

Monitoring of selected biocides – experiences from Bavaria

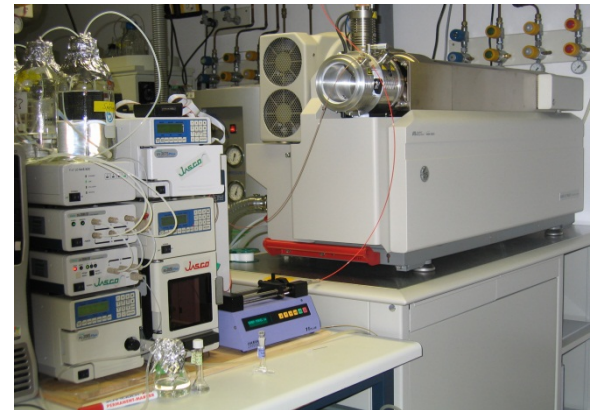
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Workshop on biocides, Berlin 05.11.2012

Outline

- introduction
- cybutryne
- triclosan and triclosan-methyl
- biocides also used as pesticides
- conclusions



Monitoring activities in Bavaria

- **no** systematic approach for biocides
- in general: surveillance monitoring according to WFD, regional monitoring programmes
- monitoring of selected biocides dependent on analytical possibilities
- cybutryne in water, triclosan and triclosan-methyl in water, suspended solids and biota
- some data for tin-organic compounds

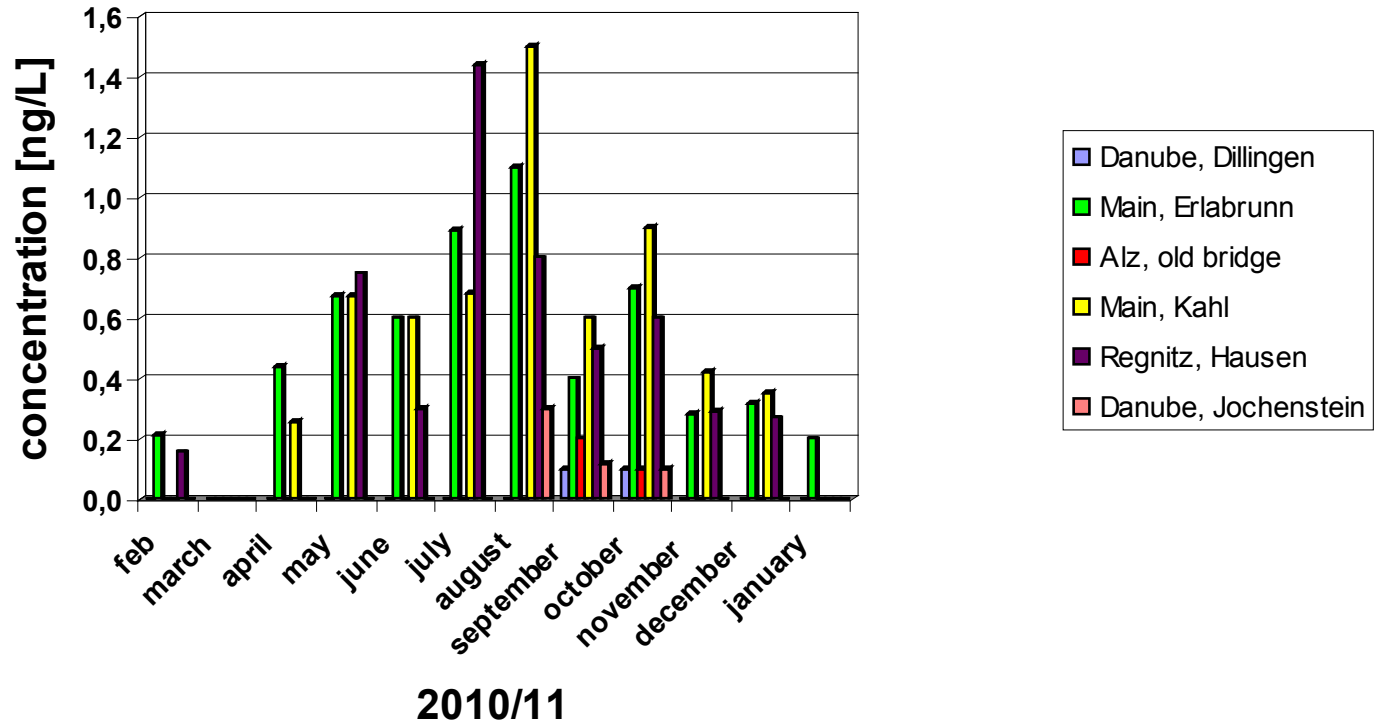
- monitoring for biocides also used as pesticides
 - lots of data in surface and ground waters
 - some data collected for compliance with former directive 76/464/EC

Cybutryne

- anti-fouling agent for boats, also other applications
- substitute for tributyl-tin since the 80ies
- risk assessment: inhibits photosynthesis, very toxic to aquatic macrophytes and algae
- UBA (Berlin) mesocosm study (e.g. effects on biomass growth – EC_{10} - at concentrations $\geq 0,06 \mu\text{g/l}$) and collection of monitoring data in Germany (inland waters)
- cybutryne is a candidate for the new list of WFD priority substances; proposed AA-EQS $0,0025 \mu\text{g/l}$ and MAC-EQS $0,016 \mu\text{g/l}$ for inland waters
- data in Bavaria:
 - 2010/11 monitoring campaign in large rivers
 - 2012 monitoring campaign in small river

Monthly analysis for selected bigger rivers 2010/11

cybutryne in Bavarian rivers



Cybutryne - analysis of smaller rivers 2012

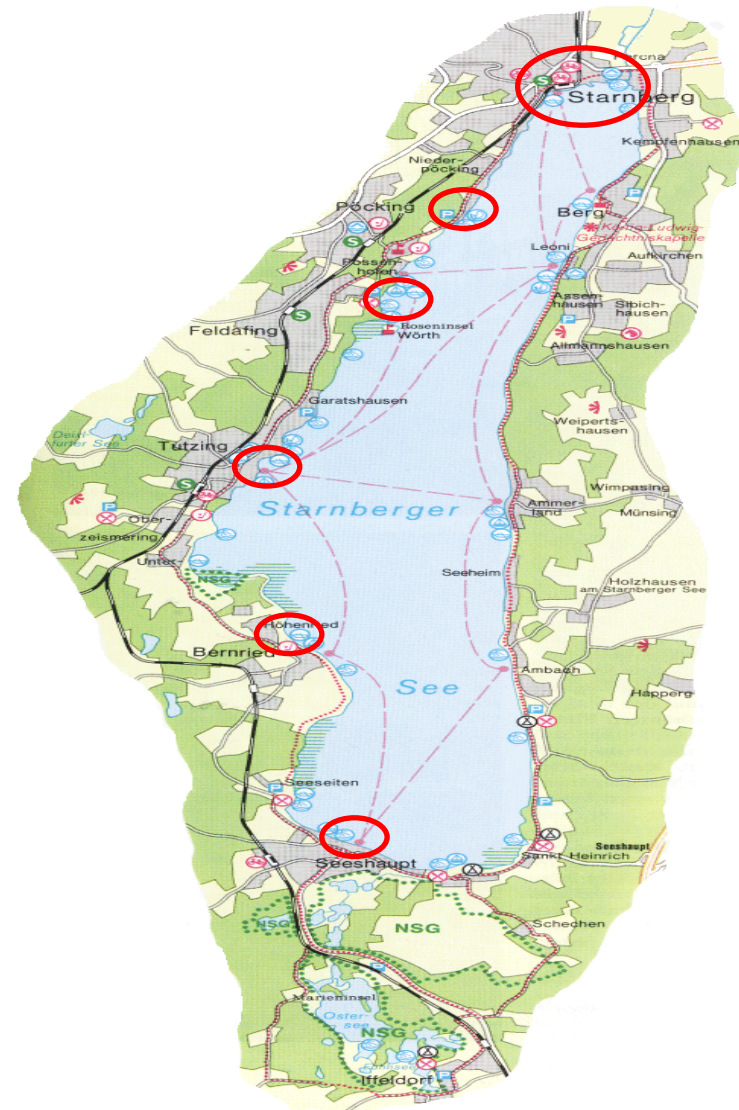
river	number of samples	positive results	min (ng/L)	max (ng/L)
Bibert	13	5	nd	0,4
Eger	11	5	nd	<0,4
Große Laber	19	17	nd	1,3
Pfatter	11	11	<0,4	0,5
Rott	11	4	nd	<0,4
Sächsische Saale	12	7	nd	0,5
Vils	11	5	nd	<0,4
Schulmühlbach	12	0	nd	nd

Cybutryne in Lake Starnberg

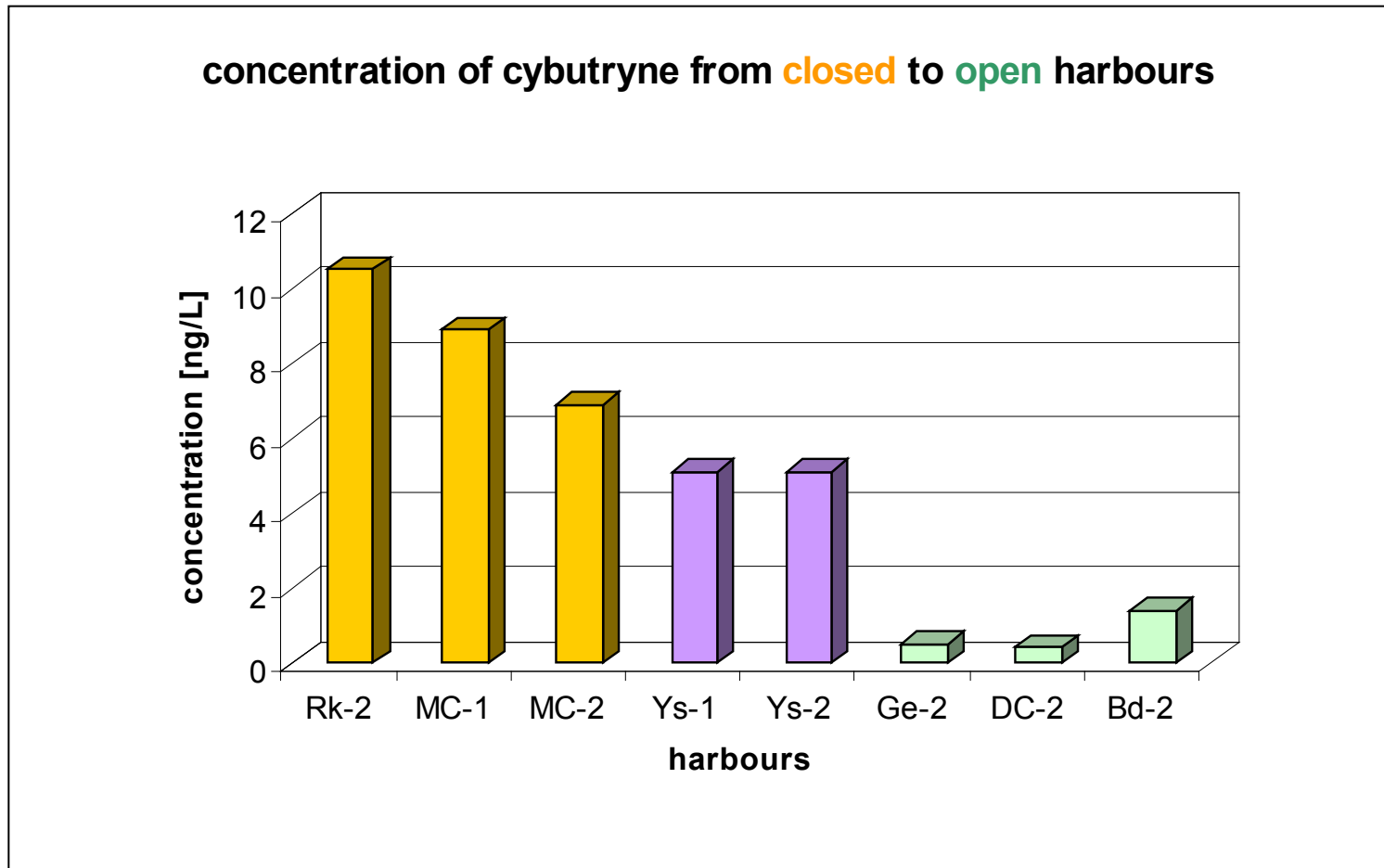
- sampling of 6 harbours in March, May and September 2010 (project in cooperation with TU Munich)

possible impacts:

- sampling close to contaminated slipping facilities
- number of boats in harbour
- intensity of boat-usage differs during the year
- type of harbour (close, open to lake)

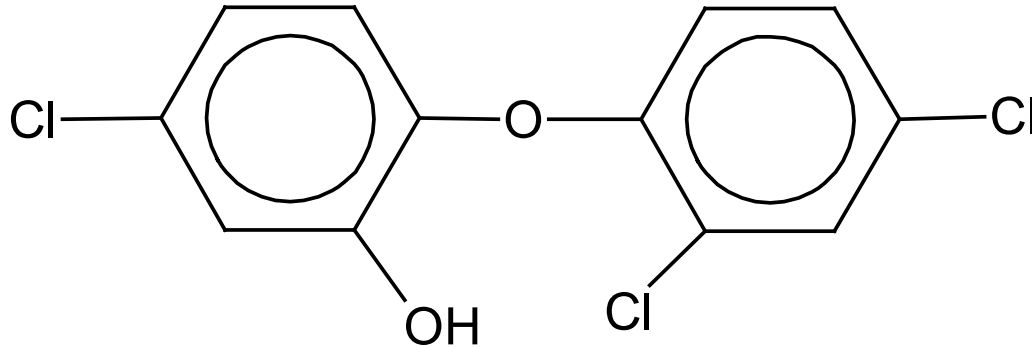


Mean concentrations in harbours at Lake Starnberg



analysis of sediments in 2011 in harbours: up to 120 µg/kg dry mass

Triclosan (5-Chlor-2-(2-4-dichlorophenoxy)phenole



O-CH₃

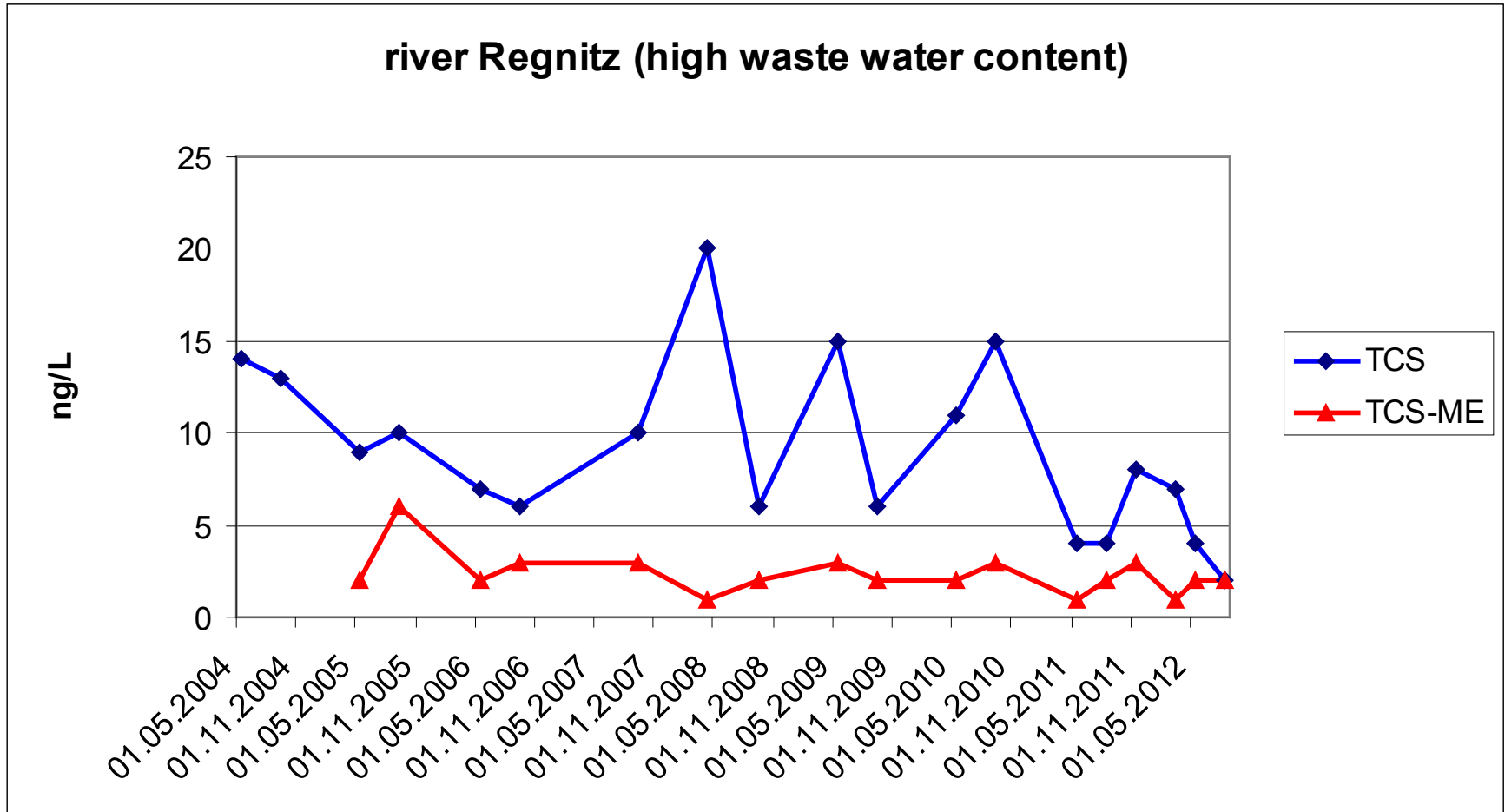
triclosan-methyl (metabolite)

available data:

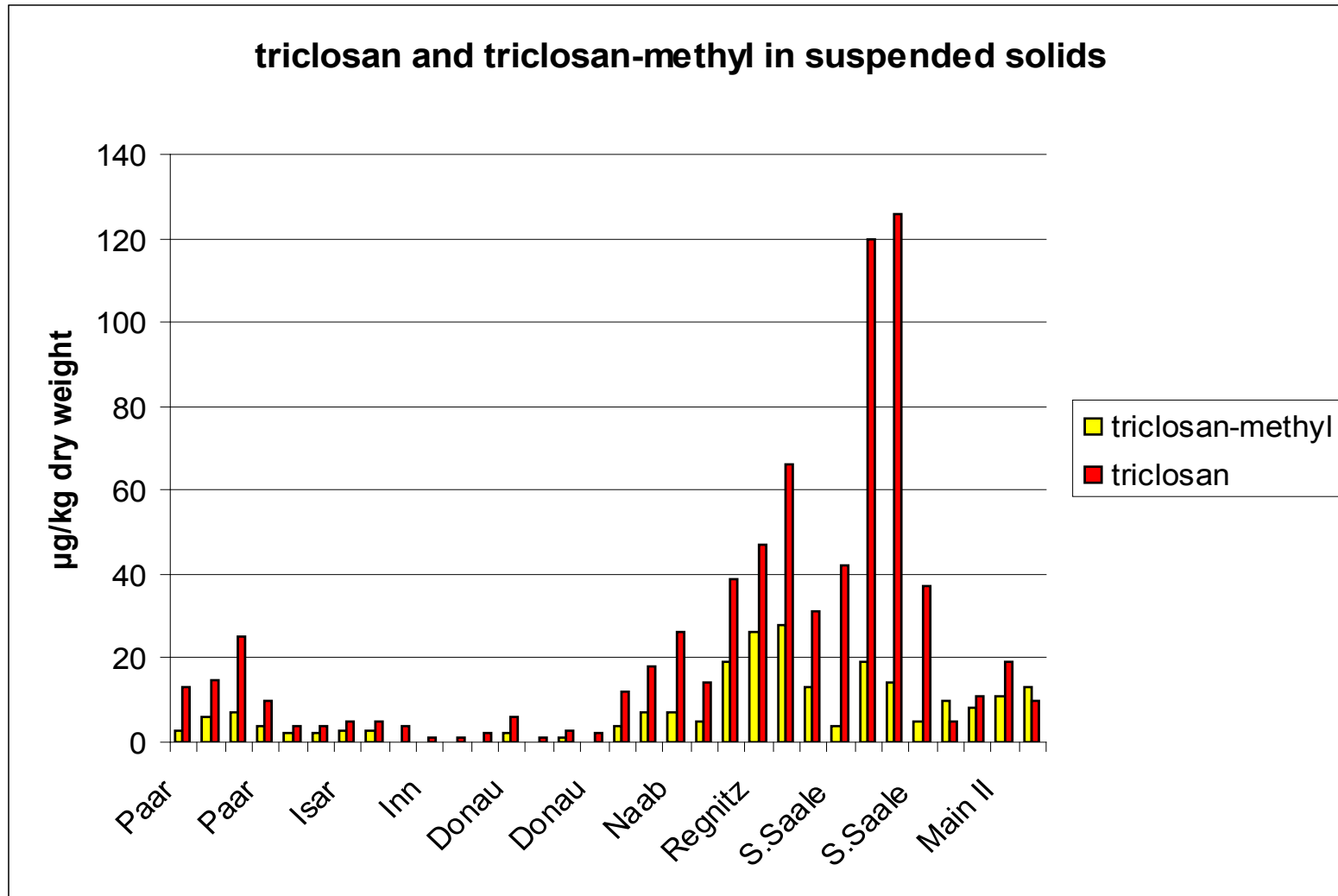
surface waters and suspended solids

biota: wild fish, carps from bioaccumulation ponds, mussels

Triclosan and triclosan-methyl in river waters (whole sample)



Suspended solids (sampling with centrifuge 2011/12)



Triclosan-methyl in biota

type of samples	n	year	min (µg/kg fw)	max (µg/kg fw)	median (µg/kg fw)
carps (muscle) from bioaccumulation ponds at WWTP	27	2003	< 1	90	15
fish (muscle) from Bavarian Rivers (different species)	55	2003	< 1	34	2
fish (muscle) from Bavarian Rivers (different species)	48	2004	<1	12	3
mussels (dreissena polymorpha) - active monitoring in Bavarian rivers	24	2003/04	<1	25	5

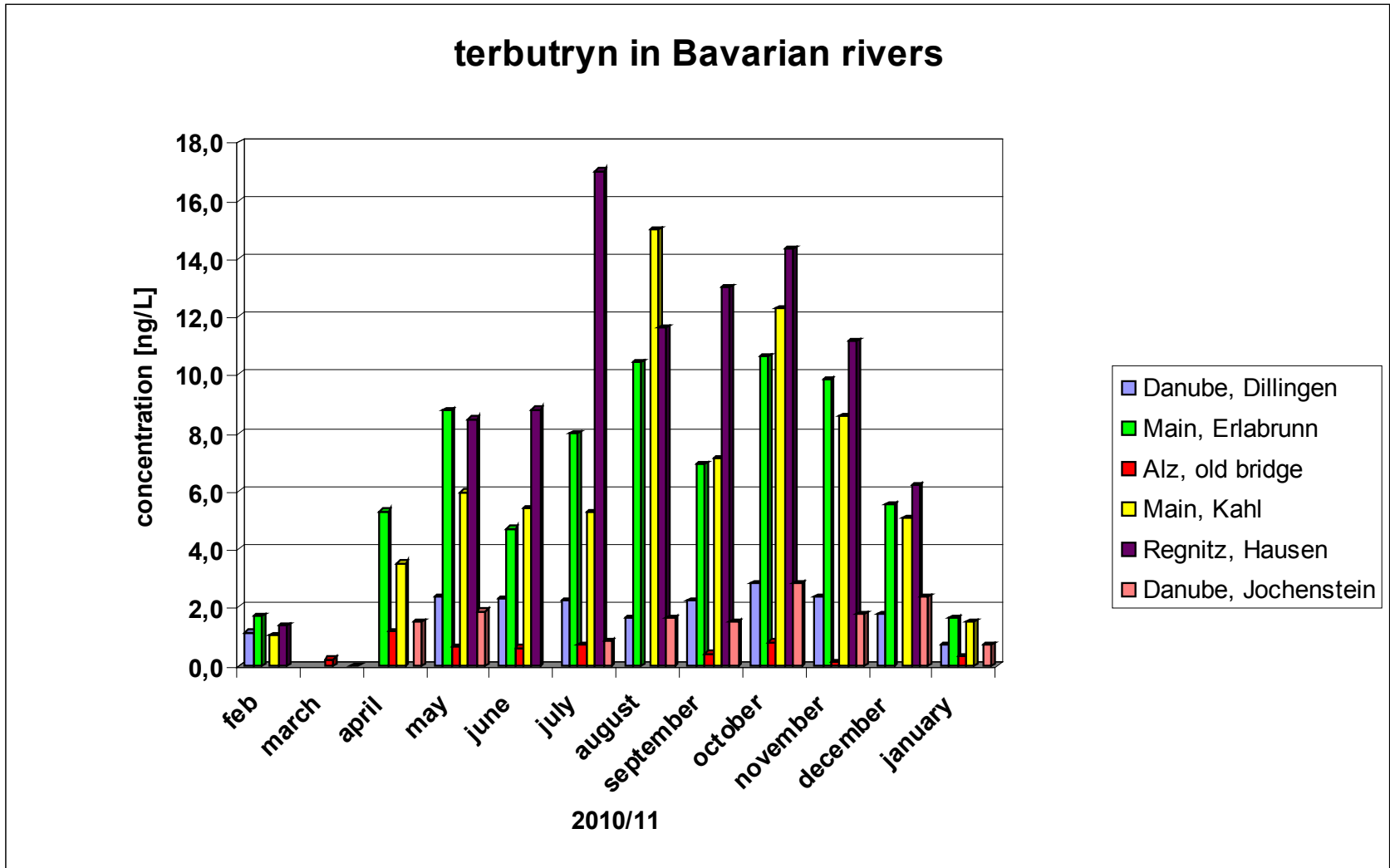
Biocides also used as pesticides

- IME-report 2012: 81 biocides listed that have/had an authorisation as pesticides (status as of 2010)
- 21 of these biocides monitored in smaller rivers (ca. 10 sampling sites taking 17 samples/year, 72h composite samples; LC-MS/MS)
- data for large rivers collected for many years

Examples

- **Terbutryn** in surface waters (authorisation 1971-2002)
1989-2012: 8438 data entries, 1336 positives, 147 values $>0,1 \mu\text{g/l}$,
maximum: $106 \mu\text{g/l}$
- **Carbendazim** in surface waters (authorisation since 1973)
- 2001-2012: 5898 data entries, 60 positives, maximum: $1,84 \mu\text{g/l}$

Terbutryn in surface waters



Conclusion

- there is a lot of data for selected biocides, especially for biocides also used as pesticides
- most data are for waters – only few data for sediments, suspended solids or biota
- development of monitoring concepts should take into regard these existing monitoring data
- a proposal for biocide monitoring based on a clearly documented prioritisation process is really welcome to fill the data gaps

Thank you for your attention