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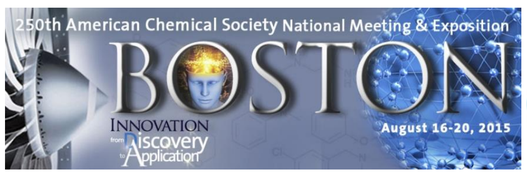

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Assessing Transformation Products by Non-Target and Suspected Target Screening: The New Frontier in Environmental Chemistry and Engineering

SUSPECTED-TARGET SCREENING STRATEGY TO INVESTIGATE DEGRADATION BY OZONATION OR PHOTOLYSIS OF URBAN MICROPOLLUTANTS IN WASTEWATERS

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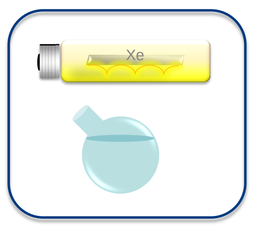
INTRODUCTION

Conventional wastewater treatment plants (WWTPs) partially eliminate micropollutants present in domestic and industrial discharges (Martin-Ruel *et al.*, 2010; Choubert *et al.*, 2011). However, some molecules still occur in effluents of WWTPs at concentrations close to 0.1 µg/L for some pesticides (e.g. diuron) and pharmaceuticals (e.g., carbamazepine, sotalol, diclofenac). The potential harmfulness of these compounds requires the development of new treatment processes (tertiary) to anticipate possible regulation changes. The aim of this poster is to present our analytical methodology to identify degradation products (DPs) created under various conditions during lab-scale or *in-situ* experiments and that will be applied to tertiary treatment processes.

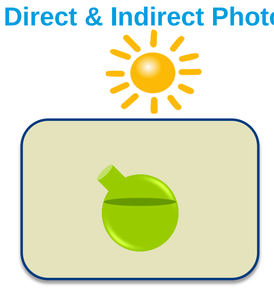
DIFFERENT TYPES OF EXPERIMENTS TO SIMULATE DEGRADATION OF MICROPOLLUTANTS

Direct Photolysis Under Controlled Conditions in Laboratory



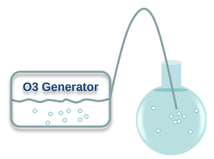
- Irradiation with UV from Xenon lamp
- Quartz R-B flasks
- Matrix: MilliQ™ water
- Spiking concentration @ 10 µg/L
- Time of exposure: 337 h.
- Quality controls: Check of no thermolysis phenomenon during experiment

Both Direct & Indirect Photolysis *in-situ*: Planted Discharge Area



- Natural sunlight
- Quartz R-B flasks
- Planted Discharge Area
- Matrix: WWTP effluent discharged by activated sludge
- Direct + indirect photolysis
- Spiking concentration @ 10 µg/L
- Time of exposure: 168 h.
- Immersion depths: 10 – 30 – 50 cm
- Quality controls: spiked samples outside water with and without exposure to sunlight

Both Direct & Indirect Ozonation In Batch Scale Reactor



- O3 dose: 0.2 g O3/g DOC
- 30L glass flask
- Matrix: WWTP effluent discharged by biofiltration
- Direct + indirect oxydation
- Spiking concentration @ 1 µg/L
- Contact time: 15 min.
- Quality controls: spiked samples without application of ozone

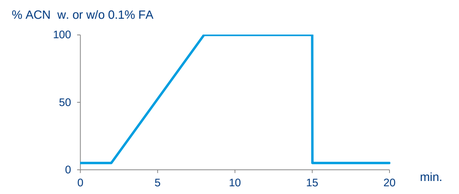
QUALITATIVE & QUANTITATIVE ANALYTICAL STRATEGY

Focus on the analytical methodology set up in our laboratory as part of the study of pharmaceuticals and pesticides: Case of Metoprolol degradation in Planted Discharge Area (at 10 cm depth)

UPLC/(Q)-TOF ANALYSIS

- **Direct injection of 50 µL sample aliquot on Waters Acquity C18 HSS T3 (100 mm x 2,1 mm, 1,8 µm) column ; 15 min. gradient (see cons) ; Flow rate: 0,3 mL/min ; Oven: 30 °C**
- **MS^E acquisition mode (Data Independent Acquisition mode): low collision energy level at 6 eV AND high collision energy level with CE ramp from 10 eV to 45 eV ; Sensitivity mode: resolution at 20000**
- **Quantification w/ internal calibration: 11 parent compounds + 8 deuterated internal standards**

Chromatographic gradient applied in both positive and negative ionization



Waters Acquity H-Class UPLC hyphenated to Xevo G2-S Q-TOF

7 STEPS SUSPECTED-TARGET SCREENING

→ Seeking DPs

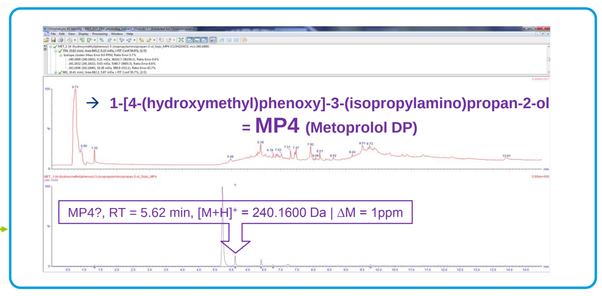
1 Construction of suspected compounds database (DB) of more than 150 expected molecules

Based on bibliographic research of average 30 papers
→ 12 potential DPs for Metoprolol

2 Software « seeking »

Waters ChromaLynx XS software:
- Exact mass ion current extraction from MSE acquisition
- Isotopic pattern verification
- Mass defect must be < 5 ppm

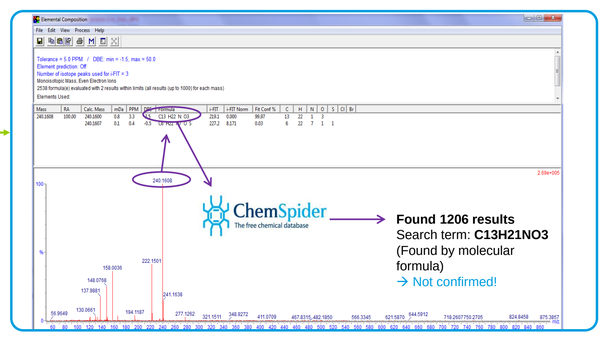
→ Suspicion of MP4 (ΔM = 1ppm)



3 Elemental composition analysis

Waters MassLynx Elemental Composition software:
- Empirical formula proposition
- Submission in the ChemSpider DB for possible structures

→ Return the right empirical formula (>99% confidence)



4 Fragmentation prediction

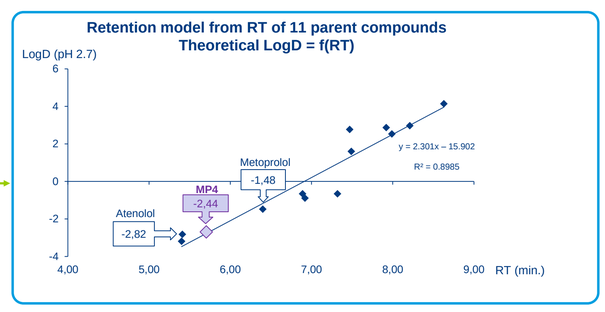
Waters MassLynx MassFragment software:
- Fragmentation explanation tentative
- Comparison with other spectral data base

→ Sensitivity is too low in this case for this compound

5 Retention prediction vs. Retention time (RT) measurement

Modeling from parental compounds RT:
- RT = f(LogD) as linear model
- Relative retention by comparison with parent compounds

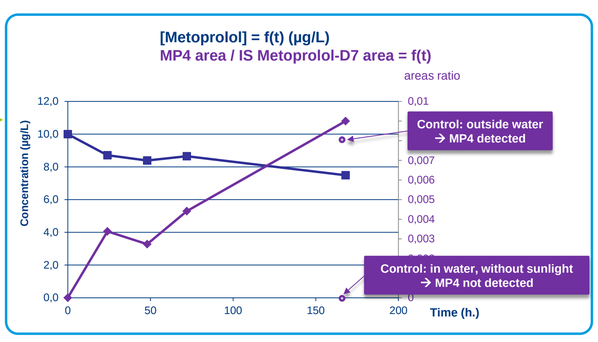
→ The experimental RT of MP4 has a 4% difference compared with predicted value
→ MP4 is well elute between Atenolol and Metoprolol as predicted



6 Diagnostic data

Other evidences:
- Kinetic appearance
- Quality Controls

→ MP4 signal intensity increase during experiment
→ No MP4 detected in control without exposure to sunlight
→ MP4 detected in control outside water at level close to the last sample one.



7 Molecule confirmation?

- Only possible if reference standard is available
- Need more analysis

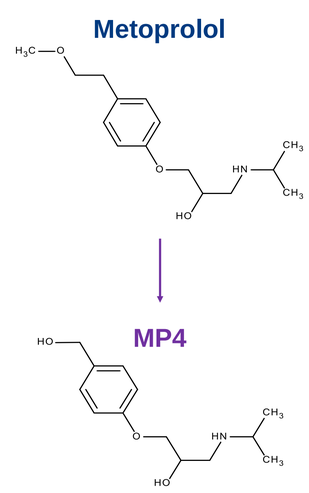
TARGETED SCREENING

→ Kinetics of parent compounds description or confirmation of DPs

Reference & deuterated internal standards

Internal calibration

Confirmed and quantified compound

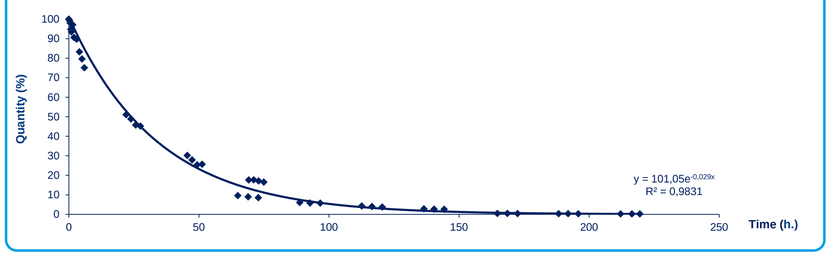


Suspicion of MP4 appearance

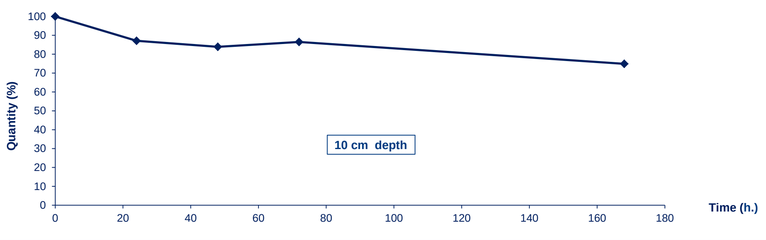
Identification Confidence
Level 3: Tentative Candidate [3]

EXAMPLE OF TARGETED SCREENING OVERCOMES FOR METOPROLOL DEGRADATION

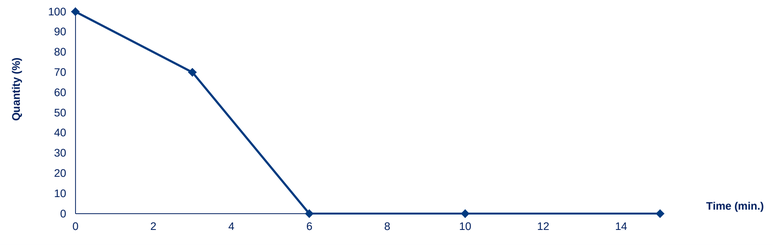
Direct Photolysis Under Controlled Conditions in Laboratory



Both Direct & Indirect Photolysis *in-situ*: Planted Discharged Area



Both Direct & Indirect Ozonation In Batch Scale Reactor



CONCLUSION & PERSPECTIVES

- The sensitivity is a critical point for identification, hence we must concentrate samples with solid phase extraction before instrumental analysis.
- To confirm, ultimately, the nature of DPs, we need to acquire, where possible, the reference standards. At this point we could consider a quantitative analysis approach.
- This strategy is being implemented on 11 compounds that are the subject of a study as part of the thesis of Baptiste Mathon. This study will be a subsequent valorization.
- We also need more tools to confirm our structures like sharing spectral databases. NORMAN MassBank is one of them [4] but nowadays it doesn't allow MS^E spectra comparisons (typically Data Independent Acquisition from Waters instrumentation).
- Working on real matrices (WWTP effluents), we need to enlarge our database to biodegradation products. To do this we will use *in-silico* computational prediction tools. Some of them are freely available (http://eawag-bdd.ethz.ch/)[4].

www.irstea.fr

[1] Martin-Ruel, S. *et al.* (2011). *Water Science and Technology* 63(11), 2486-2497
[2] Choubert, J.M. *et al.* (2011). *Water Science and Technology* 63(1), 57-65
[3] Schymanski, E. L. *et al.* (2014). *Environmental Science & Technology* 48, 2097−2098
[4] Bletsou A. A. *et al.* (2015). *Trends in Analytical Chemistry* 66, 32−44