



# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

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Pontes e Parcerias nos Países de Língua Portuguesa

Coimbra, 5 de Julho de 2016

# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## Emerging Pollutants

**“Pollutants currently not included in routine monitoring programmes at Union level but which could pose a significant risk requiring regulation, depending upon their potential ecotoxicological and toxicological effects and on their levels in the aquatic environment”**

*Directive 2013/39/EU*

# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais



**Pharmaceuticals**

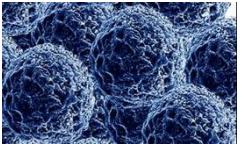
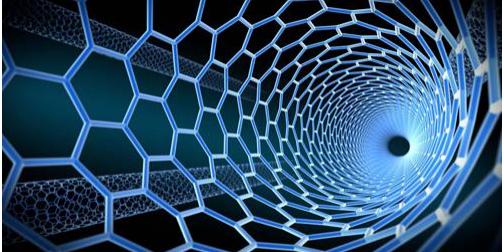


**Personal care products**

## EMERGING POLLUTANTS

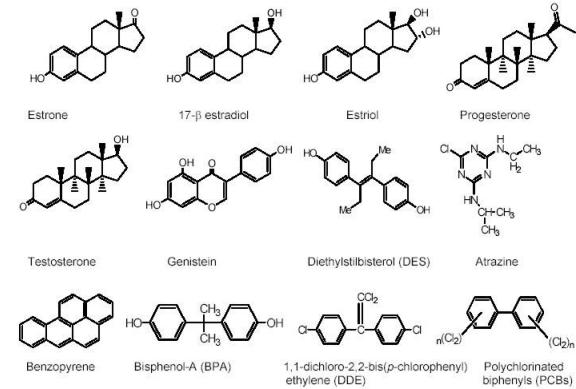


**Surfactants**



**Nanomaterials**

Cristina Delerue-Matos – 05/07/2016



**Endocrine disruptors**

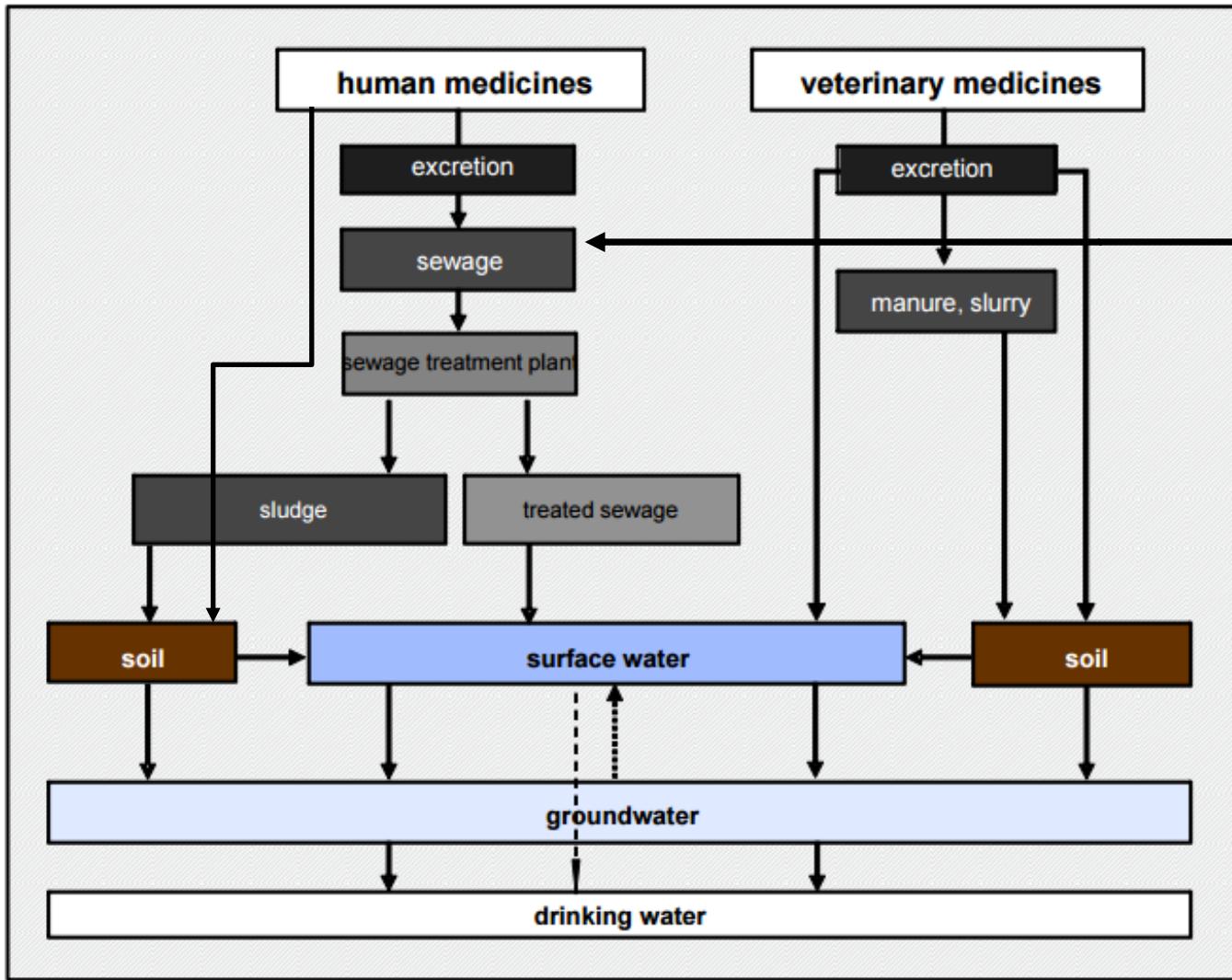


**Fuel additives**

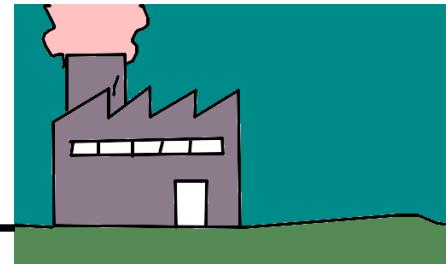


**Disinfection byproducts**

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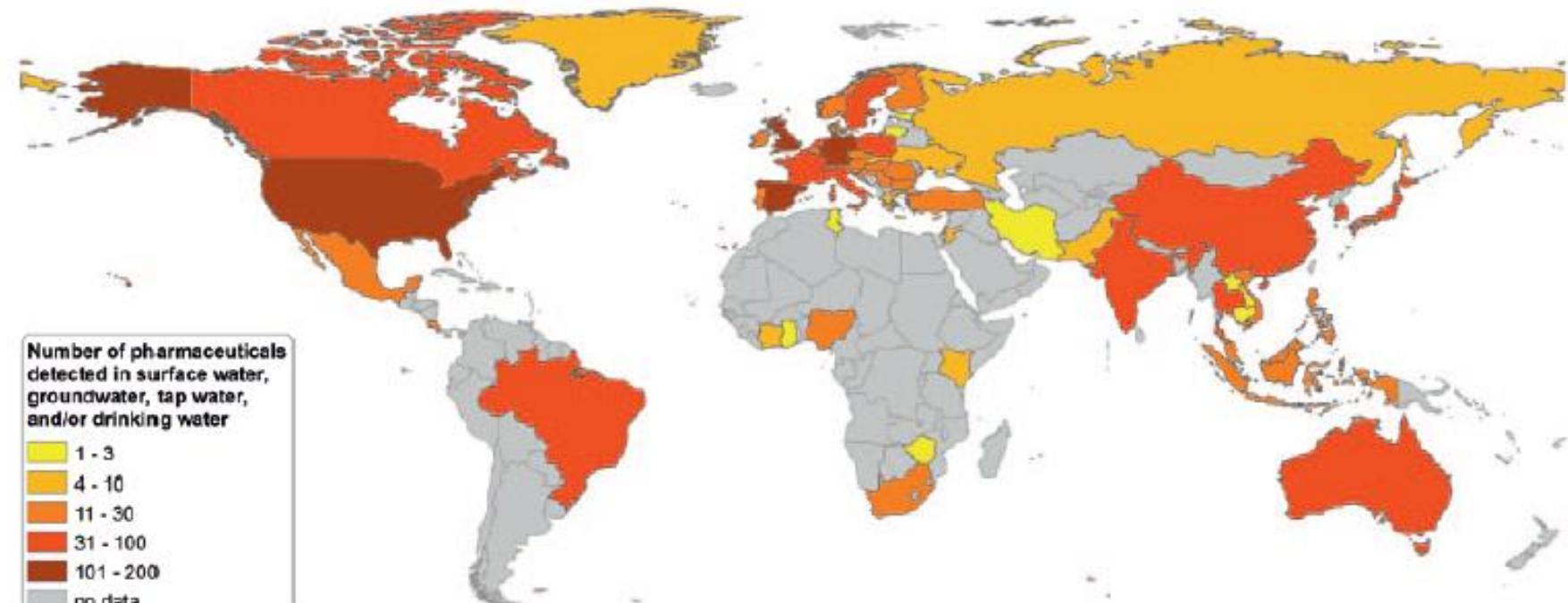
## SOURCES AND FATE IN THE ENVIRONMENT



Pharmaceuticals do not need to persist in the environment, since they are continuously introduced

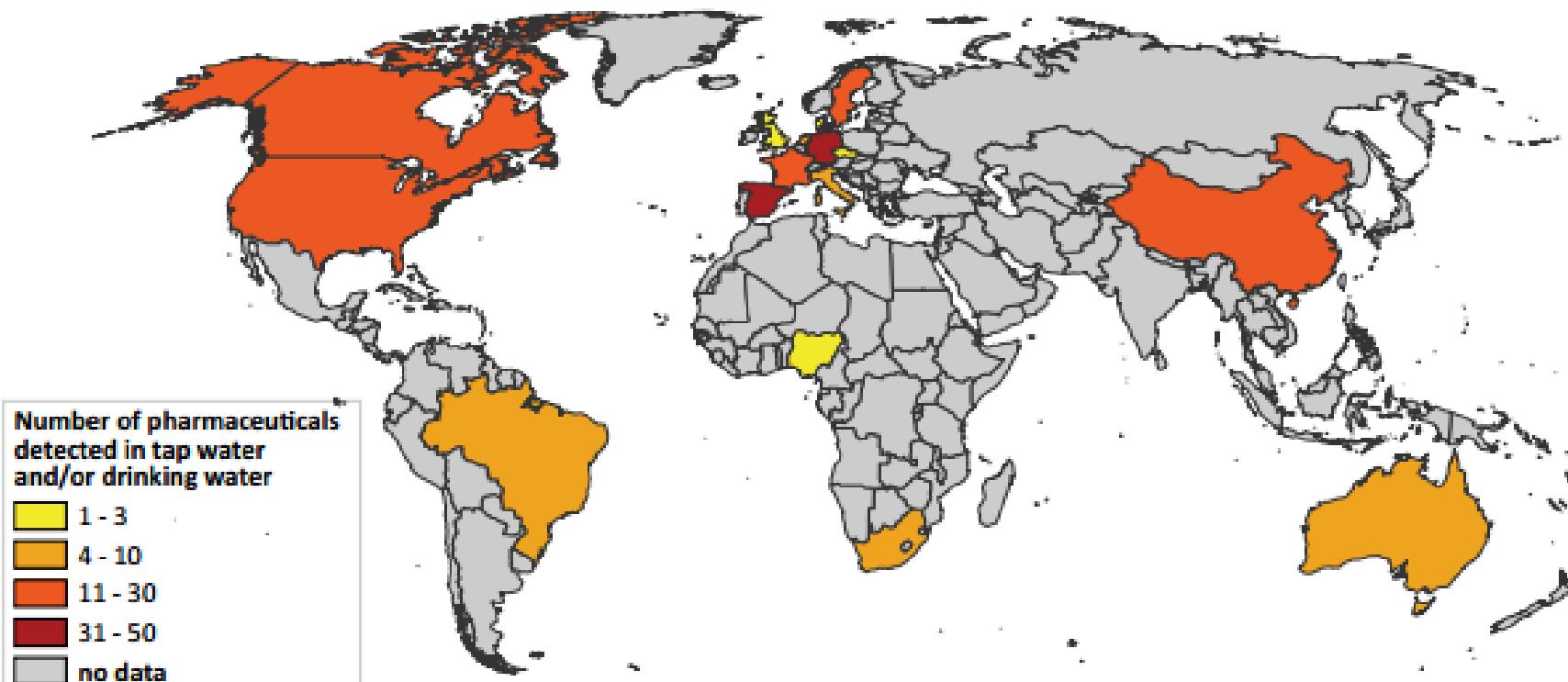
# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

- Pharmaceuticals have been detected in the environment worldwide
- Nowadays there are a few data of the presence of pharmaceuticals in developing countries



# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

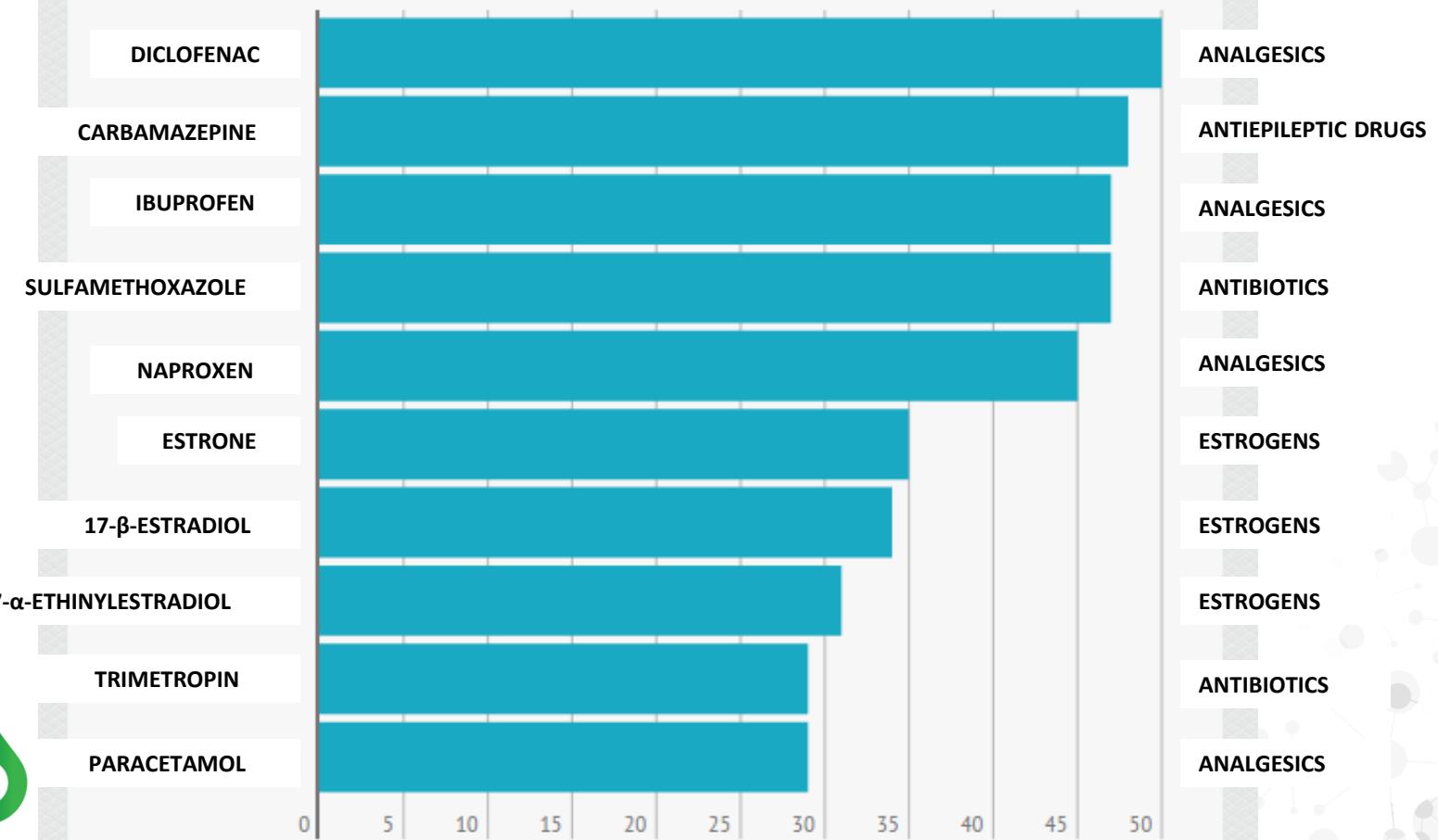
- Number of pharmaceuticals found in drinking water worldwide.



# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## Number of pharmaceuticals detected in surface water, ground water, tap water and/or drinking water

Top 10 pharmaceuticals and the number of countries in which they have been found in the aquatic environment



# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## ANALYTICAL PROCEDURE

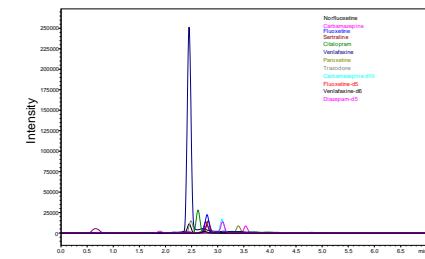
Sampling



Sample preparation



Chromatographic separation



Detection



Results



# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## PHARMACEUTICALS DETECTED BY OUR GROUP REQUIMTE/LAQV-ISEP

- ✓ PRESENCE OF PHARMACEUTICALS IN PORTUGUESE RIVERS: **IBUPROFEN**
- ✓ PRESENCE OF PHARMACEUTICALS IN PORTUGUESE RIVERS: **PARACETAMOL, PARACETAMOL-GLUCURONIDE AND P-AMINOPHENOL**
- ✓ EVALUATION OF THE PRESENCE OF PHARMACEUTICALS IN PORTUGUESE SEAWATERS
- ✓ CONTRIBUTION OF HOSPITAL EFFLUENTS TO THE LOAD OF PHARMACEUTICALS INTO URBAN WASTEWATERS
- ✓ IMPACT OF URBAN WASTEWATERS TO THE LOAD OF PHARMACEUTICALS INTO SURFACE WATERS



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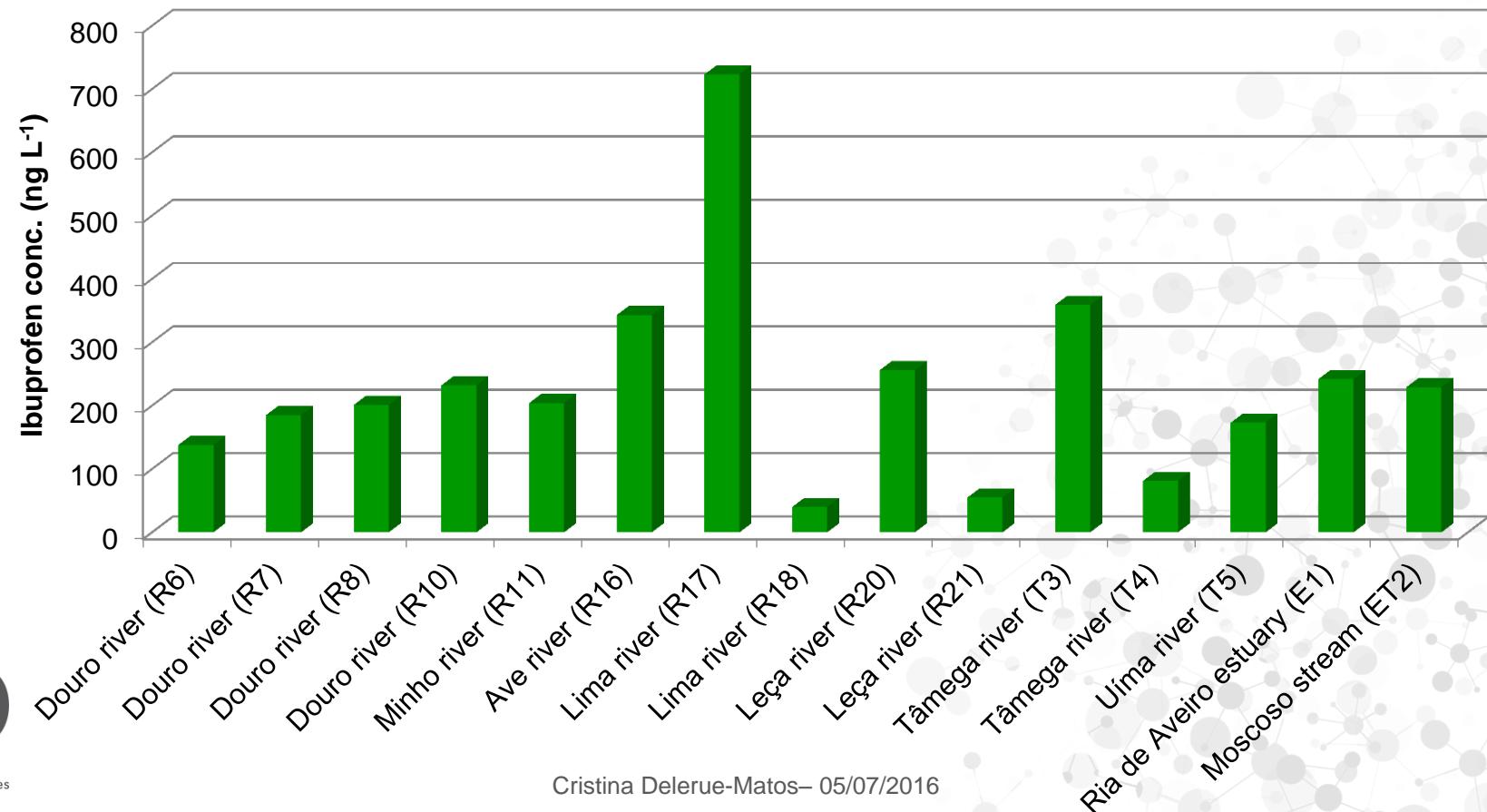
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# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## PRESENCE OF PHARMACEUTICALS IN PORTUGUESE RIVERS: IBUPROFEN

- 33 surface water samples (rivers, stream, estuaries)
- **15 positive samples** for the presence of **ibuprofen**



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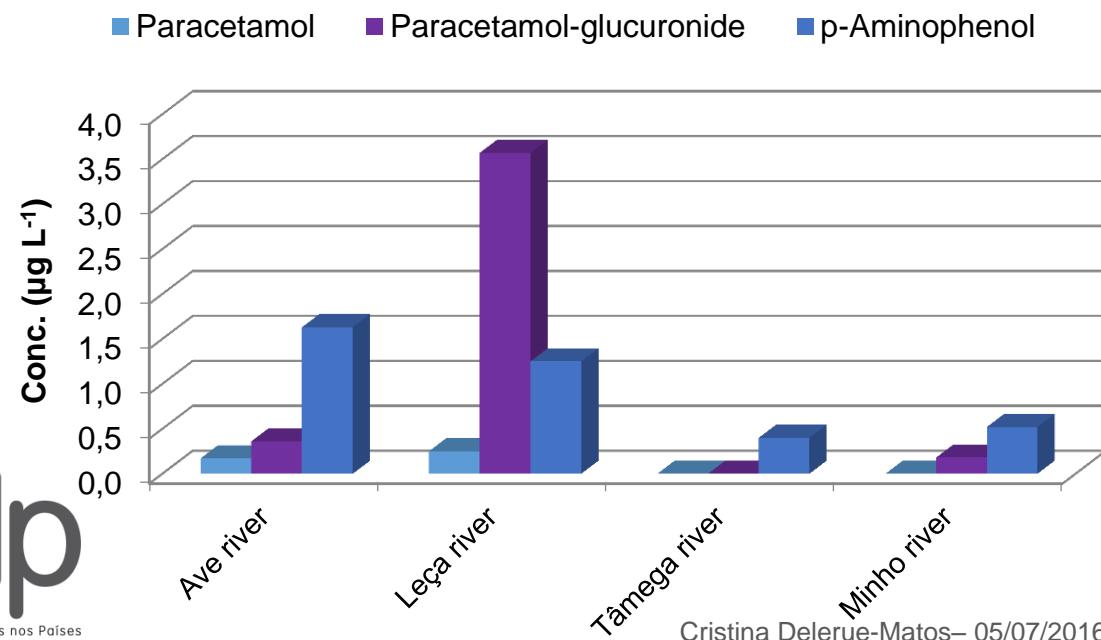
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# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## PRESENCE OF PHARMACEUTICALS IN PORTUGUESE RIVERS: PARACETAMOL, PARACETAMOL-GLUCURONIDE AND P-AMINOPHENOL

- 7 Rivers of the North of Portugal
- At least one compound detected in all the studied rivers
- **Metabolite and transformation product** detected in **higher concentrations** than the parent compound



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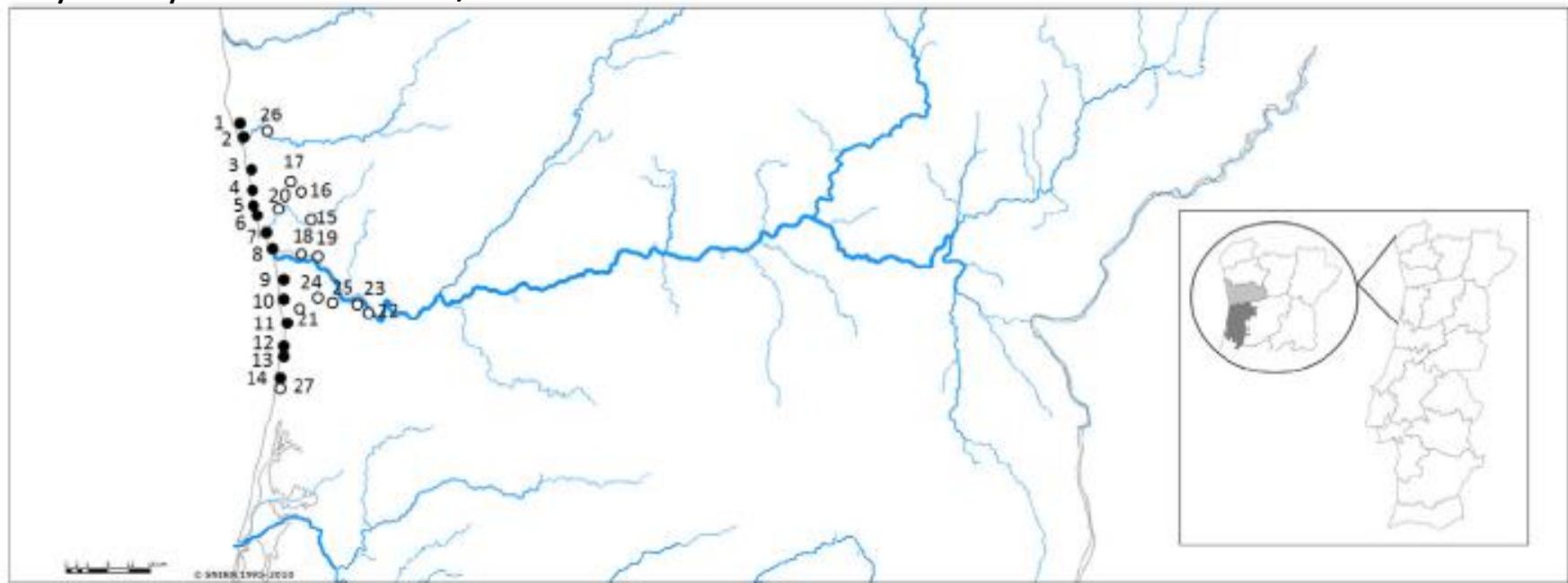
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# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## EVALUATION OF THE PRESENCE OF PHARMACEUTICALS IN PORTUGUESE SEAWATERS

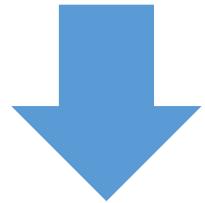
- 101 Seawater samples were collected in Atlantic Ocean
- 14 Beaches with different bathing water quality (excellent, good, sufficient)
- 5 Cities and surrounding area (Vila do Conde, Matosinhos, Porto, Vila Nova de Gaia, Espinho)
- Analyzed by SPE-UHPLC-MS/MS



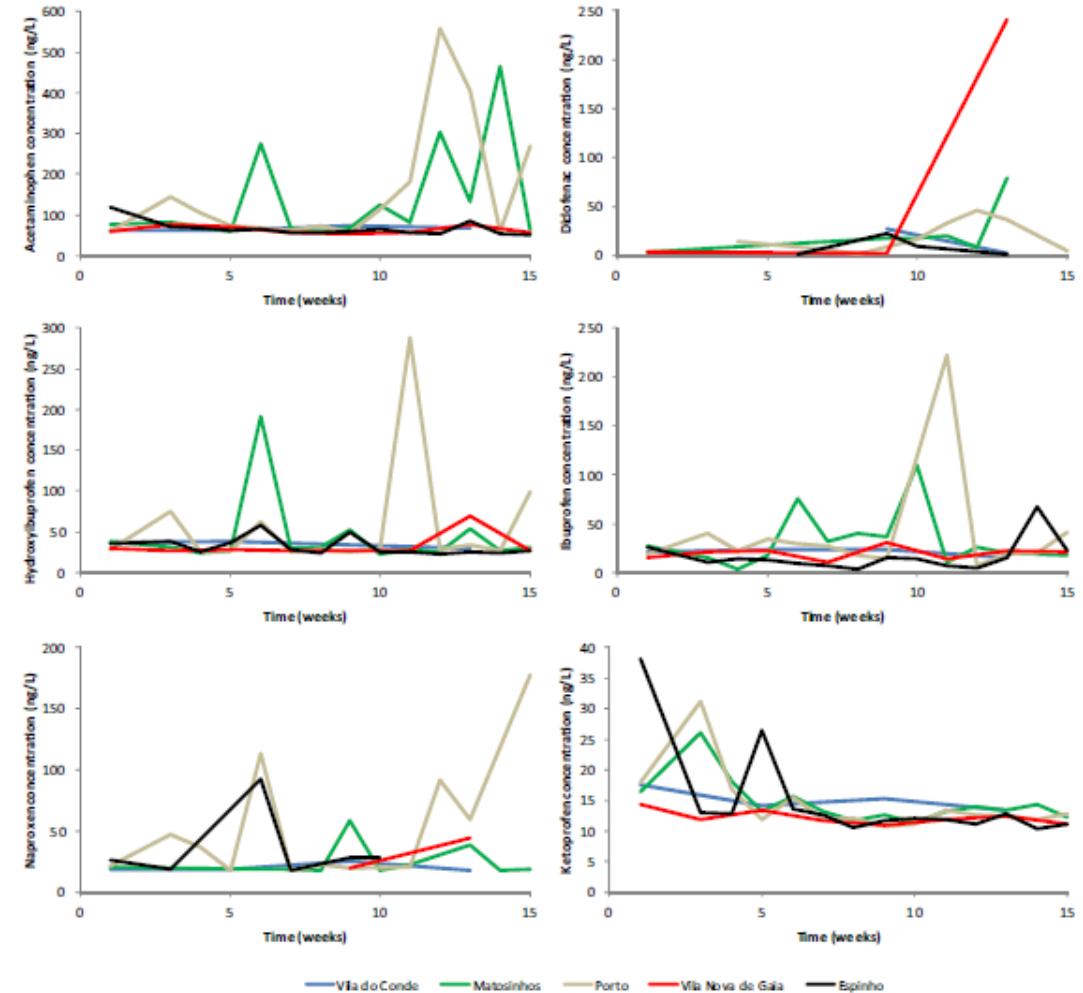
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## TEMPORAL DISTRIBUTION OF AINEs/ANALGESICS ALONG BATHING SEASON 2013

Highest concentrations detected in  
August and September



Increase of the population in the  
studied area during these months



# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## ENVIRONMENTAL RISK ASSESSMENT

### Environmental Risk Assessment

- Based on Hazard Quotient (HQ) using 3 trophic levels (algae, daphnids and fish)
- “Worst case scenario” approach

$$HQ = MEC/PNEC$$

**MEC** – Measured Environmental Concentration

**PNEC** – Predicted No-effect Concentration

$HQ \geq 1$

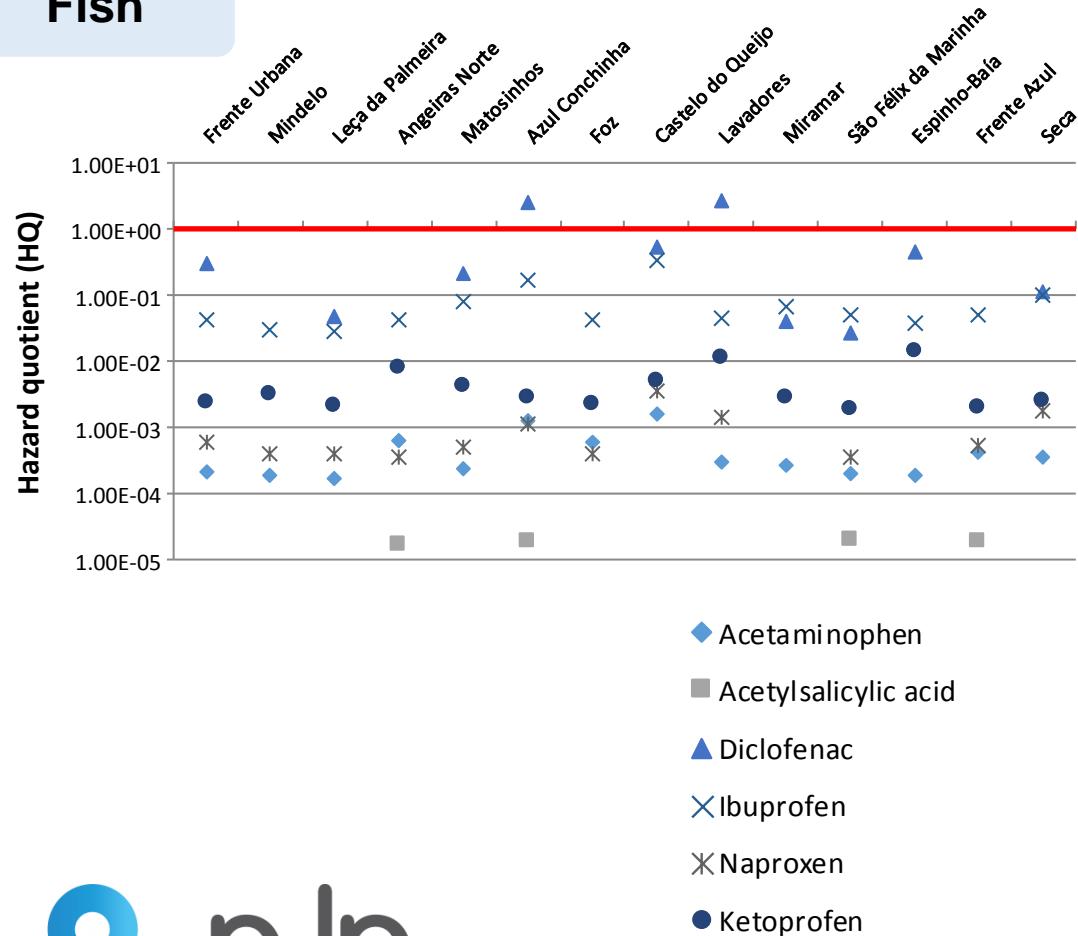
- Potential environmental risk

$HQ < 1$

- No risk is expected

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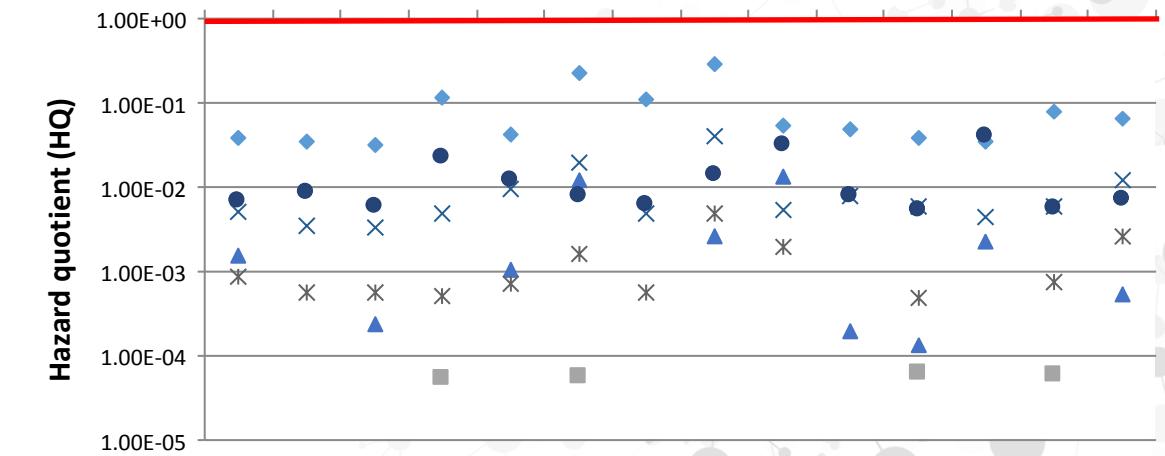
## Fish



## ENVIRONMENTAL RISK ASSESSMENT - SEAWATERS

### Diclofenac

### Daphnid

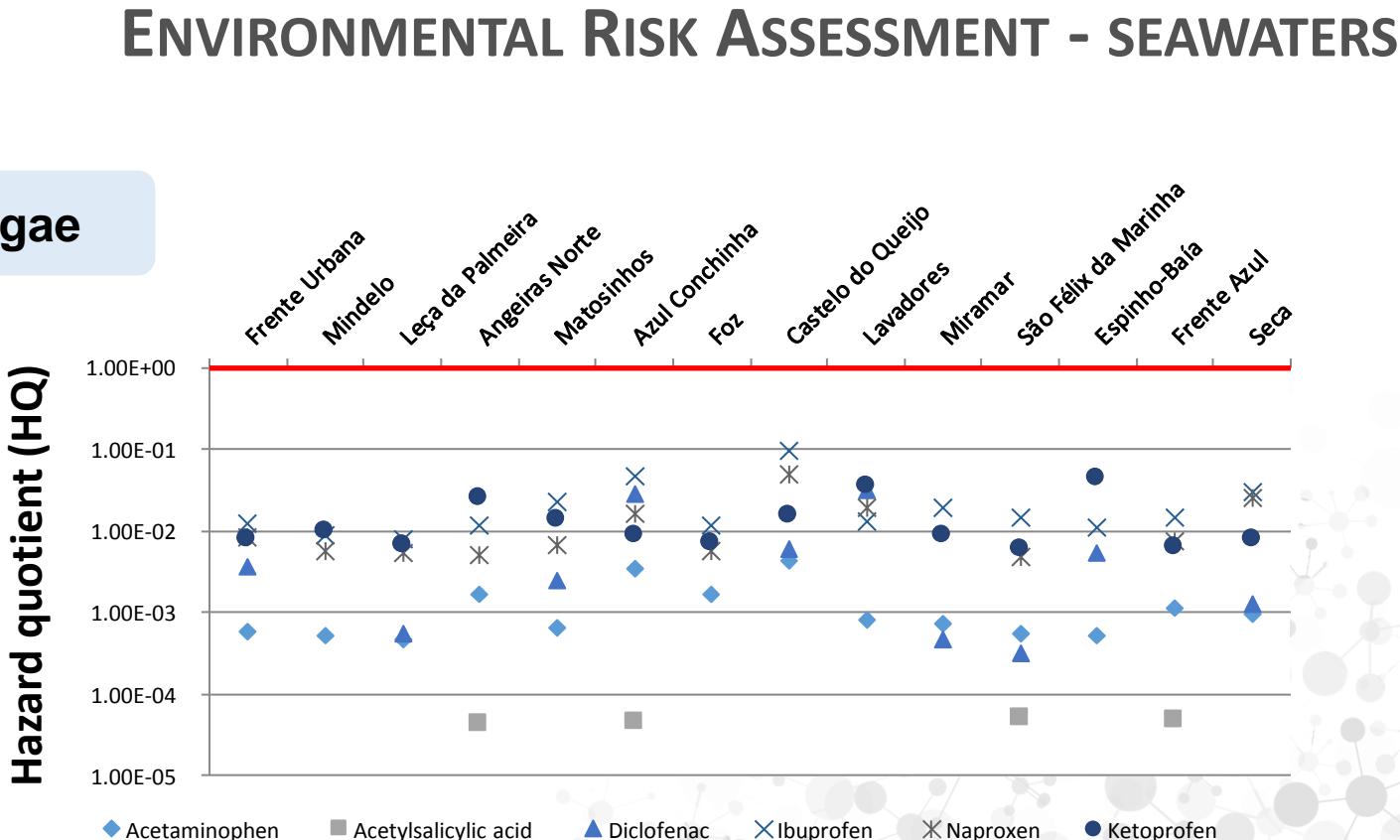


# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais



## Algae

- ◆ Acetaminophen
- Acetylsalicylic acid
- ▲ Diclofenac
- ✖ Ibuprofen
- ✖ Naproxen
- Ketoprofen



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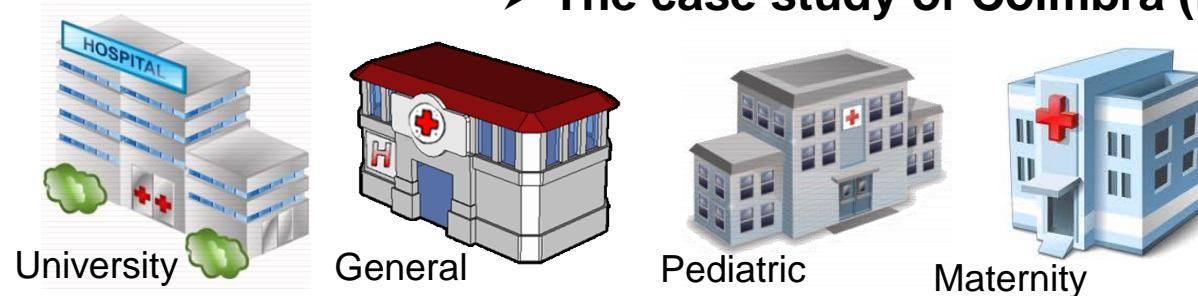
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# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## CONTRIBUTION OF HOSPITAL EFFLUENTS TO THE LOAD OF PHARMACEUTICALS INTO URBAN WASTEWATERS

➤ The case study of Coimbra (Portugal)



Number of beds			
1456	350	110	96

- ✓ 78 pharmaceuticals
- ✓ 20 therapeutic classes
- ✓ SPE-UHPLC-MS/MS
- ✓ Sampling period: February-May 2011



WWTP

# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## CONTRIBUTION OF HOSPITAL EFFLUENTS TO THE LOAD OF PHARMACEUTICALS INTO URBAN WASTEWATERS

➤ Contamination pattern (relative concentration (%)) for each therapeutic class)



University hospital



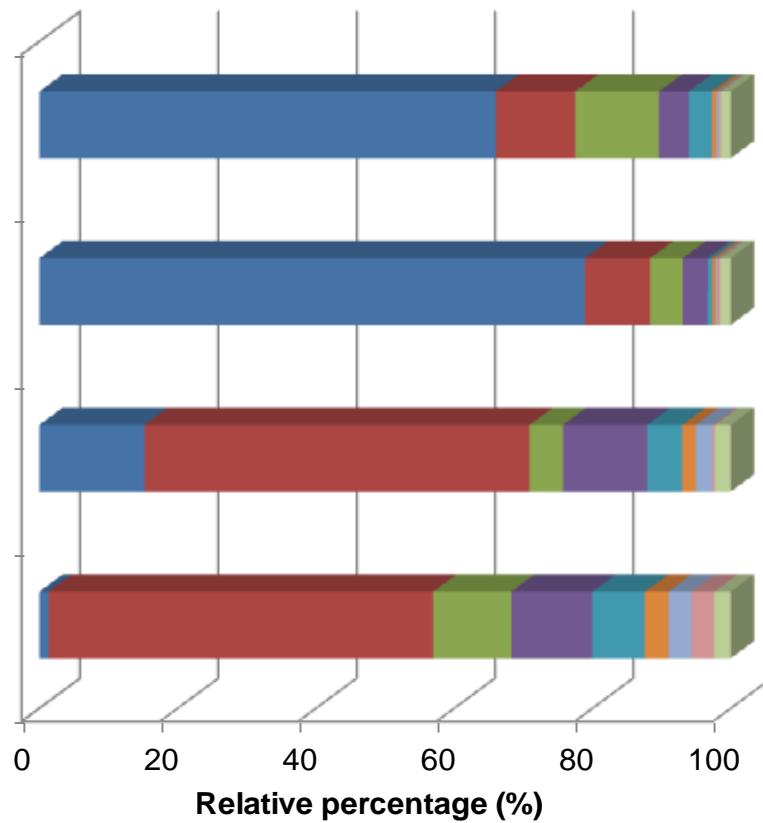
General hospital



Pediatric hospital



Maternity

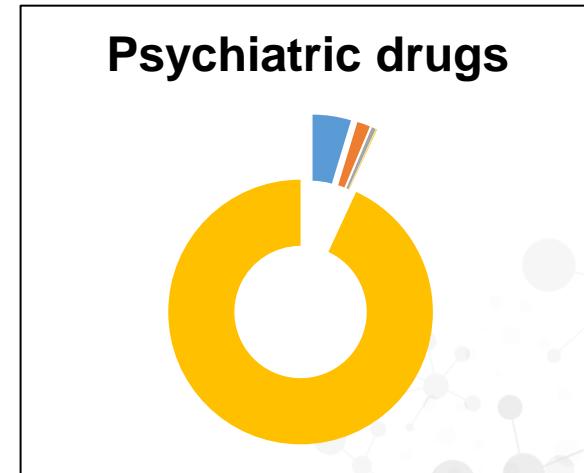
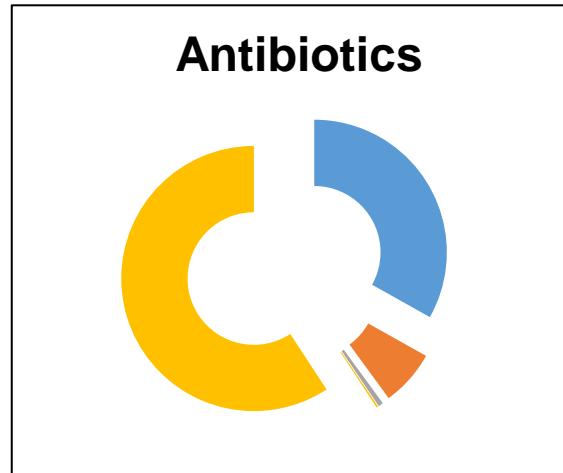
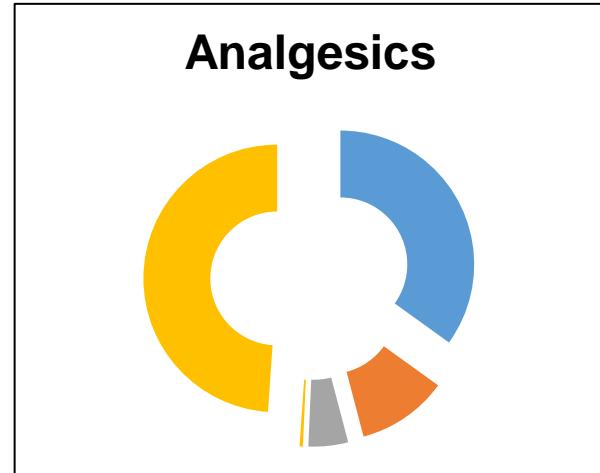


- X-ray contrast agent (iopromide)
- Analgesics/anti-inflammatories
- Antibiotics
- Diuretics
- Antihypertensives
- Psychiatric drugs
- β-Blockers
- Oral antidiabetic (metformin)
- Others

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## IMPACT OF HOSPITAL EFFLUENTS INTO URBAN WASTEWATERS

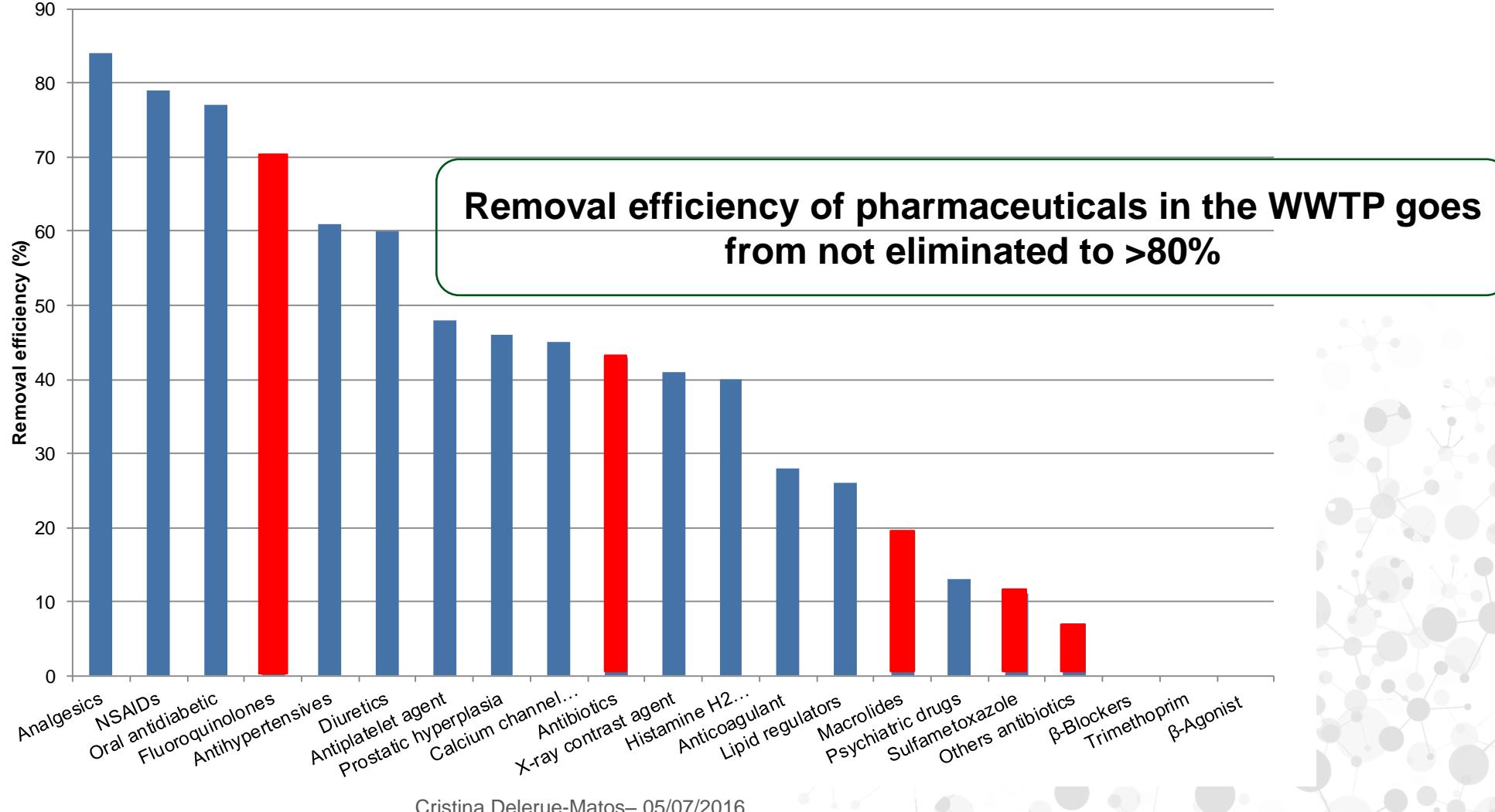
➤ Higher impact of hospital effluents



- University hospital
- General hospital
- Pediatric hospital
- Maternity hospital
- Urban input

# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## CONTRIBUTION OF HOSPITAL EFFLUENTS TO THE LOAD OF PHARMACEUTICALS INTO URBAN WASTEWATERS



# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## ENVIRONMENTAL RISK ASSESSMENT – WWTP EFFLUENTS

- Pharmaceuticals that have a potential environmental risk (HQ > 1)

The level of pharmaceuticals found in WWTP effluents showed a more pronounced potential risk for algae



Pharmaceutical	HQ algae
Sulfamethoxazole	62.6
Ciprofloxacin	279
Ofloxacin	22.9
Azithromycin	15.6
Clarithromycin	3.34
Setraline	1.20

- Antibiotics are among pharmaceuticals that have a high potential environmental risk

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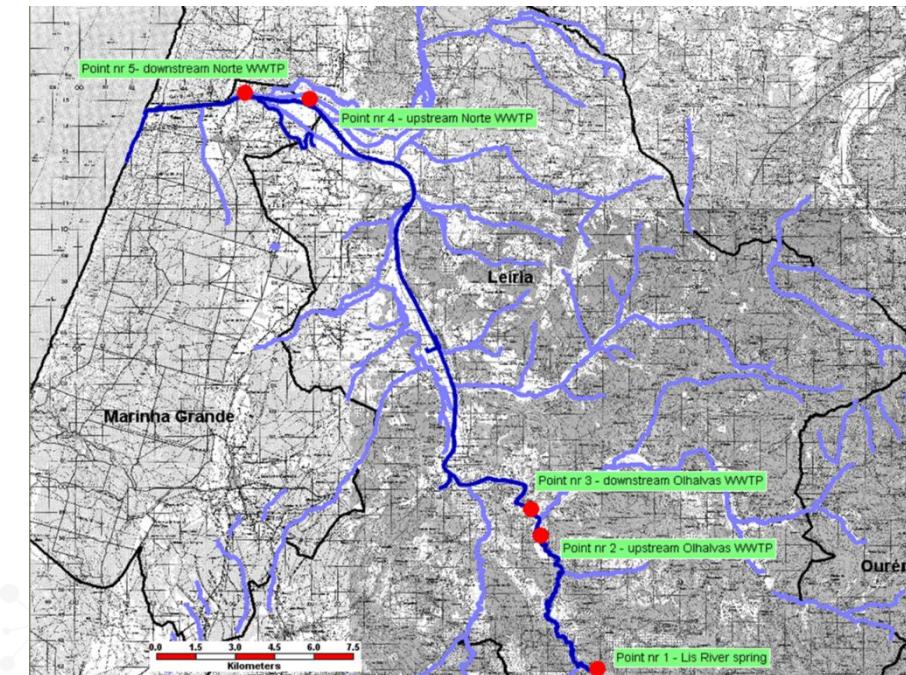
## IMPACT OF URBAN WASTEWATERS TO THE LOAD OF PHARMACEUTICALS INTO SURFACE WATERS

- The impact of WWTP effluents was evaluated using Lis river as a case study
- Sampling points were selected through the river
- WWTPs that discharge their effluent into the river were also monitored

### ✓ 9 Sampling points:

- Source of Lis River
- Upstream WWTP of Olhalvas
- Downstream WWTP of Olhalvas
- WWTP of Olhalvas (influent and effluent)
- Upstream WWTP Norte
- Downstream WWTP Norte
- WWTP Norte (influent and effluent)

### ✓ Sampling period: August 2013-June 2014



# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

WWTP 1



WWTP 2



- Designed for 49,315 p.e.
- Secondary treatment by activated sludge
- Average capacity: 6250 m<sup>3</sup>/day

- Designed for 248,685 p.e.
- Secondary treatment by activated sludge
- Tertiary treatment by UV during bathing season
- Average capacity: 37,997 m<sup>3</sup>/day

# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

Pharmaceuticals

## Anti-inflammatories/Analgesic

- ❖ Ibuprofen
- ❖ Hydroxyibuprofen
- ❖ Carboxyibuprofen
- ❖ Acetaminophen
- ❖ Naproxen
- ❖ Ketoprofen

## Psychiatric drugs

- ❖ Citalopram
- ❖ Diazepam
- ❖ Sertraline
- ❖ Fluoxetine
- ❖ Trazodone
- ❖ Venlafaxine
- ❖ Norfluoxetine
- ❖ Paroxetine
- ❖ Carbamazepine
- ❖ 10, 11-Epoxicarbamazepine

## Antibiotics

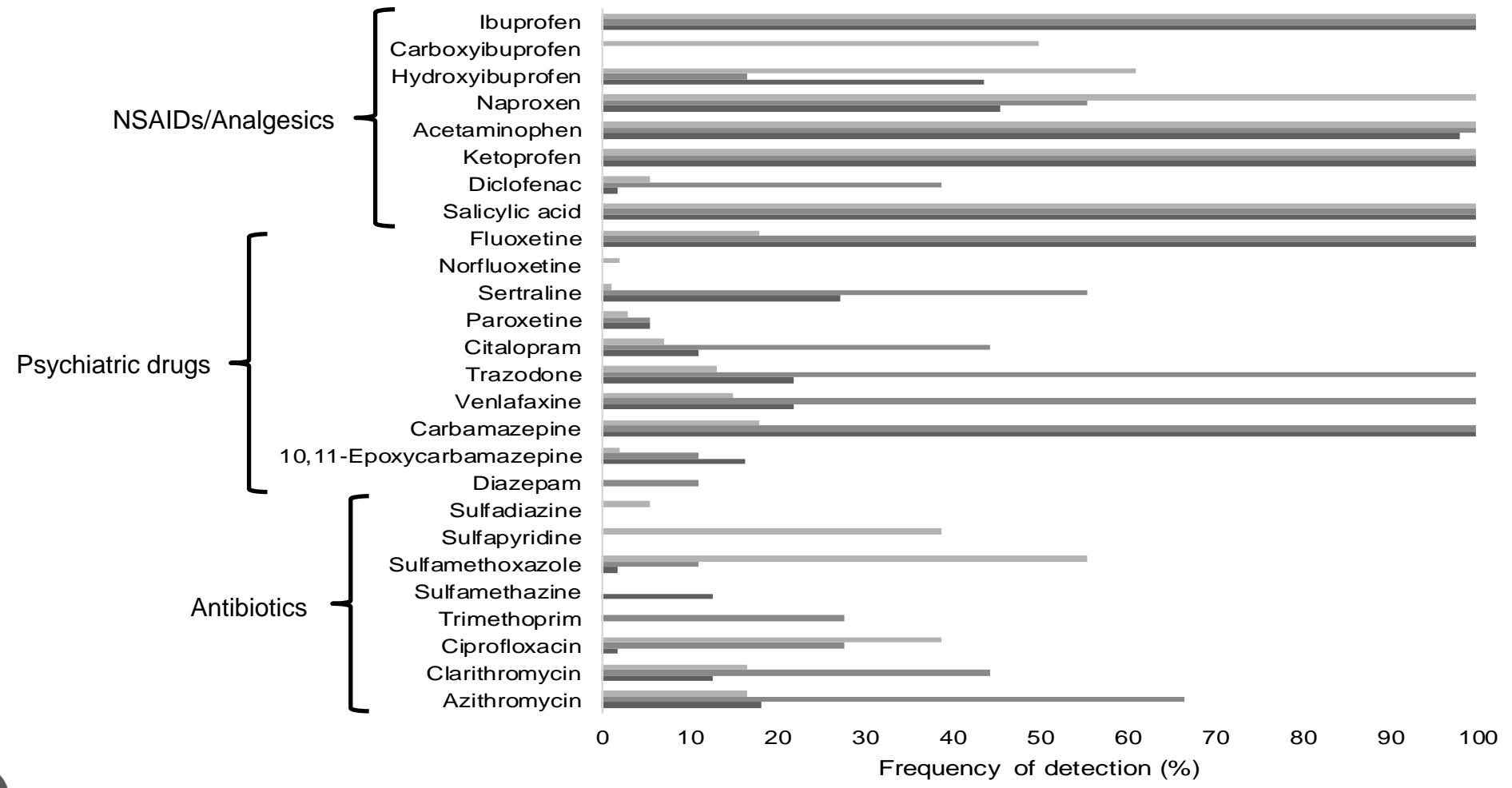
- ❖ Clarithromycin
- ❖ Sulfadiazine
- ❖ Sulfadimethoxine
- ❖ Sulfamethazine
- ❖ Sulfamethoxazole
- ❖ Trimethoprim
- ❖ Ciprofloxacin
- ❖ Sulfapyridine
- ❖ Enrofloxacin
- ❖ Sulfamethoxypyridazine
- ❖ Azithromycin
- ❖ Ofloxacin

## SPE-UHPLC-MS/MS

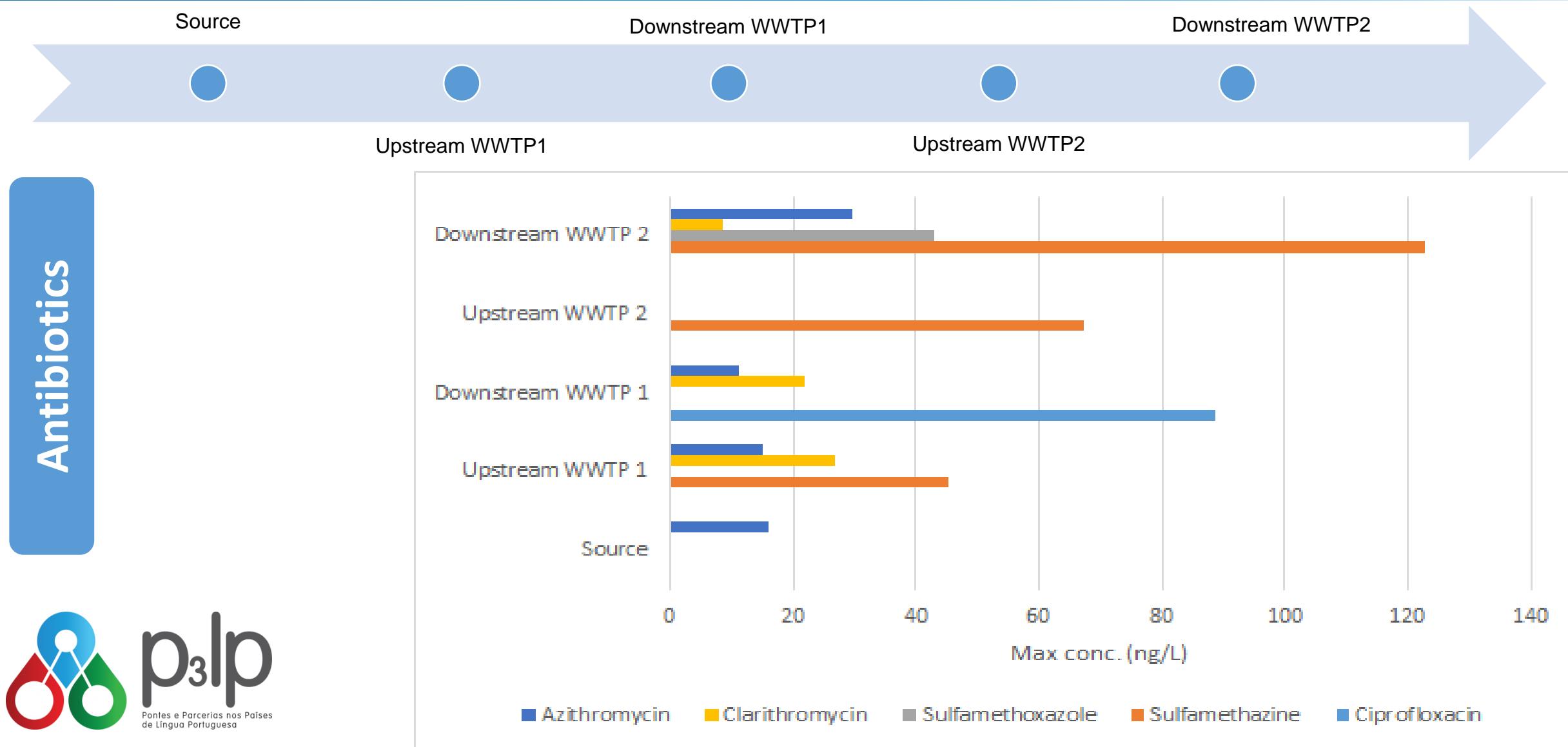
- ❖ Nimesulide
- ❖ Diclofenac
- ❖ Acetylsalicylic acid
- ❖ Salicylic acid



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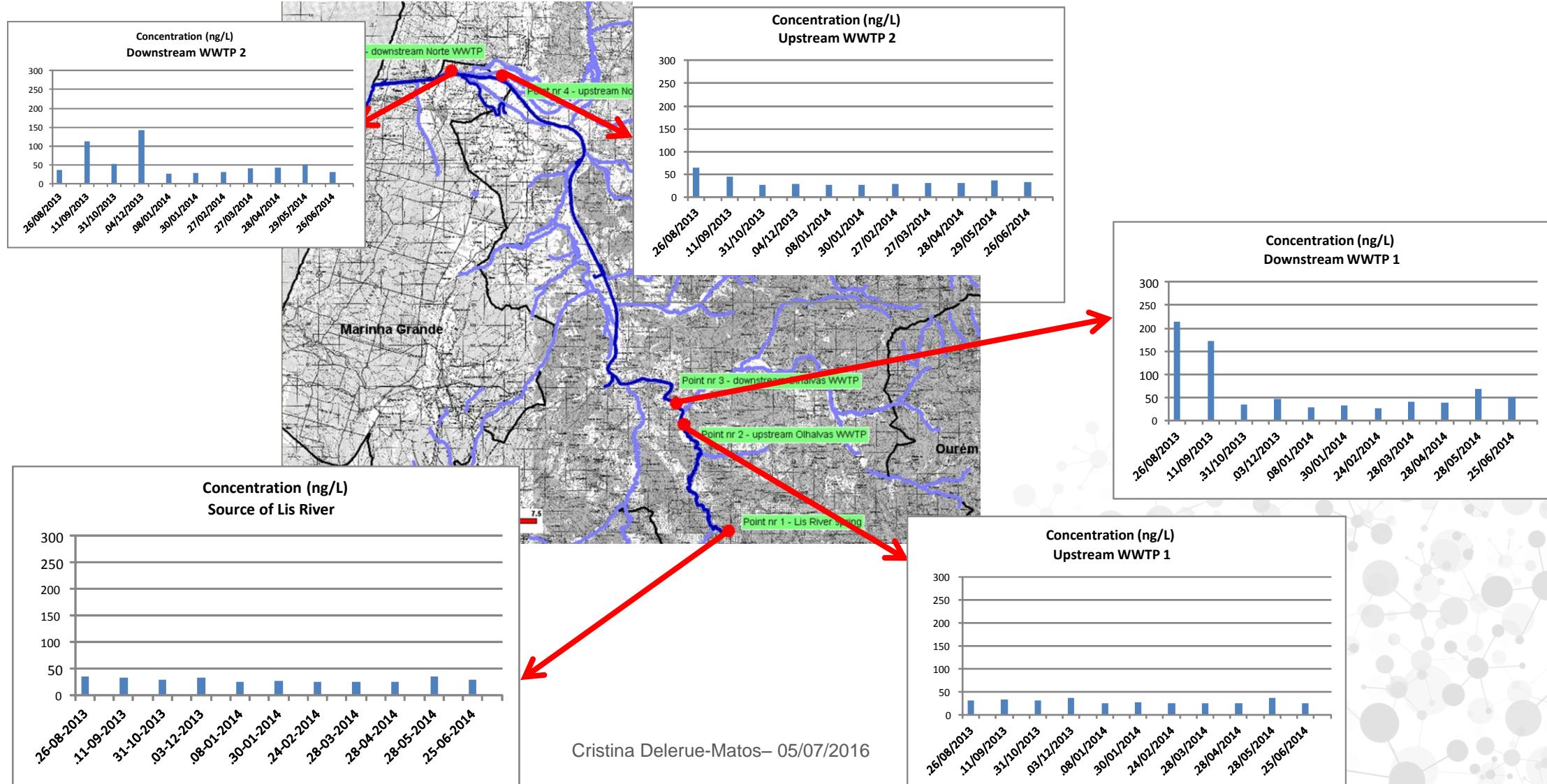


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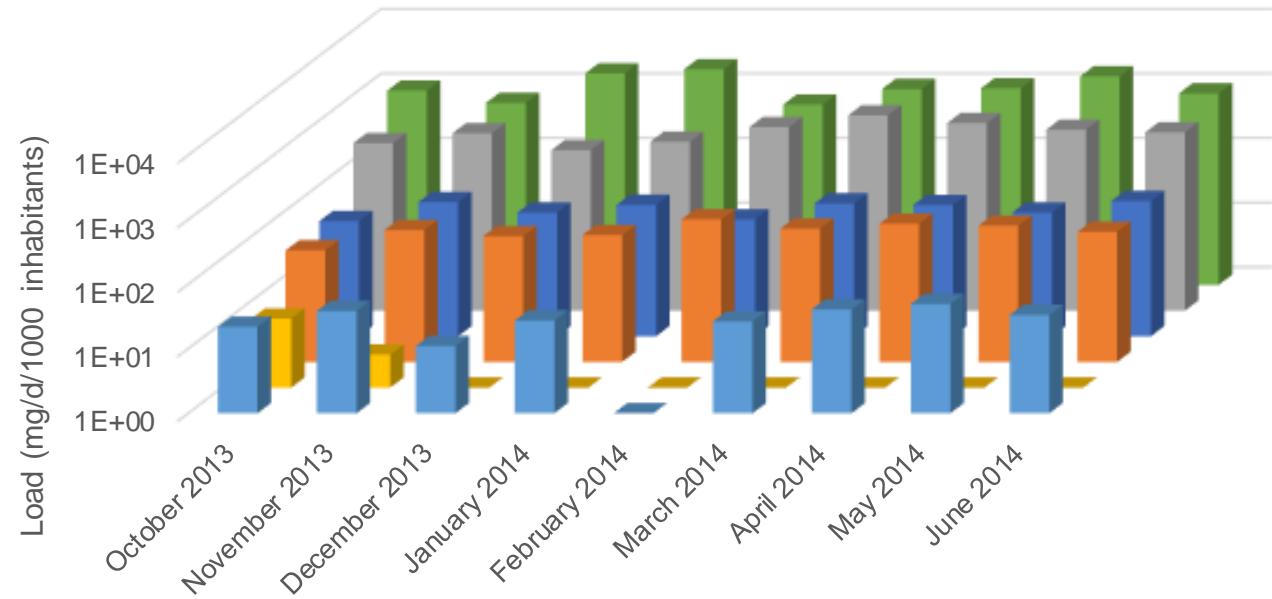
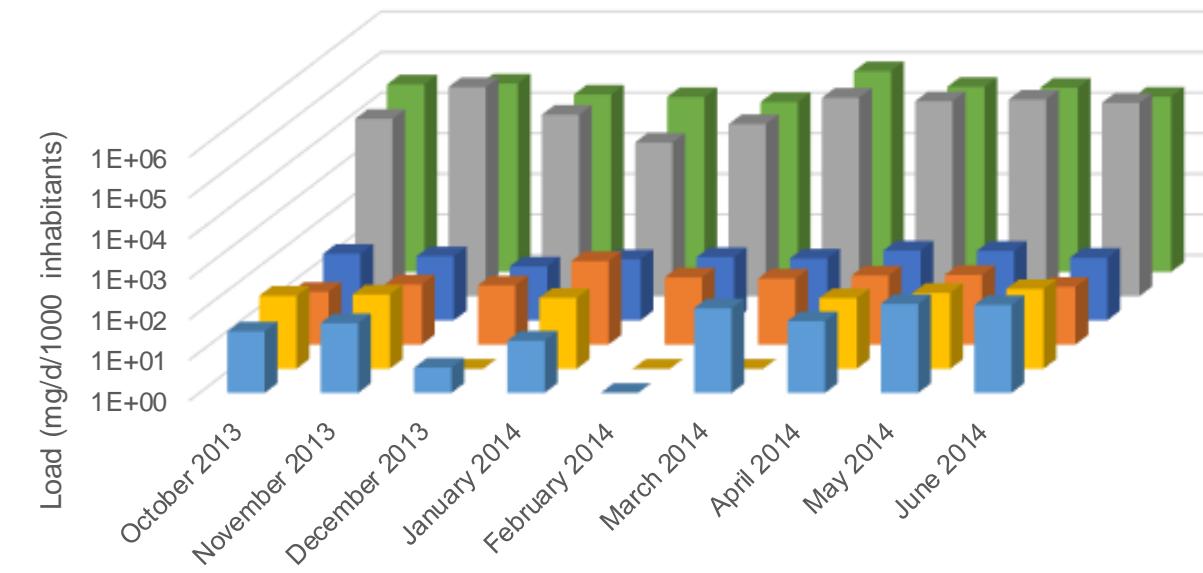


# Carbamazepine

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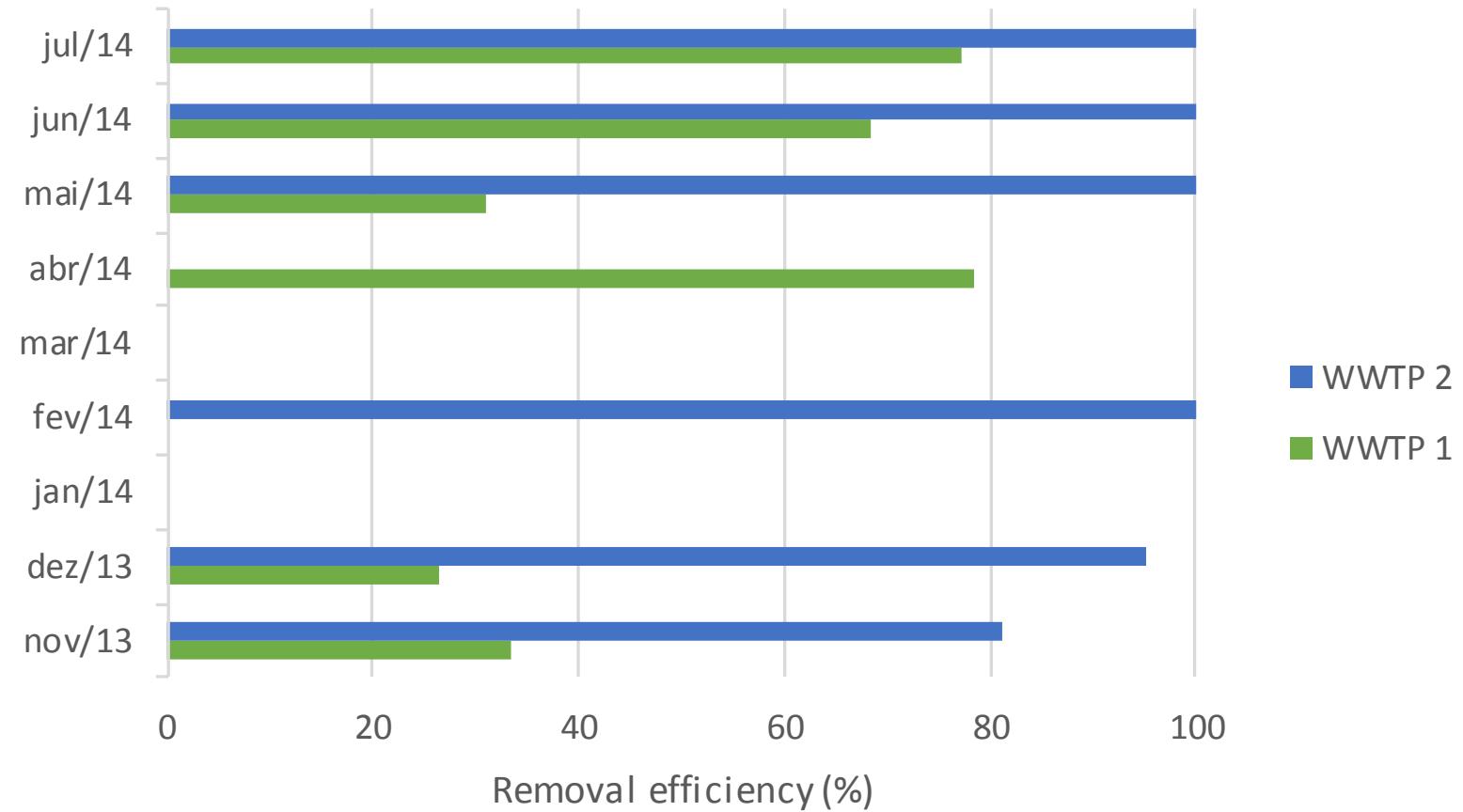


# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais



# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

## Antibiotics



- WWTP 2 shows a higher removal efficiency of antibiotics than WWTP 1

# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

Fish



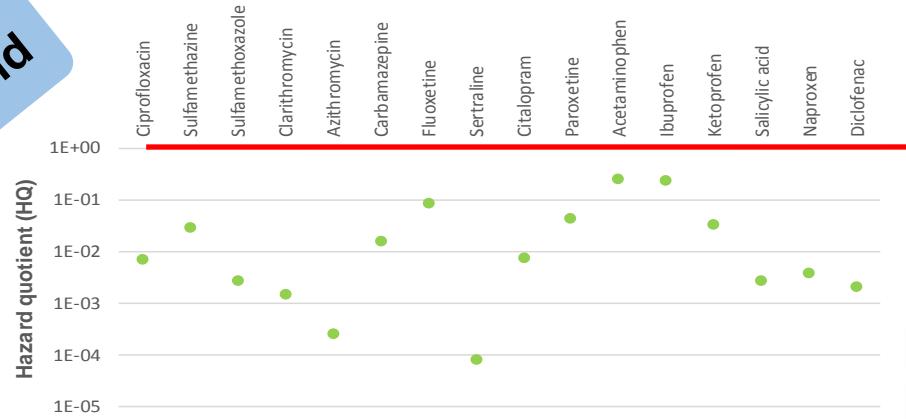
➤ Ibuprofen

Algae



## ENVIRONMENTAL RISK ASSESSMENT – LIS RIVER

Daphnid



- Ciprofloxacin
- Sulfamethozazole
- Clarithromycin
- Azithromycin

# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

WWTP 1



WWTP 2



## ENVIRONMENTAL RISK ASSESSMENT WWTP EFFLUENTS

Fish

- Ibuprofen
- Diclofenac

# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

WWTP 1



WWTP 2



## ENVIRONMENTAL RISK ASSESSMENT WWTP EFFLUENTS

Daphnid

➤ Acetaminophen

# O problema dos poluentes emergentes e a sua presença em águas superficiais e águas residuais

WWTP 1



- Ciprofloxacin
- Sulfamethoxazole
- Clarithromycin
- Azithromycin
- Fluoxetine

WWTP 2



## ENVIRONMENTAL RISK ASSESSMENT WWTP EFFLUENTS

Algae

- Sulfamethoxazole
- Fluoxetine

## CONCLUSIONS:

- ✓ The presence of different therapeutic classes was quantified in portuguese surface waters (rivers, stream, estuaries, seawaters)
- ✓ Wastewaters are an important source of entrance of pharmaceuticals into the environment
- ✓ The contribution of hospital effluents to the load of pharmaceuticals to urban wastewaters varies among therapeutic classes and from hospital to hospital
- ✓ More monitoring studies should be made in order to better understand the level of environmental pollution
- ✓ Green pharmacy approach is a challenge in nowadays
- ✓ New remediation technologies and solutions have to be found

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## ACKNOWLEDGEMENTS

- Lúcia Helena Moreira Lírio Matias dos Santos
- Paula Celeste Batista Paíga



This work received financial support from the European Regional Development Fund (ERDF) through the COMPETE - Operational Competitiveness Programme and national funds through FCT, under UID/QUI/50006/2013 and project UTAP-ICDT/CTM-NAN/0025/2014. The authors wish to acknowledge to the Agência Portuguesa do Ambiente (APA) for providing the seawater samples.



Muito Obrigada/o pela Vossa Atenção/ Thank you for your attention

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