Some highlights and present work of the IFAR and possible interactions with ECO

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Outline

Introduction

Water Cycle
Past&Present
Selected Compounds

Experimental Approach

Results and Discussion

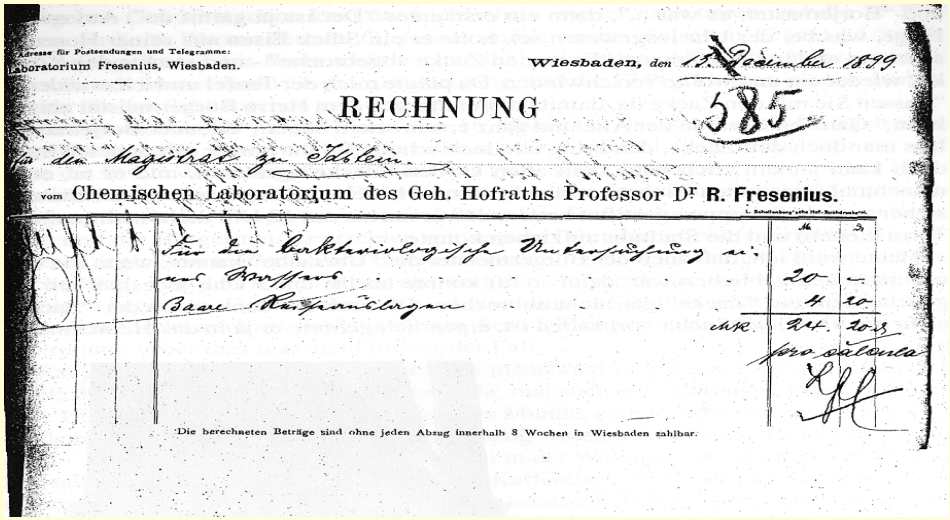
Case Studies: Biodegradation, Photodegradation and Monitoring

Conclusions & suggestions for future work within ECO

University of Applied Sciences Fresenius (HSF) Idstein, Germany

History

1848 Foundation of „Chemischen Laboratorien Fresenius“



Adresse für Postsendungen und Telegramme:
Laboratorium Fresenius, Wiesbaden.

Wiesbaden, den 13. Dezember 1899.

RECHNUNG 585

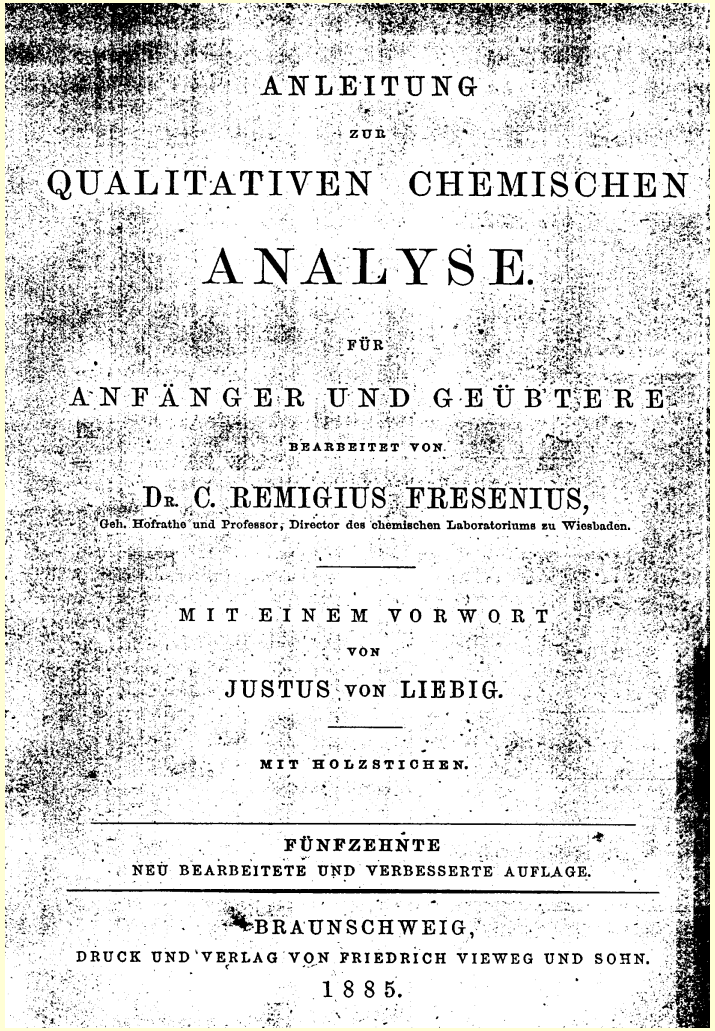
für den Magistrat zu Idstein.

vom Chemischen Laboratorium des Geh. Hofraths Professor Dr R. Fresenius.

	M.	Pf.
Für die bakteriologische Untersuchung v.	20	—
und Porto	4	20
Baare Auslagen		
zus.	24	20

pro saldo

Die berechneten Beträge sind ohne jeden Abzug innerhalb 8 Wochen in Wiesbaden zahlbar.



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.

At present: approx. 3600 Students

Department of Chemistry and Biology

Vocational Education

Chemical Technical Assistants

Biological Technical Assistants

Continuing Education

Chemical Technicians

Disinfector

Study Courses

Chemical Engineering (Degree)

Starting 2008/2009

International Bachelor of Applied Chemistry/Bachelor of Science (BSc)

Bachelor Wirtschaftschemie

Starting 2009/2010

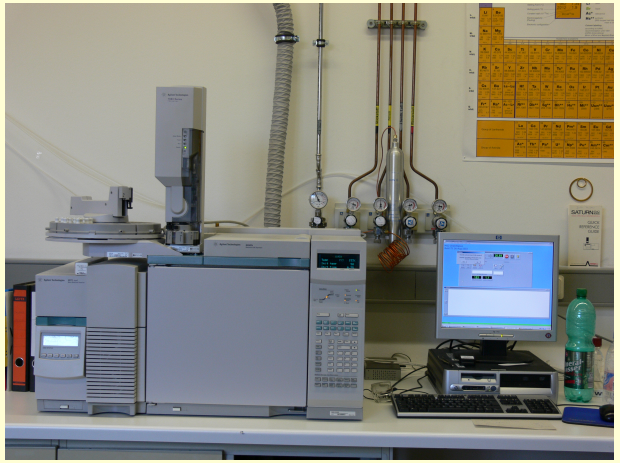
Master of Bio- and Pharmaceutial Analysis

Department of Chemistry and Biology

Institute for Analytical Research (IFAR)

Equipment f.e.

- GC-MS
- LC-MS/MS Trap
- Membrane bioreactor



Aims

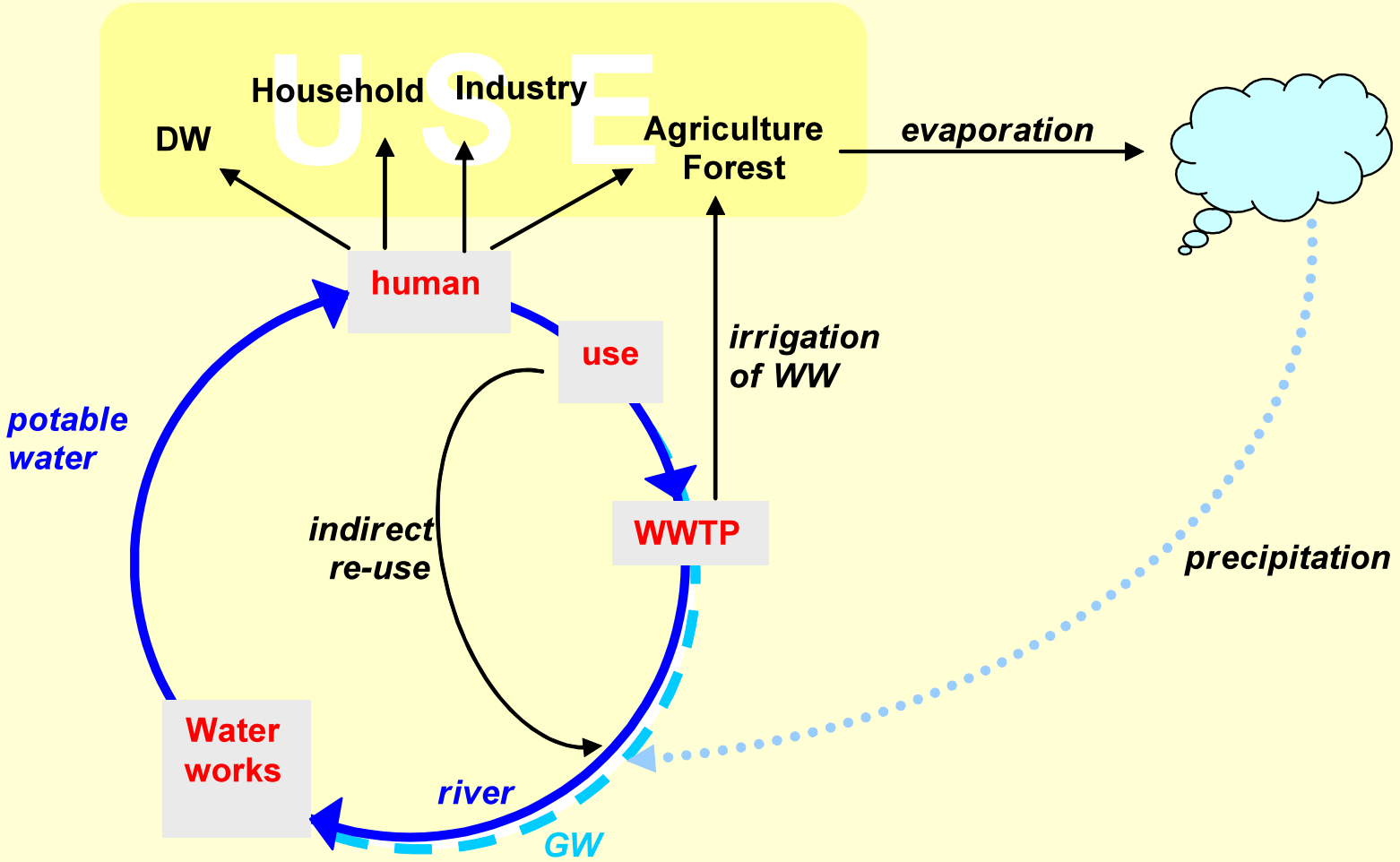
the essential products of teaching and learning, as well as practice and demand orientation, are guaranteed at the interface between teaching and practice

Innovative processes and practices for wastewater treatment and re-use in the Mediterranean region / INCO-CT-2006-517728

facts

- Supported by the European Commission
- Sixth Framework Programme
- Start date: 1. January 2007
- Duration: 42 months
- 13 participants

Contaminants in the water cycle

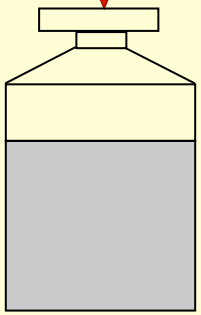


Analytical Approach

Selected conaminants
- pharmaceuticals
- pesticides
- inustrial contaminants
- personal care products
- surfactants

pharmaceuticals
pesticides
surfactants
industrial contaminants
personal care products

What's known?
What's not?

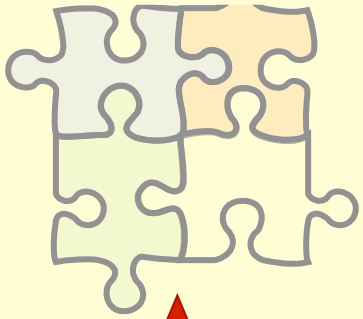


DEGRADATION TEST

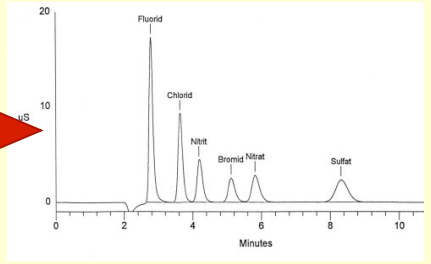
- **degradate**
- **parent compound**

mass spectrometry

IDENTIFICATION



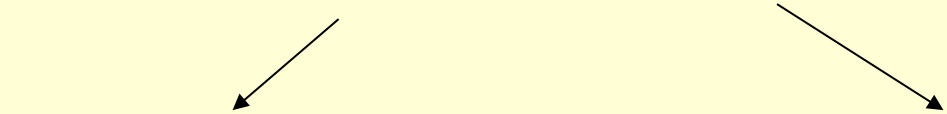
ANALYTICAL METHOD



monitoring

fate in the environment

MASS SPECTROMETRY



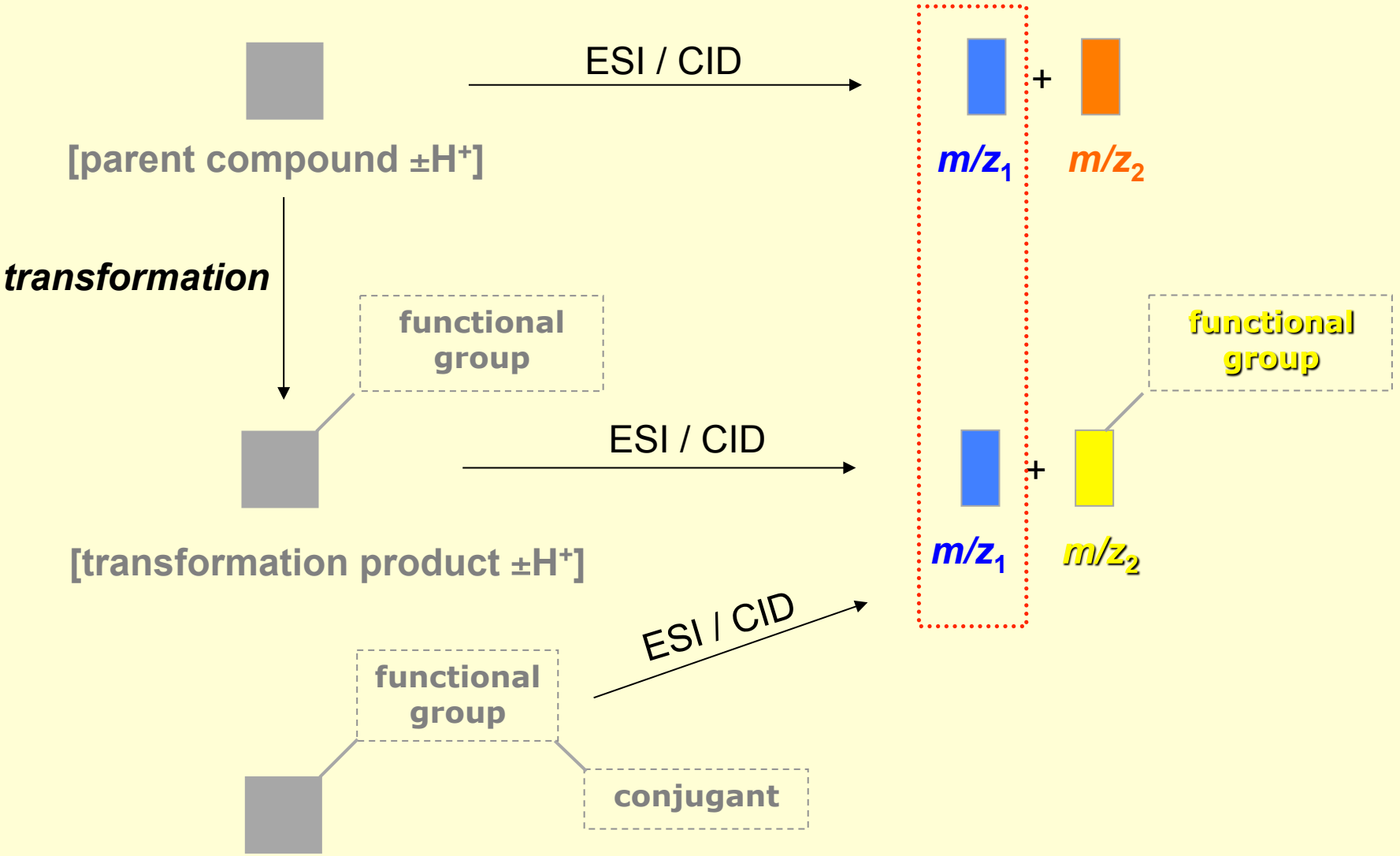
Structure
Elucidation

(degradate)

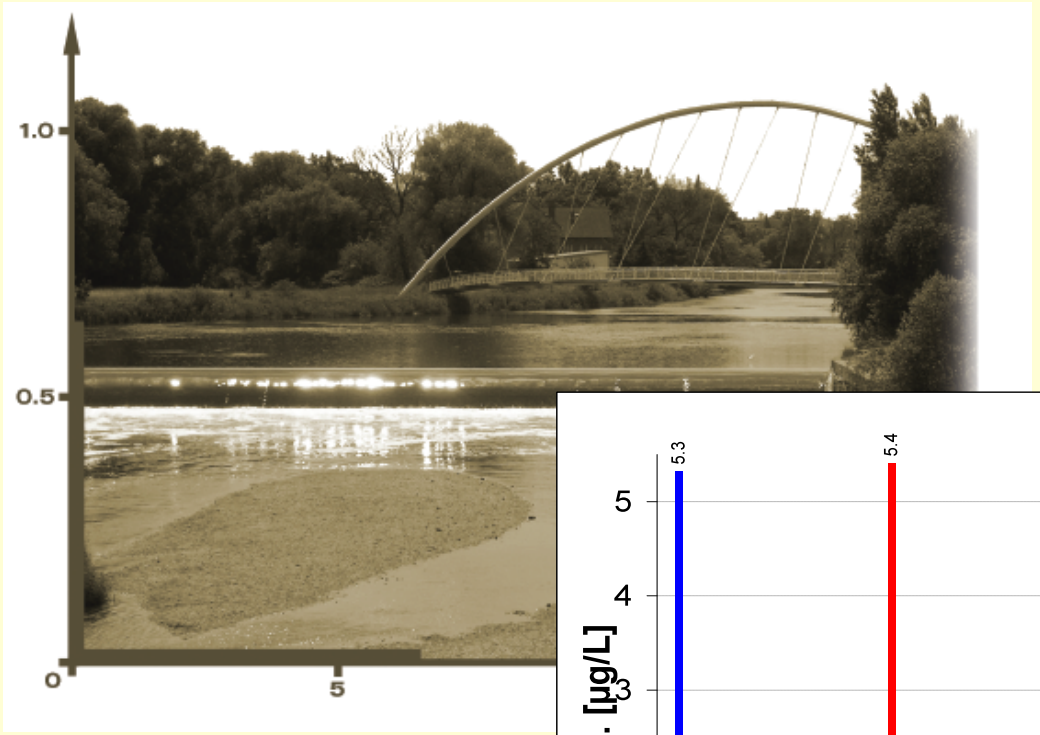
Sensitive
Detection

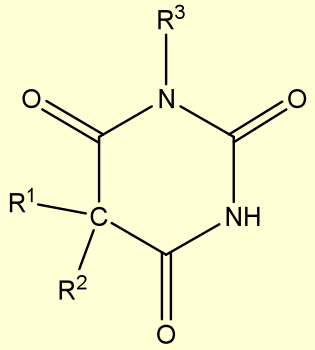
(parent compound)

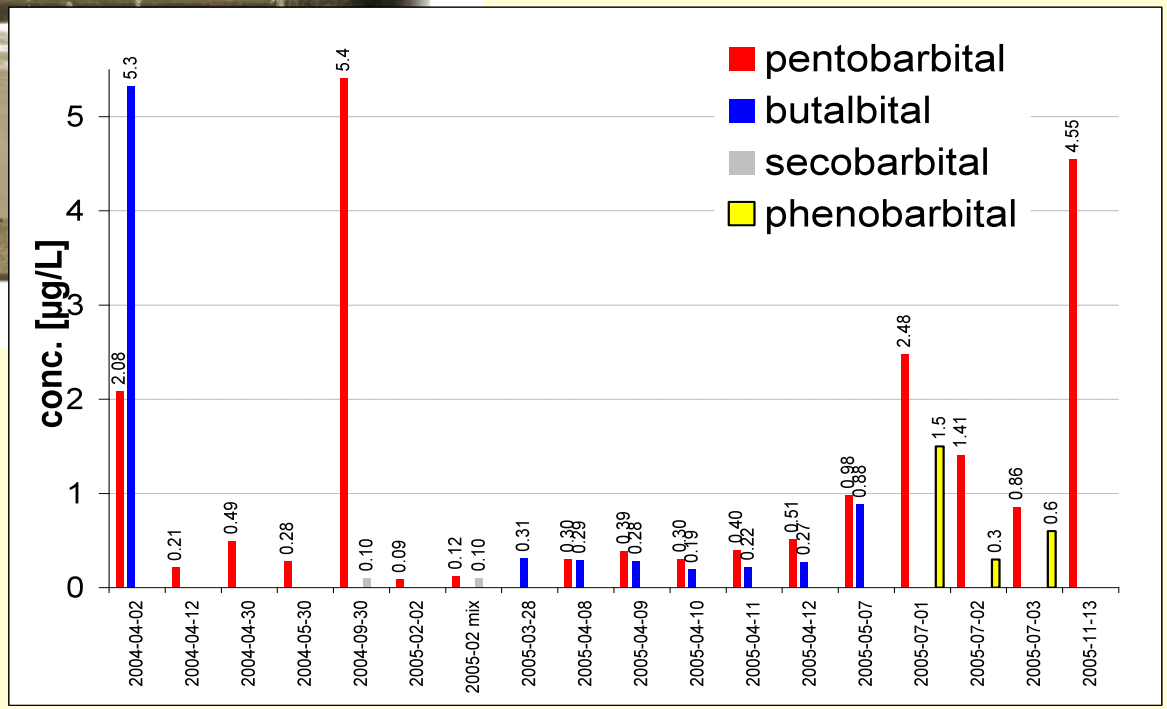
Strategy to seek for transformation products



Barbiturates



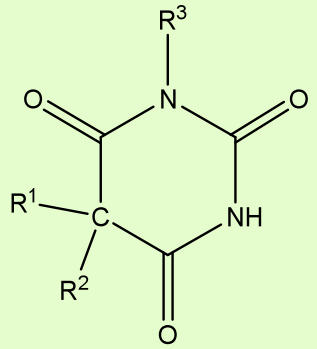




Peschka, Eubeler, Knepper; *ES & T*, 2006

Barbiturates

- pharmaceuticals (sedative hypnotics)
- peak of consumption: mid-1960s
- $\log K_{OW}$ = 1.49 – 2.24
- today only phenobarbital (antiepileptic) and
- thiopental (anaestetics)



- pentobarbital and 5,5-diallylbarbituric acid present in groundwater (30 ng/L)[1]
- phenobarbital WWTP in effluent water (1000 ng/L)[2]

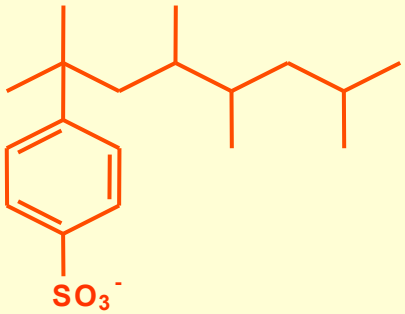
- **No biotic or abiotic biodegradability !**
- **Presence in groundwater , even after 40 years!**

[1] Eckel, Ross, Esensee; *Ground Water 31*, 1993
[2] Holm, Rügge, Bjerg, Christensen; *Environ. Sci. Technol. 29,* 1995

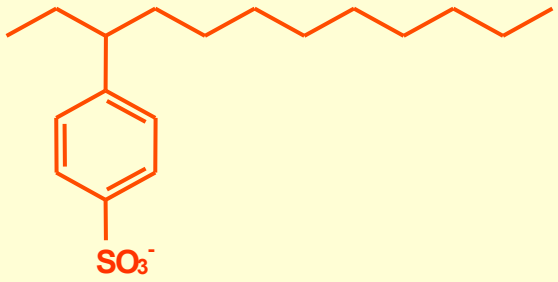
LAS and ABS in surface and ground waters in the Philippines

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)



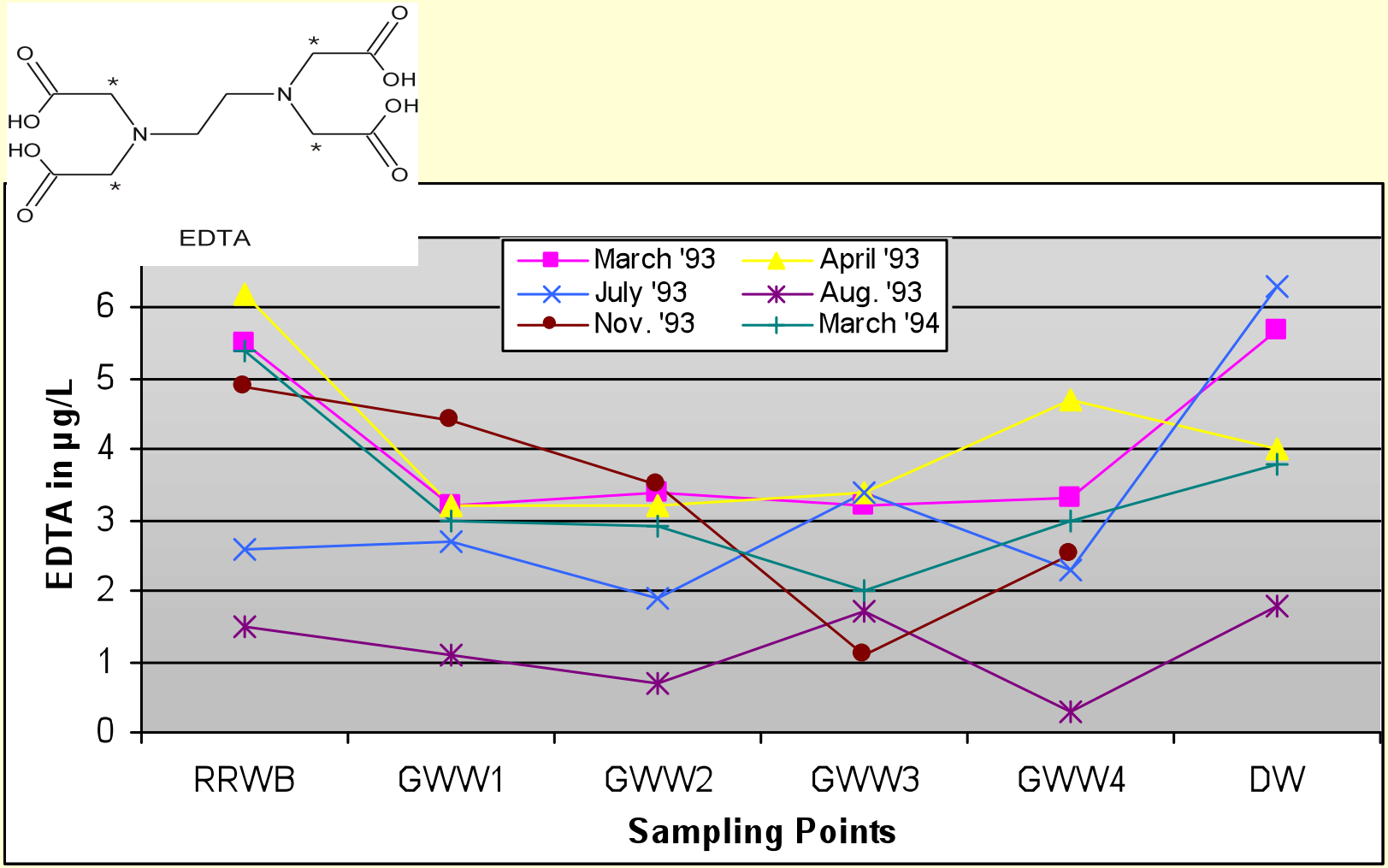
Branched alkylbenzene sulfonates (ABS)



Linear alkyl benzenesulfonates (LAS)

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

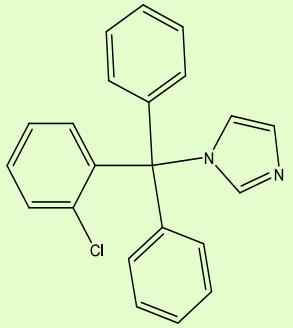
EDTA during ground water infiltration



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

Clotrimazole

- pharmaceutical (antifungal agent)
- non polar (log K_{OW} = 4.1)
- first authorised 1973
- consumed in Europe for more than thirty years with an annual quantity of approx. 20 t

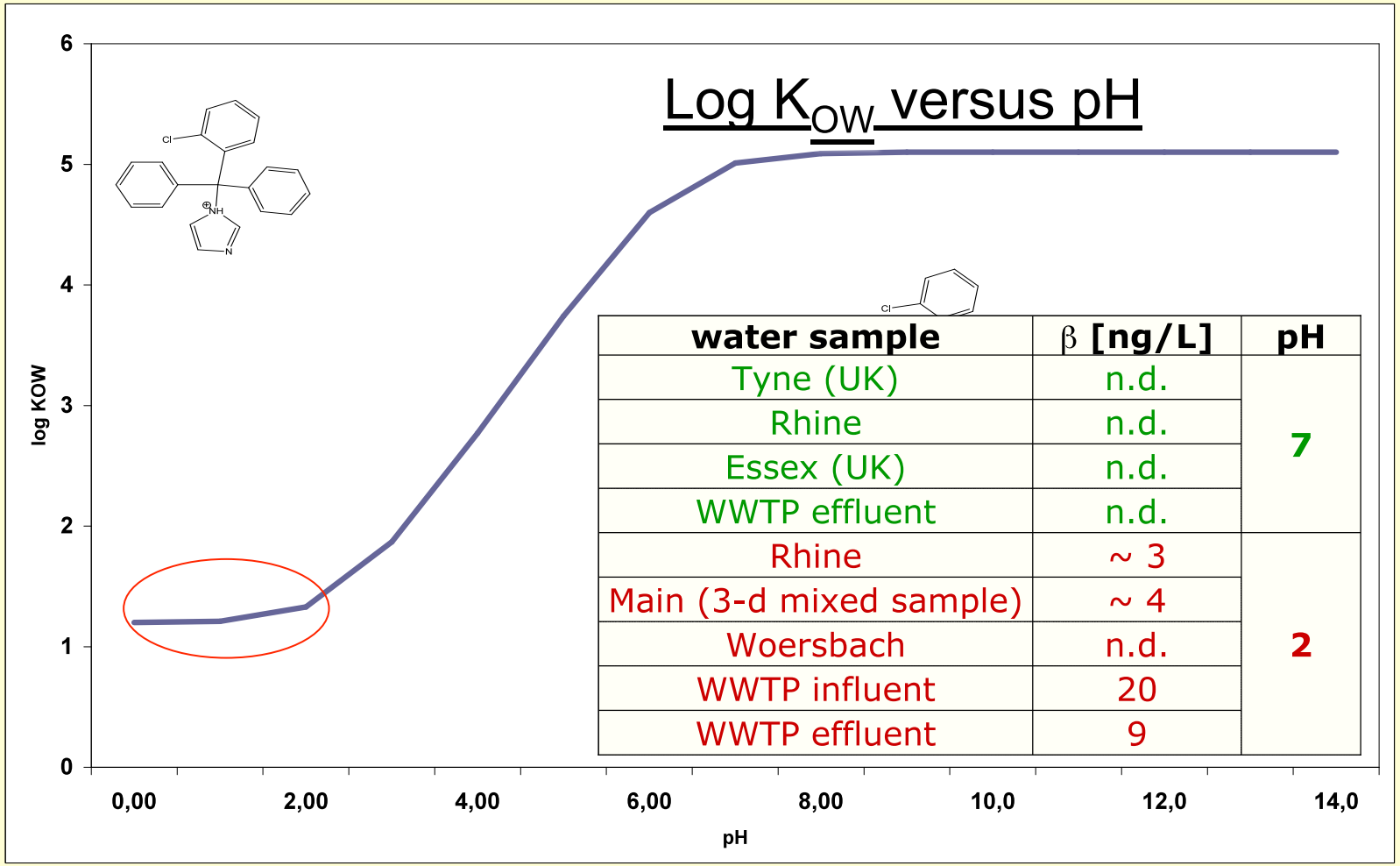


- included on the OSPAR list of substances for priority action
  BUT: degradation test was performed at a concentration which exeeds water solubilty[1]
- in surface water (~5ng/L)[2] and WWTP influent and effluent (30 and 4 ng/L)[3]

➢ **Can the P-criterion be verified?**

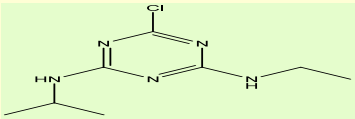
[1] OSPAR Commission; publication no 2005/199
[2] Thomas, Hilton; *Mar Pollut Bull* 49, 2004
[3] Roberts; *Cefas contract report C2483*, 2006

Monitoring of clotrimazole

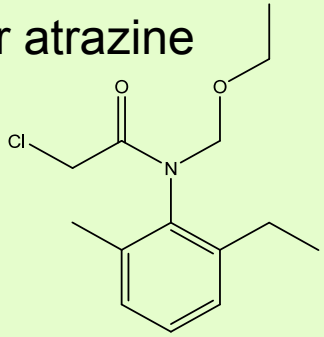


water sample	β [ng/L]	pH
Tyne (UK)	n.d.	7
Rhine	n.d.	
Essex (UK)	n.d.	
WWTP effluent	n.d.	
Rhine	~ 3	2
Main (3-d mixed sample)	~ 4	
Woersbach	n.d.	
WWTP influent	20	
WWTP effluent	9	

Atrazine & Acetochlor



- herbicides
- substitute for atrazine
- log K_{OW} 2.81



- 1950s start of application – 2004
- log K_{OW} 2.63
- on the list of priority substances (WFD)

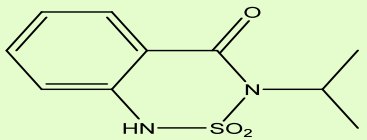
- known degradates: desethylatrazine, desisopropylatrazine, hydroxyatrazine[1]; oxanilic acid of acetochlor, ethansulfonic acid of acetochlor[2]
- atrazine and DEA in groundwater of the Bréville catchment[3] (0.2 ± 0.7 µg/L and 0.6 ± 0.2 µg/L)

➢ **Does the soil in Bréville act like a reservoir for atrazine?**

[1] Qiao, Ma, Hummel; *Agric. Food Chem. 44,* 1996
[2] Dictor, Baran, Gautier, Mouvet; *Chemosphere 71*, 2008
[3] PEGASE Final report BRGM/RP-52897-FR, 2004

Bentazone

- herbicide
- very polar (log K_{OW} = -0.46)
- herbicidal activity first reported in 1968
- one of the most applied herbicides in the Ebro river delta

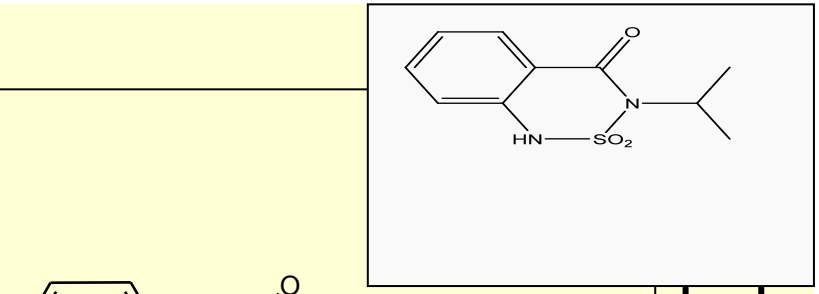


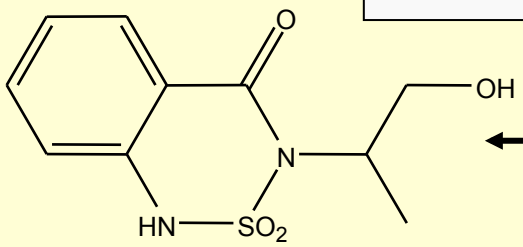
- 31 µg/L during application time (mean value); Ebro 0.27 µg/L[1]
- comparable high concentrations in river waters of the Tiber region (Italy)[2]
- not biodegradeable in a fixed bed bioreactor[3]
- passes through membrane bioractor[3]
- present in ground- and surface water[4]

➢ **If not biodegradable → photodegradation?**

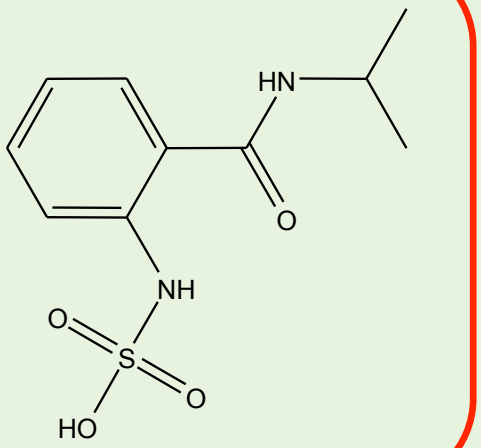
[1] Terrado, Kuster, Raldúa, Lopez de Alda, Barceló, Tauler; *Anal Bioanal Chem 387,* 2007
[2] Laganà, Bacaloni, De Leva, Faberi, Fago, Marino; *Anal Chim Acta 462,* 2002
[3] González, Müller, Petrovic, Barceló, Knepper; *Environ Pollut 144*, 2006
[4] M. Isenbeck-Schröter, Auftreten von Pflanzenschutzmitteln in Oberflächengewässern und im Grundwasser

observed mass (m/z)	elemental composition actual mass	Δ mDa
255.0432 ± 0.0013	$C_{10}H_{11}N_2O_4S$ m/z = 255.0440	- 0.8
197.0044	$C_7H_5N_2O_3S$ m/z = 197.0021	2.3
191.0826	$C_{10}H_{11}N_2O_2$ m/z = 191.0821	0.5
132.0320	$C_7H_4N_2O$ m/z = 132.0324	- 0.4





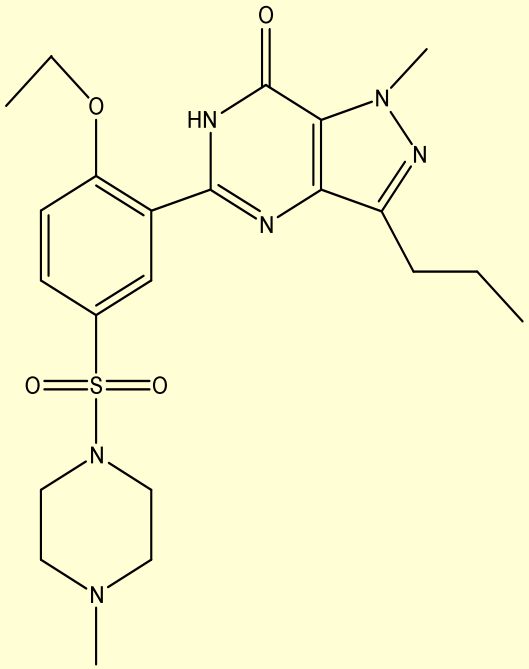
observed mass (m/z)	elemental composition actual mass	Δ mDa
257.0584 ± 0.0034	$C_{10}H_{13}N_2O_4S$ m/z = 257.0596	- 1.2
177.1024 ± 0.0003	$C_{10}H_{13}N_2O$ m/z = 177.1028	- 0.4
92.0497	C_6H_6N m/z = 92.0500	- 0.3



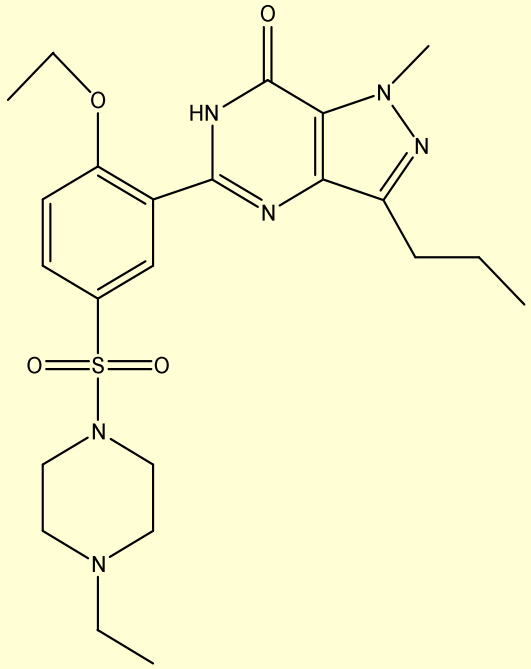
present in drainage channels on the Ebro delta

Peschka, Petrovic, Knepper, Barceló; Analytical & Bioanalytical Chemistry, 2007

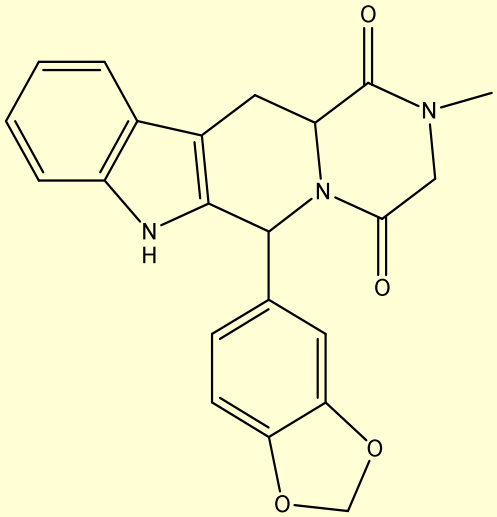
Phosphodiesterase type V inhibitors



Sildenafil



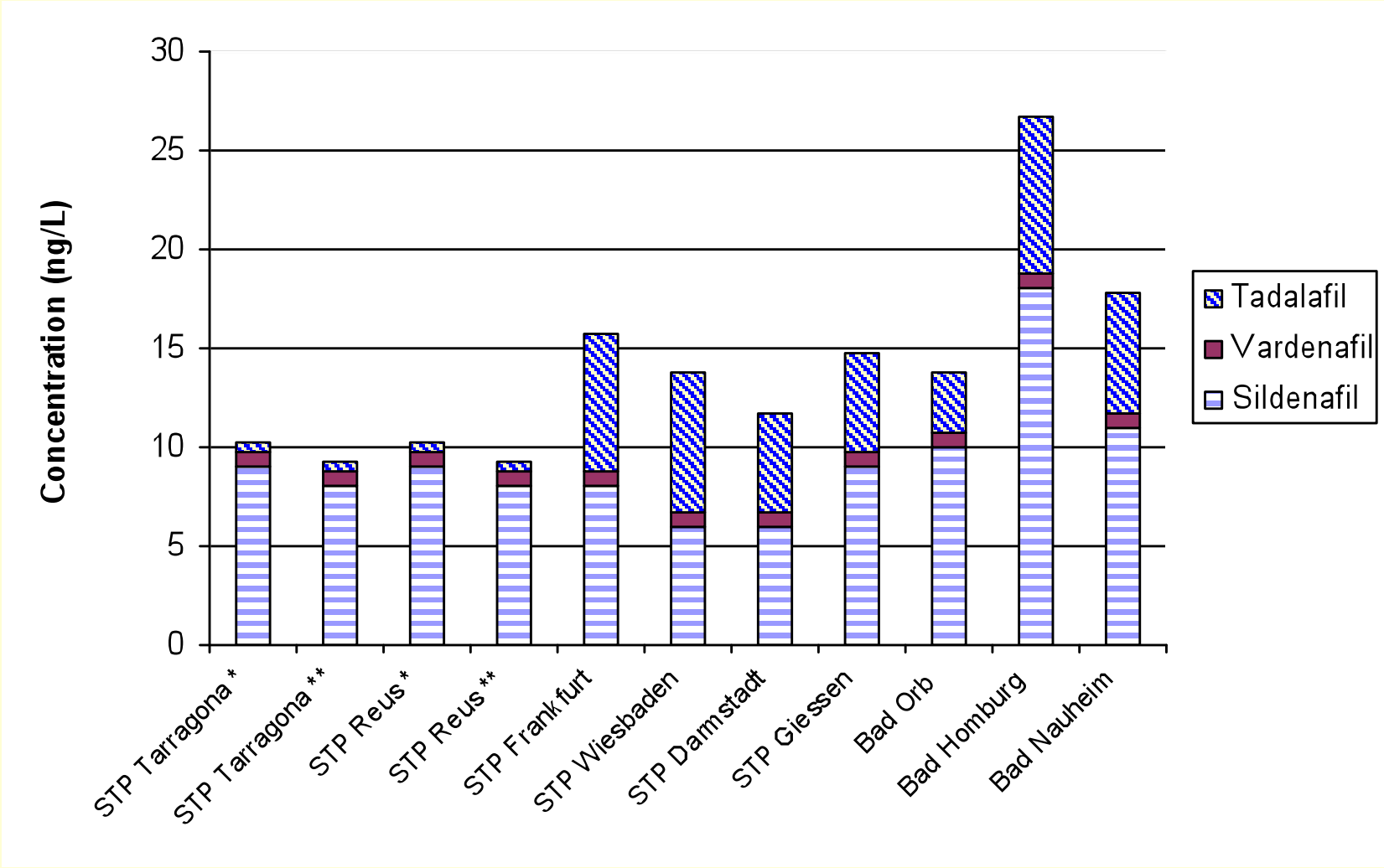
Vardenafil



Tadalafil

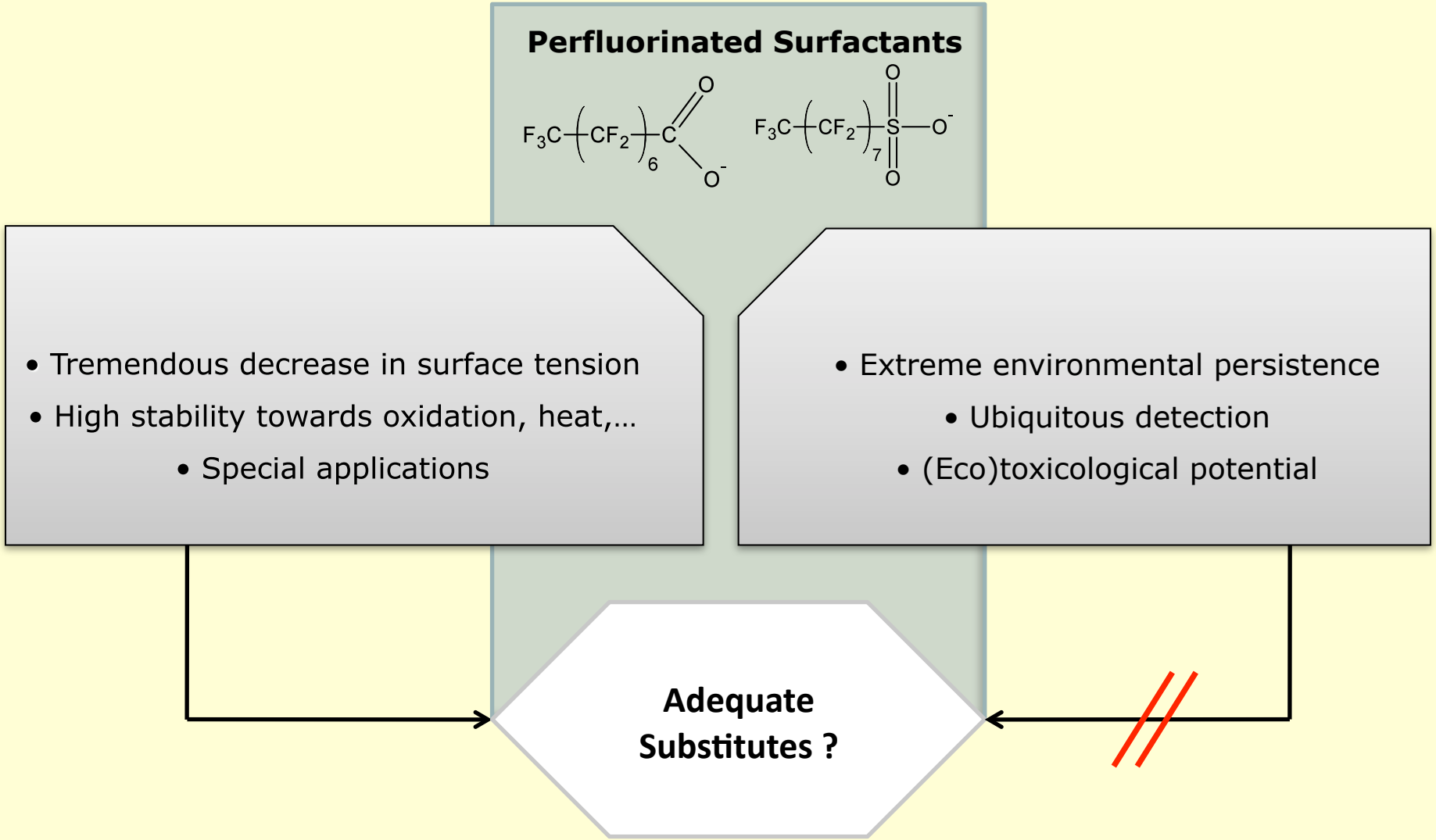
Nieto, Peschka, Knepper; *Anal. Bioanal. Chem, submitted*

Phosphodiesterase type V inhibitors



Nieto, Peschka, Knepper; *Anal. Bioanal. Chem, submitted*

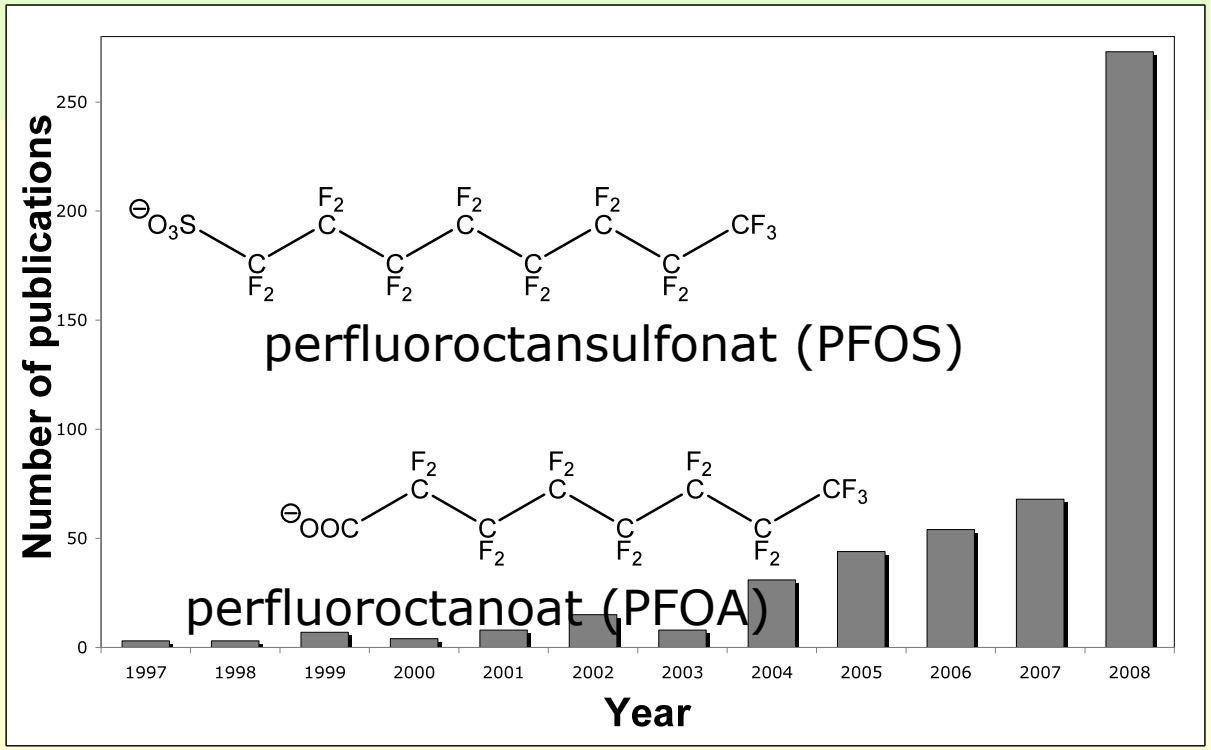
Fluorinated Surfactants



Fluorinated surfactants

- surfactants
  water soluble
  - resistant (hydrolysis/photolysis)
  - non biodegradable
  - non volatile
  - ubiquitous
  - bioaccumulative

PFOS included on the OSPAR list

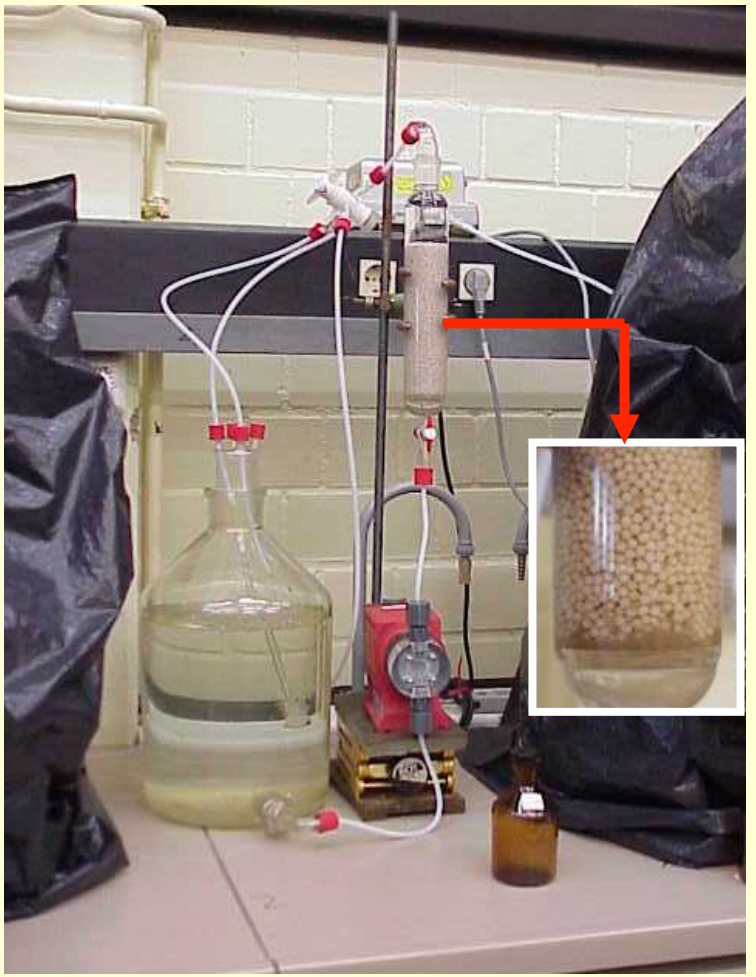


➢ **Can perfluorinated surfactants be replaced?**

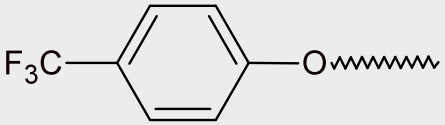
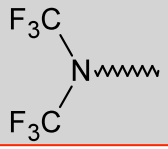
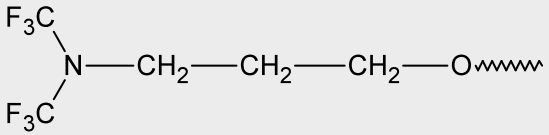
Test System

Fixed-Bed Bioreactor

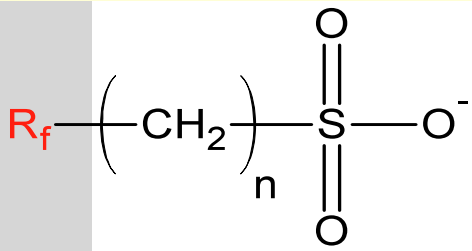
- Column used with porous glass spheres
  - Formation of a biofilm
- Filled with waste water effluent or river/creek water
  - Ubiquitous microorganisms
- Samples taken via three-way-valve



Investigated compounds

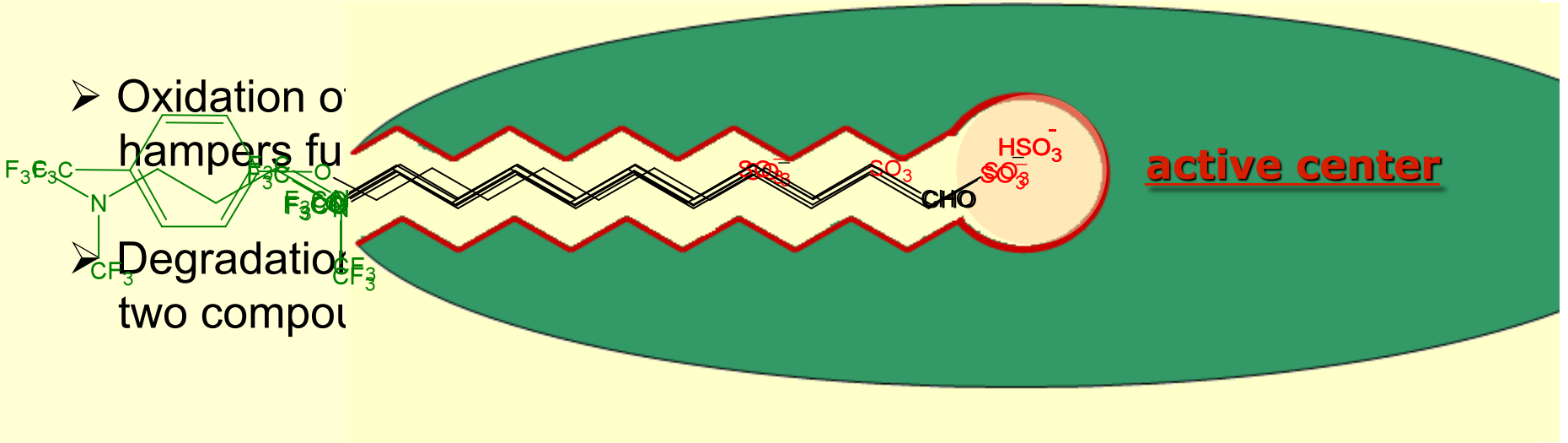
R_f	n
CF_3-O	6, 7, 9, 10, 12, 14
F_3C  O	9
F_3C  N F_3C	7 – 13
F_3C  N F_3C	6
$F_3C-CH_2-CH_2-O$	10
$F_3C-CH_2-CH_2-S$	11

? degradable

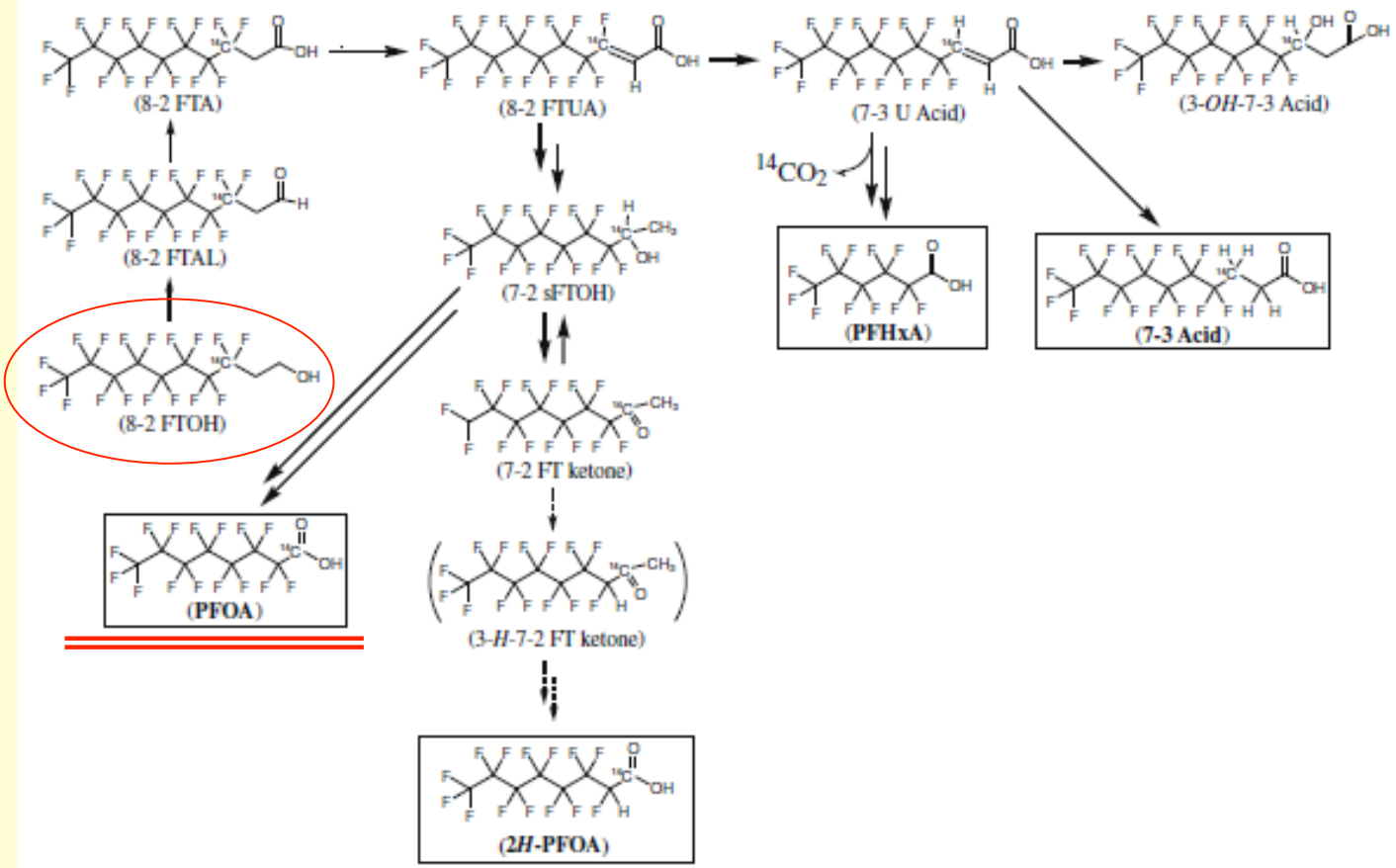


Conclusions

- There are two different primary degradation steps: desulfonation and alkyl chain oxidation
- Desulfonation as a primary degradation step depends on the alkyl chain length
- Oxidation o
  hampers fu
- Degradatio
  two compou

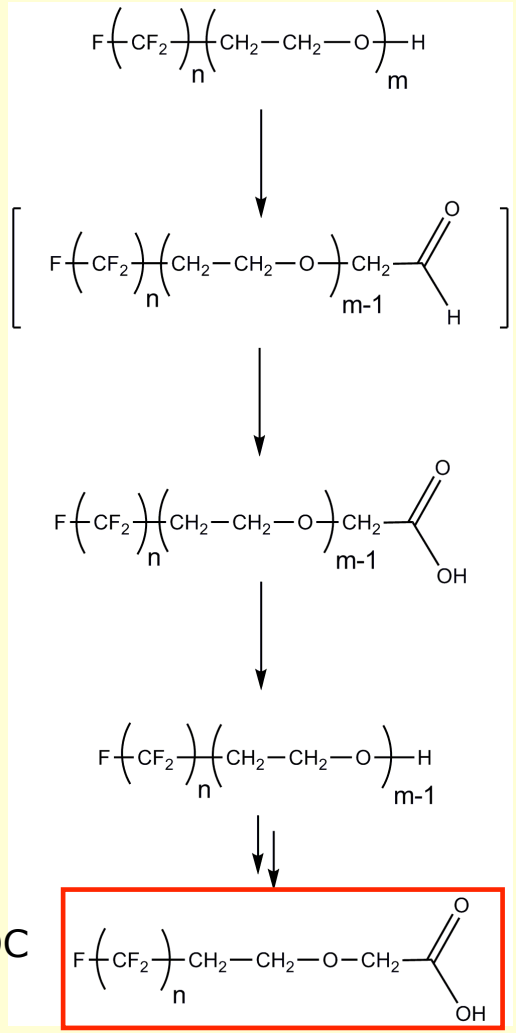


Biodegradation of Fluorotelomeralcohols (8:2-FTOH)



Wang *et al.*, Chemosphere, *in Press*

Biodegradation pathway of fluorotelomer ethoxylates (FTEO)



n = 6, 8, 10 // m = 0 - 14

→ Ethoxylate chain shortening

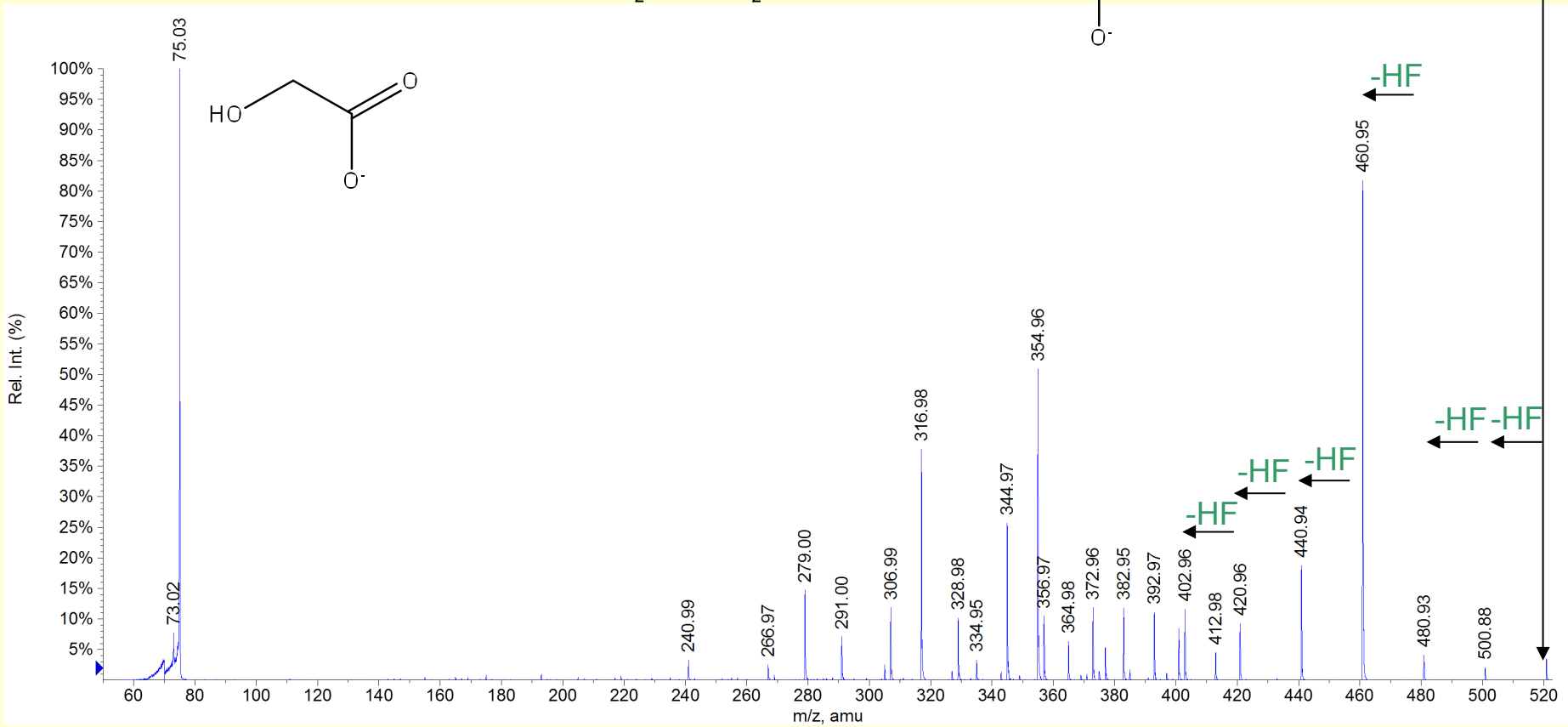
n:2-FTEOC

No formation of PFOA by FTEO biodegradation

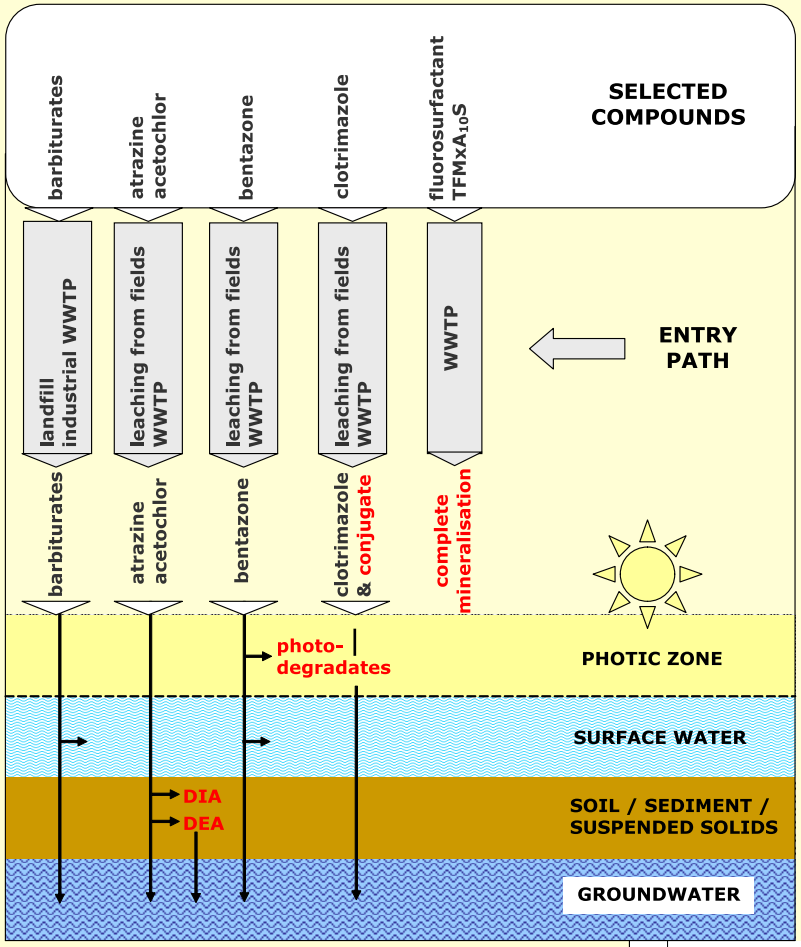
BUT

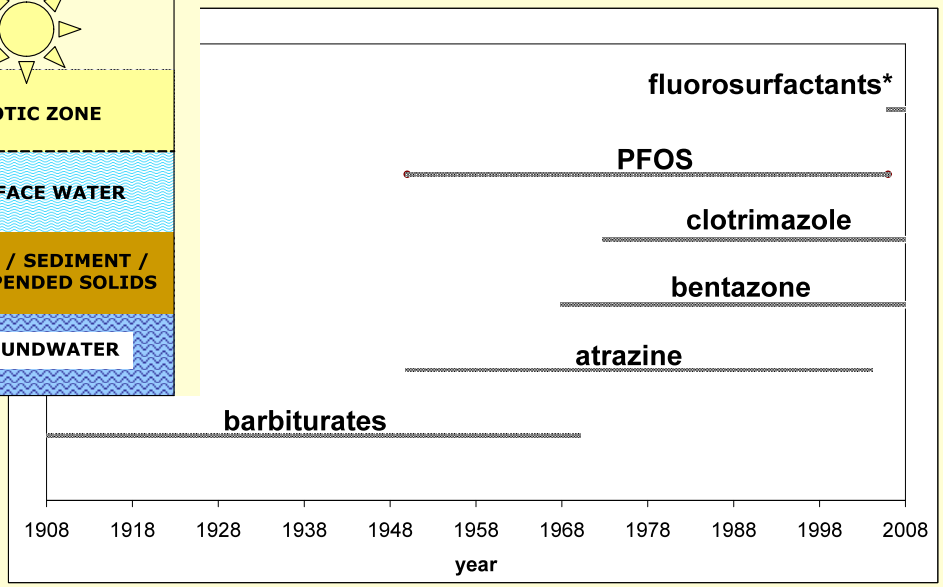
PFOA formation by residual FTOH biodegradation

Fragmentation of 6:2-FTEOC



Final remarks





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Thank you for your attention!