



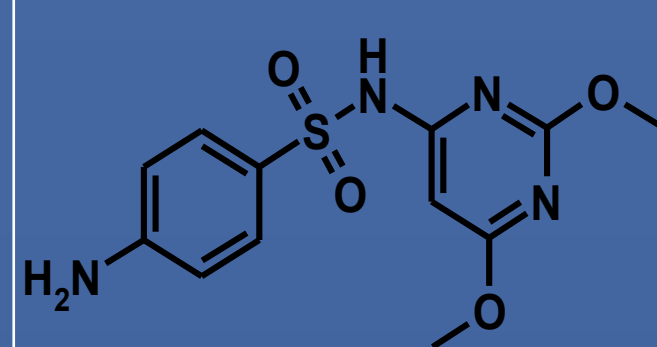
Xenobiotic concentrations in river waters of Luxembourg

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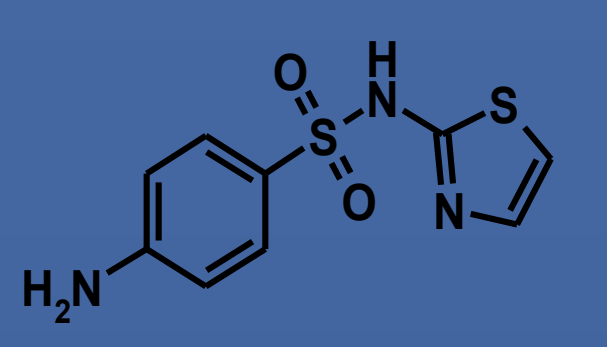
INTRODUCTION & OBJECTIVES

Introduction : Emerging contaminants like pharmaceuticals are of growing interest because of their use in large quantities in human and veterinary medicine. The amounts reaching surface waters and drinking water reservoirs depend on rainfall patterns, hydraulic conditions, consumption, metabolism, degradation and an improper disposal. The behaviour of endocrine disruptors including pharmaceuticals in the aquatic environment is widely unknown.

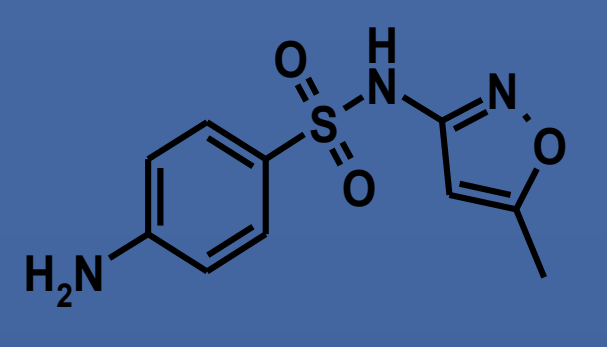
Objectives : The main goal of the project is to analyze Xenobiotics in river waters of Luxembourg by sampling the Alzette river (5 points), the contributions of the Waste Water Treatment Plant of Beggen (WWT P), as well as flood events in the Mess river.



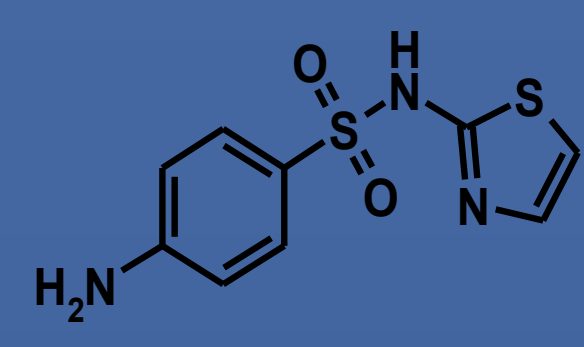
Sulfathiazole (STZ)



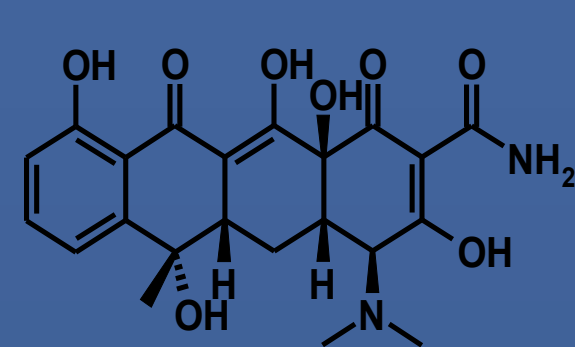
Sulfadimethoxine (SMT)



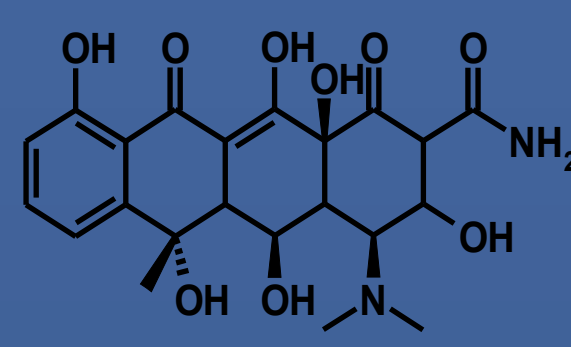
Sulfadimethoxazole (SDM)



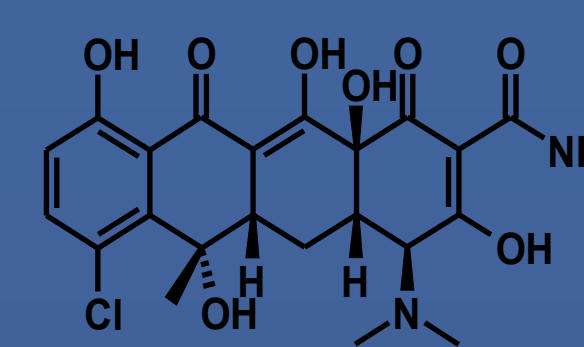
Sulfamethazine (SMZ)



Tetracycline (T)

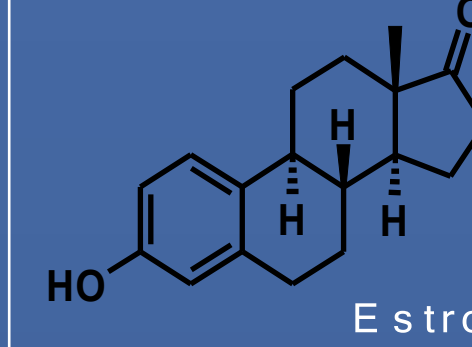


Oxytetracycline (OTC)

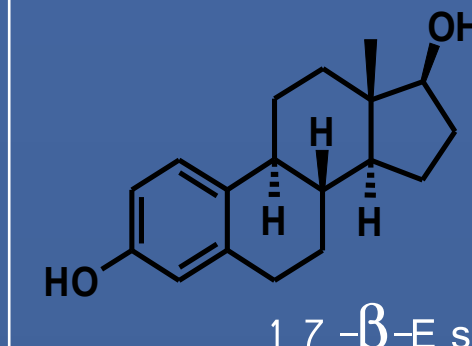


Chlortetracycline (CTC)

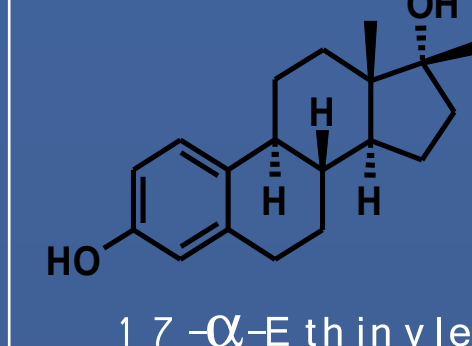
Antibiotics



Estrone (E₁)

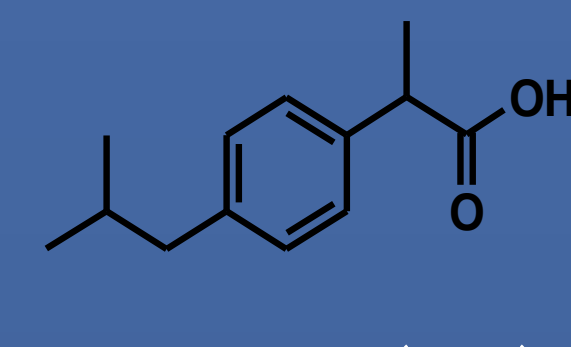


17-β-Estradiol (E₂)

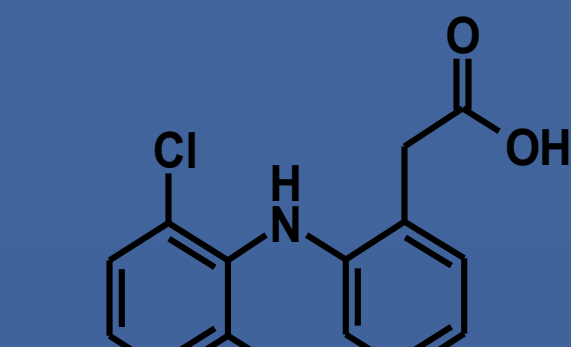


17-α-Ethinylestradiol (EE₂)

Hormones



Ibuprofen (IBU)



Diclofenac (DCL)

Analgesics

MATERIALS & METHODS

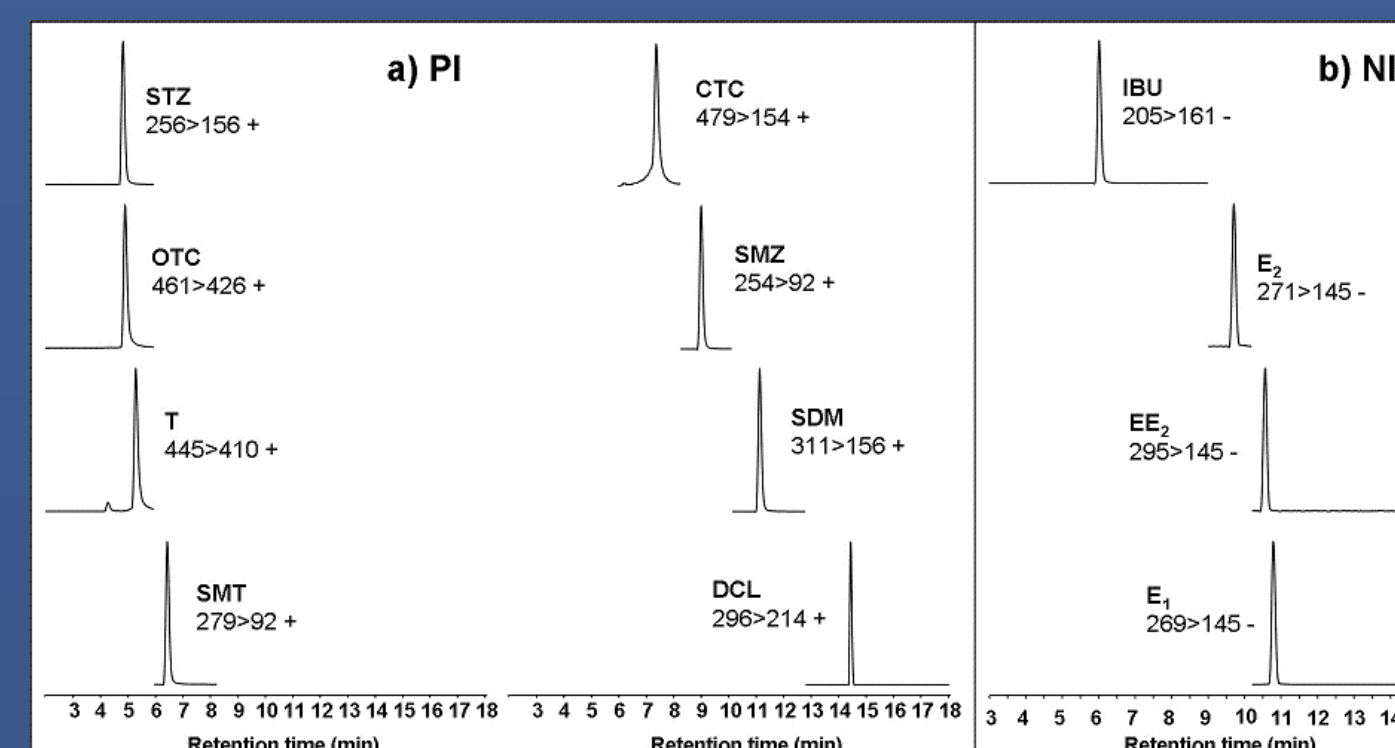
SOLID PHASE EXTRACTION (SPE)

Filtration of 1 L surface water on 0.45 μm
- pH 4 + EDTA
Loaded OASIS HLB® cartridges (200 mg, 6 mL)
- elution with methanol
2 x 5 mL extract
- drying of cartridge under N₂
1 mL Final extract



SPE automated workstation (Caliper)

HPLC/MS-MS

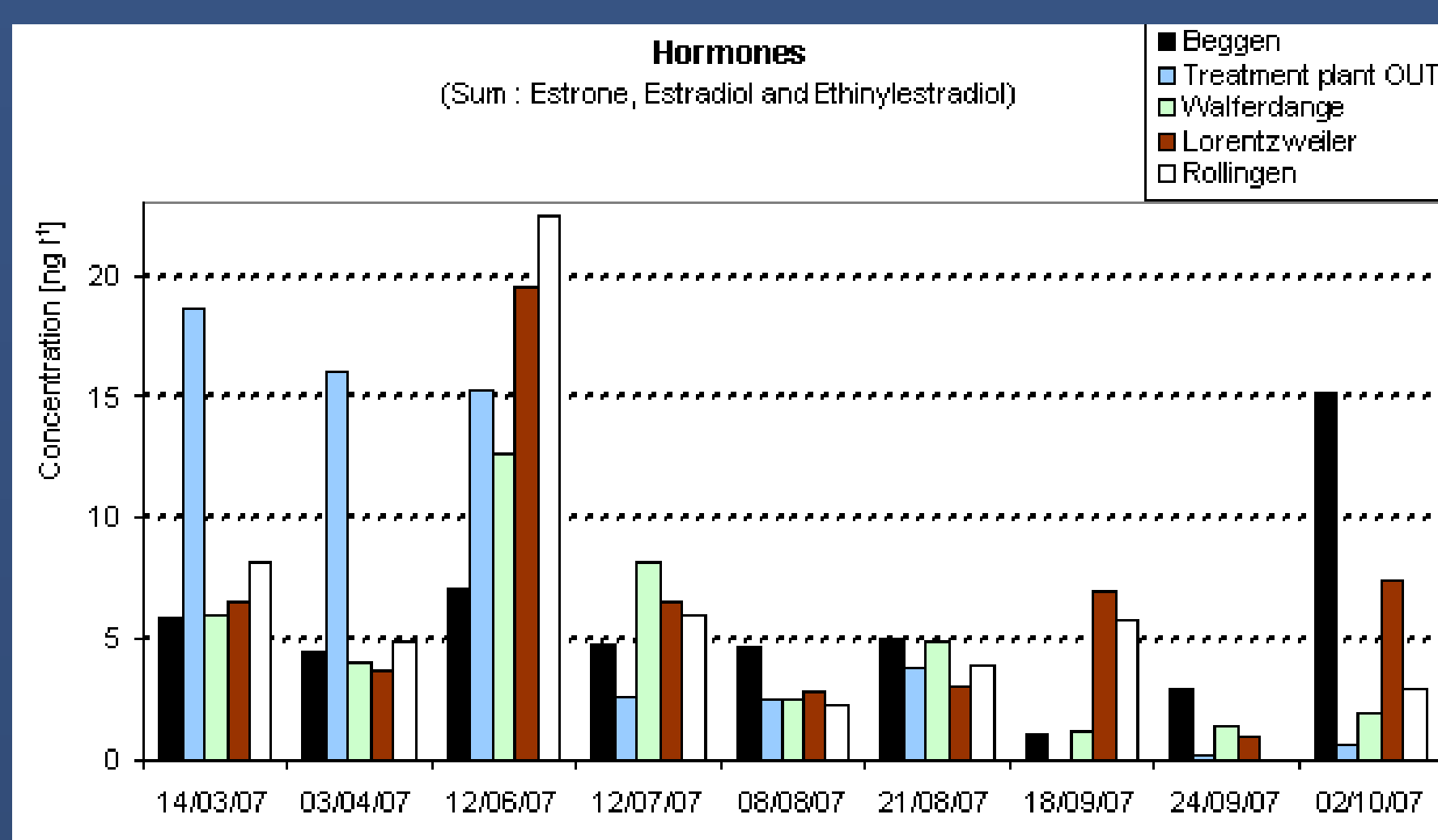


- C18 GRAVITY (125 mm, 2 mm i.d., 3 μm)
- H₂O + 0.1% FA - ACN + 0.1% FA in ESI⁺
- H₂O + 10 mM NH₄OAc - ACN in ESI⁻



HPLC Ultimate 3000 + MS/MS API 3200

RESULTS & DISCUSSION

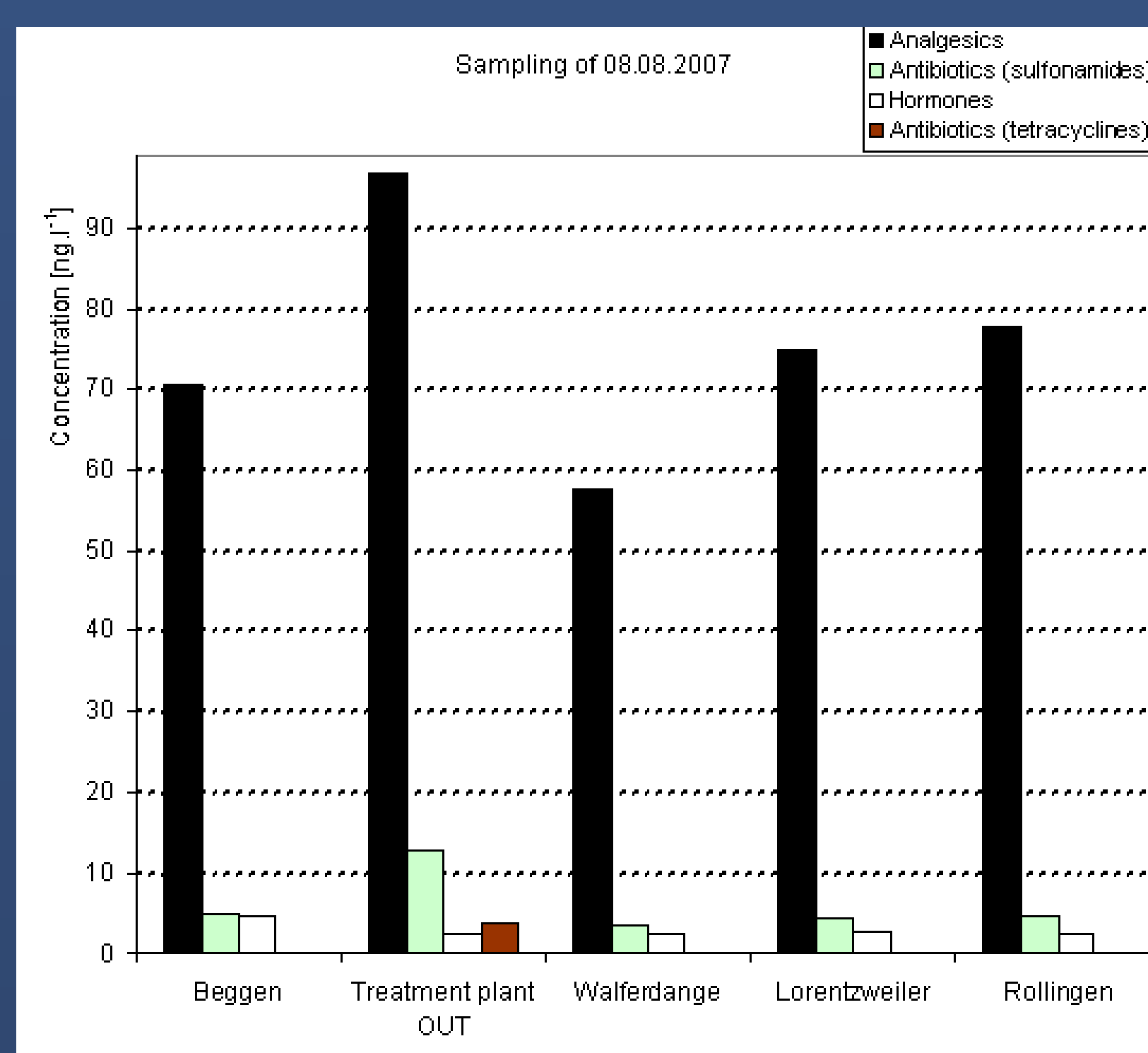


Concentration of hormones during a 6-months sampling along the Alzette (upstream of the WWTP, at the WWTP-outlet and 3 points downstream of the WWTP) :

2 different hydrological cases : during spring, hormone concentrations are two to four times higher than in summer. During summer, the discharge is mainly fed by groundwater contributions, causing a dilution of average concentrations.

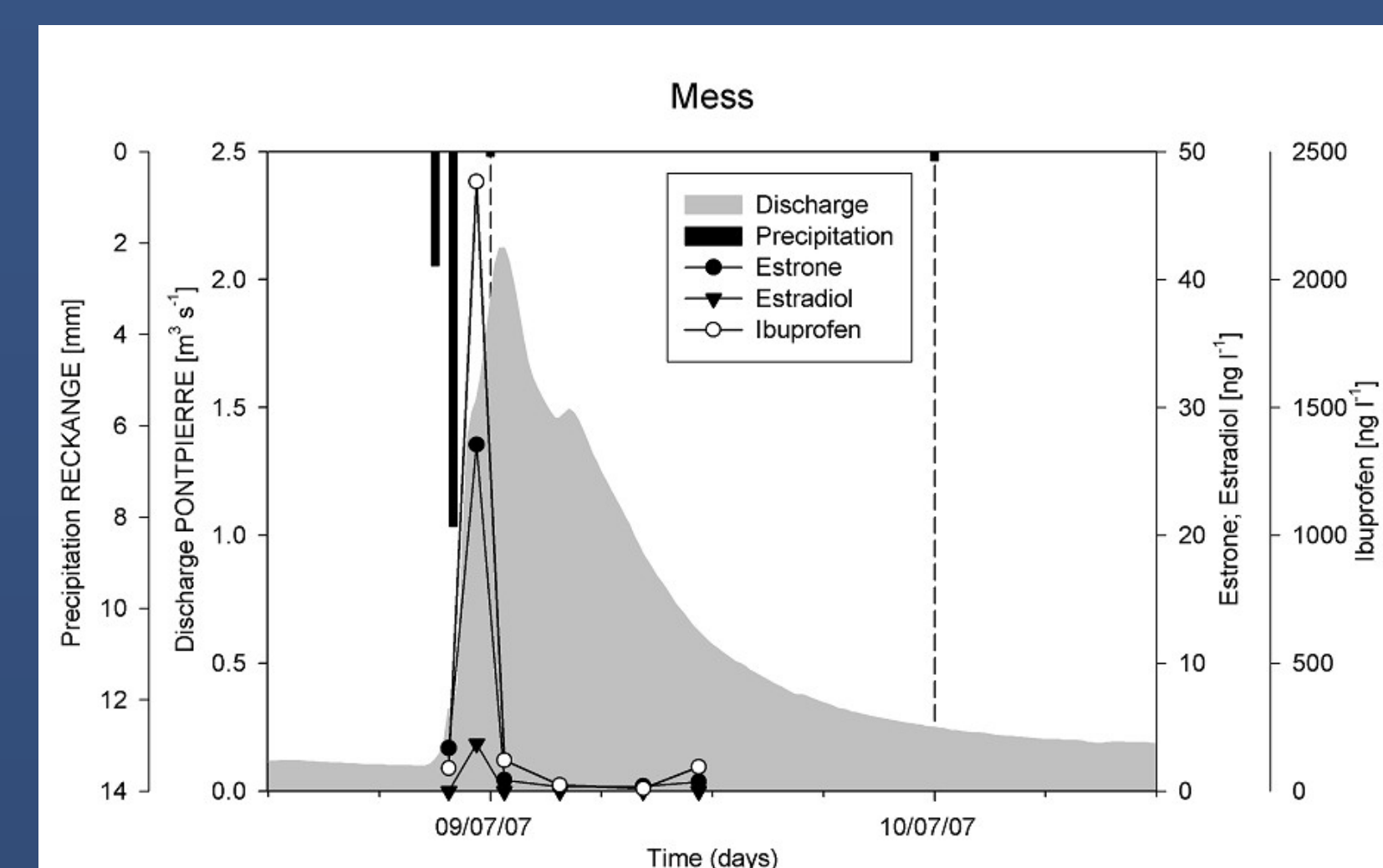
3 cases of concentration profiles compared to the WWTP-outlet :

- Accumulation of hormones (15-20 ng/L) at the WWTP-outlet (in blue) and dilution in the Alzette further downstream (sampling of 14/03/07 and 03/04/07)
- Higher concentrations in the Alzette downstream of the WWTP (12/06/07 and 12/07/07) might be due to illicit connections of household wastewater evacuation systems.
- Higher concentrations in the Alzette upstream of the WWTP (08/08/07 and 02/10/07) might be due to a malfunctioning of the WWTP.



Xenobiotics concentrations on the 08/08/07 in Alzette river water samples (upstream of the WWTP, at the WWTP-outlet and downstream of the WWTP) :

Case of accumulations of pharmaceuticals at the WWTP-outlet, followed by a dilution in the Alzette downstream of the WWTP: illustrated by the accumulation of the tetracyclines in the WWTP outlet, while they are not detected anywhere else.



Concentration of Xenobiotics during a summer flood event on the Mess river :

This flood event followed a summer drought period, causing concentrations to be very high : 2500 ng/L for IBU or 30 ng/L for E₁ (first flush effect)



Calculated Fluxes are :

- 24 000 mg of IBU
- 274 mg of E₁
- 32 mg of E₂

CONCLUSIONS AND PERSPECTIVES

- 12 Xenobiotics with very large differences in physico-chemical properties were extracted in a single method on copolymer cartridges.
- Located in industrialized areas in Luxemburg, the Alzette and Mess rivers were shown to be polluted with different Xenobiotics.
- The WWTP of Beggen obviously is not removing all pharmaceuticals from the incoming waste waters.
- The perspectives opened by the project are to analyze other micro-pollutants, like alkylphenols, and to follow these Xenobiotics during a complete hydrological year on catchments with contrasting physiographical characteristics.