

# ARMISTIQ

## Action A Traitements tertiaires intensifs

Réunion de projet

Sophie BESNAULT



# Choix des STEPs

- **ASE1-PA** : Filtration sur sable + ozonation + Charbon actif (pilote)  
⇒ *Bernières sur Mer (14), Novembre 2010 à juin 2011*

- **ASE2-PA** : BRM suivi d'un pilote d'oxydation avancée (O3/H2O2/UV)  
⇒ *Ollainville (91), Novembre-Décembre 2011*

- **ASE3-PA** : Pilote d'oxydation avancée en aval d'un FAS  
⇒ *Bernières sur Mer (14), Septembre-Octobre 2011*

# Avancement des analyses

- Résultats quasiment complets (merci !)
- Manquent seulement :
  - CIRSEE : AMQ 41 (ASE1-PA4 Bernières, seulement Echibioteb)
  - LPTC : AMQ-115 et AMQ-124 (ASE2-PA2 et 4), seulement 4 NP2EO et 4NP respectivement
  - Tous : AMQ-125 (boue BRM ASE2-PA4)

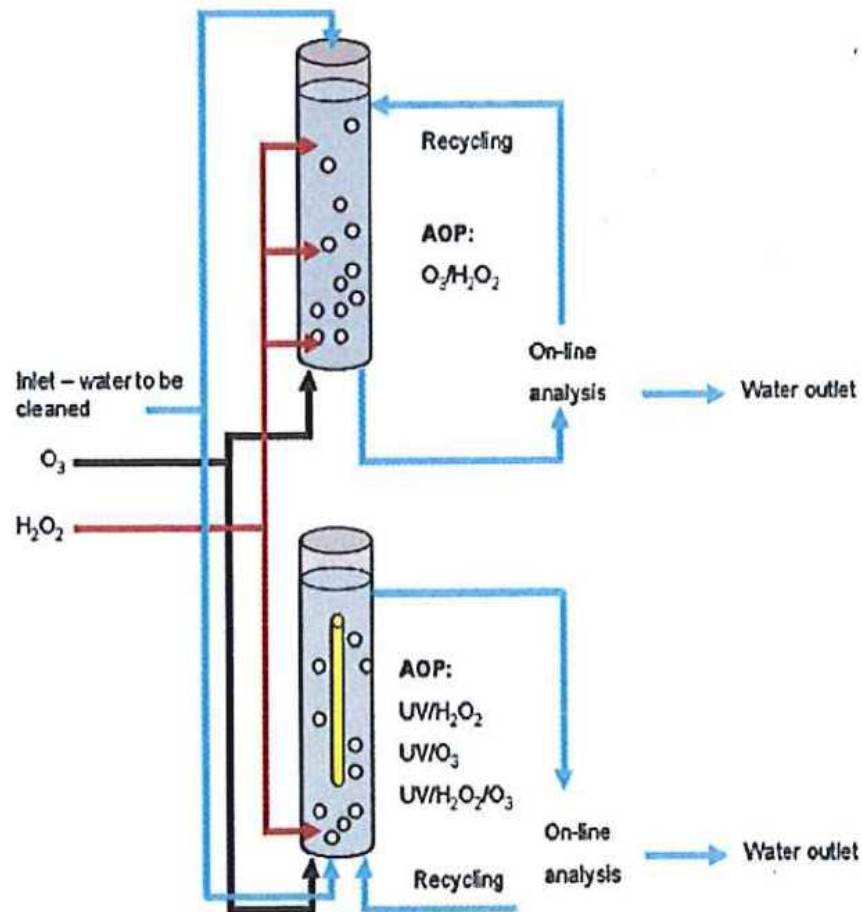
# Wastewater treatment plant selection

Biological treatment full scale + pilot tertiary treatment

Code	Size (PE)	Upstream treatment (full scale)	Tertiary treatment (pilot)
A	60 000	Membrane bioreactor	Advanced oxydation processes (O3, UV, H2O2)
B	40 000	Low load activated sludge + sand filter	Advanced oxydation processes (O3, UV, H2O2)
C	40 000	Low load activated sludge + sand filter + ozone reactor	Granular activated carbon (Filtrisorb 400)

# Advanced oxidation processes (AOP) pilot

Two parallel treatment lines :  $O_3/H_2O_2/UV$



Elements integrated in a conventional ship container

# Granular activated carbon pilot

- ▶ Material : Filtrasorb-400
- ▶ Filtration speed : 5 m/h
- ▶ Water flow : 60 L/h controlled with a floating tap
- ▶ Retro-cleaning with air & water : 1/week
- ▶ Pilot after sand filter + ozone full scale & directly after sand filter
- ▶ Pilot operating 24/24 h during 6 months
- ▶ Sampling : Day 2, Week 3, Month 3 & Month 6



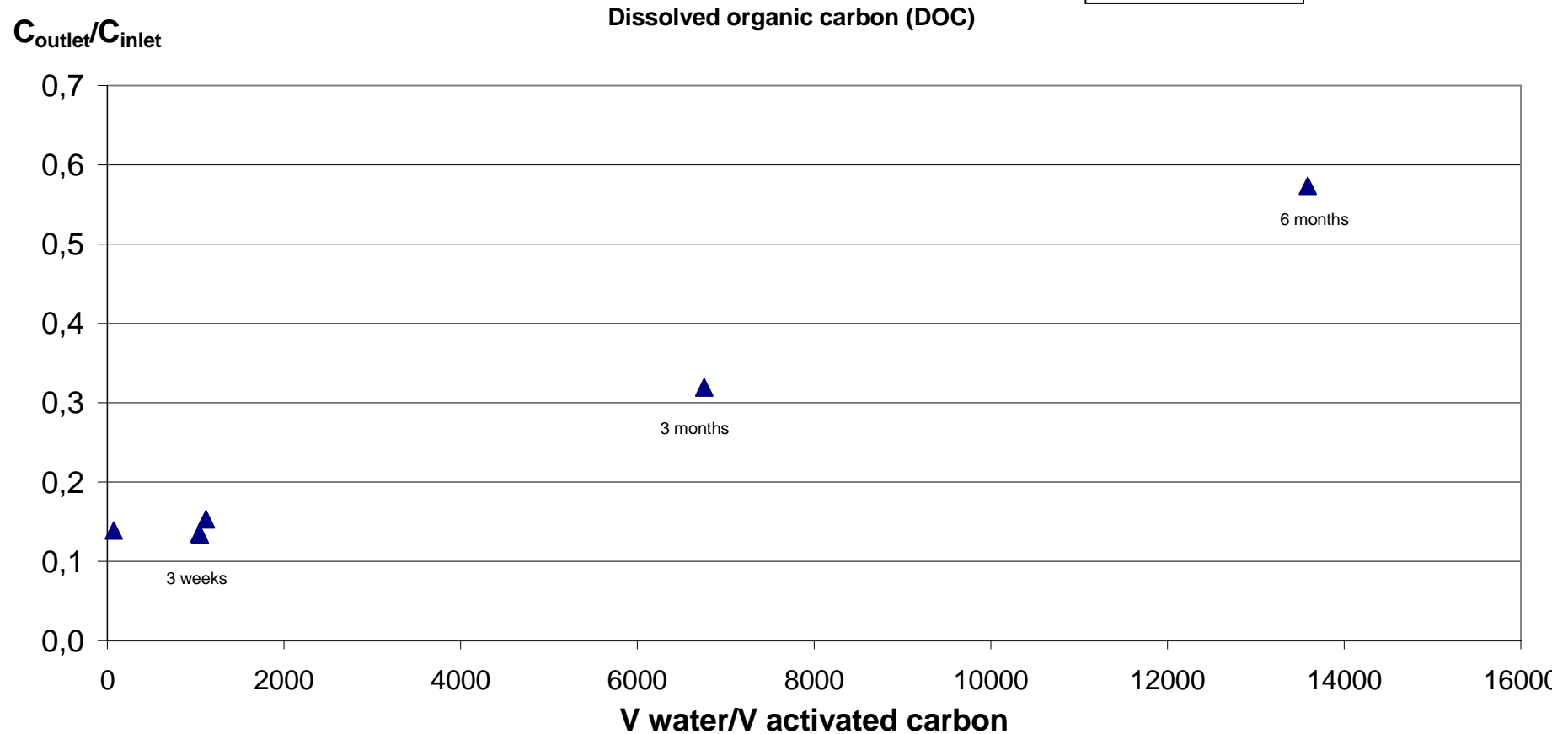
# Operating conditions AOP pilot

Condition	Description	Ozone dose (gO <sub>3</sub> /m <sup>3</sup> )	H <sub>2</sub> O <sub>2</sub> dose (mg/L)	UV dose (mJ/cm <sup>2</sup> )	Contact time (min)
I	Ozone alone	5	0	0	2,71
II.1	Ozone peroxide 0,5/1	5	1,8	0	2,71
II.2	Ozone peroxide 1/1	5	3,5	0	2,71
II.3	Ozone peroxide 1,5/1	5	5,3	0	2,71
III.1	Ozone UV 1	5	0	398	5
III.2	Ozone UV 2	5	0	795	10
IV.1	UV peroxide 1	0	5	795	10
IV.2	UV peroxide 2	0	10	795	10

Ozone, peroxide and UV doses selected according to bibliographical review

# Dissolved organic carbon removal with activated carbon pilot

WWTP C



DOC inlet : 6,8 to 8,5 mg/L C

Activated carbon not saturated after 6 months : still removing DOC



# Micropollutants removal with activated carbon pilot

## Drugs

NC : not calculable

Family of substances	Substances	Day 2	Week 3	Month 3	Month 6
Betablockers	Atenolol	99%	100%	100%	100%
	Metoprolol	98%	99%	99%	99%
	Propranolol	NC	88%	97%	99%
	Sotalol	NC	96%	99%	100%
Other drugs	Carbamazepine	NC	90%	53%	98%
	Diazepam	NC	NC	53%	85%
	Ibuprofene	93%	98%	99%	NC
	Diclofenac	88%	99%	97%	96%
Antibiotics	Sulfamethoxazole	76%	NC	NC	NC
	Erythromycin	NC	79%	73%	NC

- ▶ C°inlet : 2-210 ng/L antibiotics & other drugs, 1-7 00 ng/L betablockers

R > 70%
30% < R < 70%
R < 30 %

- ▶ Ozone pre-treatment (3 gO<sub>3</sub>/m<sup>3</sup>) not sufficient for drugs removal
- ▶ Removal efficiency always >70% on antibiotics and betablockers
- ▶ Drugs analysed are still removed after pilot operating 6 months 24/24 h

# Micropollutants removal with activated carbon pilot

## Pesticides

NC : not calculable

Priority substances of the WFD {	Substances	Day 2	Week 3	Month 3	Month 6
	Atrazine	85%	93%	91%	93%
	Diuron	NC	92%	93%	98%
	Simazine	NC	NC	87%	97%
	AMPA	100%	60%	-42%	-29%
	Glyphosate	NC	NC	33%	7%

R > 70%
30% < R < 70%
R < 30 %

- ▶ C°inlet : 5-160 ng/L urea pesticides & triazines, 1 00-1900 ng/L AMPA (Aminomethylphosphonic acid) & glyphosate
- ▶ Elimination yield >70% on urea pesticides & triazines
- ▶ Urea pesticides & triazines are still removed after 6 months 24/24 functioning
- ▶ Glyphosate & AMPA are not removed on a long term

# Micropollutants removal with activated carbon pilot

## PAH & alkylphenols

NC : not calculable

Family of substances	Substances	Day 2	Week 3	Month 3	Month 6
PAH	Napthalene	15%	NC	NC	NC
	Dibenzothiophene	48%	46%	21%	NC
	Phenanthrene	38%	21%	-8%	31%
	Anthracene	NC	NC	36%	NC
	Acenaphtene	70%	12%	-2%	NC
	Fluorene	52%	NC	-3%	30%
	Fluoranthene	50%	21%	23%	NC
	Pyrene	75%	35%	0%	79%
	Chrysene + Triphenylene	NC	NC	48%	NC
	Benzo(b+j+k)Fluoranthene	NC	85%	NC	NC
Alkylphenols	4-Nonylphenol monoethoxylate	15%	17%	92%	NC
	4-Nonylphenol diethoxylate	NC	NC	98%	NC
	4 Nonylphenol	21%	39%	52%	40%
	4-ter octylphenol	41%	69%	20%	6%
	4-Nonylphenoxyacetic-acid	100%	100%	100%	97%
	4 ter butylphenol	-12%	NC	60%	NC

- ▶ C°inlet : 0.1-3.3 ng/L PAH, 2-1204 ng/L alkylphenols
- ▶ PAH, although in reduced C° at the inlet, are partly removed
- ▶ 4-nonylphenoxyacetic acid was well removed by GAC during all the tests
- ▶ Removals varied for the other alkylphenols

R > 70%
30% < R < 70%
R < 30 %

# Micropollutants removal with activated carbon pilot

## Metals

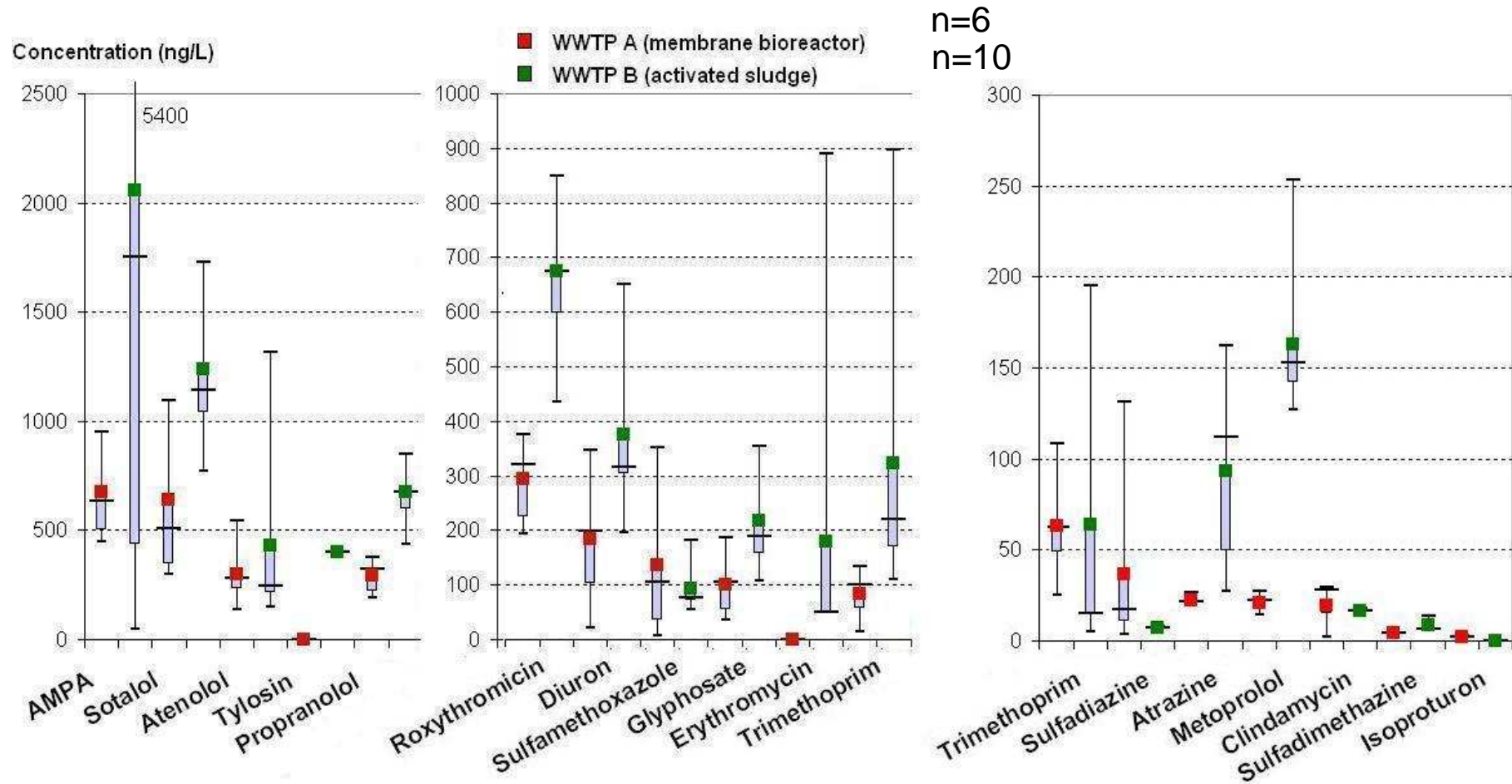
NC : not calculable

Substances	Day 2	Week 3	Month 3	Month 6
Bore	59%	9%	17%	22%
Titane	NC	24%	9%	-2%
Vanadium	NC	NC	NC	-37%
Chrome	99%	92%	9%	0%
Cobalt	NC	NC	NC	33%
Nickel	-165%	34%	6%	0%
Cuivre	-25%	17%	-91%	33%
Zinc	94%	42%	4%	3%
Arsenic	-256%	-3%	9%	10%
Molybdène	-72%	34%	-20%	-15%
Cadmium	NC	-200%	NC	NC
Etain	NC	NC	NC	NC
Barium	-36%	1%	-10%	-16%
Plomb	54%	89%	75%	32%
Uranium	-16%	54%	5%	-555%

R > 70%
30% < R < 70%
R < 30 %

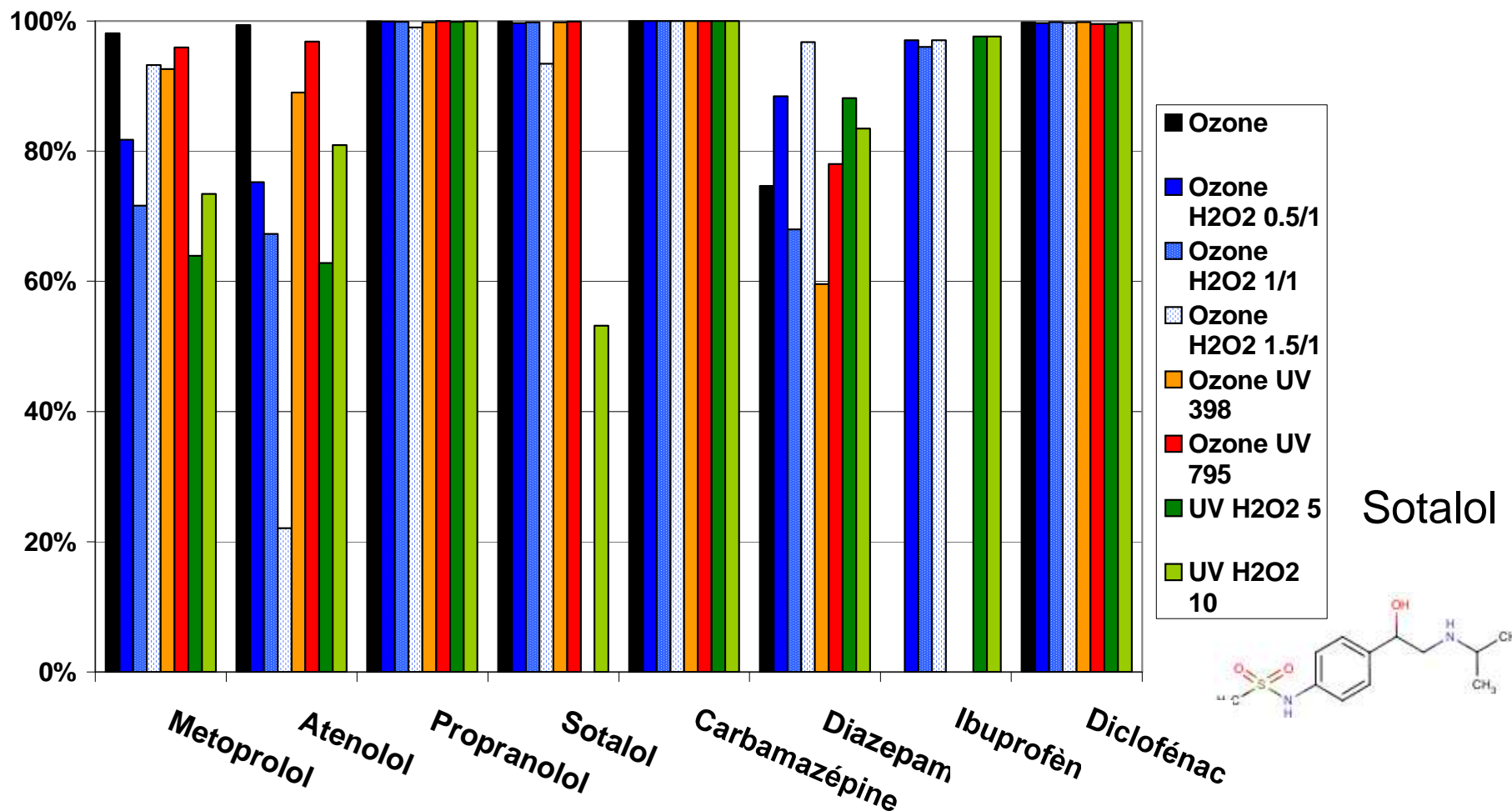
- ▶ C°inlet : 0.1-207 µg/L
- ▶ Some metals partly removed, in particular at the beginning of the tests (B, Cr, Zn, Pb)

# Quality of the inlet water



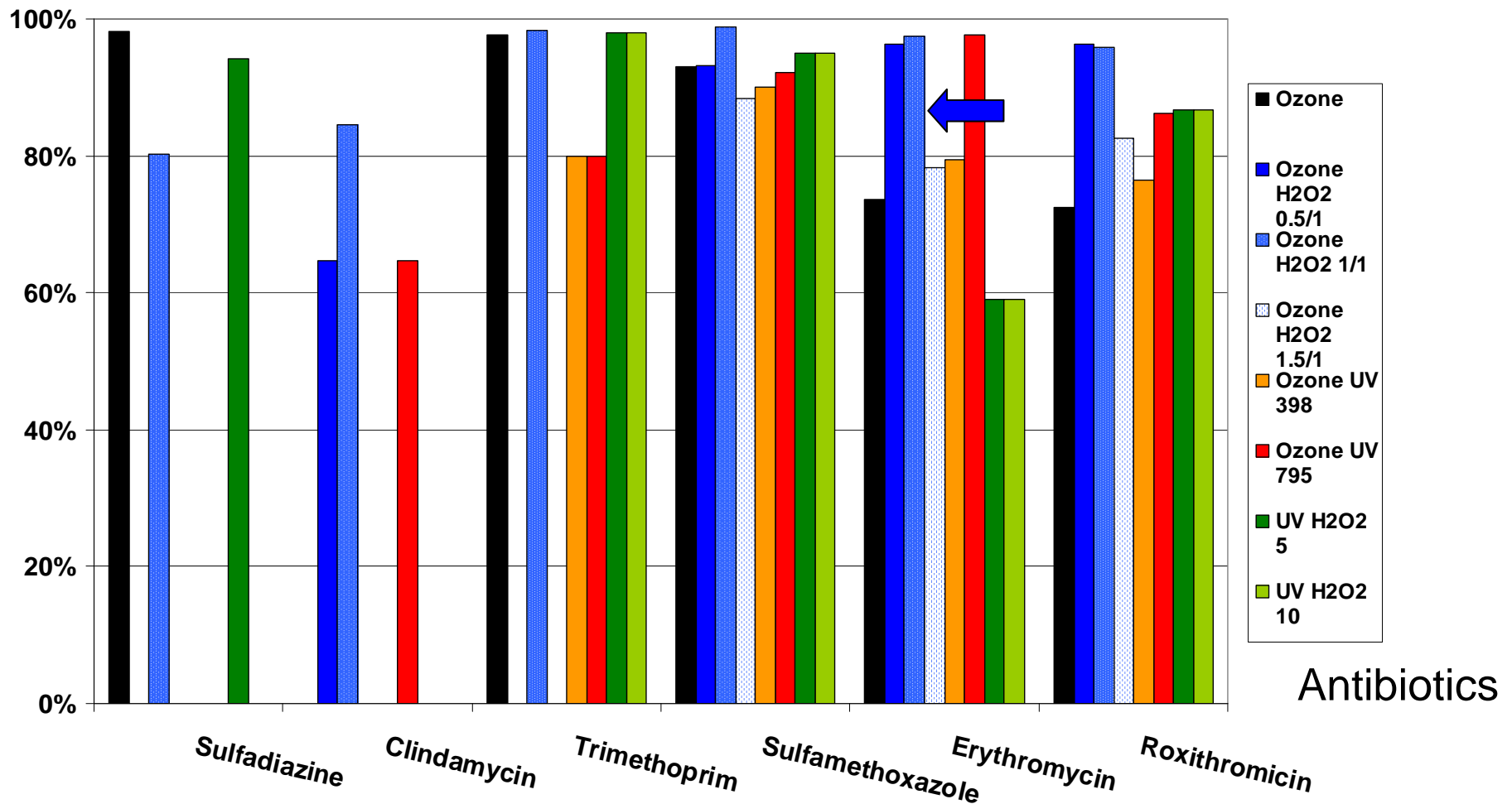
Higher micropollutants concentrations after CAS + sand filter,  
wider ranges

# Micropollutants removal with AOP pilot



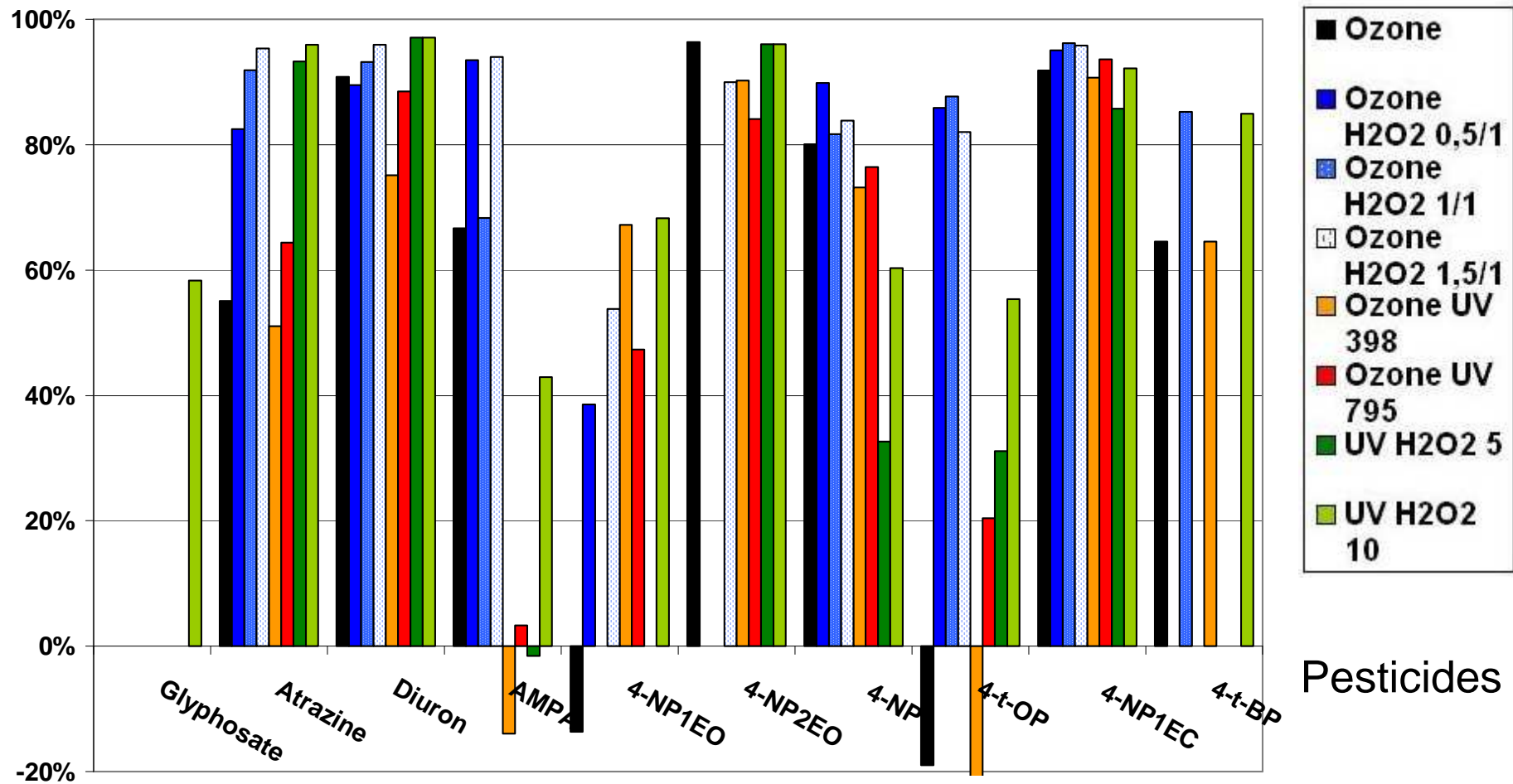
Betablockers well eliminated (> 98%) with ozone alone : promotion of the radical oxidation pathway by using AOP reduced the removal of betablockers

# Micropollutants removal with AOP pilot



Removal increases with H<sub>2</sub>O<sub>2</sub> addition to ozone, optimal H<sub>2</sub>O<sub>2</sub> dose ←

# Micropollutants removal with AOP pilot



Pesticides

Pesticides removal optimised with H<sub>2</sub>O<sub>2</sub> addition to ozone

Higher H<sub>2</sub>O<sub>2</sub> dose, better removal -> still performing in H<sub>2</sub>O<sub>2</sub> excess



# Micropollutants removal with AOP pilot

Metals not affected by AOP (B, Ti, V, Ba, As, Co) : removal between –5 to 6%

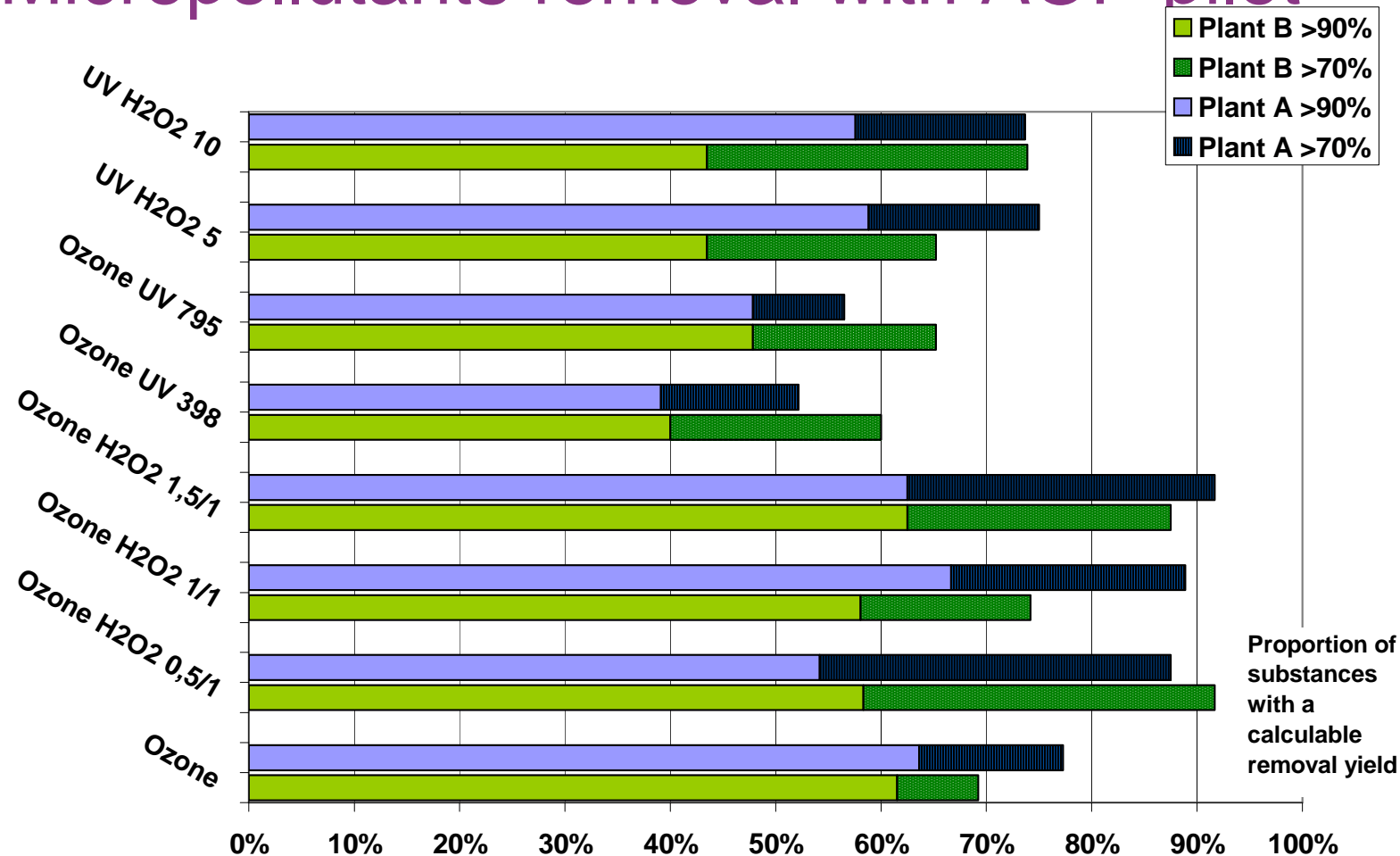
Metals in higher concentrations at the outlet (Cr, Mo, Sn (H<sub>2</sub>O<sub>2</sub>), U)

Metals partly removed (Cu, Zn) <30%

Metals removed (Pb, Cd) >50%

Variable behaviour (Ni)

# Micropollutants removal with AOP pilot



- ▶ Addition of  $\text{H}_2\text{O}_2$  increases number of substances well removed (>70%) by 10 to 20%
- ▶ Not necessary to have an excess of  $\text{H}_2\text{O}_2$

# Conclusions

- ▶ Granular activated carbon and advanced oxidation processes ( $O_3/H_2O_2/UV$ ) efficient on most of the « refractory » micropollutants studied
- ▶ Activated carbon lifespan evaluated : still efficient after 6 months functioning 24/24 h (adsorption & biological activity)
- ▶ Ozone alone enough for betablockers removal
- ▶ Advanced oxidation processes optimise removal of most of the pesticides and antibiotics
- ▶ Some pesticides (glyphosate & AMPA) incompletely removed
- ▶ Environmental impact, cost, toxicity & by-products are currently being studied
- ▶ For smaller plants, extensive treatments, currently being evaluated, could be an interesting option