

RETROSPECTIVE MONITORING OF METHYLTRICLOSAN IN FRESHWATER FISH COVERING THE PERIOD 1994 - 2008

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INTRODUCTION

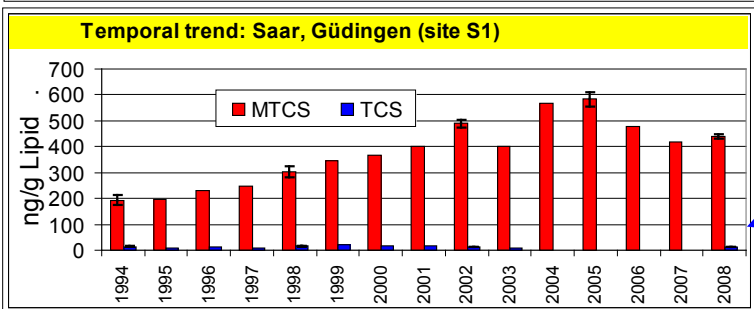
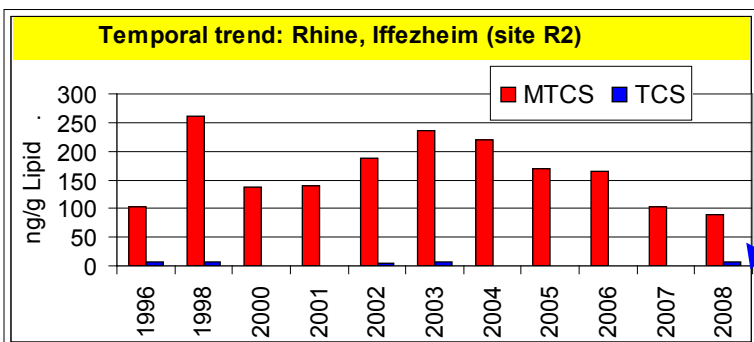
During the last years there were several reports on the appearance of the biocide triclosan (TCS) and methyl-triclosan (MTCS), a transformation product of TCS, in the environment. TCS is used in numerous personal care products like toothpaste and soaps, but also in textiles and shoes. The current annual consumption in Germany is estimated to be 40 t (0.5 g per capita and year). In order to investigate the exposure of aquatic organisms towards TCS and MTCS in Germany a retrospective monitoring of breams from representative rivers was initiated. Samples from the period 1994 to 2003 (1st study) and 2004 to 2008 (2nd study; TCS only analyzed in 2008) were taken from the archive of the German Environmental Specimen Bank (ESB) to evaluate temporal changes and regional differences of the occurrence of TCS and MTCS.

ORIGIN OF FISH

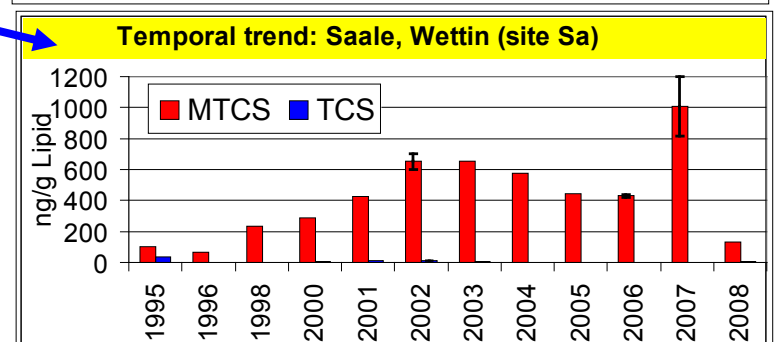
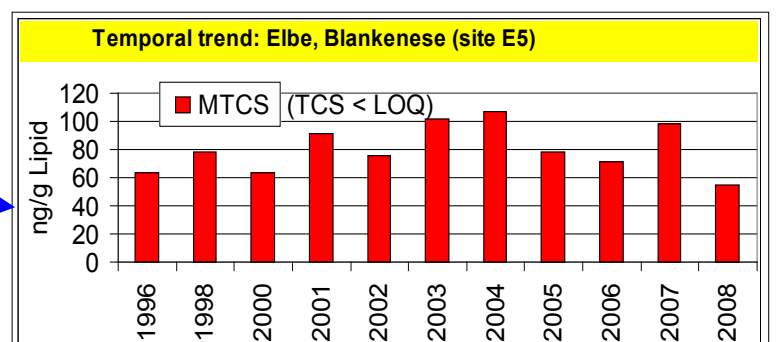
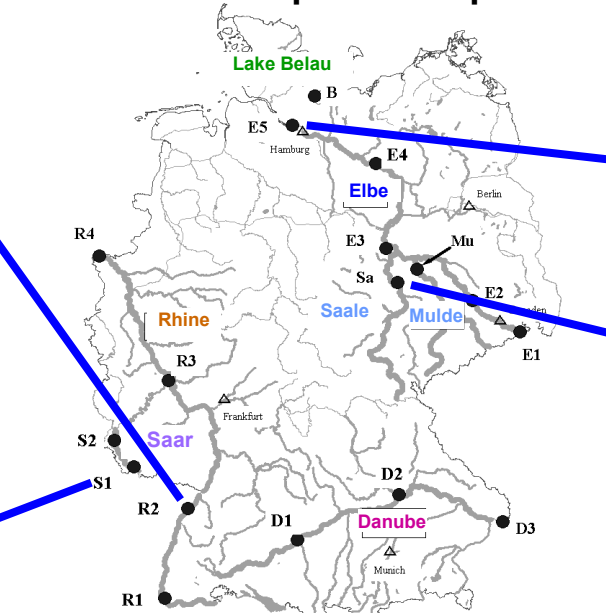
In the framework of the German ESB bream (*Abramis brama*) are sampled annually from 16 sampling sites in German rivers and one lake site (see map below). Both, muscles and livers are archived as pooled annual samples (20 - 40 individuals; [UBA 1996, Klein et al. 2003]). For this study archived bream muscle samples were retrieved.



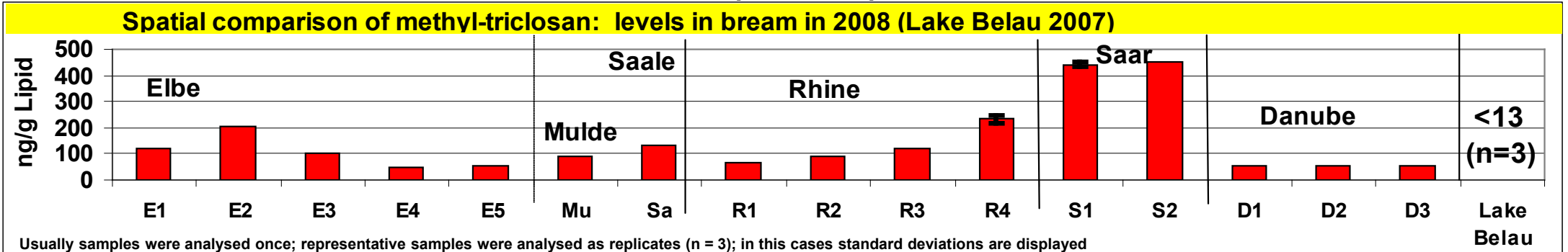
The authors acknowledge the excellent work of the ESB team of the Institute of Biogeography of the University of Trier which is responsible for the biota sampling.



RESULTS: Temporal comparison



RESULTS spatial comparison



PROPERTIES OF TARGET COMPOUNDS

- TCS:** 5-chloro-2-(2,4-dichlorophenoxy)phenol (CAS No. 3380-34-5); log Pow 4.8, photodegradable, water solubility 10 - 17 mg/L, PNEC for aquatic organisms 50 ng/L
- MTCS:** 5-chloro-2-(2,4-dichlorophenoxy)anisole (CAS No. 4640-01-1); log Pow 5.22, persistent in water, solubility 0.2 - 0.7 mg/L, estimated PNEC for aquatic organisms 15 ng/L

MATERIALS AND METHODS

- Details of the method are published elsewhere [Böhmer et al. 2004].
- 1 - 2.5 g of frozen and grinded ESB sample is mixed with sodium sulfate (ratio 1:6, w/w)
- Accelerated Solvent Extraction (ASE, Dionex) with cyclohexane (100°C, 14 MPa)
- Clean-up by gel permeation chromatography on Bio-Beads S-X3
- Clean-up on an activated silica gel column
- Non-polar fraction containing MTCS eluted with n-hexane was analyzed directly with a Finnigan MAT Magnum GC/MS/MS
- Polar fraction containing TCS and CP was derivatized with PFBB (2,3,4,5,6-pentafluorobenzylbromide) and analyzed by GC/MS with negative chemical ionization with an Agilent quadrupol 5973 MSD)
- For quantification, TCS (from Ehrenstorfer, Augsburg) and MTCS (from VeZerf Labor-synthesen, Idar-Oberstein) were used. ¹³C₆-TCS (provided by CIBA, Basel) and MTCS-D₃ (from Syntheselabor Dr. Weiss, Stahnsdorf) were used as internal standards.
- Limit of quantification (LOQ) for TCS/MTCS: 0.2 - 0.3 ng/g wet weight corresponding to about 3 - 60 ng/g lipid weight (depending on fat content of the fish)
- Estimated expanded measurement uncertainty: 12 % for MTCS and 26 % for TCS.

CONCLUSIONS

- Triclosan levels in bream from German rivers were in the range **< 0.2 - 3.4 ng/g wet weight**. No temporal trends could be identified
- Methyl-triclosan levels in bream muscles were in the range **< 13 - 1200 ng/g lipid weight**. In most rivers increasing trends were detected until about 2003/2005; afterwards concentrations stayed constant or even decreased (e.g. Rhine, site Iffezheim R2)
- Highest methyl-triclosan levels were detected for bream from both river Saar sites and single sites in rivers Rhine and Elbe (R4, E2); **no contamination was found for fish from reference site Lake Belau**
- The recent decrease of MTCS fish levels is probably a result of a **voluntary renunciation of the use of TCS in washing and cleaning agents by the member companies of the German Cosmetic, Toiletry, Perfumery and Detergent Association (IKW) as announced in 2001**

REFERENCES

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Information on the German ESB is available via the internet at www.umweltprobenbank.de. At this web-site also standard operating procedures (SOPs) for ESB working steps can be retrieved. Moreover, research reports and monitoring data are accessible.



Currently the archive of the German ESB contains more than **1,400 different samples** (approx. 230,000 sub-samples). Specimens are now **available for retrospective analysis of all kind of target compounds**.