Le contrôle des pollutants organiques dans le WFD: Pourquoi et Comment?

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Europa University of Applied Sciences Fresenius, Germany.

Innova-Med

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Monitoring organic pollutants within the WFD:
Why and relevance for water reuse

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Innova-Med

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Outline:

- Why do we need to monitor within the WFD ?

  Strategy of monitoring

  Results of monitoring

  (WWTP-influent & -effluent; surface & ground water; soil)

- Relevance for water reuse

  Persistence (parent compounds and metabolites)

  Innovative waste water treatment

Strategy of monitoring (WFD):

Each ***compound***
- and also ***metabolite*** –
which could possibly appear has to be investigated.

....*if an analytical method is available and the analysis not too costly*

Time schedule WFD:

Dec. 2000	In force
Dec. 2003	National law implementation
Dec. 2004	Characterisation and inventory
Dec. 2006	Programs for monitoring are ready for application
Dec. 2009	Program for measures and plans for management of river basin are finished
Dec. 2012	Program for measure is implemented
Dec. 2015	„good condition“ (ecological + chemical); new plans for management of river basin

Priority Substances and Other Pollutants

The Commission proposal (COM(2006)397 final) setting environmental quality standards for surface waters of 41 dangerous chemical substances includes the 33 priority substances and 8 other pollutants.

Chemical status - 33 priority compounds

Organic compounds (n = 16)

(2) Anthracene
(4) Benzene
(5) Brominated diphenylethers
(7) Chloroalkanes (C_{10} -C_{13})
(10) 1,2-Dichloroethane
(11) Dichloromethane
(12) DEHP
(15) Fluoranthene
(17) Hexachlorobutadiene
(22) Naphthalene
(24) Nonylphenols (4-para-N)
(25) Octylphenols (para-tert-O)
(26) Pentachlorobenzene
(28) PAK (Benzo-a-pyrene, Benzo-b-fluoranthene, Benzo-g,h,i-perylene, Benzo-k-fluoranthene, Indeno-1,2,3-cd-pyrene)
(31) Trichlorobenzenes (1,2,4-TB)
(32) Trichlormethane

Metals (n = 4)

(6) Cadmium
(20) Lead
(21) Mercury
(23) Nickel

Pesticides (n = 13)

(1) Alachlor
(3) Atrazine
(8) Chlorfenvinphos
(9) Chlorpyrifos
(13) Diuron
(14) Endosulfan
(16) Hexachlorobenzene
(18) HCH (Lindan)
(19) Isoproturon
(27) Pentachlorophenol
(29) Simazine
(30) TBT-cation
(33) Trifluralin

Identified as priority dangerous compounds (n = 13)

European Water Framework Directive (WFD)

Starting 2007 the EU-member states have to conduct monitoring programs upon organic pollutants and others.

Hesse, Germany carried out a prelimary monitoring to find appropriate sampling points.

- 119 sampling locations
- 95 substances, including pesticides, pharmaceuticals, industrial chemicals & metabolites

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Pesticide monitoring in 2004/2005

pesticide	quality standard [µg/L]	90-perc. [µg/L]	maximum value [µg/L]
Isoproturon	0.3 / 1.0 *	0.47	15
Mecoprop (MCPP)	0.1	0.12	11
Dichlorprop (2,4-DP)	0.1	0.11	10
n-Chloridazon	0.1	0.1	9.7
Bentazone	0.1	0.14	9
MCPA	0.1	0.16	7.7
Metazachlor	0.4	< l.d.	4.6
Diuron	0.2 / 1.8 *	0.21	4.5
Metobromuron		< l.d.	4.4
Metamitron		0.2	4.3
Ethofumesate		0.12	3.9
Terbuthylazine	0.5	0.04	2.5
Metolachlor	0.2	< l.d.	1.6
Atrazine	0.6 / 2.9 *	< l.d.	1.4
Terbutryn	0.03	0.09	1.3
Epoxiconazole		0.04	1
2,4-D	0.1	< l.d.	0.91
Propiconazole		0.07	0.8
Metribuzin		< l.d.	0.75
Fluoxypyr		0.04	0.55
Tebuconazole		0.05	0.51
Fenpropimorph		< l.d.	0.49
Terbutylazine-desethyl		< l.d.	0.47
Dichlobenil		< l.d.	0.46
Haloxyfop		< l.d.	0.46

approx. 700 samples

74 pesticides found, therefrom

25 with max. values

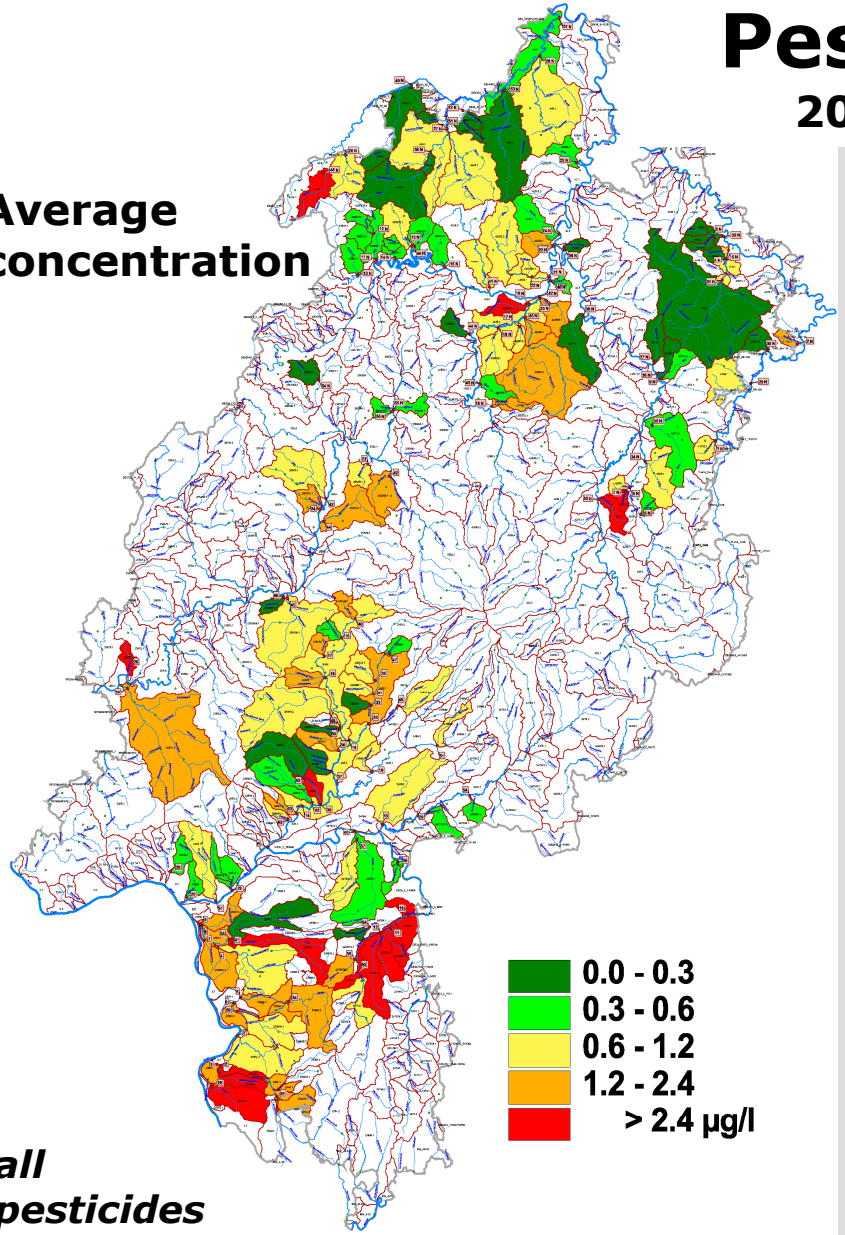
l.d. = limit of detection

•annual average value / maximum value

Pesticides

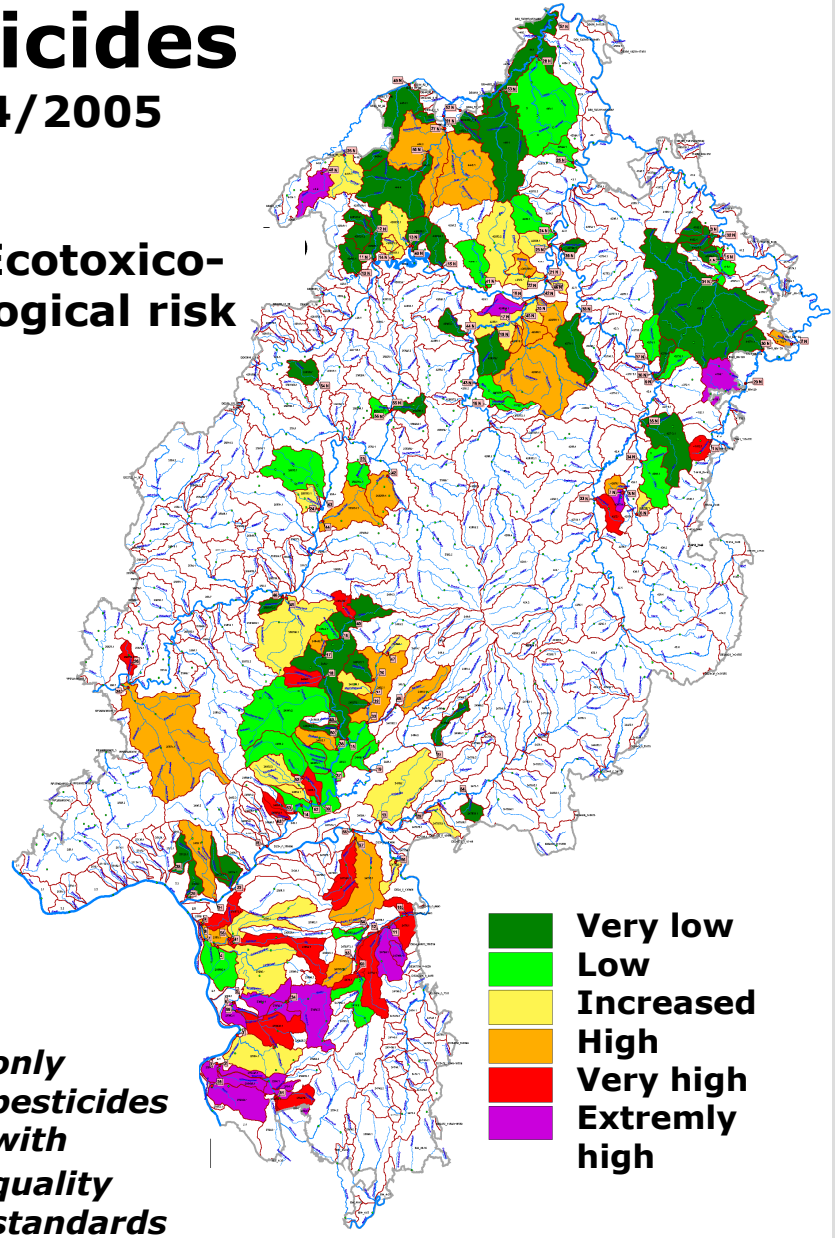
2004/2005

Average concentration



all pesticides

Ecotoxico-logical risk



only pesticides with quality standards

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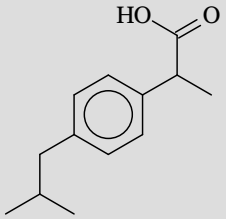
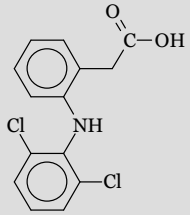
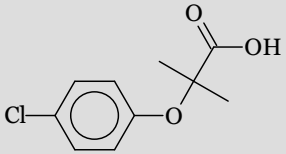
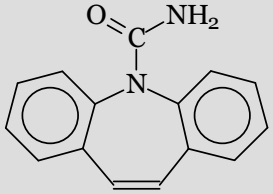
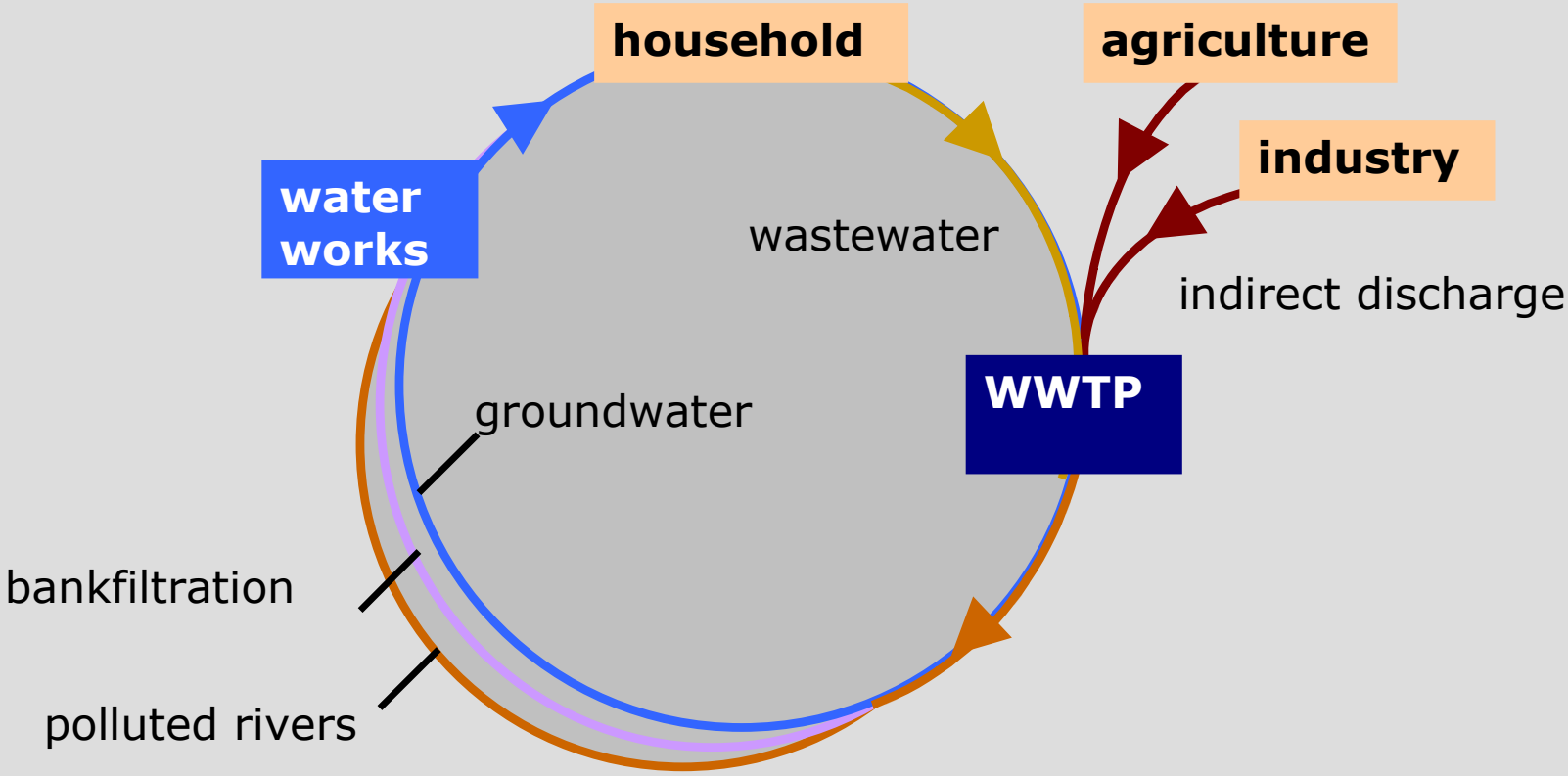
Selection pharmaceuticals, which might be regulated within the EU

Compound class	Formula	Name
Analgetics		**Ibuprofen**
Analgetics		**Diclofenac**
Lipid regulator		**Clofibric acid**
Anti depressiva		**Carbamacepine**

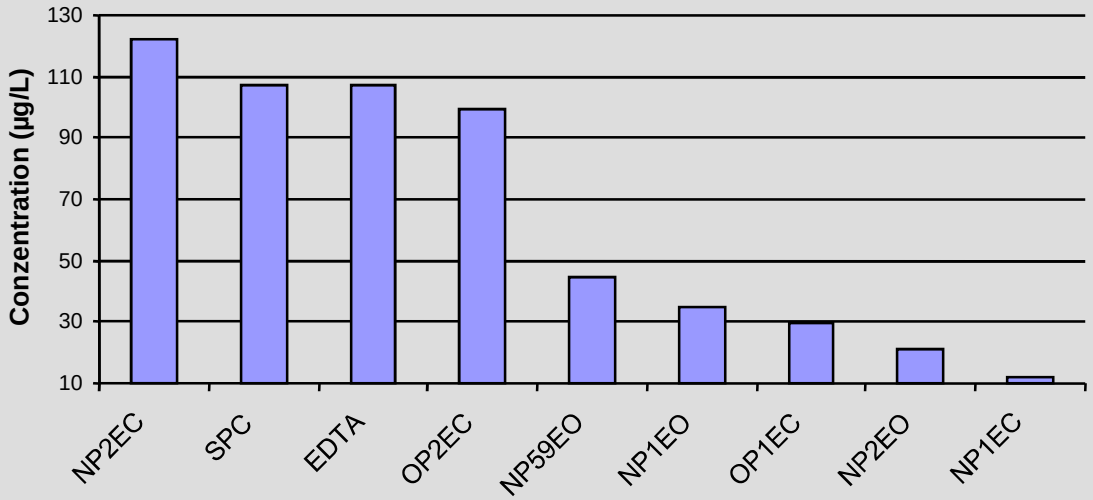
Polar Persistent Pollutants (P^3): Entry into the watercycle



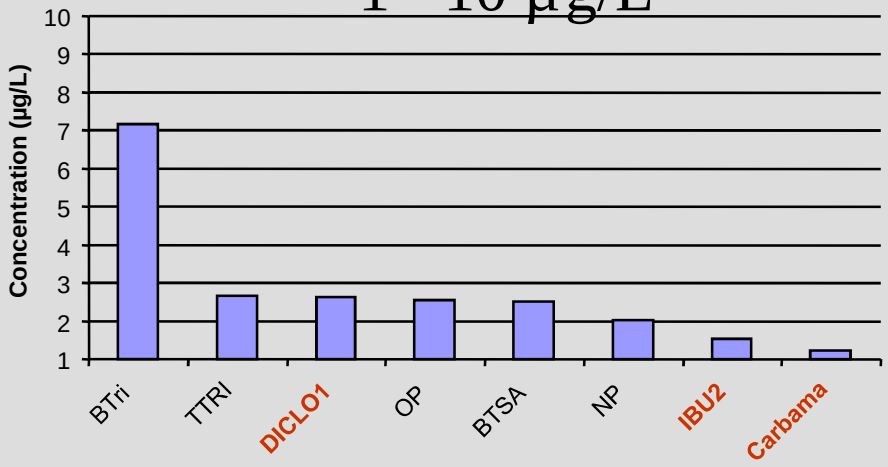
Uncontrolled Re-use????

P3-compounds in European wastewaters

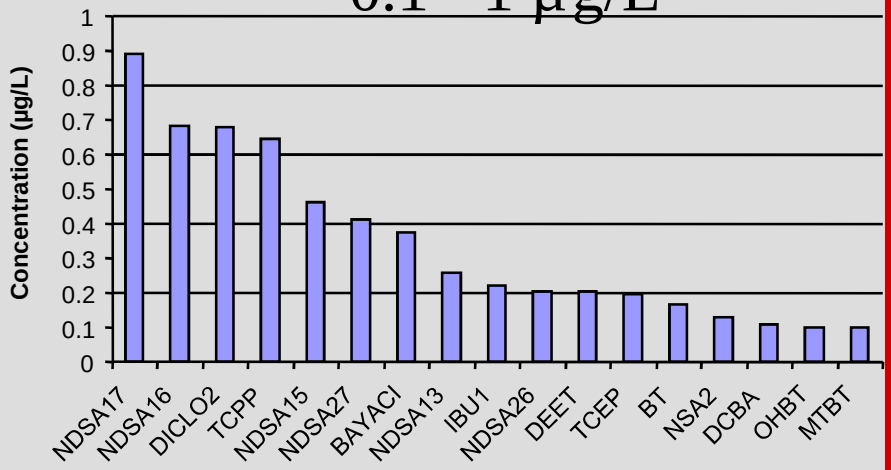
10 - 100 µg/L



1 - 10 µg/L

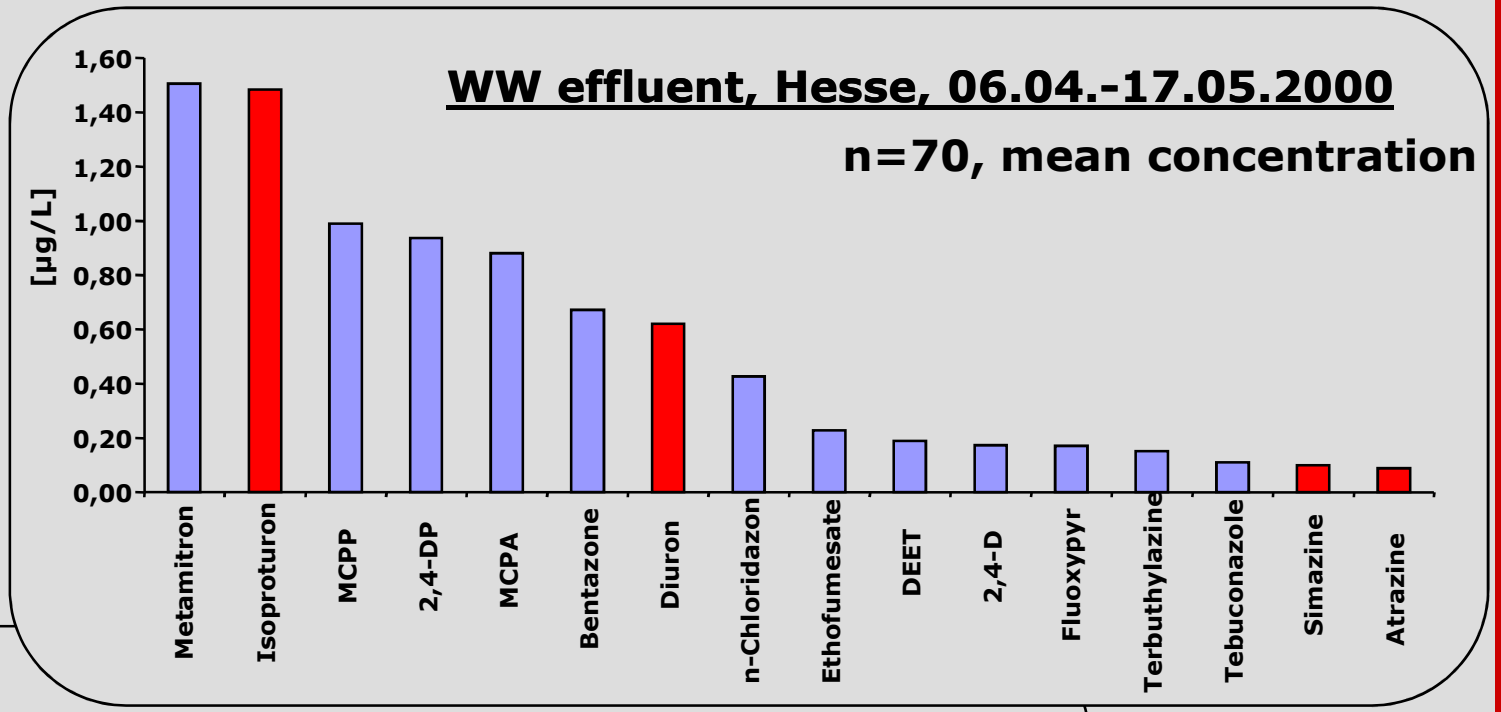


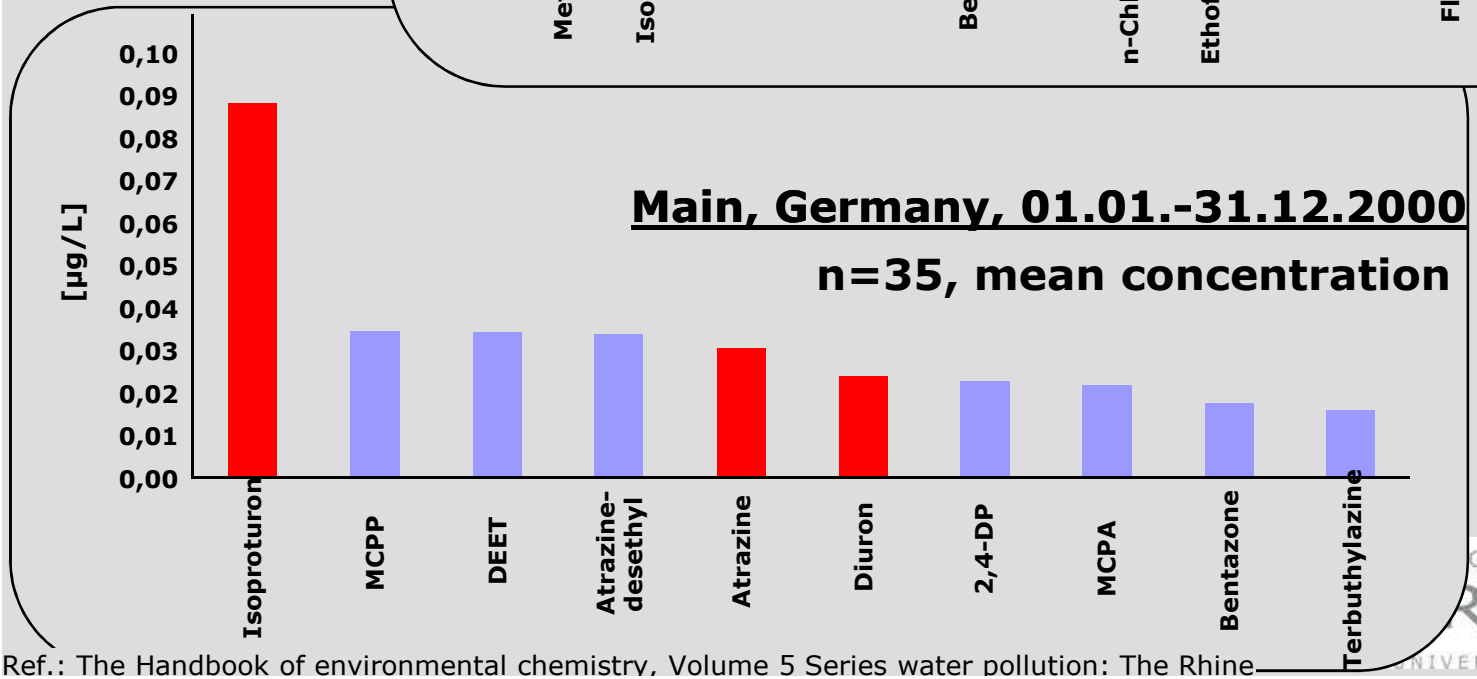
0.1 - 1 µg/L



T.Reemtsma[1], S.Weiss[1], J.Mueller[2], M.Petrovic[3], S.González[3], D. Barcelo[3] F.Ventura[4], T.P.Knepper[2*] EST 2006

Comparison of pesticide concentrations in waste and surface waters





Ref.: The Handbook of environmental chemistry, Volume 5 Series water pollution: The Rhine

Balance of the stream Nidda to bordering WWTPs

Compound	Waste water treatment plant pestcide load in kg	Nidda pesticide load in kg	Share of load of pesticides from WWTP to total load in Nidda in %
Atrazine	1,9	3,4	57
MCPP	5,2	7,7	67
2,4-DP	4,4	6,9	63
Isoproturon	8,5	14,0	61
Diuron	6,6	10,4	64

Data gained 23/04/1994 to 24/05/1994

How is the concentration in the water cycle correlated with the elimination during wastewater treatment??

Comparison of “Acitivated Sludge” and “Membrane Bioreactor”

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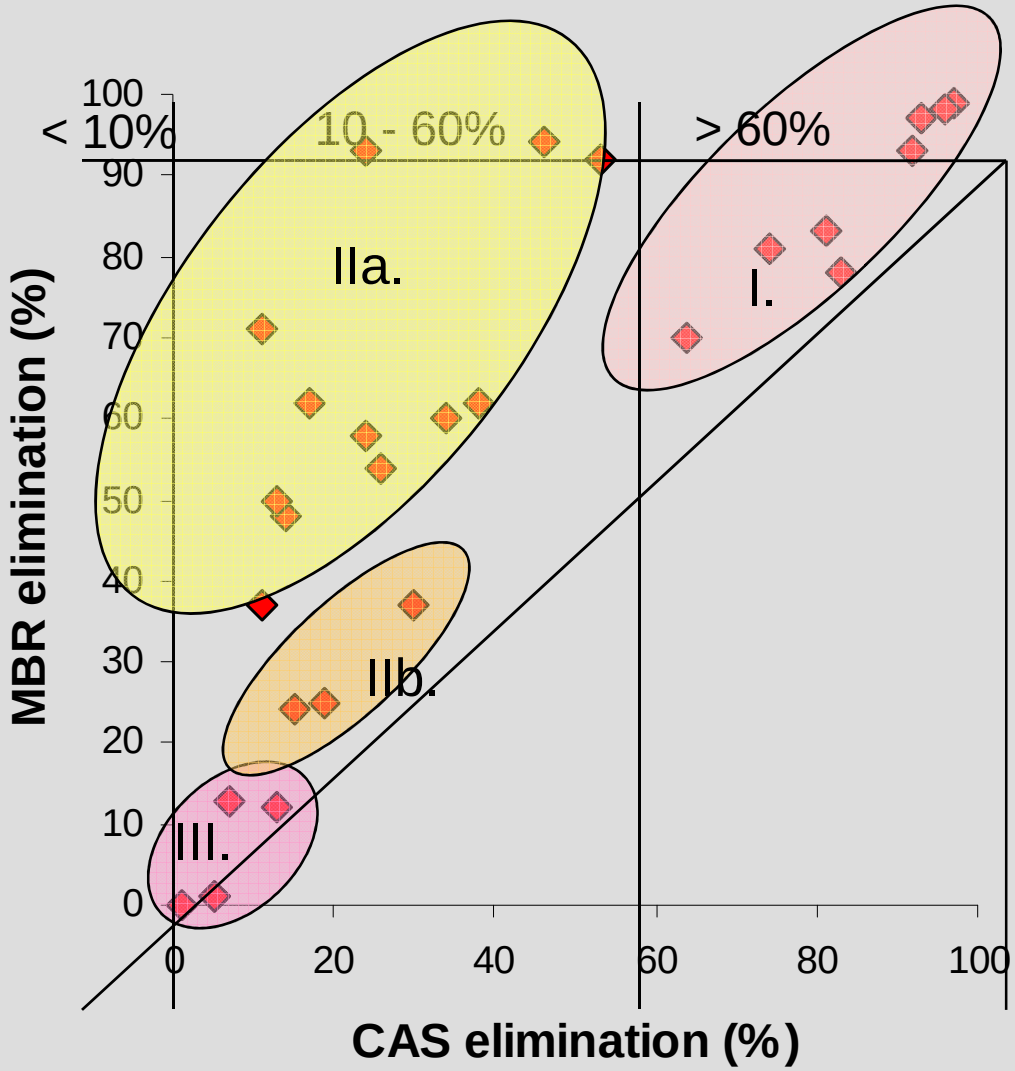
MBR - CAS Comparison



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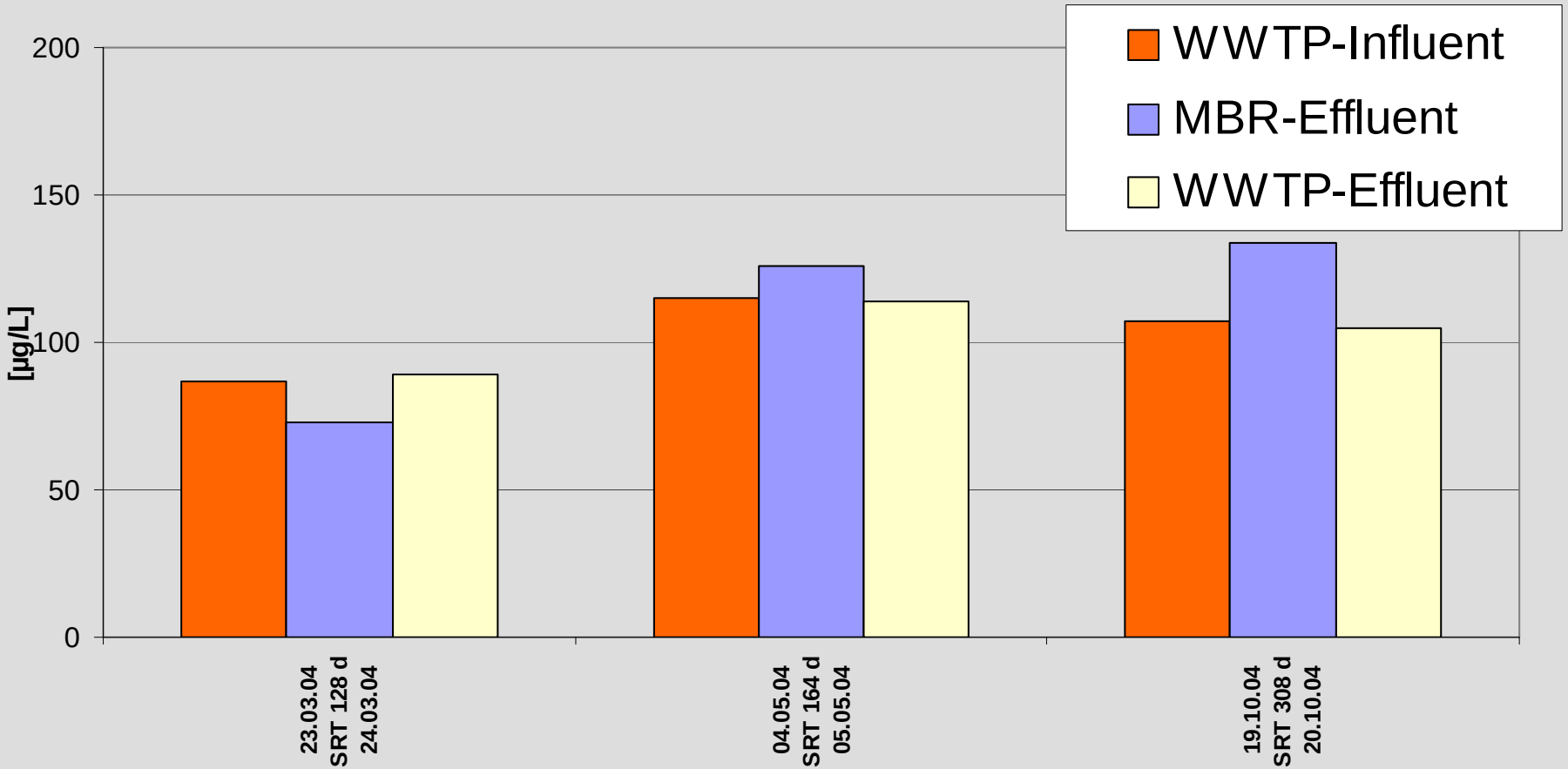
EDTA / Atrazine !!



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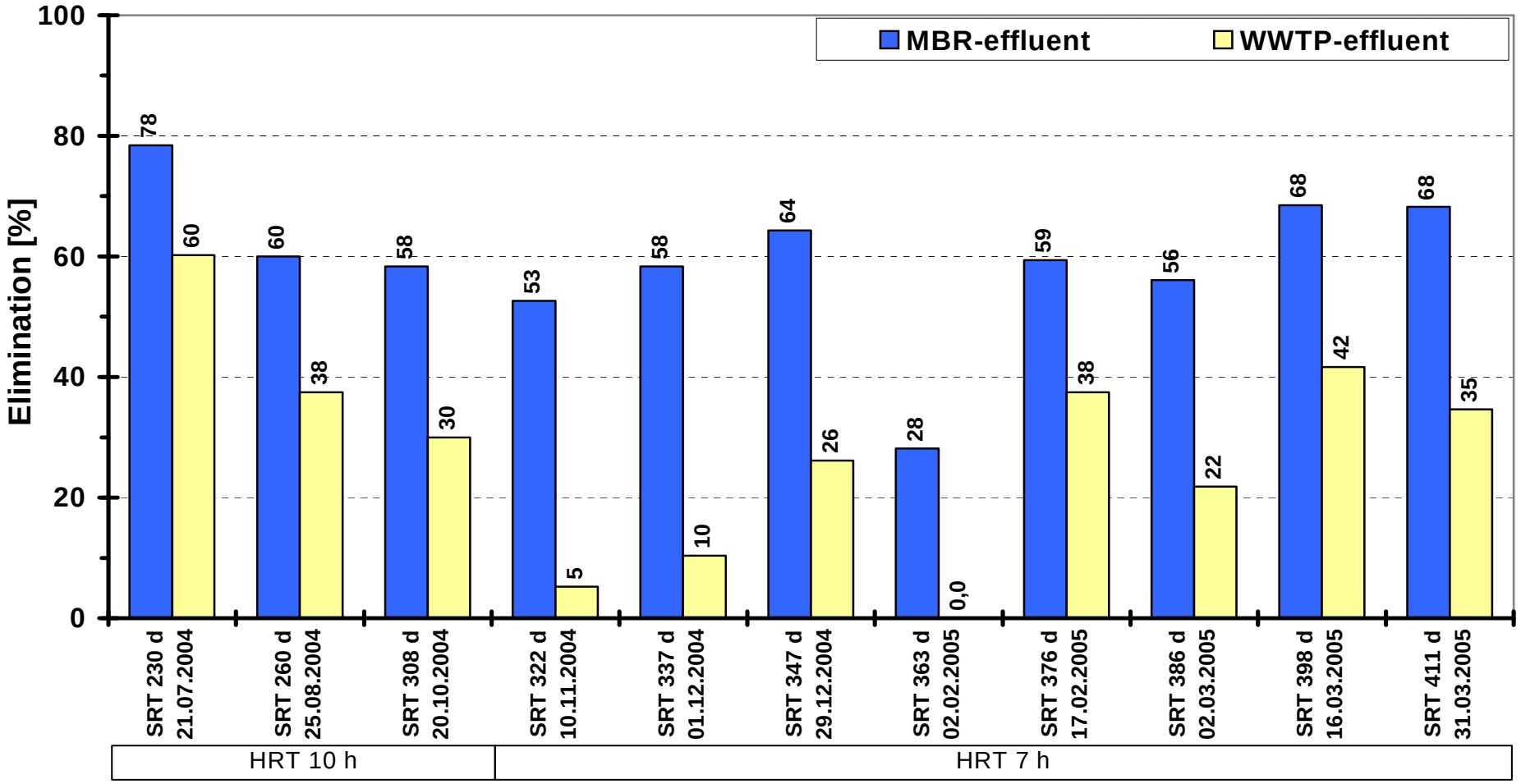
Elimination rates of diclofenac



No adsorption to sludge!

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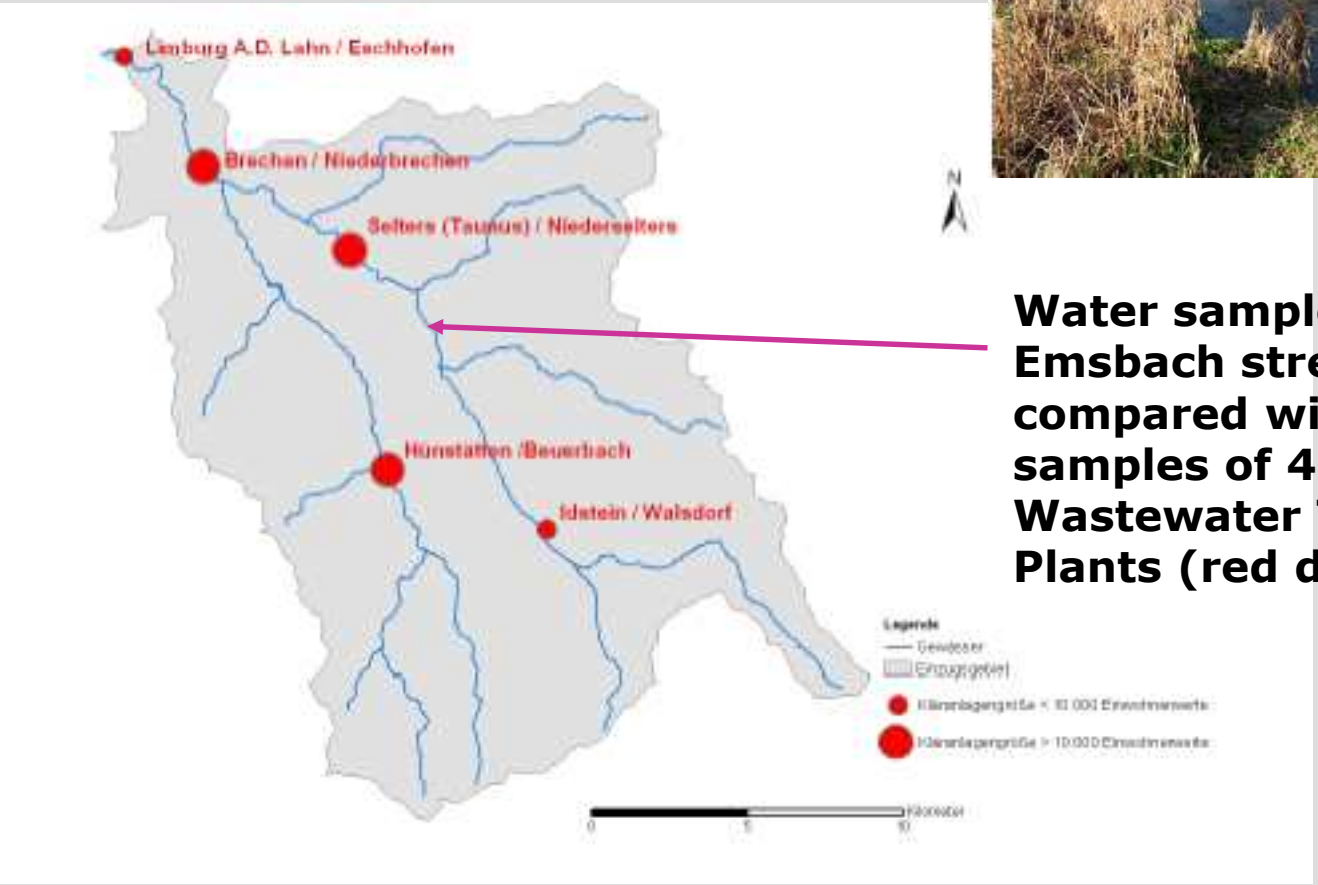
Balance of data gained for Hessian project* to fulfill requirements of WFD



Water samples of Emsbach stream compared with water samples of 4 Wastewater Treatment Plants (red dots)

***„Auswahl der kosteneffizientesten Maßnahmenkombinationen unter Berücksichtigung der Umweltziele und Ausnahmen nach Art. 4 WRRL anhand ausgewählter Wasserkörper im hessischen Teil des Bearbeitungsgebiets Mittelrhein"**

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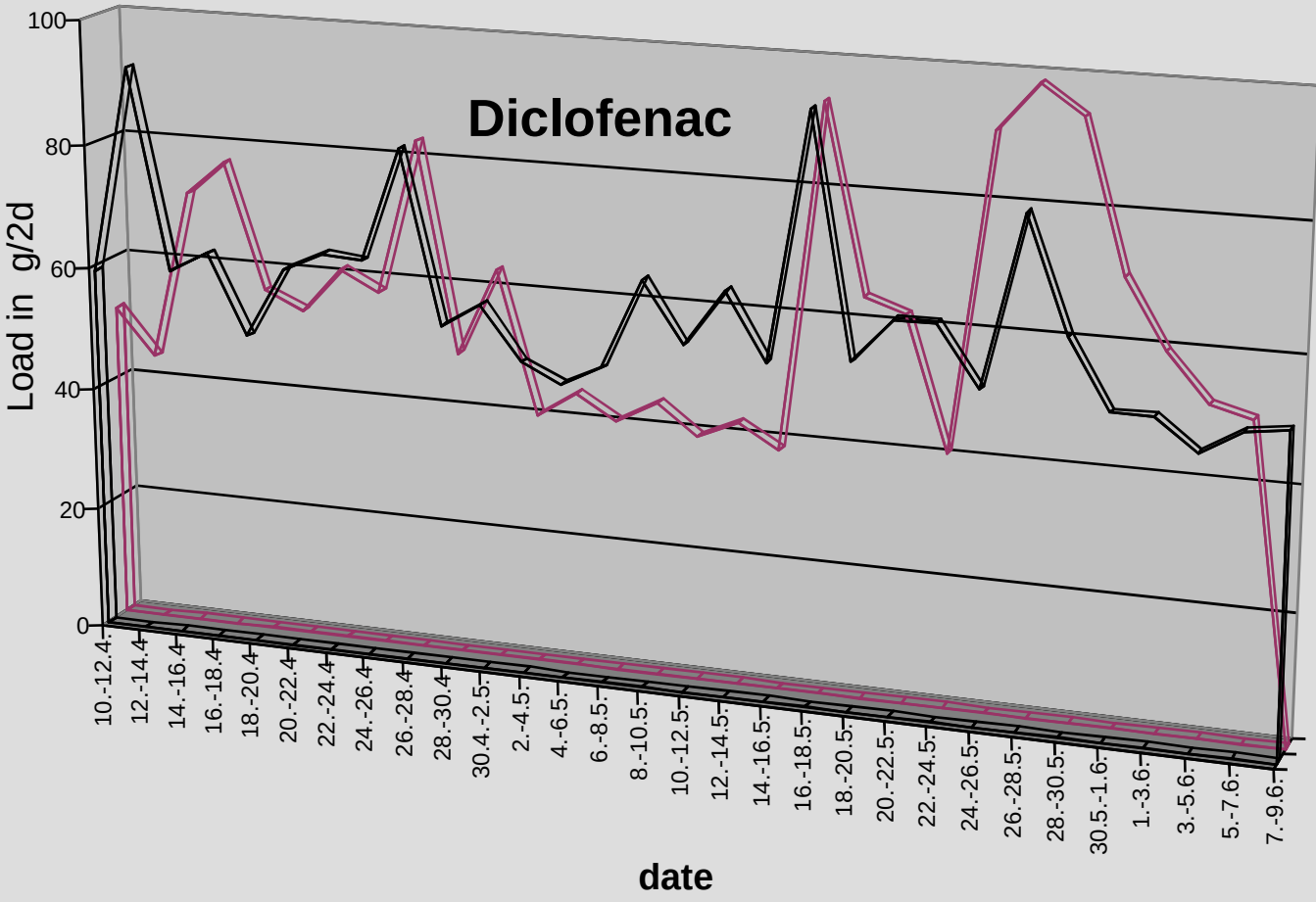
Balance of entry of emerging contaminants into the aquatic environment via WWTP:



Total for 2 month analysis (2006):

WWTP: 1.83 kg

Stream: 1.77 kg

(result different for degradable compounds)

Stream

Total of 4 WWTP effluents

HLUG

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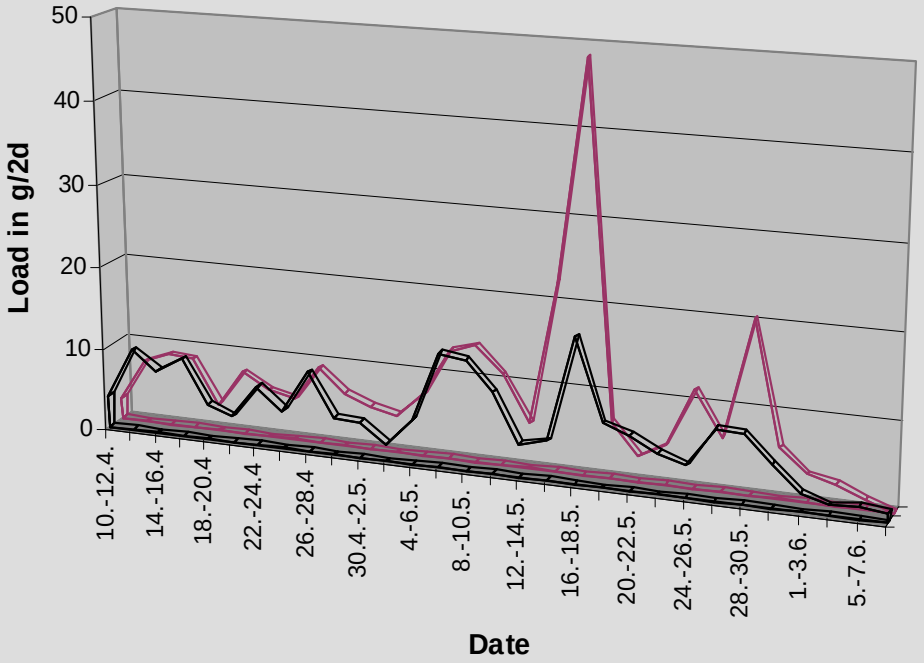
Isoproturon



Stream Emsbach

Total of 4 WWTP effluents

Where do persistent polar priority pesticides and metabolites remain in the environment?

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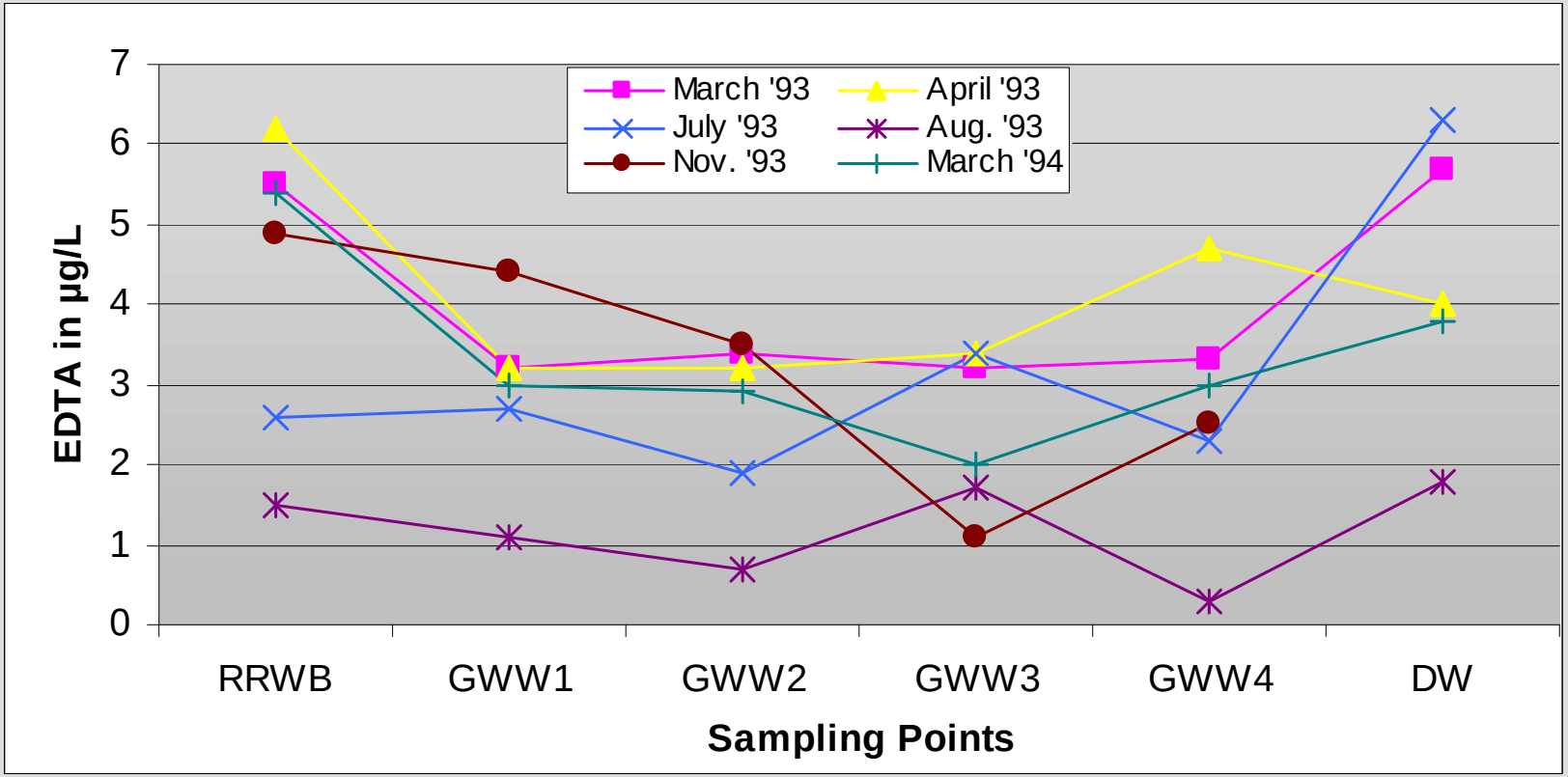
Values of EDTA in ground water wells



RRWB = River Rhine Water Basin; GWW1 = Groundwater Well (1 m); GWWW2 (80 m); GWW3 (145 m); GWW4 (160 m); DW = Drinking Water

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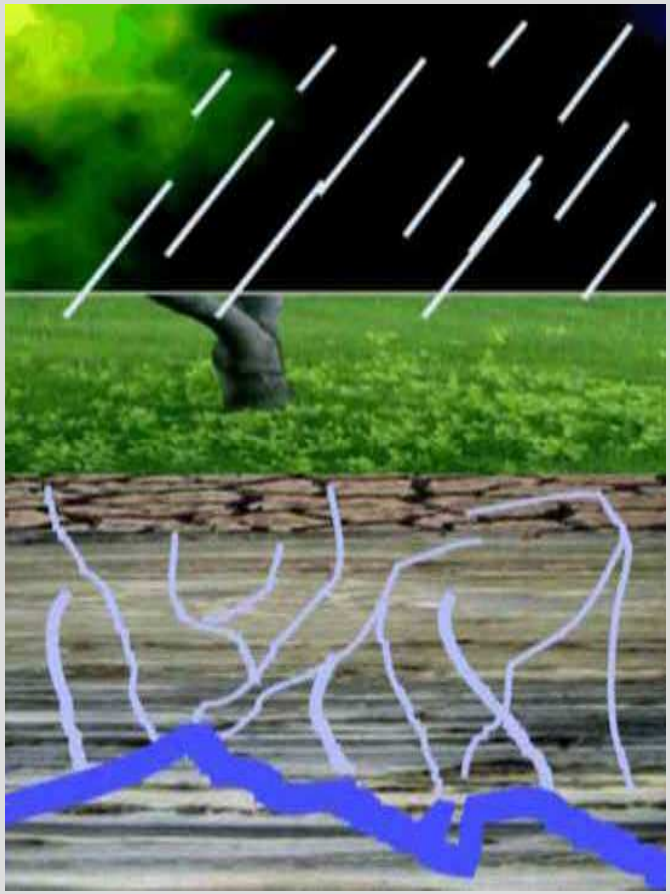
Occurrence of barbiturates in irrigated ground water (Berlin)

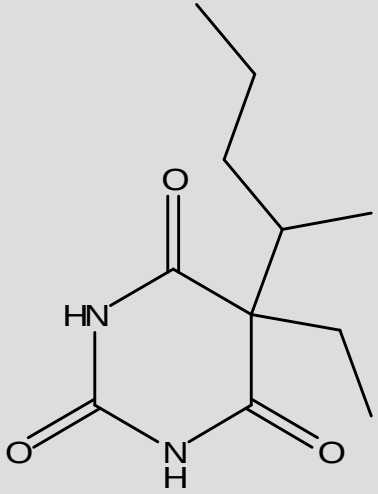


Groundwater, Berlin

WW infiltration 40 y ago:

Phenobarbital:

up to 1.3 µg/L



Others:

between 0.05 and 0.08 µg/L

Science News – July 26, 2006

Barbiturates' environmental legacy

Pharmaceuticals can persist in the environment, even after a sharp decline in use.

Although the use of barbiturates peaked more than 3 decades ago, the drugs are still being detected in surface water and groundwater in Germany, according to new research published today on *ES&T*'s Research ASAP website (DOI: 10.1021/es052567r). Scientists report that some pharmaceuticals can linger in the environment well past their date of use. Furthermore, the data suggest that manufacturers should consider a product's potential to degrade when they develop new pharmaceuticals.

"This is the first time that anyone has systematically looked for barbiturates in the environment," says corresponding author Thomas Knepper of the Europa University of Applied Sciences Fresenius (Germany). "Since these compounds are polar—therefore don't adsorb to soils—and are hardly biodegradable, we suspected that they could still be around," he adds.

The Mulde, an idyllic river in Germany, is significantly impacted by barbiturates from an unknown source.

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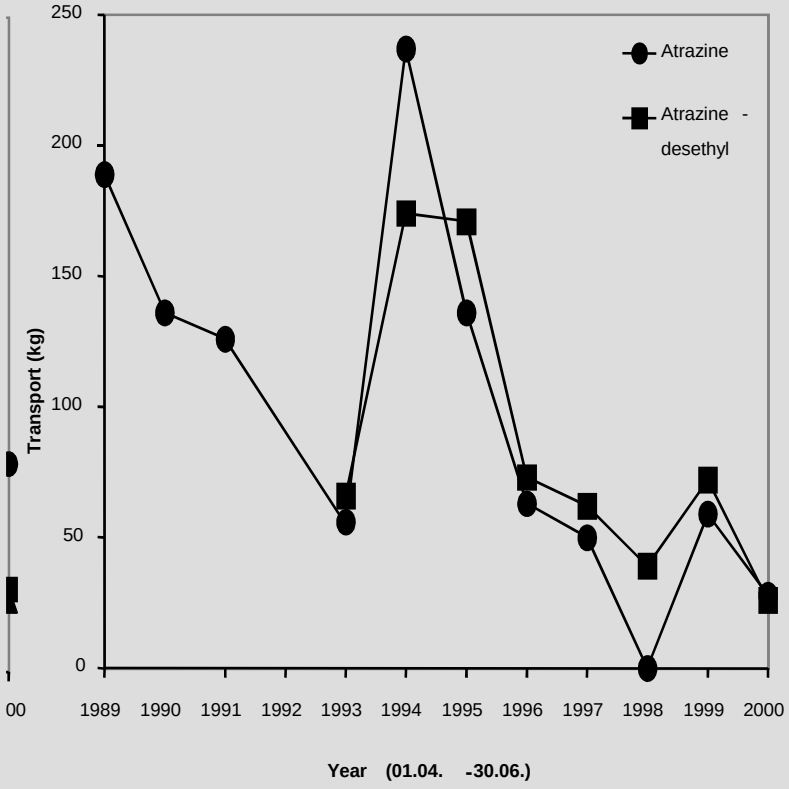
Atrazine in surface water

In Germany baned since 1991, but still detectable

Formation of metabolites in soil



Transport rates of atrazine, atrazine-desethyl in the Main river during the period of 01.04.-30.06. over the years 1989 to 2000.

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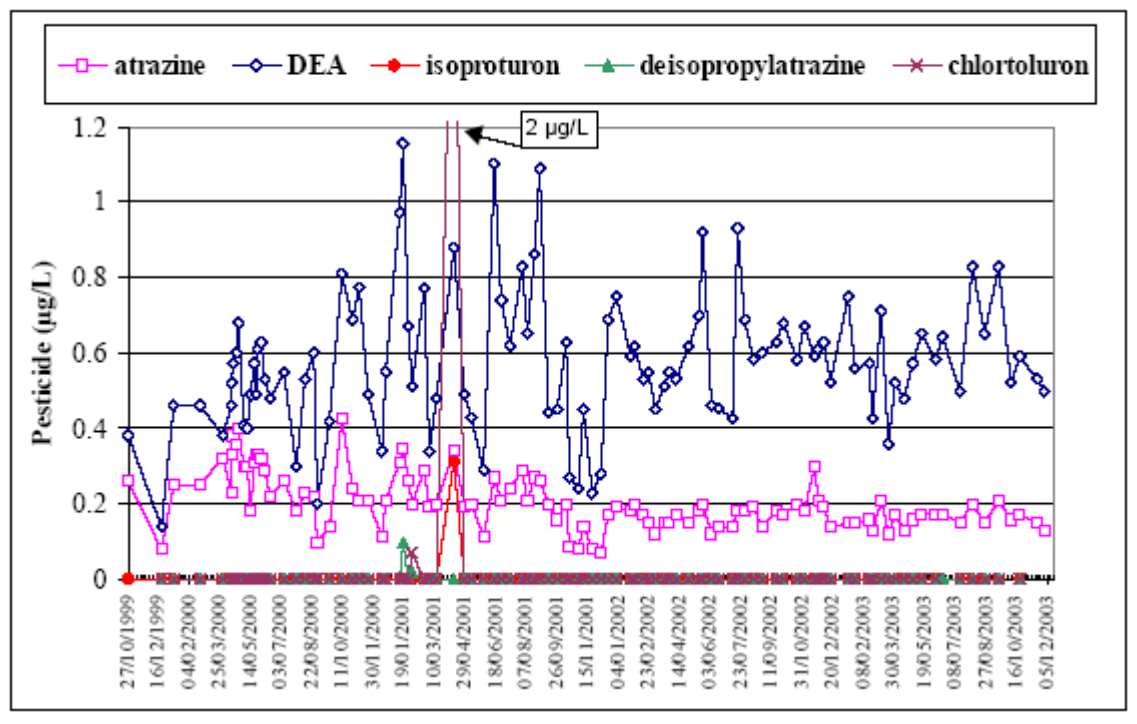
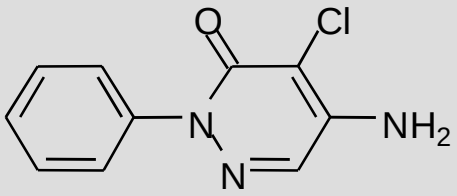
The problem:

- atrazine application in the watershed was stopped in 2000 (replaced by acetochlor)
- groundwater of the Brévilles spring still exhibits contamination by atrazine and desethylatrazine with concentrations of 0.19 ± 0.7 µg/L and 0.59 ± 0.18 µg/L, respectively

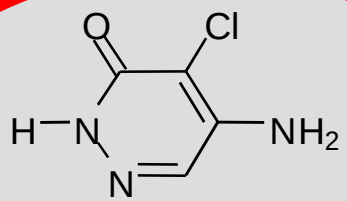


Do soil/rocks act as „storage tank“ ?

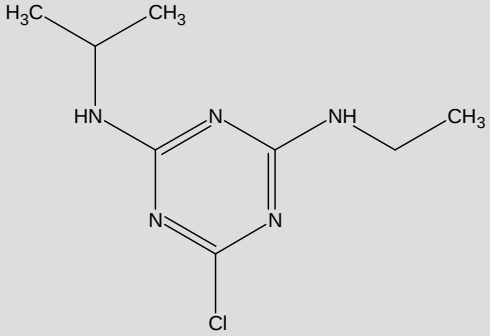
Selected pesticides and metabolites



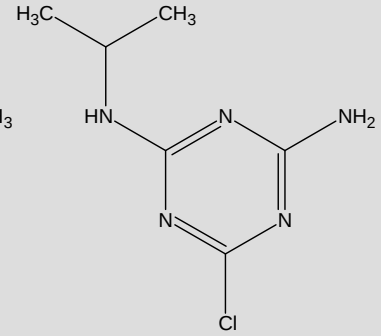
Chloridazon



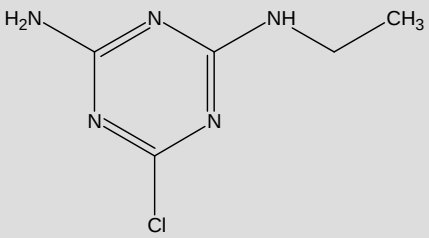
Desphenyl - chloridazon



atrazine



desethyl-atrazine



desisopropyl-atrazine

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Concentrations of LAS and ABS in surface and groundwatres in the Philippines

Surface Water sample	ABS (µg/L)	LAS (µg/L)	ABS/LAS ratio
Bucal Stream	3.5	25	0.14
San Pedro River	66	102	0.65
San Christobal River	9.2	8.4	1.1
Napindan Channel	1.0	2.2	0.45
Pasig River (Guadalupe)	4.1	8.0	0.51
Pasig River (Manila Bay)	22	27	0.81
Ground Water sample			
Spring – Drinking Water	3.2	0.35	9.1
Spring – Drinking Water-	7.2	2.6	2.8
Public Spring - Cabuyao	128	7.3	18
Spring – Cabuyao [1)]	253	4.9	52
Cabuyao Residential area	574	7.0	82
Cabuyao Highway, industrial	792	9.9	80

[1)] (intensive use for laundry washing between 1950 and 1970)

Eichhorn et al, Sci. Tot. Env. 2001;

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Conclusions

- The more pollutants are analysed the more can be detected – main source for entry into the aquatic environment are WWTP.
- Monitoring campaigns need to be well thought of and organized – metabolites need to be included
- Organic pollutants are present in surface waters all over Europe at comparable concentrations (for pesticides during application time)

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Acknowledgement

EFF:

Jutta Müller

Manuela Peschka

Marco Bernhard

Jan Eubeler

Heike Weil

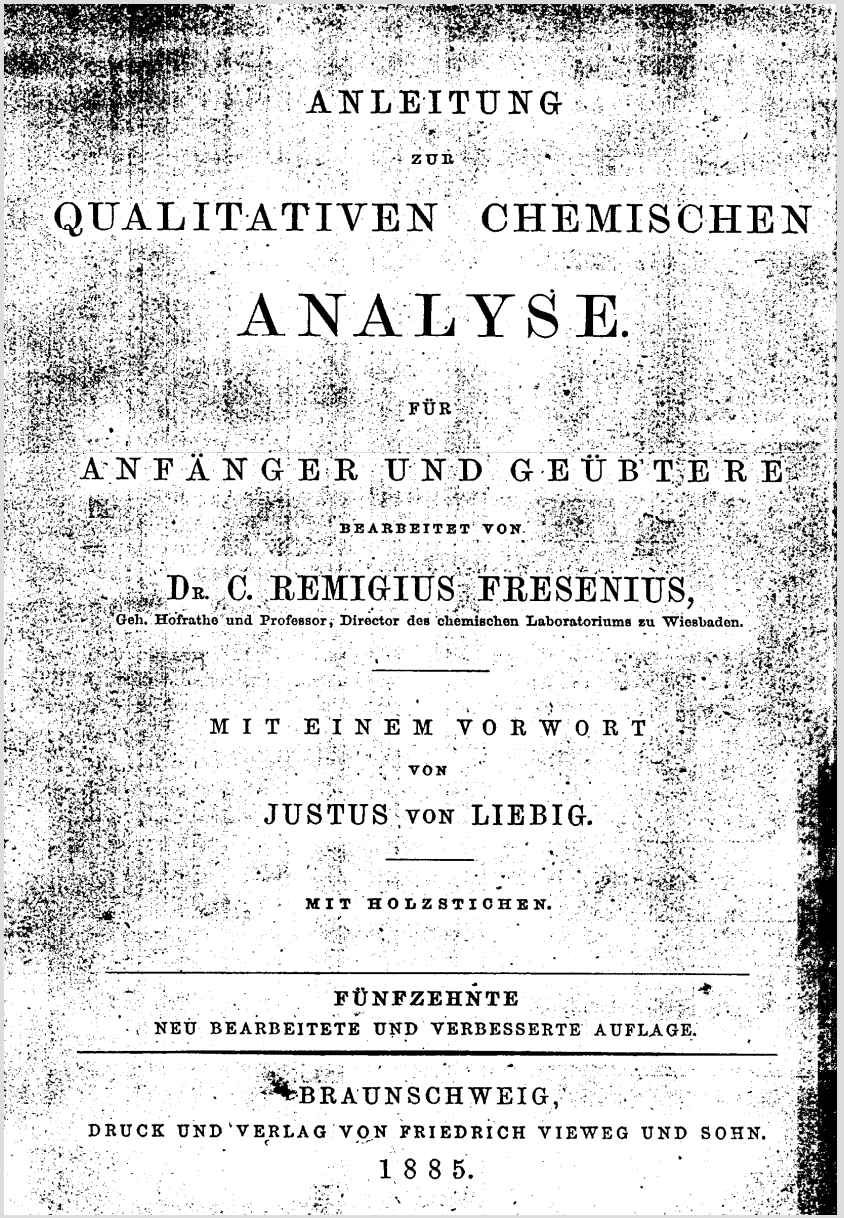
European Commission

(Projects P-THREE; EMCO; Aquaterra;

Innovamed

Hessian Ministry for Environment

Peter Seel



ANLEITUNG

ZUR

QUALITATIVEN CHEMISCHEN

ANALYSE.

FÜR

ANFÄNGER UND GEÜBTERE.

BEARBEITET VON

Dr. C. REMIGIUS FRESENIUS,

Geh. Hofrathe und Professor, Director des chemischen Laboratoriums zu Wiesbaden.

MIT EINEM VORWORT

VON

JUSTUS von LIEBIG.

MIT HOLZSTICHEN.

FÜNFZEHNTE

NEU BEARBEITETE UND VERBESSERTE AUFLAGE.

BRAUNSCHWEIG,

DRUCK UND VERLAG VON FRIEDRICH VIEWEG UND SOHN.

1885.

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How is the effective treatment for re-use ?

What are the relevant compounds to monitor?

Groundwater has not to be deterioated!

What are the long-term effects?

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