

LOGROS Y RETOS EN LA REMOCIÓN DE CONTAMINANTES EMERGENTES EN AGUAS RESIDUALES URBANAS MEDIANTE HUMEDALES CONSTRUIDOS

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Instituto de Diagnóstico Ambiental y Estudios del Agua (IDAEA-CSIC)

CSIC
1^{er} OPI en España
3^o en Europa

DEPARTAMENTOS

- **Química Ambiental***
 - Geociencias
- *incluye ecotoxicología



Técnicas avanzadas de análisis químico
Ecotoxicología acuática
Microbiología molecular



Categorías Contaminantes Químicos

- Priority substances (Framework Directive 2000/60/CE)



- Emerging pollutants: Pharmaceuticals and Personal Care Products (PPCPs)



Widespread use. ca. 100 t y⁻¹ in Germany or England



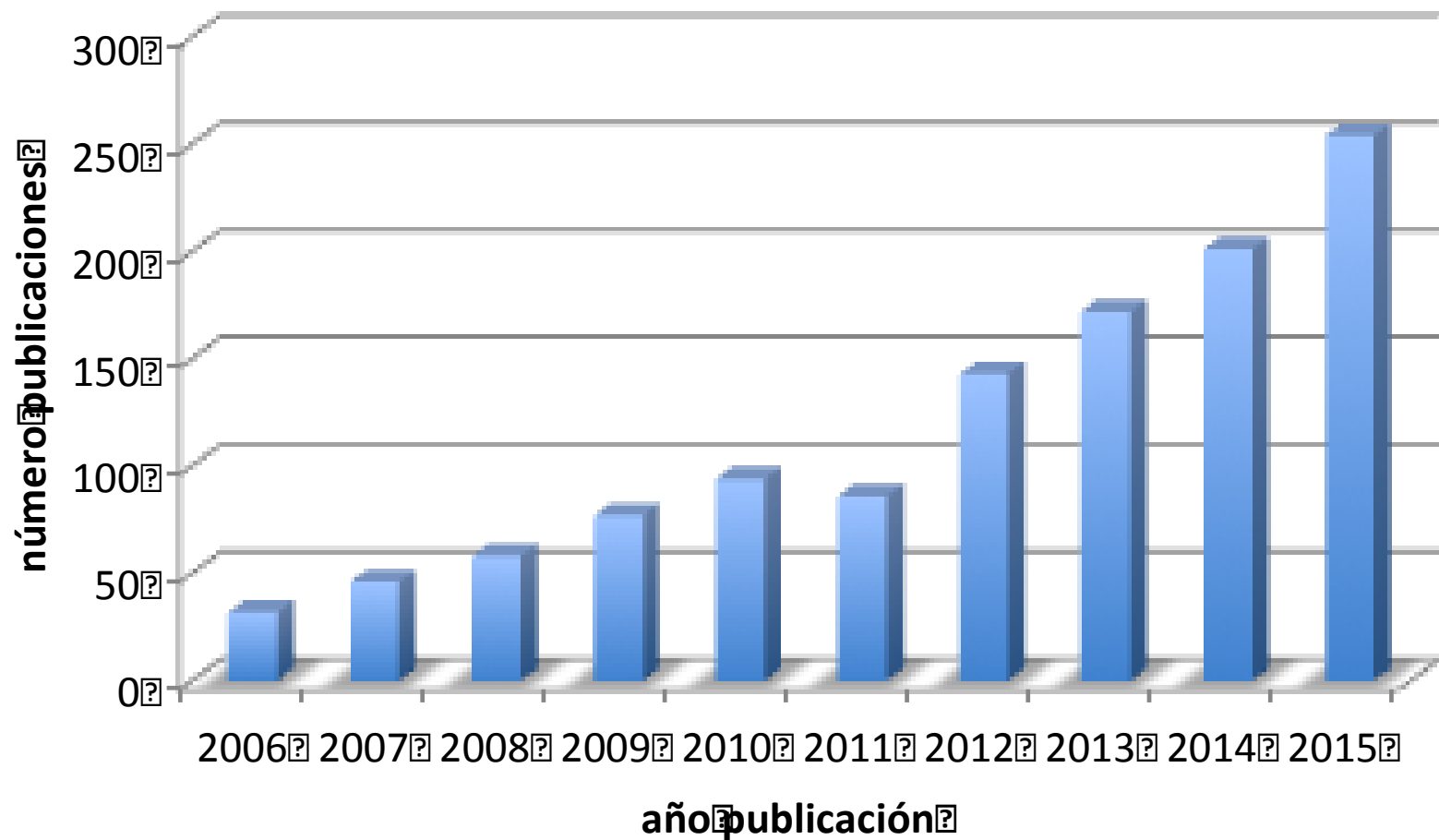
550.000 t y⁻¹ in Germany

Watch List Contaminants 2008/105/EC, 2015/495/EC

Clases Contaminantes Emergentes

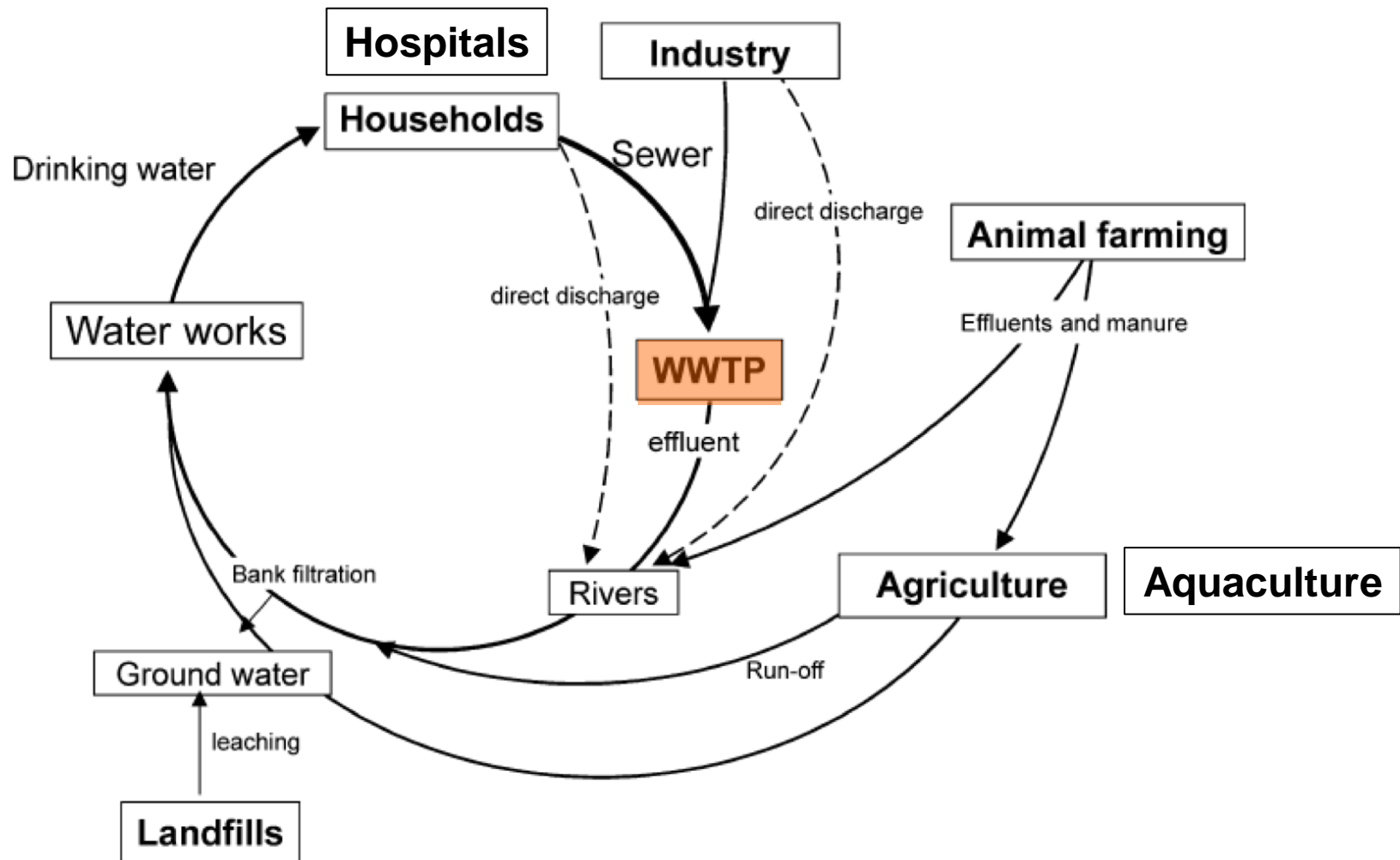
- Fármacos (todas las categorías)
- Hormonas (naturales y sintéticas)
- Fragancias (polycyclic musks)
- Estimulantes (cafeína)
- Biocidas (triclosan)
- Polímeros y derivados (monómeros, plastificantes)
- Tensioactivos y derivados
- Toxinas naturales (microcistinas)
- Subproductos desinfección agua no regulados

Publicaciones contaminantes emergentes 2006-2015



Pharmaceutical & Personal Care Products (PPCPs)

Origin and Final Fate of PPCPs in the Aquatic Environment



Reducción población de buitres en el subcontinente indio. Atribuido al diclofenaco



Figure 1 Oriental white-backed vultures, *Gyps bengalensis*—alive, feeding on the carcass of a buffalo, and dead.

Lindsay Oaks et al. 2004. *Nature* 427, 630

Transferencia de genes resistencia bacteriana

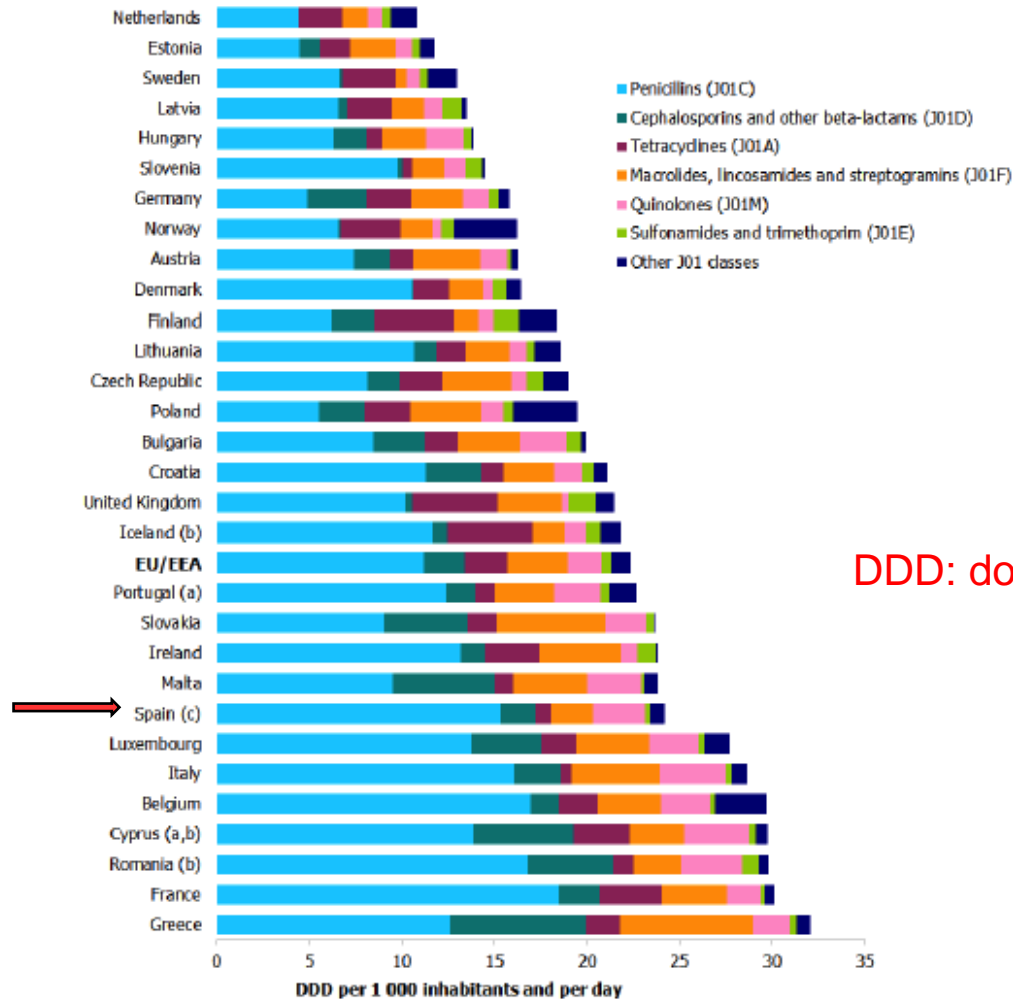
- Ocurren en presencia de residuos antibióticos. Potenciado por otros contaminantes (metales).
- Durante el tratamiento de aguas residuales se puede incrementar la resistencia bacteriana.

CONSECUENCIAS:

- Disminución de la eficiencia de los antibióticos en el tratamiento de enfermedades infecciosas bacterianas, parasitarias, fúngicas, etc.

<http://www.who.int/mediacentre/factsheets/fs194/es/>

Consumo antibióticos uso humano en la UE. 2014



DDD: dosis diaria recetada

Disrupción endocrina

Una amenaza a la salud humana y ecosistemas

Incremento enfermedades crónicas

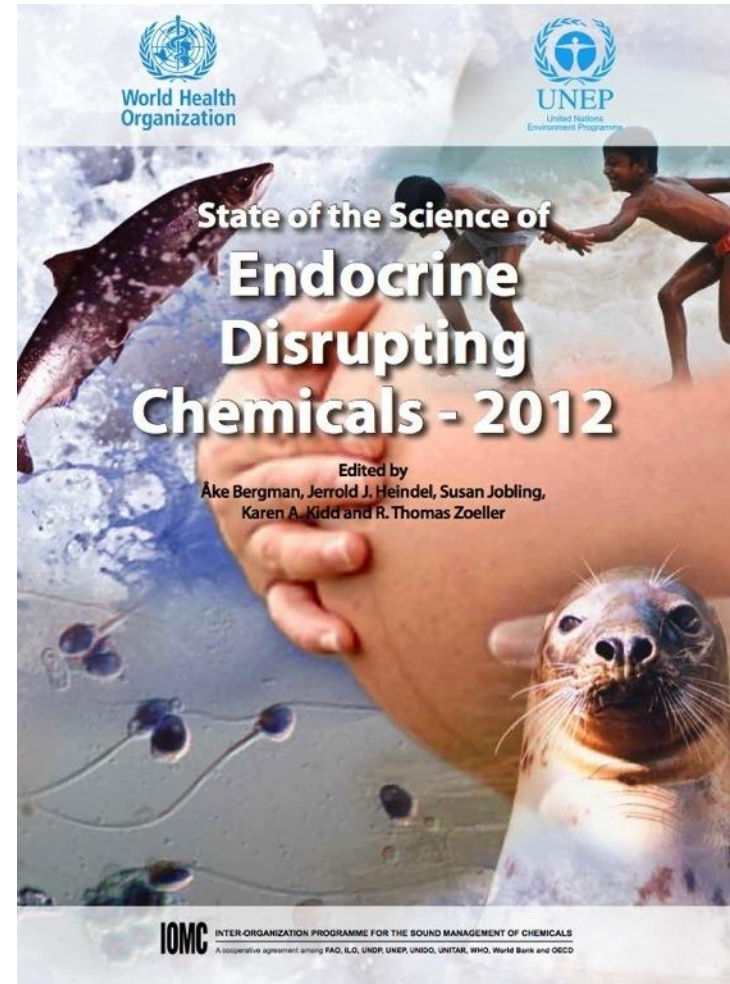
- Cardiovasculares
- Cáncer,
- Obesidad
- Diabetes

Incremento enfermedades reproductivas

- Infertilidad masculina o femenina
- Parto prematuro

Incremento enfermedades infantiles

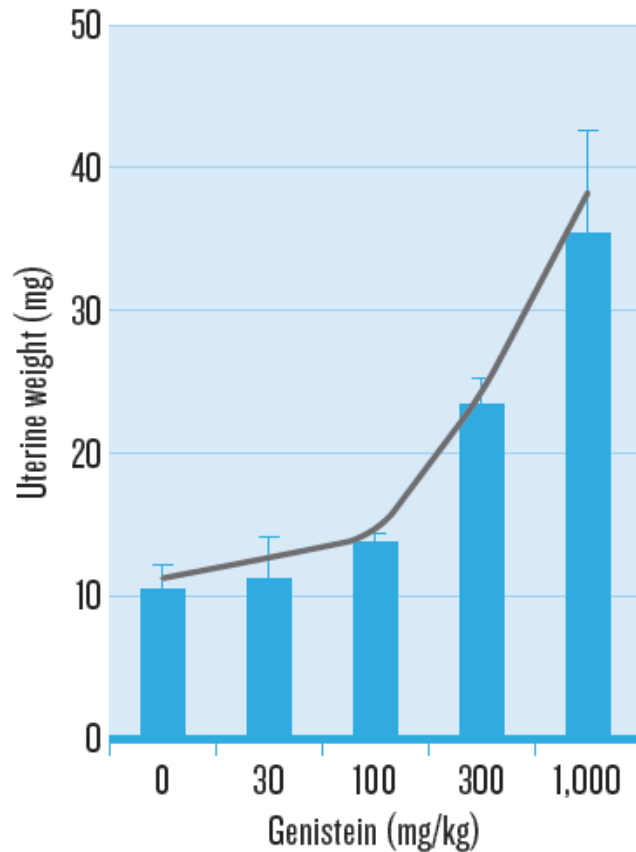
- Hiperactividad y autismo.
- Dislexia
- Tiroides
- Asma
- Leucemia y cáncer cerebral.
- Adelanto pubertad



Epigenetics.

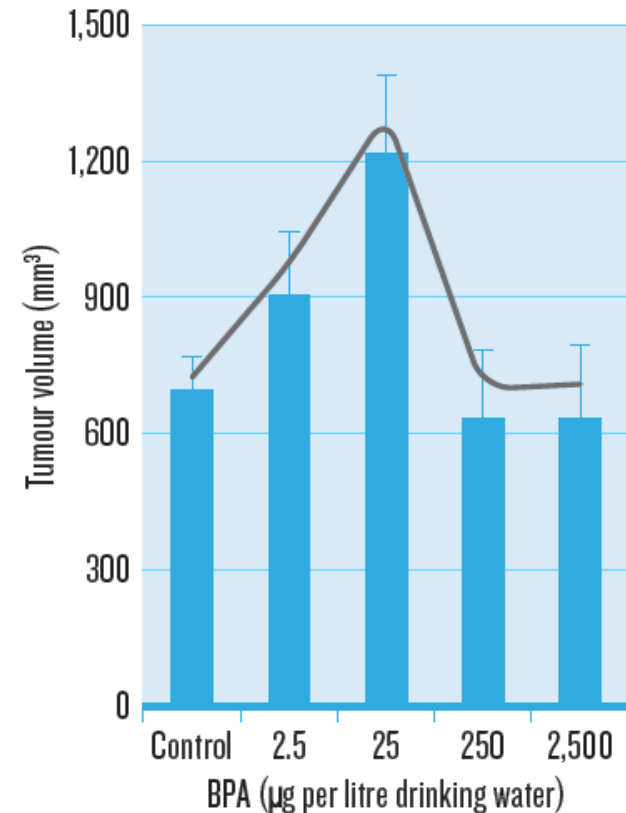
Unpredictable dose-response of EDs

Monotonic curve



SOURCE: Ohto, R. et al. *J. Toxicol. Sci.* **37**, 879–889 (2012)

Non monotonic curve



SOURCE: Jenkins, S. et al. *Environ. Health Perspect* **119**, 1604–1609 (2011)

Constructed wetlands (CWs)

Mature technology: 50 years of experience

- **Secondary**
- **Tertiary**
- **Quaternary**

- **Suspended solids**
- **BOD**
- **Nutrients**
- **Pathogens**
- **Trace elements**
- **Organic contaminants**

500 inhabitants (Almatret south, Lleida, NE Spain)

MAIN REMOVAL PATHWAYS:

1. SYSTEM CONFIGURATION
2. OPERATION

REMOVAL KINETICS: NATURAL CONDITIONS

PHYSICAL

- Sedimentation
- Volatilization

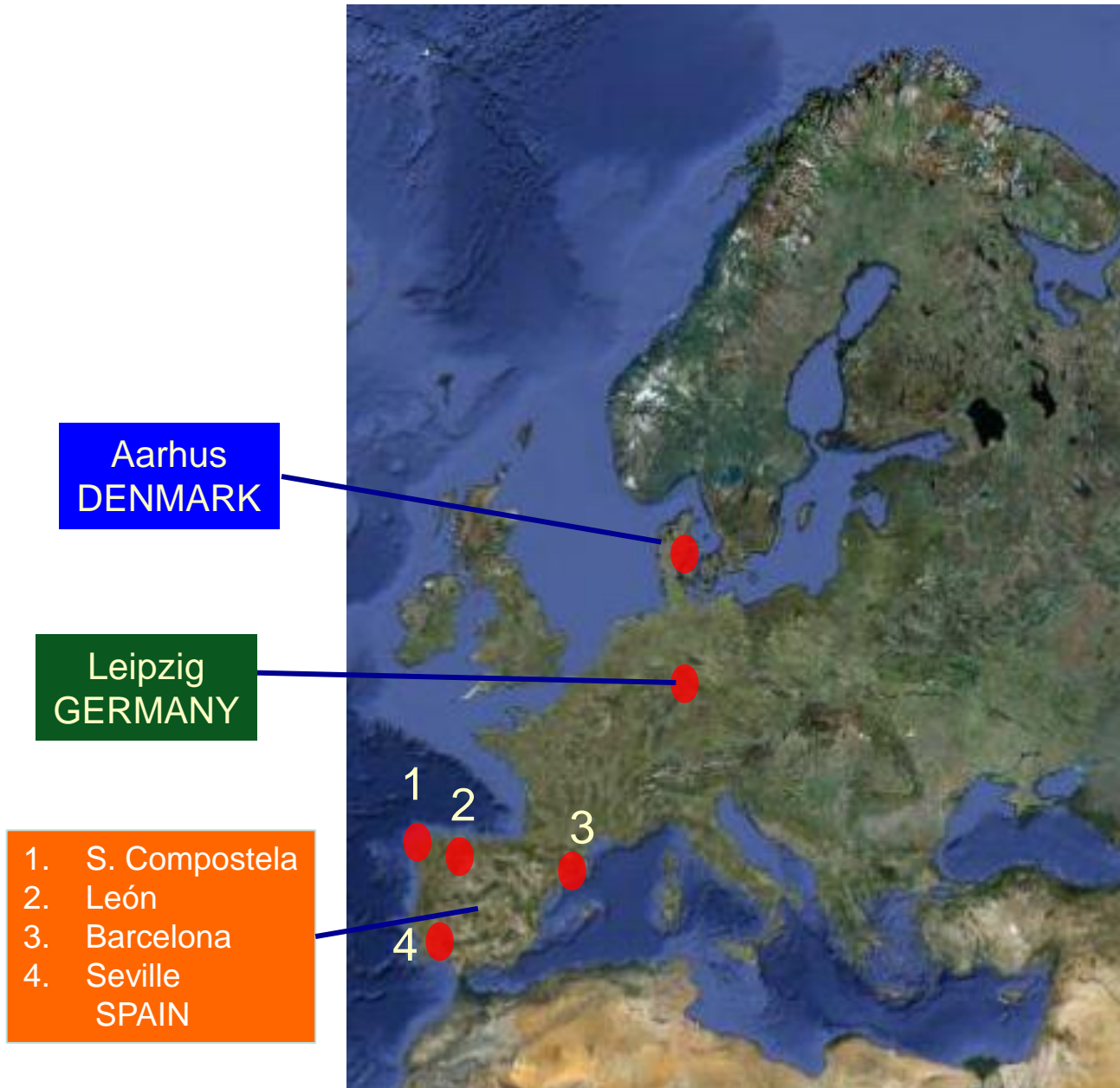
CHEMICAL

- Redox
- Hydrolysis
- Photooxidation

BIOLOGICAL

- Biodegradation
 - Aerobic
 - Anaerobic
- Plant uptake
 - Metabolism

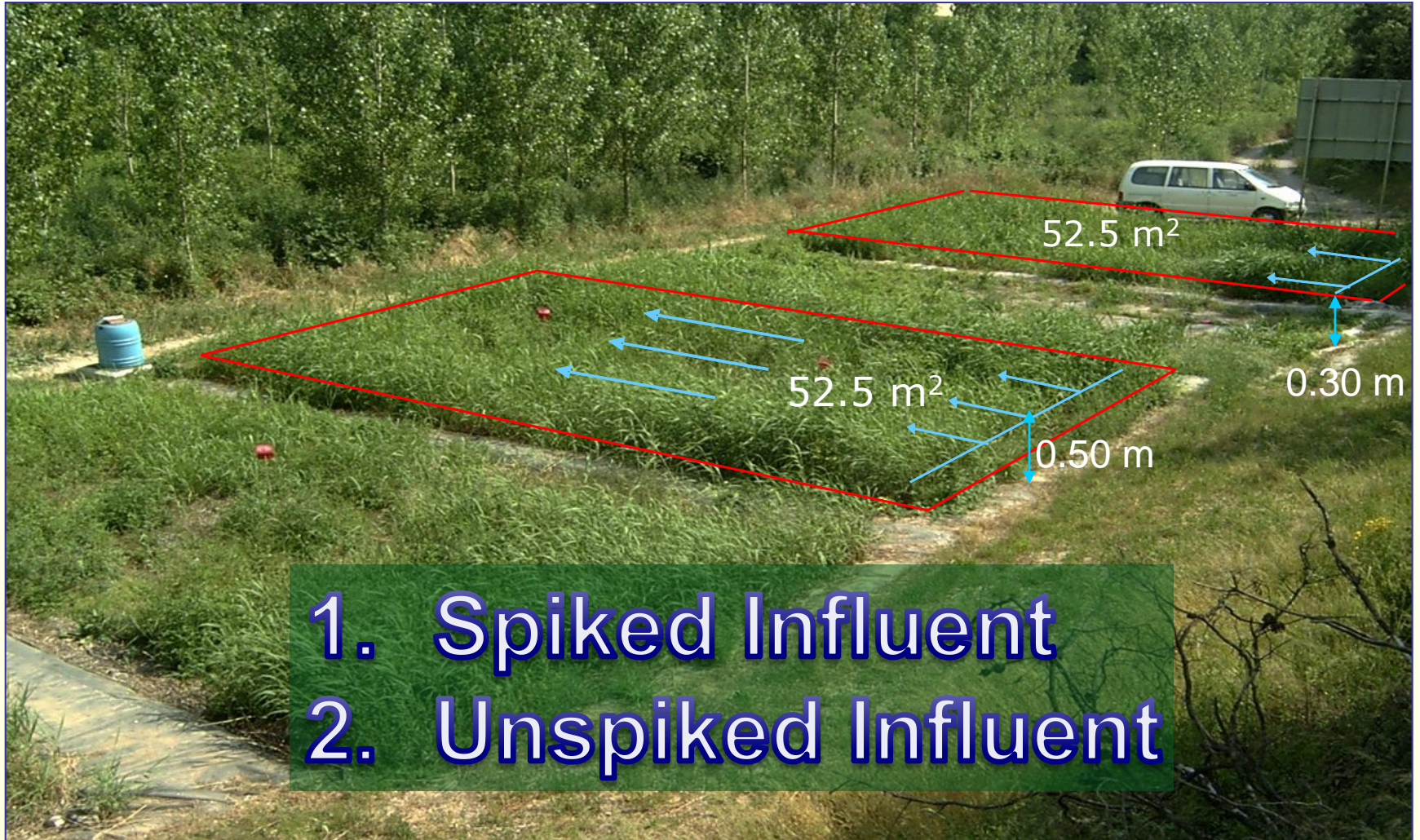
Case Studies



SISTEMAS EXPERIMENTALES

- Mesocosmos
- Plantas piloto

HORIZONTAL SUBSURFACE FLOW CONSTRUCTED WETLAND



Continuous Injection Subsurface Flow CW. LFV, Barcelona. SP

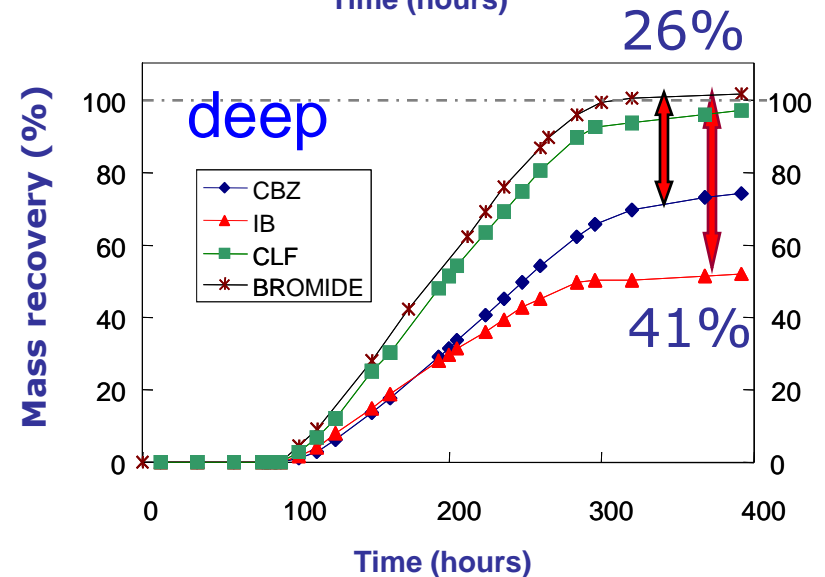
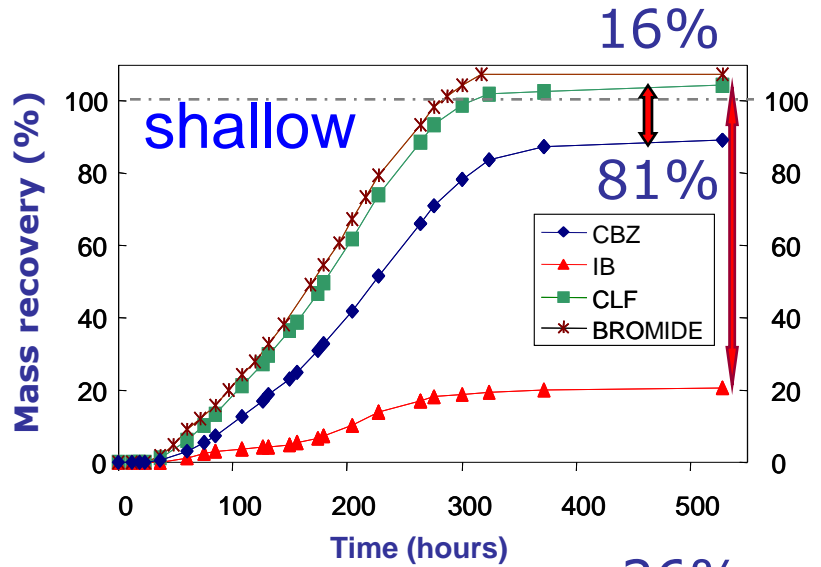
CBZ: Carbamazepine
IB: Ibuprofene
CLF: Clofibric Acid

Mass recovery percentage after the injection experience

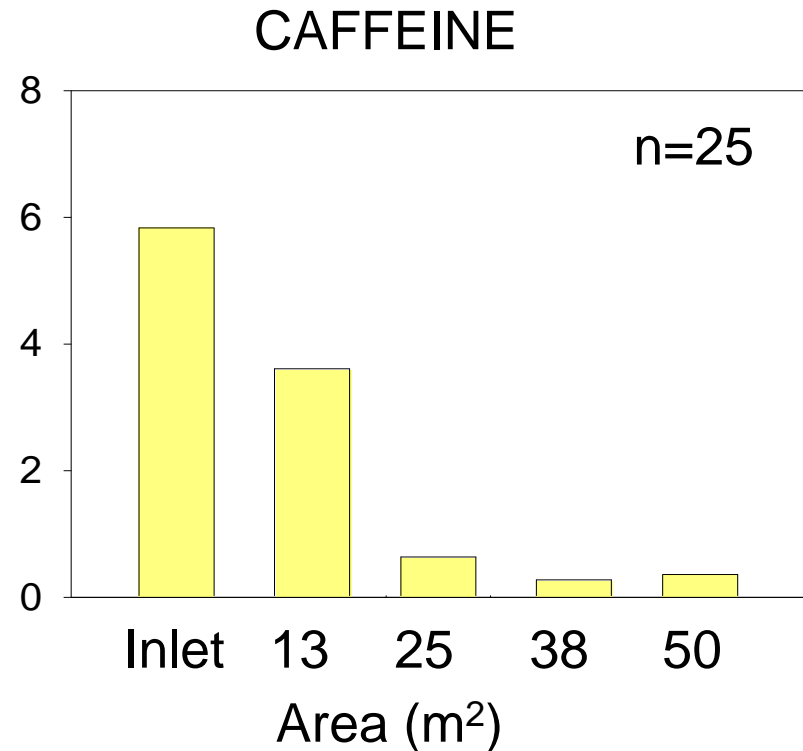
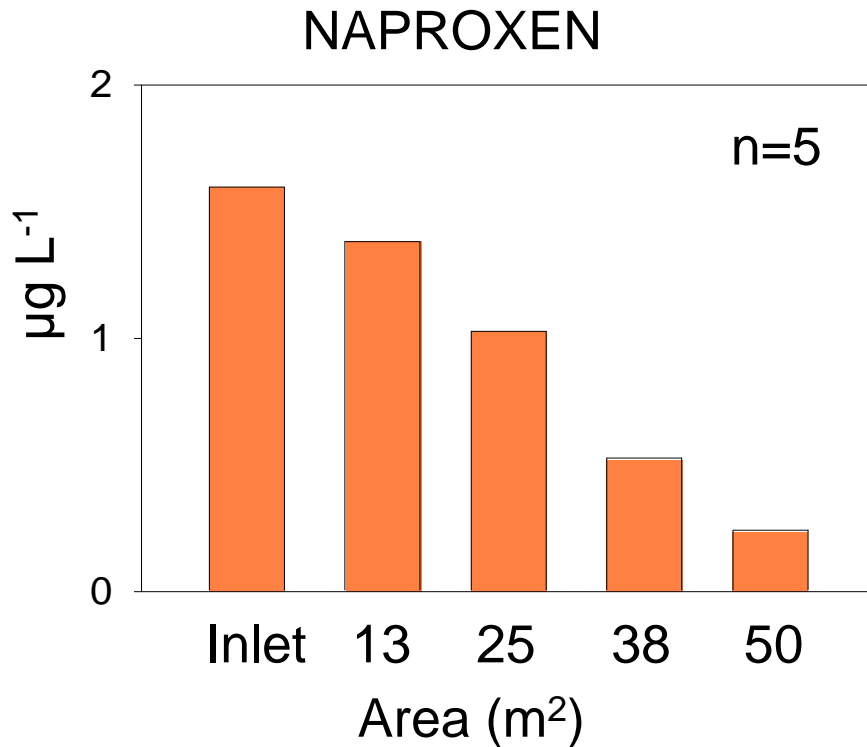
Ibuprofene

Shallow bed
(81%)

Deep bed
(41%)



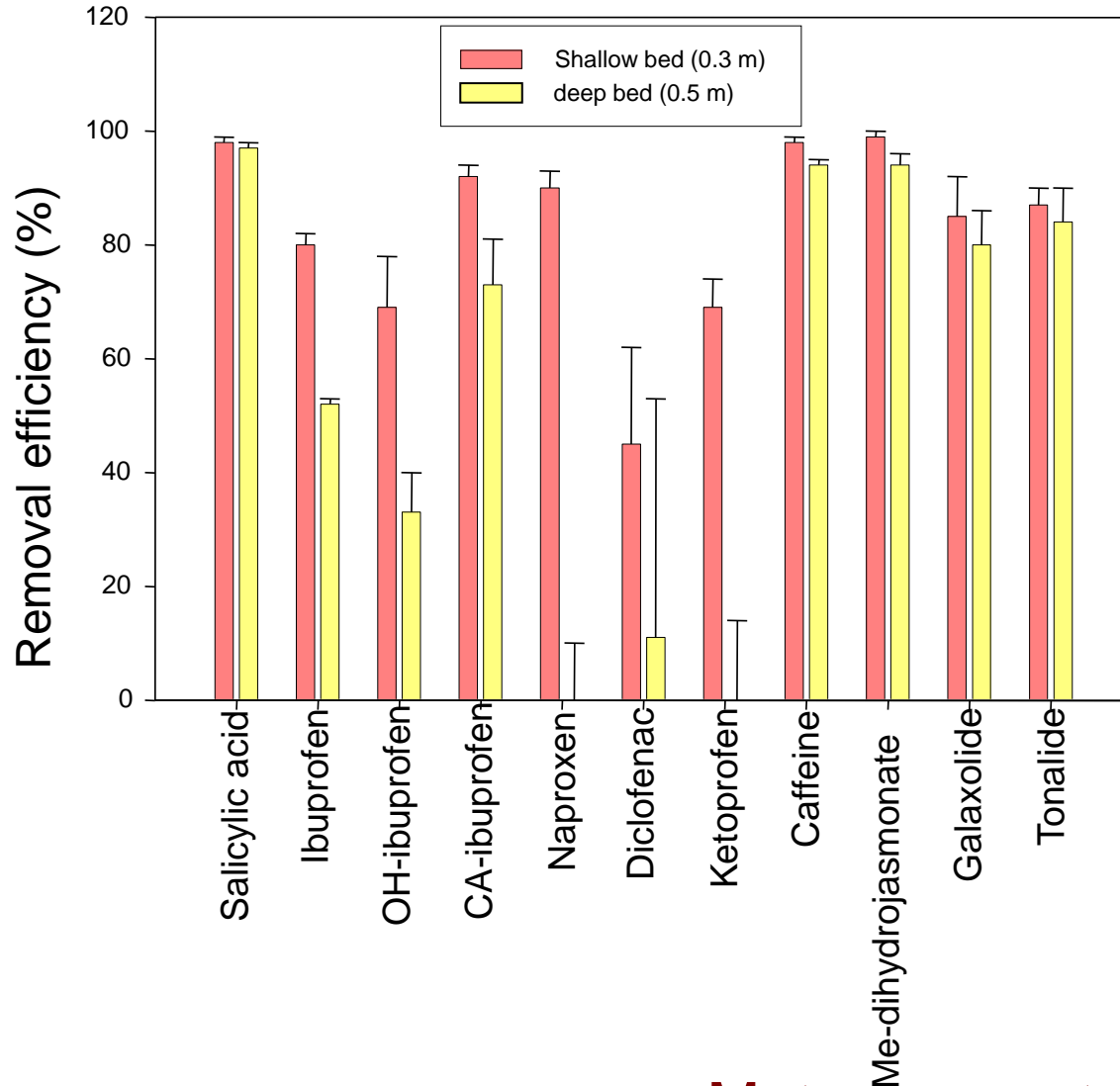
Surface area



➤ High surface area dependence on PPCP removal, first-order kinetics vs zero-order kinetics

FACTORS AFFECTING PPCP REMOVAL IN HF-SSF

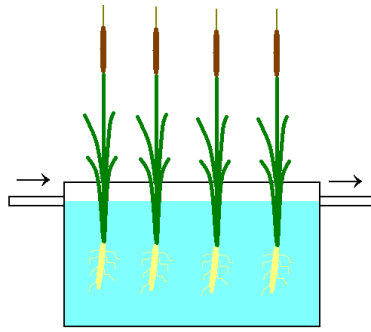
May 2004 (n= 5)



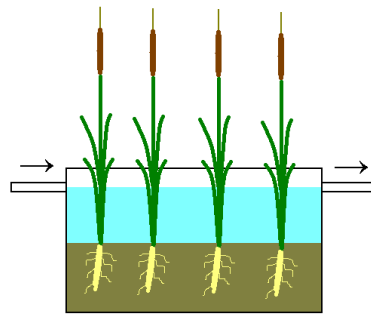
Water depth

➤ Easily biodegradable compounds are less sensitive to water depth.

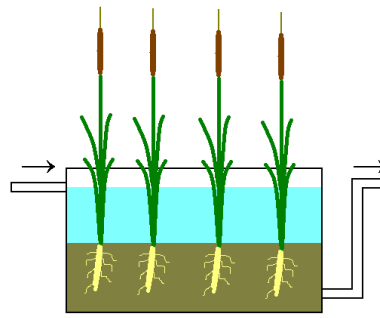
Experimental setup. Univ. Leon mesocosms



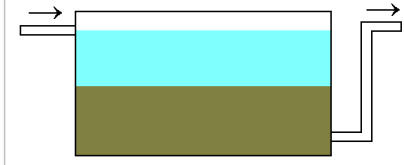
CW1
Planted with *Typha* sp.
Without gravel bed.
Free-water surface flow.



CW2
Planted with *Typha* sp.
With gravel bed.
Free-water surface flow.

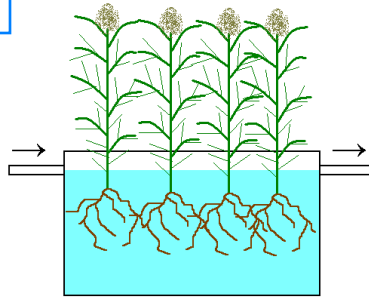


CW3
Planted with *Typha* sp.
With gravel bed.
Free-water subsurface flow.

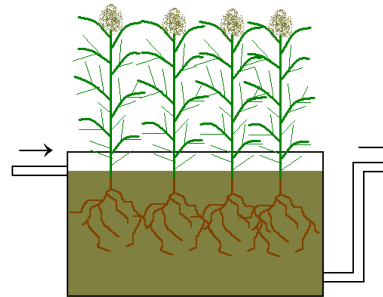


CW4
Unplanted.
With gravel bed.
Free-water subsurface flow.

HRT: 2-3 d



CW5
Planted with *Phragmites australis*.
Without gravel bed.
Free-water surface flow.



CW6
Planted with *Phragmites australis*.
With gravel bed.
Subsurface flow.



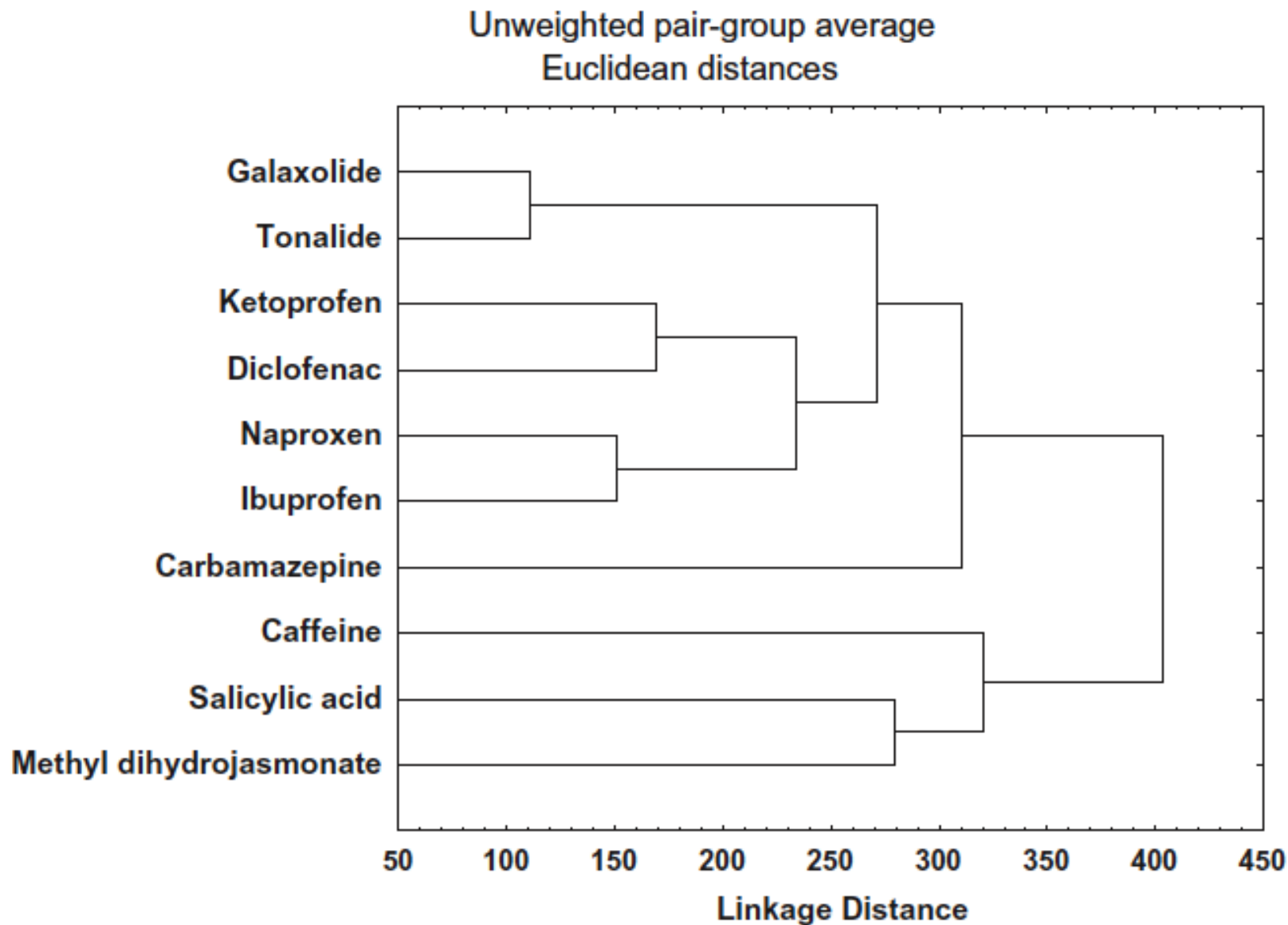
CW7
Unplanted.
With gravel bed.
Subsurface flow.

HLR: 50 mm d⁻¹

N=6

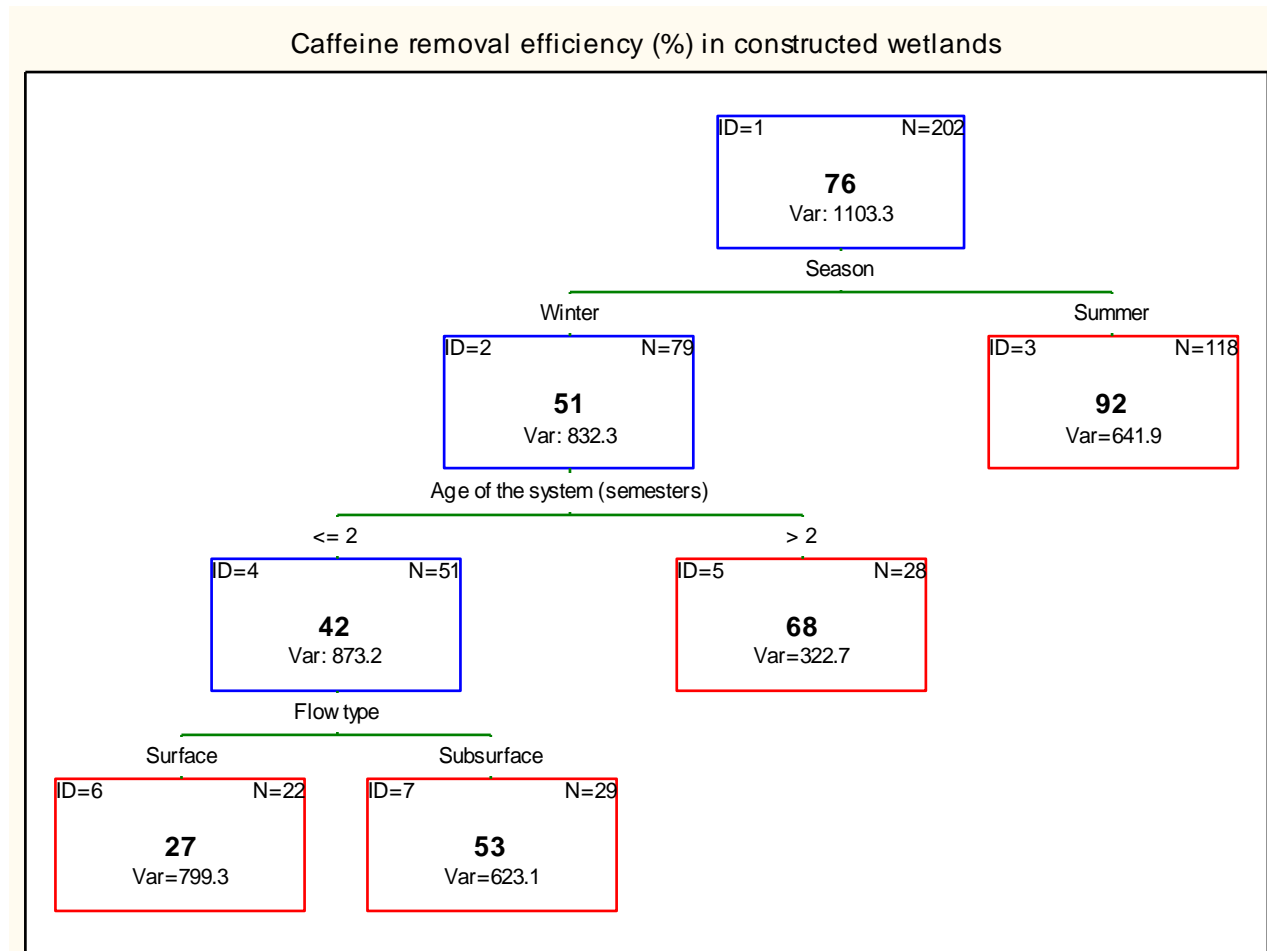
Dimensions (cm): 80 width x 130 length x 50 depth. $d_{10} = 4$ mm

Clustering Tree Diagram. Removal Efficiencies



Regression Tree Model (CHAID's algorithm)

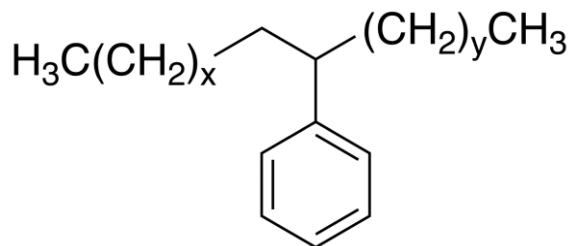
CAFFEINE: 39 month study



GRAVEL BED. ORGANIC MATTER BIODEGRADATION

System Configuration Effect

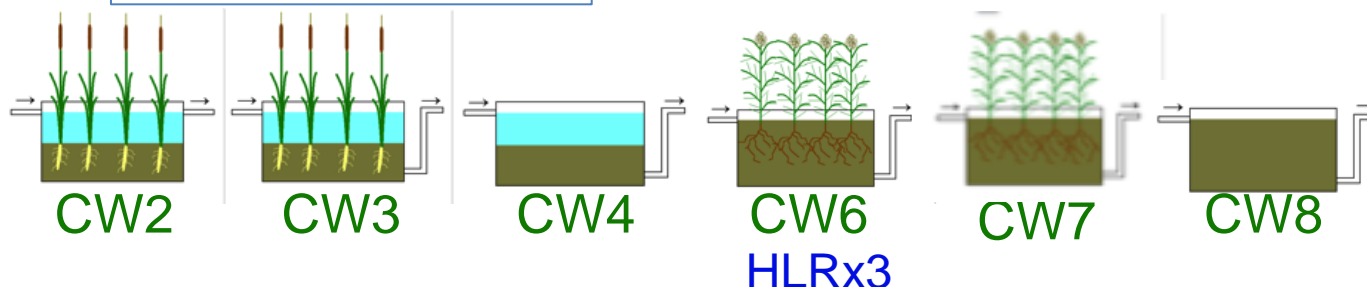
Linear Alkylbenzenes (LABs)



$$\frac{I}{E} = \frac{(6C12 + 5C12)}{(4C12 + 3C12 + 2C12)}$$

1: no biodegradation
>1 biodegradation

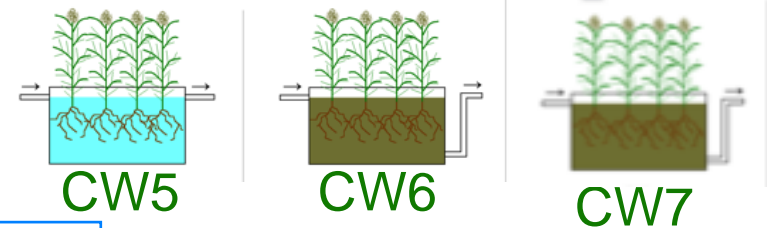
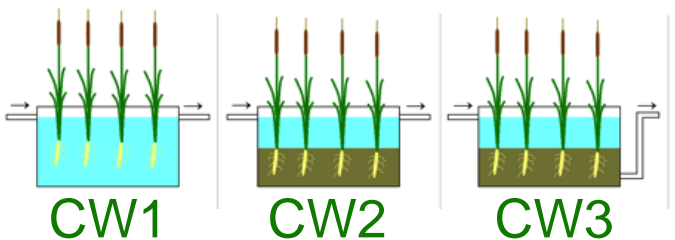
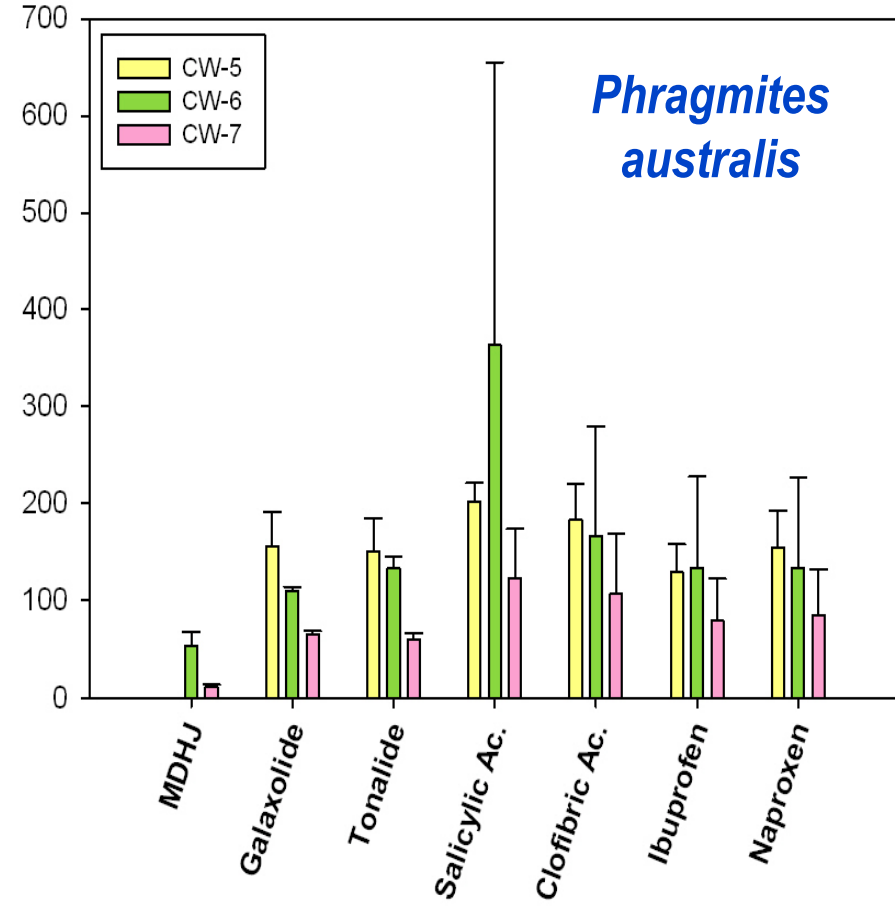
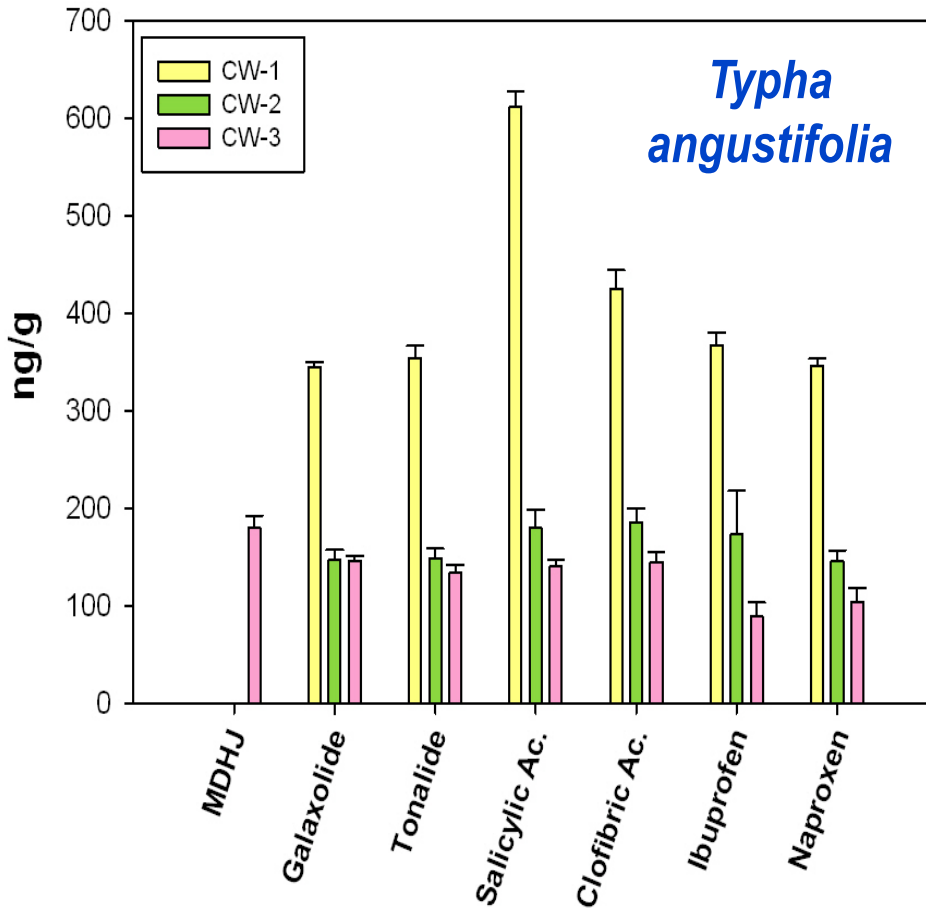
- Log Kow 6.8-9.99
- Anionic surfactant precursor
- Isomer specificity biodegradation
- Aerobic pathway



	CW2	CW3	CW4	CW6	CW7	CW8
I/E Ratio	3.07 ± 0.70	2.16 ± 0.21	2.02 ± 0.31	2.01 ± 0.17	2.09 ± 0.55	0.96 ± 0.09

UPTAKE RIZOSPHERE.

Plant Species vs System Configuration

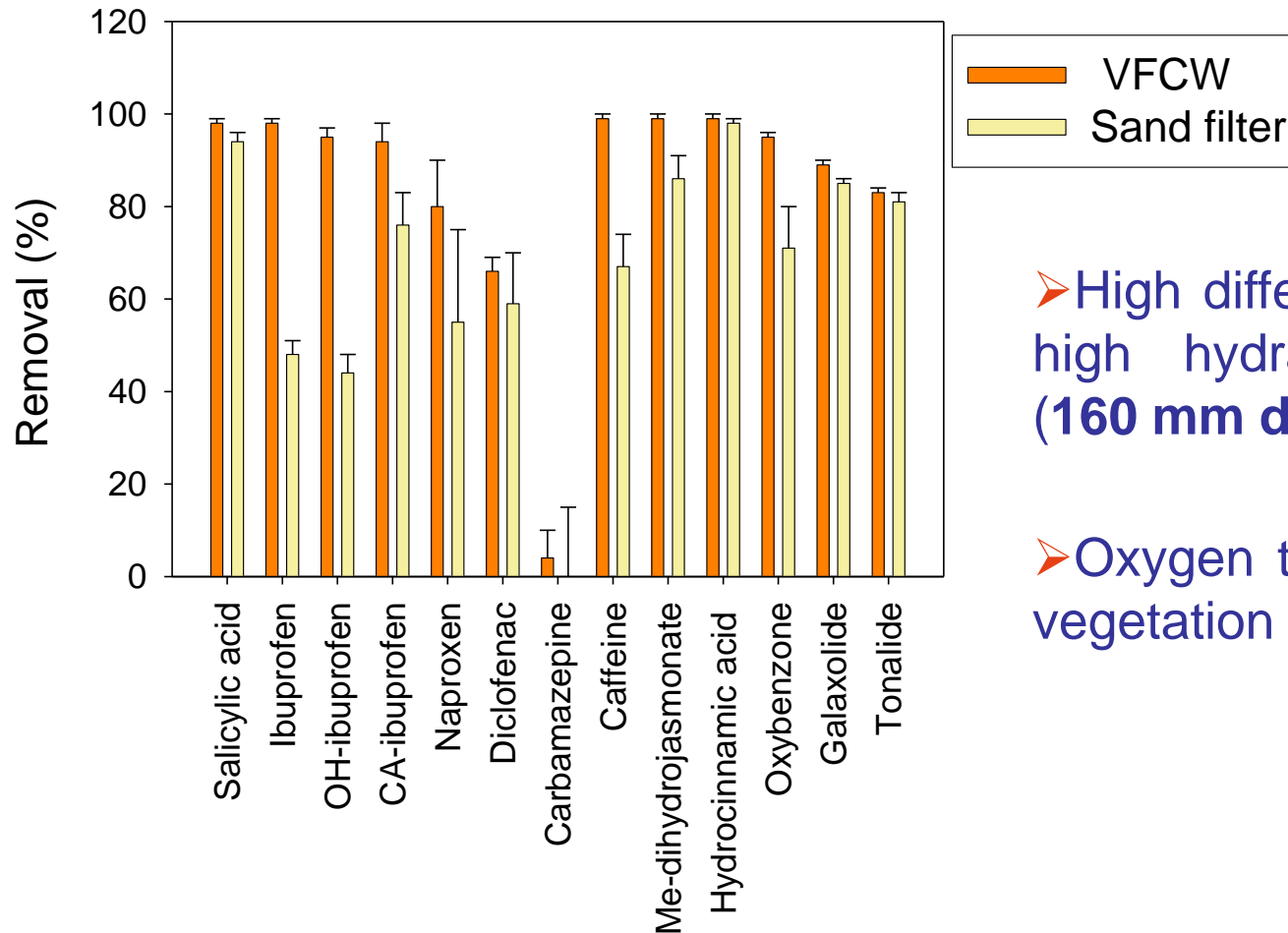


Dimensions (cm): 80 width x 130 length x 50 depth $d_{10} = 4$ mm

HLR_{x3}

Vertical Flow subsurface flow. Plant Effect.

Trigge, Denmark

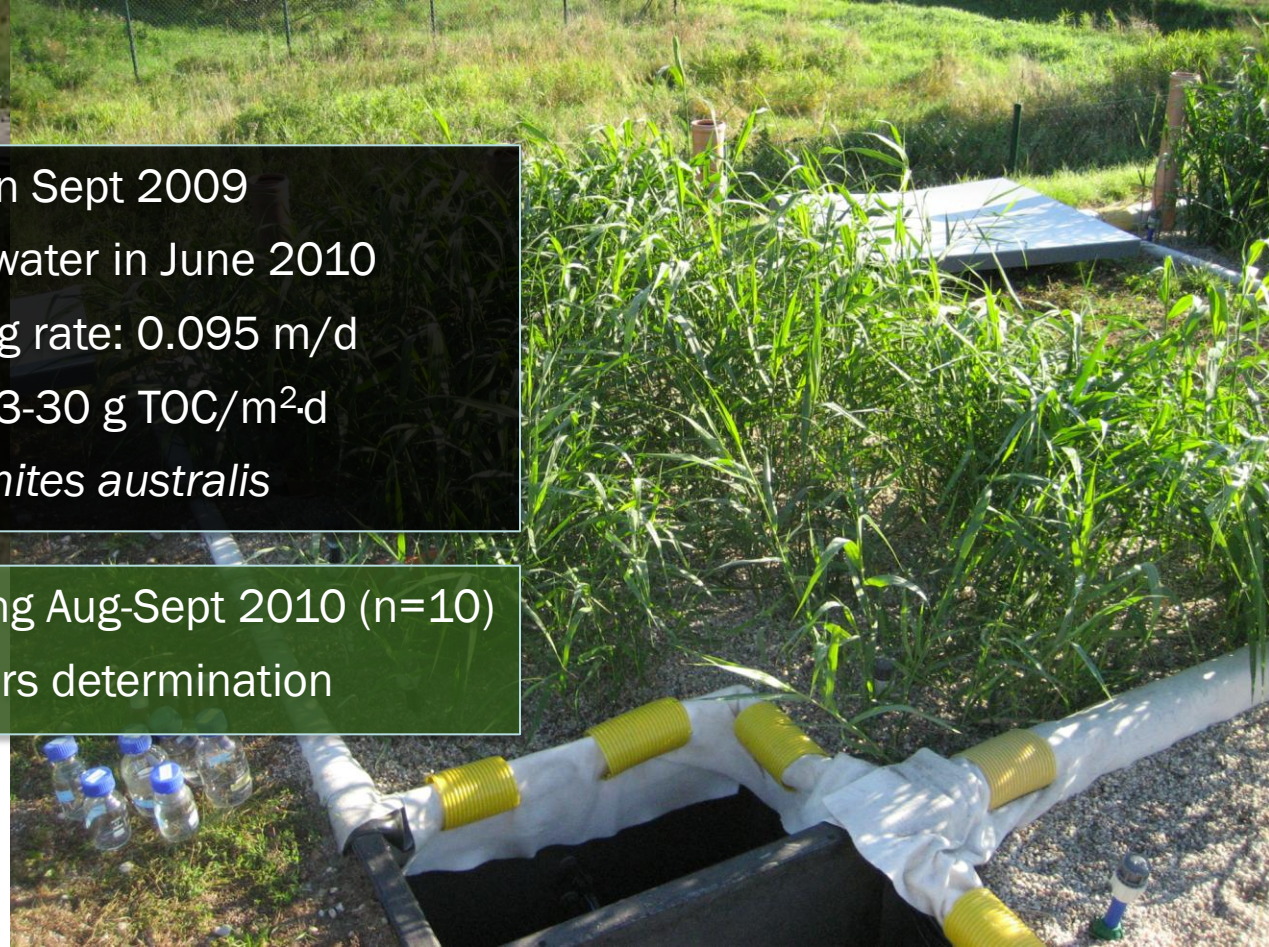


➤ High difference on removal at high hydraulic loading rates (160 mm d^{-1}).

➤ Oxygen transfer increased by vegetation

Vertical systems

Pilot treatment plant (Leipzig, Germany)

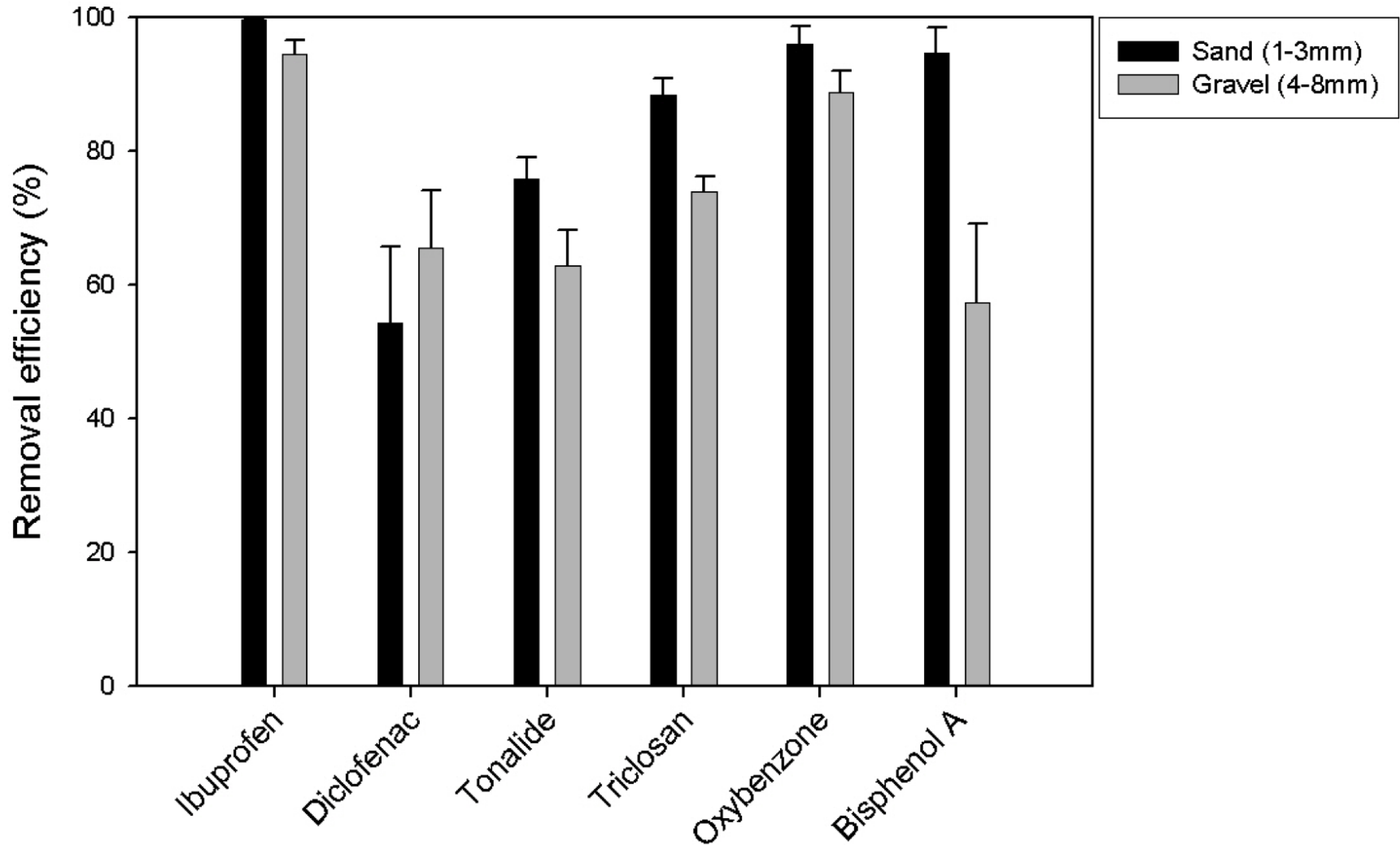


Started operation in Sept 2009
Operated with real wastewater in June 2010
Average hydraulic loading rate: 0.095 m/d
Organic loading rate: 13-30 g TOC/m²-d
Planted with *Phragmites australis*

Grab samples twice/week during Aug-Sept 2010 (n=10)
Water quality parameters determination

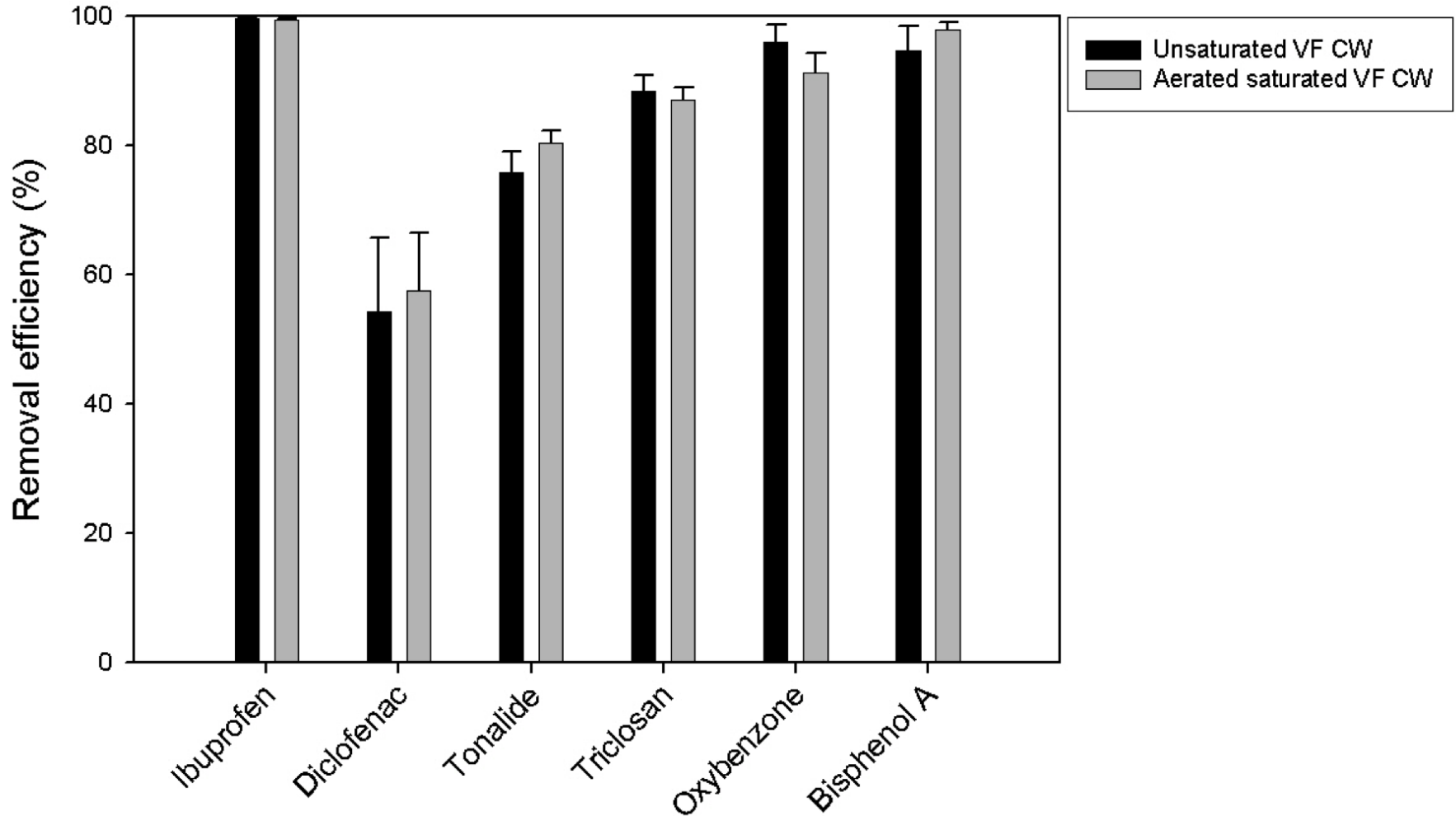
Vertical systems

Effect of granulometry

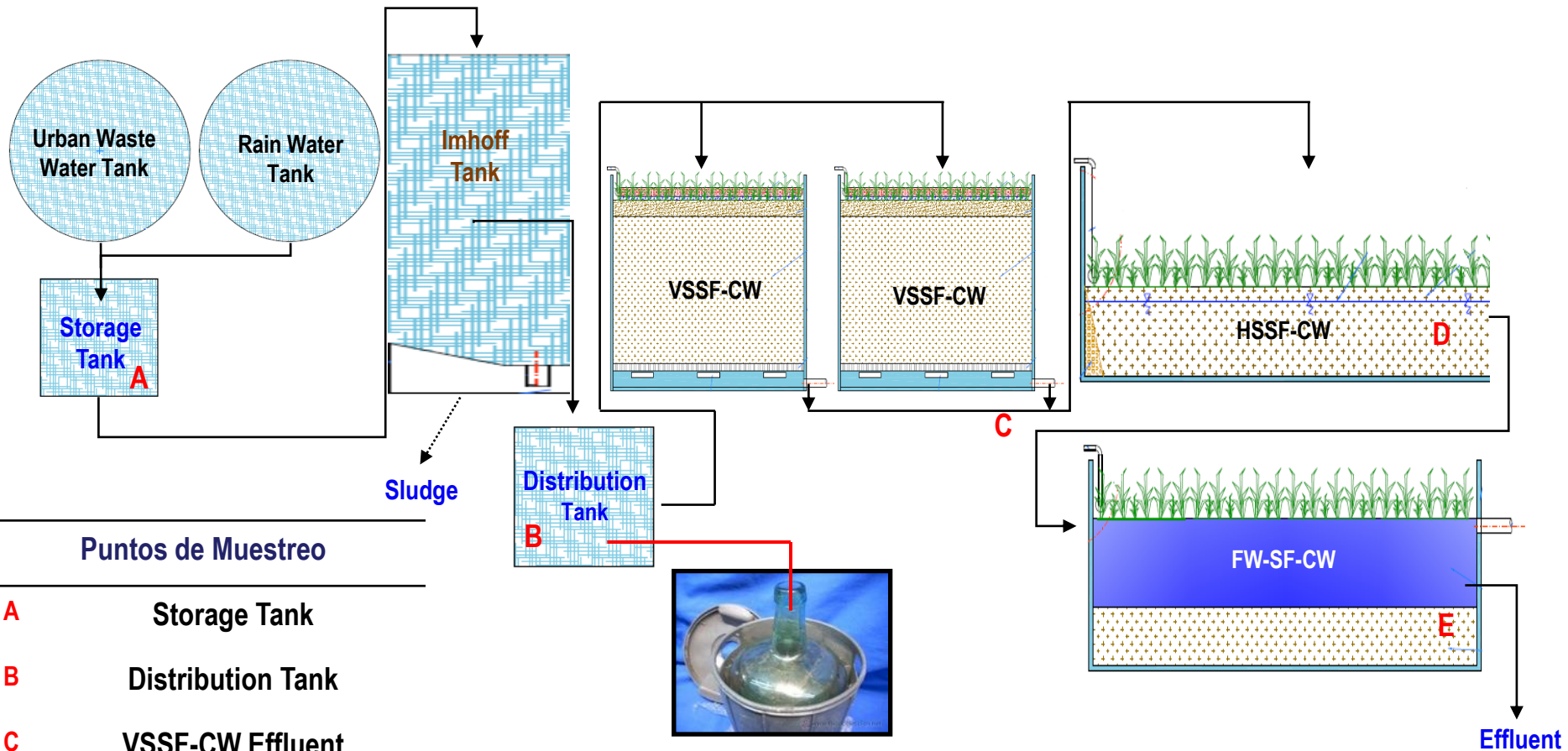


Vertical systems

Effect of use of active aeration



Continuous Injection. VF-HSSF-FWSF Pilot Plant



Puntos de Muestreo

- A** Storage Tank
- B** Distribution Tank
- C** VSSF-CW Effluent
- D** HSSF-CW Effluent
- E** FW-SF-CW

SISTEMAS HÍBRIDOS. UPC. Barcelona

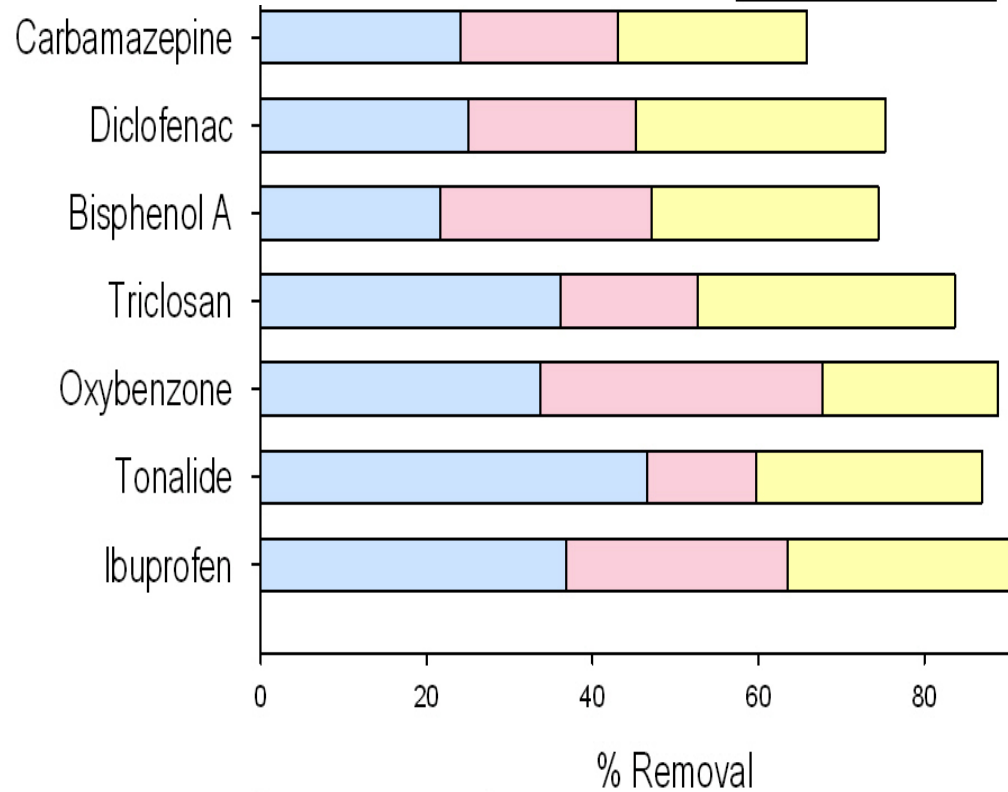
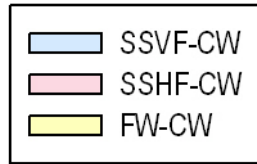


Continuous Injection Analytes. VSSF-HSSF-FWSF Pilot

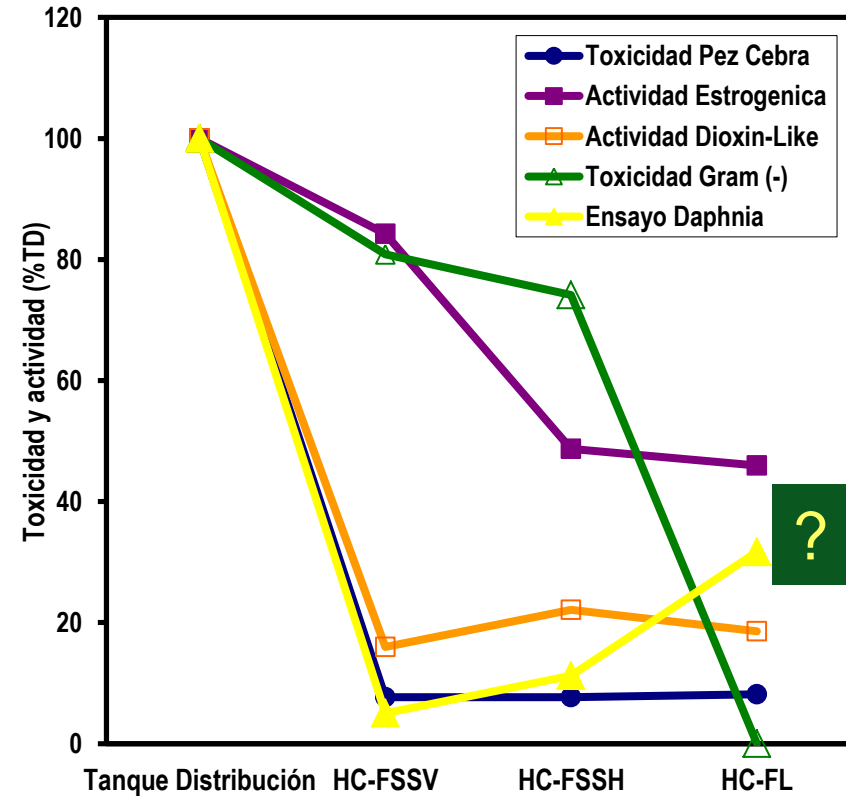
Antibiotics	Pharmaceuticals and Personal Care Products	Metals
Lincomycin Sulfamethoxazole Erythromycin Doxycycline Enrofloxacin	Tonalide Carbamazepine Triclosan Ibuprofen Diclofenac Ethinylestradiol Oxybenzone Bisphenol A	Mercury Hg Cl ₂

Inyección continua de analitos. Planta Piloto Híbrida

Eliminación PPCP

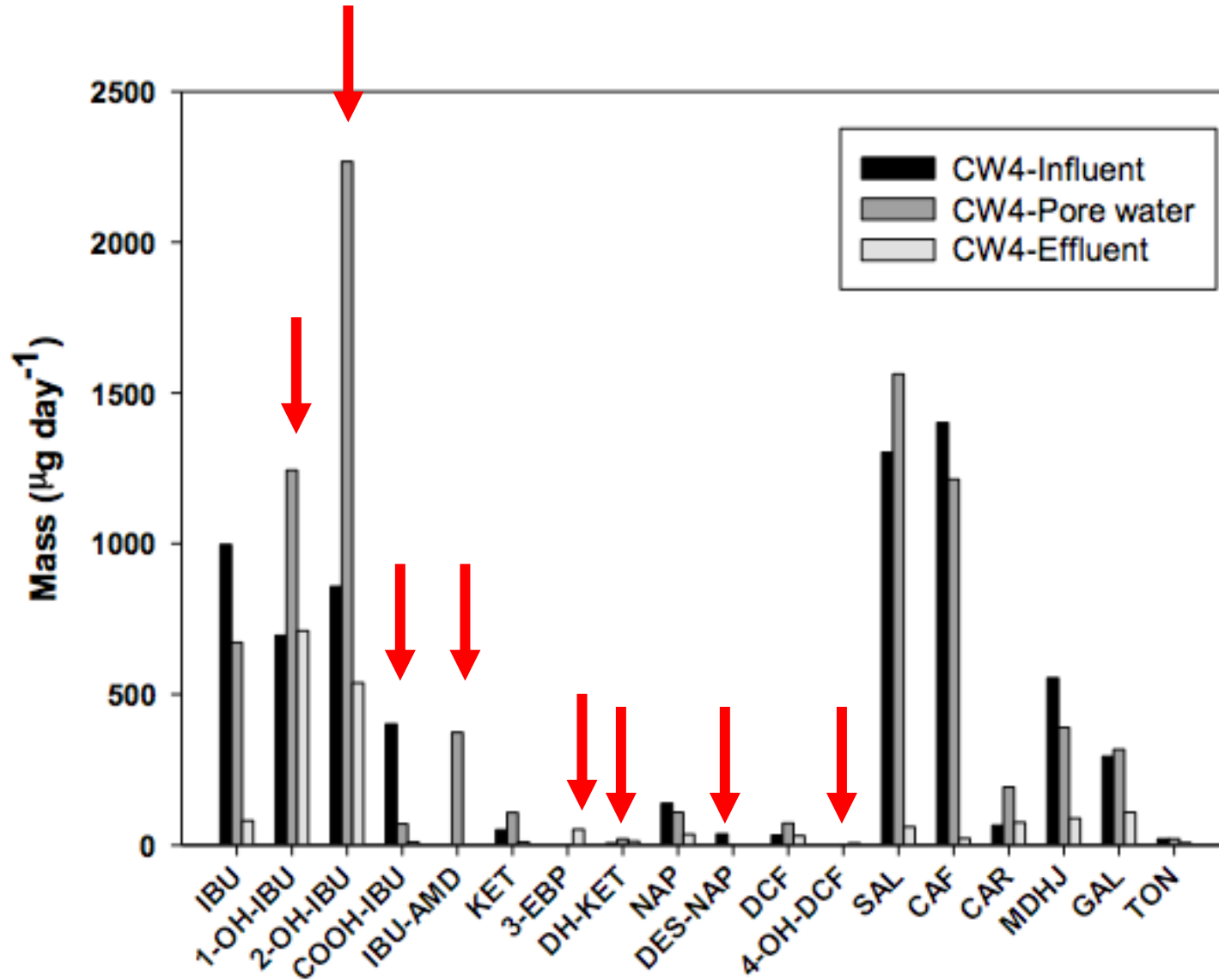


Eliminación Toxicidad



FSSV: flujo subsuperficial vertical; FSSH: flujo subsuperficial vertical; FL: Flujo libre

Transformation products. Influent, pore water & effluent



Continuous Injection Analytes. VF-HSSF-FWSF Pilot Plant

Antibiotics

Class

Compounds

Lincosamide

Lincomycin

Sulfonamide

Sulfamethoxazole

Macrolide

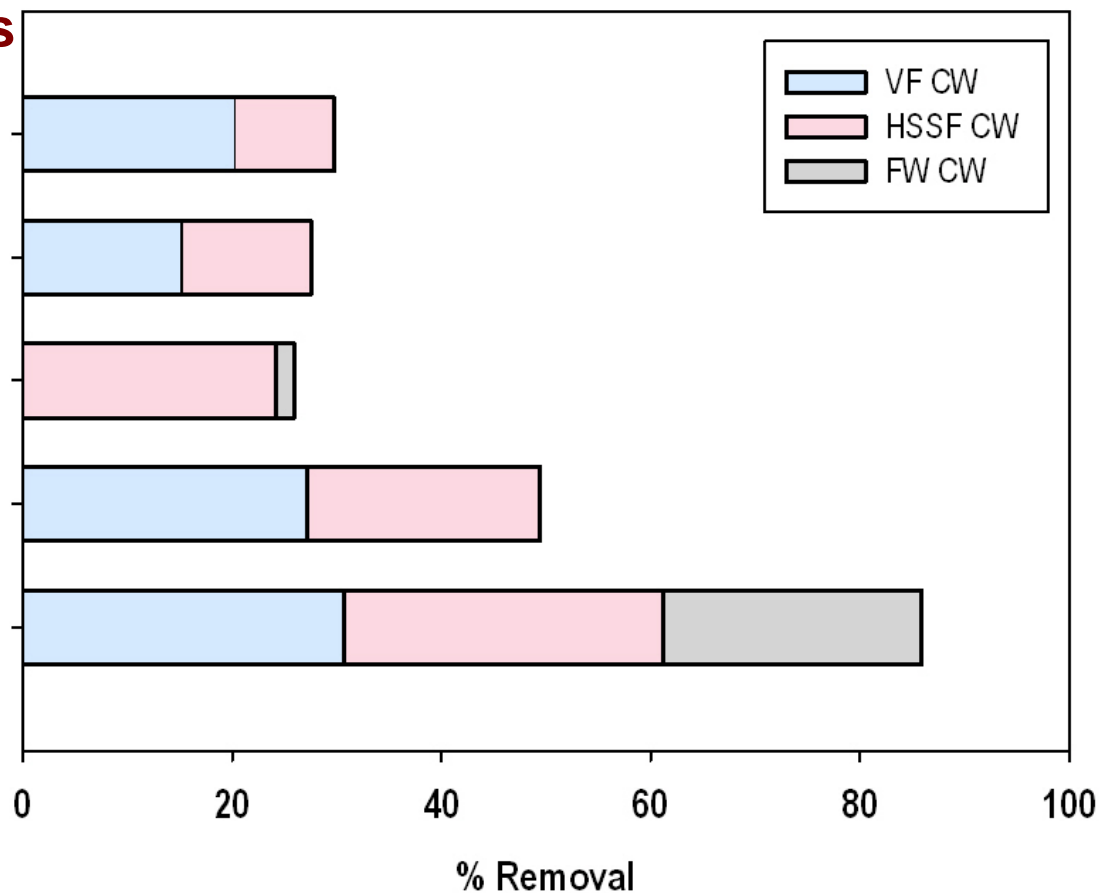
Erythromycin

Tetracycline

Doxycycline

Fluoroquinolone

Enrofloxacin



SSVF: subsurface vertical flow; SSHF: Subsurface horizontal flow; FW: Free water surface flow

Hybrid systems

Hydraulic loading rate: 0.044 m/d
Organic loading rate: 9 g BOD₅/m²-d

Planted with *Phragmites australis* and other species

Pilot hybrid plant (Seville, Spain)

1

Imhoff tank

2

Vertical flow CW

317 m²



3

Horizontal flow CW

229 m²



Sampling of emerging contaminants (May-Jun 2011),
twice/week
24-h composite samples (n=8)

4

Free water surface CW

240 m²



5

Water tank for reuse

20 m³

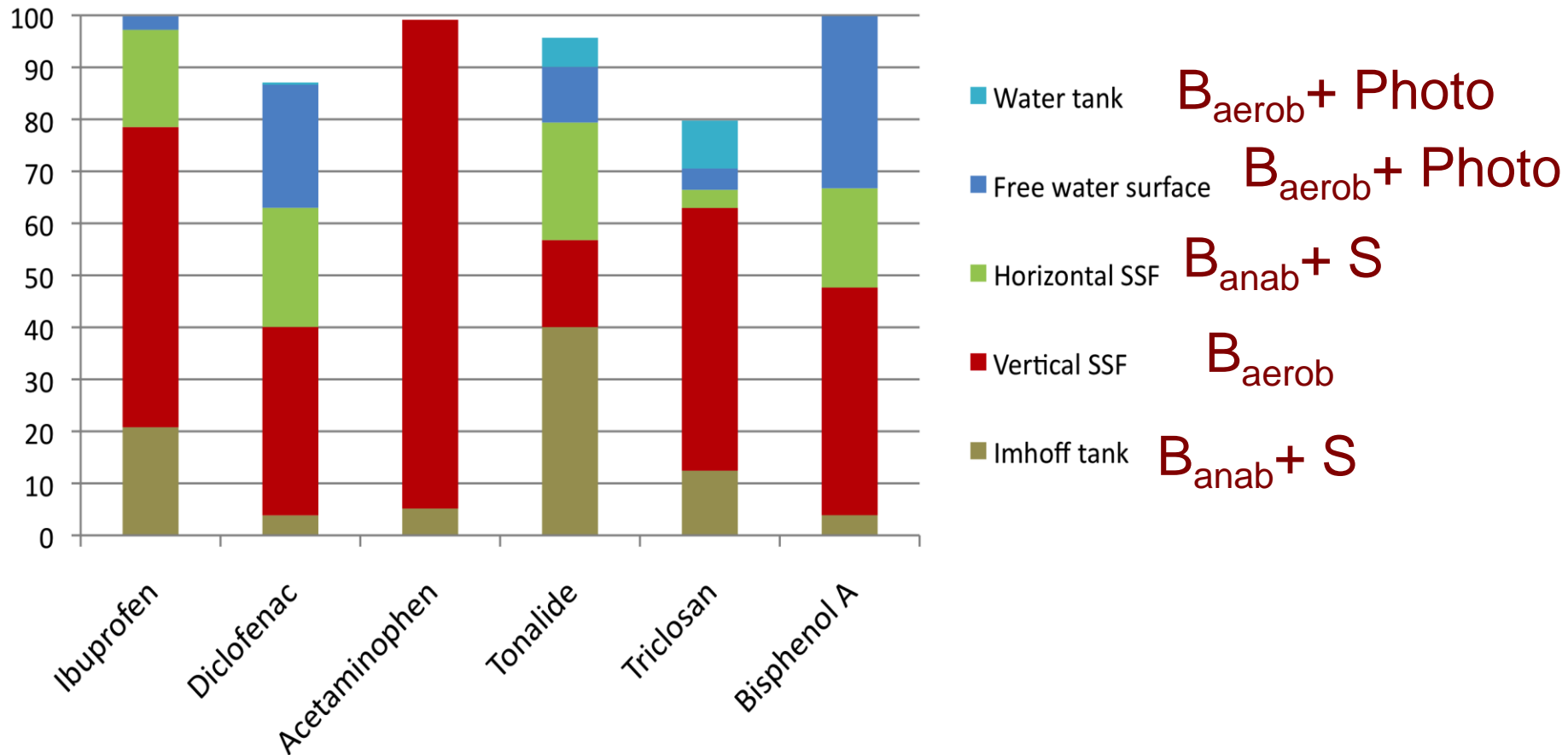


Hybrid systems

Behavior of emerging organic contaminants

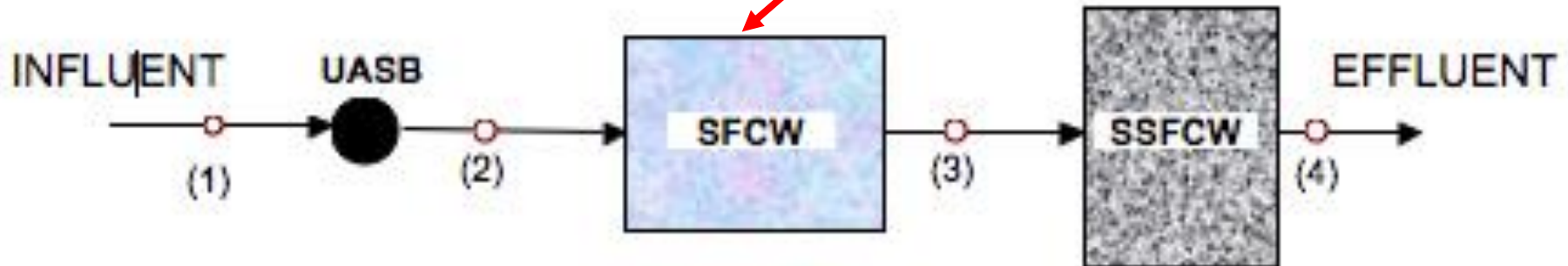
Influent concentrations: ng/L-ug/L; Ethinylestradiol and oxybenzone <LOD

Removal efficiency (%)



Hybrid Systems. Anaerobic Digestion- Constructed Wetlands. Phase Distribution & Seasonality

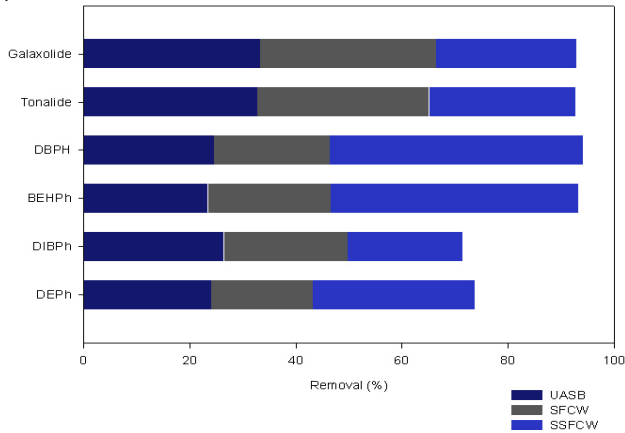
Silvouta, Santiago Compostela. Spain



Hybrid Systems. Anaerobic Digestion- Constructed Wetlands. Phase distribution & seasonality

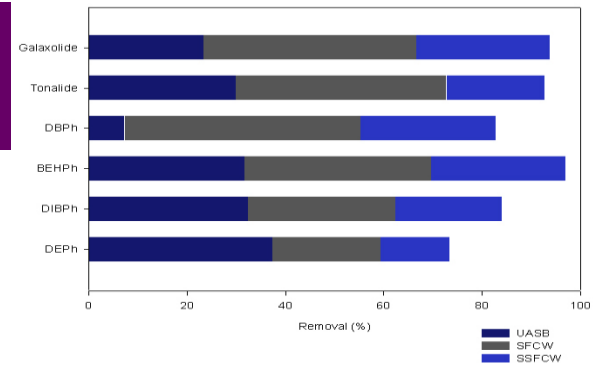
UASB-SFCW-SSFCW

Winter 2008, N=6

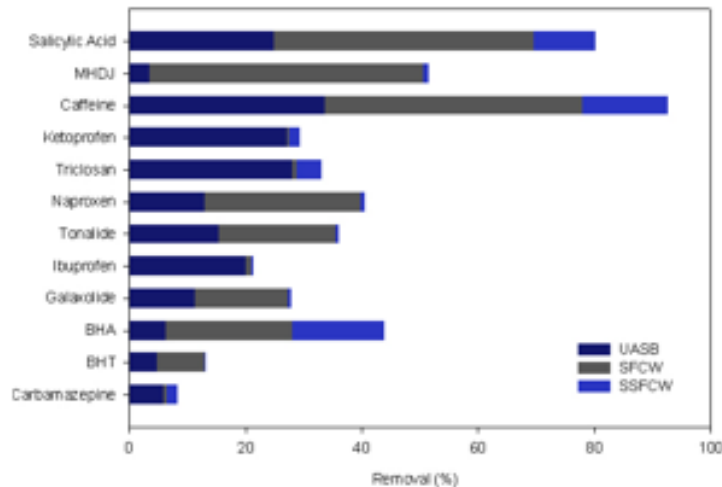


Suspended solids

Summer 2008, N=6

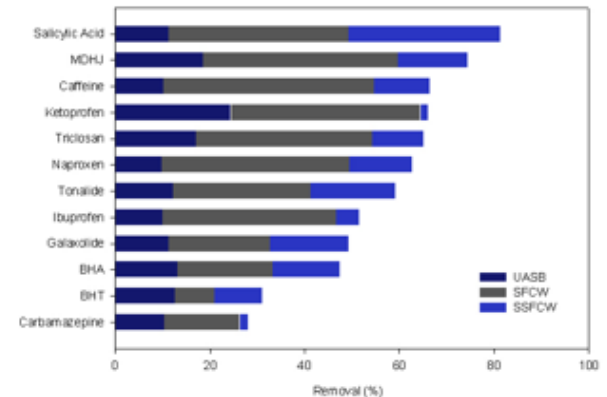


Winter 2008



Dissolved phase

Summer 2009



Humedales a escala real

Full-Scale Hybrid System



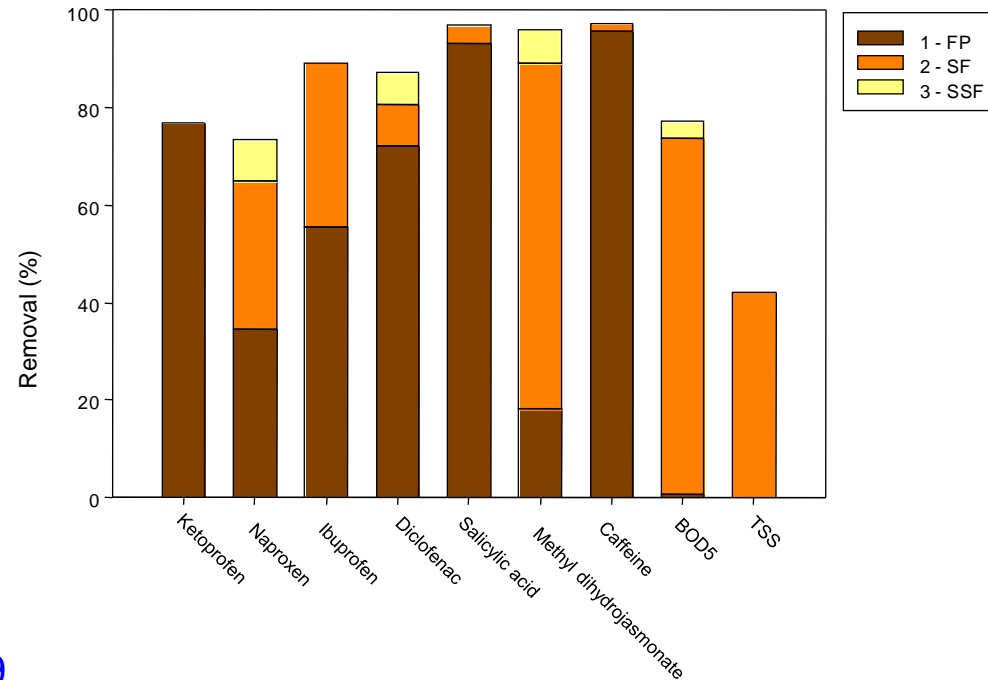
FP + SF + SSF

FP: facultative pond
SF: Surface flow
SSF: subsurface flow

180 h
Bustillo de Cea (León)
56 m³ d⁻¹
4070 m²
22 m² h⁻¹

The combination of ponds & wetlands allows an overall high removal efficiency

BUSTILLO DE CEA



TERTIARY TREATMENT. FULL SCALE

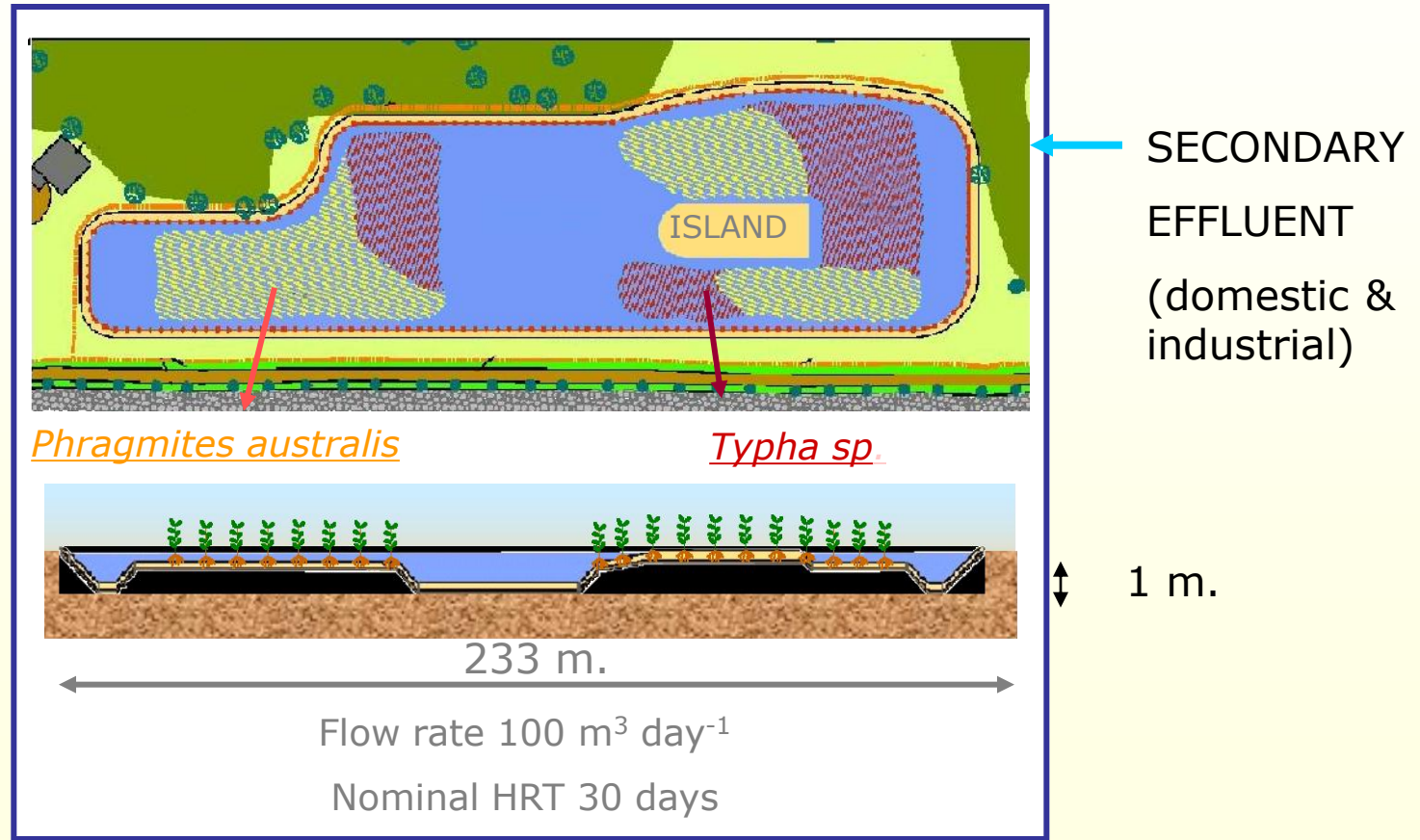


CAN CABANYES

SURFACE FLOW CONSTRUCTED WETLAND (SFCW)

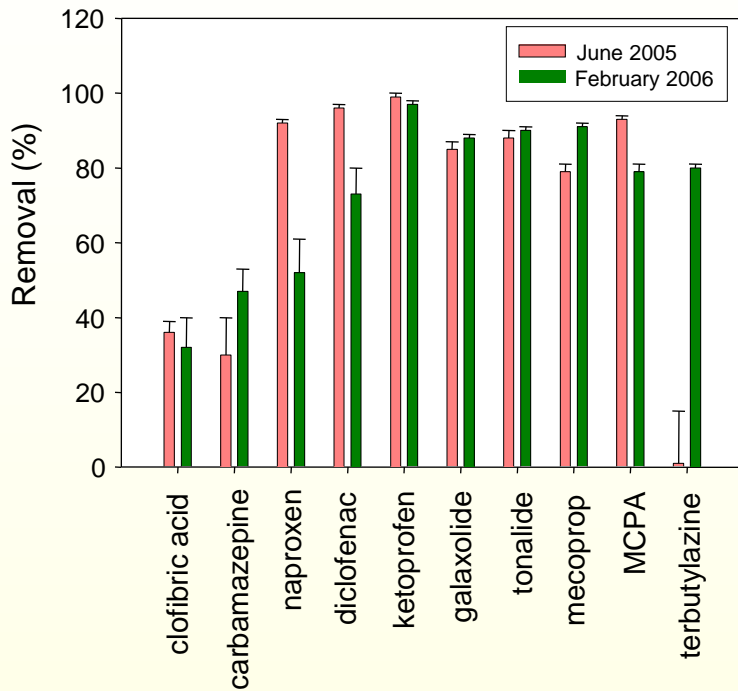
TERTIARY TREATMENT. FULL SCALE

SURFACE FLOW CONSTRUCTED WETLAND (SFCW)

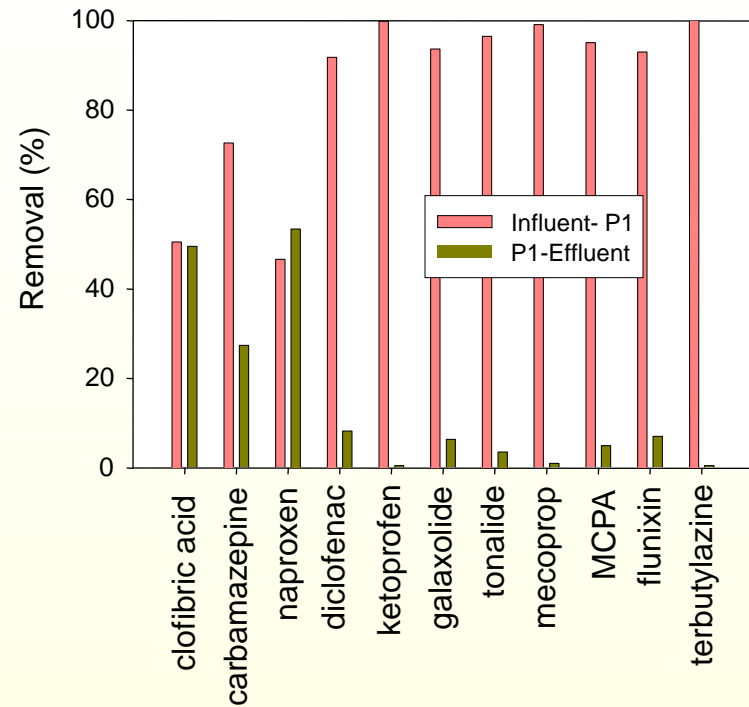


TERTIARY TREATMENT. FULL SCALE

Seasonal trend



Spatial trend

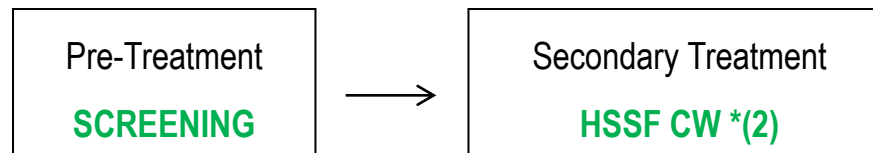


- Seasonal variability was shown for compounds with a poor elimination by biodegradation in contrast with high photodegradation rates (i.e. ketoprofen and diclofenac).
- The first part of system made a greater contribution to elimination than the latter part, with the exception of recalcitrant compounds (clofibrac acid and cabamazepine).

Full-Scale Subsurface Flow Constructed Wetland

- ✓ Gualba (Barcelona, Spain)
- ✓ 2002
- ✓ Population: 1072 P.E.

Parameters	Influent	Effluent
BOD ₅ (mg/L)	309 ± 260	20.7 ± 18.5
TSS (mg/L)	407 ± 245	25.9 ± 23.0



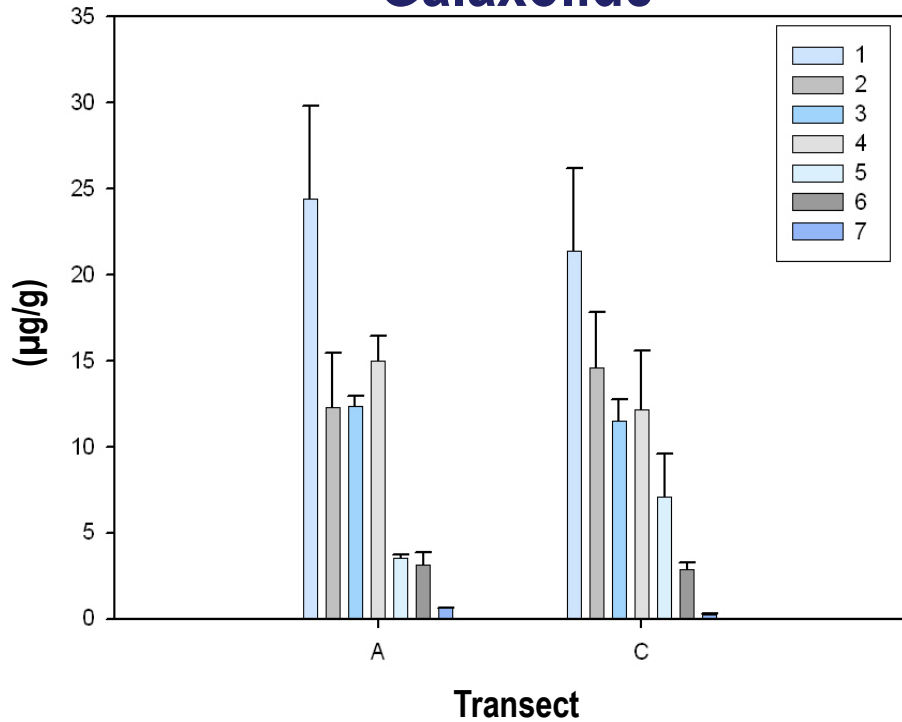
* Horizontal Subsurface Flow Constructed Wetland

Granular Medium

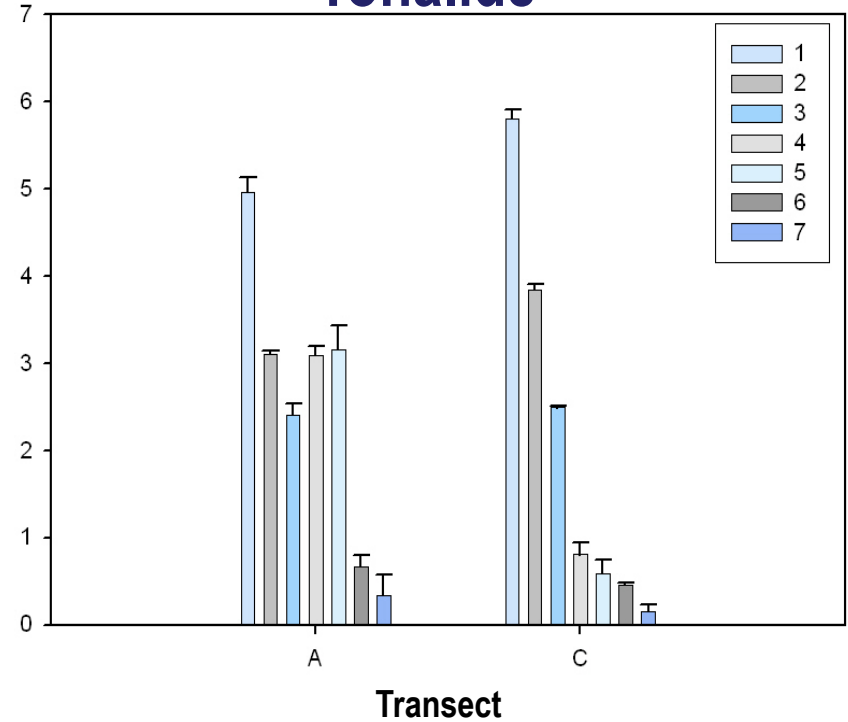
Flow Rate (m ³ /d)	Surface Area (m ²)	Water depth (m)	D ₅₀ (mm)	Porosity (%)	Initial Hydraulic Conductivity (m/d)
207	1404	0.35	7.5	45	181

Full-Scale Subsurface Flow Constructed Wetland

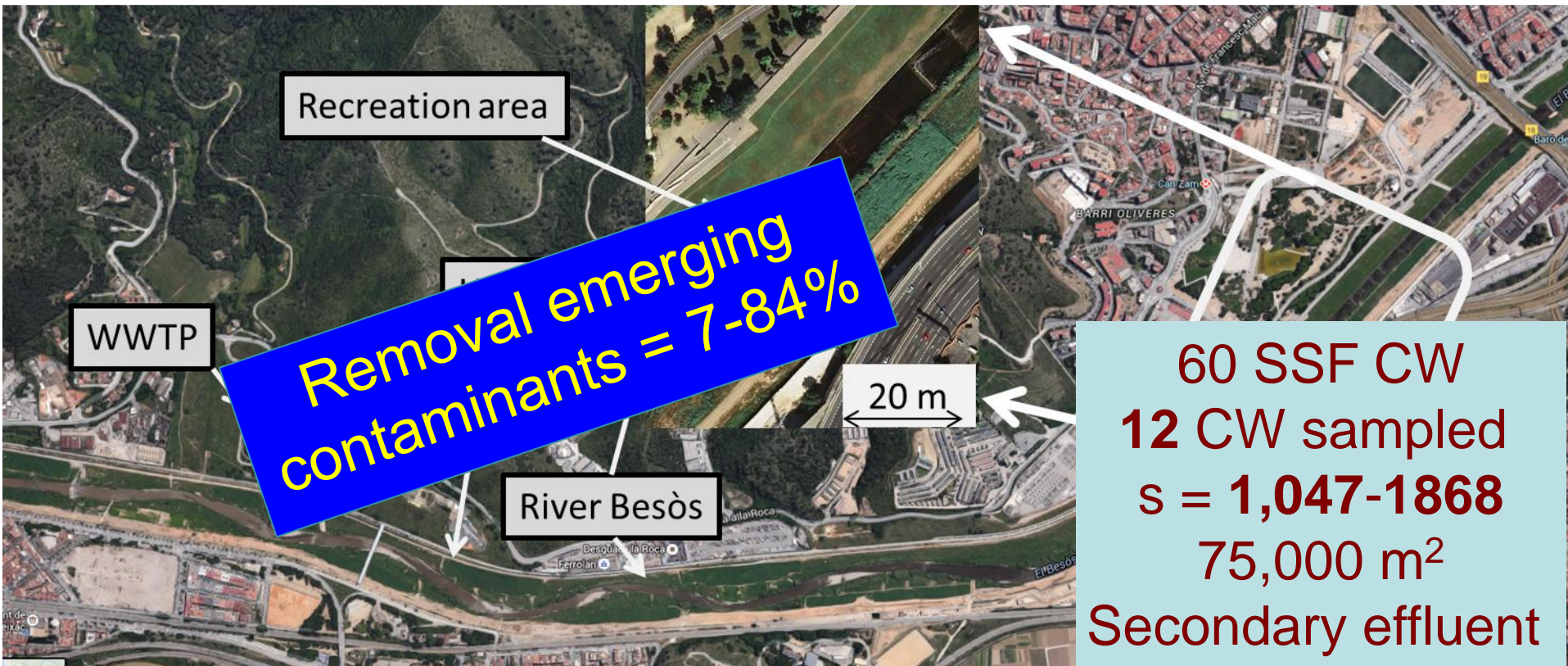
Galaxolide



Tonalide



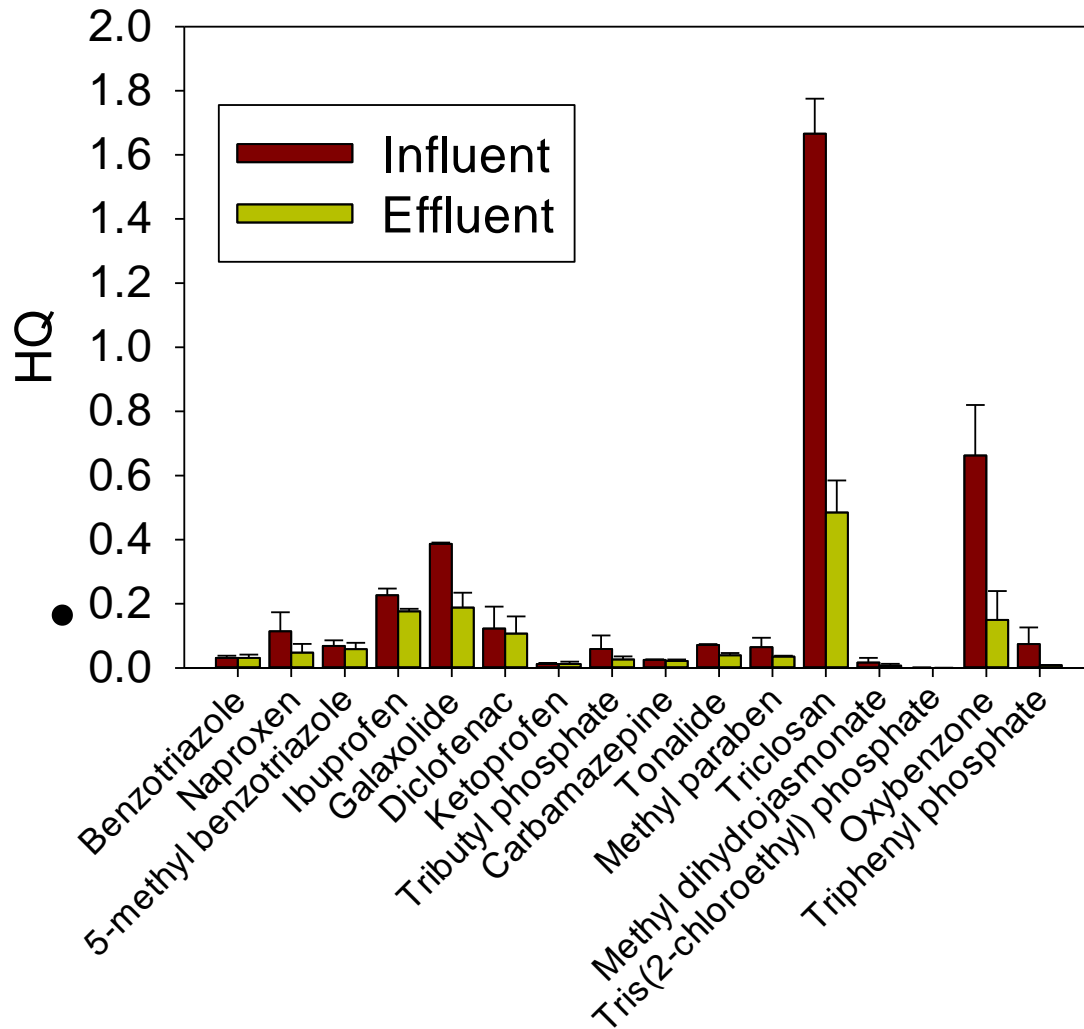
Riparian wetlands. Besós River



	T (°C)	Cond ($\mu\text{S cm}^{-1}$)	DO (mg L^{-1})	($\text{NH}_4\text{-N}$) (mg L^{-1})	TSS (mg L^{-1})	COD (mg L^{-1})
May Influent	21	1500	7	61	42	158
May Effluent	18±1	1600±500	0.4±0.1	58±11 (5)	12±5 (72)	74±17 (53)
July Influent	25	1901	8	42	15	58
July Effluent	23±1	1920±200	0.5±0.2	34±8 (20)	8±5 (45)	44±8 (25)

Estimated Acute Toxicity

Daphnia magna



$$HQ = MEC / PNEC$$

MEC: Measured environmental concentration

PNEC: Predicted non effect concentration

HQ > 1 potential risk

Conclusions

➤ CWs can be used for the elimination or attenuation of PPCPs in urban wastewater (secondary or tertiary treatment):

✓ **Positive factors:**

- ✓ Vegetation
- ✓ Ambient temperature

▪ **Negative factors:**

- Large surface area

hybrid systems (aerobic-anaerobic) are **the best**.

➤ PPCP removal efficiency of CWs is similar or better to conventional activated sewage sludge but...

- ✓ Low energy consumption
- ✓ Less sewage sludge production
- ✓ Much better landscape integration
- ✓ No off-flavors

Agradecimientos

- Colaboradores

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- Dr. J. Nivala (UFZ, Leipzig, Alemania)
- Dr. C. Arias y Prof. H. Brix (Univ. Aarhus, Dinamarca)
- Dr. J.L. Salas. CENTA.

- Posdocs

- Dr. Maria Hijosa Valsero (INIA, León, España)
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Empuriabrava WWTP: Pond-CW system



**Muchas gracias
por su atención**



Credits: Ruud Kampf