Evaluating pesticide pressure on freshwater mussel habitats: monitoring requirements and methodological limitations

Tom Gallé, Andreas Krein, Viola Huck, Michael Bayerle & Denis Pittois

LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY
LIST

MEASURING CHEMICAL IMPACT

Can we link chemical exposure to decline of natural populations?

LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY LIST

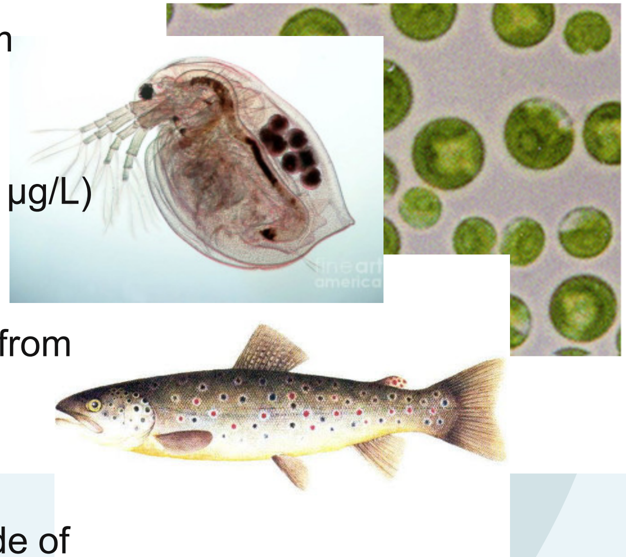
- River mussels are decaying everywhere in Europe
- Their natural habitats are larger rivers with developed gravel river beds
- Their life-cycle makes them very vulnerable to anthropogenic pressures
- Routinely addressed pressures are siltation of beds and eutrophication
- But what about chemical pressure in rural areas?
- LIFE Unio project interested in investigation
- Challenging task with limited budget (passive sampler application)

LifeUNIO

ASSESSING RELEVANT STRESSORS
A WFD conundrum

How to find out which pressure is the most impacting?

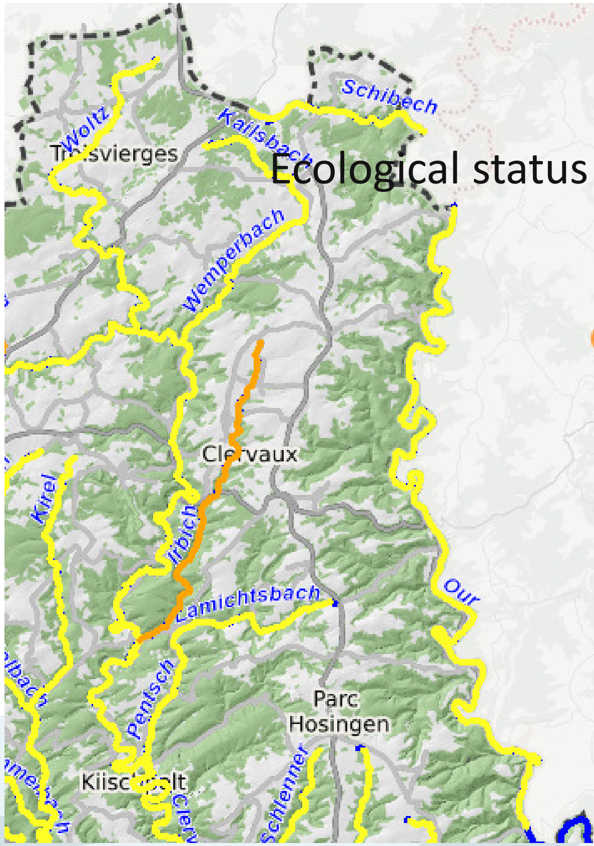
- Through **statistical analysis** of pressures on sites with varying populations or biological indicator scores
  - Gradient of population levels and pressures available (causality)?
  - Is your monitoring reflecting the exposure of the biota (periodicity)?
  - Indistinguishable pressures because of co-occurrence (urban stream syndrome, intensive agriculture)
- Delineation of chemical pressure from **ecotoxicological tests**
  - Data on freshwater mussels scarce and eclectic (pesticide EC >100 µg/L)
  - Depending on lifestage relevance and exposure during that time (glochidia, juveniles, adults)
  - General risk assessments of target analysis like WFD-EQS derived from standard test species (AA vs. MAC)
  - MOA and organism-toxtests on water/sediment samples addressing mixtures (ED, luminescence, algae, mutagenicity)
  - Chronic effects -> physiological markers in animals (thresholds, mode of action)

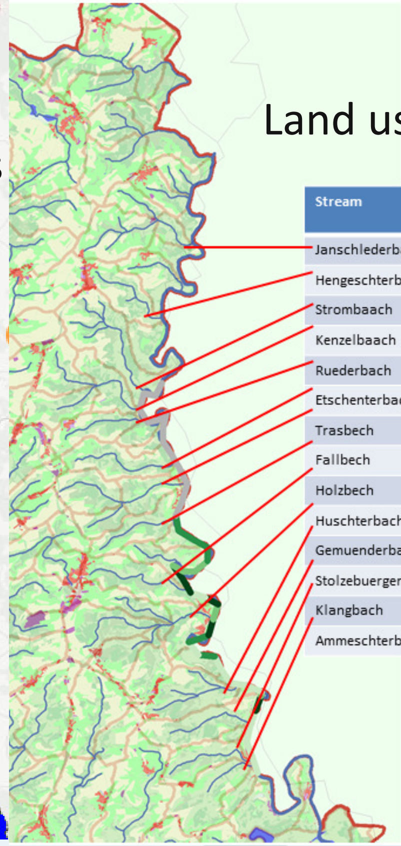


SELECTING MONITORING SITES

Which concept? Emission vs immission

- One longitudinal profile with population size variation and only small tributaries contributing
- Transboundary rivers Our and Sure
- Different information situation (FLIK vs. CORINE)
- We opted for a mixed approach (immission for mussel colonies and emission form catchments)
- Emission loads normalized by landuse & crops



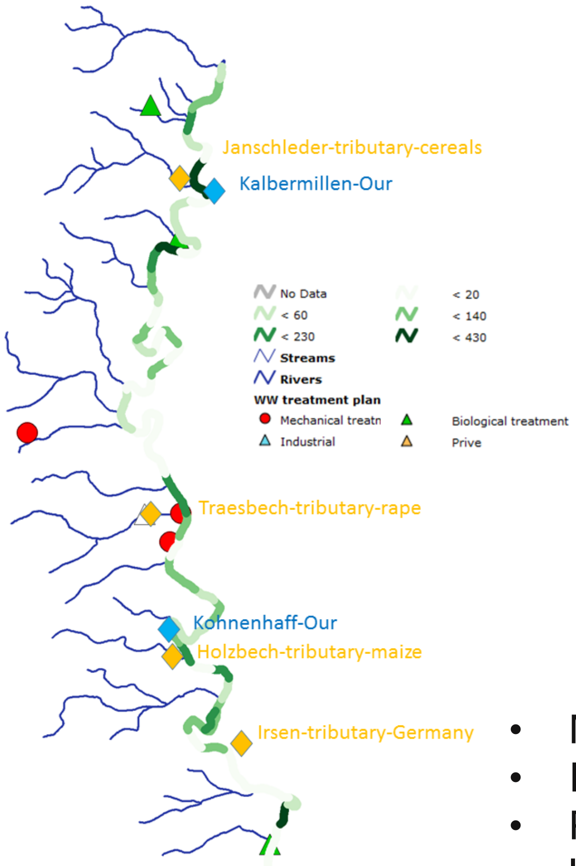


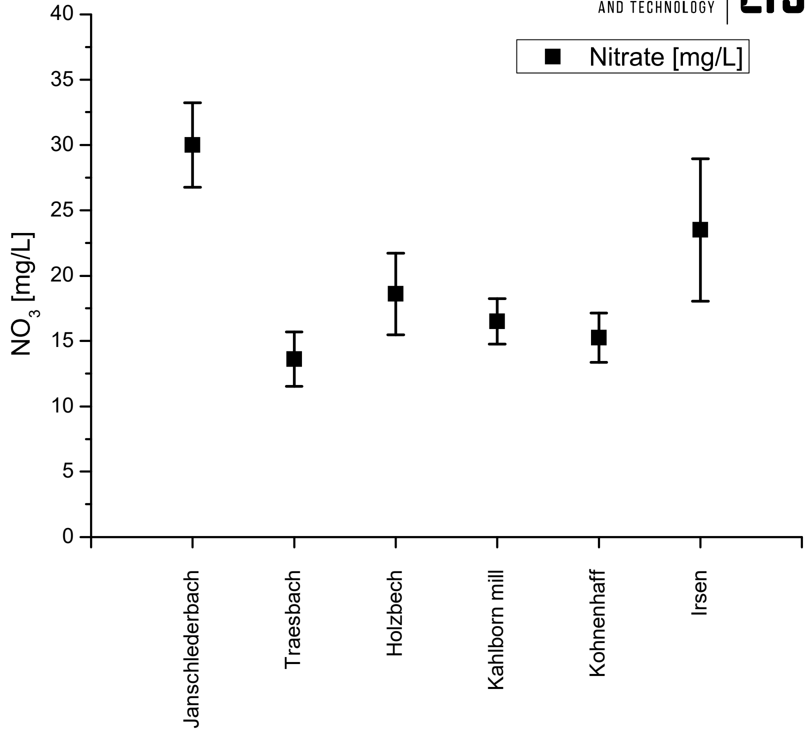
Land use/crop pressure

Stream	Cereals [%]	Maize [%]	Rape[%]	Potatoes [%]
Janschlederbaach	19.73	4.93	3.41	0.16
Hengeschterbaach	11.99	4.5	2.45	0.02
Strombaach	9.68	2.30	1.79	0.37
Kenzelbaach	14.76	3.36	2.06	0.18
Ruederbach	11.08	5.58	1.81	0.1
Etschenterbach	12.91	2.29	1.81	0.1
Trasbech	8.84	1.76	2.46	0
Fallbech	8.42	2.05	1.40	0
Holzbech	11.45	5.70	0.69	0
Huschterbach	11.54	4.48	1	0.05
Gemuenderbach	4.13	4.46	0.05	0.03
Stolzebuergerbach	6.46	5.81	0.2	0.19
Klangbach	6.49	8.11	0.52	0.01
Ammeschterbach	6.54	1.59	1.51	0.01

MUSSEL POPULATIONS OUR

Chemical gradients?

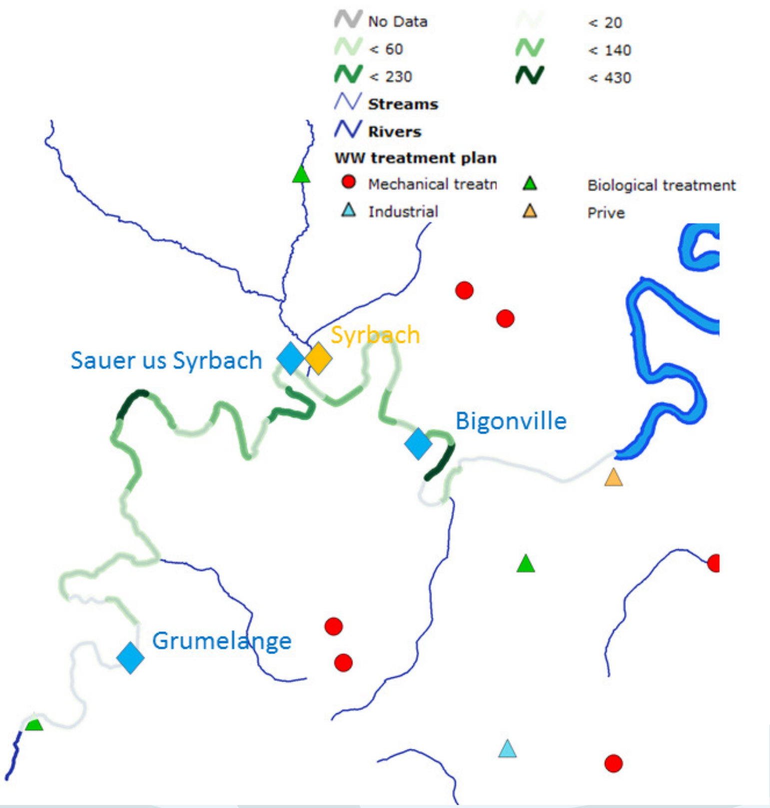


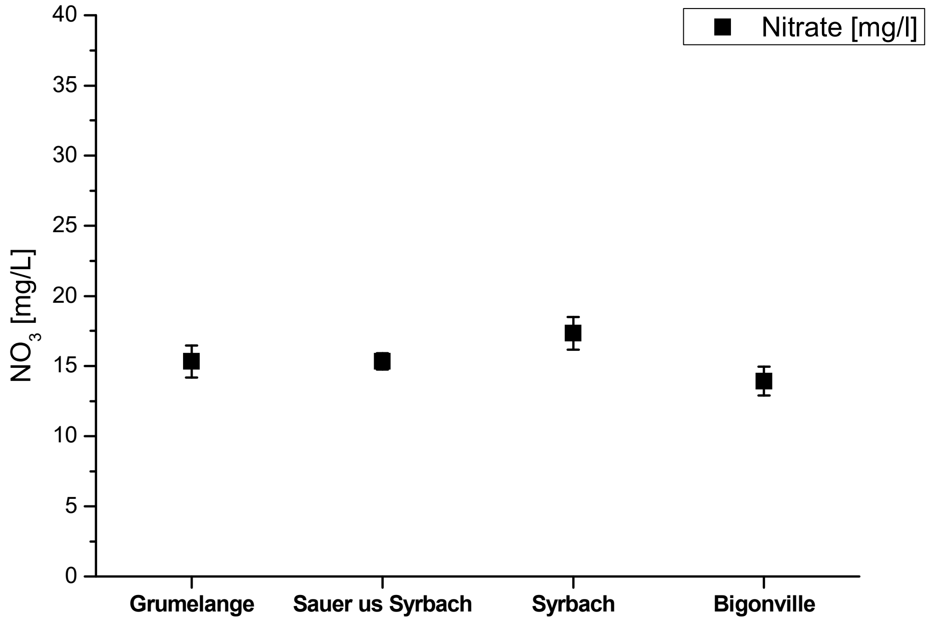


- Mussel colonization is discontinuous and patchy
- Impact of small tributaries (excessive loads?) or dilution?
- Polar pesticides will not be attenuated along the longitudinal profile (photodegradation, sorption)

MUSSEL POPULATIONS SÛRE

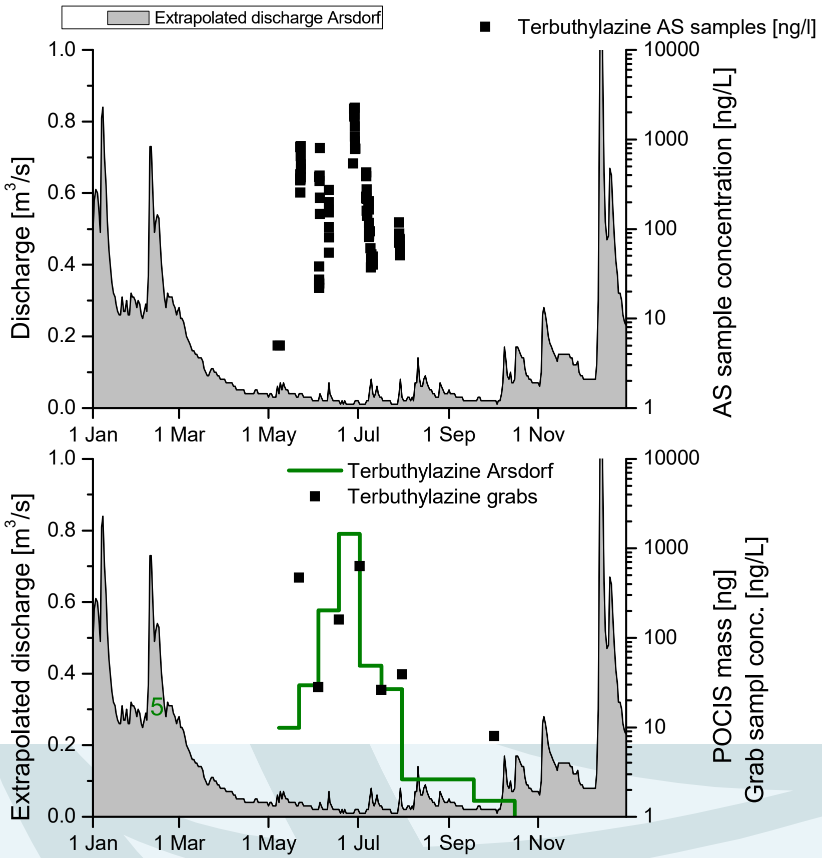
Chemical gradients?





- Even less variability on the Sûre in basic chemistry
- Substantial longitudinal variation in population

PESTICIDE EXPOSURE
Episodic mobilisation during application time

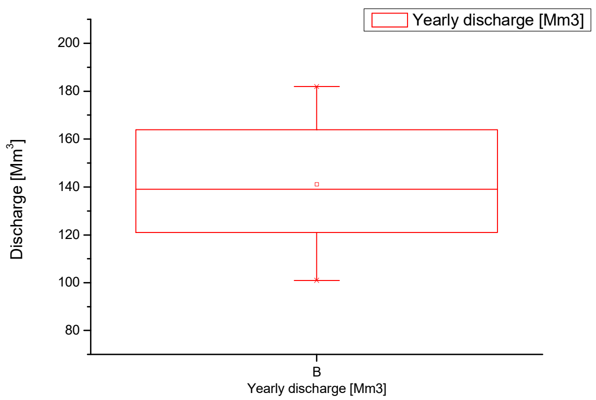


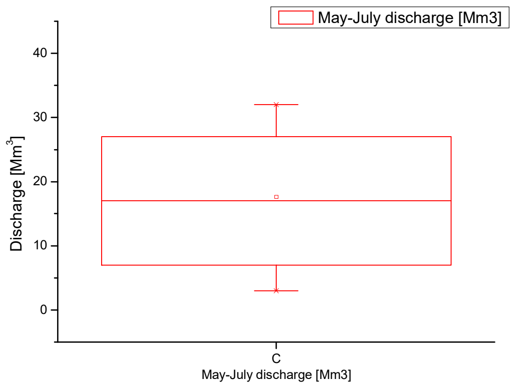
- Pesticide occurrence periodic (season) and episodic (flood waves)
- Main application period of relevance is May-June (herbicides in maize, fungicides and insecticides in cereals & rape)
- Passive sampler are the only monitoring technique providing continuous sampling

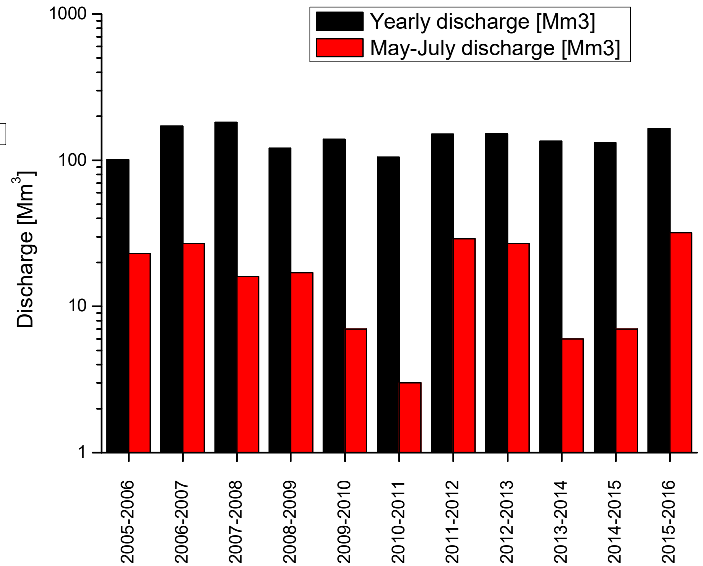
POCIS-passive sampler
Polar compounds (log K_{OW} 1-4)
14 day exposure
Calibration during base-flow

MONITORING PERIOD

You've got to deal with the weather





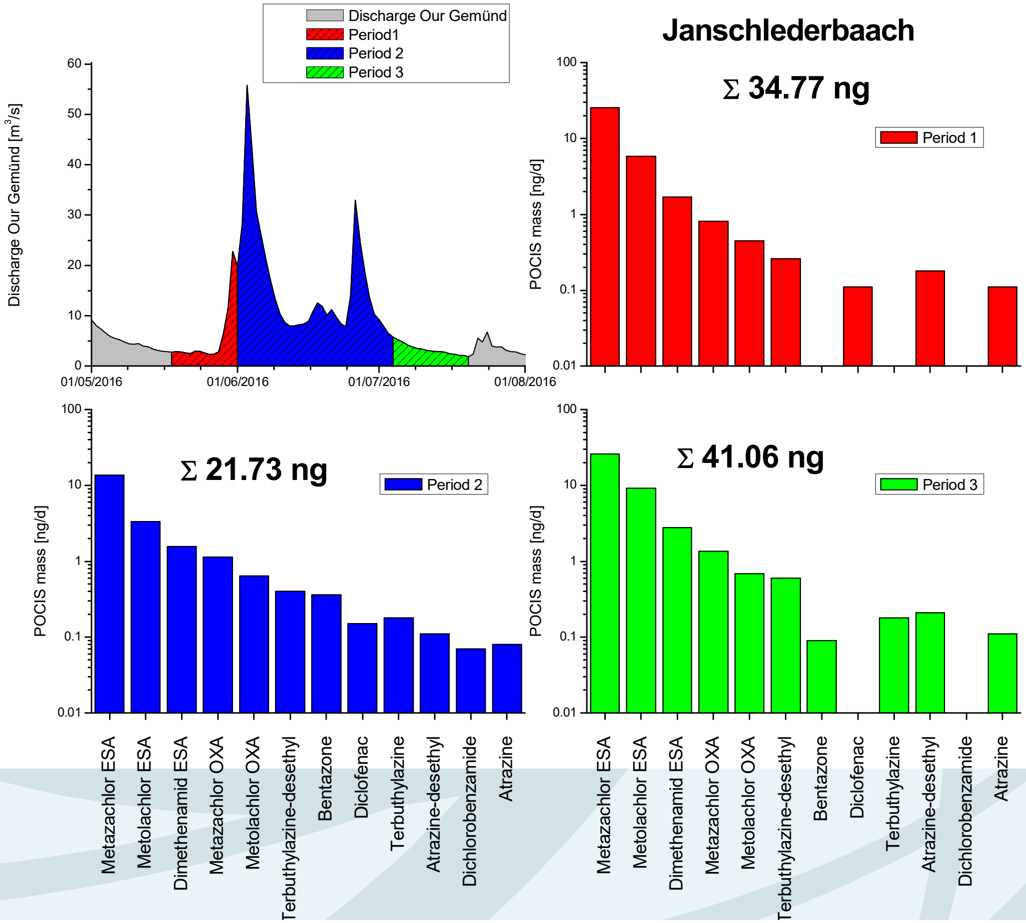


- May-July period is the highest in pesticide emissions and normally low in discharge
- However in 2016, June was rainy and produced a strong month long flood wave

THE ARRAY OF COMPOUNDS

Raw results from POCIS: mass ranking

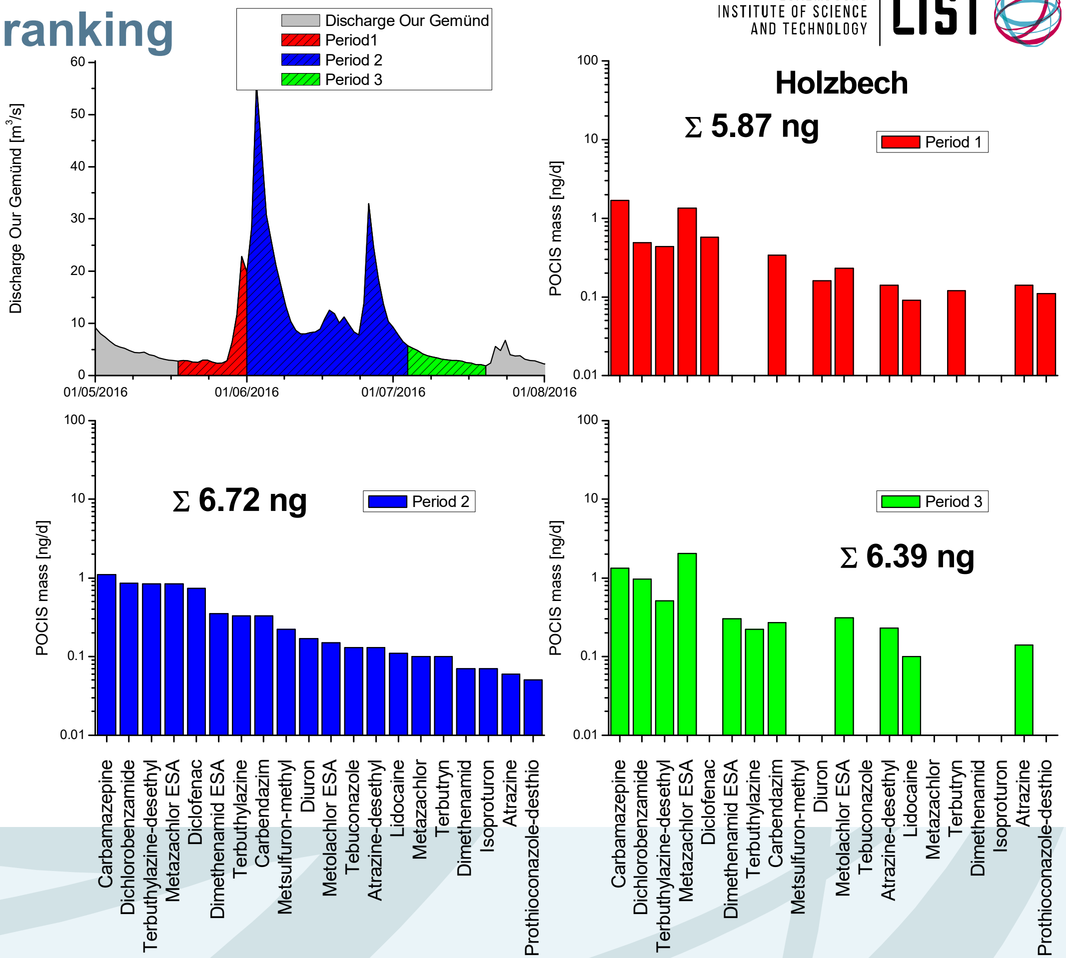
- Three periods of exposure covered
- Janschhleder Bach is the most agriculturally intensive catchment
- Very few detections of currently applied compounds (only TPs)
- Low overall level



THE ARRAY OF COMPOUNDS

Raw results from POCIS: mass ranking

- Holzbech receives (treated?) waste waters form Hosingen
- Many pharmaceuticals and biocides detected
- Larger array of currently applied compounds in Maize

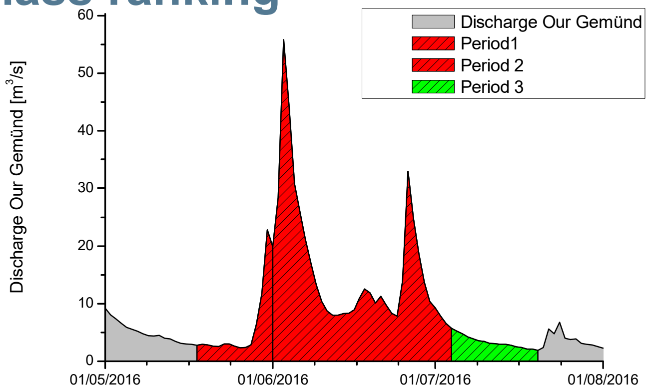


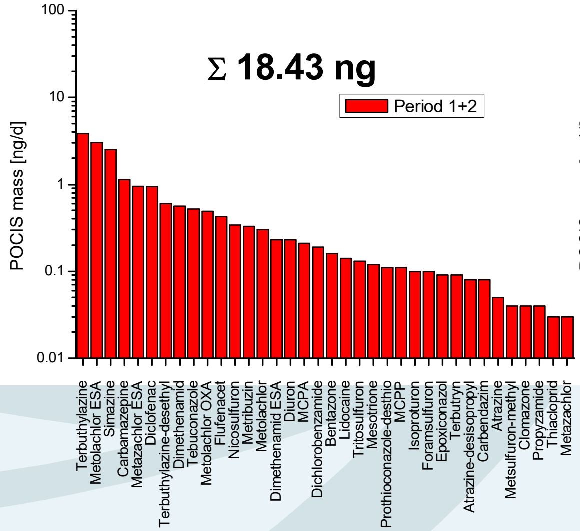
THE ARRAY OF COMPOUNDS

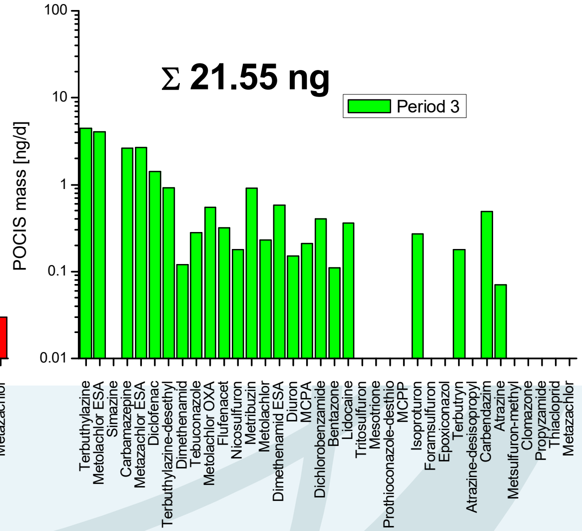
Raw results from POCIS: mass ranking

Kohnenhaff-Our

- This site hosts a mussel population
- Due to the size of the river, access in June was not possible
- The array of coumpounds is much larger
- Maize herbicides dominate the picture
- Overall mass is relatively low





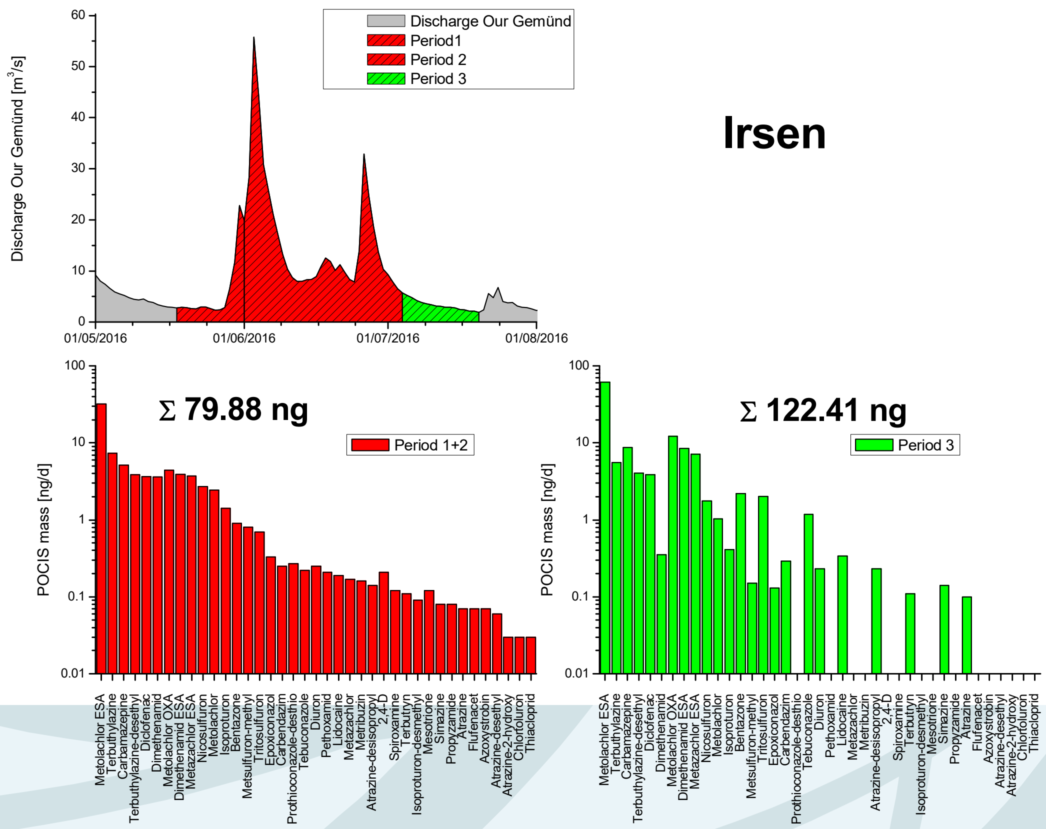


LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY

THE ARRAY OF COMPOUNDS

Raw results from POCIS: mass ranking

- This site characterizes the input of a tributary with strong maize cultures
- Overall mass much higher
- Distinct shifts towards old school maize herbicides like s-metolachlor, terbuthylazine, dimethenamide



CALIBRATION

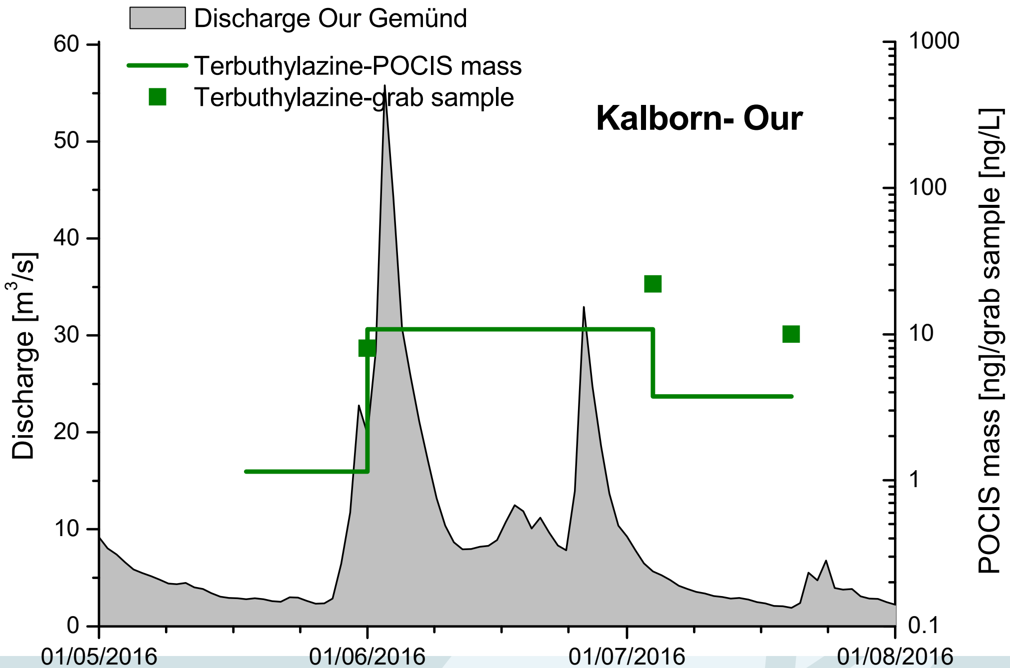
From POCIS masses to Time Weighteg Averages

LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY LIST

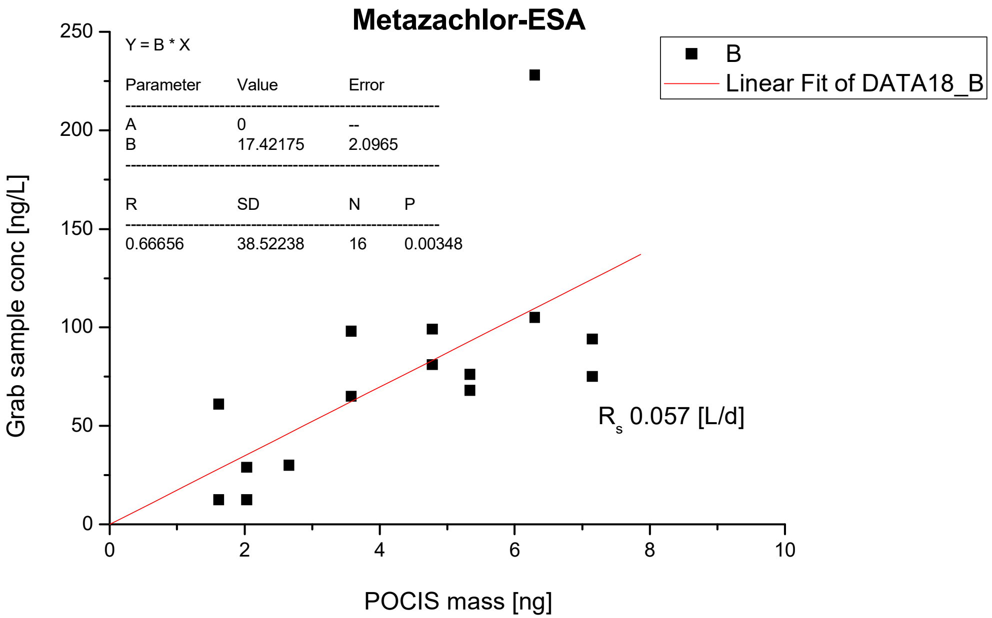
$$C_w = \frac{M_{POCIS}}{R_s\ t}$$

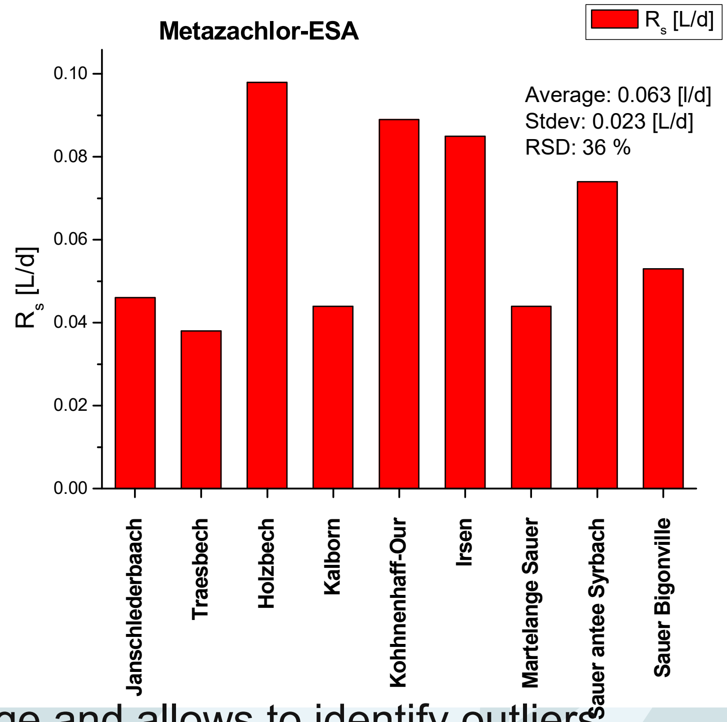
C_w	Concentration in water (TWA) [ng/l]
M_{pocis}	POCIS mass [ng]
R_s	Sampling rate [L/d]
t	exposure tmie [d]

Grab samples to verifiy R_s and compare them to lab determined values



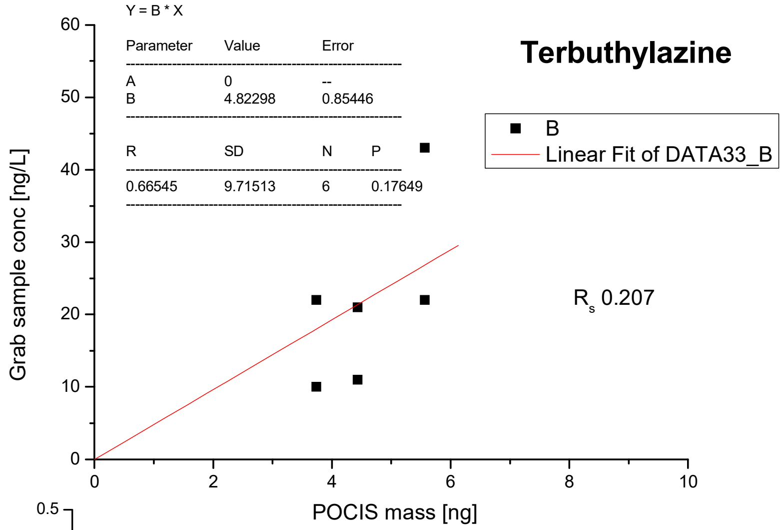
CALIBRATION
From POCIS masses to Time Weighteg Averages

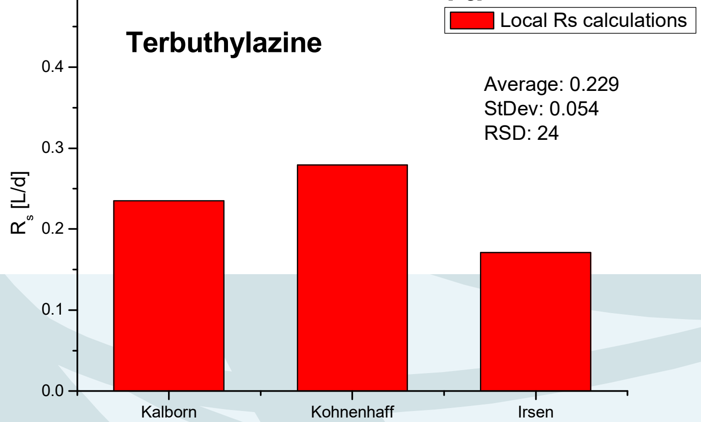




- Regression of all sites gives an overall average and allows to identify outliers
- Locally calculated Rs used where a stronger deviation is obvious

CALIBRATION

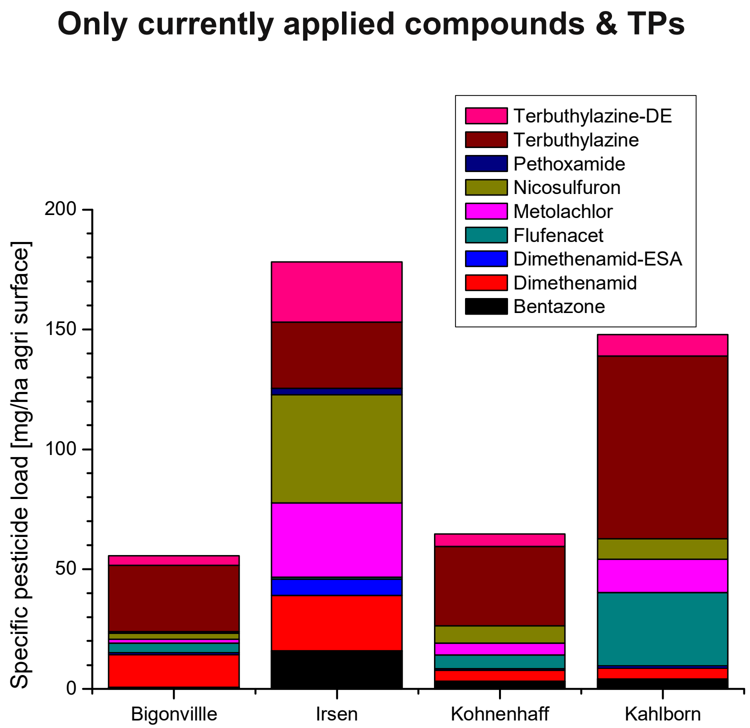


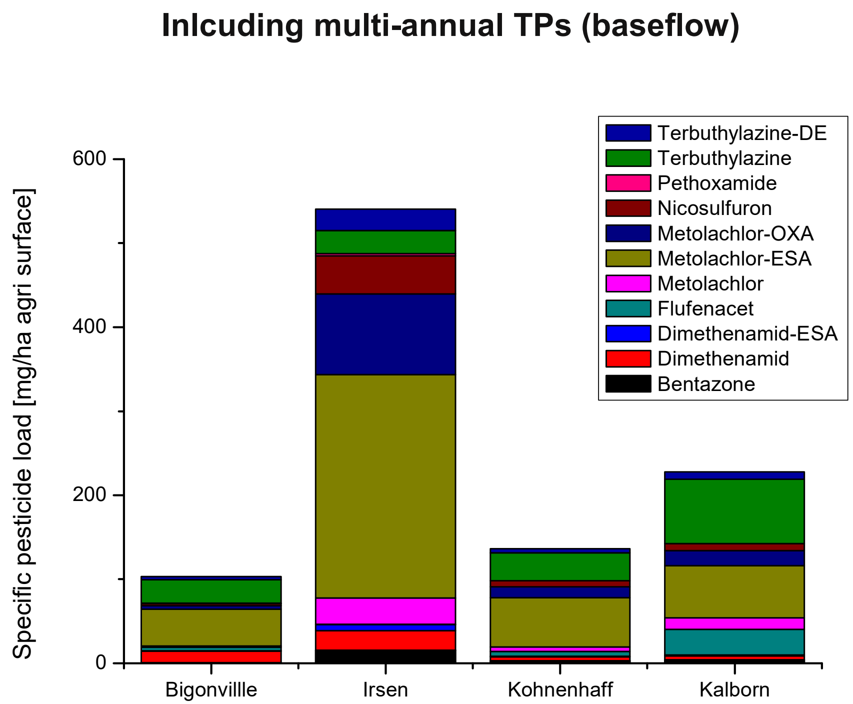


Rs [L/d]	Lab calibration	Field regression	Field average	Moschet
Bentazone	0.04		0.082	
Carbamazepine	0.23	0.231	0.226	0.1
Clomazone	0.13			
Diclofenac	0.07	0.223	0.162	0.06
Epoxiconazol	0.11			0.08
Flufenacet	0.13			0.1
Isoproturon	0.16			0.08
MCPA	0.06			
Mesotrione	0.05			
Metazachlor	0.22			0.2
Metazachlor ESA	0.05	0.047	0.063	0.04
Metolachlor	0.19		0.102	
Metolachlor ESA	0.07	0.093	0.099	0.04
Metolachlor OXA	0.04		0.068	0.03
Metribuzin	0.20			
Metsulfuron-methyl	0.06			
Napropamide	0.13			0.1
Propyzamide	0.14			
Pymetrozine	0.19			
Terbuthylazine	0.17	0.207	0.229	
Terbuthylazine-desethyl	0.19		0.208	0.08
Dimethenamid				0.1
Dimethenamid-ESA			0.081	
Metazachlor-OXA			0.025	
Nicosulfuron			0.079	

NORMALIZED PESTICIDE LOADS

A fingerprint of land use





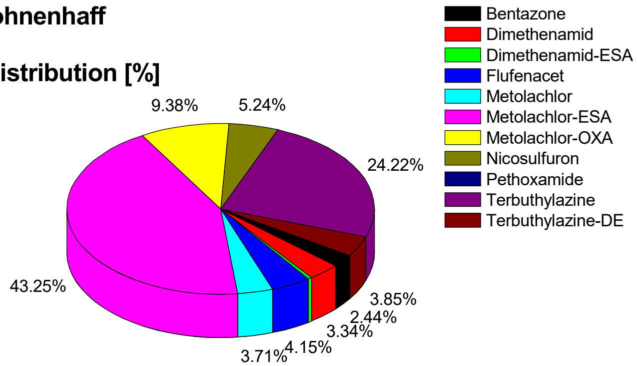
- Long-lived TPs make up for a large proportion of the load

PESTICIDE LOADS

Relative distributions

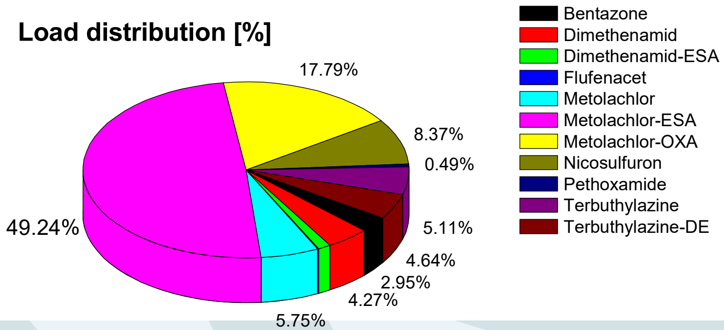
Our-Kohnenhaff

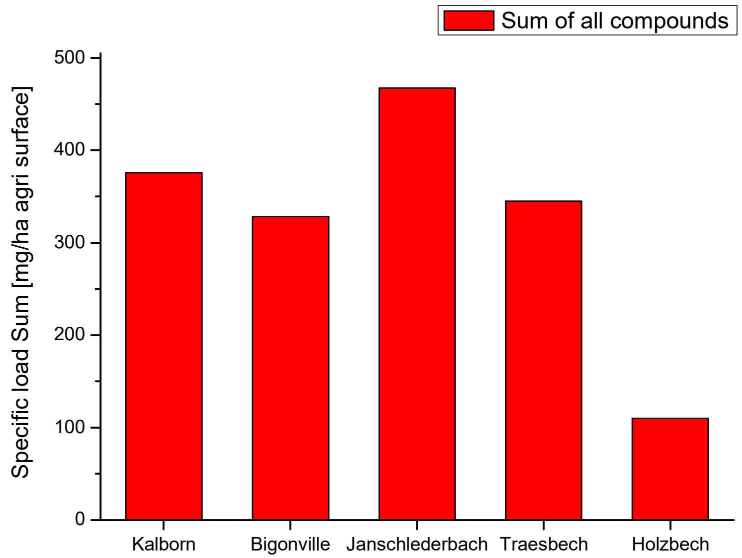
Load distribution [%]



Irsen

Load distribution [%]





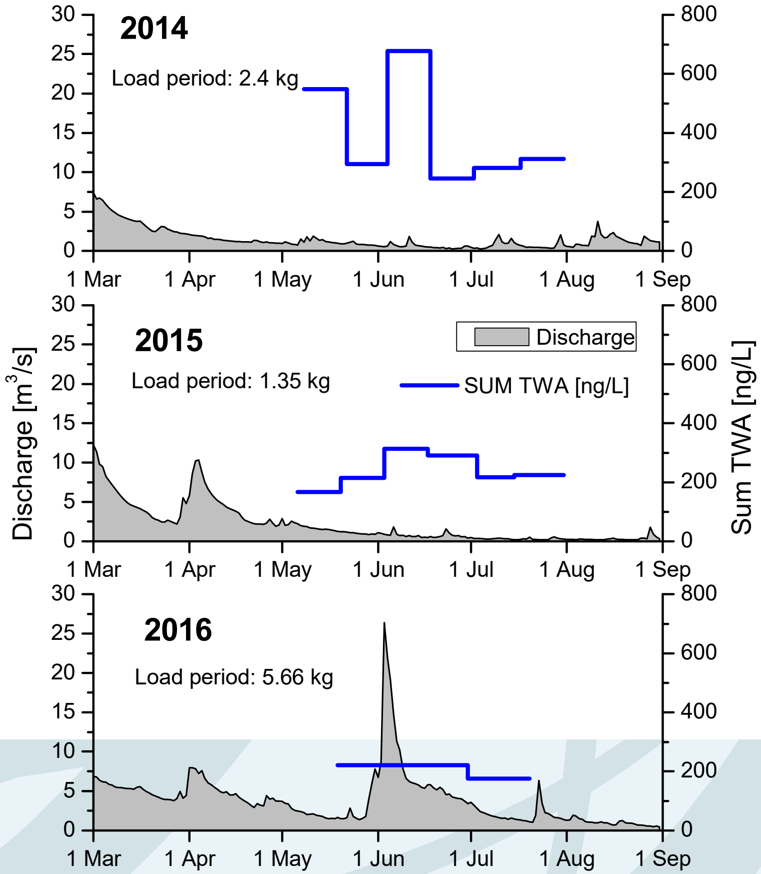
- Specific pesticide profiles for different countries (Lux, Belgium, Germany)
- Unusual: higher order river shows higher loads than tributaries (international dimension)

REPRESENTATIVENESS

How does 2016 compare to previous years?

LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY LIST

- Bigonville (Sure) has been monitored in 2014 + 2015
- Loads in 2016 are larger but TWA (exposure) is lower
- Small events (2014) can lead to great exposure in application period



EVALUATING IMPACT

The concept of summed risk quotients

$$RQ_i = \frac{TWA}{AA - EQS}$$

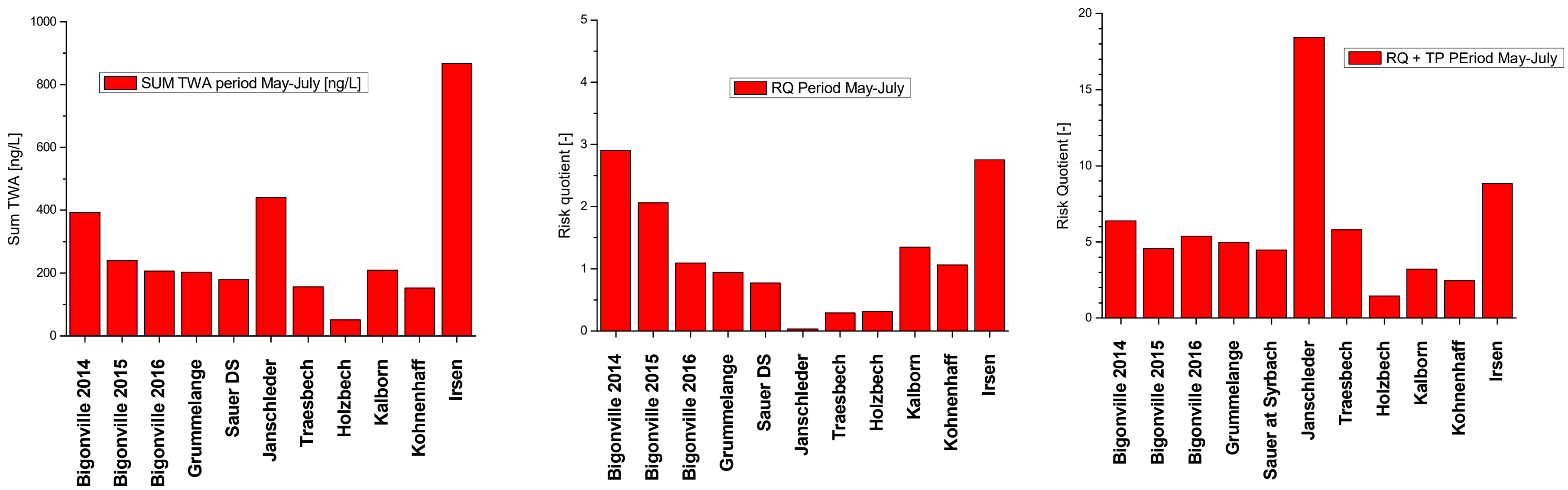
$RQ_i > 1$ ecotxicological risk

Sum of RQ_i global impact

No classification of Sum RQ_i

Compound	AA-EQS [ng/L]	Compoud	AA-EQS [ng/L]
2,4-D	200	MCPP	3600
Atrazine	600	Mefenpyr-Diethyl	1650
Azoxystrobin	950	Mesotrione	80
Bentazone	73000	Metazachlor	20
Carbamazepine	2000	Metolachlor	270
Carbendazim	340	Metosulam	15
Chlortoluron	600	Metribuzin	120
Clomazone	2000	Metsulfuron-Methyl	4000
DEET	41000	Napropamid	5120
Diclofenac	50	Nicosulfuron	35
Dimethenamid	130	Pethoxamid	79
Diuron	20	Propyzamide	6000
Epoxiconazol	190	Prosulfocarb	600
Fluaxastrobin	572	Pymetrozin	500
Flufenacet	137	Spiroxamine	60
Fluroxypyr	20	Sulcotrione	5000
Foramsulfuron	7	Tebuconazole	1200
Isoproturon	320	Terbuthylazine	220
Kresoxim-Methyl	630	Terbutryn	65
Linuron	260	Thiacloprid	10
MCPA	1340	Tritosulfuron	150

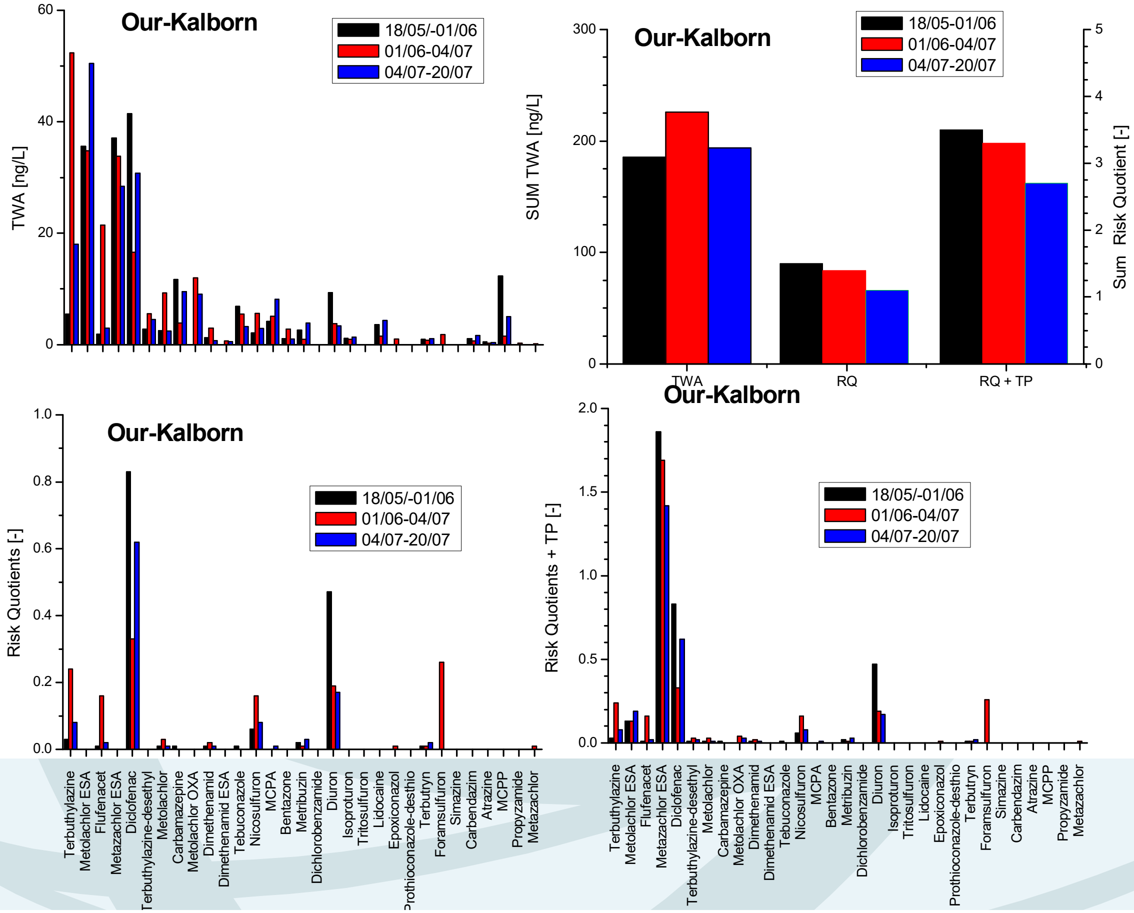
SUMMARY RQS
The inclusion of transformation products



- The inclusion of transformation products dramatically changes the picture

THE DETAIL OF RQ

Pharmaceuticals and biocides matter



LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY LIST

CONCLUSIONS

- Mussel distribution is very patchy with no strict relationship to pesticide exposure although higher exposures seem to affect presence. Limited array of independent sites precludes conclusions.
- Luxembourgish tributaries of the Our are at a lower pollution level than the German/Belgian side.
- Mixture toxicity can be addressed by the Risk Quotient approach but there are certain limits
  - AA-EQS are derived from 3 lab test species - > field relevance
  - There is no interpretation for Sum of RQs
  - There is no ecotoxicological data for transformation products although these are dominant
- Further research could involve the measurement of biomarkers in (exposed) biota in the rivers since exposure levels are sublethal and only stress can be measured.
- Better alignement with WFD biological indicators – further inquiry into common traits of species and deficits in mussel sensitivity respresentativeness.