Removal of Endocrine Disrupting Compounds from Urban Waste Water using a novel process combining PAC (Powder Activated Carbon) and ballasted clarification

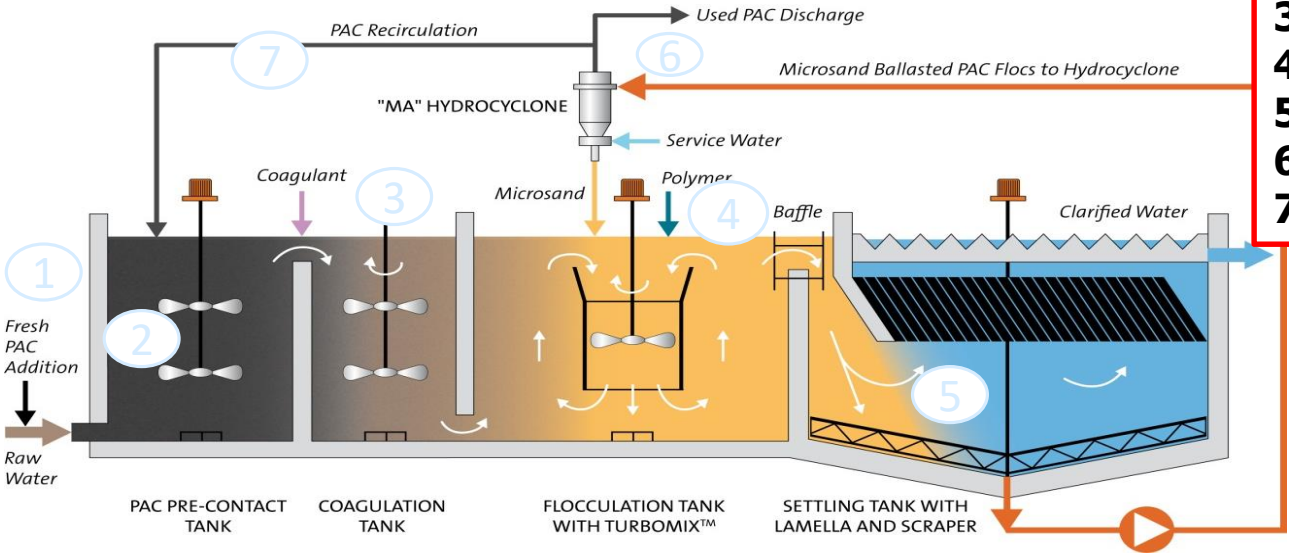
Agenda

- Actiflo® Carb
  - Process descriptions
  - Applications
  - References
- Micropollutants within urban waste water
  - A wide range of pollutants and concentration
  - Typical performance data of biological waste water plants
- Micropollutants removal with Actiflo® Carb
  - Process descriptions
  - First References
  - Perspectives using Frogbox®

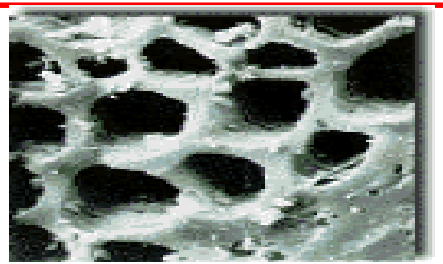
Actiflo® Carb
Proces description, usages and references

Process descriptive

- ***Ballasted clarification:***
  - Short floculation time
  - High clarification rate : 40 to 60 m/h (waste water)
- ***Benefits of recirculated PAC***
  - Constant availability of PAC for adsorption
  - Continuous removal



1 = New PAC
2 = PAC reactor
3 = Coagulation
4 = Flocculation
5 = Clarifier
6 = Cycloning PAC removal
7 = PAC recirculation



PAC under microscope

Applications

- Any pollutants with an affinity with PAC

Waste water

- Endocrine Disruptors (hormones...)
- Drugs residues (antibiotic, anti-inflammatory, anti-epilectic...)
- Biocides

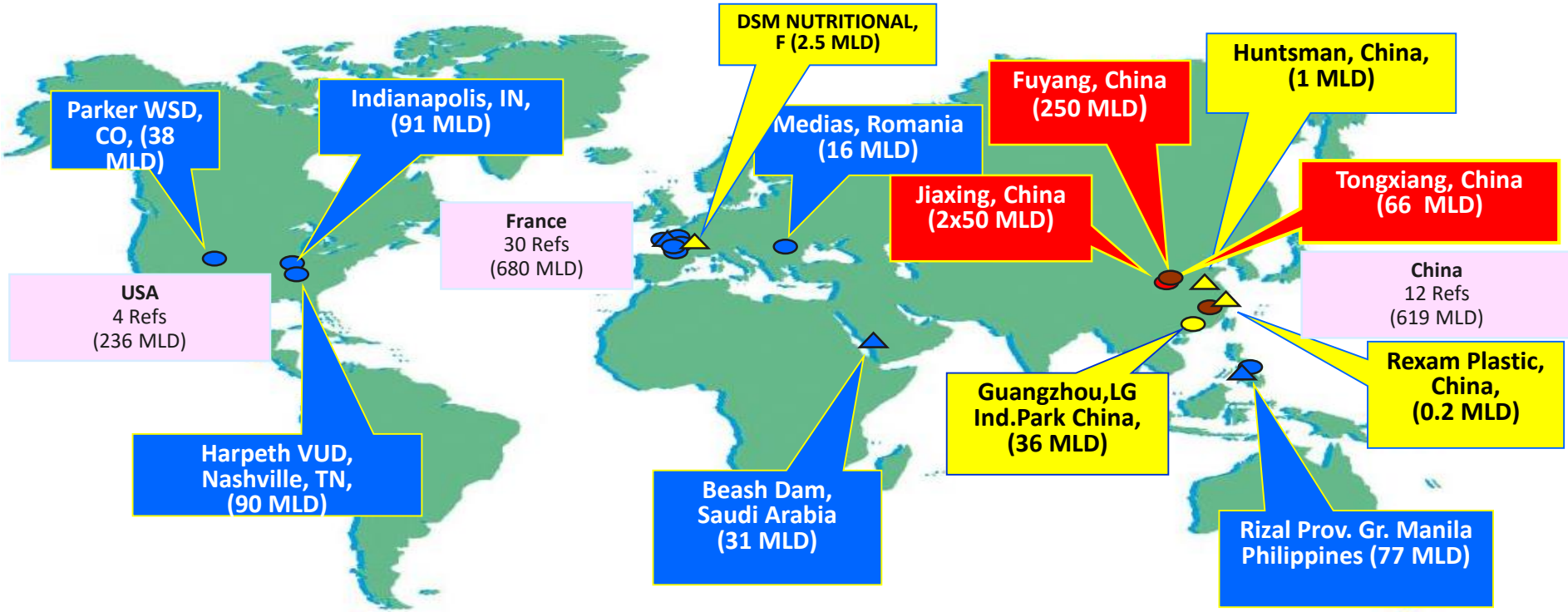
Drinking water

- Natural Organic Matter
- Disinfection By Products
- Pesticides (atrazine, metaldehyde, DEA...)

Actiflo®Carb

Over 12 years of experiences

A world wide extension



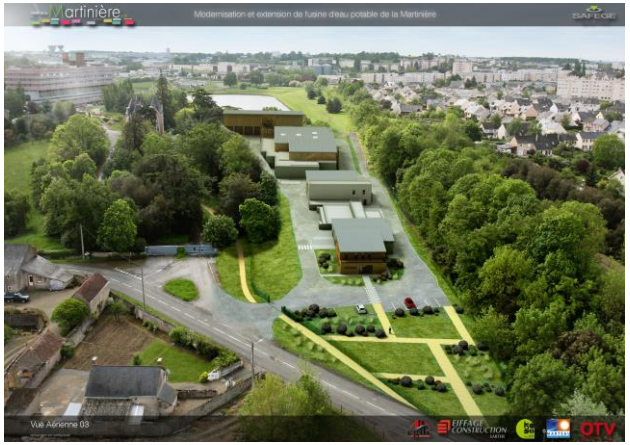
Design & Build

Solutions

Drinking Water (40 Ref / (total 1,138 MLD)
Municipal Wastewater (5 Ref. / (total 446 MLD)
Industrial Water & WW (6 Ref./ (total 76 MLD)

Actiflo® Carb – Drinking water plants in operation

SITE / FACTORY / PLANT NAME	COUNTRY	YEAR OF COMPLETION	DESIGN FLOW
AIRE-SUR-LA-LYS	France	2010	4,167 m3/h
BOUIL DE CHAMBON	France	2009	500 m3/h
CHÉZY-SUR-MARNE	France	2013	450 m3/h
CHOLET	France	2015	1,200 m3/h
FEURS	France	2013	350 m3/h
INDIANAPOLIS (TW MOSES), IN	USA	2011	3,785 m3/h
KERMORVAN	France	2012	TBC
LA CHESNAIE COUTURES	France	2014	500 m3/h
LANDIVISIAU	France	2009	500 m3/h
LANMEUR	France	2014	200 m3/h
LE CREUSOT	France	2015	450 m3/h
LUCIEN GRAND	France	2008	3,000 m3/h
MERVENT, SITE DE LA BALINGUE	France	2014	2,200 m3/h
MIRE MORANNES	France	2009	200 m3/h
MONTLUÇON EP	France	2016	1,200 m3/h
MONTRY (SIPAEP MARNE ET MORIN)	France	2011	530 m3/h
NANTES LA ROCHE EP	France	2020	8,000 m3/h
PARKER W&SD, CO	USA	2011	1,577 m3/h
PERROS GUIREC EP	France	2009	400 m3/h
PONT SCORFF	France	2015	300 m3/h
RIZAL	Philippines	2017	2,083 m3/h
ROMORANTIN – LANTHENAY	France	2016	460 m3/h
SABLE USINE DE LA MARTINIERE	France	2015	1200 m3/h
SAINT MEZARD EP	France	2011	250 m3/h
TREGAT 2	France	2016	400 m3/h
USINES NORD CMCU	France	2015	450 m3/h
VIENNE COMBADE	France	2013	150 m3/h
VITRE - USINE DE LA GRANGE	France	2015	580 m3/h
GRANVILLE	France	2018	350 m3/h
AVRANCHE	France	2018	350 m3/h

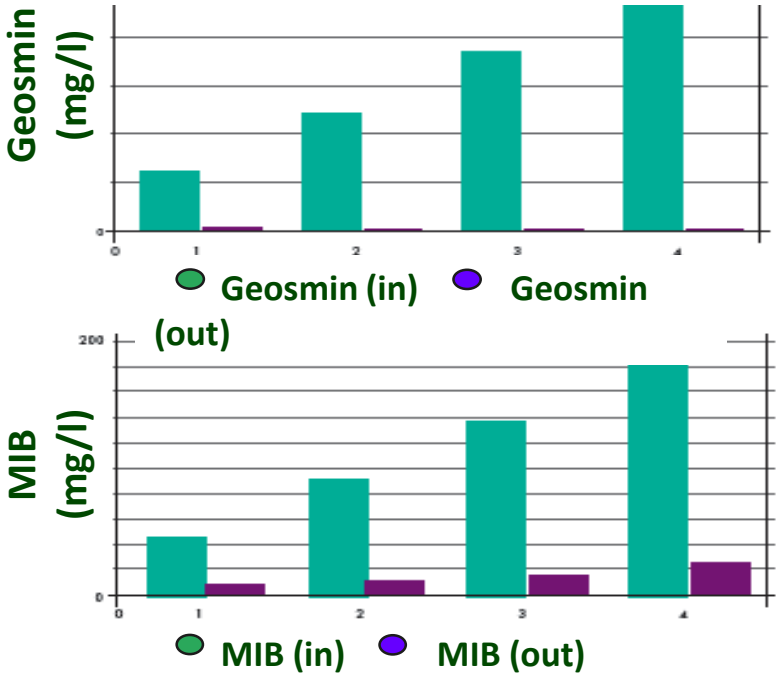


In green: Actiflo® Carb plants operating with green polymers

Actiflo® Carb – Moses Indianapolis

- Surface water with colour and Algae
- TOC 3 to 6 mg/l & pesticides (50 to 75% removal)

Geosmin & MIB Tests Results

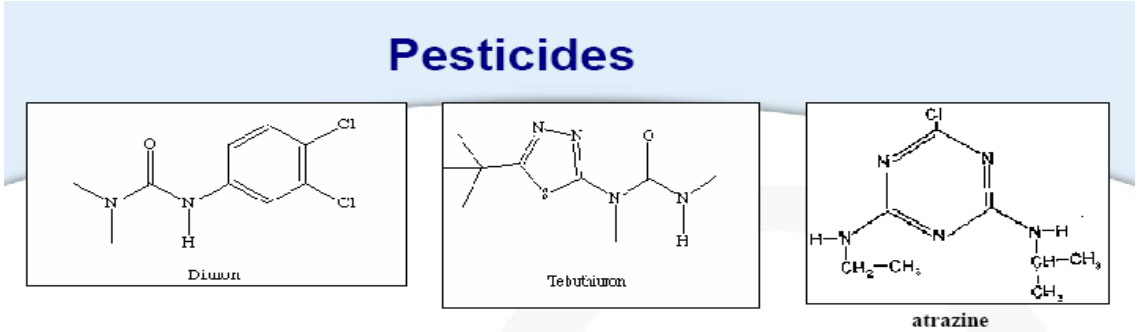


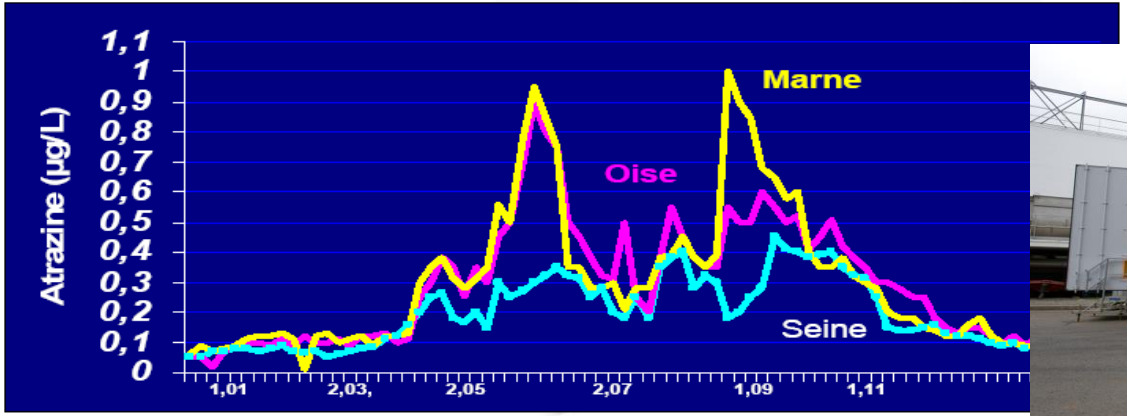
	IN (ppb)	Out (ppb)	Removal (%)
Atrazine	0.36	0.05	86
DEA	0.26	< LQ	> 93
DEDIA	0.37	0.03	92
Isoproturone	0.40	< LQ	> 98
Acetochlorine	0.77	< LQ	> 94
Bentazone	0.37	0.04	89
Glyphosate	0.23	< LQ	> 68
Acetochlorine	0.22	< LQ	> 68

Actiflo® Carb
for pesticides removal

Pesticide Removal : testing under “live” conditions

- ***Dosing of pesticides in the raw water (reservoir) to simulate peaks of concentrations***





Pesticides removal

- ***Target concentration in the raw water: 0.3 µg/L***

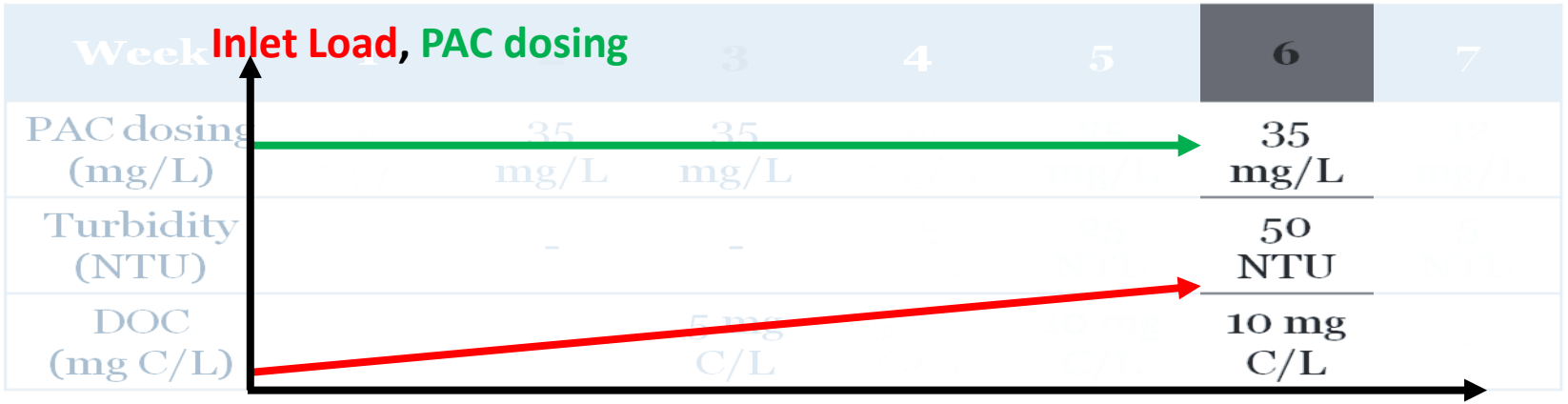
Compounds	Inlet T +1h	Outlet T + 1h	% removal	Outlet T + 24h	% removal
	[µg/L]	[µg/L]	[%]	[µg/L]	[%]
Atrazine	0.39	n.d.	>95	n.d.	>95
DEA	0.34	n.d.	>94	n.d.	>94
DEDIA	0.36	n.d.	>94	n.d.	>94
Isoproturon	0.66	n.d.	>97	n.d.	>97
Acetochlore	0.81	n.d.	>97	0.24	70.4
Bentazone	0.27	n.d.	>92	0.03	89.0
Glyphosate	0.35	n.d.	>77	n.d.	>77
AMPA	0.46	n.d.	>82	n.d.	>82

n.d.: below detection level

Eff. Removal > 77 to 97%

Spiking program

- Main conditions target for each week



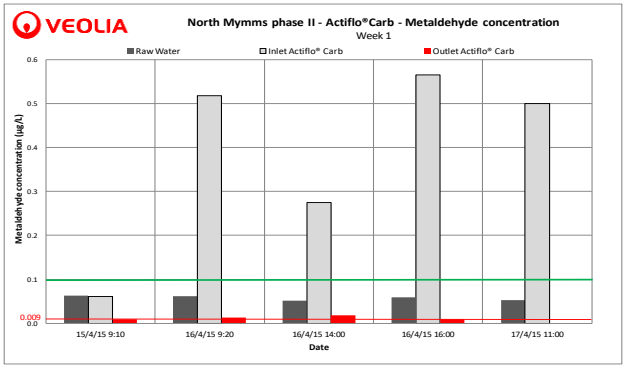
- Pesticide spiking changed each day (up to 1.5 µg/L)
  - Metaldehyde, carbetamide, metazachlor and propyzamide

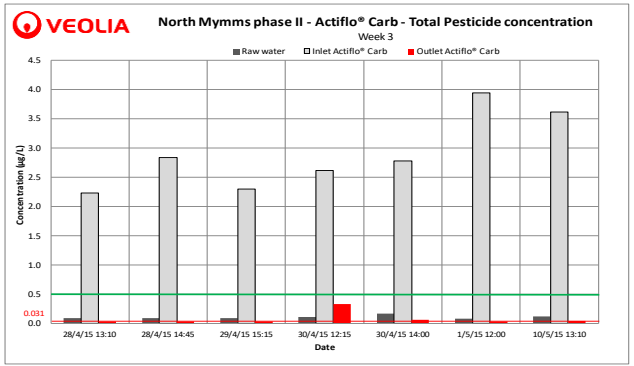
<u>Target:</u> Test upper limits of Actiflo®Carb process

Actiflo® carb (most recent tests)

- Trials in 2015 for Metaldehydes removal: North Mymms WTW with Affinity Water **– DTP support of VWT (UK) for** Metaldehyde $(CH_3CHO)_4$

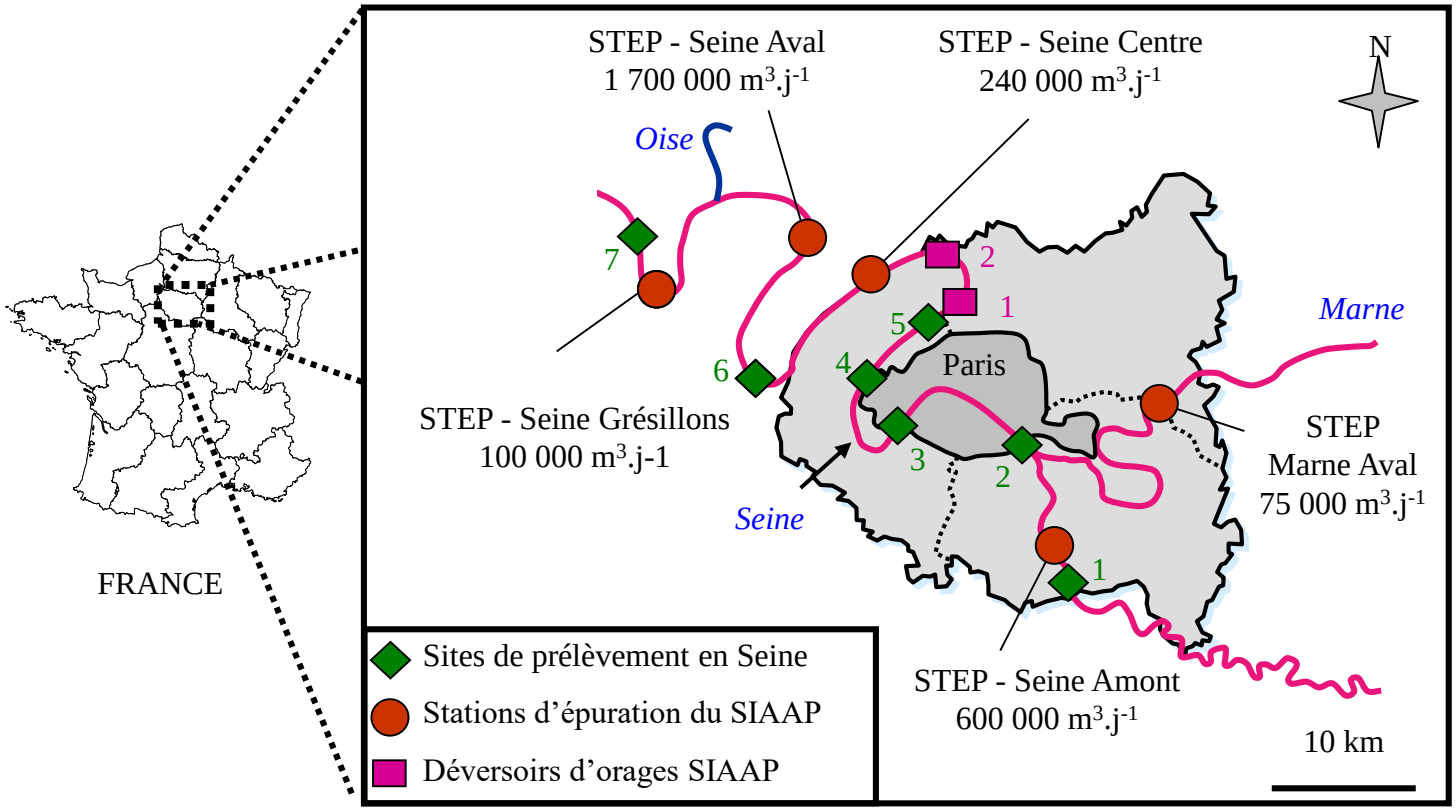
Particularly challenging compound for traditional technologies eg GAC
LogKow < 0



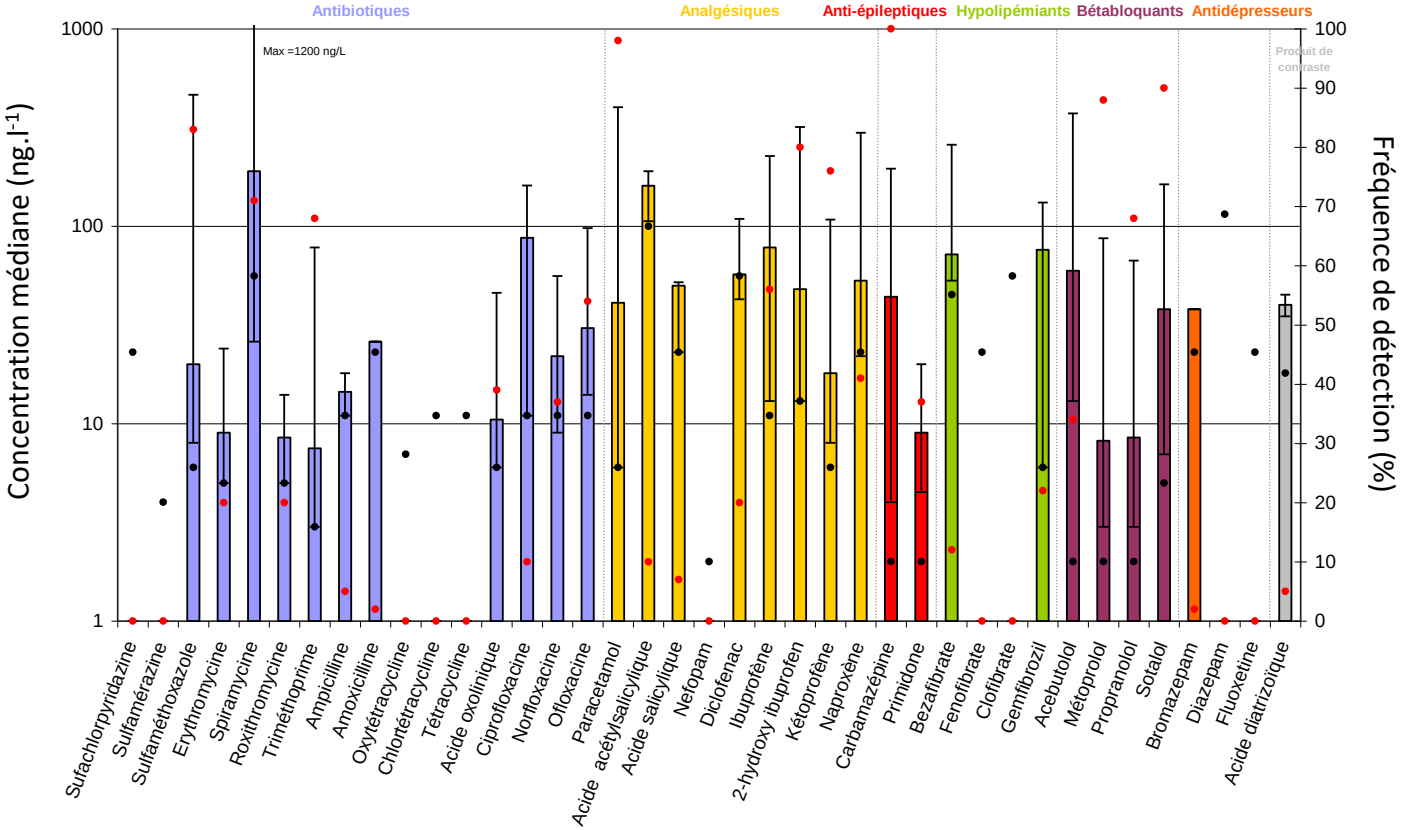


Micropollutants in urban waste water

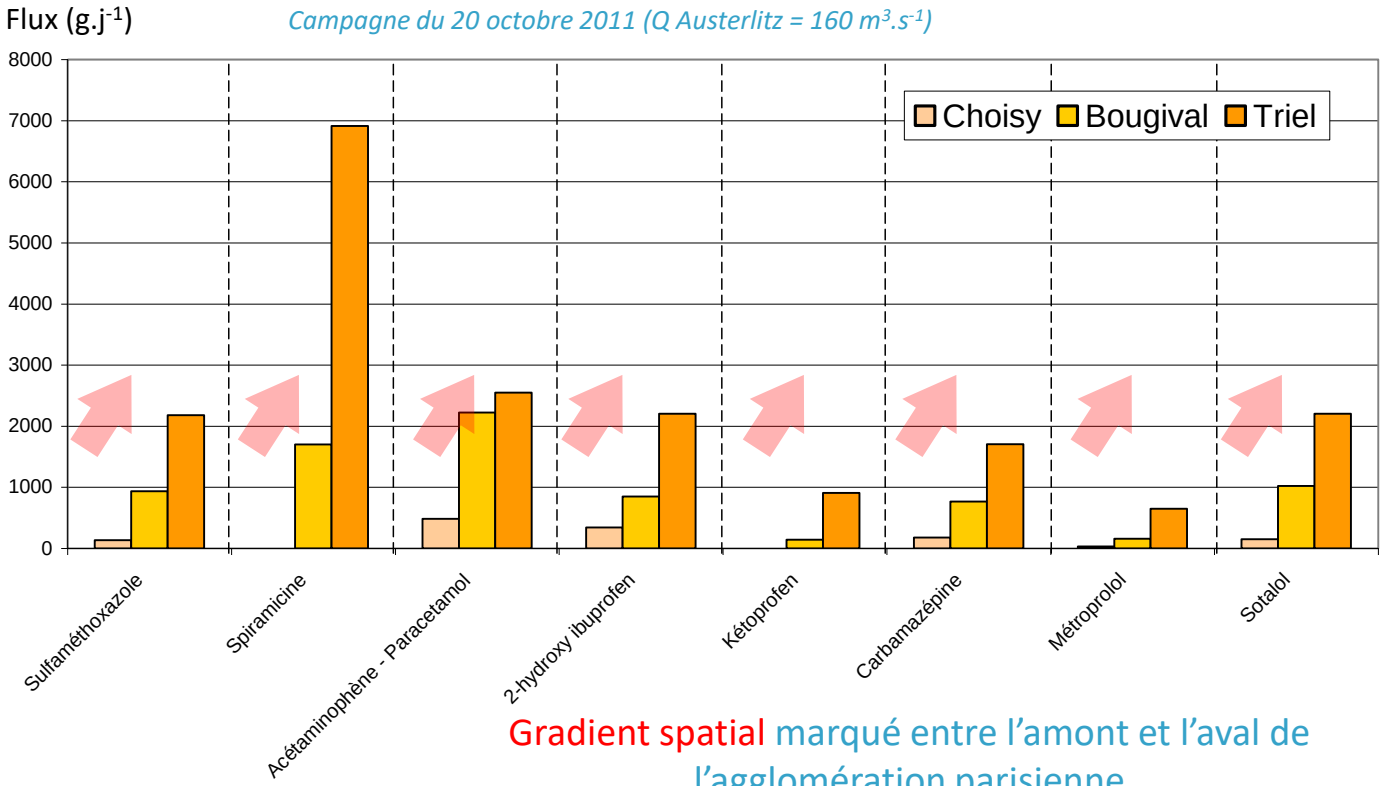
Pharma residuals during 2010 - 2011



Pharma residuals during 2010 - 2011

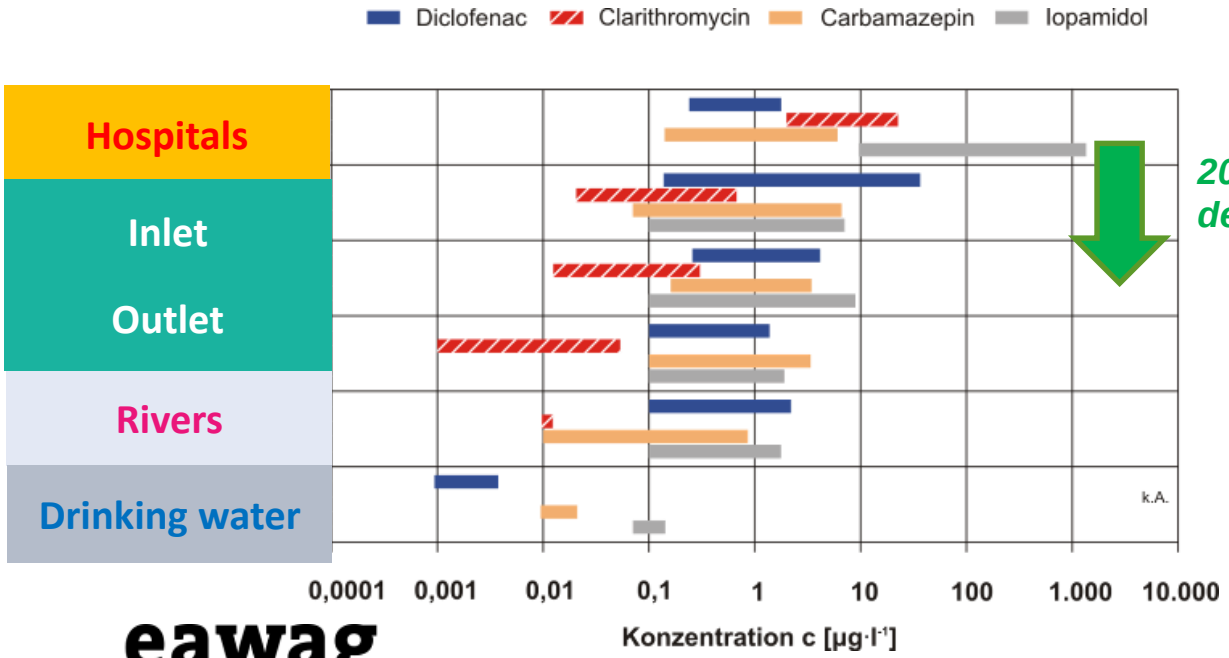


Overview of some molecules across Paris



Gradient spatial marqué entre l'amont et l'aval de l'agglomération parisienne

The context: typical WwTW performances



20 à 40% removal depending on molecules

eawag aquatic research

Verschiedene Quellen (1996-2010) aus Beier, S. et al. 2010

12 months operational study with SIAAP*

- Organisation & scientific plan
  - To operate on a real plant
  - 138 micropolluants analysed

Daily monitoring

TSS, DOC, BOD, DOC, TKN, NO_3, NO_2, Pt, P-PO_4, Colour , Turbidity, Abs. UV 254 nm

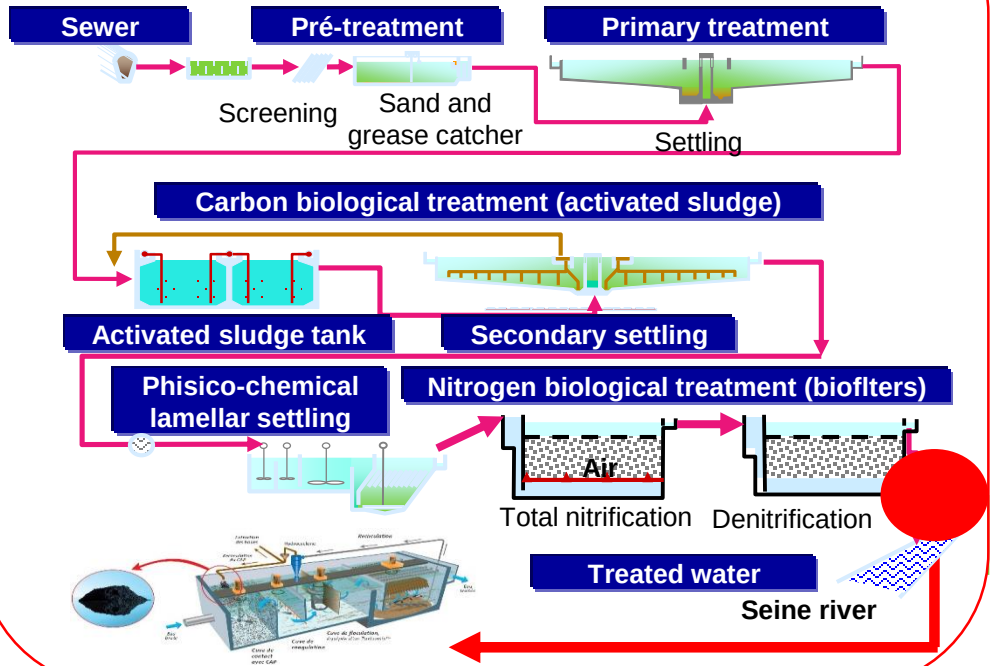
Pharmaceutical and Hormones

Antibiotiques (humains et vétérinaires), analgésiques, bétabloquants, hypolipémiants, antidépresseurs, antiépileptiques, diurétiques, antifongiques, hormones

Other micropollutants

HAP, solvants chlorés, Alkylphénols, herbicides/insecticides, acides perfluorés, bisphénol A, Métaux

WwTW Seine Aval (Achères) 6 million Pop. eq. – removal C/N/P



Micropollutants analysed

Always found | Often found | Seldom found

Micropolluants organiques

LISTE DCE		MEDICAMENTS HUMAINS	MEDICAMENTS VETERINAIRES	HORMONES	DIVERS
Naphtalène	Alachlore	Metronidazole	Florfenicol	α oestradiol	PFOA
Acénaphtylène	Atrazine	Trimethoprim	Sulfanilamide	β oestradiol	PFOS
Acenaphtène	Chlorfenvinphos	Sulfamethoxazole	Dicyclanile	Estrone	Bisphénol A
Fluorene	Diuron	Ofloxacine	Sulfadiazine	Estriol	
Phenanthrene	Isoproturon	Ciprofloxacine	Sulfathiazole	Norethindrone	
Anthracene	Pentachlorophénol	Roxithromycine	Marbofloxacine	Androstenedione	
Fluoranthene	Simazine	Paracétamol	Ampicilline	Gestodène	
Pyrène	Trifluraline	Kétoprofene	Norfloxacin	Testosterone	
Benzo[a]anthracene	HCH alpha	Diclofenac	Tétracycline	Levonorgestrel	
Chrysène	HCH béta	Ibuprofène	Oxytetracycline	Progesterone	
Benzo[b]fluoranthène	HCH gamma	Naproxen	Sulfabenzamide		
Benzo[k]fluoranthène	HCH delta	Acide salicylique	Danofloxacine		
Benzo[a]pyrène	Chlopyrifos	Aténolol	Enrofloxacine		
Indeno[1,2,3-cd]pyrène	Aldrine	Propranolol	Orbifloxacine		
Dibenz[a,h]anthracène	Isodrine	Fenofibrate	Difloxacin		
Benzo[ghi]perylène	Endosulfan alpha	Bezafibrate	Sulfadimethoxine		
1,2,4-trichlorobenzène	DDE pp	Fluvoxamine	Chlortetracycline		
Hexachlorobutadiène	Dieldrin	Oxazepam	Penicilline G		
Hexachlorobenzène	Endrin	Lorazepam	Tylosine Tartrate		
BPA	DDD pp	Carbamazepine	Erythromycine		
Nonylphénol	DDT op	Furosemide	Monensin		
4-nonylphénol	Endosulfan béta	Econazole	Narasin		
Octylphénol	DDT pp		Sulfameter		
Para-ter-octylphénol			Sulfadimerazine		

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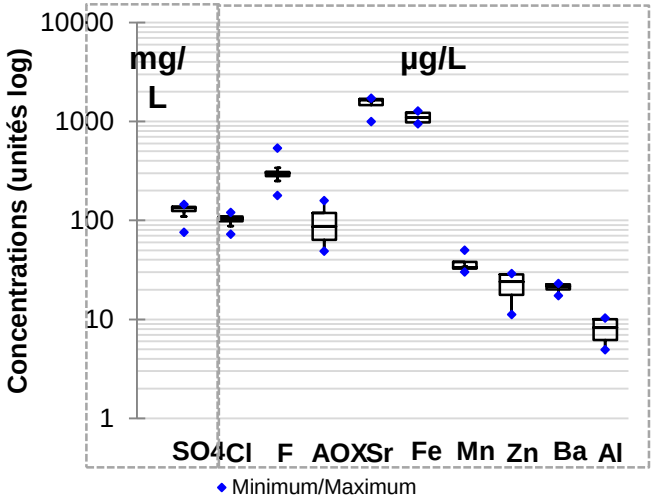
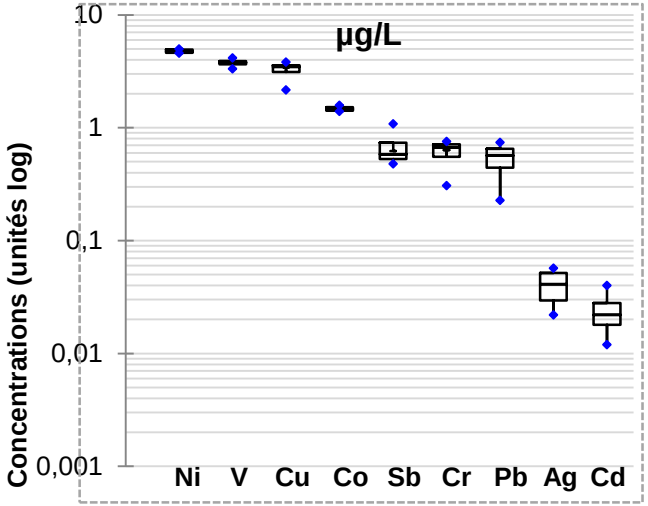
HAP | Herbicides / insecticides | Antibiotiques | Bétabloquants | Antidépresseurs / anxiolytiques | Diurétique | Hormones

Solvants chlorés | Alkylphénols | Analgésiques | Hypolipémians | Antiépyleptique | Antifongique | Perfluorés

Box plot final effluent quality

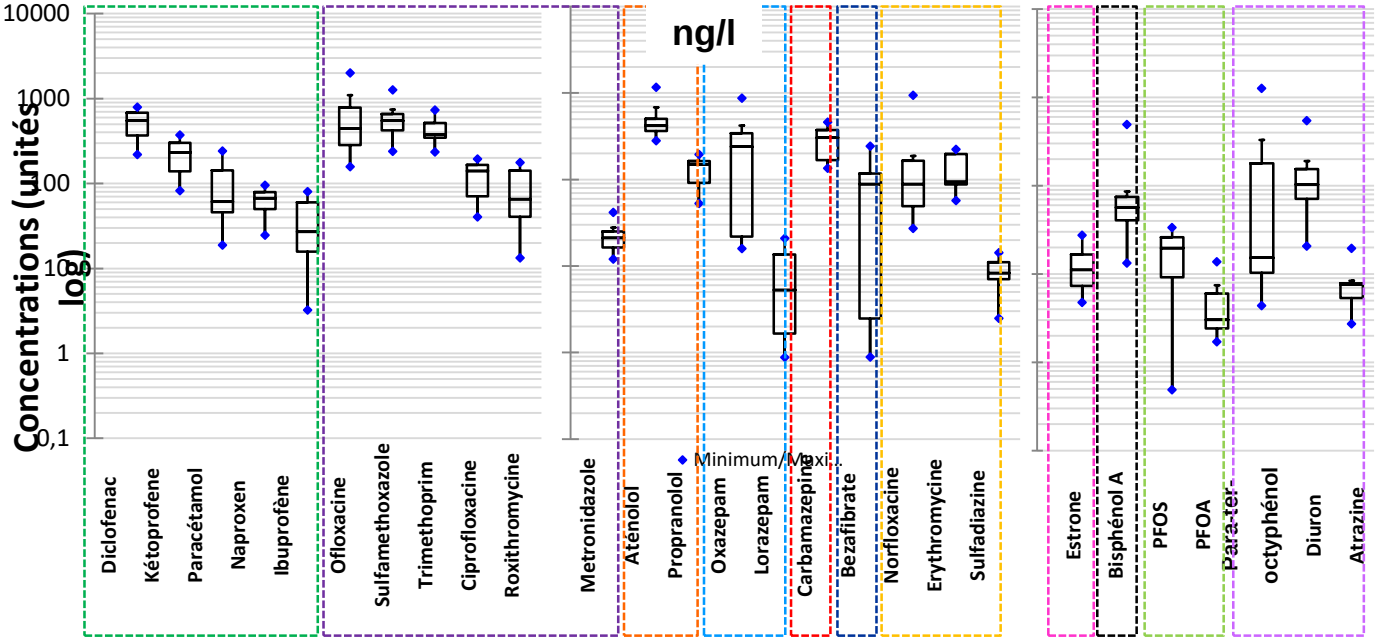


Résultats métaux (4 campagnes – 2 configurations, 11 campagnes en attente de résultats)



Faible variabilité des concentrations et ordres de grandeur conformes aux suivis RSDE des usines du SIAAP

Box plot organic micropollutants



Analgésiques
Ab humains
Bêtabloquants
Anti-dépresseurs
Antiépileptiques
Hypolipémiants

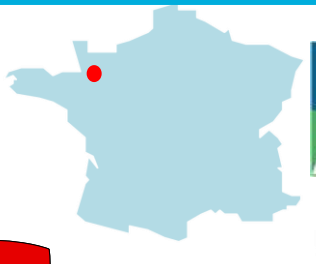
Ab vétérinaires
Hormones
Bisphénol A
Perfluorés
DCE - herbicides

Plus forte variabilité des concentrations

Actiflo® Carb
Micropollutants removal

Over 10 pilot plants trials since 2010

- **Avranches (France) – Pilot trials**
  - 18 months Actiflo Carb (2010 – 2012)
  - PAC alone and combined with O3
- **Industrial prototype – Cham (Lucerne, CH)**
  - 6 months trials in 2011 in cooperation with :
  - Industrial unit 50 to 100 m3/h
- **Industrial prototype – Milwaukee (USA)**
  - 4 months trials in 2011
  - Industrial unit 50 to 100 m3/h
- **Aachen (Germany) – Pilot trials**
  - 6 months trials **- RWTH Aachen**



Avranches

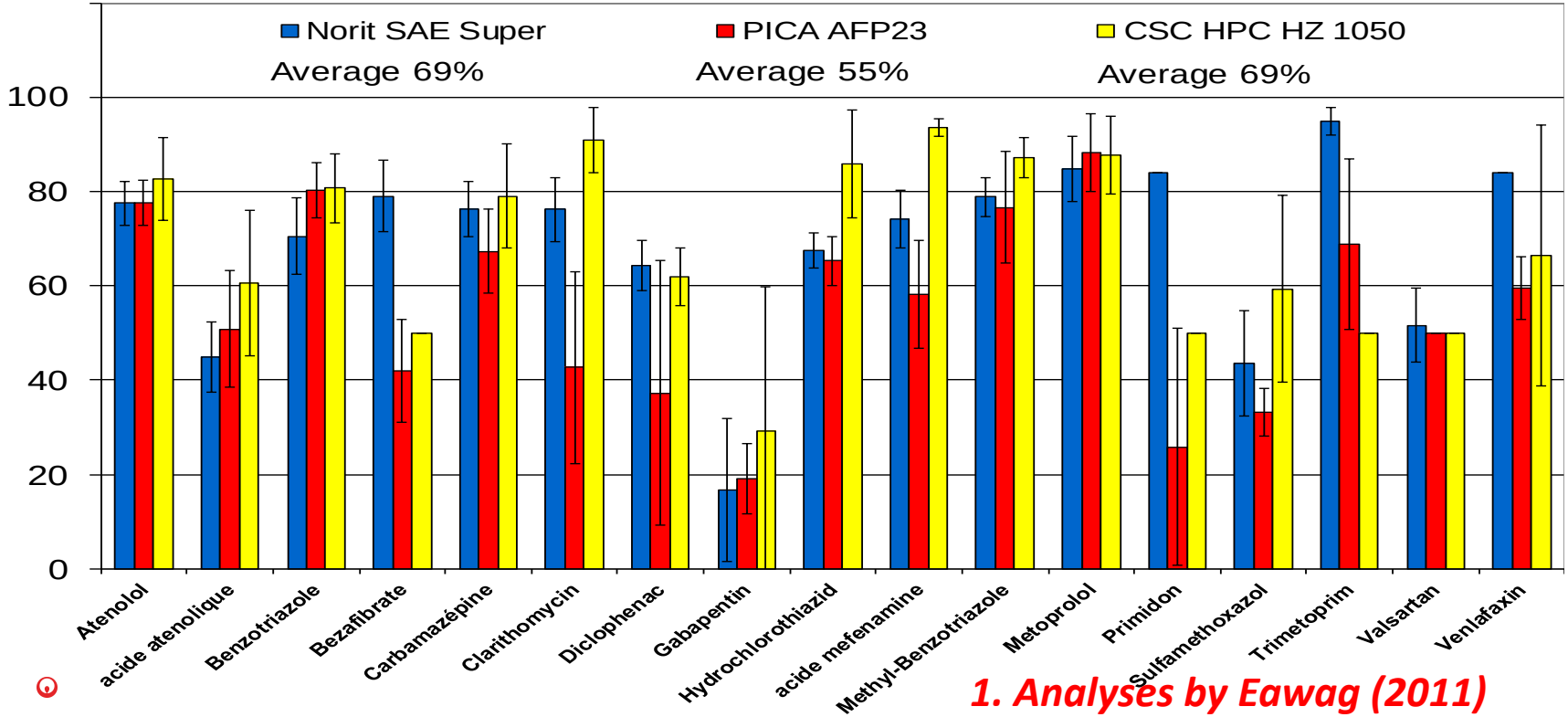
eawag 75 aquatic research

UWM UNIVERSITY of WISCONSIN MILWAUKEE

WERF Water Environment Research Foundation Collaboration. Innovation. Results.

Various PAC tested (Norit, Jacobi, Calgon, etc…)

- CAP dose 10 ppm, CAP concentration in reactor 1 – 2 g/l
- Contact time 10 mn



1. Analyses by Eawag (2011)

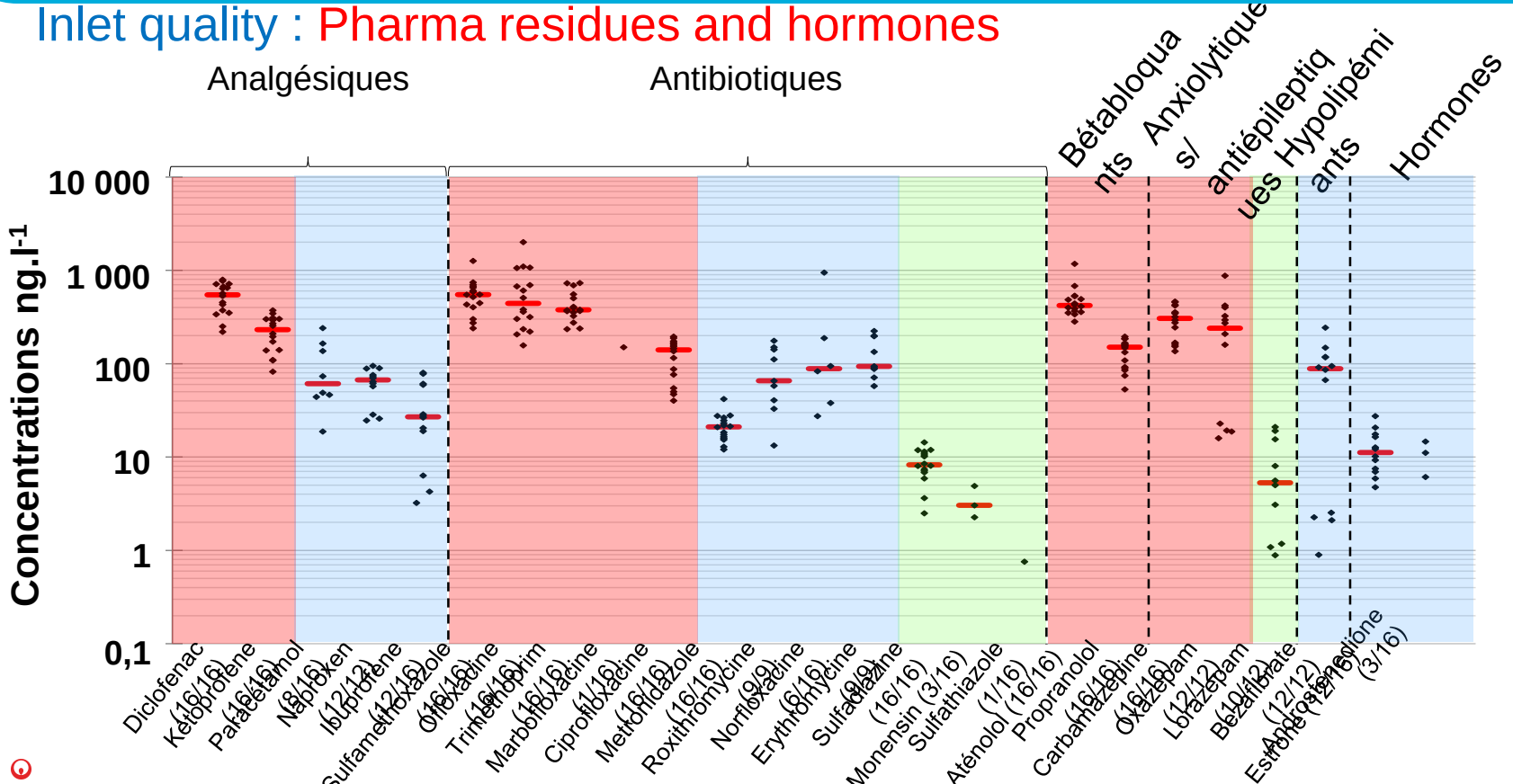
Micropollutants removal

- Actiflo® Carb : micropollutants removal

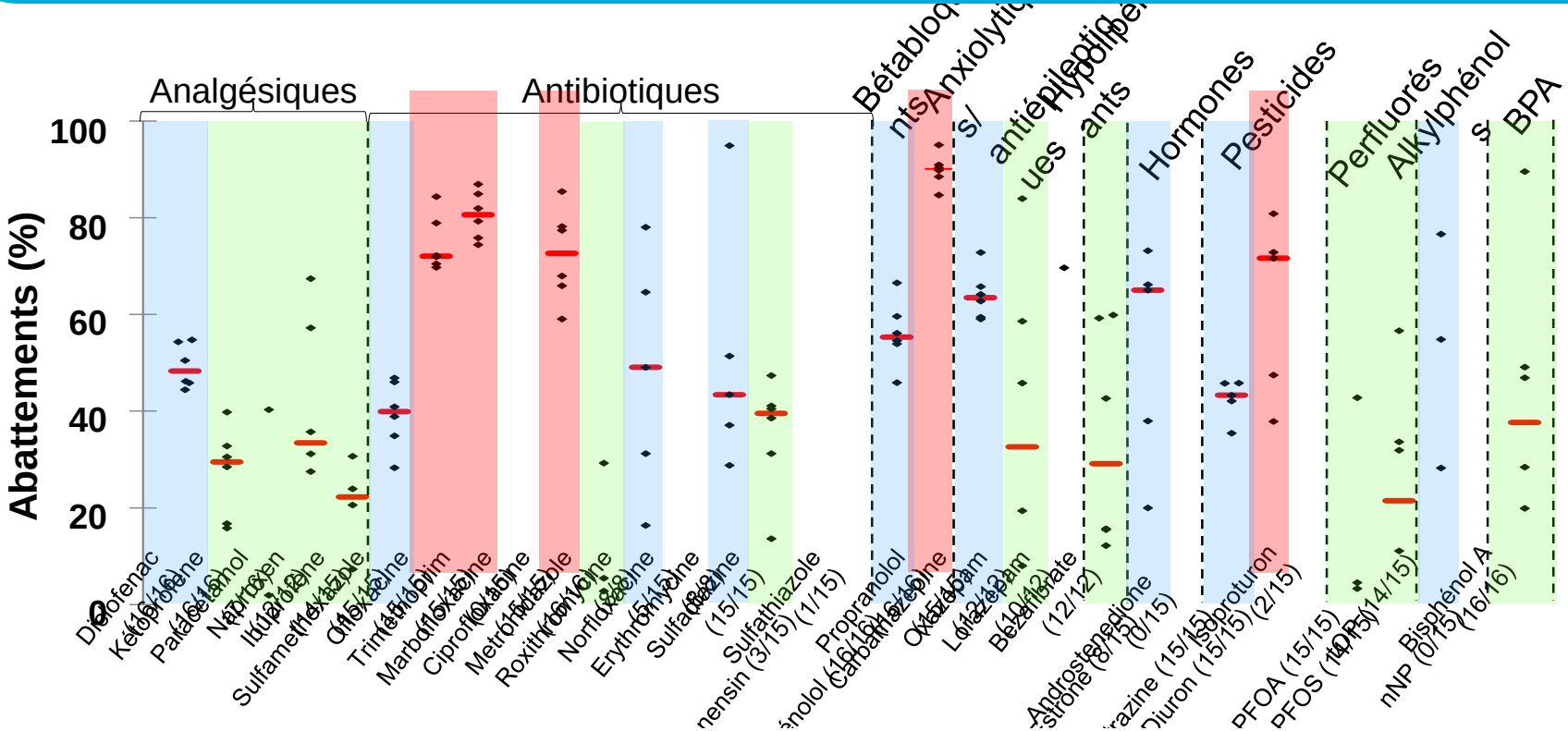
Micropolluants	Abattement en %									
	Sites et quantités de CAP									
	Aachen			Achères			Avranches		Bruxelles	Lucerne
	10 ppm	20 ppm	30 ppm	5 ppm	10 ppm	15 ppm	20 ppm	20 ppm + O3	15-20 ppm	10 ppm
Atenolol	/	/	/	38	47	67	90	92	/	76
Metoprolol	88	91	95	/	/	/	69	76	82	85
Propanolol	/	/	/	75	88	95	/	/	88	/
Clarithromycine	37	70	63	/	/	/	/	/	79	76
Sulfamethoxazole	28	68	74	28	39	39	77	88	69	45
trimethoprim	/	/	/	68	72	80	/	/	79	95
Diclofenac	57	89	91	38	45	60	82	97	71	65
Bezafibrate	/	/	/	20	15	30	/	/	31	78
Carbamazepine	83	94	96	40	60	72	98	99	82	76

Analysis results over 24 campaigns of sampling

- Inlet quality : Pharma residues and hormones



Median removal

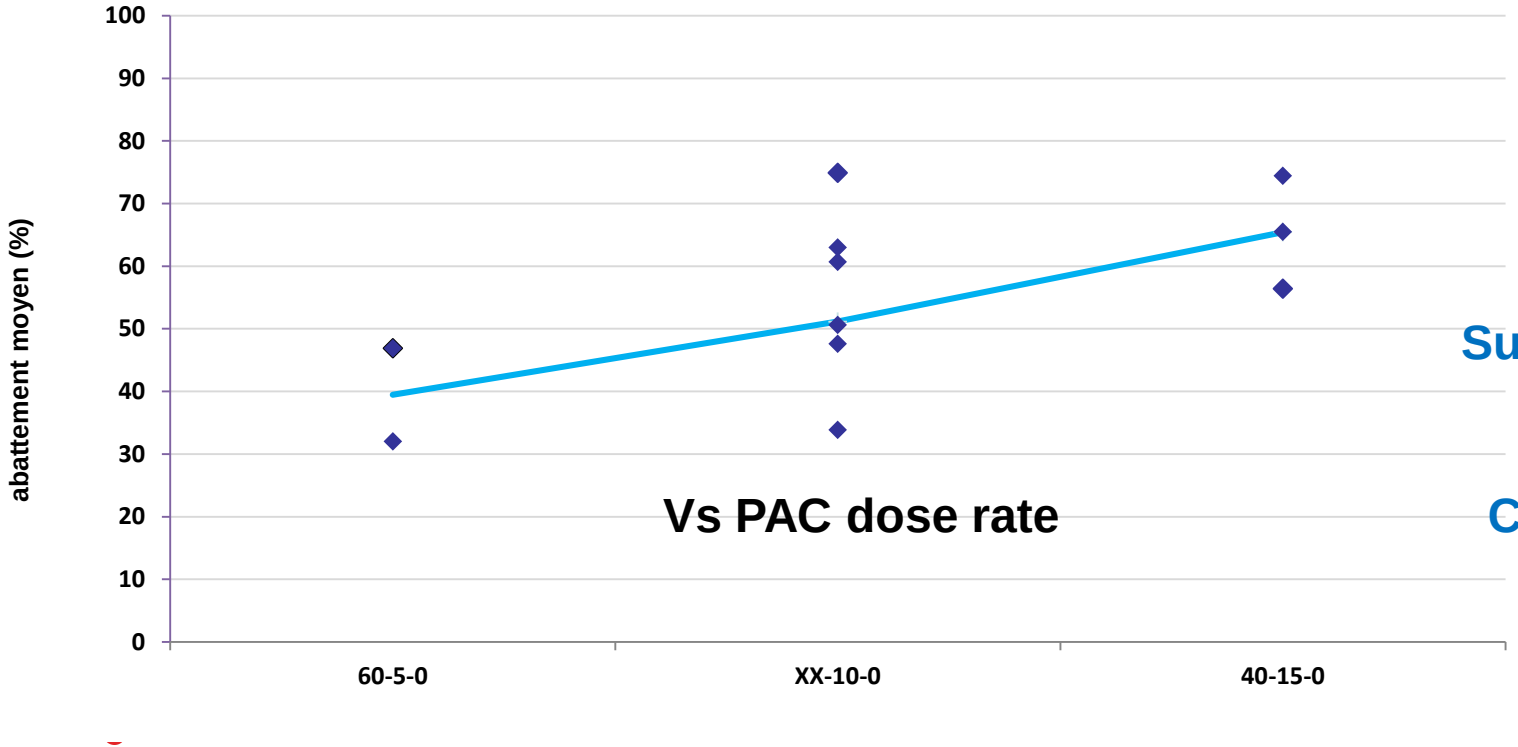


Average removal over 33 molecules :

> 70% for 5 molecules, [40 – 70%] for 11 molécules and < 40% for 9 molécules

Mass removal

Synthesis over 6 molecules (cumulative concentration)



Molecules of reference

Diclofenac
Ibuprofene
Sulfamethoxazole
Atenolol
Propanolol
Carbamazepine

Actiflo® Carb
“hard” COD removal

Actiflo® Carb for industrial effluents (« Hard COD »)

Municipal waste water	China	Zhejiang	Fuyang	Tertiary	Actiflo Carb operation as needed to reduce refractory COD from nearby paper mill
Industrial waste water	China	Shandong	Huntsman, Qingdao	HPI / CPI	Tertiary; removal of refractory COD from WW with dye chemicals used in textile industry; very high COD up to > 900 mg/l
Industrial waste water	France	haut-rhin	DSM Nutritional Products France, Village-Neuf (close to Basel, Switzerland)	Pharma	Tertiary treatment after AS for TSS & refractory TOC/COD removal; and pharma micropoll removal
Industrial waste water	Italy	SIC	Raffineria di Milazzo, Milazzo (Sicily)	HPI / CPI	Secondary clarification of MBBR effluent with Actiflo Carb; removal of refractory COD up to 200 mg/l; reuse for fire protection water system

DSM references : Mulhouse, France

DSM : results (Commissioning)

- Synthèse des essais de mise en route

Date	Débit alim	Vitesse	MES alim	COT alim	Dosage polymère	Dosage FeCl3	Dosage CAP	Type CAP	pH rejet	MES rejet	COT rejet
	m3/h	m/h	mg/l	mg/l	mg/l	mg/l	g/l		upH	mg/l	mg/l
21/04/2015	60	30	500	40	0,7	100	_	_	7,0	7	
22/04/2015	35	12	240	30	0,7	100	_	_	7,4	9	
22/05/2015	65	32	65	140	1,5	250	1	HCAP2	6,9	19	15
08/06/2015	65	32	30		1,5	250	1	HCAP2	6,5	21	
09/06/2015	65	32	15		1,5	350	1	HCAP2	6,4	25	
22/06/2015	70	35	250	140	1,5	350	1	CPL	6,9	14	25
23/06/2015	70	35	140	150	1,5	350	1	CPL	6,8	13	30
29/06/2015	70	35	120	200	1,5	550	1,7	CPL	6,3	12	25

Taux de sable réglé à 7-10 g/L

Messages to take home

These processes deliver :

- TOC & Colour Removal
  - TOC < 2 ppm
  - When used in combination with upstream clarification UVT > 90 / 92%
- Taste & Odour Removal
- Pesticides Removal
- Algal Toxins removal
- THM Removal when using Actiflo Carb; Filtraflo Carb or Opacarb MF
  - THMs are formed by the reaction of free chlorine with natural organic matter (NOM), man-made organic matter or bromide
  - The NOM responsible for THMs consists of humic and fulvic acids produced by decaying organic matter
  - Chloroform is typically found at higher concentrations in potable water than any other THM.
  - THM5 < 100 ppb and generally below 50 ppb

Many thanks for your attention

We welcome your questions