

Degradation products of pesticides in natural waters, favorable export conditions and seasonal variability



Oslo, 06.21.2017



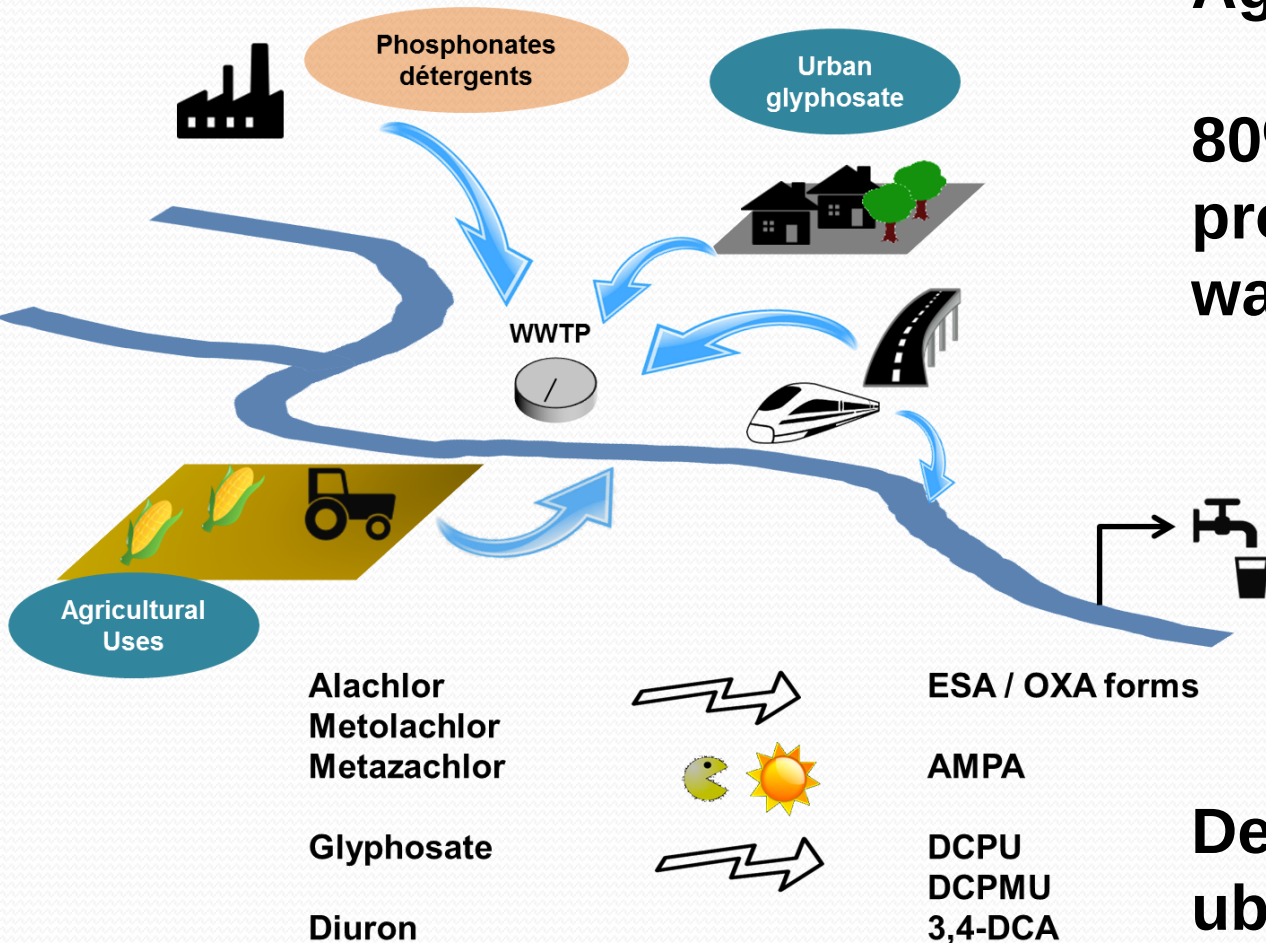
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Directors: Baurès E., Piel.S



Context: Vilaine watershed

Agricultural watershed

80% of drinking water produced from surface water



Adapted from
Grandcoin et al., 2017

Degradation products
ubiquitous in this
watershed

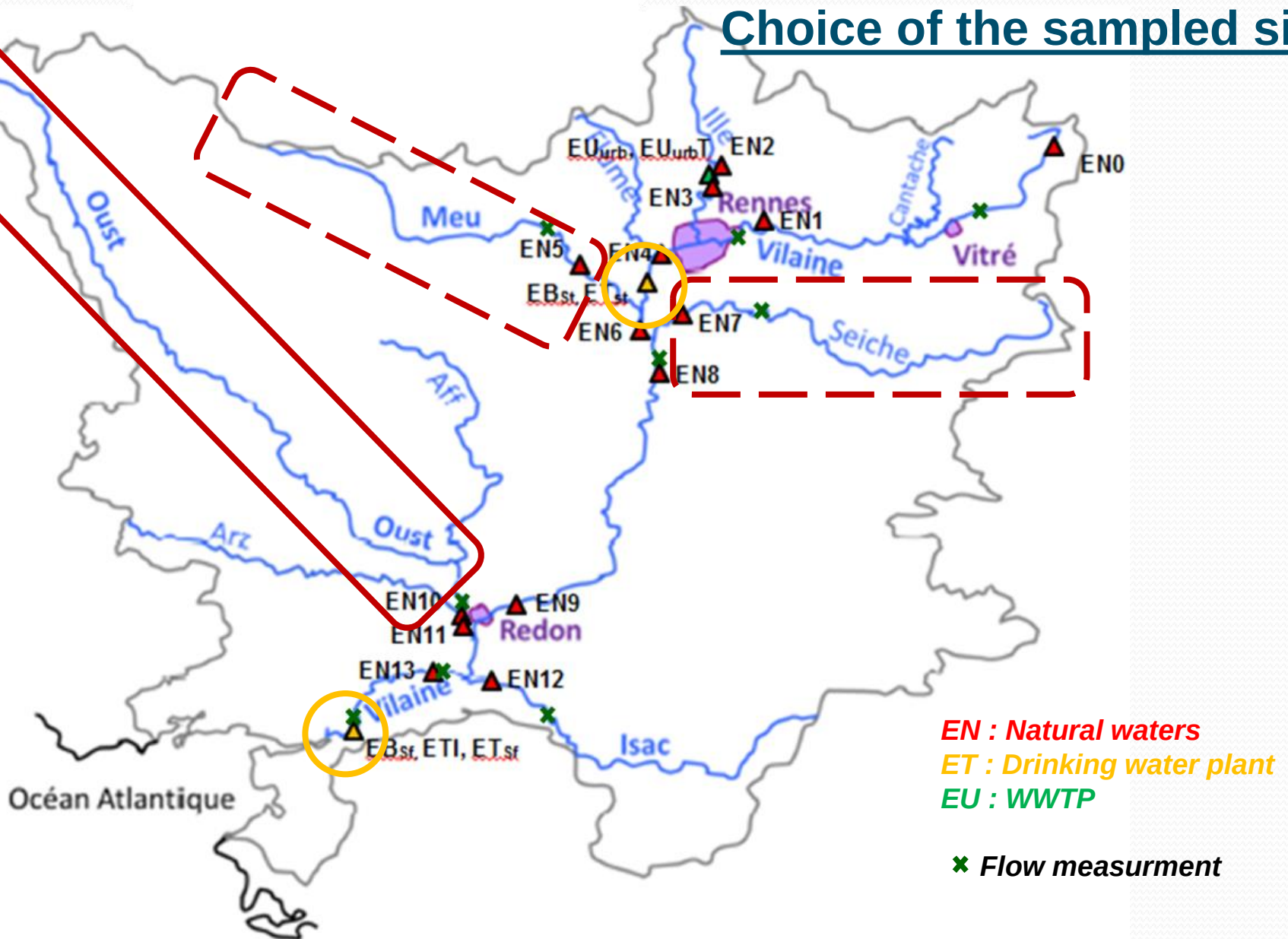
Does a link between degradation products and hydroclimatic conditions can be emphasized?



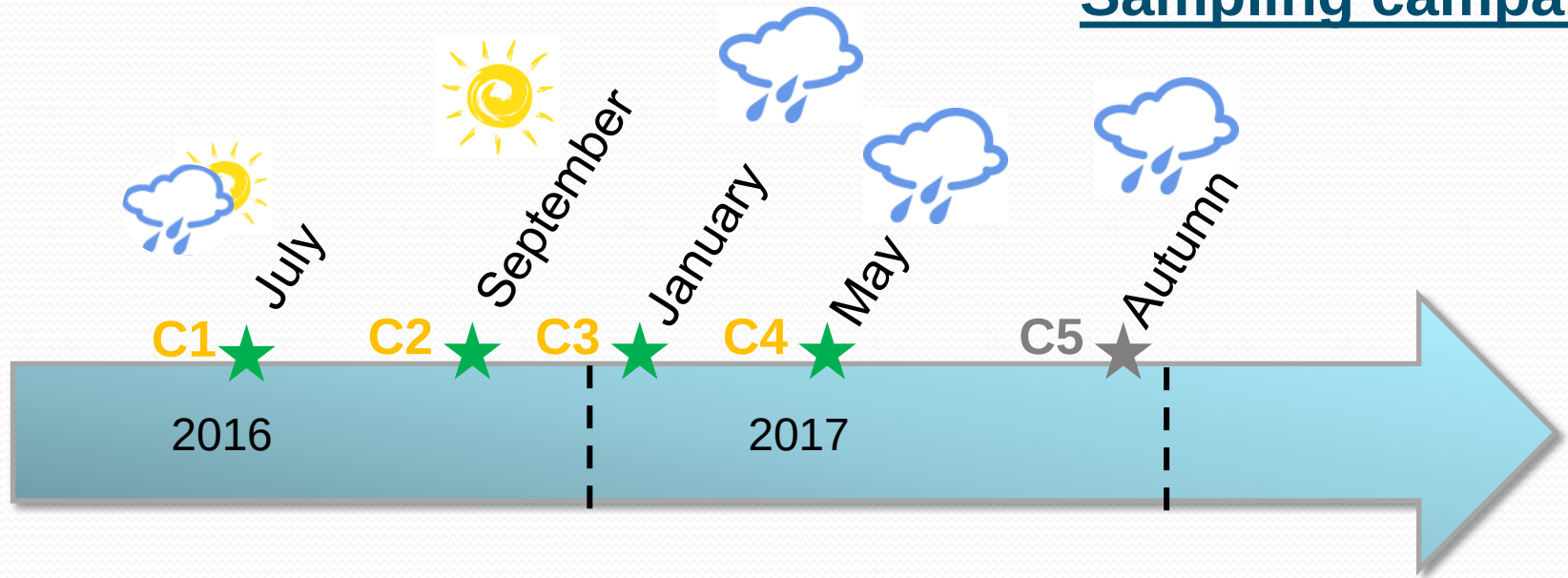
Also true for parent compounds and physico-chemical parameters

Is it possible to predict and simply verify a contamination?

Choice of the sampled sites



Sampling campaigns



Ponctual sampling of natural waters (2 days)
(AFNOR standard FD T90-523-1, 2008)

Rain conditions C3 and C4 (>10 mm / 24h)



Analysis

Parameter	Equipment	LOQ
Temp, pH, cond, fDOM, Chlorophyll, %O ₂ , salinity, redox	EXO 2 probe	-
Diuron, DCPU, DCPMU, 3,4-DCA, S-Metolachlor, Alachlor, Metazachlor and their ESA/OXA forms	RRLC-MS/MS	20 ng/L
Glyphosate, AMPA	HPLC-Fluorimetry	50 ng/L
NO ₂ , NO ₃ , NK, NH ₄ , P _{tot} , PO ₄ , UV Spectra, DOC, TOC, MES, DCO, DBO.	Various	-

Hydroclimatic data

$\Sigma RR (-1s)$: Cumulative Rainfall (-1 week)

$\Sigma RR (-2s)$: (-2 week)

$\Sigma RR (-4s)$: (-4 week)

$RR (Vmax-1s)$: Maximum daily rainfall (-1 week)

TM_d : median temperature the day of sampling

$INST (day)$: Insolation duration the day of sampling

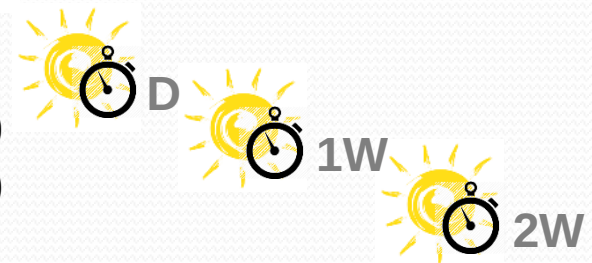
$\Sigma INST (-1s)$: Cumulative insolation duration (-1 week)

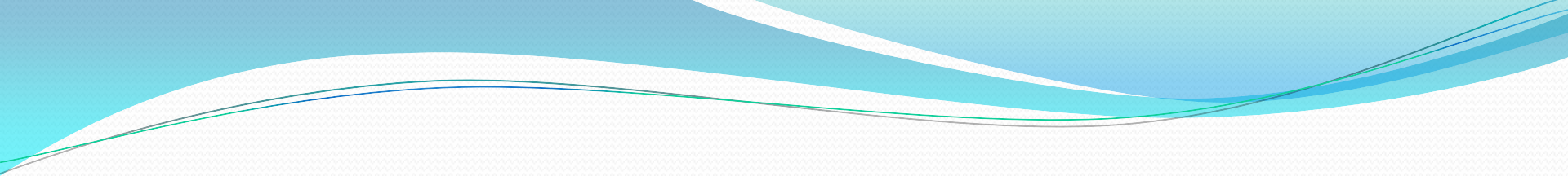
$\Sigma INST (-2s)$: Cumulative insolation duration (-2 week)

$\Sigma GLOT (-1s)$: Cumulative solar radiation (-1 week)

$\Sigma GLOT (-2s)$: Cumulative solar radiation (-2 week)

Q : Median flow the day of sampling





Preliminary results

Selected compounds

(µg/L)	C1 				C2 				C3 			
	Max	Med	Min	FOD%	Max	Med	Min	FOD%	Max	Med	Min	FOD%
Diuron	0.02	0.02	0.02	23	0.22	0.06	0.02	43	0.06	0.04	0.02	69
Alachlor ESA (ALA ESA)	0.26	0.09	0.04	100	0.16	0.07	0.03	93	0.11	0.07	0.05	54
Metazachlor ESA (MTZ ESA)	0.15	0.08	0.05	100	0.12	0.05	0.02	100	0.1	0.06	0.03	100
MetazachloreOXA (MTZ OXA)				0				0	0.04	0.03	0.02	38
S-Metolachlor (SMOC)	0.06	0.05	0.03	54	0.06	0.05	0.03	64				0
Metolachlor ESA (MESA)	0.84	0.34	0.14	100	0.38	0.17	0.06	100	0.61	0.2	0.09	100
Metolachlor OXA (MOXA)	0.23	0.09	0.03	100	0.11	0.04	0.02	93	0.17	0.05	0.02	100
Glyphosate	0.17	0.1	0.08	31	0.26	0.17	0.1	43	0.56	0.26	0.09	23
AMPA	2.1	0.69	0.23	100	2.48	1.1	0.18	93	1.15	0.61	0.1	100

DCPMU, DCPU, 3,4-DCA, Alachlor, Alachlor OXA,
Metazachlor *below LoQ*

AMPA, MESA presents greatest concentrations and fluxes

AMPA and MESA variations along the river Vilaine-1

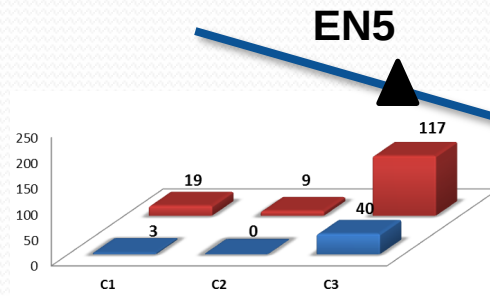
■ MESA ■ AMPA

C1 ☁️☀️

C2 ☀️

C3 ☁️

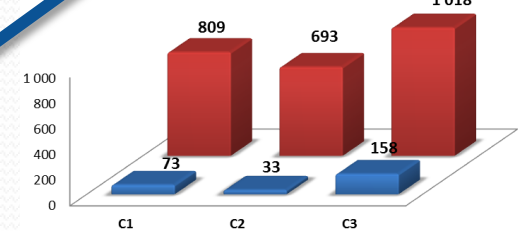
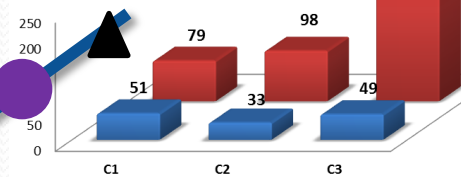
Fluxes in *kg/day*



Rennes

EN4

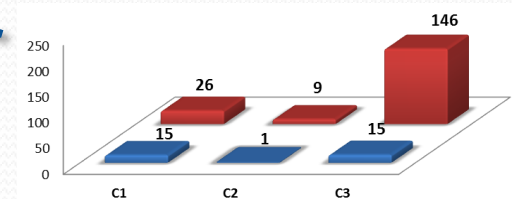
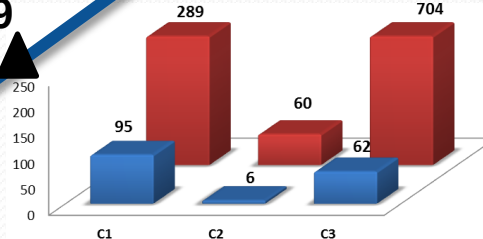
EN1



Seiche

EN7

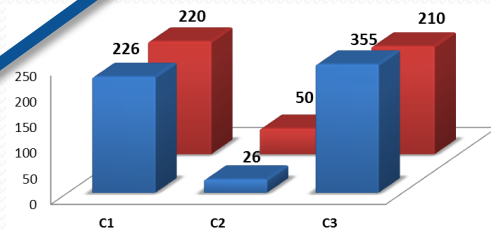
EN9



Redon

EN10

Oust



Drinking water plant



AMPA and MESA variations along the river Vilaine-2

Agglomeration increases **AMPA** load (all seasons)

Meu and *Seiche* rivers are small contributors to loads (mainly **AMPA** in winter)

Fluxes : **C2** ☀️ < **C1** ☁️☀️ < **C3** ☁️ but [**C2**] > [**C1**] > [**C3**]

Oust river is the main influent (40-50% Q_{Vilaine}) and carry mainly **MESA**

Winter **C3** ☁️ is the most favorable period to metabolites export towards surface waters

C1 Correlations physicochemical / followed compounds

Spearman rank correlation (p-values < 0.05) on R 3.4.1

+

AMPA

MESA

NH4	0.58
PO4	0.70
fDOM	0.88
TOC	0.58

ALA ESA	0.63
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MTZ ESA

ALA ESA

ALA ESA	0.69
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MESA	0.63
MTZ ESA	0.69

-

AMPA

MESA

ALA ESA	-0.73
MESA	-0.79

AMPA	-0.79
Cond	-0.80
DOC	-0.56
fDOM	-0.73

MTZ ESA

ALA ESA

fDOM	-0.56
NH4	-0.77

AMPA	-0.73
Cond	-0.71
PO4	-0.70
fDOM	-0.73

AMPA, Correlated to OM and waste water

ESA forms correlated between them; negatively correlated with AMPA, OM and waste water

C2 Correlations physicochemical / followed compounds

Spearman rank correlation (p-values < 0.05) on R 3.4.1

+

AMPA

MESA

NH4

0.62

ALA ESA

0.64

PO4 / Pt

0.66 / 0.56

MTZ ESA

0.60

fDOM

0.93

TOC / DOC

0.66 / 0.67

MTZ ESA

ALA ESA

MESA

0.60

MESA

0.64

AMPA, still correlated to OM
and waste water

ESA forms correlated between
them

-

AMPA

MESA

ALA ESA

-0.70

AMPA

-0.79

Cond

-0.88

MESA

-0.79

TOC / DOC

-0.73 / -0.68

MTZ ESA

-0.71

fDOM

-0.92

PO4 / Pt

-0.73 / -0.71

NK

-0.67

MTZ ESA

ALA ESA

AMPA

-0.79

AMPA

-0.79

TOC / DOC

-0.73 / -0.67

Cond

-0.60

fDOM

-0.73

TOC / DOC

-0.63 / -0.61

PO4 / Pt

-0.57 / -0.64

fDOM

-0.74

NK

-0.59

PO4 / Pt

-0.57

NH4

-0.59

C3 Correlations physicochemical / followed compounds

Spearman rank correlation (p-values < 0.05) on R 3.4.1

+

AMPA

MESA

ALA ESA	0.74
MOXA	0.79

MTZ ESA

ALA ESA

MOXA	0.66	MESA	0.74
		MOXA	0.73

MTZ OXA

MOXA

MTZ ESA	0.66	ALA ESA	0.73
TOC	0.57	MESA	0.79

-

AMPA

MESA

ALA ESA	-0.77	Cond	-0.95
		PO4 / Pt	-0.78 / -0.89
MESA	-0.72	NK	-0.58

MTZ ESA

ALA ESA

AMPA	-0.77
Cond	-0.83
Pt	-0.64

MTZ OXA

MOXA

AMPA	-0.72
Cond	-0.75
PO4 / Pt	-0.77 / -0.82

AMPA and ESA forms, still have different sources/influences

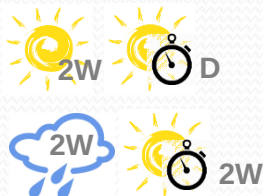
ESA / OXA forms coexists and are correlated between them

Correlations hydroclimatic data / followed compounds

Spearman rank correlation (p-values < 0.05) on R 3.4.1

C1 

AMPA /



Conclusions

AMPA can be linked to waste waters parameters and solar radiation

ESA forms of chloroacetamids are always present together

OXA forms presence increases in winter

No clear link between **ESA/OXA** forms and hydroclimatic/water parameters has been yet shown



LERES Lab Team 2016

Thank you for your attention!

