

Étude des produits de transformation des biocides : analyse par spectrométrie de masse haute résolution

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16 juillet 2021



laboratoire eau environnement systemes urbains



Introduction générale

● Les biocides

- Inhibition de la croissance d'organismes « nuisibles »
- Utilisés seuls ou en combinaison

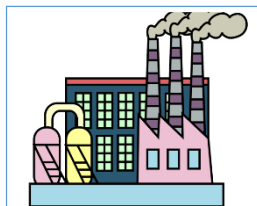
● De multiples domaines d'utilisation



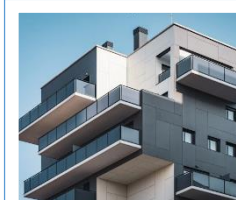
Produits cosmétiques



Produits d'entretien



Industrie



Bâtiment

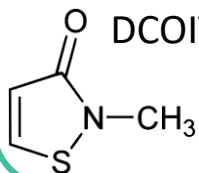


Répulsif

Introduction générale

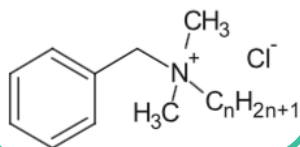
Isothiazolinones

MIT
CMIT
BIT
OIT
DCOIT



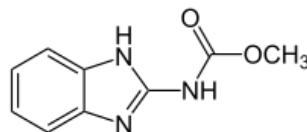
Ammoniums quaternaires

DDAB
Benzalkoniums
(C12 à C18)



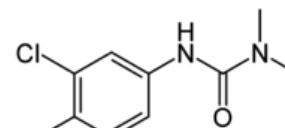
Carbamates

Carbendazime
IPBC



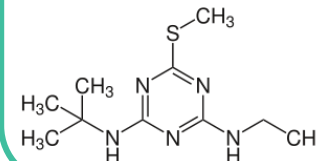
Urées

Diuron
Isoproturon
Hexaflumuron
Diflubenzuron



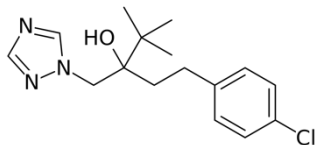
Triazines

Terbutylazine
Terbutryne
Cybutryne



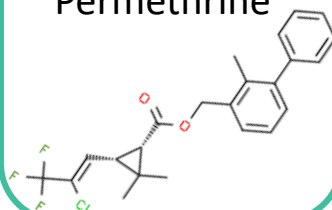
Azoles

Propiconazole
Tébuconazole
Thiabendazole



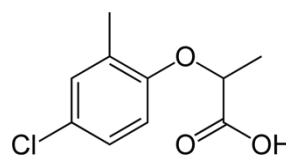
Pyréthrinoïdes

Bifenthrine
Cyperméthrine
Deltaméthrine
Perméthrine



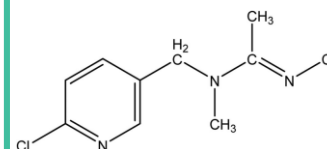
Phénoxy acide

Mécoprop



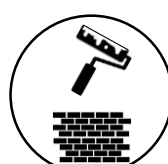
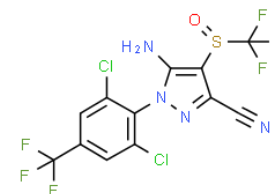
Néonicotinoïde

Acétamipride



Phénylpyrazole

Fipronil



1. État de l'art des produits de transformation

- La photodégradation
- Présence dans l'environnement
- Connaissance des TPs dans la littérature

2. Matériel et méthodes

- Expériences de photodégradation
- Traitement de données

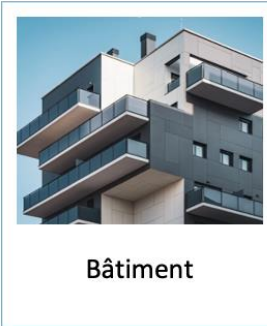
3. Résultats préliminaires

4. Conclusions et suite du stage

État de l'art

● Les voies de dégradation

Bâtiment : limiter les développements biologiques

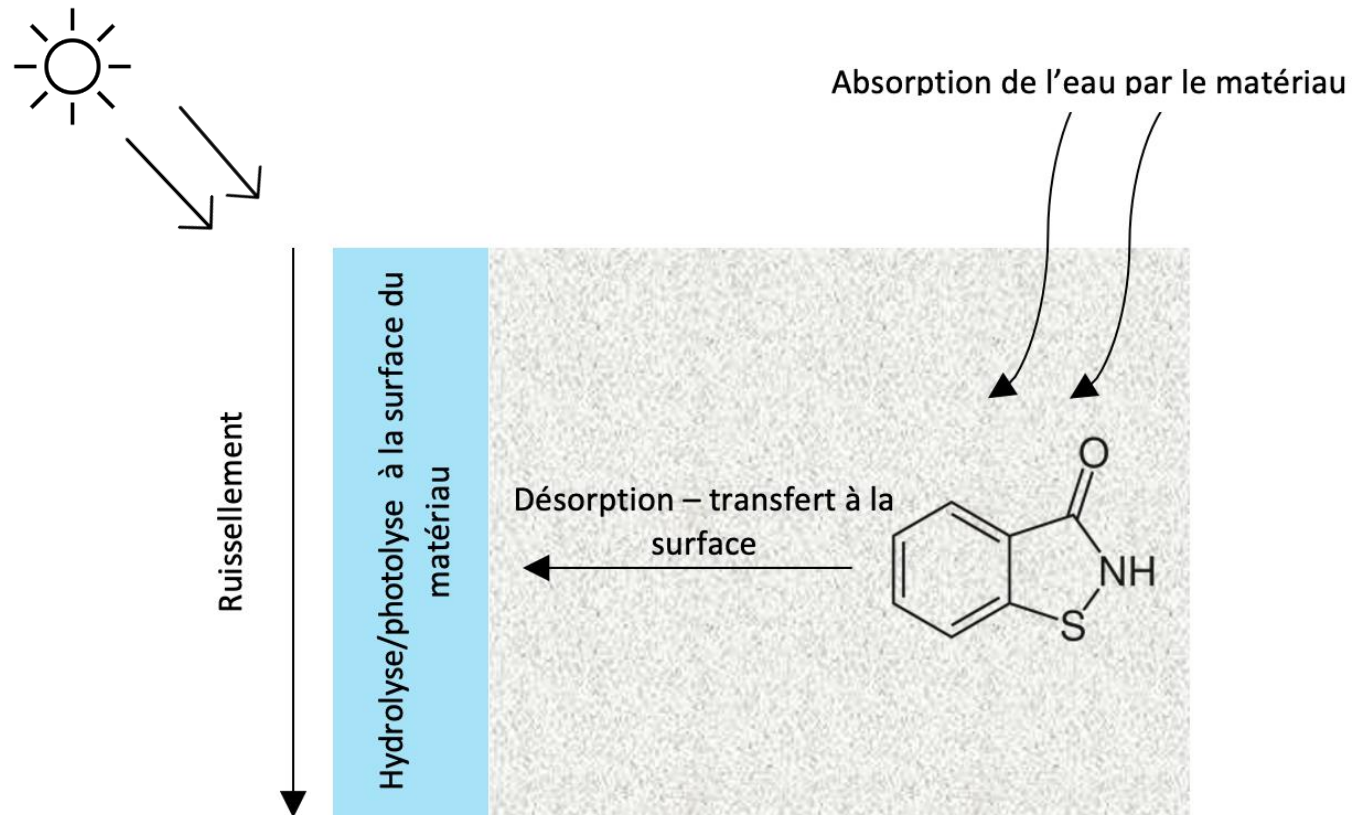


hausinfo.fr



francehumidite.com

● La photodégradation solaire



Phénomène de photodégradation et lixiviation

État de l'art

● Présence dans l'environnement

— Eaux de ruissellement

Lixiviation : transfert vers les eaux pluviales puis vers l'environnement

- Hensen et al., 2018

Arrosages d'une toiture et suivi des eaux de ruissellement

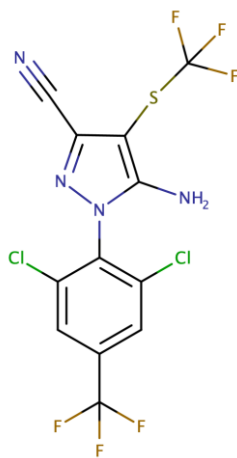
	Diuron	Terbutryn	DIU_TP-219
Ruissellement de façade	17,7 ng/L	0,4 ng/L	691,8 ng/L
Ruissellement par drainage	7 ng/L	1,9 ng/L	

État de l'art

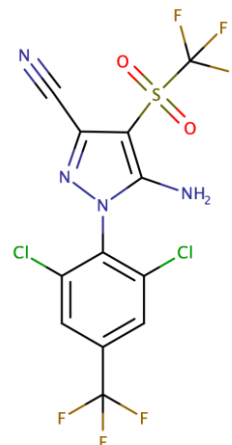
Eaux de surface

Cas du Fipronil (Justine Cruz, 2018)

- Fipronil Sulfide (FP-SFI) : entre 0,13 et 0,29 ng/L
 - Fipronil Sulfone (FP-SFO): entre 0,43 et 0,89 ng/L
- } PNEC = 0,77 ng/L (ANSES, 2018)

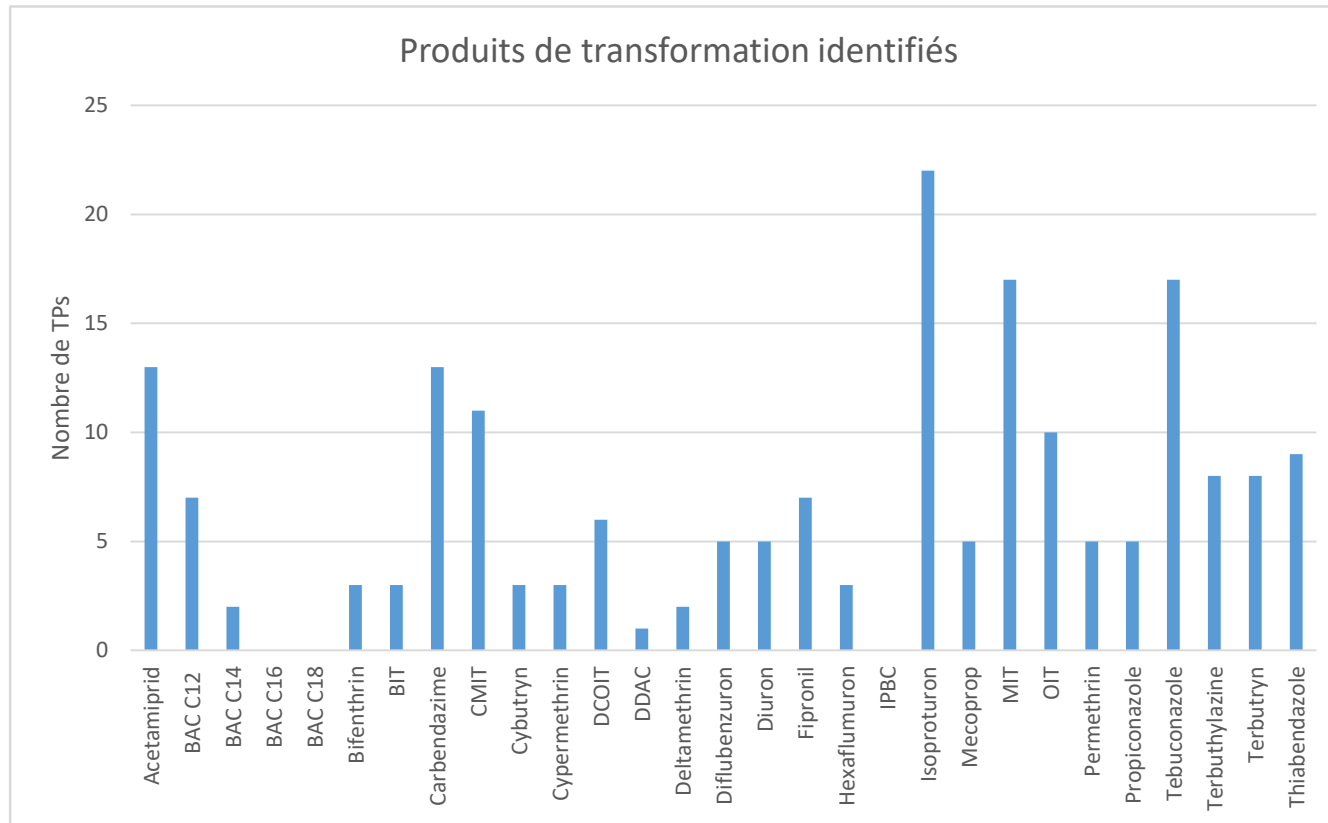


FP-SFI



FP-SFO

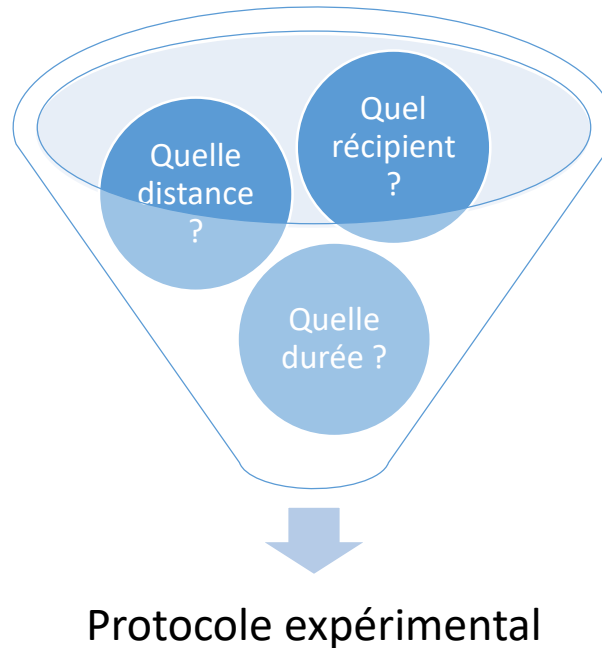
- Connaissance des TPs dans la littérature
 - Inégalité des connaissances



Matériel et méthodes

Matériel et méthodes

- Expériences de photodégradation
 - Optimisation du protocole expérimental



Matériel et méthodes

- Expériences de photodégradation
 - Optimisation du protocole expérimental

Récipient : Cristallisoir ou bécher ?

Tests avec EUP seule, durant des expositions UV de 2h

	1	2
Récipient	Cristallisoir	Bécher 50 mL
Volume irradié	35 mL	35 mL
Volume évaporé	10 mL (28%)	1 mL (2,8%)

Matériel et méthodes

- Expériences de photodégradation
 - Optimisation du protocole expérimental

Récipient : Cristallisoir ou bécher ?

Tests avec EUP seule, durant des expositions UV de 2h

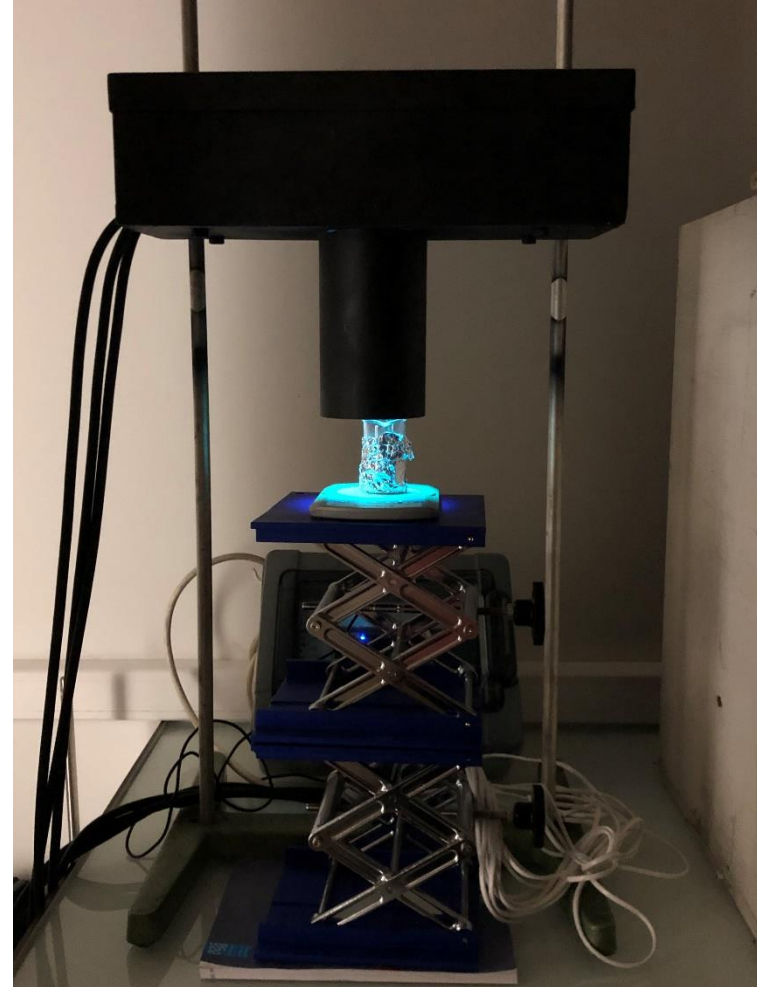
	1	2
Récipient	Cristallisoir	Bécher 50 mL
Volume irradié	35 mL	35 mL
Volume évaporé	10 mL (28%)	1 mL (2,8%)
ΔT	-6,5 °C	+1,4 °C

Matériel et méthodes

● Expériences de photodégradation

Paramètres retenus :

- Bécher de 50 mL, $V_{EUP} = 35$ mL
- Concentration à 1 mg/L dans EUP
- 17 cm de distance
- Agitation magnétique
- 6h d'exposition



Matériel et méthodes

Expériences de photodégradation

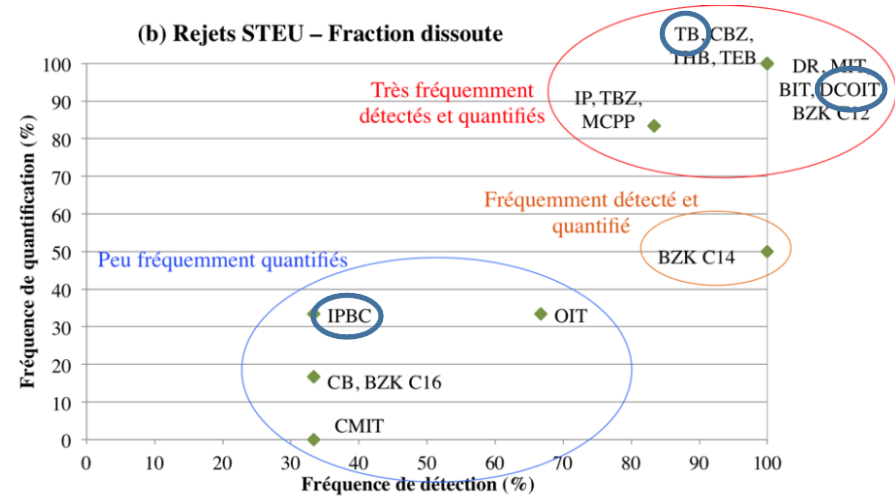
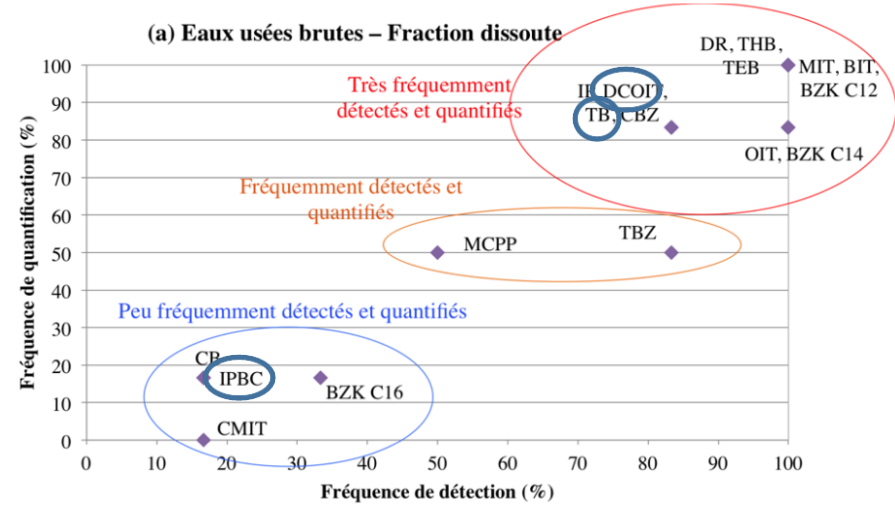
Choix des molécules à dégrader

Deux critères :

1. Quantité d'informations
2. Fréquence de détection/quantification dans les eaux

4 biocides retenus :

- Terbutryn
- DCOIT
- DFB
- IPBC



Thèse Claudia Paijens, 2019

Matériel et méthodes

● Protocole d'analyse

Analyse par HRMS

- 4 dimensions :
 - Masse
 - Temps de rétention
 - Temps de vol
 - Section efficace de collision (CCS)
- Injection directe
 - Mélange 80/20 EUP/MeOH
- Duplicat d'analyse



LC-QTOF Vion

● Traitement de données



— Analyse suspecte

- Établissement d'une nouvelle librairie
 - 195 produits de transformation

— Analyse non-ciblée

- Recherche de nouveaux TPs

Matériel et méthodes

Waters UNIFI - 20210607_TP-UVbiocide: Analysis Center

My Work LC-MS Explorer 20210614_TP_UVbiocide... Rinsing Jun 14, 2021: An... 20210607_TP-UVb... Search folders...

Review Investigate Report

Review Results Limit faults Process Edit Tools File

Workflow

Tray: 1:E,3 TB_SOL_t0_2 Candidate Mass 242.... Filters

Workflow

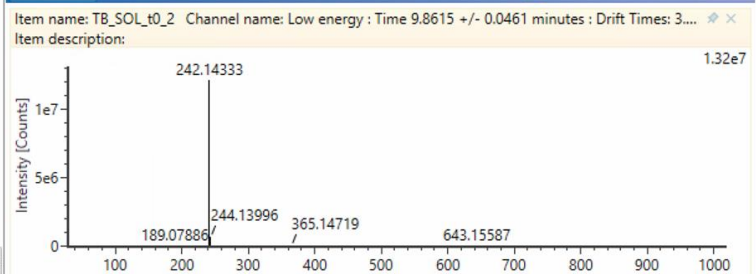
- Summary
 - Batch Overview
- Accurate Mass Screening
 - Identified Components
 - Unobserved Components
 - Unknown Components**
 - Binary compare unknown unique
 - Identified components across all inject...
 - component evolution across samples
 - unknown components peak table
 - Test

Component name	Observed m/z	Observed RT (min)	Observed CCS (Å ²)	Response	Label
1 Candidate Mass 242.1433	242.1433	9.86	161.90	1337946	
2 Candidate Mass 186.0806	186.0806	9.85	139.93	214855	
3 Candidate Mass 326.3776	326.3776	18.29	215.23	100277	
4 Candidate Mass 242.1433	242.1433	9.86	193.26	63708	
5 Candidate Mass 365.1354	365.1354	15.93	186.68	51833	
6 Candidate Mass 242.1433	242.1433	9.86	236.74	43417	

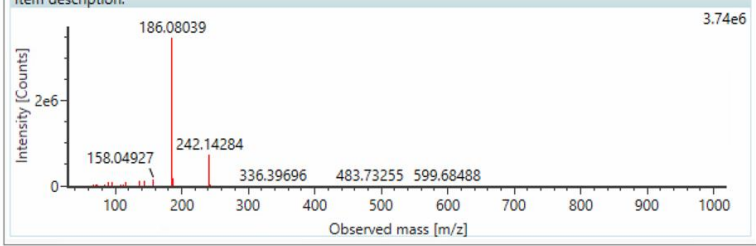
Component Hierarchy Show 10 compounds

No hierarchy to display

Spectra



Item name: TB_SOL_t0_2 Channel name: High energy : Time 9.8615 +/- 0.0461 minutes : Drift Times: 3...
Item description:



OSU, User [Chemist] Rinsing Jun 14, 2021 (LC-MS) 20210614_TP_UVbiocideNeg (LC-M...

Matériel et méthodes

The screenshot displays a mass spectrometry software interface with the following components:

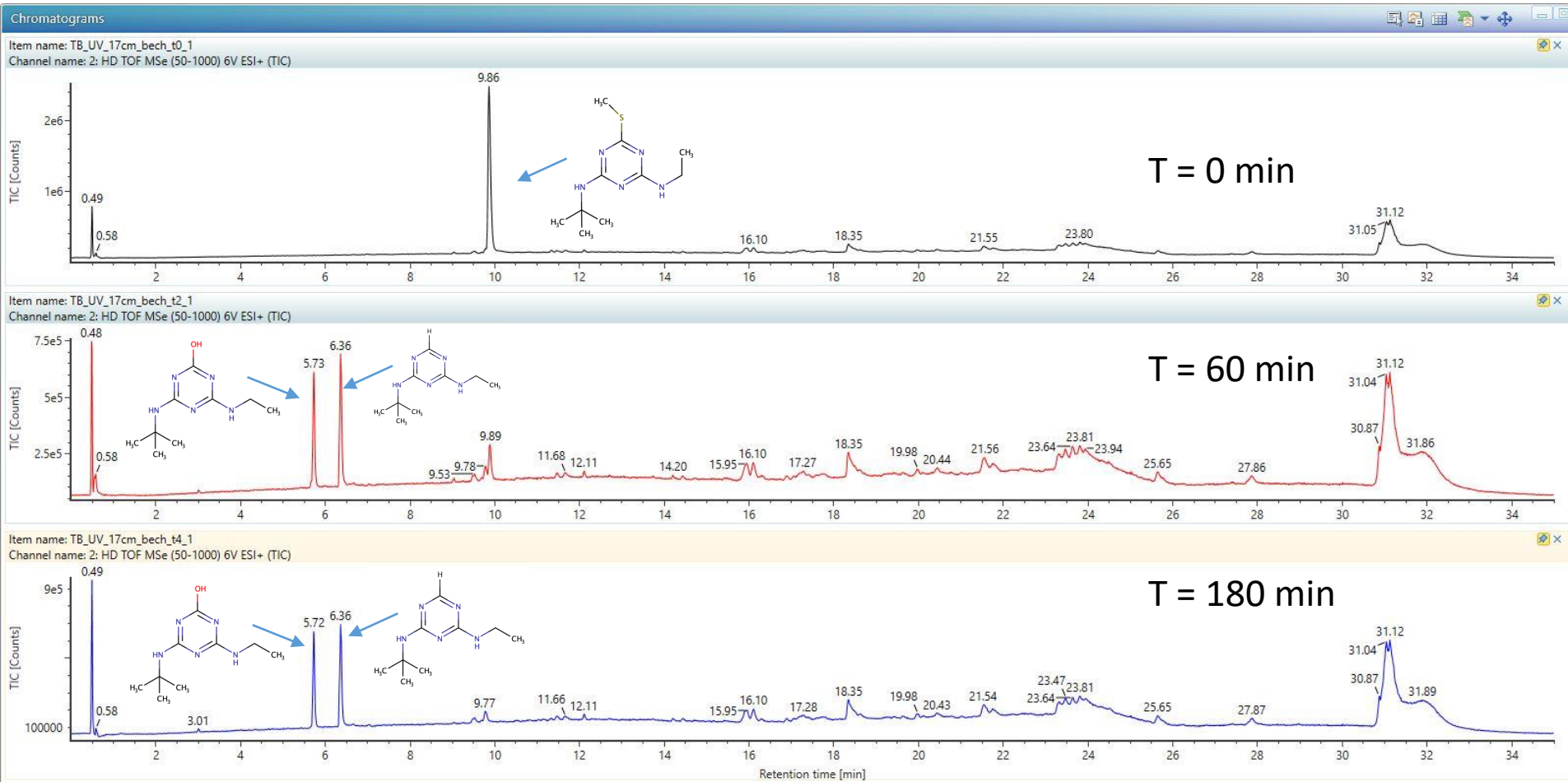
- Workflow Panel:** Shows a summary of the analysis process, including 'Accurate Mass Screening' and 'Elucidation Toolset'.
- Spectra Panel:** Contains two mass spectra:
 - Top Spectrum:** Item name: TB_SOL_t0_2, Channel name: Low energy; Time 9.8621 +/- 0.0461 minutes; Dr...; Item description: 4.27e5. The x-axis is 'Observed mass [m/z]' (0-1000) and the y-axis is 'Intensity [Counts]' (0-4e5). Major peaks are labeled at m/z 186.08056, 242.14333, 244.13996, 315.26482, 545.19910, and 911.82379.
 - Bottom Spectrum:** Item name: TB_SOL_t0_2, Channel name: High energy; Time 9.8621 +/- 0.0461 minutes; D...; Item description: 2.81e4. The x-axis is 'Observed mass [m/z]' (0-1000) and the y-axis is 'Intensity [Counts]' (0-25000). Major peaks are labeled at m/z 96.05554, 187.08222, 242.14284, 288.03450, 545.20333, 547.20349, 795.49149, and 932.96511.
- Discovery Panel:** Shows search parameters and results.
 - Parameters:** Available libraries include abcr, Acros Organics, Activate Scientific, ACToR, Adrian Hobson, and Advanced ChemBlocks. Selected libraries include ChemBank, enviPath, EPA DSSTox, EPA Toxcast, MassBank, NIST, and PubChem.
 - Results (4 found):**

Component Name	m/z	Elemental Composition	i-FIT Confidence (%)	Common Name	Fragment Matches	Predicted Intensity
Candidate Mass 242.1433278477	242.1433	C10H19N5S	100.00	Terbutryn		
Candidate Mass 242.1433278477	242.1433	C10H19N5S	100.00	6-(Methylsulfonyl)-N,N-dipropyl-1,3,5-triazine-2,4...		
Candidate Mass 242.1433278477	242.1433	C10H19N5S	100.00	N-sec-Butyl-N'-ethyl-6-(methylsulfonyl)-1,3,5-triaz...		
Candidate Mass 242.1433278477	242.1433	C10H19N5S	100.00	6-(Methylsulfonyl)-N,N-dipropyl-1,3,5-triazine-2,4...		
 - Information Panel:** Lists synonyms for Terbutryn, including 200-835-2, 212-950-5, 886-50-0, N2-(tert-Butyl)-N4-ethyl-6-(methylsulfonyl)-1,3,5-triazine..., HS 14260, and n-tert-butyl-n'-ethyl-6-(methylsulfonyl)-1,3,5-triazine-2,4...
- Chemical Structures:** Two chemical structures of Terbutryn are shown. The top one is a skeletal structure with a tert-butyl group, an ethyl group, and a methylsulfonyl group on a 1,3,5-triazine ring. The bottom one is a ball-and-stick model of the same molecule. A small inset graph shows the S:H ratio as 0.50 B: 1 H:2.

Résultats

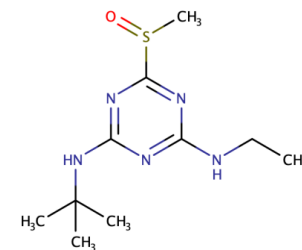
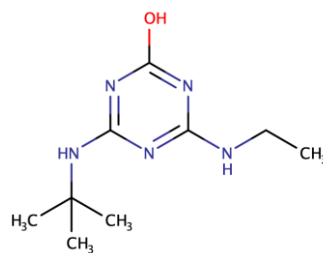
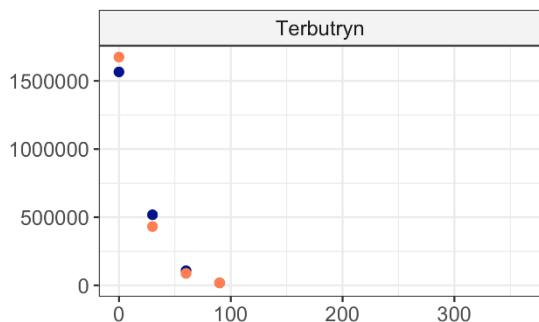
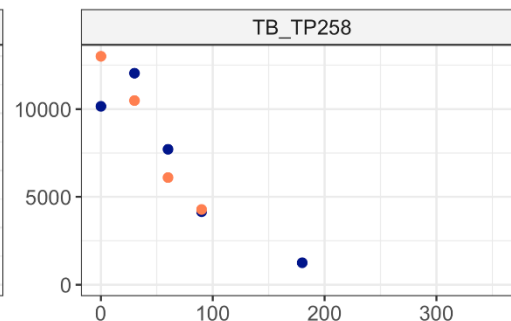
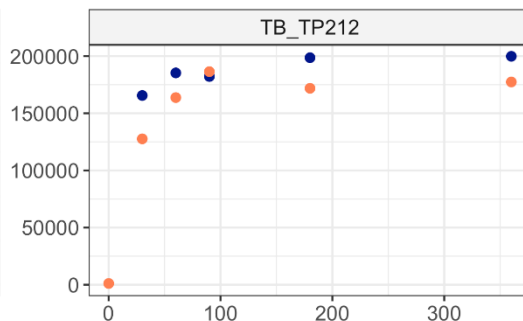
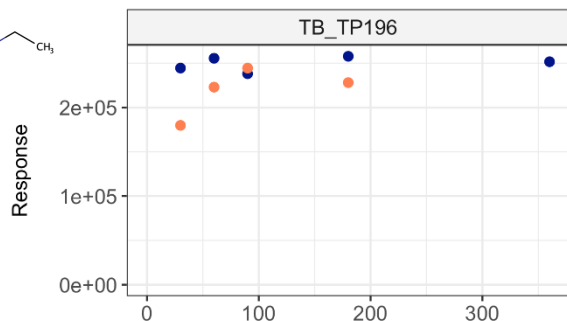
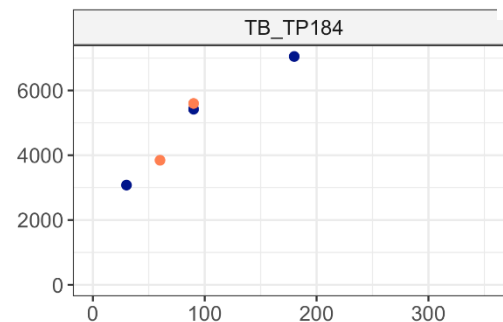
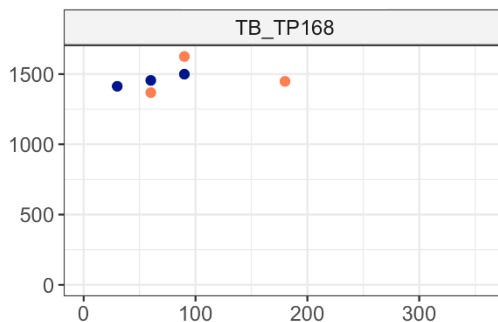
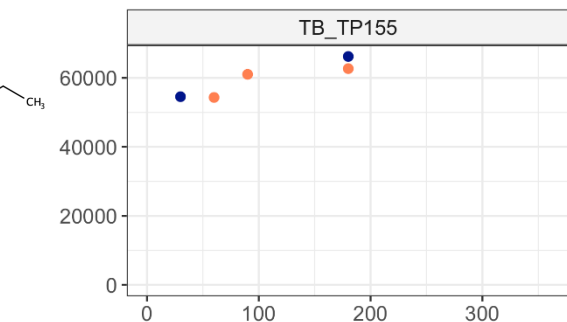
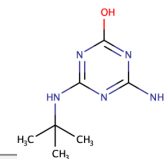
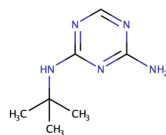
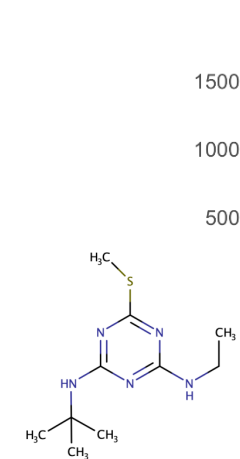
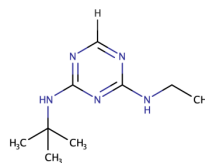
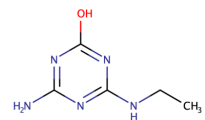
Résultats

Terbutryn



Résultats

Terbutryn



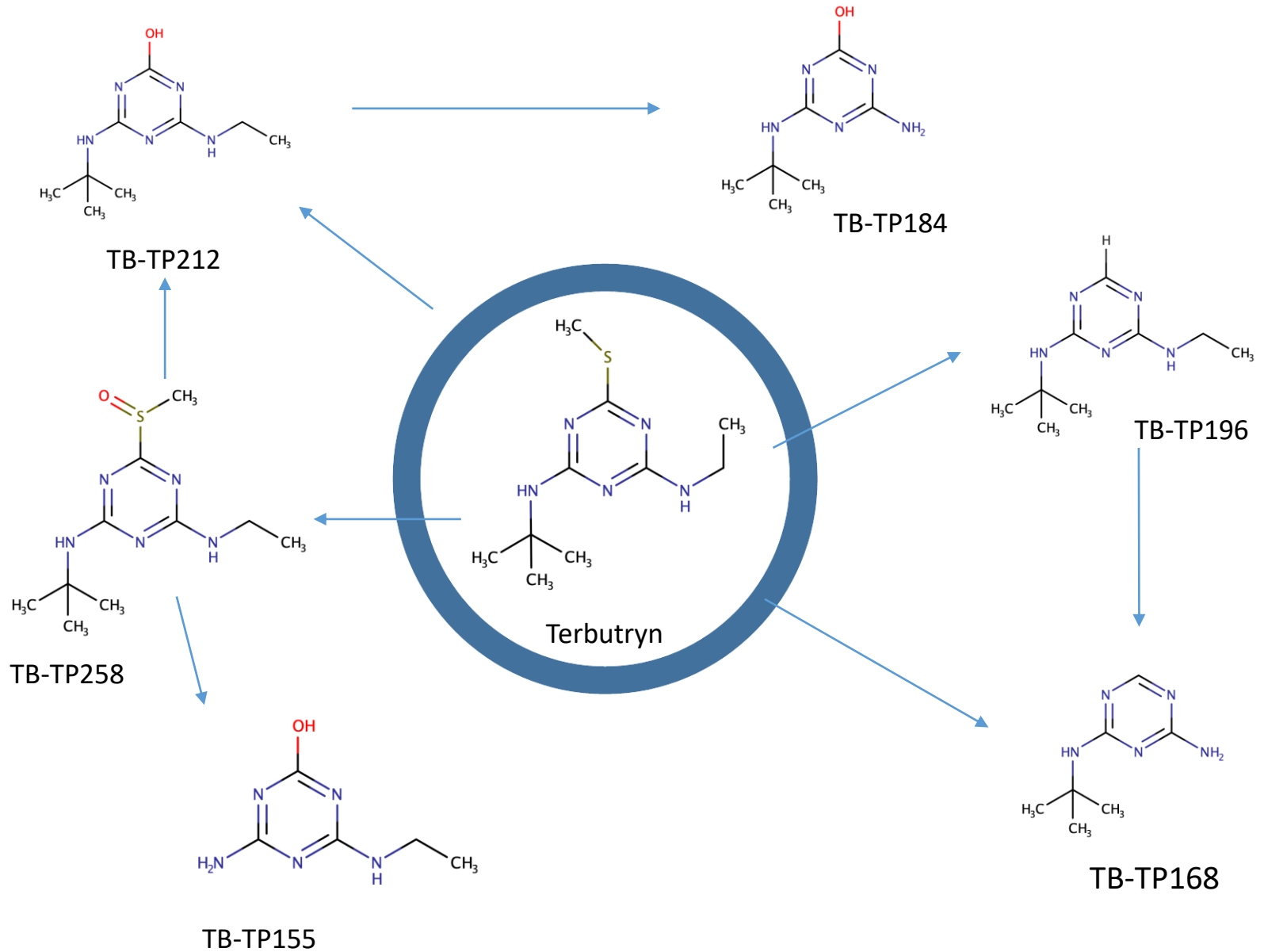
$T_{1/2} = 13$ minutes ; ordre 1

Comparaison avec Bollmann et al., 2016 :
 $T_{1/2} = 11,9$ h (3 lampes UV de 5W)

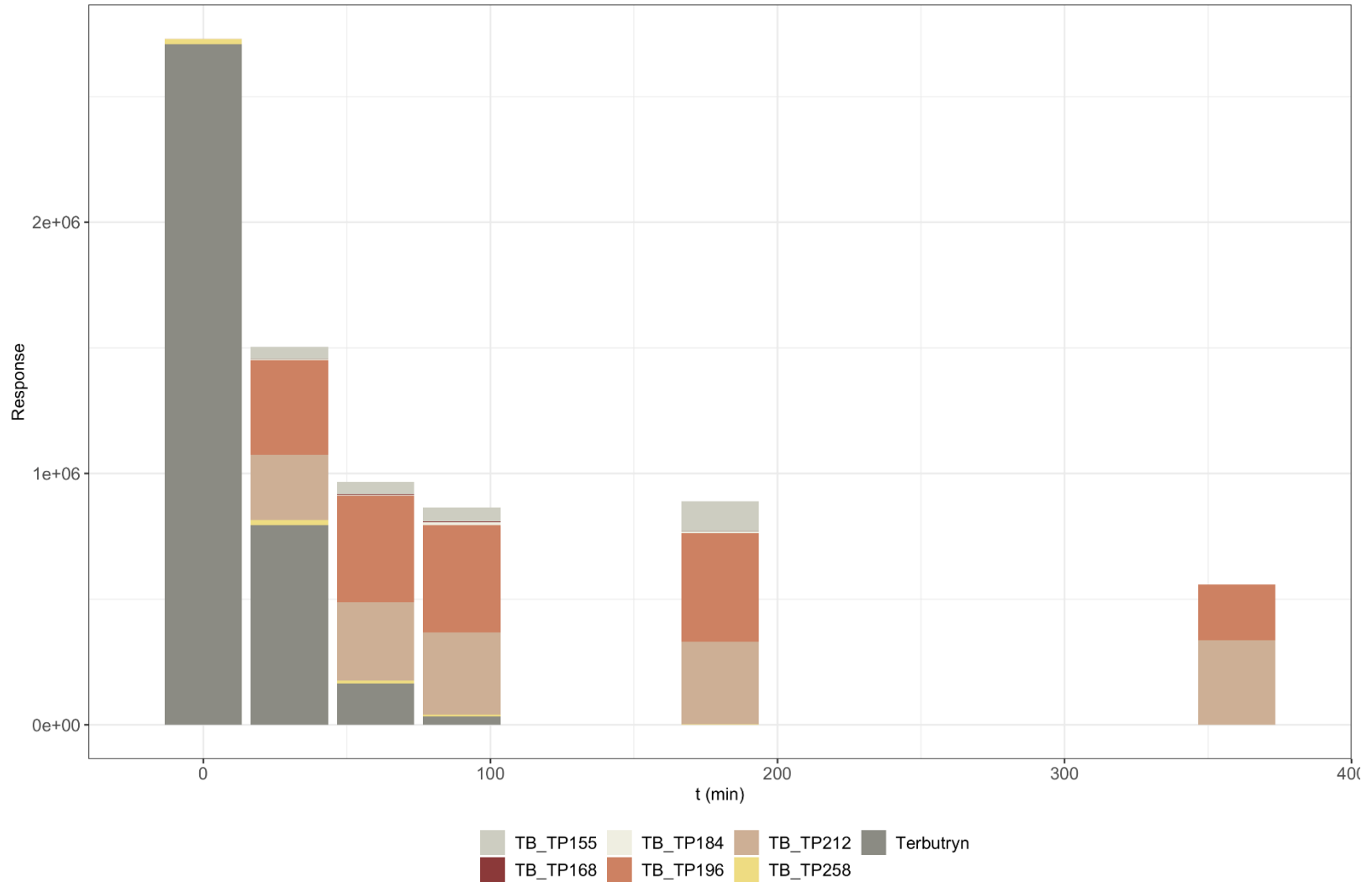
t (min)

● 1 ● 2

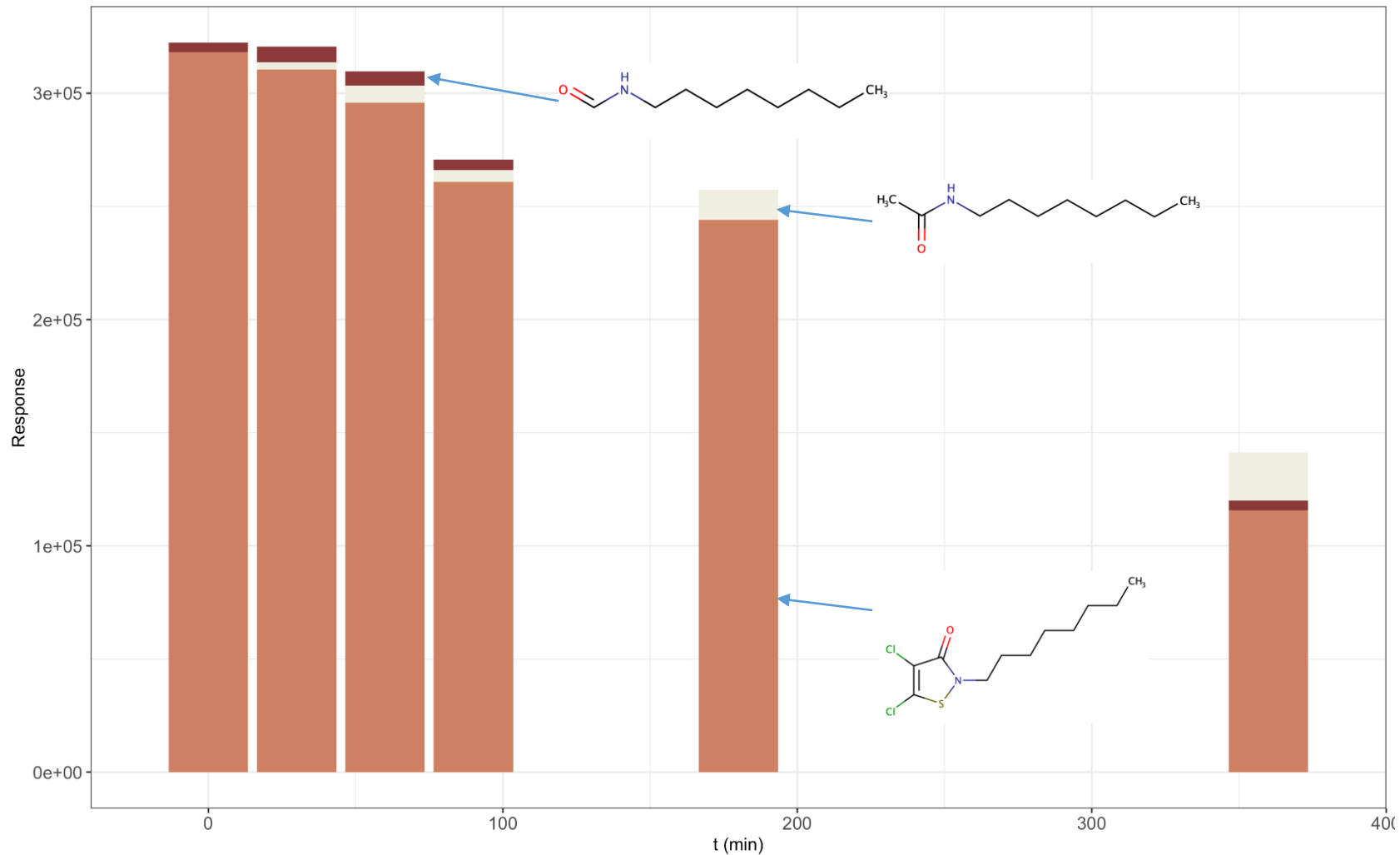
Résultats



Terbutryn



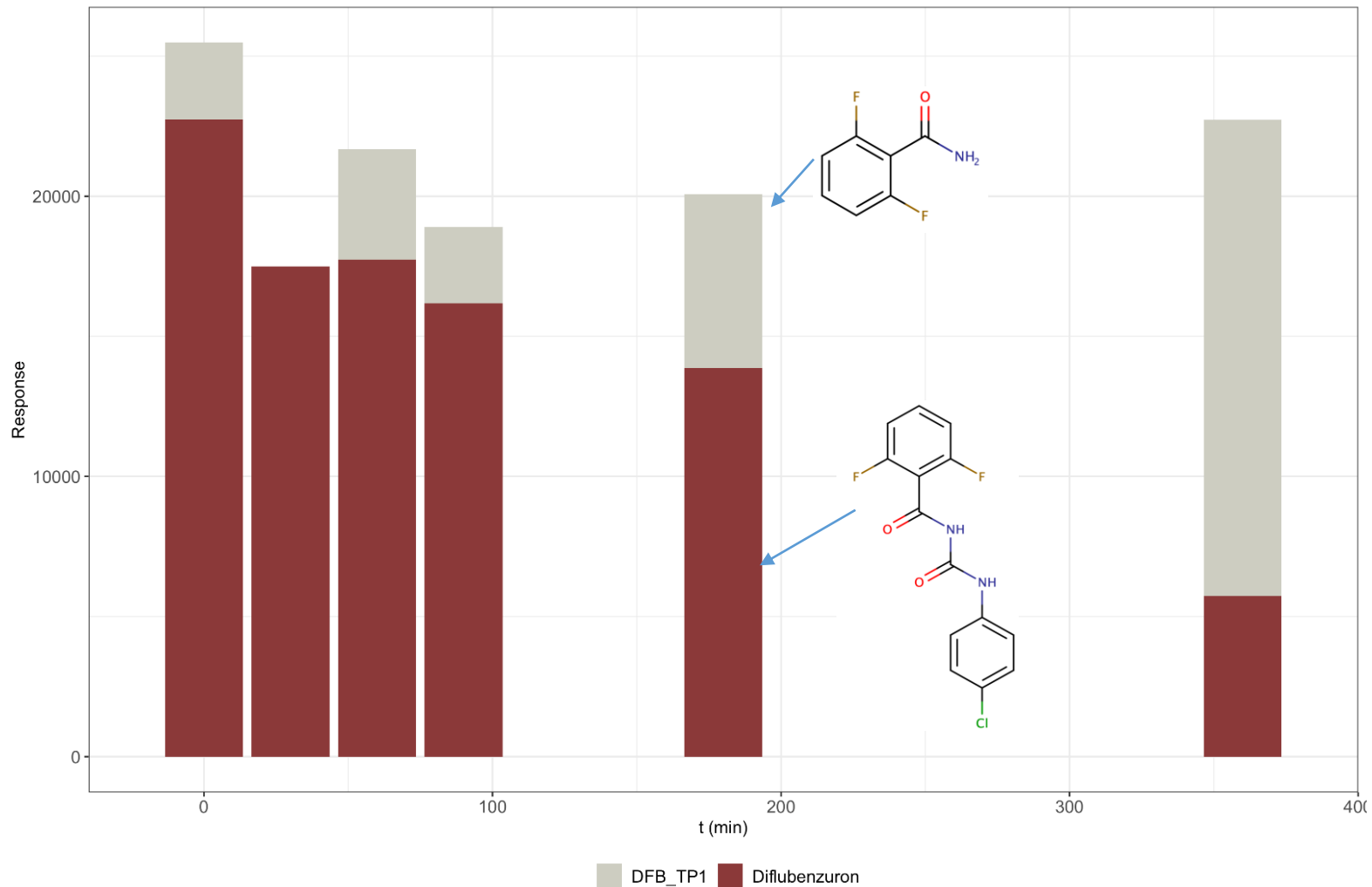
DCOIT



$T_{1/2} = 4$ heures ; ordre 1

DCOIT_TP172 OIT_TP158 DCOIT

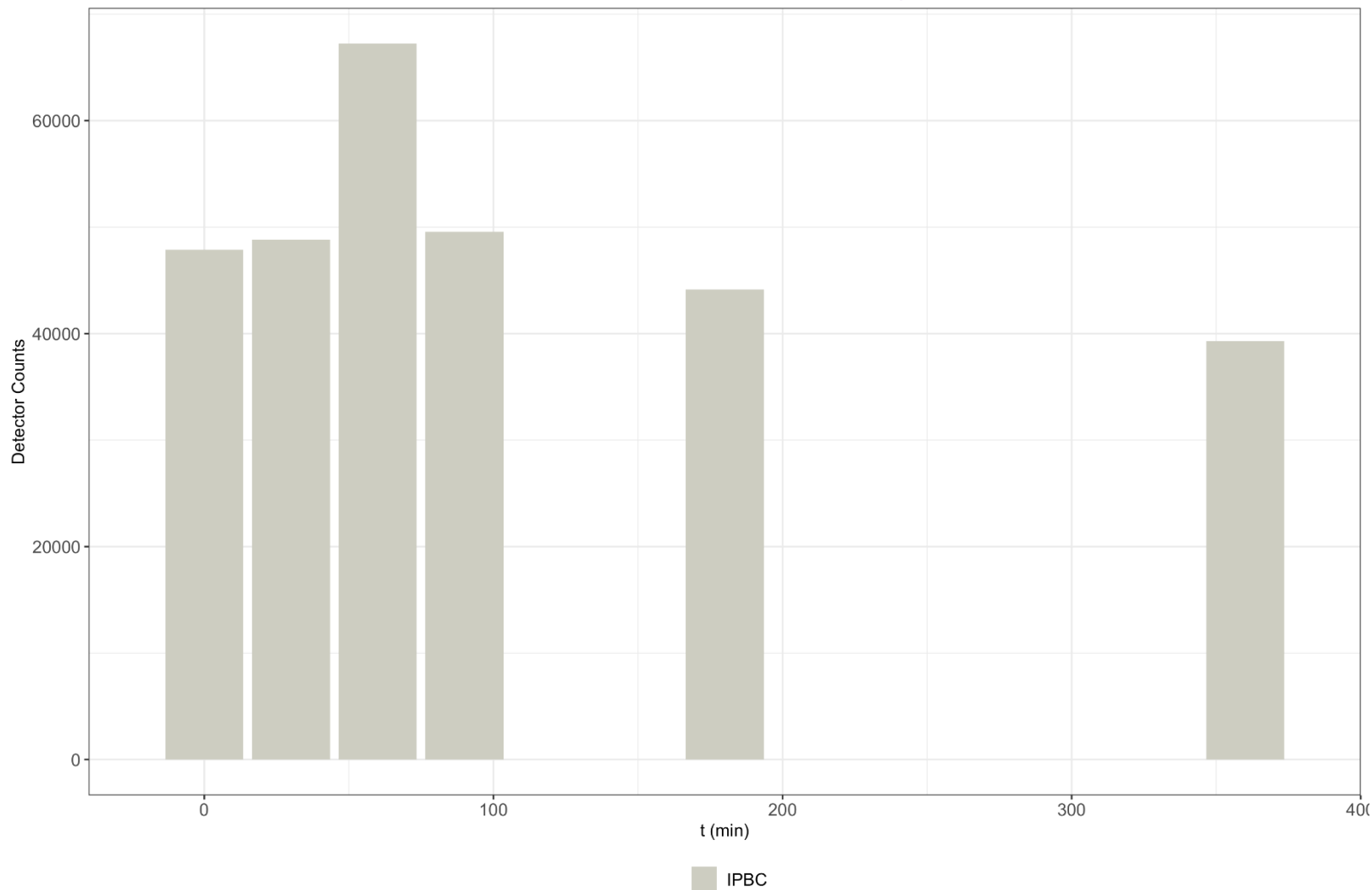
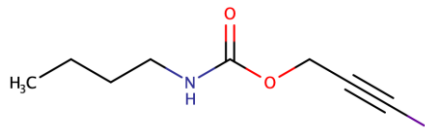
● Diflubenzuron



$T_{1/2} = 3,2$ heures ; ordre 1

Résultats

IPBC



Conclusions et suite du stage

- Meilleure compréhension de la dégradabilité des composés face aux UVs

- Variabilité

- À venir

- Dégradation de nouveaux biocides

- Triplicats d'analyse

- Essai d'identification de nouveaux TPs

- Analyse de spectres réels

- Eaux sortie STEU
 - UV – UV/H₂O₂
 - Chlorées

leesu

laboratoire eau environnement systemes urbains

Merci pour votre attention



École des Ponts

ParisTech



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