 528/2012) cause changes of the use of biocides**
- **Consequently it is expected that environmental concentrations of biocides will change:**
  - **for (new) biocides included in the list of approved substances levels may increase**
  - **decreasing environmental levels are expected for substances for which non-approval decisions were taken or for which risk mitigation measures were implemented**
- **How to check such consequences?**
  One approach - implementation of an appropriate environmental monitoring
  - **to check whether the environmental levels of biocides are changing - temporal and spatial trends**
  - **to check whether biocide concentrations are above the derived no-effect levels (PNEC, environmental quality standards)**

Are appropriate biocide monitoring data already available?

- Can biocides monitoring data from existing monitoring programmes be used? Unfortunately biocides are often not appropriately covered
- Traditionally, e.g., in surface waters mainly plant protection products (partly also approved as biocides), compounds from industrial sources and legacy chemicals are monitored
- Monitoring of biocides in other media is marginal (e.g., in soil and air)
- However, there is some coverage of rodenticides - both from plant protection and biocide use - in raptors in some countries
- As a consequence of the scarce data the German Environment Agency (UBA) aims to develop a comprehensive monitoring concept for biocides
  - main purpose is to achieve a better coverage of biocides in existing monitoring programmes - no new monitoring programme
  - proposed monitoring activities should be organized in a stepwise approach – starting with research projects or screening studies, followed by surveys in selected regions, finally inclusion of relevant biocides in routine monitoring programmes

Categorisation of monitoring approaches

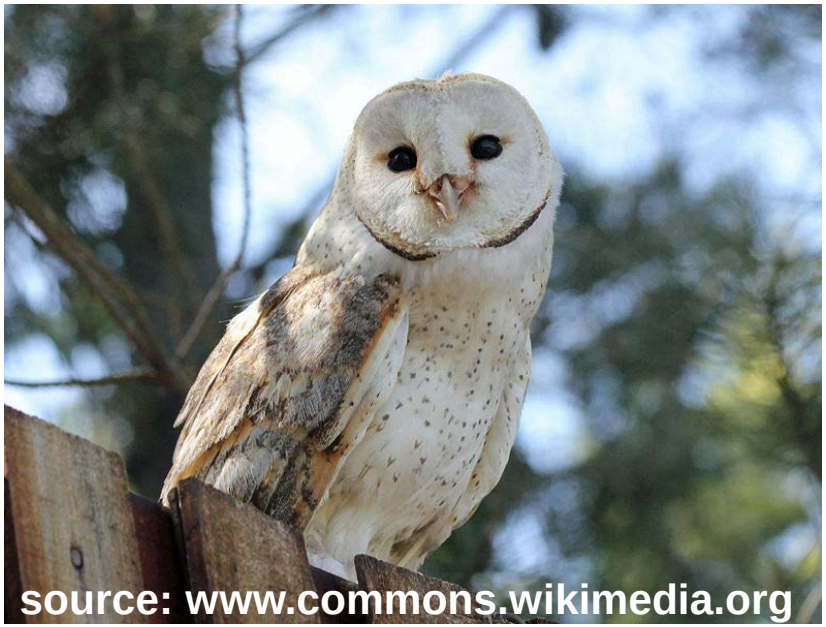
- **Research projects: special investigations on one or a few compounds at one or a few sampling sites; e.g., to characterize emission patterns**
- **Screening (or snapshot monitoring): analysis of one or more target compounds, one or a few sampling time points, local to regional scale - e.g., as feasibility study to test whether a target compound is consistently detectable in the selected compartment**
- **Survey: approach at one or a few sampling time points to get data on the concentrations of one or more target compounds in an environmental compartment at a regional to national scale; survey data should allow a conclusion on the relevance of the target compounds for the investigated compartment**
- **Routine monitoring: assumed to be performed on a national scale and covers ideally all relevant target compounds in an environmental compartment on a long-term basis (e.g., > 5 years); allows the detection of temporal trends and recognition of spatial patterns**

Categorisation of monitoring approaches

Monitoring approach	Number of compounds covered	Number of sampling sites	Number of sampling events
Research projects (short period)	1 – 3	1 – 3	1 – > 10
Screening (short period)	1 – 9	3 – 9	1 – 5
Survey (limited period)	1 – > 10	> 10	1 – 9
Routine monitoring (permanent)	All relevant compounds	Coverage of representative sites	Not limited; frequency: monthly – annually

Example 1: Approach for a monitoring of raptors in Germany (1)

- most rodenticides are (potentially) persistent, bioaccumulative, toxic (PBT)
- rodenticides taken up with prey may cause secondary poisoning of predators
- studies in the UK or Scandinavia demonstrate presence of second-generation anticoagulant rodenticides (SGARs) in raptors, e.g., Christensen et al. 2012, Walker et al. 2012, Hughes et al. 2013, Langford et al. 2013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Example 1: Approach for a monitoring of raptors in Germany (2)

Criterion	Specification	Comment
Matrix	Raptors	Raptor tissue (e.g., liver) or eggs
Relevant PTs and typical substances	PT 14 (rodenticides)	examples for detected PT 14 compounds: Brodifacoum, Bromadiolone, Difenacoum, Flocoumafen
Monitoring approach	Survey: opportunistic biota monitoring Screening: regional sampling	Sampling of raptors found dead Egg monitoring (non-destructive)
Scale of monitoring	Depends on availability of samples; in Germany, samples are only available for certain regions	Retrospective monitoring possible since appropriate samples are available in specimen banks
Relevant sites	Selection criteria: nearby potential biocide applications in near-natural environments	e.g., near farm buildings or in suburban areas

Example 1: Approach for a monitoring of raptors in Germany (3)

Criterion	Specification	Comment
Relevant monitoring programmes in Germany/Europe (examples)	1) Peregrine falcon egg monitoring (LUBW Karlsruhe; von der Trenck 2012) 2) Raptor specimen bank of dead found organisms (IZW Berlin) 3) Programmes, e.g., in UK, Norway, Denmark 4) EURAPMON network: www.eurapmon.net (overview)	In some programmes samples are only stored (specimen bank), but up to now no study on relevant rodenticides was performed Samples from IZW Berlin (Leibniz Institute for Zoo and Wildlife Research, Berlin, Dr. Oliver Krone) may be used in a cooperation project
Appropriate analytical methods	Available, e.g. Christensen et al. 2012, Hughes et al. 2013, Langford et al. 2013	Studies applied multi-methods covering most of the relevant rodenticides
Limits of detection (LOD) / Limits of quanti-fication (LOQ)	Walker et al. 2008: LODs were 0.045, 0.013, 0.002 and 0.050 µg/g wet weight for Bromadio-lone, Difenacoum, Flocoumafen and Brodifacoum	1 g of tissue was applied; for quantification an HPLC method with fluorescence detection was used
Availability of labelled standards	e.g., Bromadiolone-D5, Chloro-phacinone-D4, Warfarin-D5	in Germany, e.g., from Campro Scientific GmbH, Berlin

Example 2: Monitoring of suspended particulate matter / sediment (1)

- suspended particulate matter (SPM) and sediment are covered by the Water Framework Directive (WFD) monitoring in some EU member states
- SPM and sediment bind compounds by different mechanisms, both polar and non-polar compounds; polar compounds are not completely bound to SPM, but it can be assumed that the bound fraction at a certain site is fairly constant over time
- in some cases it may be appropriate to perform a retrospective monitoring (e.g., to allow evaluating the success of risk mitigation measures)
- the German Environmental Specimen Bank (ESB) programme is archiving SPM samples since about one decade
- while for a real-time monitoring of polar compounds the water phase would be appropriate, investigation of archived SPM allows also a retrospective monitoring

Example 2: Monitoring of suspended particulate matter / sediment (2)

Criterion	Specification	Comment
Matrix	Suspended particulate matter (SPM) and sediment	According to WFD requirements some compounds may be monitored also in SPM or sediments; SPM samples may be available from certain programmes
Relevant PTs and typical substances	PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 from direct inputs; PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19 from indirect inputs via STPs	Examples for detected compounds: organotin compounds (now banned antifouling compounds) are frequently detected in sediments; Triclosan (PT 1) and several quaternary ammonium compounds (QAC; PT 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13) were found in sediments/SPM
Monitoring approach	Screening or survey: SPM: e.g., monthly sampling with sedimentation traps Grab sampling for sediment Sampling of sediment cores	 Advantage: time-integrative sampling For surface sediment sampling Cores allow a dating of sediment burden

Example 2: Monitoring of suspended particulate matter / sediment (3)

Criterion	Specification	Comment
Scale of monitoring	National scale, coverage of all water bodies (rivers and lakes)	Parallel to WFD water phase monitoring
Relevant sites	SPM monitoring in larger rivers, sediment sampling in lakes	Sites in urban regions and those influenced by STP effluents; smaller rivers may not contain sufficient SPM
Relevant monitoring programmes in Germany/ Europe	WFD compliance monitoring (in Germany by federal states) German Environmental Specimen Bank (ESB)	In Germany measurement of some compounds in SPM is mandatory Archived samples allow a retro-spective monitoring
Appropriate sampling methods	A standard operating procedure for the sampling of SPM with traps is available from the German ESB (German language) Guidance on chemical monitoring of sediment and biota (EC 2010)	SPM is also sampled by several of the German federal states (e.g., at the Elbe river) Procedure according to WFD requirements

Example 2: Monitoring of suspended particulate matter / sediment (4)

Criterion	Specification	Comment
Appropriate analytical methods	GC or HPLC methods according to substance properties	see, e.g., Wick et al. (2010) for a HPLC multi-method for biocides
Limits of detection (LOD) / Limits of quantification (LOQ)	LOD for Triclosan and Methyl-triclosan in SPM: 0.1 ng/g dry weight LOD for Cybutryne (Irgarol), Tebuconazole and Propiconazole in SPM: 0.1 ng/g dry weight	Rüdel et al. (2013) Schulz (2013)#
Availability of labelled standard compounds	examples: Triclosan (ring-$^{13}C_{12}$, 99%), Methyltriclosan (ring-$^{13}C_{12}$, 99%), trans-Permethrin (phenoxy-$^{13}C_6$, 99%), cis-Permethrin (phenoxy-$^{13}C_6$, 99%)	standards available from, e.g., CIL, Inc. (in Germany via LGC Standards GmbH, Wesel)

see poster P08, Pohl et al.: Cybutryne and azole fungicides in SPM

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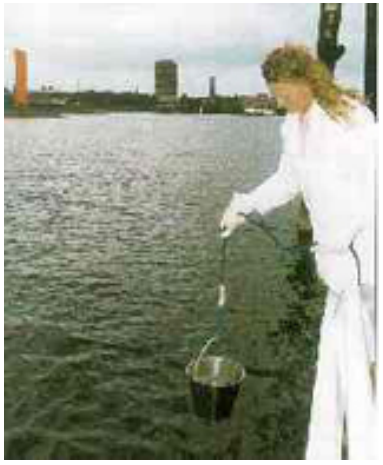
Example 3: Water phase monitoring (1)

- **the monitoring of the water phase of surface waters is well established in most European countries**

- **compliance monitoring is required by the Water Framework Directive (WFD; 2000/60/EC, EC 2000) and daughter directives (2008/105/EC and 2013/39/EU)**

- **for the WFD surface water monitoring a guidance document is available: Guidance on surface chemical water monitoring under the Water Framework Directive (EC 2009)**



Example 3: Water phase monitoring of biocides (2)

Criterion	Specification	Comment
Matrix	Water phase	according to WFD analysis of whole water phase for organic compounds required (i.e. unfiltered)
Relevant PTs and typical substances	PT 7, 8, 10, 11, 12, 14, 16, 18, 19, 21 from direct inputs; PT 1, 2, 3, 4, 7, 10, 11, 12, 18, 19 from indirect inputs via STPs	Examples for detected compounds: Triclocarban (EU non-approval decision, phase-out 2009); Triclosan (PT 1 until 2015 also authorized for PT 2, 7, 9) and transformation product Methyl-triclosan; Cybutryne/Irgarol (PT 21, until 2011 also authorized for PT 7, 9, 10); Diuron (PT 7, 10)
Monitoring approach	Routine monitoring of water bodies: e.g., monthly sampling (WFD surveillance monitoring)	Ideally pooled samples (e.g., weekly) are taken and combined to a monthly sample; this approach allows detecting substances with intermittent emission characteristics
	For biocides: focus on urban sites / certain time periods	To differentiate between plant protection product / biocide usage for dual use compounds

Example 3: Water phase monitoring of biocides (3)

Criterion	Specification	Comment
Scale of monitoring	National scale	Some biocides are already covered by monitoring obligations of the WFD (as amended in EU 2013) e.g., Cybutryne/Irgarol, Cypermethrin, Diuron, Isoproturon, Terbutryn
Relevant sites	Due to the varying emission patterns of the different PTs all kind of water bodies seem relevant	To monitor indirect inputs: sites in larger rivers which are influenced by effluents of STPs seem most relevant Measurements in smaller water bodies may be relevant if specifically exposed, e.g., potential exposure to biocides leached from façades which are transported via stormwater to water bodies
Relevant monitoring programs in Germany/ Europe	WFD compliance monitoring (in Germany performed by federal states)	Data from about 260 monitoring sites (LAWA) are reported to the EU commission Data from EU member state monitoring are available at the European Environment Agency (EEA) internet portal, data base “waterbase rivers”

Example 3: Water phase monitoring of biocides (4)

Criterion	Specification	Comment
Appropriate sampling methods	Guidance on surface water chemical monitoring (EC 2009) Guidance on sample preservation (ISO 5667-3 2012)	Procedures according to WFD requirements, application of national or international standards (e.g., for sampling and sample conservation)
Appropriate analytical methods	GC-MS or HPLC-MS methods according to substance properties	see, e.g., Wick et al. (2010) for a HPLC-MS multi-method for biocides
Limits of quantification (LOQ)	Largely varying depending on compound and applied analytical method	LOQ should be lower than PNEC / environmental quality standard (EQS); e.g., 30% of the EQS according to WFD daughter directive
Availability of labelled standard compounds	Triclocarban (4'-chlorophenyl-$^{13}C_6$, 99%); Isoproturon-D_6; Imazalil-D_5 (2-propenyl-D_5); Propiconazole-D_5, Tebuconazole-D_6, Irgarol-D_9	Especially for biocides which are also used as PPP labelled standards are available (e.g. from Sigma-Aldrich or Dr. Ehrenstorfer)

Proposal: implementation of a biocide monitoring programme (1)

- As a first step, relevant compartments were identified and relevant biocides prioritised; lists are provided to monitoring authorities

- For the better coverage of biocides in surface water monitoring, cooperation with the German federal states which operate the Water Framework Directive monitoring is recommended

- For soil monitoring, cooperation with federal states which operate permanent soil investigation sites is recommended; e.g., for investigating biocide input from liquid manure or sewage sludge

Proposal: implementation of a biocide monitoring programme (2)

- **To allow also a retrospective following of changes, the utilisation of samples from existing specimen banks is suggested:**
  - **archived biota samples - e.g., fish or raptor tissues - may be used to identify trends of non-polar biocides in aquatic and terrestrial compartments**
  - **for more polar compounds from freshwaters archived suspended particulate matter (SPM) from rivers may be analysed**

- **Special aspects may be investigated in a snapshot monitoring, e.g., antifouling biocides in marinas**

Conclusions (1)

- **The proposed biocide monitoring approach relies mainly on cooperation with existing programs**
- **Proposals to cover additional biocides should be supported by**
  - **basic information on the respective compounds - e.g., use pattern, estimated annual consumption, important properties;**
  - **data on effect concentrations in the respective compartment - e.g., PNEC for freshwater or soil organisms;**
  - **information on analytical methods available from assessment reports**
- **In some cases samples from environmental specimen banks may be useful; if an analytical method for the respective compound is available, the investigation can be conducted quickly - times series of archived samples can provide fast information on possible recent trends**

Conclusions (2)

- **The proposed monitoring activities should be organized in a stepwise approach - starting with research projects or screening studies, followed by surveys in selected regions, finally inclusion of relevant biocides in routine monitoring programmes**

- **The elaborated monitoring concept will be further discussed with the German Federal States**

- **In order to validate the monitoring concept further experimental investigations are planned**

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