CENTRE DE RECHERCHE PUBLIC
HENRI TUDOR
www.tudor.lu

CENTRE DE RESSOURCES DES TECHNOLOGIES POUR L'ENVIRONNEMENT
UNE STRUCTURE DU MINISTÈRE DE L'ENVIRONNEMENT ET DU CRP HENRI TUDOR

Pesticide and pharmaceutical emission profiles from WWTPs: Monitoring with passive and auto-samplers

M3 conference
17.06.2010

Michael Bayerle, Tom Gallé, Denis Pittois

Structure

1. Description of the project
2. Passive sampling with POCIS
3. Dynamics of xenobiotics in WWTPs
4. Floodwave
5. Conclusion

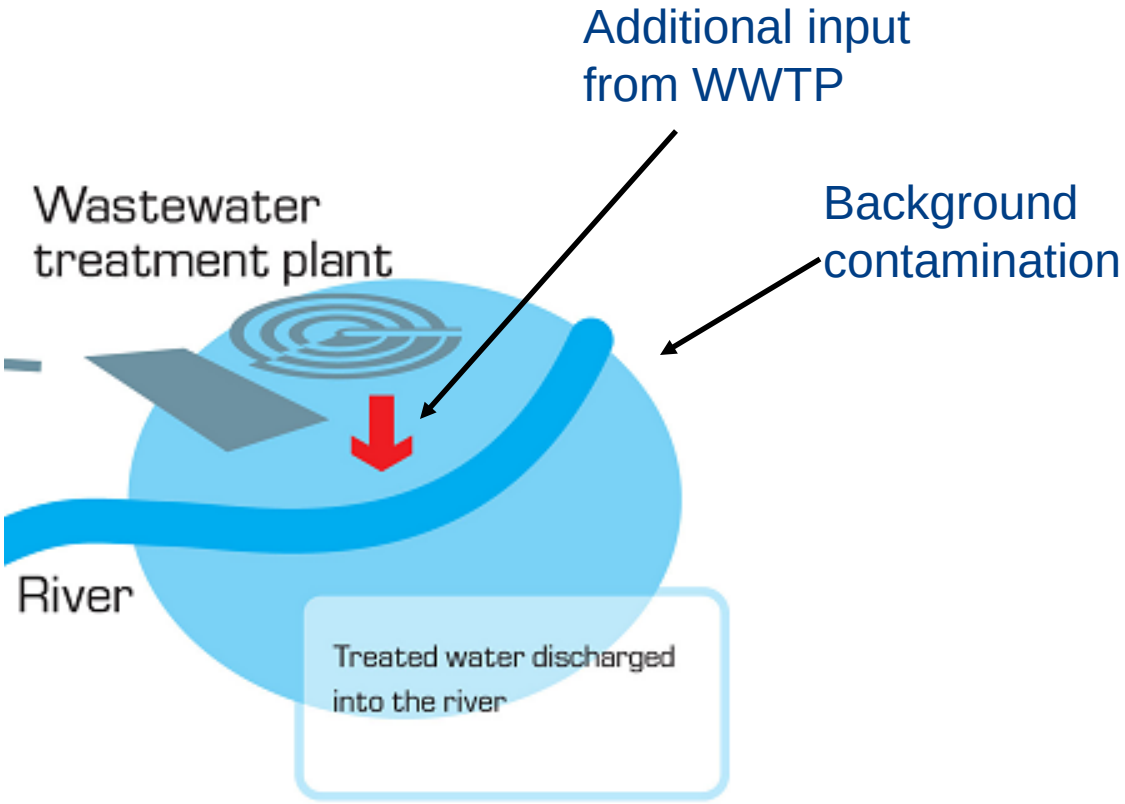
1. Project description

Project context

- Application of pesticides on sealed surfaces (maintenance of places and roads or cleaning of spraying equipment)
- WWTP effluents as an important source for surface water contamination

- => Quantification of pesticide emission through sanitation systems to surface waters
- => Verification of applicability of passive sampling techniques to monitor organic micropollution

1. Project description



Grab sampling only gives a snapshot of the contamination situation

Passive sampling leads to time weighted average concentrations

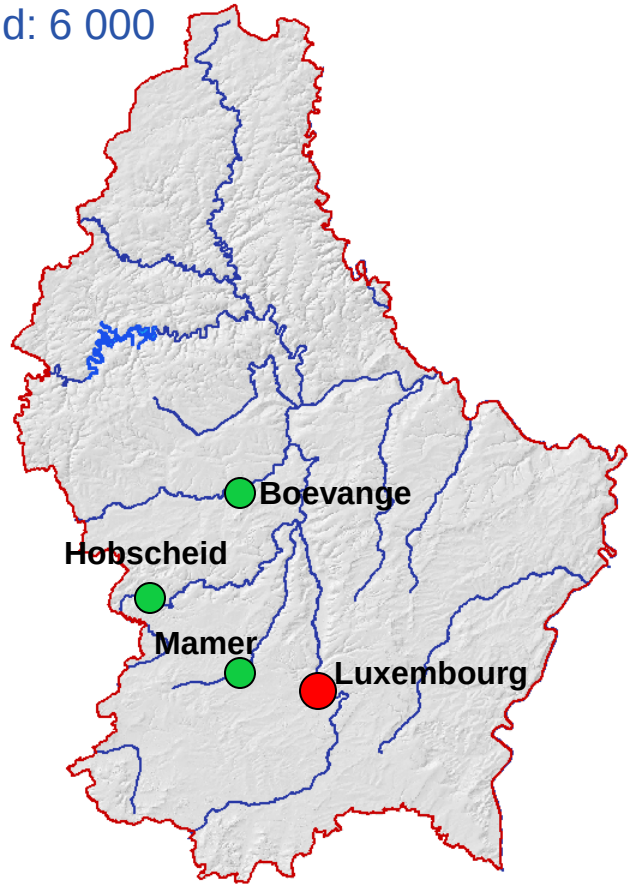
1. Project description

Discrete sampling

- Autosamplers have been installed at the WWTP inlet and outlet and in the river (in Mamer additionally in the pretreatment and denitrification tank)

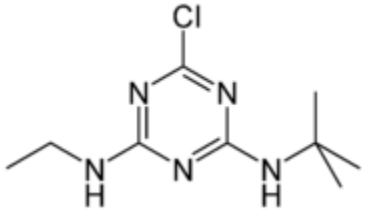
- Samples were taken as 2 or 3-hour composite samples during a period of 24 hours

Population equivalents
Boevange: 2 700
Mamer: 20 000
Hobscheid: 6 000

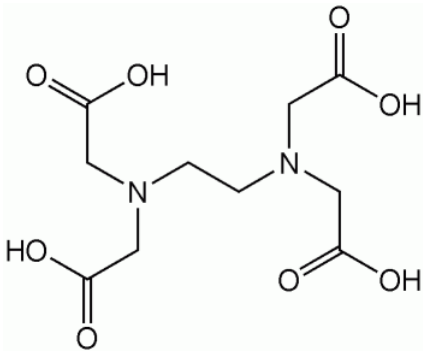


1. Project description

Measured parameters



Terbuthylazine



Ethylenediaminetetraacetic (EDTA)

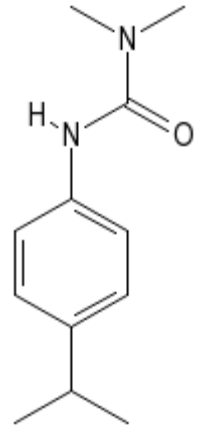
Discrete samples:

- Anions, ammonium, TOC, BOD, COD, suspended matter, pH, conductivity

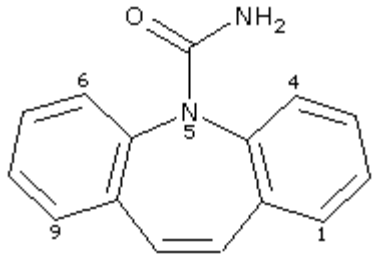
-Xenobiotics: ca. 30 substances (pesticides, complexing agents, pharmaceuticals)

Online-probes: conductivity, turbidity, temperature

Polar Organic Chemical Integrative Sampler



Isoproturon



Carbamazepine

2. Passive sampling

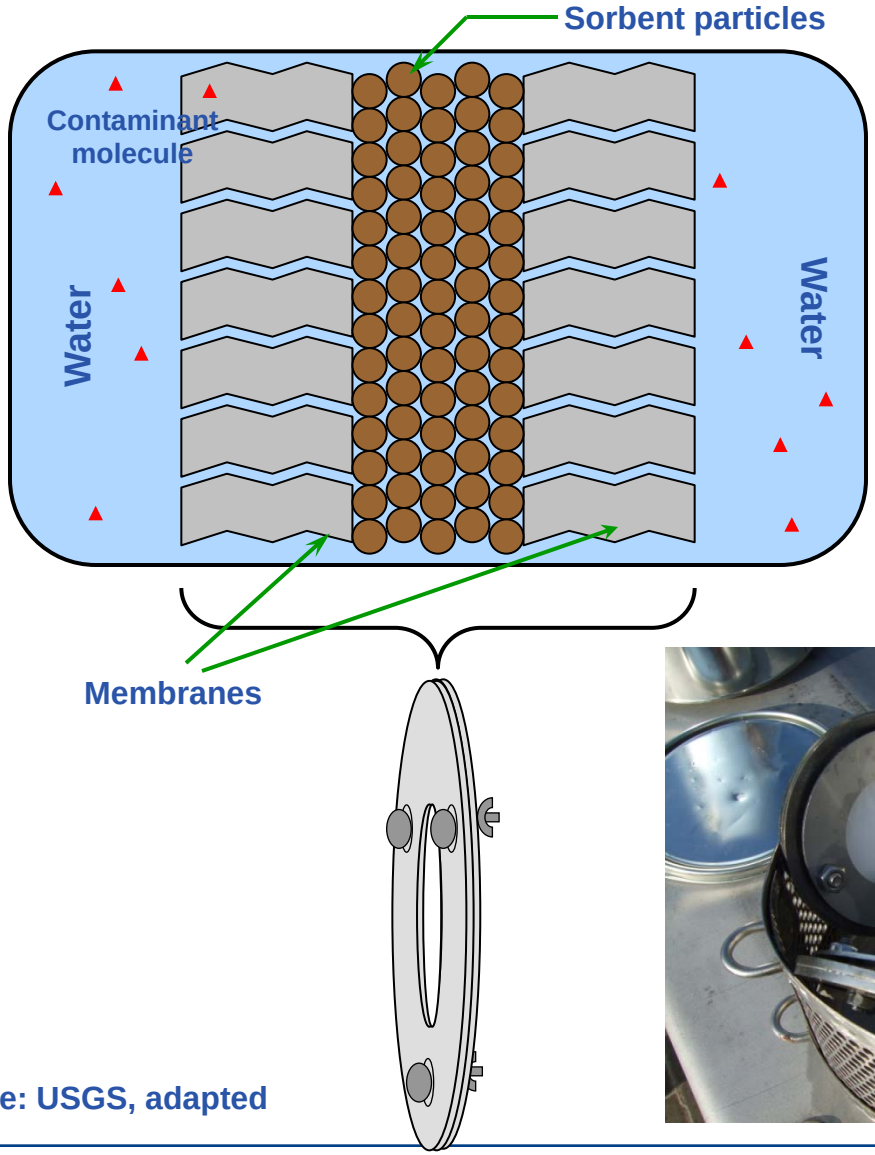


Figure: USGS, adapted

2. Passive sampling

POCIS theory

- Specific sorption of substances: determination of sampling rates in the laboratory

$$M_S(t) = C_W R_S t$$

$M_S(t)$: the compound mass accumulated in the receiving phase

t: exposure time

C_W: concentration of the compound in the water phase

$$R_S = k_u V_T$$

R_S: sampling rate [L/d]

k_u: uptake rate constant

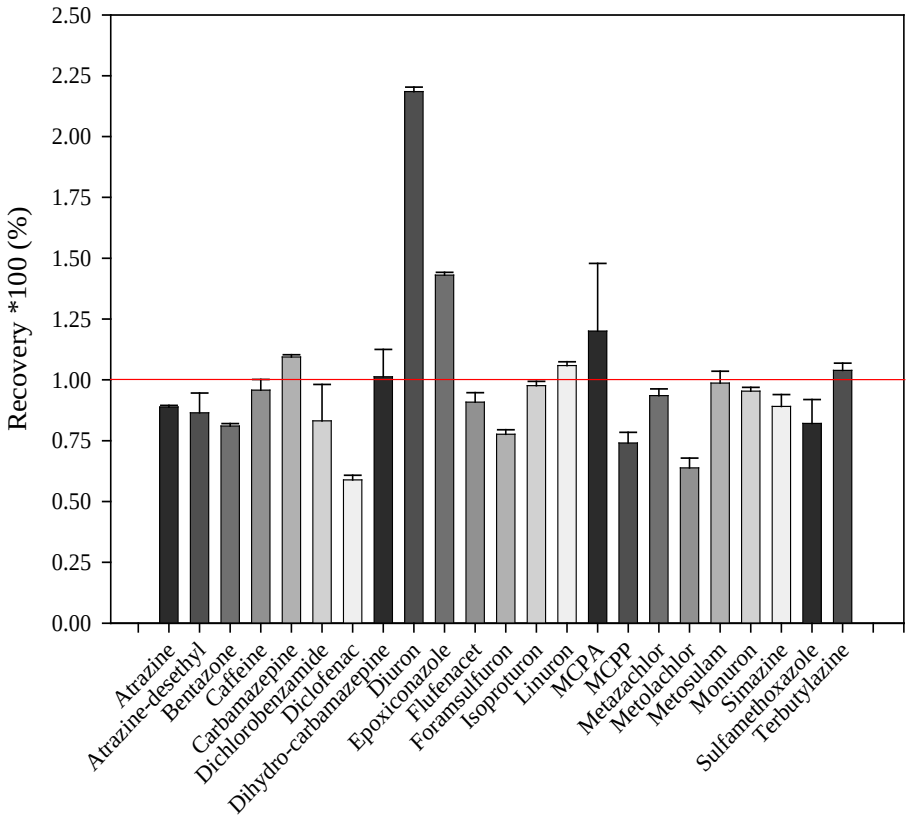
V_T: volume of water tank

2. Passive sampling

POCIS treatment

- Transfer of sorbent into SPE column
- Extraction with methanol
- Evaporation
- Analysis at LC-MS/MS
- Calculation of concentrations during deployment

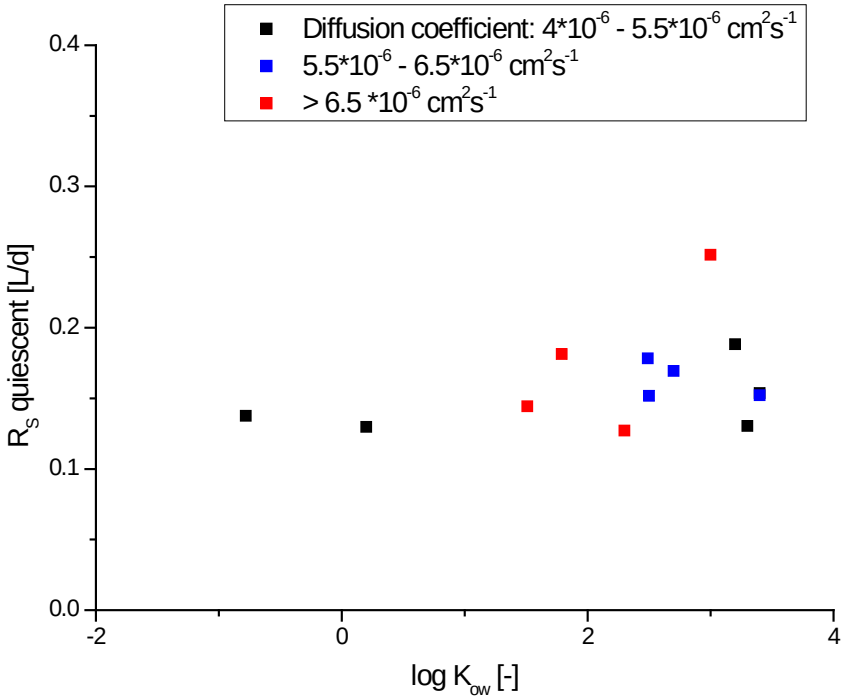
Recovery obtained during extraction tests of POCIS fortified with the analytes



2. Passive sampling

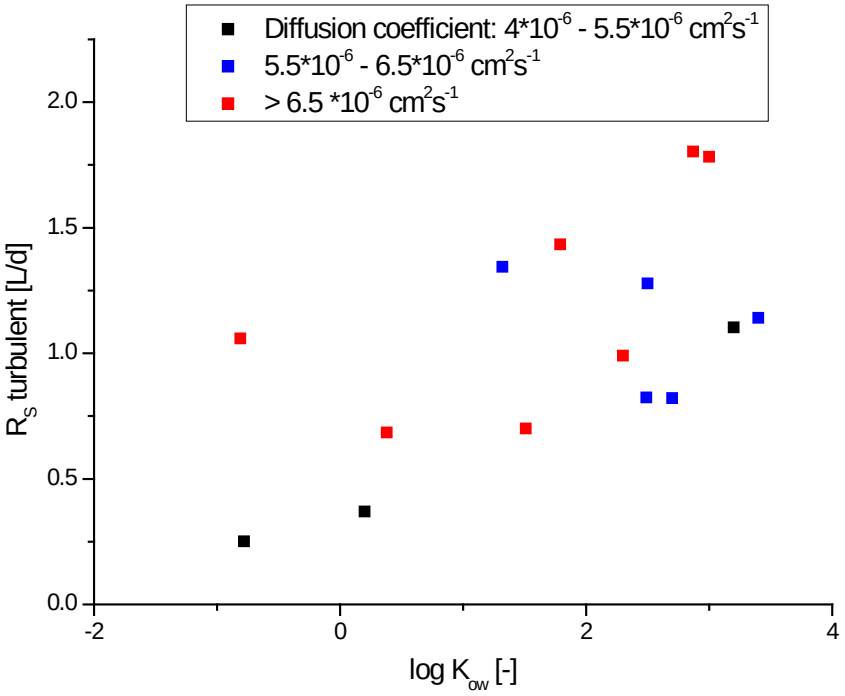
Sampling rates R_S are influenced by K_{ow} and diffusion coefficient

Quiescent mode



Transport limited by aqueous diffusion

Turbulent mode



Transport limited inside sampler

2. Passive sampling

Comparison of lab and field derived sampling rates:

Field data are between lab values => grade of turbulence

		Sampling rate R_S [L/d]			
	Log K_{OW}	turbulent lab	quiescent lab	effluent Mamer	RSD field
Atrazine	2.70	0.82	0.17	0.27	8.6%
Diclofenac	4.51	0.63	0.12	0.22	8.4%
Isoproturon	2.50	1.28	0.15	0.18	11.6%

	river Mamer	RSD field	river Attert	RSD field
Atrazine	0.23	14.5%	0.59	18.4%
Diclofenac	0.19	13.4%	0.40	23.7%
Isoproturon	0.16	16.5%	0.59	5.8%

2. Passive sampling

Limits of detection with POCIS

Depending on the exposure time and sampling rate R_S

In theory:

- 24 hour exposure with an R_S of 0.2 L/d: 5 ng/L
- 14 day exposure: 0.36 ng/L
- Limit of detection for online-extraction (auto-sampler data):

  5 – 10 ng/L

Practically:

Around 1 ng/L, because matrix effects due to high pollutant loads in the extracts have to be taken into account

2. Passive sampling

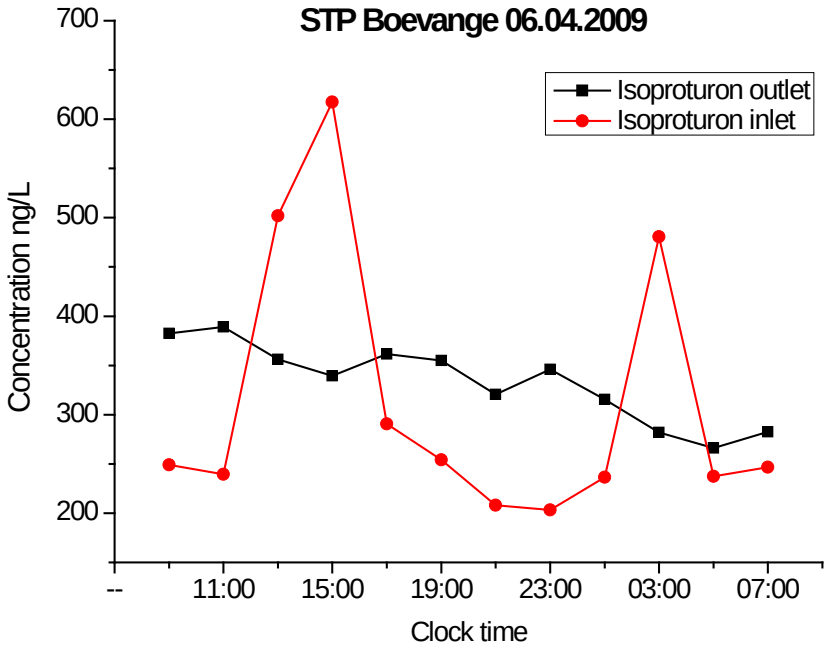
POCIS deployed for 14 days:

Ranges indicate the uncertainty of R_S determination and the three deployed replicates

	Time weighted average concentrations [ng/l]		
	Atrazine	Isoproturon	Diclofenac
Boevange			
upstream WWTP	2.8 – 8.9	6.0 – 21.4	2.4 – 3.7
downstream WWTP	3.3 – 7.2	5.8 – 12.1	3.6 – 6.8
effluent WWTP	3.0 – 4.8	102 – 166	382 – 493
Mamer			
downstream WWTP	16.2 – 35.9	20.4 – 32.1	99.7 – 215
effluent WWTP	4.9 – 13.2	34.5 – 113	264 – 1030

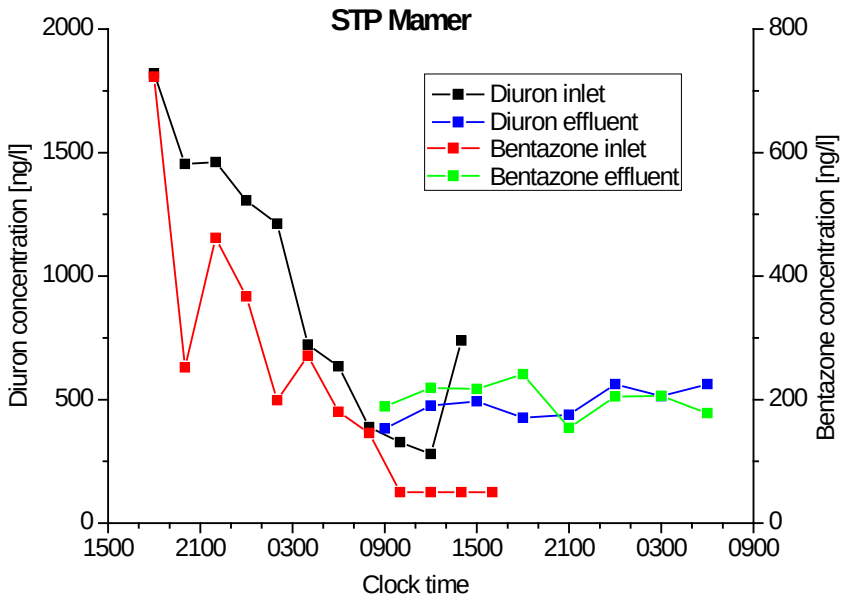
3. Xenobiotic dynamics

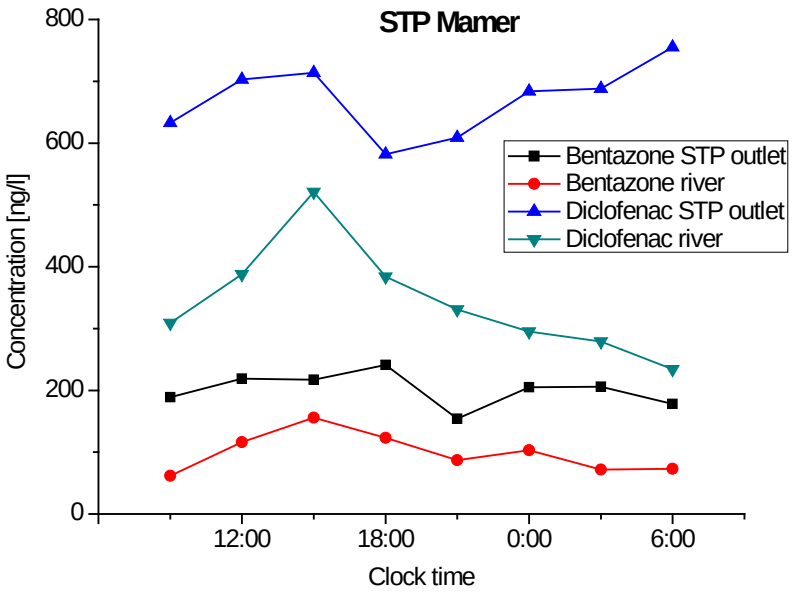
Pesticides in the sewage treatment plant



3. Xenobiotic dynamics

Low elimination rates of xenobiotics





Elimination rate by calculating loads:

Bentazone: 17%

Diuron: 49 %

Dilution factor between outlet and river varies (1,4 – 3,2)

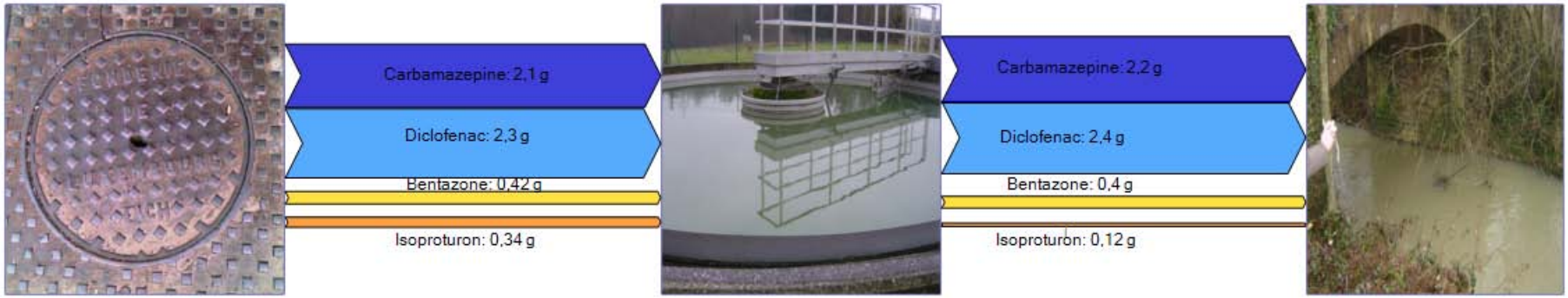
=> additional input upstream

3. Xenobiotic dynamics

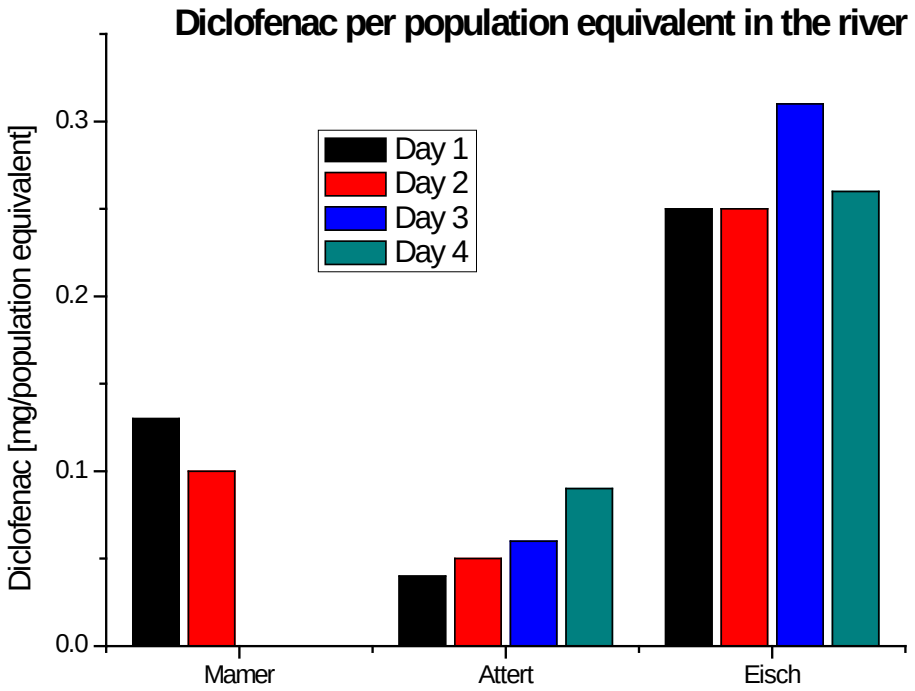
Daily loads of pharmaceuticals and pesticides released into the river

- Boevange

- Mamer



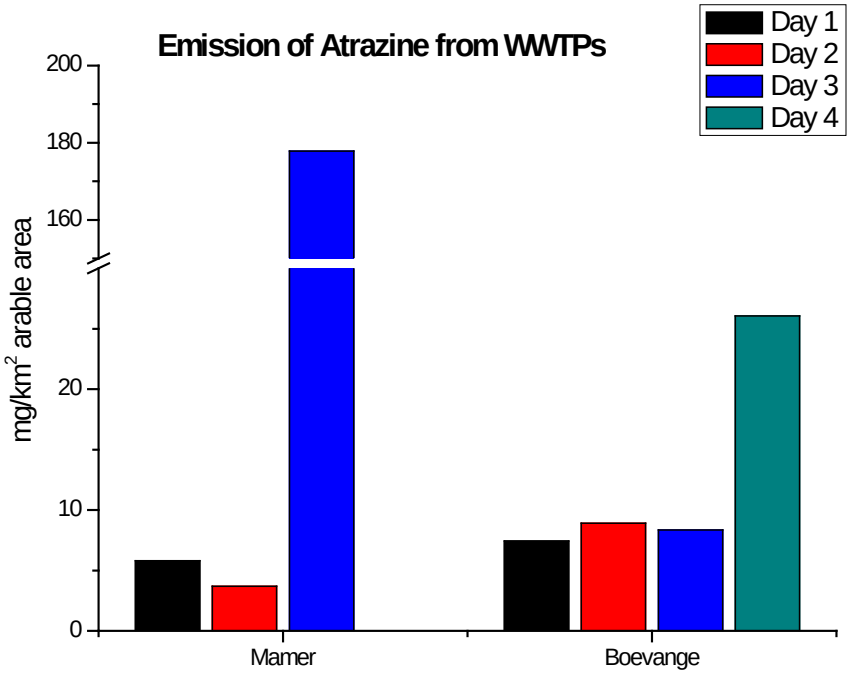
3. Xenobiotic dynamics

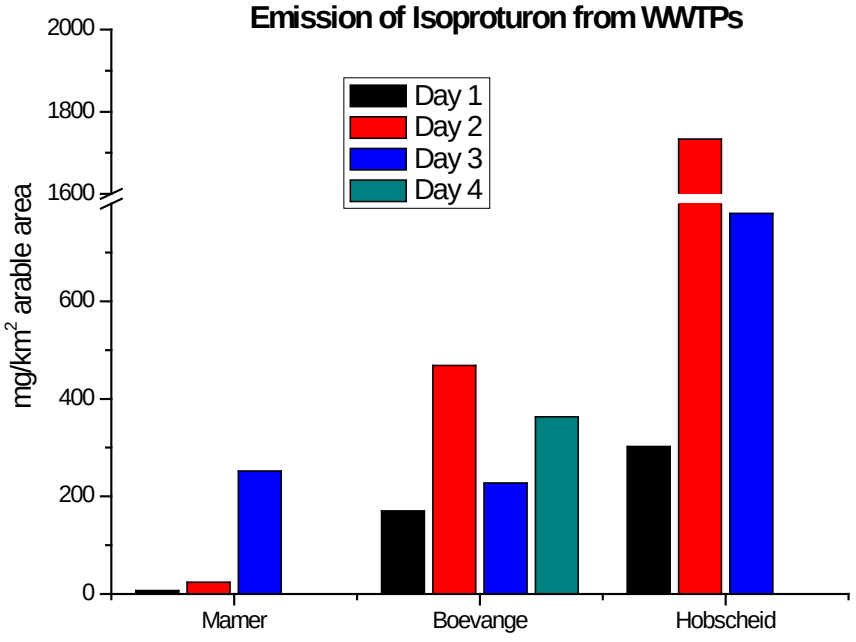


3. Xenobiotic dynamics

Atrazine is still released from WWTPs , mainly under high flow conditions

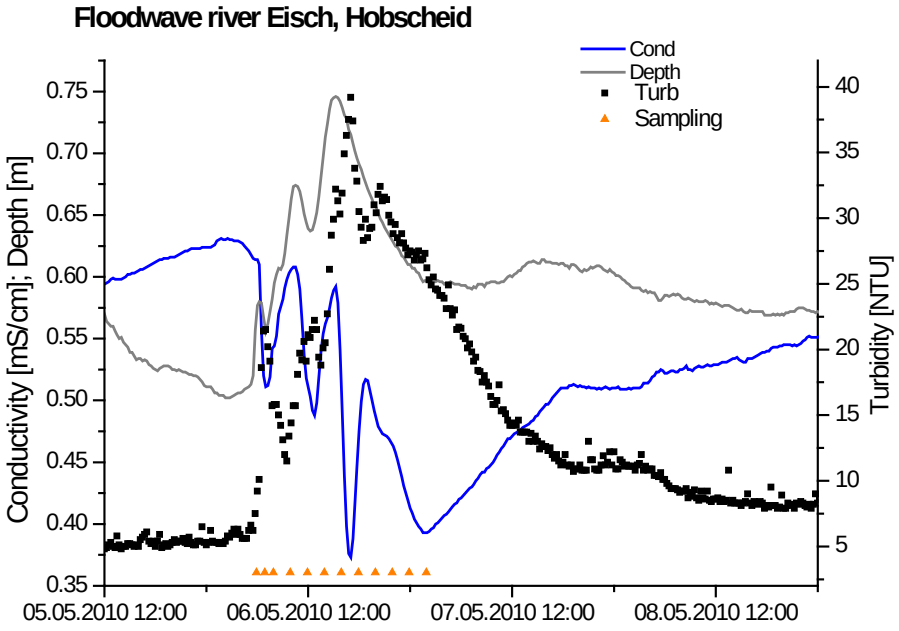
Isoproturon loads discharged into the rivers are much higher with a bigger variability

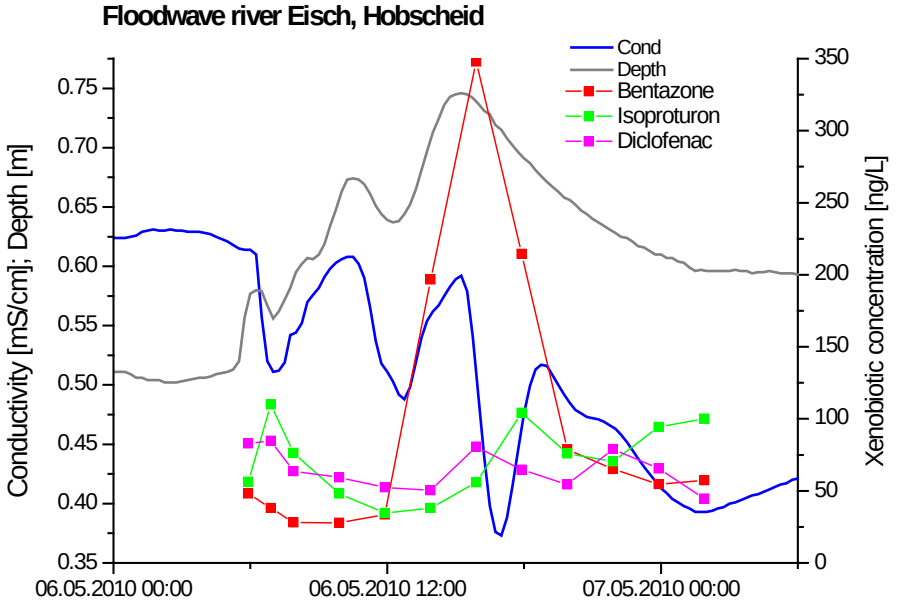




4. Floodwave

Floodwave sampling at the river Eisch, downstream of WWTP Hobscheid

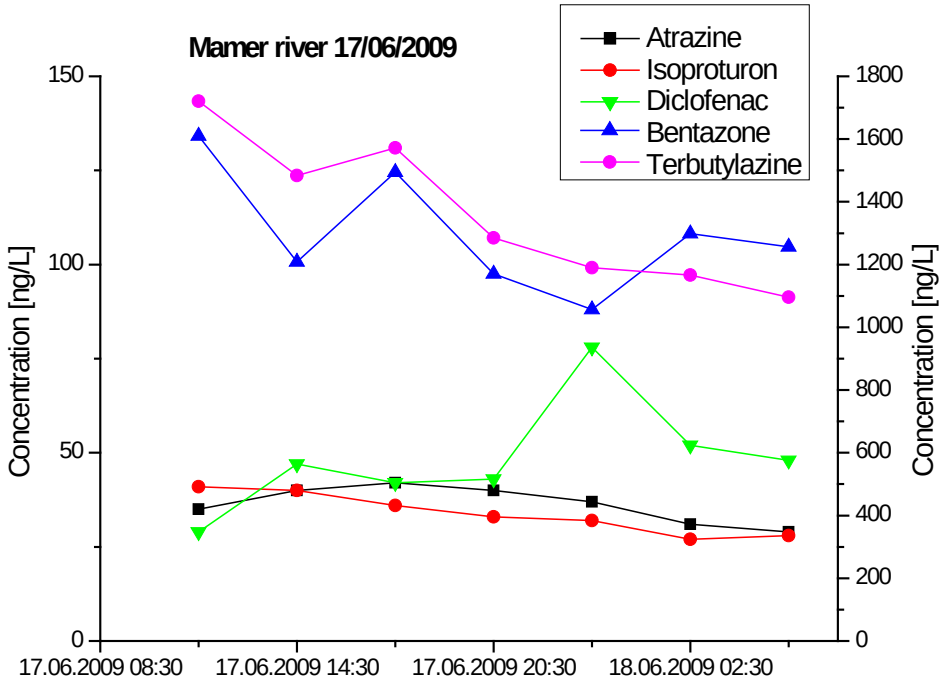




Different dynamics (and sources) for some pesticides

4. Floodwave

Floodwave during the sampling at the river Mamer, downstream of WWTP



Surface runoff => higher concentrations

Lower impact of WWTP effluent => dilution effect

5. Conclusion

Monitoring with POCIS

- Easy to handle
- Reliable results under constant conditions
- Turbulence of the system is important

Open question:

Influence of high concentration pulses (short term) on sampling rates in comparison to permanent low concentration (long term)

=> High-resolved wave sampling (POCIS + auto-sampler)

Funding: Ministry of the Interior

In Cooperation with:

Wastewater Syndicate SIDERO

Administration de la gestion de l‘eau, Laboratoire

Thank you for your attention!