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Discharge of endocrine disrupting chemicals by combined sewer overflows into receiving waters : case-study of the Paris conurbation

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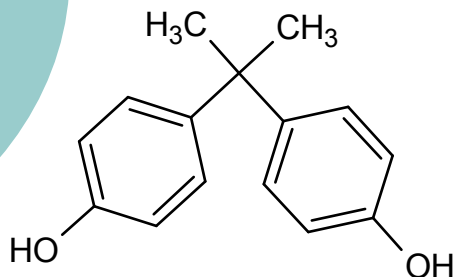
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Alkylphenols and bisphenol A



*Bisphenol A
(BPA)*

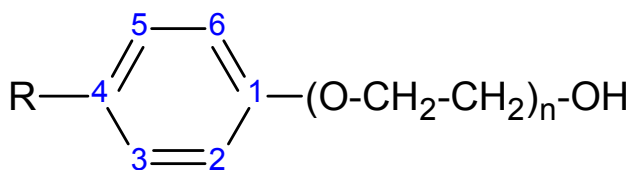


4-4'- dihydroxy-2,2- diphenylpropane

Uses : monomer in the manufacture of polycarbonate plastics (water bottles, baby bottles); epoxy resins (food contact lacquers : cans, tin cans).

World annual consumption : 450 000 t/year (Vanderberg 2007)

Alkylphenols (APs)



Uses: non-ionic surfactants, detergents, industrial wetting agents or emulsifiers.

n could range from 1 to 50 units, ex : NP₁EO

World annual consumption : 500 000 t/year (Ying 2002)

R = 9	R = 8
Nonyl-	Octyl-
80 %	20 %

Studied compounds



Structures	Nomenclatures	Names
	NP₂EO	Nonylphenol diethoxylate
	NP₁EO	Nonylphenol monoethoxylate
	NP	Nonylphenol
	NP₁EC	Nonylphenol acetic acid
	OP₂EO	Octylphenol diethoxylate
	OP₁EO	Octylphenol monoethoxylate
	OP	Octylphenol
	BPA	Bisphenol A

Interest of studying BPA and APs?



Compounds ubiquitous in environment (*Uguz et al. 2003*)

Toxicity → NP, OP and BPA have estrogenic effects on wildlife
Endocrine disrupting chemicals (EDC) (*Correa-Reyes et al. 2007*)

Disruptions on wildlife:

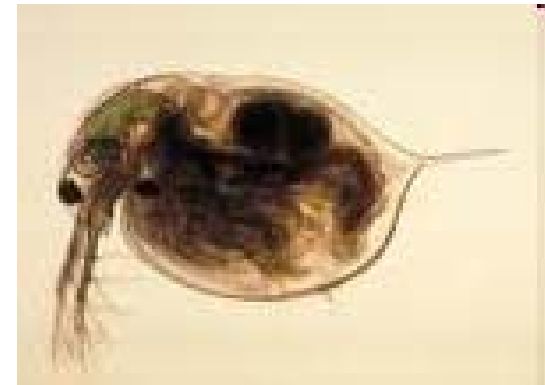
Deformity (gills, liver, kidneys) Rosy barb (*Battcharaya et al. 2008*)

Reproductive toxicity : male mice (*El-dakdoki and Helal 2007*)

Embryo development: *Daphnia magna* (*Zhang et al. 2002*)



Rosy Barb

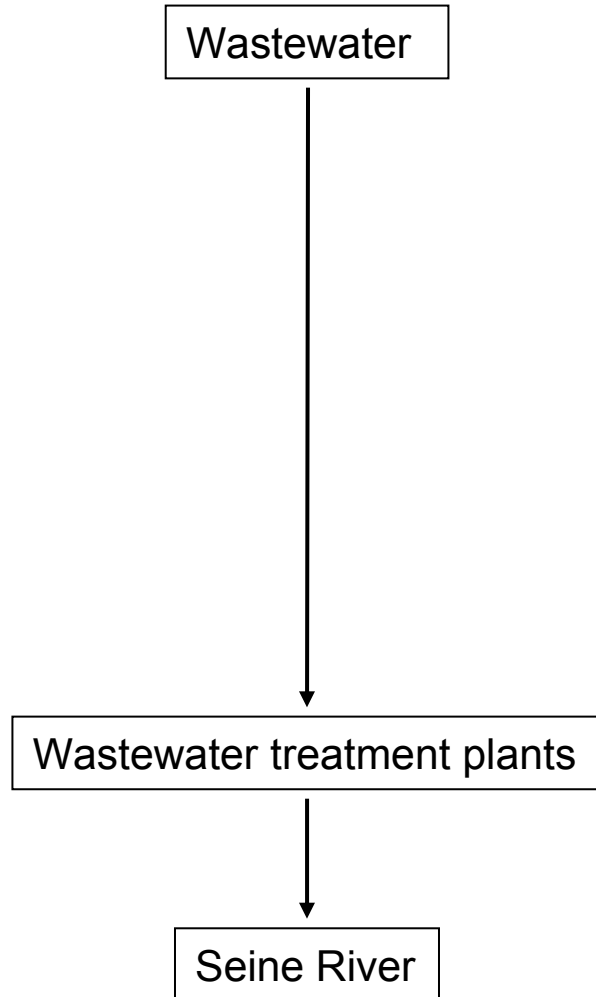


Daphnia magna

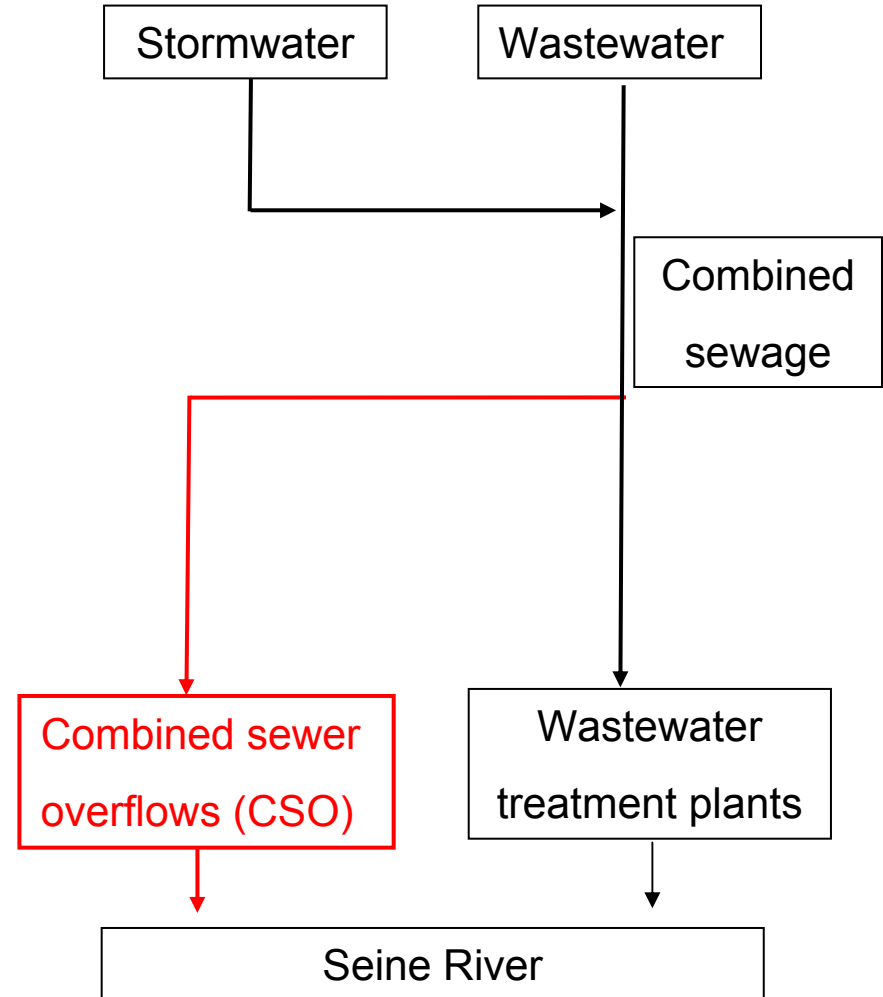
Combined sewerage systems



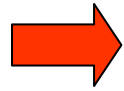
Dry weather periods



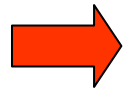
Wet weather periods



Objectives



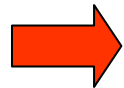
Evaluate the concentrations of APs and BPA in CSO



Comparison of loads discharge at the scale of an event

Against daily wastewater treatment plant loads

Against daily exported loads by the Seine River

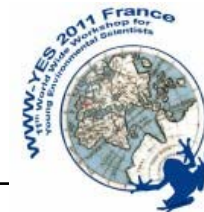


Comparison of loads discharge at the scale of a year

Against annual wastewater treatment plant loads

Against annual exported loads by the Seine River

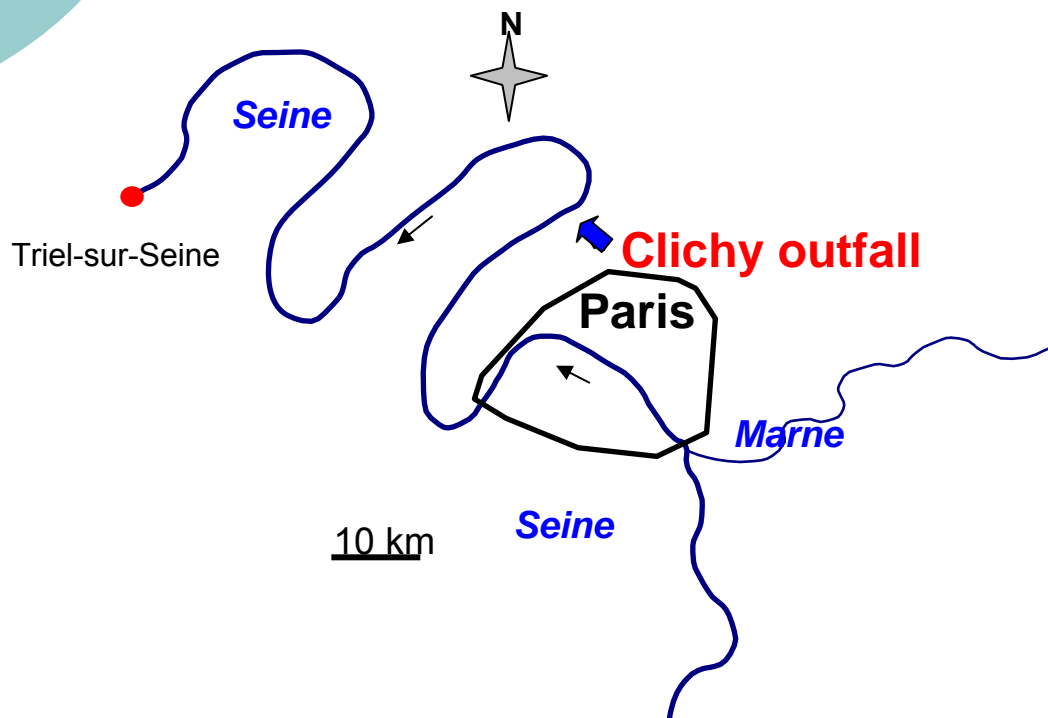
Clichy outfall



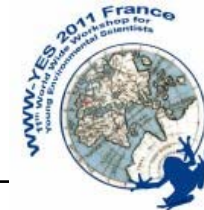
Sampling :

250 ml every 5 min

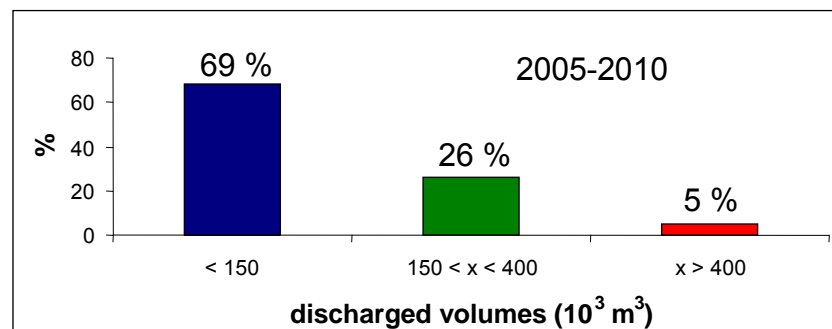
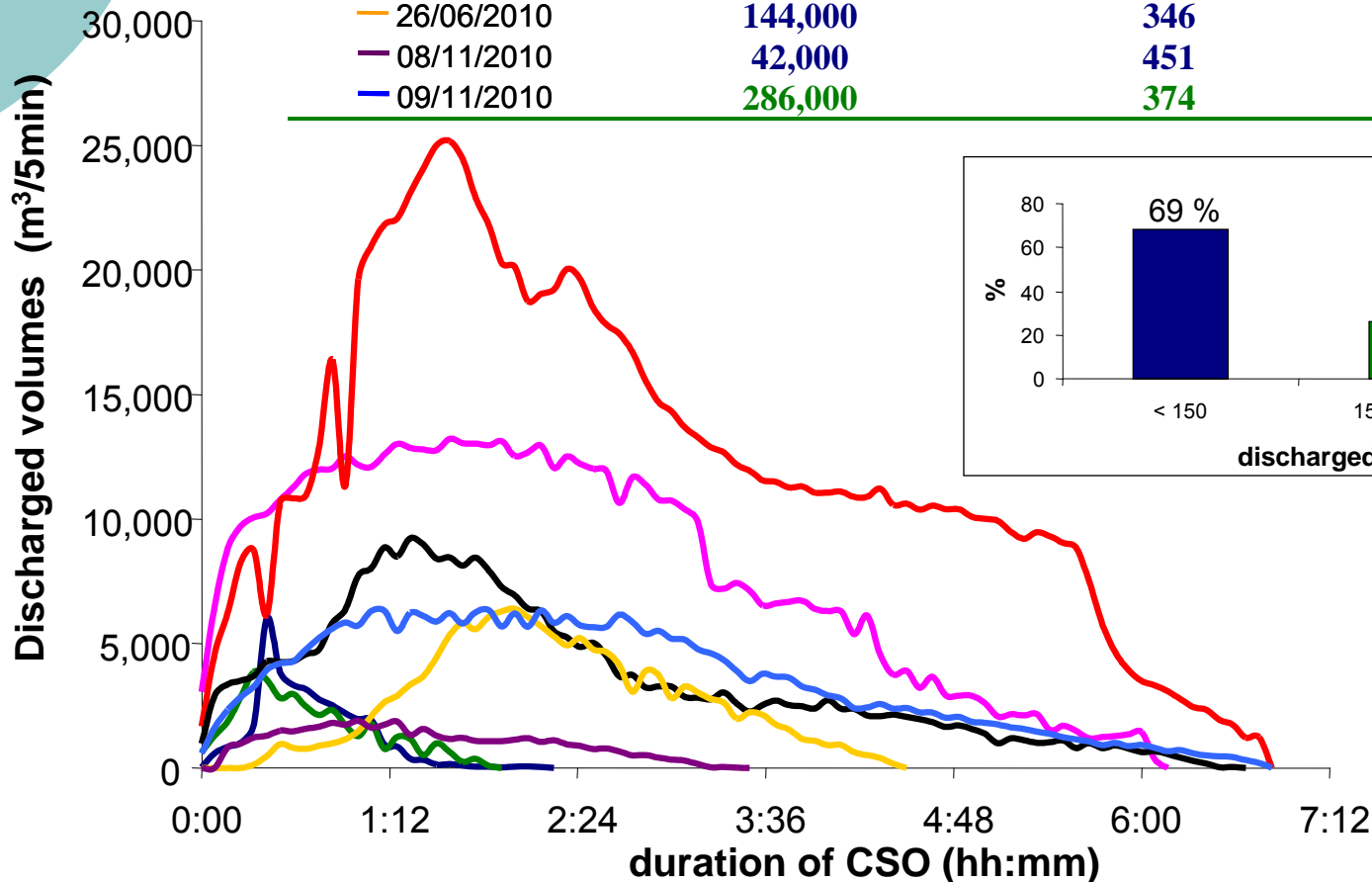
Total duration : 3h



Sampling campaigns



Sampling campaigns	Discharged volumes (m ³)	Conductivities (μS.cm ⁻¹)	% wastewater
— 16/06/2010	34,000	449	39
— 12/07/2010	580,000	284	20
— 14/07/2010	1,000,000	201	11
— 08/09/2010	38,000	380	31
— 24/06/2010	279,000	260	18
— 26/06/2010	144,000	346	27
— 08/11/2010	42,000	451	39
— 09/11/2010	286,000	374	30



Analytical procedure



Calliper: AutoTrace SPE

Extraction (SPE)

OASIS HLB (200 mg/ 6ml)



Waters : UPLC-MS-MS

Combined water

Filtration

GF/D (2.7 μm)
GF/F (0.45 μm)

Dissolved

Particulate



Anton Paar: Multiwave 3000

Freeze dry

Alpha 1-2 LDplus

Extraction

Microwave : Multiwave 3000

Purification

SPE cartridge OASIS HLB

UPLC-MS-MS

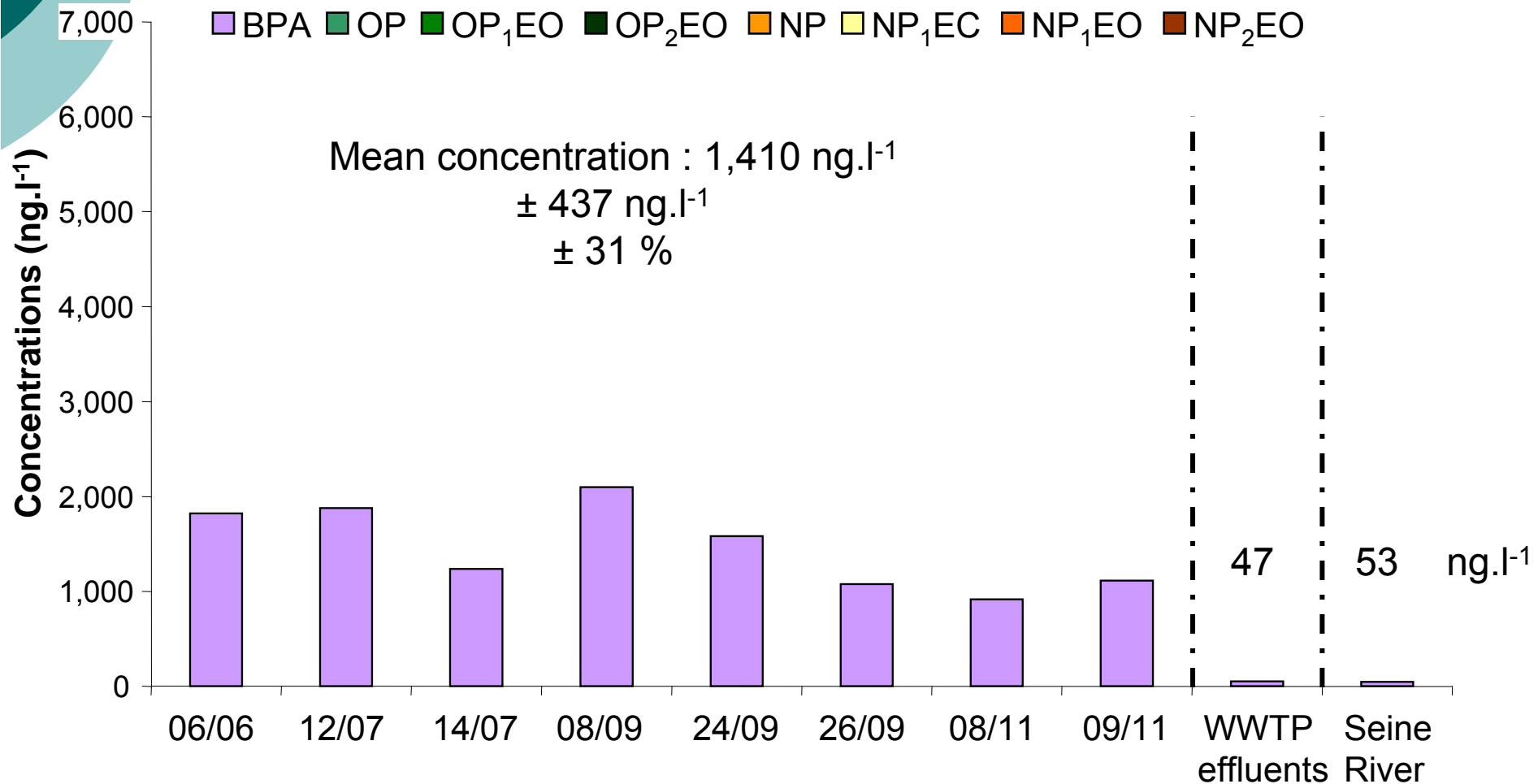
Internal standard
(BPA-d16, 4-n-NP, 4-n-NP₁EO)

Results: Total concentrations



Huge concentrations of BPA: 917 – 2,098 ng.l⁻¹; WWTP effluents : 47 ng.l⁻¹

Literature (wastewater): 226 – 12,000 ng.l⁻¹

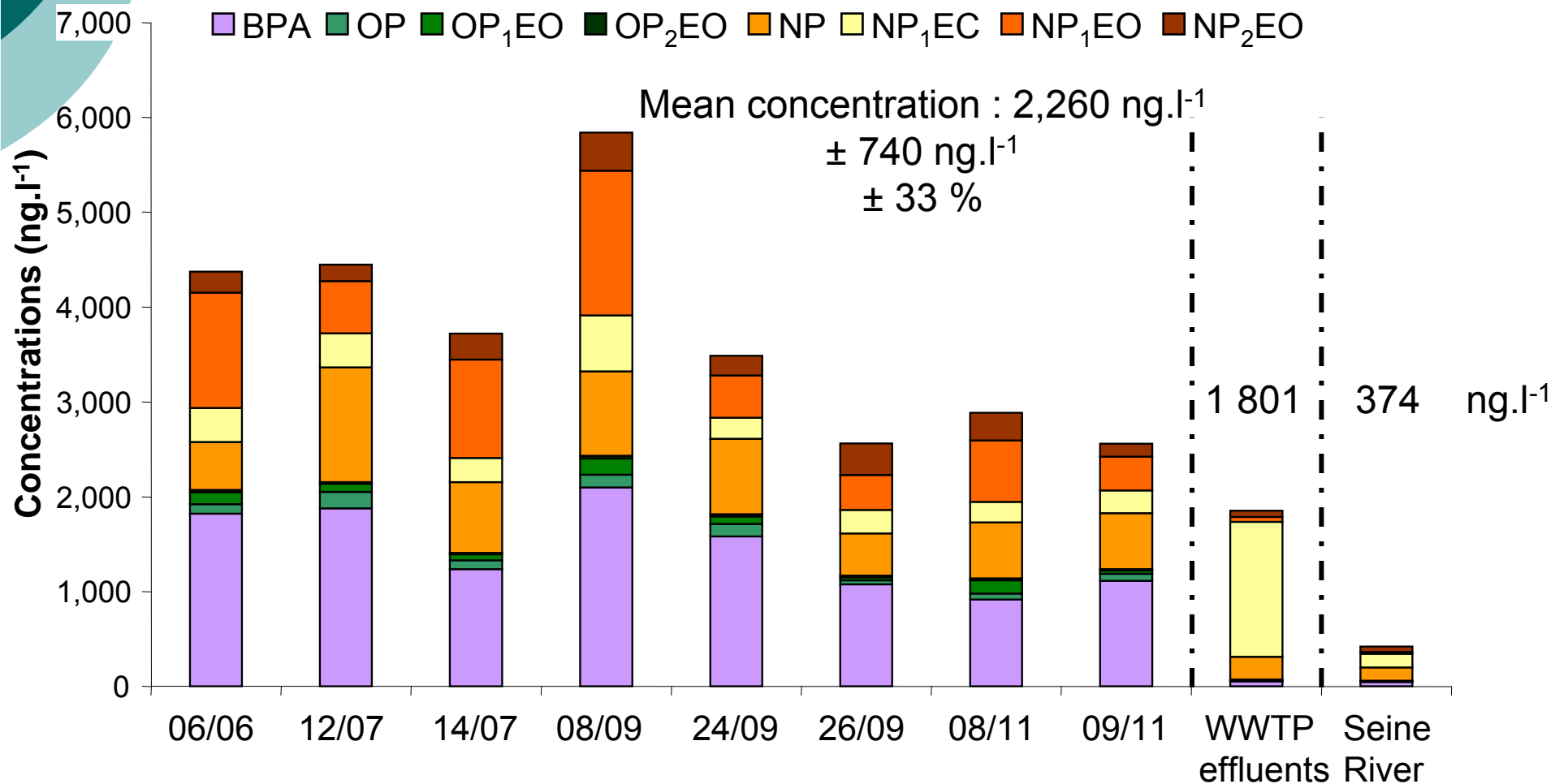


Results: Total concentrations



Mean concentration CSO \approx WWTP effluent concentration

CSOs: low NP₁EC : 207 – 572 ng.l⁻¹ ; WWTP effluents : 1,454 ng.l⁻¹



CSO loads vs. WWTP loads

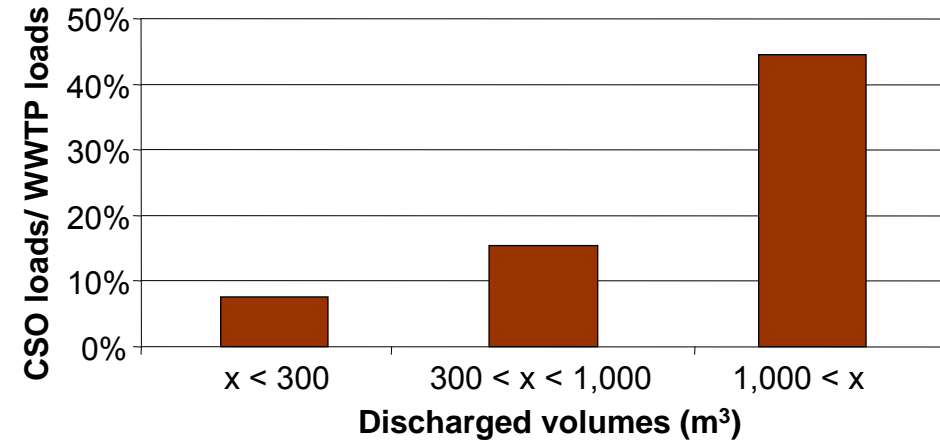
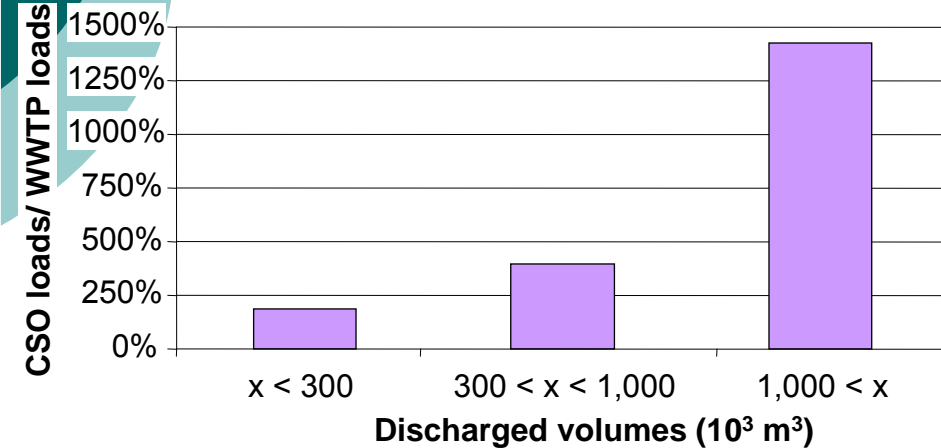


CSO loads vs. daily loads Σ WWTP (5 WWTPs \rightarrow 8 million inhabitant equivalent)

CSO loads = sum of loads of all CSO outfalls of the Greater Paris

BPA

Σ APs



Loads of BPA:

Small \rightarrow 2 times higher than WWTP loads

Medium \rightarrow 4 times higher than WWTP

High \rightarrow 13 times higher than WWTP

CSOs could be important sources of BPA within receiving waters at the scale of the event

Loads of APs:

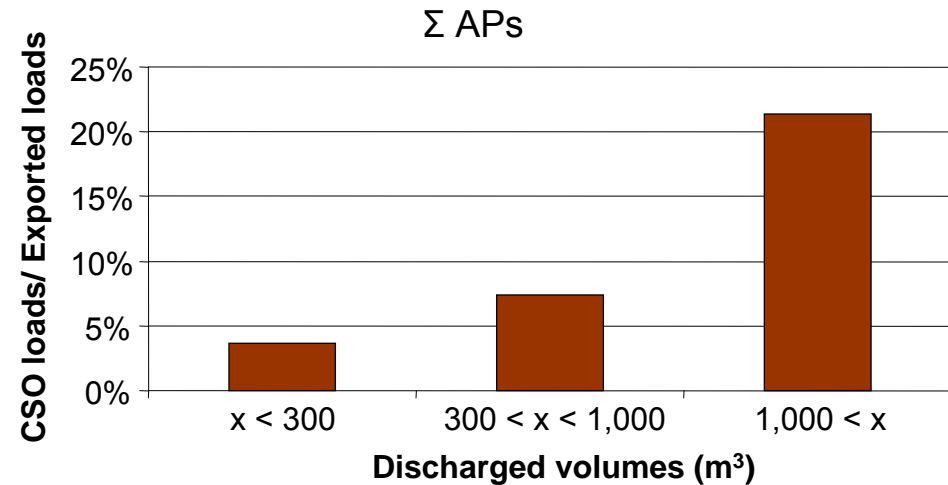
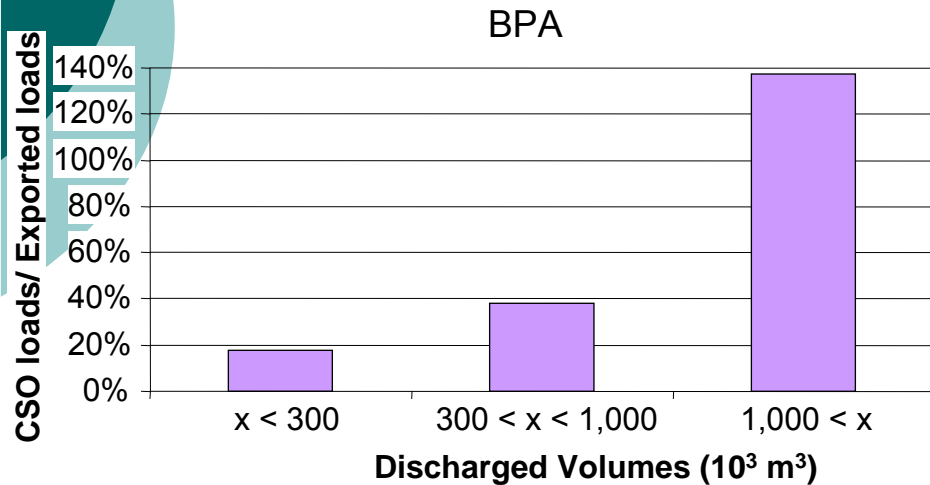
Small – medium – high : $< 50\%$ of WWTP loads

CSOs do not appear as important sources of APs within receiving waters at the scale of the event

CSO loads vs. Seine River loads



CSO loads vs. daily exported loads by the Seine River (dry weather)



Loads of BPA:

Small → Exported loads are 20 % higher

Medium → Exported loads are 40 % higher

High → Exported loads can double

CSOs may play a key role for exported loads of BPA by the Seine River during wet weather periods

Loads of APs:

Small – medium – high : ≤ 20 % of exported loads by the Seine River

CSOs do not play an important role for exported loads of APs by the Seine River during wet weather periods

First assessment of annual loads



CSO annual loads → estimation thanks to total volumes discharged from 2005 to 2010

WWTP annual loads → estimation thanks to 5 monthly sampling campaigns: 2010-2011

Seine River loads → estimation thanks to 10 monthly sampling campaigns: 2010

	Σ Paris outfalls	Σ WWTP effluents	Seine River	% Σ Paris outfalls	% Σ WWTP effluents
Volume (m ³ .y ⁻¹)	14,443,482	772,705,000	9,486,374,400	0.2	8.1
BPA	17.3	33	468	3.7	7.1
4-t-OP	0.9	28	101	0.9	27.6
OP ₁ EO	0.9	-	-	-	-
OP ₂ EO	0.2	33	29	0.8	115.4
4-NP	9.8	251	777	1.3	32.3
NP ₁ EC	4.0	923	1,007	0.4	91.7
NP ₁ EO	4.4	344	469	1.0	76.6
NP ₂ EO	2.9	501	449	0.5	106.8
Sum APEOs	22.8	2,080	2,831	0.8	73.5

Loads : kg/year

At the scale of a year → CSOs are not relevant sources of BPA and APs within Seine River

Conclusions and outlooks



Conclusions :

High concentrations of BPA ($1,410 \text{ ng.l}^{-1}$) within CSO

Concentrations of APs in CSOs similar to WWTP effluents

At the scale of an event: CSOs could play a key role for BPA loads but not for APs

At the scale of a year: CSOs are not relevant sources of BPA and APs within Seine River

Outlooks :

Improve our estimation of CSO loads and exported loads by modeling (PROSE)

Improve our understanding of the influence of CSO on exported loads (particulate loads)

Evaluate the proportion of contamination owed to wastewater or runoff for each event



Thank you for your attention

Acknowledgement:

SIAAP and Paris Municipality: Providing sampling site, and volumes discharged from 2005 to 2010

LEESU: Florent Leroy, Mohamed Saad and Alexandre Segor for their technical assistances

14/07/2010

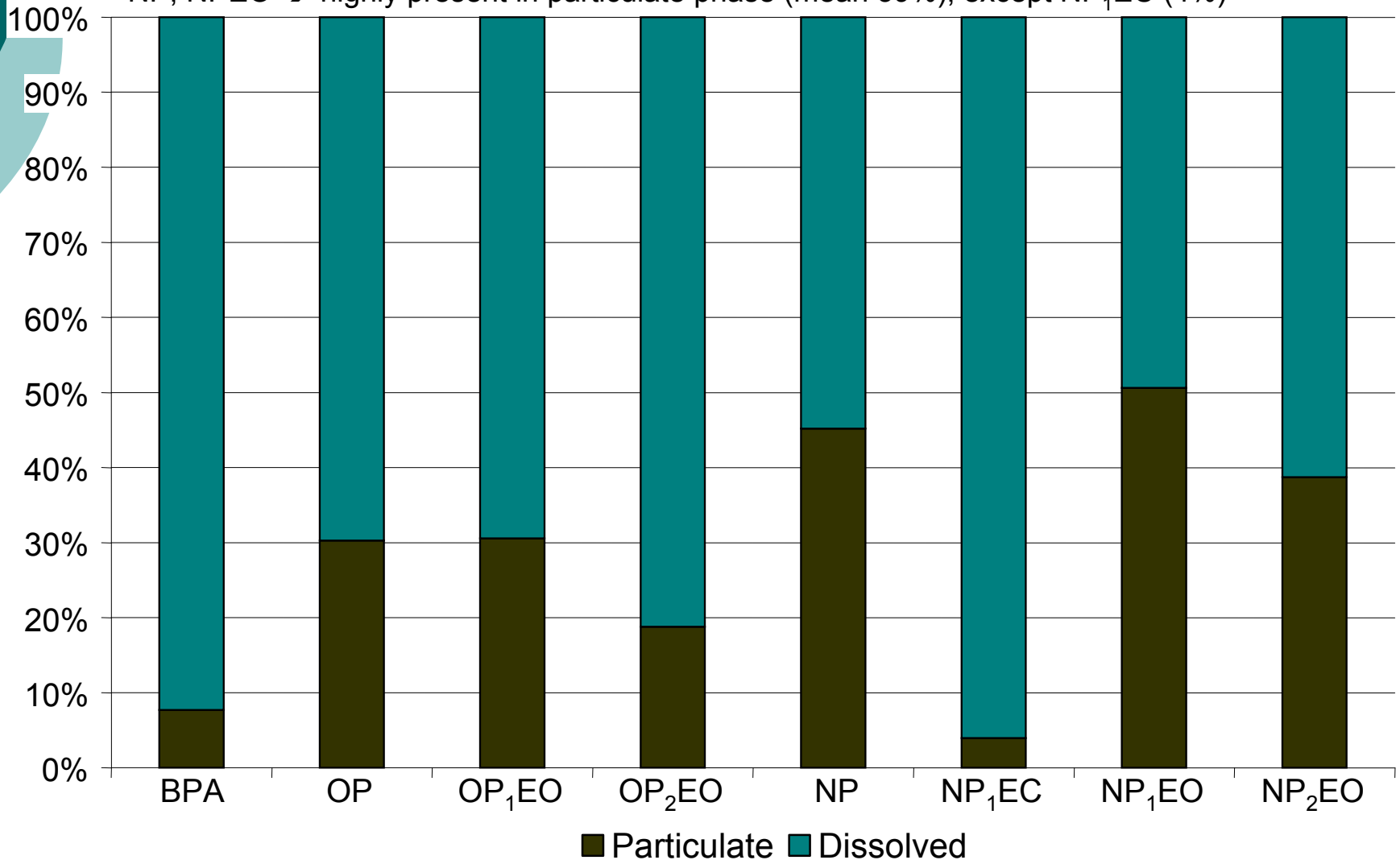
Source : DDP SIAAP

Distribution dissolved / particulate



BPA → 92 % in dissolved phase

NP, NPEO → highly present in particulate phase (mean 39%), except NP₁EC (4%)



Simplified NP_nEO biodegradation

