Environmental Monitoring of Biocides – Cybutryne and Azole Fungicides in Suspended Particulate Matter Samples

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Introduction and Aim

❖ Data on applied amounts and emission rates of biocidal active substances to the environment is limited in Germany.
❖ Data from environmental monitoring campaigns which could exclusively be attributed to biocidal uses are rare.
❖ Consequently, the assessment of biocides in the context of the Biocidal Product Regulation (EU) No. 528/2012 (BPR) has started without any information regarding the actual situation of biocide emission into the environment.
❖ We are interested if the effects of the BPR are already observable (e.g. practicability of risk mitigation measures, exclusion, and substitution of active substances with very high concern (SVHC).
❖ The substance cybutryne is assumed to be an suspected endocrine disruptor and has been identified as a potential candidate for substitution according to the BPR (criteria for persistence and toxicity are fulfilled).
❖ The antifouling cybutryne (Irgarol) was banned as construction material preservative for façades and insulating material in 2011.
❖ An increase in use of other material preservative substances (e.g. tebuconazole, propiconazole) as substitutes for cybutryne was therefore expected.

→ The aim of this study was to investigate the occurrence of the biocides cybutryne, propiconazole and tebuconazole retrospectively by analyzing suspended particulate matter (SPM) samples.

Methodology

❖ The three substances were analyzed in SPM samples provided by the German Environmental Specimen Bank (ESB).
❖ SPM samples were collected monthly using passive sedimentation boxes permanently installed in surface waters.
❖ At the end of each year, samples were pooled to form one homogenate (see standard operating procedure from the ESB, 2012).
❖Samples were taken from six different sampling areas (the rivers Rhine, Elbe, Saar and Saale)
❖ All areas are assumed to be impacted by urban environments (e.g. emission of municipal waste water and storm water), whereas the influence of agricultural emission is expected to be rather secondary.
❖ For example, the sampling site Rehlingen documents the water status of the river Saar after passing the Saarland conurbation and how it is influenced by a sewage treatment plant.
❖ One further sampling site (Blankenese) is located downstream of the Hamburg port in the estuary of the river Elbe into the North Sea.
❖The analytical method based upon accelerated solvent extraction (ASE technique) in connection with a HPLC triple quadrupole system (HPLC-MS/MS).
❖ Samples covered a period of 6 years, starting in 2006.
❖ Average recovery rates of 85.5% ± 9.0% and 64.8 % ± 7.5% were obtained for propiconazole and tebuconazole; for cybutryne a lower recovery rate of 34.1% ± 6.2 was found.

Results and Discussion

❖ All three substances were detected at all sampling sites in the lower µg/kg range with a detection limit of 0.1 µg/kg.
❖ For cybutryne, concentrations were found between < 0.1-4.2 µg/kg, for propiconazole between 0.77-5.9 µg/kg and for tebuconazole between 0.51-5.7 µg/kg.
❖ From 2006 to 2012 cybutryne concentrations decreased significantly at the sampling sites of the rivers Saar (figure 1) and Rhine.
❖ No definite trends could be observed at the other sampling sites (table 1).
❖ In cases of propiconazole and tebuconazole, the amounts extracted from SPM samples decreased only at one sampling site of the river Rhine significantly during the observation period (see table 1).
❖ At most sampling sites no significant trend could be observed over time (figure 2).
❖ Concentrations of all three substances were higher in the year 2007 for the sampling site at the river Saale → This increase was assumed to be caused by floodwater occurrence in this year.
❖ The higher concentrations of cybutryne in SPM samples at the Elbe (Blankenese) in comparison to both azole fungicides (not shown) can be attributed to its use as antifouling coating.

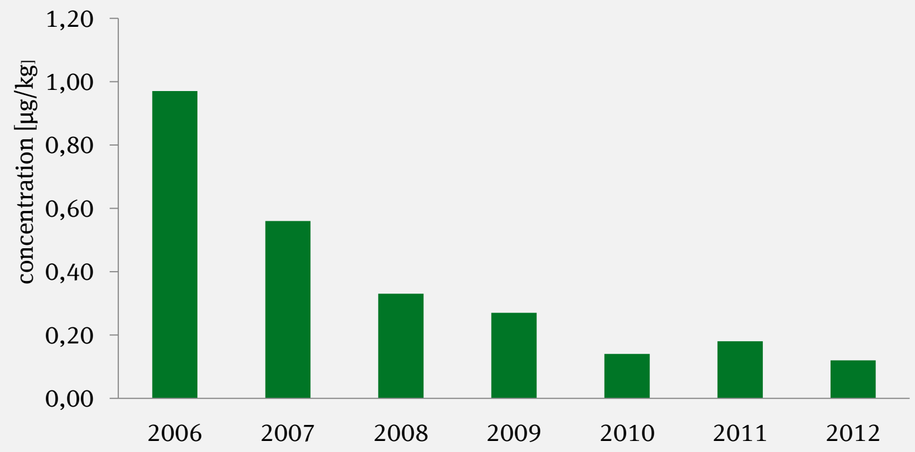

Figure 1: Significant decrease of the substance cybutryne at the sampling site Saar (Rehlingen) during the years 2006 and 2012

Table 1: Observed changes in cybutryne, propiconazole, and tebuconazole contaminations of SPM samples over a period of six years (2006-2012)

Sampling site	cybutryne [µg/kg]	cybutryne [%]	propiconazole [µg/kg]	propiconazole [%]	tebuconazole [µg/kg]	tebuconazole [%]
Saar /Rehlingen	-0.13	-91***	-0.02	-1	-0.02	-4
Rhine/ Koblenz	-0.09	-70***	-0.05	-18	-0.03	-19
Rhine/ Bimmen	-0.13	-56	-0.33	-71**	-0.30	-82**
Elbe/ Blankenese	-0.18	-42	-0.06	-22	+0.08	+68
Elbe/ Zehren	-0.02	-17	+0.04	+7	-0.02	+0.1
Saale/ Wettin	-0.31	-88	-0.28	-0.3	-0.31	-42

*** significance level p < 0.01; ** significance level p < 0.05

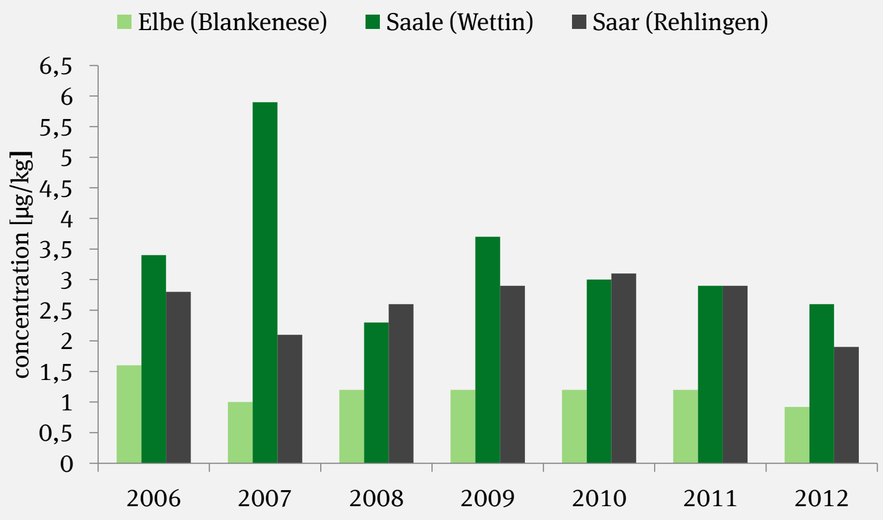

Figure 2: Contamination of SPM samples with propiconazole over time at three different sampling sites (rivers Elbe, Saale and Saar)

Conclusion and Outlook

❖ A trend of decreasing concentrations of cybutryne (Irgarol) was observed over the time period → First effects of substitutions of active ingredients?
❖ Expected increase of azole fungicides concentration could not be confirmed.
❖ Further investigations over a longer period are necessary to confirm possible effects of substance exclusions and substitutions.
❖ Additional consideration of further environmental matrices (e.g. sediment, biota) may be reasonable.

This study is part of a Research and Development Project (F&E) of the Federal Environment Agency (UBA) aiming at the *"Validation of a prioritisation concept for biocides and development of a monitoring programme for biocides in Germany"*. Final results of this project with further experimental studies, will be available at the end of the year.

(Reference: Volker Schulz, 2013. Time-related concentration levels of the biocide cybutryn and the azole fungicides propiconazole and tebuconazole in suspended matter of the German Environmental Specimen Bank)

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