

Attenuation of emerging contaminants by wetland systems

Dr. Victor Matamoros











Institute of Environmental Assessment and Water Research



Contaminants of emerging concern





(UNEP, 2009)

The Universe of Chemicals Globally


- 73,000,000 organic + inorganic substances (2013)
- Commercially available: 19,184,000
- in commerce in USA, EU, Japan, China ~150,000
- production > 1 tonne/year ~ 30,000

<500 of them are routinely measured in the aquatic environment

Contaminants of emerging concern



"Emerging pollutants" can be defined as pollutants that are currently not included in routine monitoring programmes at the European level, and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments.



Drugged Waters
Does it matter that pharmaceuticals are turning up in water supplies?
By JAMIE HULLOFF
MARCH 21, 1998 SCIENCE NEWS, VOL. 153

In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognized until new detection methods were developed.

Contaminants of emerging concern





Pharmaceuticals
antiinflammatory/analgesics (ibuprofen, naproxen, diclofenac), diuretics (furosemide), antibiotics (erythromycin, sulfonamides)

Personal care products
fragrances (galaxolide, celestolide o tonalide), sun filters (oxibenzone) cosmetics (parabens, siloxanes)



Plasticizers
Phthalats (Di-n-butyl phthalat), plastic additives (bisphenol A, bisphenol F, bisphenol S...)

Microplastics
sorb and concentrate persistent organic pollutants (POPs), which can increase exposure to contaminants when these plastics are ingested

Disinfection by-products (except THMs)
iodo-THMs, N-nitrosamines...

Contaminants of emerging concern

Surfactants/ detergents
PFOA & PFOS (Perfluorooctanoic acid and Perfluorosulfonates)







Flame retardants
Polybrominated diphenyl ethers (PBDEs), organophosphates (tris(2-chloroethyl) phosphate)

Pesticides
Piretrines (permetrine)
Phenoxyacid herbicides (mecoprop, 2,4-D, MCPA...)



Antiseptics
triclosan, triclorcarban,

Nanoparticles (1-100 nm)
Silver nanoparticles added to socks to kill the bacteria

Anticorrosives
Benzotriazole, chlorophen

Contaminants of emerging concern

Ecotoxicological effects of the presence of ECs in the aquatic environment

Triclosan (antiseptic)




Oc1ccc(Cl)c(Cl)c1

Negative effects on frog metamorphosis
Tiroxine (T4)

Diclofenac (nonsteroidal anti-inflammatory drug)
Effects on fish gills and liver (0.5-1 µg/L)

DCF consumption as a human and veterinary pharmaceutical drug is >1000 tons/year

17-Ethinylestradiol (EE2) (birth control pill)
Feminization of male fishes: 5-6 ng/L (*Fathead minnow*)
Collapse of a fish population after exposure to a synthetic estrogen

Miyata and Ose. J Toxicol Pathol. 2012; 25(1): 1-9.
V. Christen et al. Aquatic Toxicology 96 (2010) 167-181
Kidd, K.A et al. 2007. PNAS, 104(21), 8897-8901

Contaminants of emerging concern

Effects

- Reduction of macroinvertebrates diversity in rivers
- Behavioural changes in mosquito fish
- Reproductive disruption in fish

Effects at Different Levels of Biological Organization

Mechanistic Understanding

Ecological Significance

Molecular Cellular Systems Organism Population Community

Source: <http://christinafontmayor.weebly.com/cellular-biology.html>

W. Brack et al. / Science of the Total Environment 503–504 (2015) 22–31

Contaminants of emerging concern

"No substance is a poison by itself. It is the dose that makes a substance a poison..."
Paracelsus (1493-1541)

Occurrence (Chemical exposure) → Ecosystem (structural and functional changes)

Example of a Pareto distribution
Vilfredo Pareto (1848-1923) Italian economist who stated in 1906 the so called "80:20" (Pareto Principle)
Sociology: "20 % of people own 80% of wealth"
Quality Control: "20 % of causes account for 80% of failures"
"Few compounds are responsible for most of the risk"

Source: W. Brack et al. 2013. Solutions Project kick-off Presentation

Contaminants of emerging concern

Watch list

COMMISSION IMPLEMENTING DECISION (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council (notified under document C(2015) 1756) (Text with EEA relevance)

Name of substance/group of substances	CAS number (1)	EI number (2)	Indicative analytical method (3) (4)	Maximum acceptable method detection limit (mg/l)
Estrogens 17-Alpha-ethinylestradiol (EE2)	57-61-6	200-342-2	Large-volume SPE — LC-MS-MS	0,035
17-Beta-estradiol (E2), Estrone (E1)	53-28-2, 53-18-7	200-023-8	SPE — LC-MS-MS	0,4
NSAID Diclofenac	15307-86-5	239-348-5	SPE — LC-MS-MS	10
2,6-Di-tert-butyl-4-methylphenol	128-37-0	204-881-4	SPE — GC-MS	3 160
Personal Care Products 2-Ethylhexyl 4-methoxycinnamate	5466-77-3	226-775-7	SPE — LC-MS-MS or GC-MS	6 000
Antibiotics Macrolide antibiotics (5)			SPE — LC-MS-MS	90
Methocarb	2032-65-7	217-991-2	SPE — LC-MS-MS or GC-MS	10
Pesticides Neonotroinids (7)			SPE — LC-MS-MS	9
Oxadiazon	19666-30-9	243-215-7	LLE/SPE — GC-MS	88
Tri-allate	2303-17-5	218-962-7	LLE/SPE — GC-MS or LC-MS-MS	670

(1) Chemical Abstracts Service.

Contaminants of emerging concern

High amount of unknown transformation products (TPs) are discharged or produced in the surface water bodies

Pharmaceuticals & Personal care products
e.g.: antibiotics
0.1-0.2 × 10⁶ tons/yr

Synthetic organic chemicals
300 × 10⁶ tons/yr

& metabolites...

Pesticides
2.3 × 10⁶ tons/yr

Some are more recalcitrant and toxic than the parental compounds

Elodie Passeport's Lab

Coelho AD, Sans C, Agüera A, Gómez MJ, Esplugas S, Dezotti M (2009). Sci. Total Environ. 407, 3572-3578

Contaminants of emerging concern

Crop's uptake and human health risk

Crops irrigated with treated wastewater

The threshold of toxicological concern for a child is of 60 g/day (half a carrot)

Source: Malchi, T et al. 2014. Environ. Sci. Technol., 48(16), 9325-9333. Wu, X., et al. 2015. Sci. Total Environ., 536, 655-666.

Intake of crops irrigated with reclaimed water

Carbamazepine (Genotoxic)

Source: Goldstein, et al. 2014. Environ. Sci. Technol., 48(10), 5593-5600

Wetland systems

Conventional treatments

Intensive systems

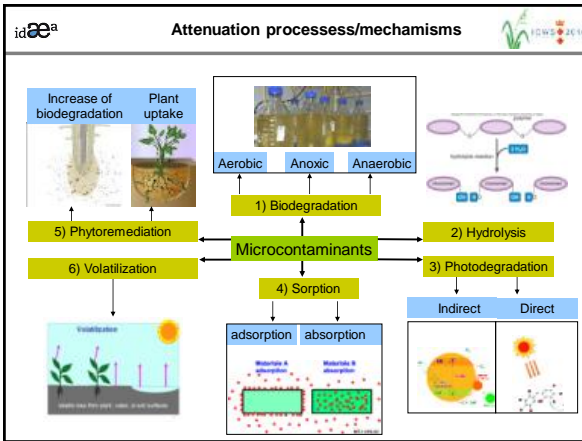
- Activated sludge,
- Membrane biological reactors,
- Advanced oxidation processes (ozone, TiO₂...)
- Membrane-based treatments

Wetland systems

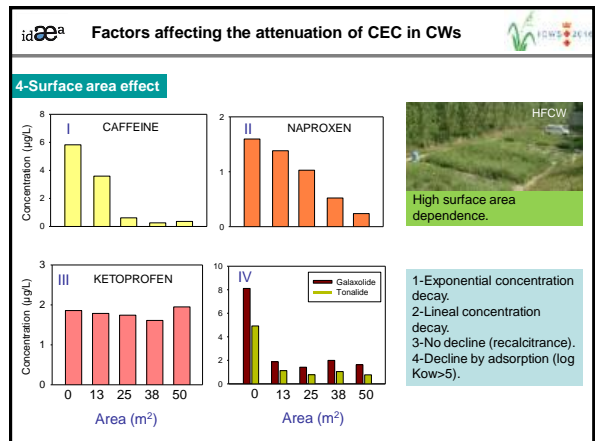
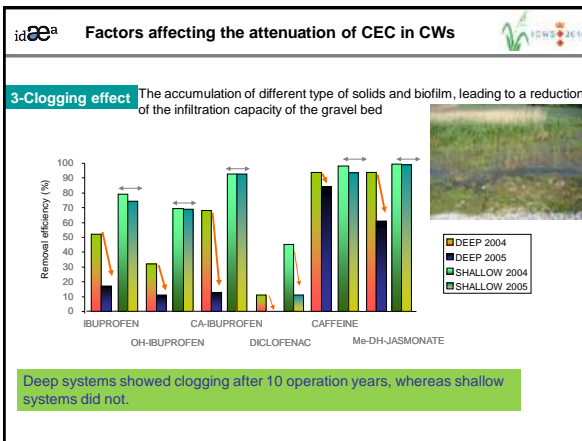
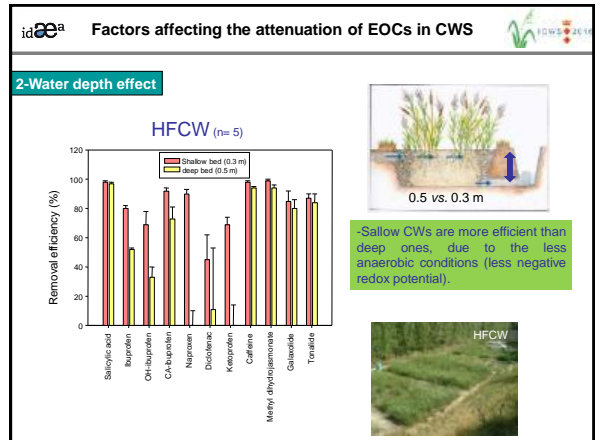
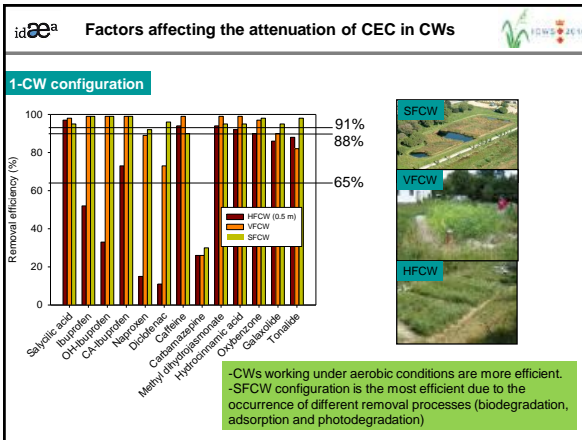
Extensive systems

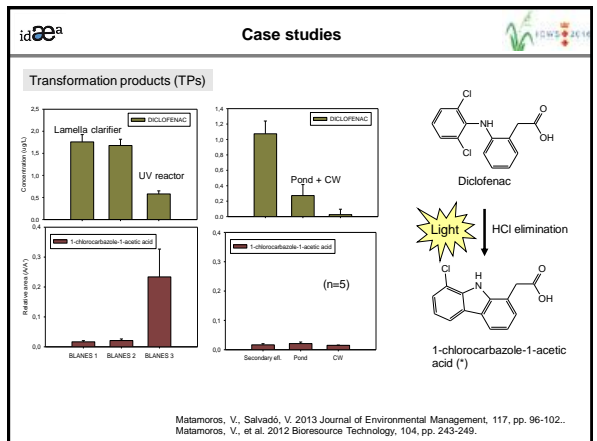
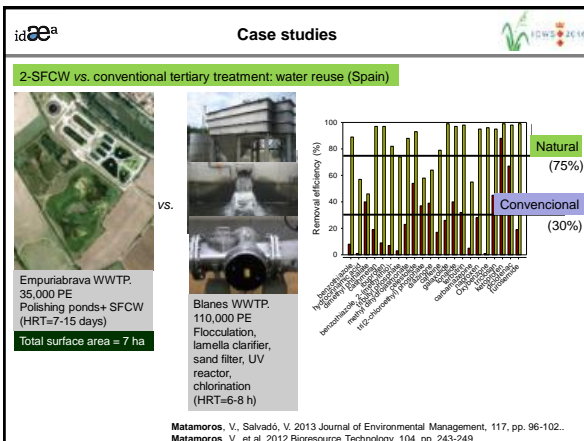
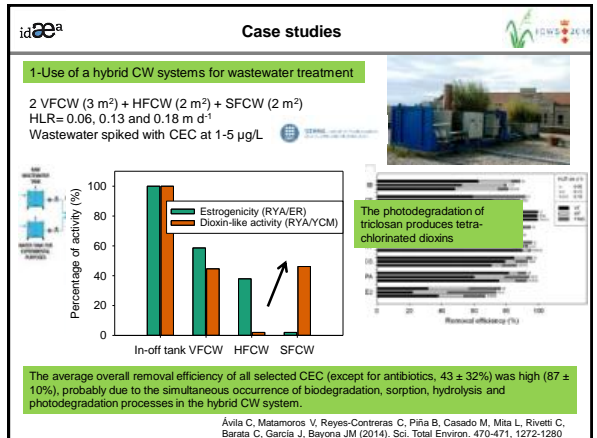
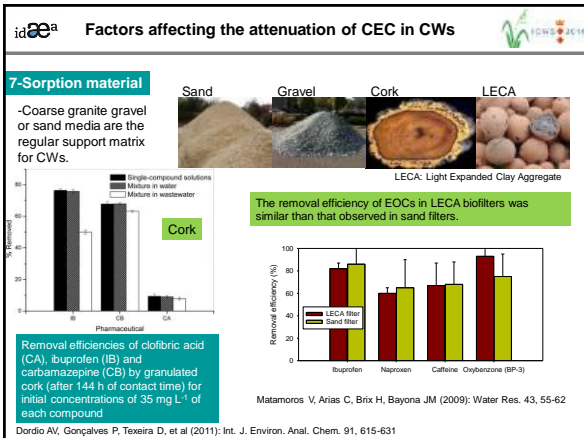
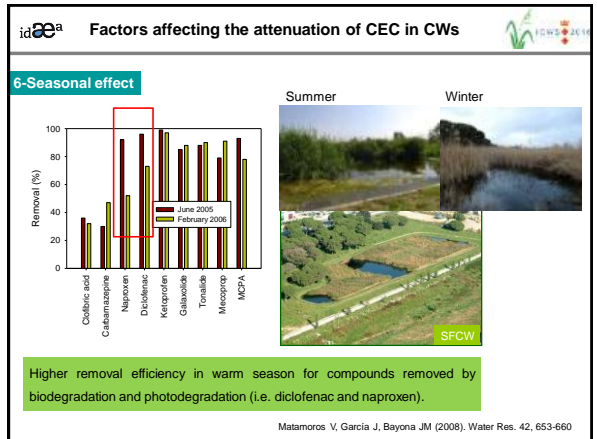
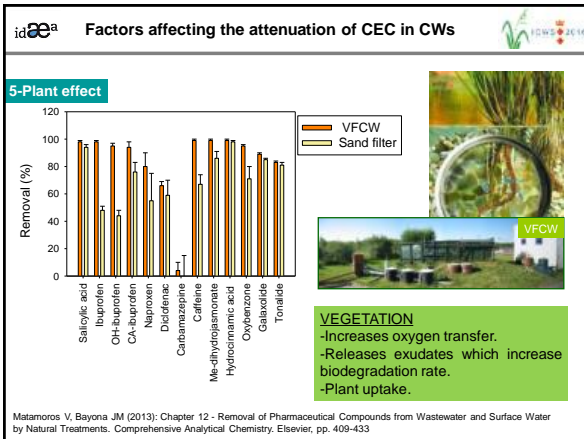
- Constructed wetlands,
- Buffer strips
- Restored wetlands
- Recharge basins...

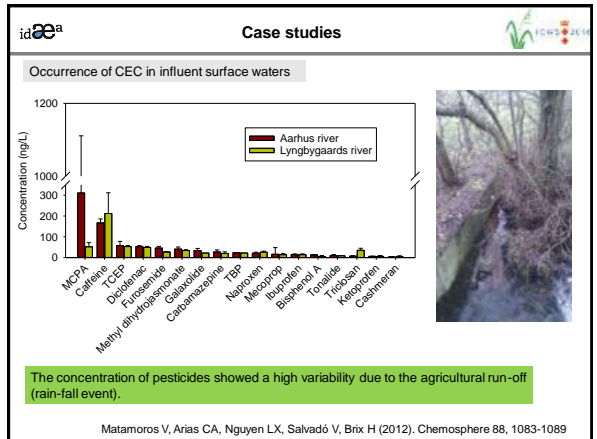
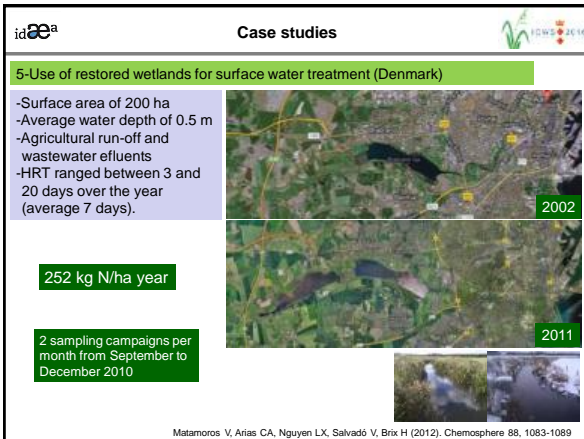
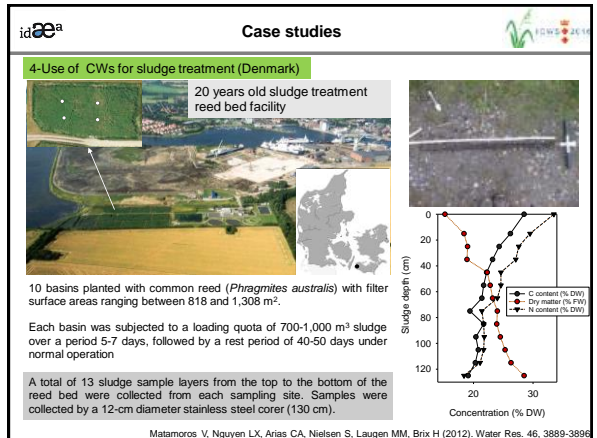
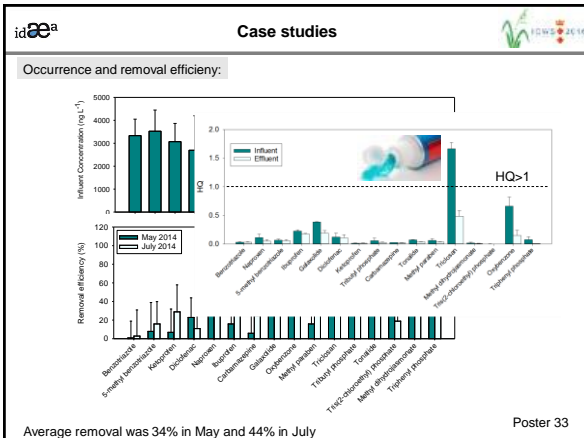
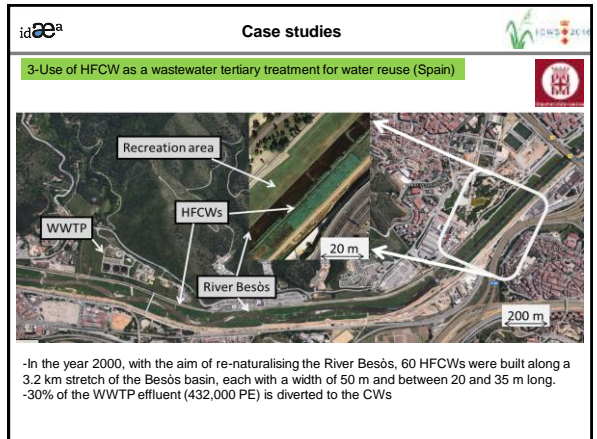
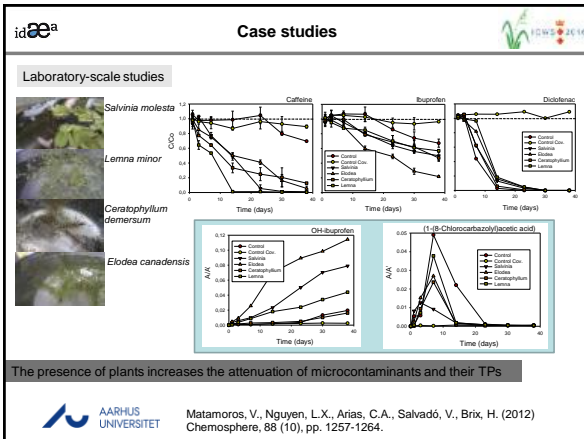
-Urban and industrial wastewater,
-Surface and agricultural run-off water effluents

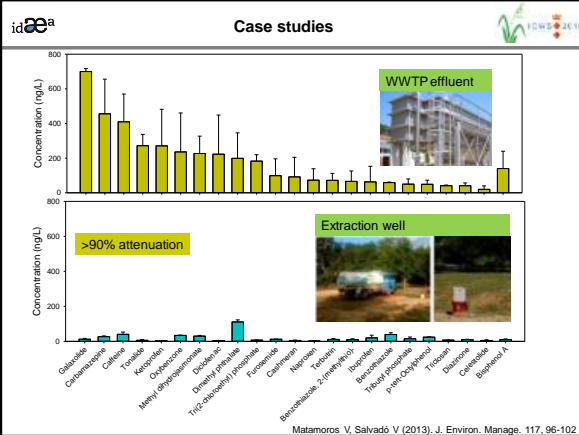
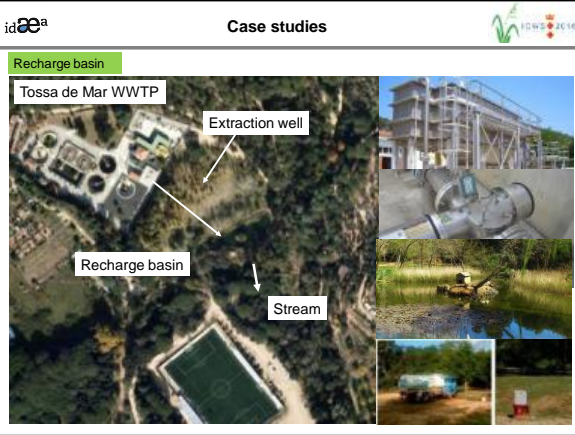
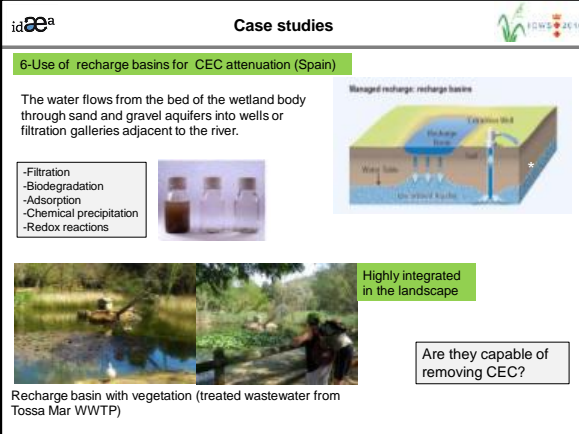
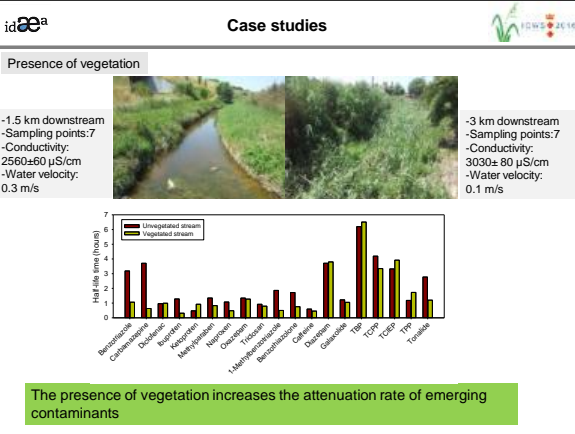
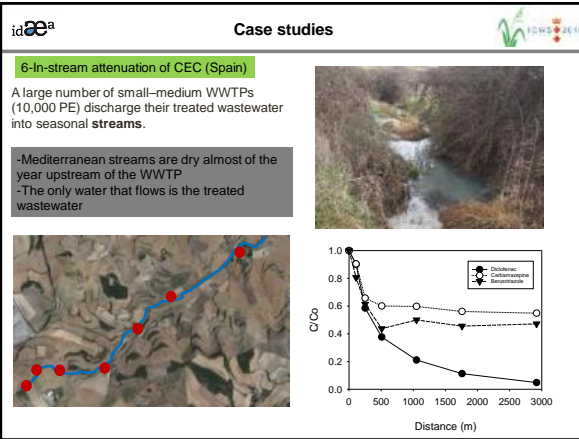
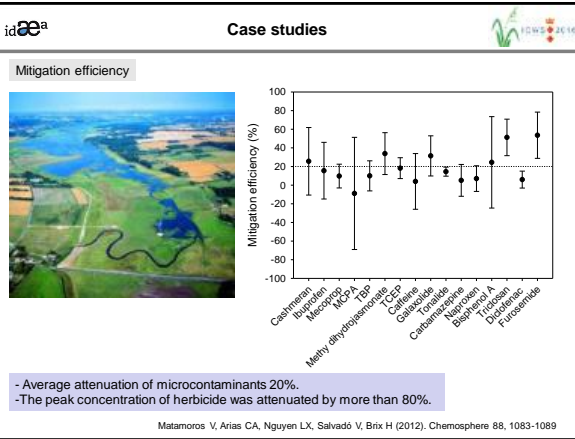


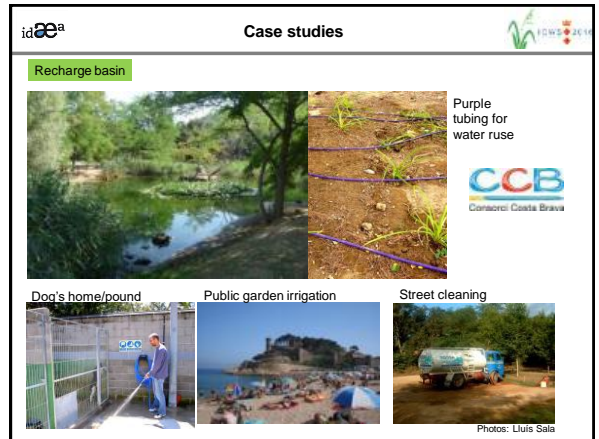
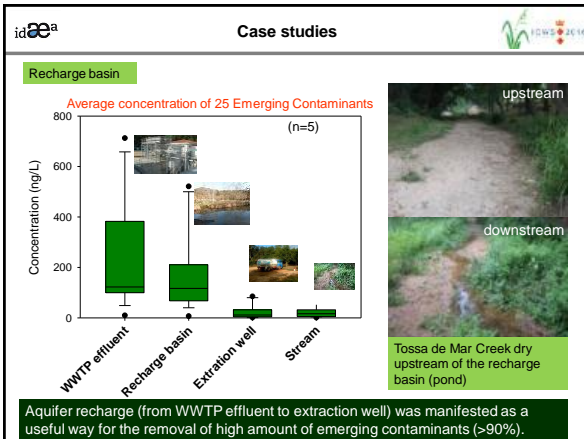
- ### Factors affecting the attenuation of CEC in CWs
- Different factors promote different attenuation processes
1. CW configuration (HFCW, VFCW vs. SFCW)
 2. Water depth (HFCW)
 3. Clogging (HFCW and VFCW)
 4. Surface area (HFCW and SFCW)
 5. Plant effect (VFCW)
 6. Seasonality (SFCW)
 7. Sorption material (HFCW)











Concluding remarks

- The attenuation of CEC in CWs depends on different factors (CW configuration, clogging, surface area, presence of plants, seasonality, sorption material...).
- The use of Hybrid CWs improves attenuation of CEC
- CWs used as tertiary treatment technology are able to remove CEC more efficiently than conventional tertiary systems
- Reed bed sludge systems, restored wetlands, recharge basins and buffer strips are useful for attenuating the discharge of CEC into the aquatic environment.
- The presence of vegetation enhances the attenuation of CEC.

Future trends

- Include other CEC and toxicological studies of both influent and effluent waters. For example only some of the pollutants included in the EU watch list have been studied until now.
- Assessment of TPs, some of them can be more toxic than the parental ones.
- Understand removal mechanisms, interactions soil-plant (rhizosphere). Explore the capacity of plant exudates and uptake for removing pollutants.

