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Determination of biocide transformation products using suspect and non-target screenings by high-resolution mass spectrometry

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Introduction

Biocidal substances

Used in various fields to inhibit the growth of micro-organisms^{1,2}



Degradation

Photolysis
Photocatalysis
Biodegradation
(...)

Transformation products (TPs)

Some of these TPs are identified in the literature but there are still gaps in the knowledge for some biocides, for which the TPs are unknown.

Objectives

- To create a **library** containing many biocides and their TPs using non-target screening based on **high-resolution liquid chromatography-mass spectrometry** (UPLC-HRMS).
- To **identify new TPs** through UV degradation experiments followed by HRMS in order to complete the library.
- To **search TPs in environmental samples** using suspect screening

Materials and methods

Database building

TPs of 29 biocides* were collected from the literature for many degradation processes: biodegradation (soil, bacteria), photolysis, photocatalysis... The 29 biocides and their TPs were added in a database (containing these characteristics: biocide, TP name, degradation process, empirical formula, molar mass, structure, reference). These biocides and TPs were added in our UPLC-HRMS library (name and structure).

Biocides and their TPs in water samples

Water samples: Groundwater (GW) WWTP : membrane bioreactor

Solid phase extraction:

Multiphasic cartridges to improve selectivity

Multi-DPA:

Oasis HLB
XAW
XCW
DPA

Multi-ENV:

Oasis HLB
XAW
XCW
ENV+

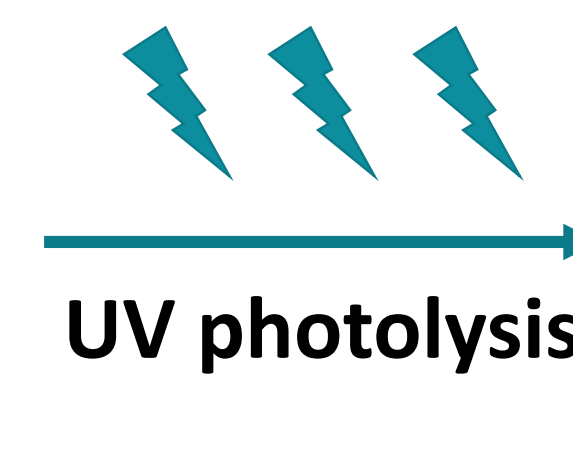
Comparison

Degradation experiment

CBZ, DCOIT, DFB, IPBC, TB, TEB and THB solution

1 mg L⁻¹ except for DFB (0,2 mg L⁻¹)

Low-pressure Hg UV lamps (3 × 15 W)



500 µL were collected after 0, 10, 20, 30, 60, 90, 180 and 360 minutes of exposure.

→ Degradation kinetics

Analysis by UPLC-HRMS

Vion ESI-IMS-QTOF (Waters)

- Suspect screening:** Search for biocides and their TPs present in sample in the library
- Non target screening:** Identification of new TPs
Molar mass between 100 and 1000 Da

* Benzalkonium chlorides (DDAB, BAC-C12/C14/C16/C18), propiconazole (PPC), tebuconazole (TEB), diflubenzuron (DFB), hexaflumuron (HFU), iodopropynyl butylcarbamate (IPBC), isothiazolinones (MIT, CMIT, BIT, OIT, DCOIT), acetamiprid (ACE), fipronil (FIP), diuron (DIU), isoproturon (IPU), bifenthrin (BFT), Cypermethrin (CPMT), deltamethrin (DMT), permethrin (PMT), cybutryn (CBY), terbutylazine (TBZ), terbutryn (TB), thiabendazole (THB), carbendazim (CBZ) and mecoprop (MCP)

Results and discussion

Degradation experiment

Suspect screening

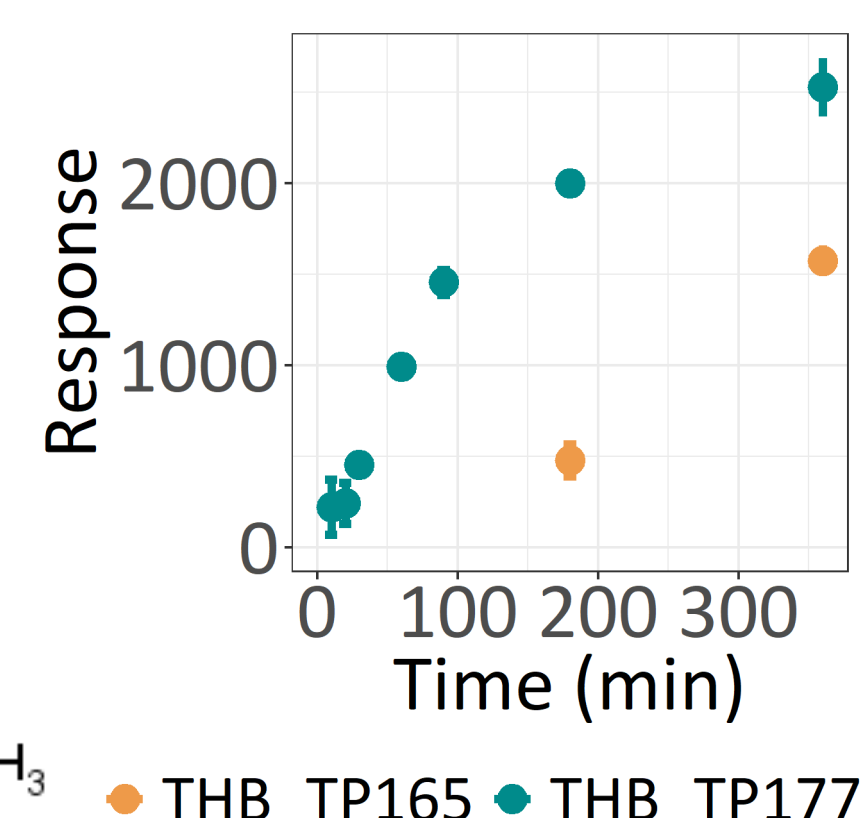
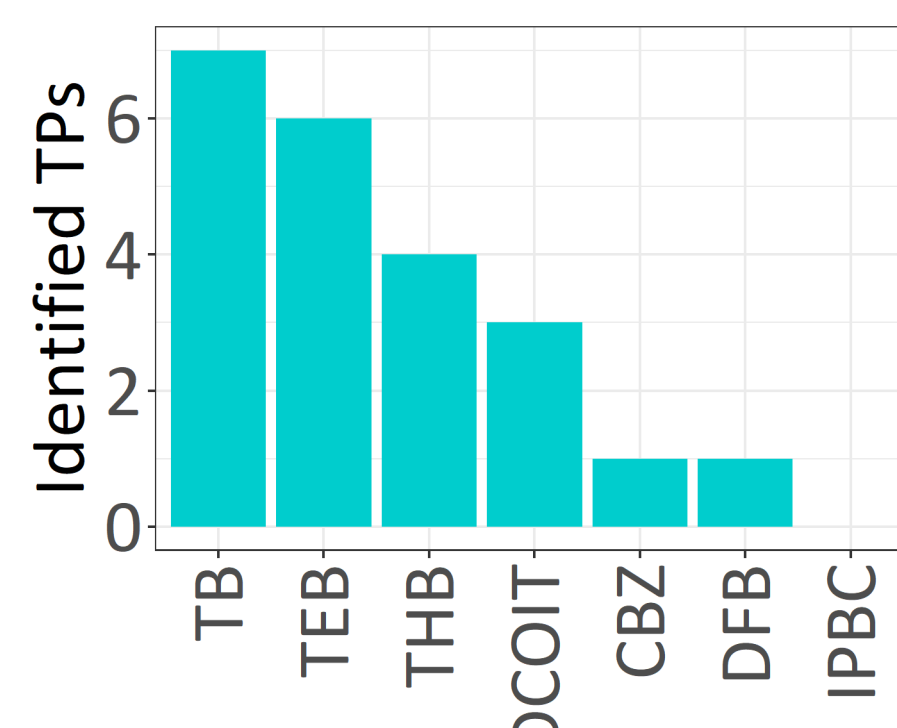
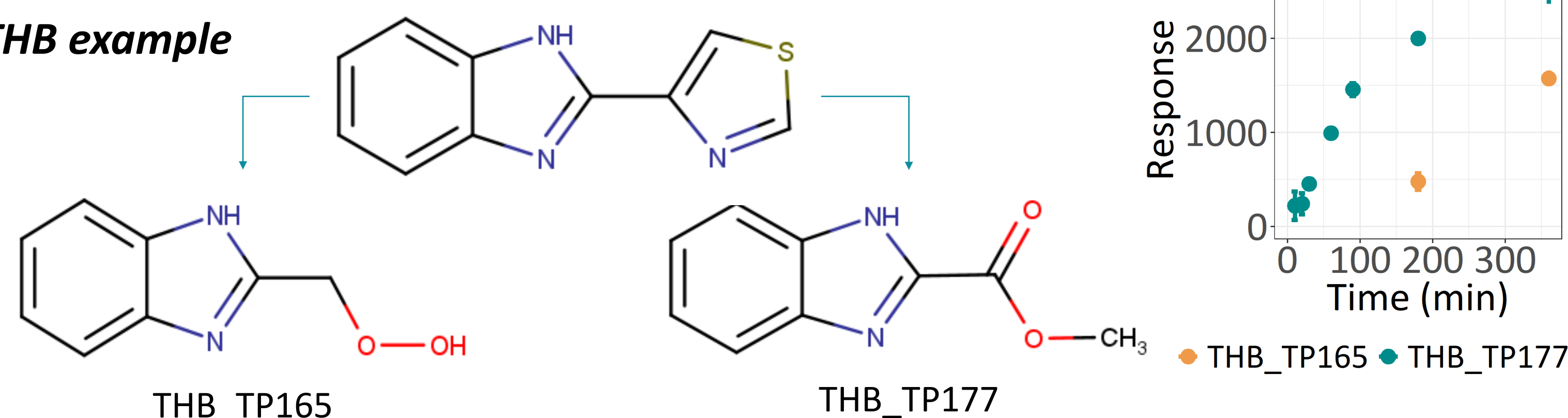
TB was completely removed during irradiation, followed by DFB (75%), DCOIT (63%), CBZ (52 %), TEB (51 %), IPBC (16 %) and THB (14 %).

Some of the TPs from literature were identified in our samples. TPs found were identified as biodegradation and photolysis products in literature.

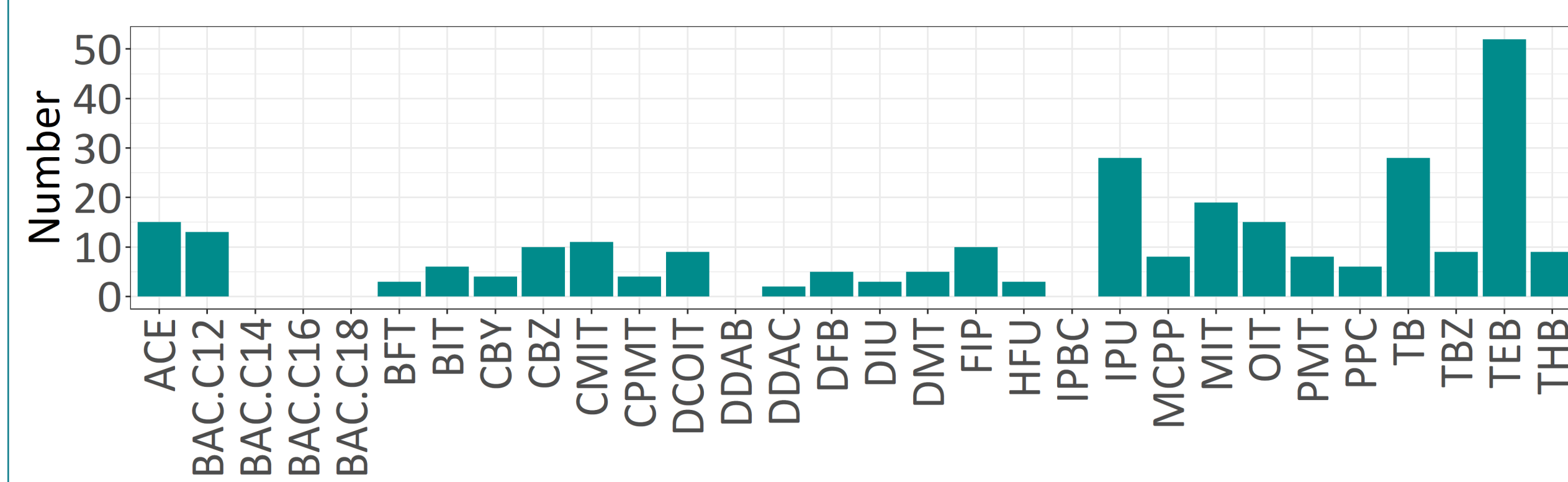
Non target screening

New TPs identified (level 2/5 on confidence : probable structure³) for THB (×2), CBZ (×2), TEB (×2) and DFB (×1).

THB example



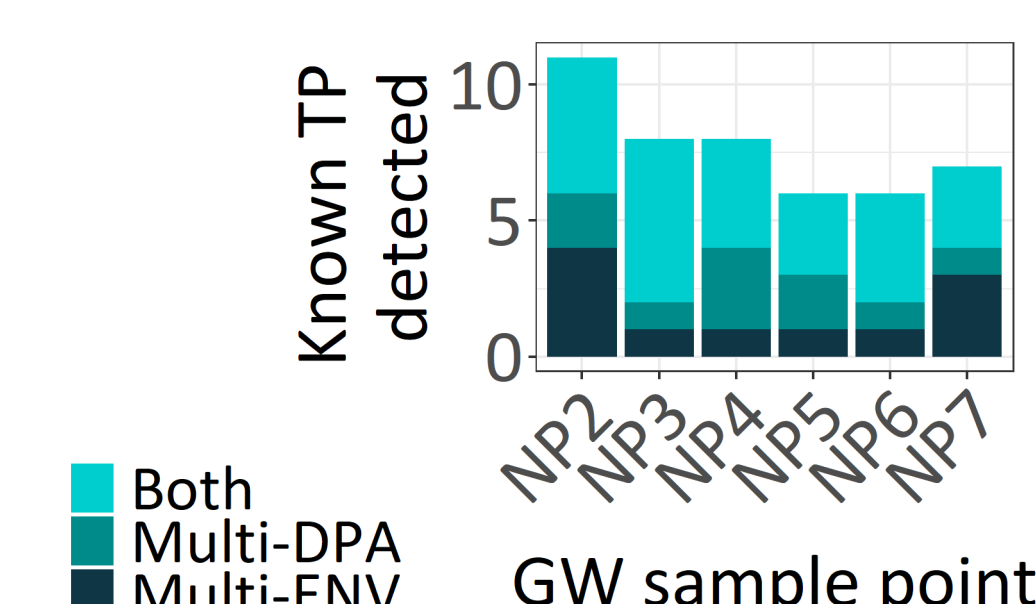
TPs database



- 211 TPs** found in 43 articles
- 7 TPs newly identified** from the degradation experiment
- Few studies about the occurrence of TPs in real samples
- Mainly biodegradation (85) and photolysis (69) products

Comparison of cartridges

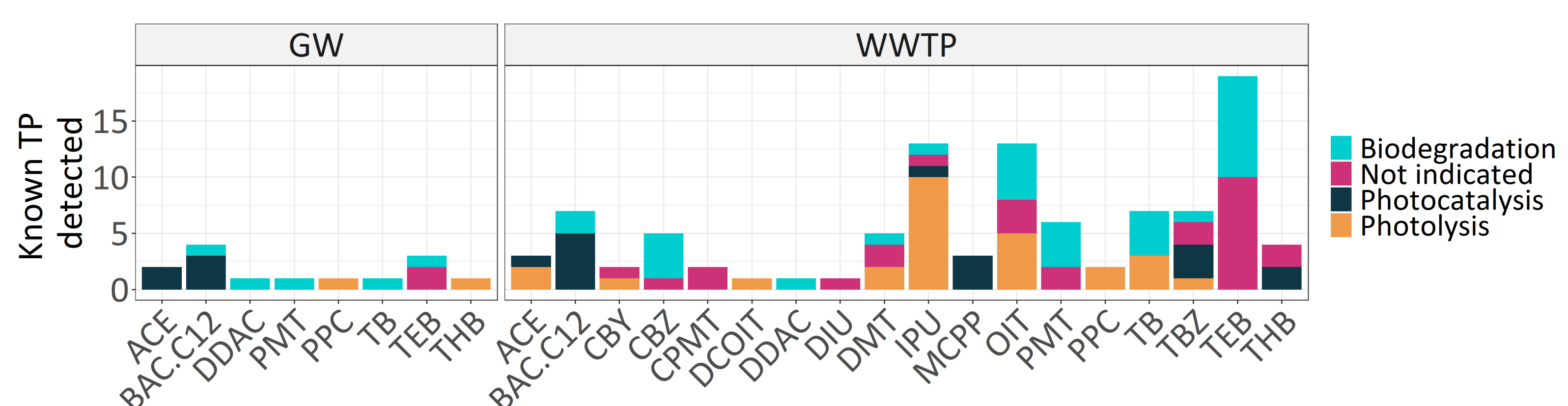
- Similar number of TPs** detected between the two cartridges
- Some TPs only detected with one cartridge



Occurrence of biocides and their TPs

Multi-ENV

- 3 biocides detected in groundwater samples and 7 biocides detected in WWTP samples.
- TPs from biocides used in cosmetics, detergents, paints, wood protection...
- Mainly biodegradation and photolysis products



References

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- Paijens et al. 2020. Environ. Sci. Pollut. Res. 27, 3768–3791
- Schymanski et al. Anal. Bioanal. Chem. 407, 6237–6255

Acknowledgments

