

SPATIAL EVOLUTION OF PHARMACEUTICALS IN SUSPENDED PARTICULATE MATTERS AND BED-LOAD SEDIMENTS OF A PERI-URBAN STREAM

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HS9.5: Transfer of sediments and contaminants
in catchments, rivers systems and lakes*

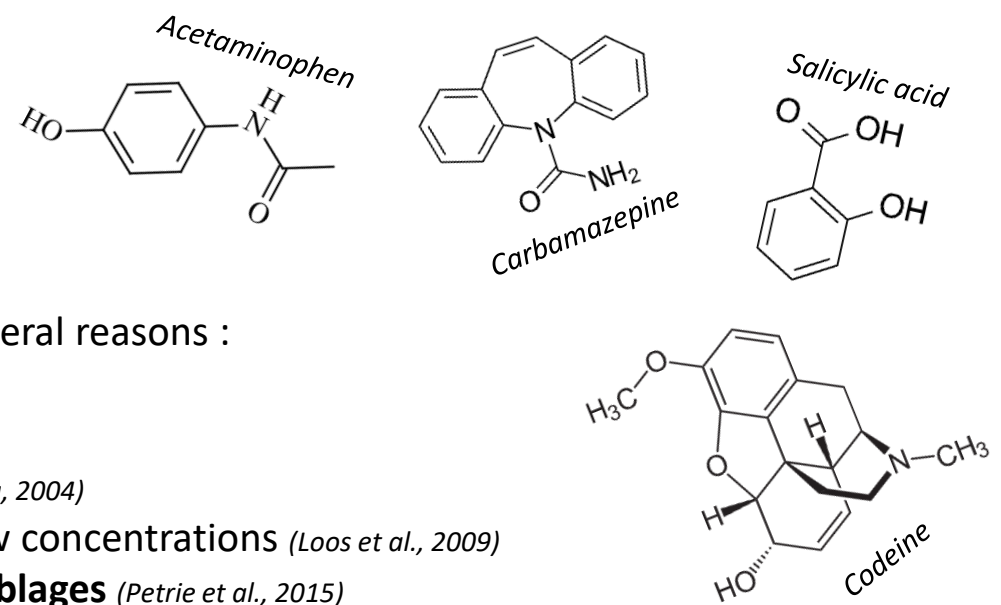


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Pharmaceutical products constitute an **emerging environmental concern** for several reasons :

- Being **worldwide** consumed (*Jjemba, 2004*)
- Being **continuously** emitted at low concentrations (*Loos et al., 2009*)
- Being released as **complex assemblages** (*Petrie et al., 2015*)
- Having **biological effects** (*Halling-Sørensen et al., 1998*)
- Including a **wide variety** of compounds with **various properties** (*Zhou and Broodbank, 2014*)

Main sources are the partial removal of the compounds in **sewage treatment plants** (*Munoz, 2009*)

Medical institutions wastewaters released **strong levels** (*Verlicchi et al., 2010*)

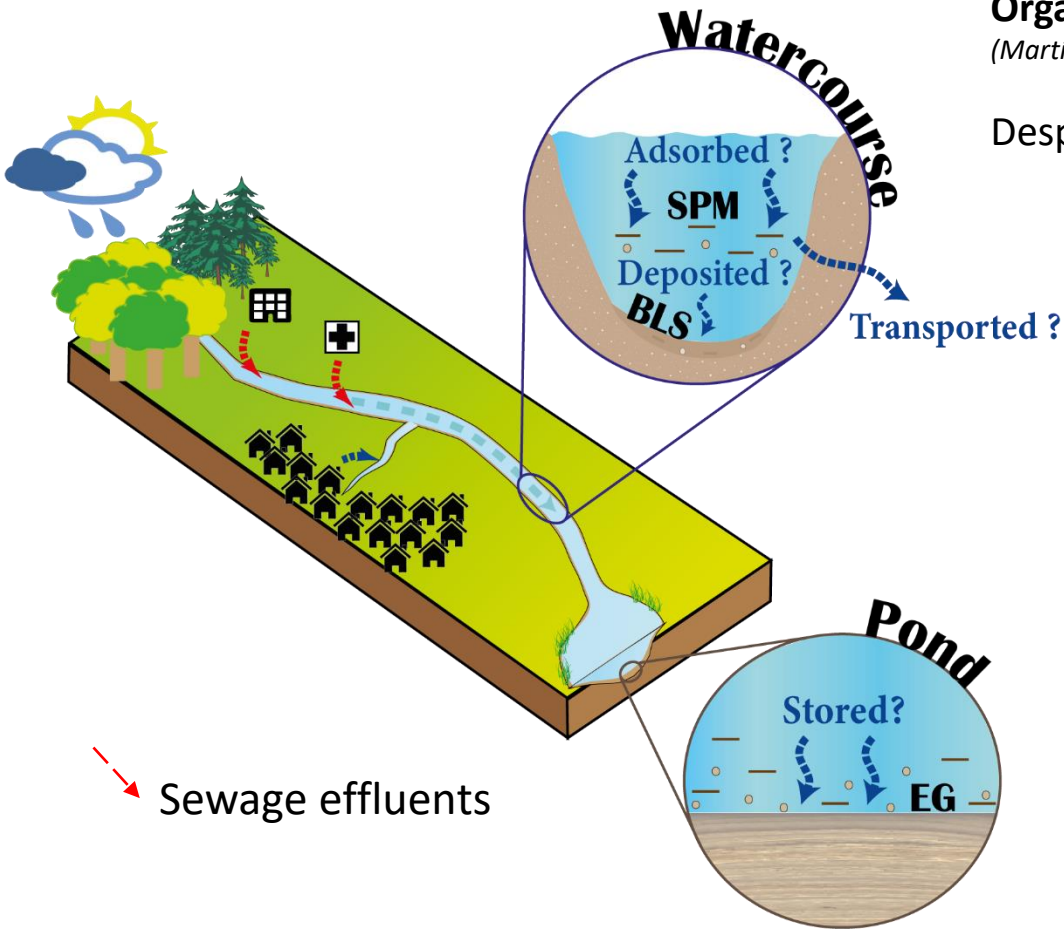
France is one of the **higher drugs consumer** in the European Union (*Bouvier et al., 2010*)

Among the hydrological systems of the Loire Bretagne basin, the **Loire River** show the **larger contamination levels**

(*Amalric et al., 2011*)



A hospital sewage effluent



Organic and mineral particles of solid matrices can **adsorb** pharmaceutical products
(Martínez-Hernández et al., 2014; Svahn and Bjorklund, 2015)

Despite that, **particulate material** analyses are **neglected** (Munoz, 2009)

Understanding sorption processes and compounds dynamics is however needed to manage environmental contaminations (Dobor et al., 2012; Martínez-Hernández et al., 2014; Petrie et al., 2015)

Sorption processes were mostly evaluated by batch experiments
(Scheytt et al., 2005; Stein et al., 2008; Yamamoto et al., 2008)

Suspended particulate matter is rarely evaluated (Maskaoui and Zhou, 2010)

Comparison between different compartments are poorly investigated
(Da Silva et al., 2011)

Spatial-temporal evolution is even more unclear (Fairbairn et al., 2015)

How occur drugs adsorption and spatial evolution into different compartments of the particulate phase at a catchment scale ?

Study site

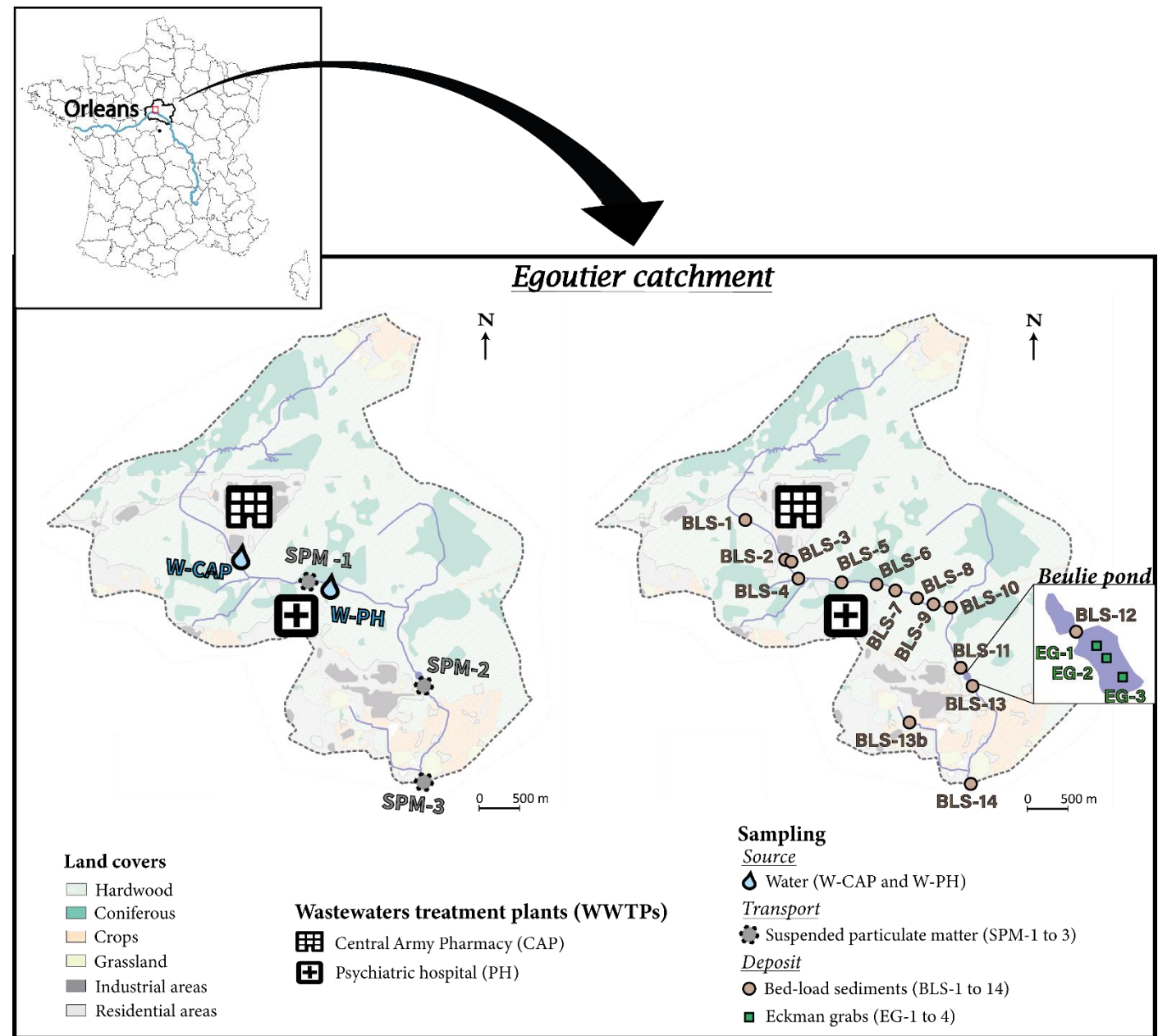
Egoutier stream :

Tributary of the **Loire River** flowing on **hydromorphic subsoils** (Soucémariadin and Verbèque, 2007) developed on **Sologne sands and clays** and **Orleanais sands** (Berger and Desprez, 1969)

Collects two sewage effluents :

- ✓ One from a Central Army Pharmacy (CAP) with continuous releases
- ✓ One from a psychiatric hospital (PH) with periodical releases

Discharge into a **pond** (the Beulie pond) in its central part

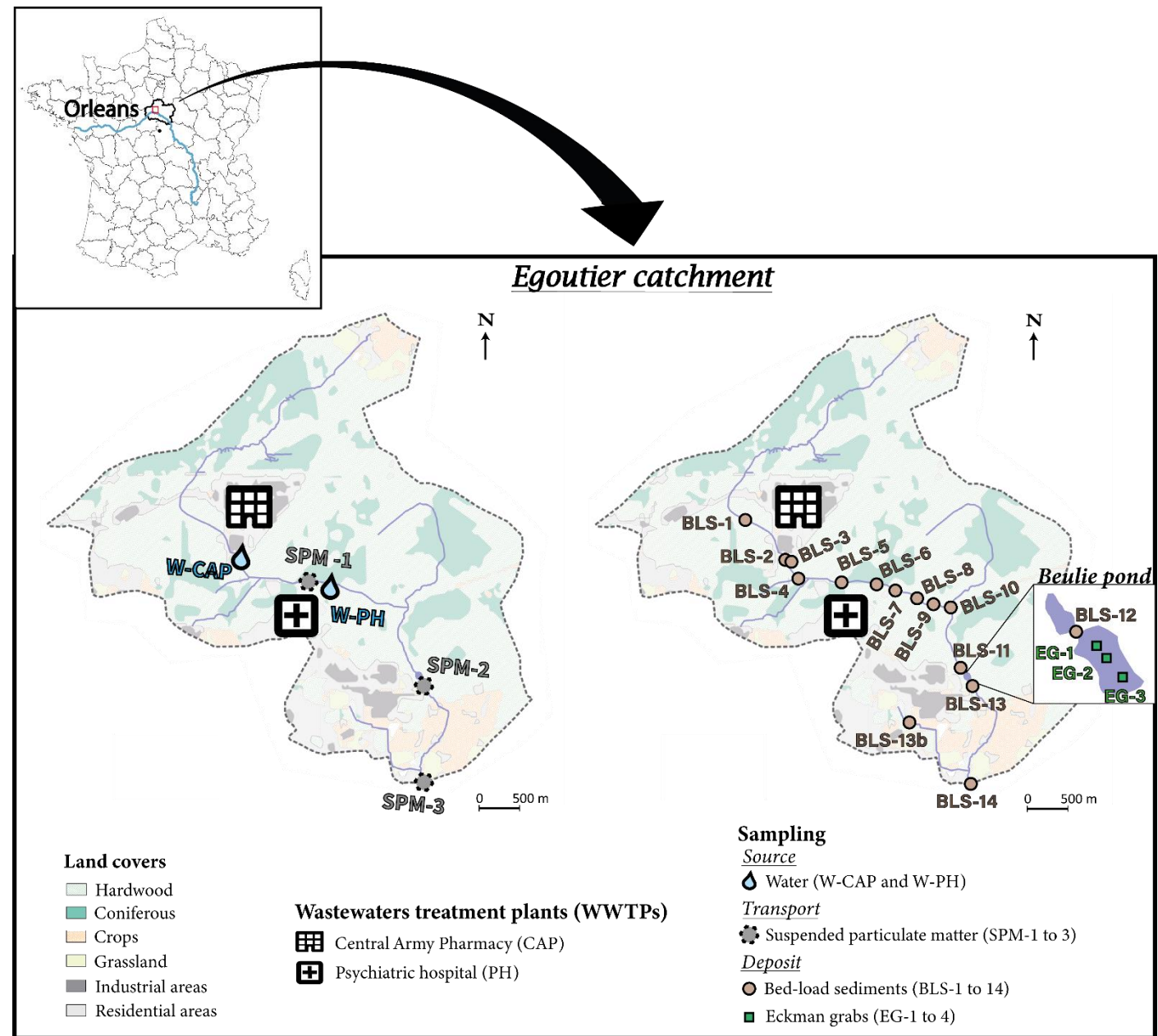


(Land cover: Inglada et al., 2017)

Sampling

4 compartments analysed :

- 💧 **The two water sources (W)**
-> Once with plastic bottles
- ⚙️ **Three locations of suspended particulate matter (SPM)**
-> 3 periods of 2 months with GEACOS
(Simonneau et al., 2020)
- 🟤 **15 samples of bed-load sediments (BLS) along the watercourse**
-> 4 sets in spring and summer of two years with Flacon tubes
- 🟩 **A transect of the pond interface sediments (EG)**
-> 3 eckman grabs collected once



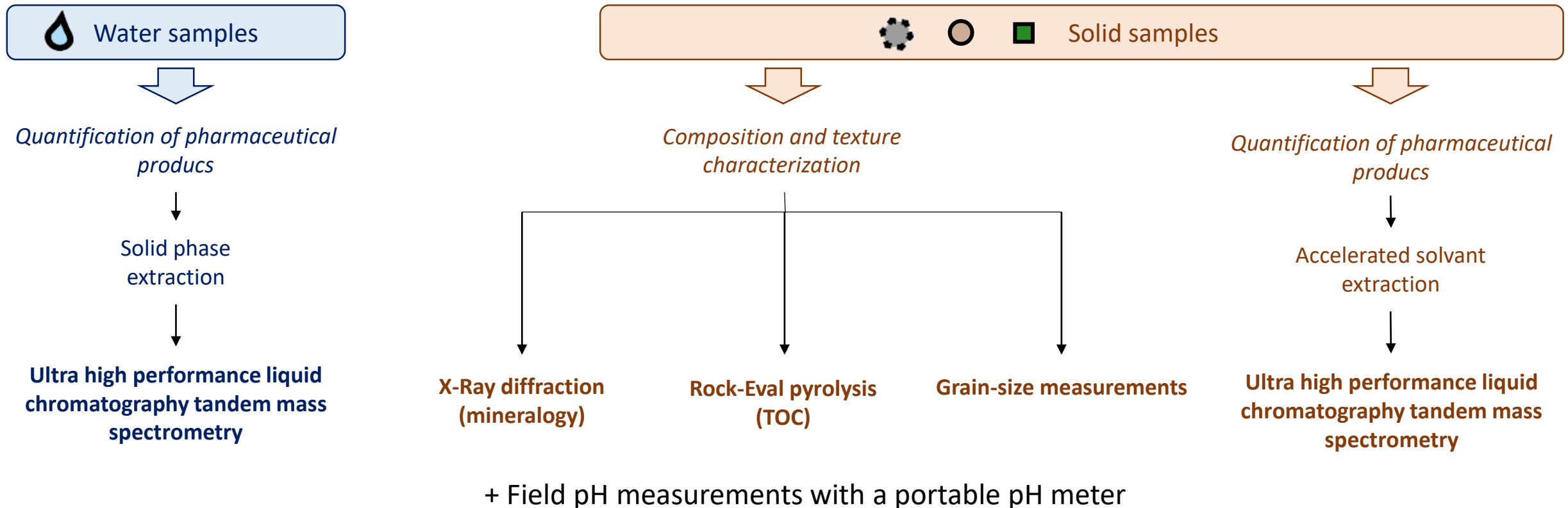
(Land cover: Inglada et al., 2017)

Methods

Quantification of different groups of drugs with different properties :

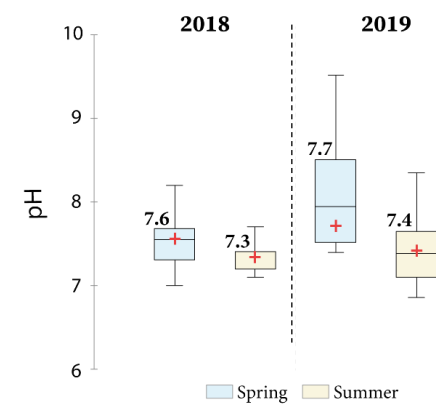
- Cationic compounds : *atenolol (ATE)*, *codeine (COD)*, *tramadol (TRA)*, *trimethoprim (TRI)*
- Neutral compounds : *acetaminophen (ACM)*, *carbamazepine (CBZ)*, *diazepam (DIA)*, *oxazepam (OXA)*
- Anionic compounds : *diclofenac (DIC)*, *salicylic acid (SCA)*

And their influencing factors

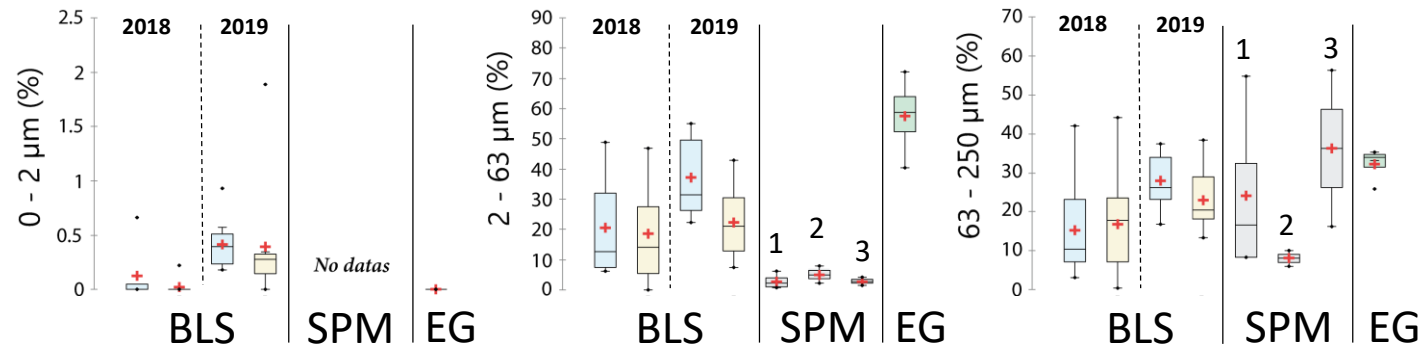


- **Minerals** : Quartz (dominant), calcite, albite, orthoclase, smectite (except downstream the pond), pyrite (only in the pond)

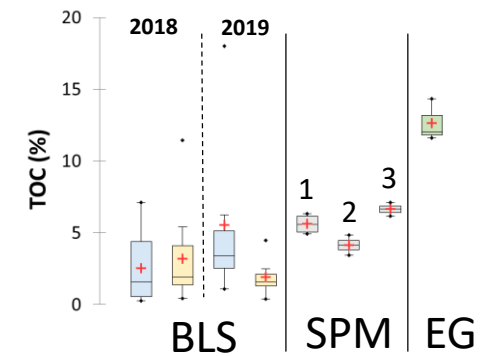
Physical-chemical conditions



Grain sizes of the particulate material



Organic content



➤ Physical-chemical conditions :

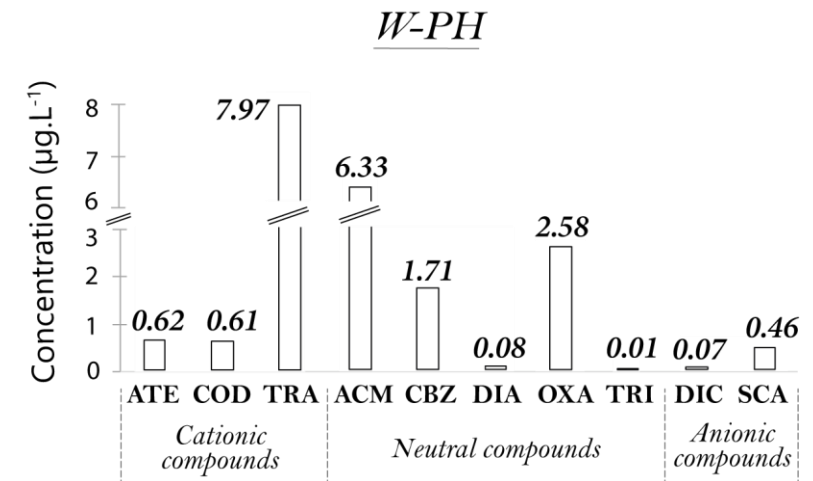
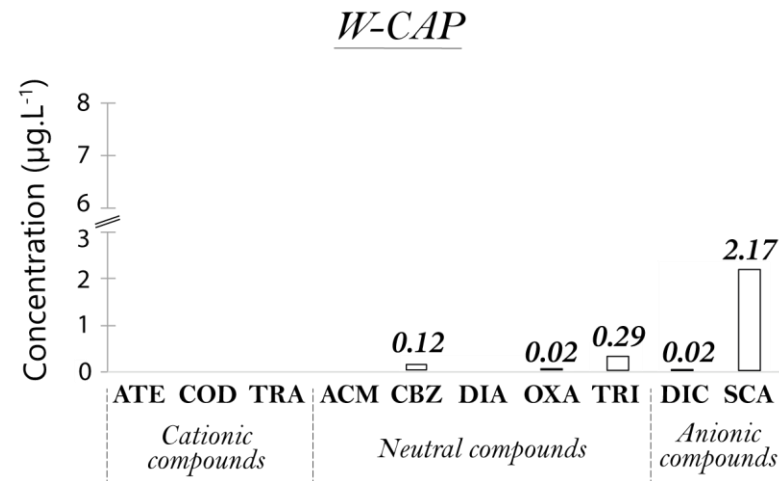
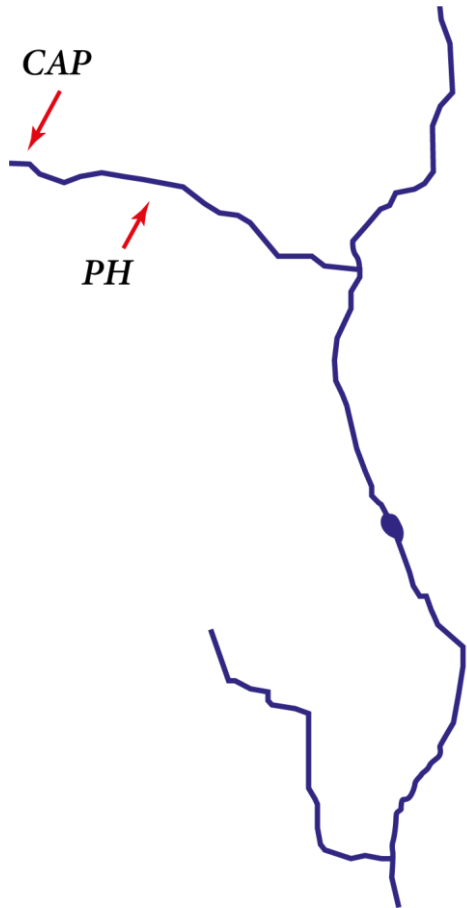
- Around **neutrality**
 - On average **higher** in **spring**
 - Slightly **variable** at **catchment scale** in summer
- (the only molecule influenced by such variations is TRI, passing from a cationic form to a neutral one)*

➤ Grain-sizes :

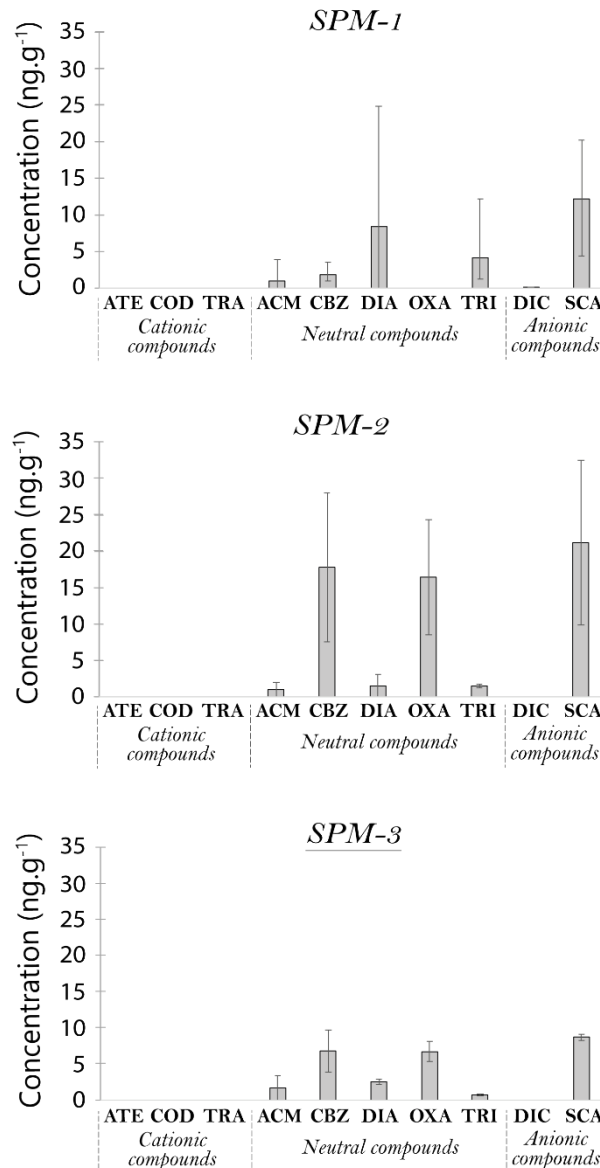
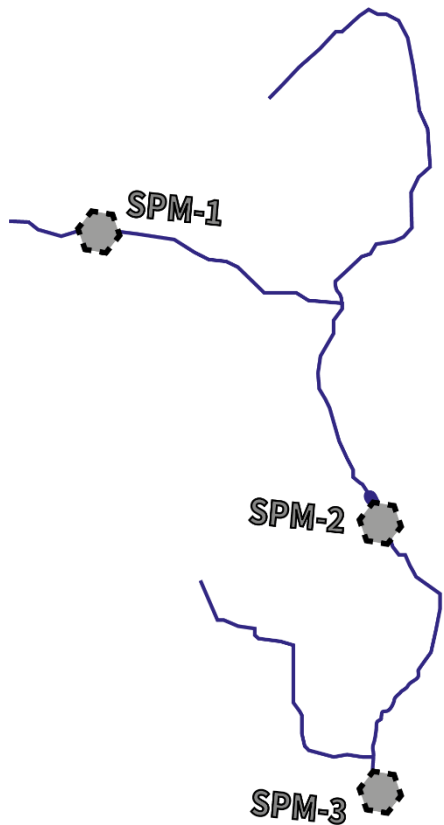
- **BLS** were **coarse** and seasonally **homogeneous** in 2018, **finer** in 2019, mostly in **spring**
- **SPM** have similar proportions in **2 – 63 µm** fraction
- The presence of the pond only **decrease** intermediate grain-size particles (**63 – 250 µm**) in **SPM**
- **Beulie pond** sediments are mainly composed of fine grain-size particles (**2 – 63 µm**)

➤ TOC :

- Moderate, the **pond** present the **higher** amounts
- **Low variations** in **BLS** from 2018 and in **SPM**
- **Seasonal dissimilarities** were higher in **BLS** from 2019



- The **PH** consume a **higher variety** of pharmaceutical products than the CAP
- The **CAP** treatment plant seems **more efficient** than the PH one, exhibiting much lower amounts of compounds. Despite that, **TRI and SCA** are released in **higher rates**
- The **PH** sewage effluent released **high levels** of compounds, with **TRA, ACM, CBZ and OXA** in several $\mu\text{g.L}^{-1}$.



➤ Only 6 compounds quantified

➤ Except the **apparition** and the **disparition** of **OXA** and **DIC**, respectively, **adsorbed compounds** were the same

➤ Amounts between the different compounds were **variable** :

- **CBZ, OXA** and **SCA** presented the **highest** mean concentrations
- **ACM, DIA, TRI** and **DIC** the **lowest**

➤ Amounts **fluctuated** at catchment scale :

- **CBZ, OXA** and **SCA** are on average **higher downstream the pond** and **decreased towards the outlet**
- **DIA** exhibited **higher** amounts **upstream the pond**
- **ACM, TRI** and **DIC** were only **slightly variable**

Results

Accumulated rates (bed-load sediments)



Cationic compounds										Neutral compounds										Anionic compounds										
	ATE			COD			TRA			ACM			CBZ			DIA			OXA			TRI			DIC			SCA		
	M	SD	DF	M	SD	DF	M	SD	DF	M	SD	DF	M	SD	DF	M	SD	DF	M	SD	DF	M	SD	DF	M	SD	DF	M	SD	DF
1	0	/	0/2	0	/	0/2	0	/	0/2	0	/	0/2	0.2	/	1/2	0	/	0/2	0	/	0/2	4.2	0	1/2	0	/	0/2	8.3	±0.1	2/2
2	0	/	0/4	0	/	0/4	0	/	0/4	0	/	0/4	0.6	±0.2	2/4	7.0	±7.0	3/4	0	/	0/4	3.6	±2.0	2/4	0.1	/	1/4	8.6	±11.5	3/4
3	0	/	0/4	0	/	0/4	0	/	0/4	0	/	0/4	2.3	±2.8	2/4	3.4	±2.1	2/4	0.8	/	1/4	3.1	±2.7	2/4	0	/	0/4	18.5	±28.1	4/4
4	0	/	0/4	0	/	0/4	41.9	/	1/4	0	/	0/4	0.6	±0.6	2/4	1.9	/	1/4	0	/	0/4	1.5	±0.4	3/4	0.4	/	1/4	8.9	±10.6	3/4
5	0	/	0/4	0	/	0/4	0	/	0/4	0.6	/	1/4	0.6	±0.4	3/4	3.7	±0.4	2/4	0.1	/	1/4	2.8	±1.2	2/4	0	/	0/4	7.6	±11.1	3/4
6	0	/	0/4	0	/	0/4	0	/	0/4	0	/	0/4	0.3	±0.1	3/4	4.9	±1.8	2/4	0	/	0/4	1.0	±0.5	3/4	0.1	/	1/4	8.1	±10.3	3/4
7	3.4	±4.4	2/4	12.3	/	1/4	0	/	0/4	3.5	/	1/4	51.1	±53.1	4/4	0	/	0/4	33.2	±22.9	4/4	7.1	0	1/4	0.4	/	1/4	26.2	±25.1	4/4
8	3.8	/	1/4	8.1	/	1/4	0	/	0/4	2.5	/	1/4	4.7	±3.0	4/4	1.3	±0.6	2/4	6.3	±5.3	4/4	1.5	±1.2	3/4	0	/	0/4	26.6	±34.0	3/4
9	3.0	±3.2	2/4	17.3	±4.3	2/4	58.12	/	1/4	10.1	/	1/4	30.1	±6.3	4/4	9.1	±3.8	4/4	30.9	±13.2	4/4	6.8	±7.9	4/4	3.7	±4.2	2/4	29.0	±25.4	2/4
10	0	/	0/4	0	/	0/4	0	/	0/4	1.2	/	1/4	3.7	±3.5	4/4	2.5	±1.4	3/4	5.8	±4.6	4/4	1.4	±0.4	2/4	0.2	/	1/4	37.3	±47.0	4/4
11	0	/	0/2	4.2	±5.9	1/2	0	/	0/2	16.9	/	1/2	1.3	±1.8	1/2	39.6	/	1/2	141.4	/	1/2	4.5	±2.6	2/2	4.9	/	1/2	1.7	/	1/2
12	0	/	0/2	0	/	0/2	0	/	0/2	0.7	/	1/2	6.0	±5.1	2/2	2.4	±2.0	2/2	10.8	±11.2	2/2	0	0	0/2	0.2	±0.3	2/2	57.9	/	1/2
13	0	/	0/4	0	/	0/4	0	/	0/4	0	/	0/4	1.6	±0.9	4/4	0	/	0/4	2.0	±1.1	4/4	2.5	±2.1	2/4	0.1	/	1/4	11.4	±13.0	4/4
13b	0	/	0/4	0	/	0/4	0	/	0/4	0	/	0/4	1.4	/	1/4	4.7	/	1/4	0	/	0/4	11.2	0	1/4	0.1	/	1/4	30.5	±17.7	2/4
14	0	/	0/4	0	/	0/4	0	/	0/4	0	/	0/4	2.1	±1.1	2/4	2.2	/	1/4	2.1	±1.9	3/4	15.3	±17.2	2/4	0	/	0/4	49.0	±81.0	4/4

All compounds quantified

Detection frequencies :

- **CBZ, TRI and SCA** were **ubiquitous**, already present before CAP sewage effluent
- **DIA and OXA** also frequent
- **ATE and COD** local presence in some sample sets
- **ACM and DIC** rare and in variable locations
- **TRA** even more rare

Variability and rates :

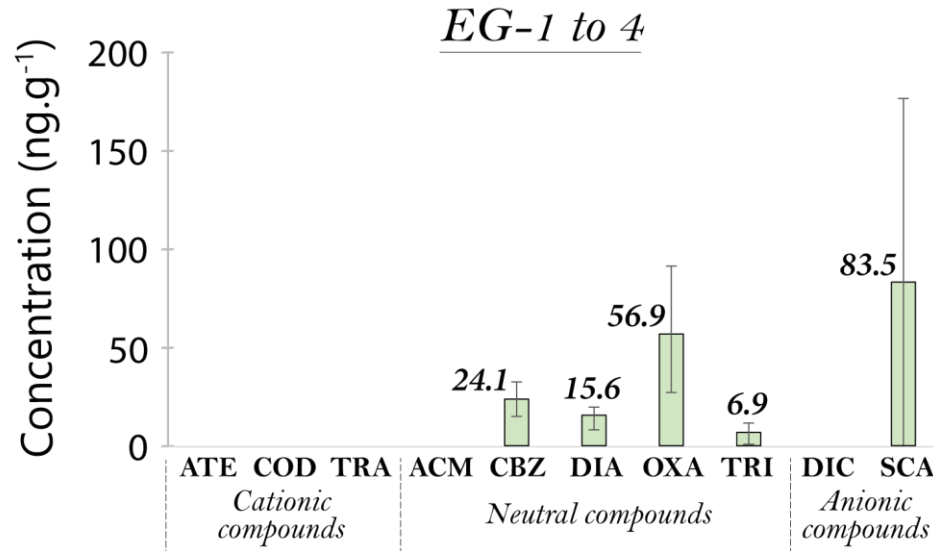
TRA > OXA > SCA > CBZ > DIA > ACM > TRI > COD > DIC > ATE

Most contaminated samples :

BLS-9 > BLS-11 > BLS-7

Surprisingly, samples collected at storm waters discharges (BLS-2 and 13b) presented concentrations in CBZ, DIA, DIC, TRI and SCA

■ Stored rates (the Beulie pond interface sediments)



- Only 5 compounds quantified
- SCA was the **more concentrated** with an increasing concentration towards the pond outlet
- OXA presented **high levels**

- CBZ and DIA had **intermediate concentrations**
- TRI was the compound with **lowest amounts**

Therapeutic group	Compound	Log K_{ow}	Persistence	Major degradation processes
Analgesics	ACM	0.46	Low ^{q,w}	BT ^{q,w}
	SCA	2.26	Low ⁱ	Both ⁱ
Antibiotic	TRI	0.91	High ^{k,q}	Debated ^{i,q}
Anti-inflammatory	DIC	4.98	Low ⁱ	PH ^{m,p}
B-blocker	ATE	0.16	Moderate ^{k,u}	BT ^{s,u,v}
Opioids	COD	1.19	High ^a	PH ^r
Psychotropics	TRA	1.34	High ^l	None ^l
	CBZ	2.45	High ^{k,q}	PH ^q
	DIA	2.63	High ^t	PH ^{m,n}
	OXA	2.24	Moderate ^t	BT ⁿ

References

www.drugbank.ca

ⁱAshton et al., 2004
^jBaena-Nogueras et al., 2017
^kBendz et al., 2005
^lBergheim et al., 2011
^mBoreen et al., 2003
ⁿCalisto and Esteves, 2009
^oFekadu et al., 2019
^pKoumaki et al., 2015
^qLam et al., 2004
^rLin et al., 2014
^sLiu et Williams, 2007
^tLöffler et al., 2005
^uRamil et al., 2010
^vYamamoto et al., 2008
^wYu et al., 2006

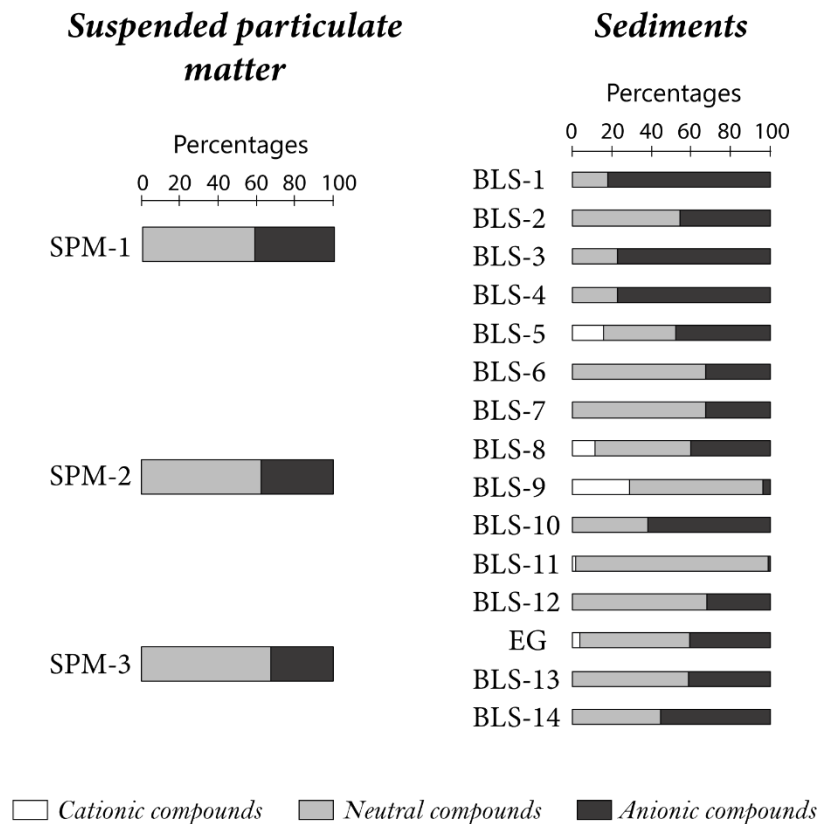
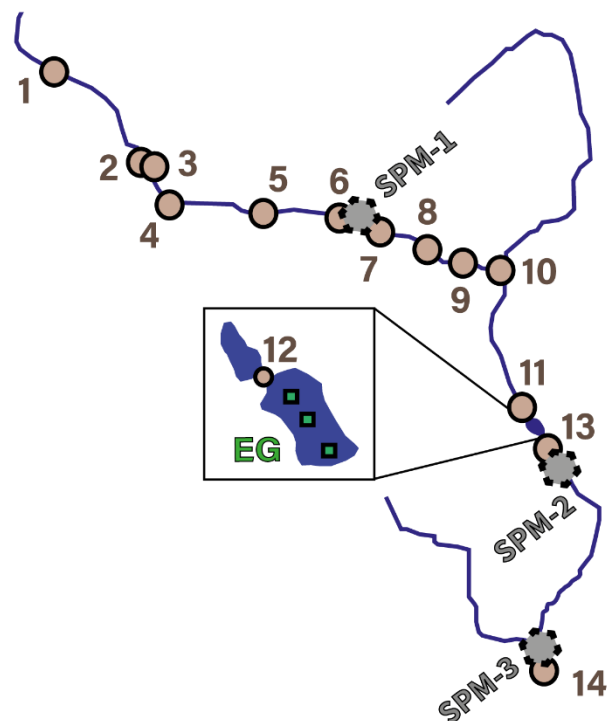
- ACM, SCA and DIC are known to have low persistencies :

ACM and DIC scarcity in every particulate compartments is **consitent**

SCA has an **ubiquitous** presence, probably because of a **low solubility** ($\log K_{ow}$) and **high releasing rates**

- CBZ and TRI ubiquity is congruent with their high persistence in spite of not being the stronger emitted compounds
- OXA is **moderatly** submitted to **biotransformation** but **high releasing rates** and being **DIA** main **metabolite** (Klaminder et al., 2015) explain its **high levels** and **presence**
- DIA** **intermediate concentrations** despite **low amounts** in the **dissolved** phase correspond to a **high persistence**
- ATE** and **COD** have **local presence** even if they are **moderately to highly persistent**, probably due to their **solubility** and **suggesting other driving factors**
- TRA** is the **more discharged** compound and is **highly persistent**, in accordance with the **high concentrations** observed in BLS but can be **desorbed** (Stein et al., 2008) which can explain its **general absence**

Compounds abundance depends on their resistance to degradation but that is not the main process explaining their levels



Neutral compounds are **predominant** in **SPM** and in the Beulie **pond sediments**

Neutral compounds are also **mostly prevalent** in **BLS**

Resulting from **three factors** :

- High **releasing rates**
- High **persistence**
- High **hydrophobic interactions** with **organic matter** as solid matrices have **low contents** of **clay minerals**

Thus compounds rates were mostly driven by their lipophilicities

Few **exceptions** because of **SCA** presence **upstream** sewage effluents (**BLS-1**), **SCA higher releasing rates** at CAP wastewaters discharges (**BLS-3**) and **high sorption rates** of neutral compounds at the **accumulation zone** (**BLS-9**) with an **important level of organic matter** (8,5 %)

Neutral compounds have the better affinity with particulate phases because of their persistence and low contents of clay grain sizes limiting potential ionic interactions

Sorption coefficient : $K_d = [X]_{PP}/[X]_{DP}$ (Williams et al., 2009)

(A pseudo- K_d for the PH because water and sediments were not sampled together)

K_d values could not be calculated for **TRA**, **DIA** and **DIC** because of their absence in the dissolved or particulate phase

Calculated K_d values were in the same ranges than those observed in others studies

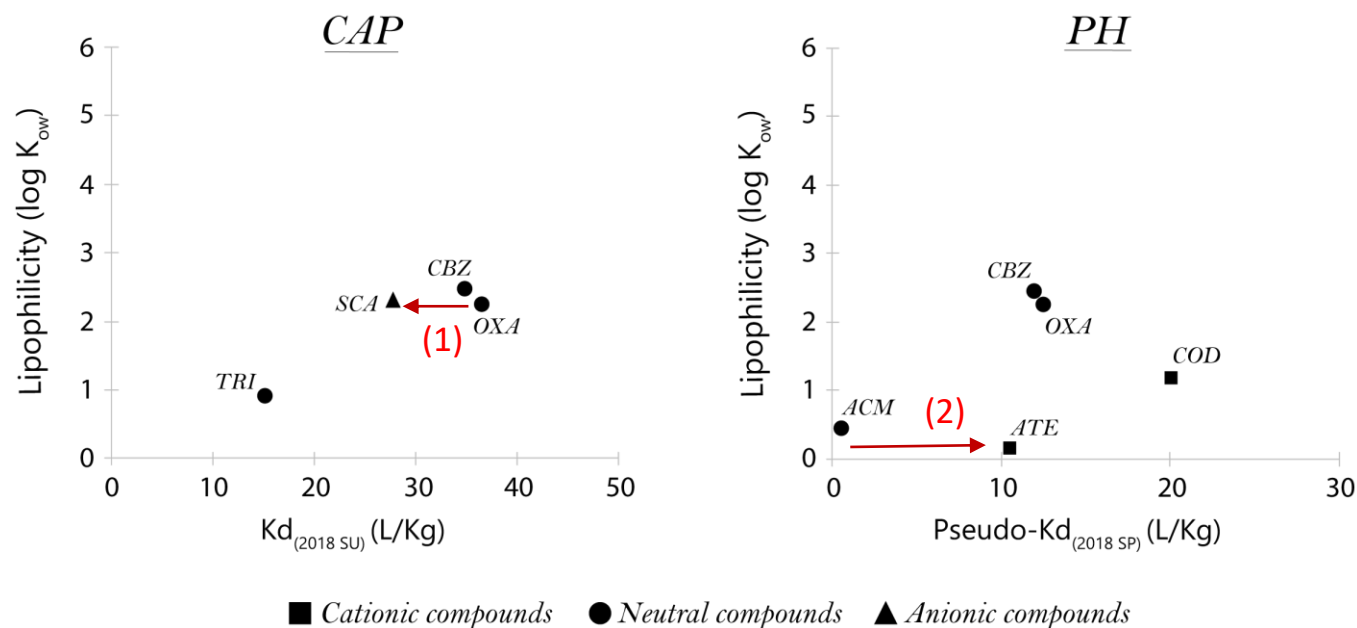
Few exceptions were observed mainly because of different contents in organic matter

Sorption coefficients increased with increasing lipophilicity ($\log K_{ow}$)

TRI and *SCA* exhibited extreme pseudo- K_d for PH sewage effluent, probably because of variable consumption levels

K_d coefficients were different between anionic, cationic and neutral compounds with similar lipophilicities

Effect of the less interactions or contributions of ionic bounding ?



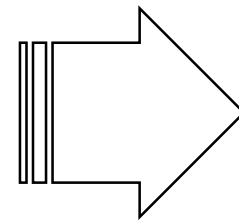
(1) Hydrophobic interactions are less important for anionic compounds with a similar lipophilicity ?

(2) Sorption of cationic compounds does not only occur through hydrophobic interactions ?

Compounds have thus a good affinity with particulate phases

Assemblages founded in BLS samples collected at CAP and PH sewage effluents were the same than in the dissolved phase

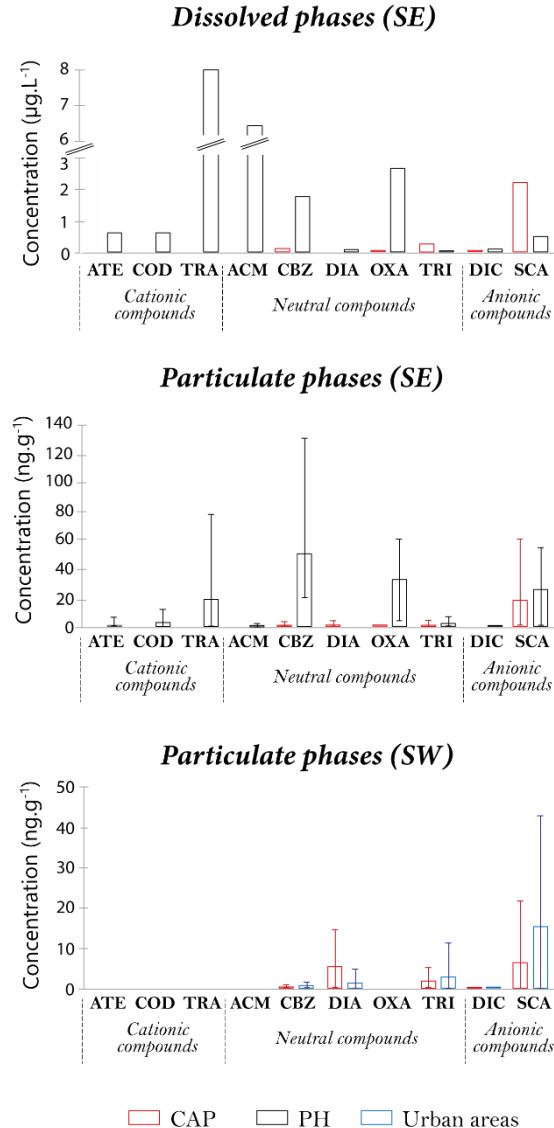
Only DIA and DIC presented dissimilarities but these compounds were released in the lower amounts



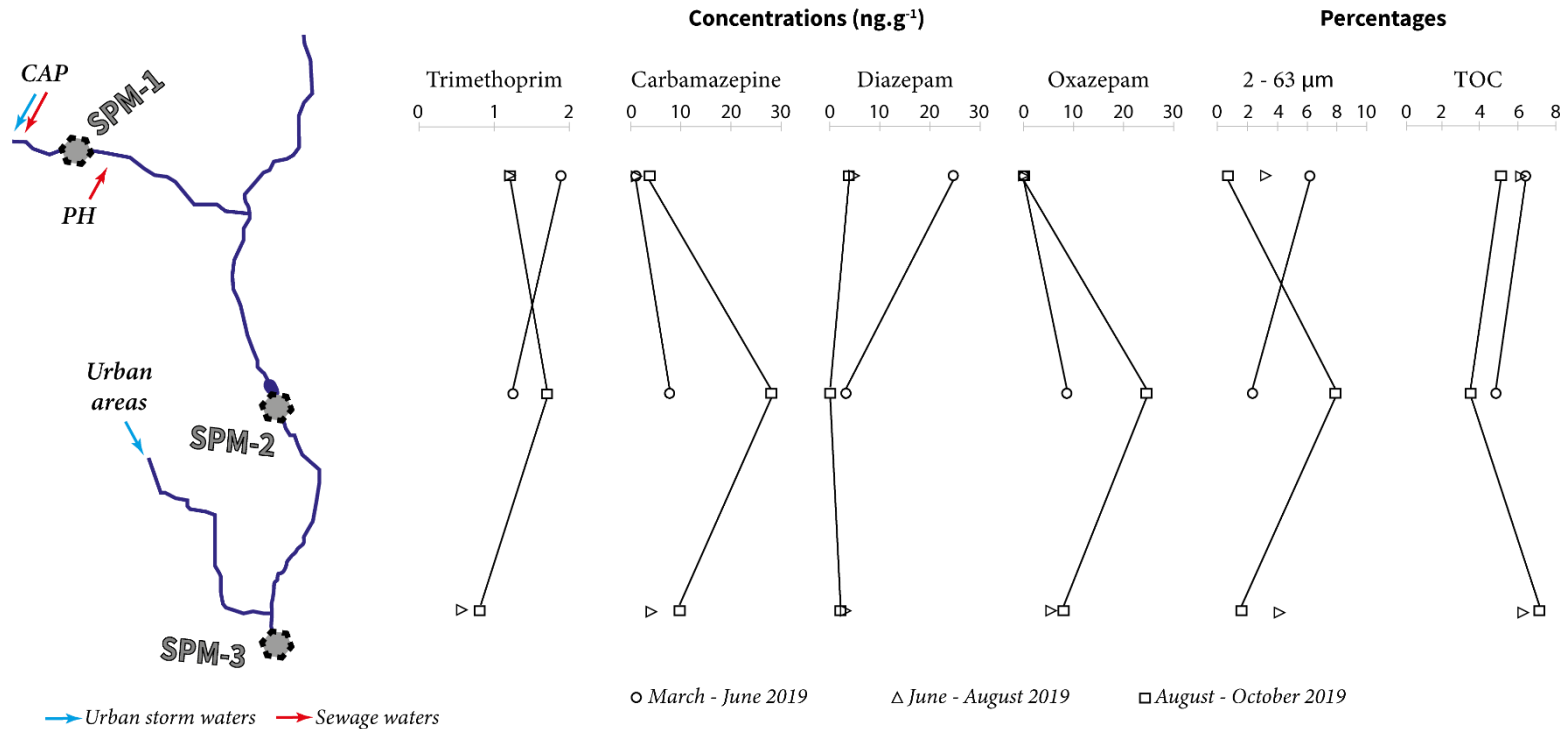
It can also be consider that mixtures observed at storm waters releasing reflect others sources linked to leaks of domestic wastewaters

In this way, households consumption mostly emitted CBZ, DIA, TRI, DIC and SCA

Which is also consistent because both CAP and urban areas storm waters presented the same mixture



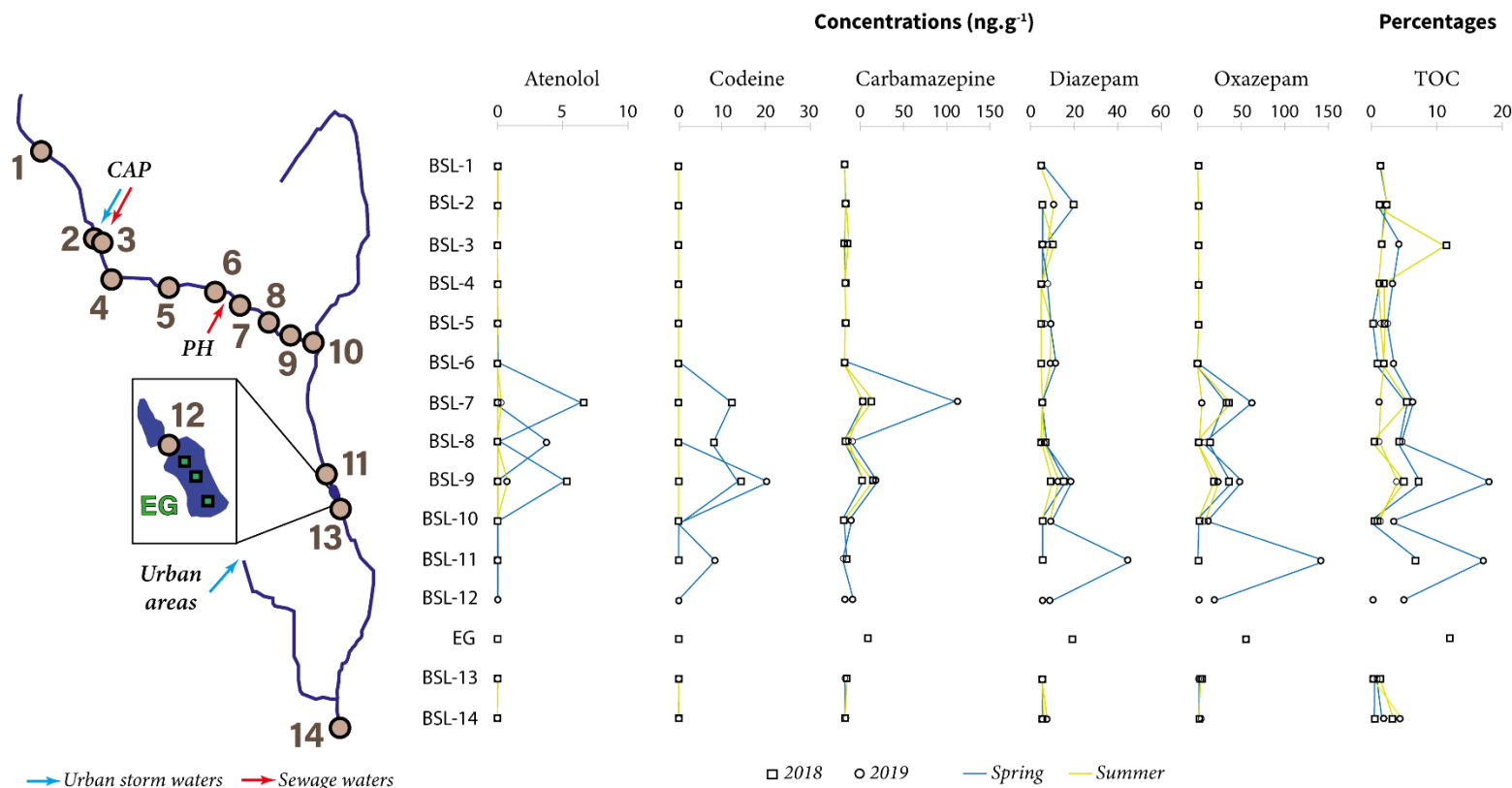
Resistant to degradation processes, 4 neutral compounds with different sources were represented : TRI mostly from the CAP sewage effluent, CBZ and OXA mostly from the PH one and DIA mostly from domestic wastewaters



- With the lowest lipophilicity and low releasing rates, **TRI** exhibited a **low variability** at catchment scale, slightly following the 2 – 63 μm grain – size fraction
- CBZ** and **OXA** increased downstream the pond and **decreased toward the outlet** :
 - > Because of the **adding contribution of the PH** effluent
 - > **High amounts** are **transported** at catchment scale despite the presence of the pond
 - > Amounts do not reach the outlet because of the presence of an accumulation zone between SPM-2 and SPM-3
- DIA** is the **lowest released** compound and **slightly followed the TOC** contents

In SPM, compounds with low concentrations tend to have low variations following their bearing phases, but amounts mainly reflect sources contributions independently of bearing phases levels

Resistant to degradation processes, 5 cationic and neutral compounds with different properties and some already used as tracers were represented (OXA, Maskaoui and Zhou, 2010; CBZ, Amalric et al., 2011)

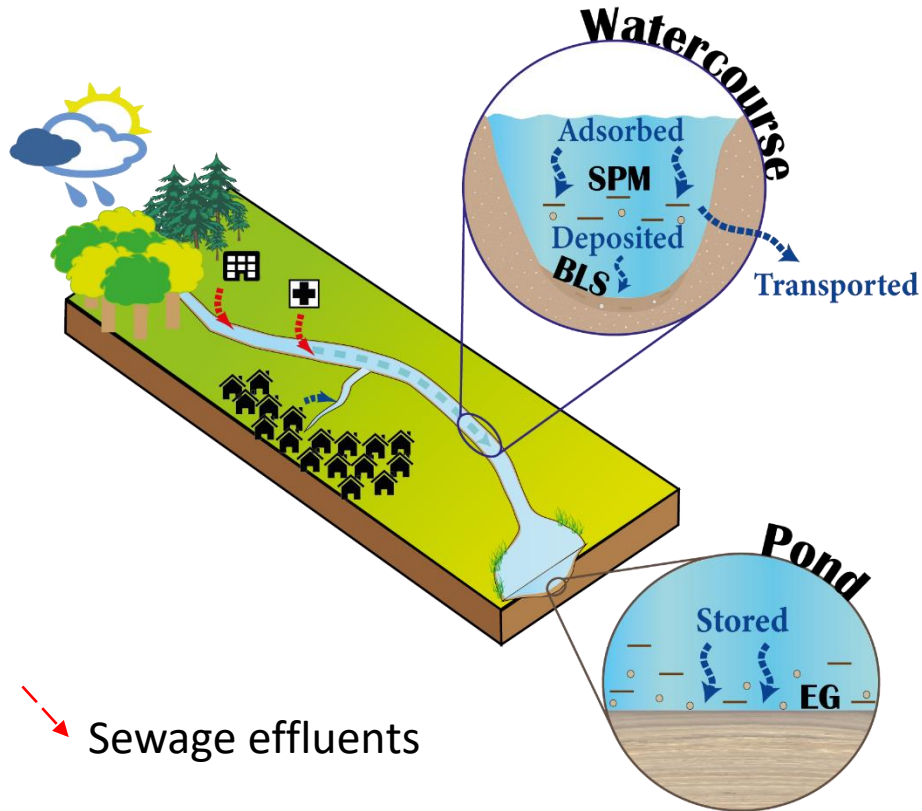


- Pharmaceutical products are **concentrated at discharging sites** and where **organic matter** levels are the highest
- In BLS downstream the pond, contamination levels were very low evidencing the **strong storage capacity of the pond** and the limited presence of accumulation zones demonstrated by lower fine grain-size particles (2 – 63 μm)
- Higher levels are observed in **spring** probably because of **lower degradation processes efficiency** resulting from **higher flow rates** (Amalric et al., 2011), a **colder weather** (Kim and Carlson, 2007) and **higher organic matter inputs**

In sediments, spatial distribution of compounds mainly reflect discharging sites and the sedimentary dynamic of the stream
Seasonal variations linked to the degradation processes efficiency appear too

Conclusions

- ✓ All investigated compounds presented an affinity with the particulate phase and mixture observed in bed-load sediments collected at discharging sites reflected the dissolved phase content



- ✓ Degradation processes play a role in compounds abundance but releasing rates and compounds solubilities were the major factors driving compounds sorption
- ✓ Neutral compounds were predominant because of higher releasing rates and persistence
- ✓ Organic matter is the main bearing phase as clay grain sizes were very low, promoting hydrophobic interactions
- ✓ Hydrophobic interactions seem lower for anionic compounds and in addition to ionic ones for cationic compounds
- ✓ Spatial distribution in suspended particulate matter mainly reflect sources contributions but this fraction have a good transportation capacity at a catchment scale

- ✓ Spatial distribution in sediments is linked to discharging site and the sedimentary dynamic of the watercourse depending on compounds bearing phases

- ✓ Further investigations will be needed to demonstrate :
 - If sorption processes are different between a dynamic environment like in suspended particulate matter and a stagnant one like in bed-load sediments
 - If the K_d coefficient can highlight different kinds of interactions contributing to compounds sorption
- ✓ The Egoutier stream can be a good opportunity to observe the particulate content and evolution for other groups of compounds
- ✓ The Beulie pond can be a perfect candidate to investigate the archive of contamination levels temporal evolution as it is present since centuries

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