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Modelling the fate of the transformation products generated by the degradation of carbamazepine in various water treatment processes

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Carbamazepine and water treatment

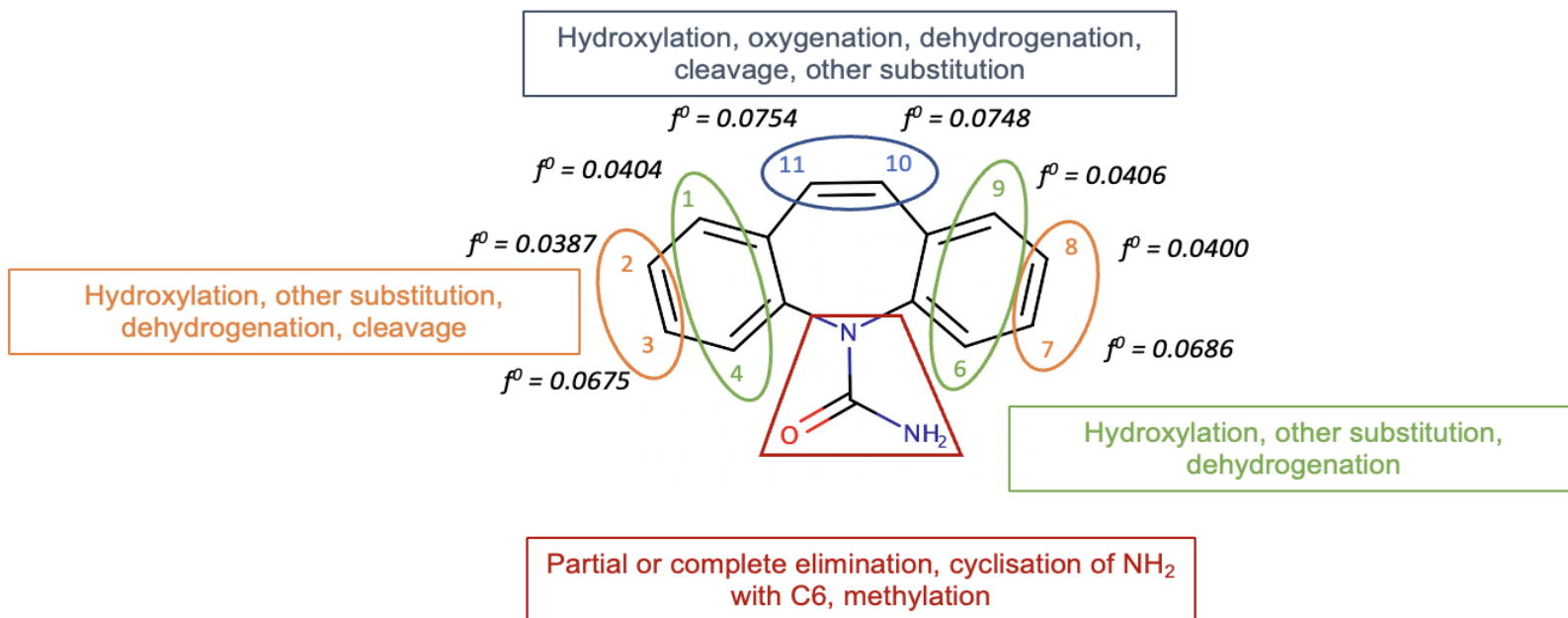
Carbamazepine (CBZ) = anticonvulsant drug (treatment of epilepsy, bipolar disorder and trigeminal neuralgia)

- Worldwide consumption > 1000 t/year
- Poor removal (< 25%) by conventional secondary processes
- 500-1000 ng.L⁻¹ in WWTP effluents

AOP: radicals attack on CBZ structure



Generation of **transformation products (TPs)**

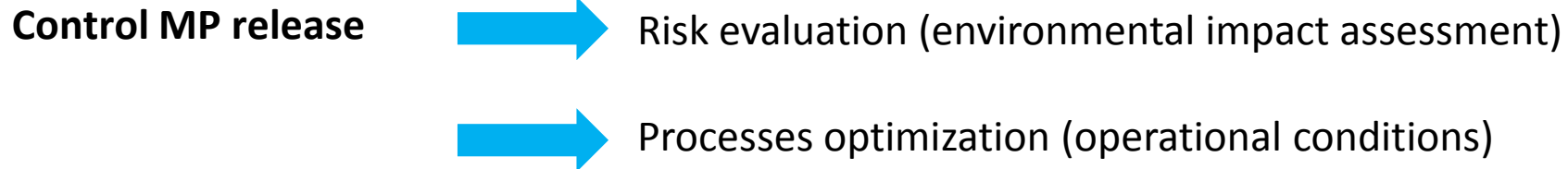


Trognon, Albasi and Choubert, *Sci. Tot. Env.* (2024)

- **Various** TPs (structures, physico-chemicals characteristics, concentrations)
- Many **unknown** about the fate and behavior of such diversity of TPs

Computer-based modelling

Computer-based modelling as a promising tool to predict the fate of MPs and their TPs



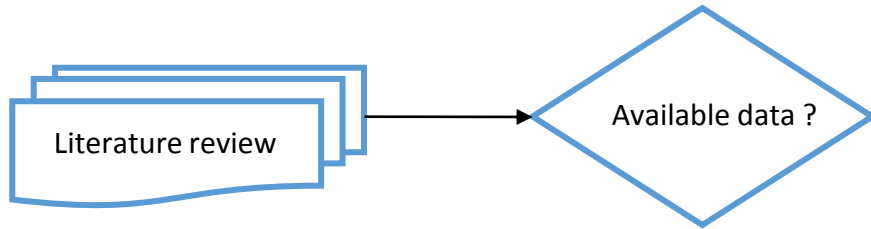
Aim: improve the knowledge on the **nature**, **fate** and **dynamics** of CBZ and its TPs

- 1) **Identification** of CBZ transformation pathways in various oxidation processes and
- 2) **Modelling** of CBZ transformation products to improve the knowledge of their dynamics

1) Trognon et al, *Sci. Tot. Env.*, 2024

2) Trognon et al, *in prep.*

Scientific approach: development of individual models



Scientific approach: development of individual models

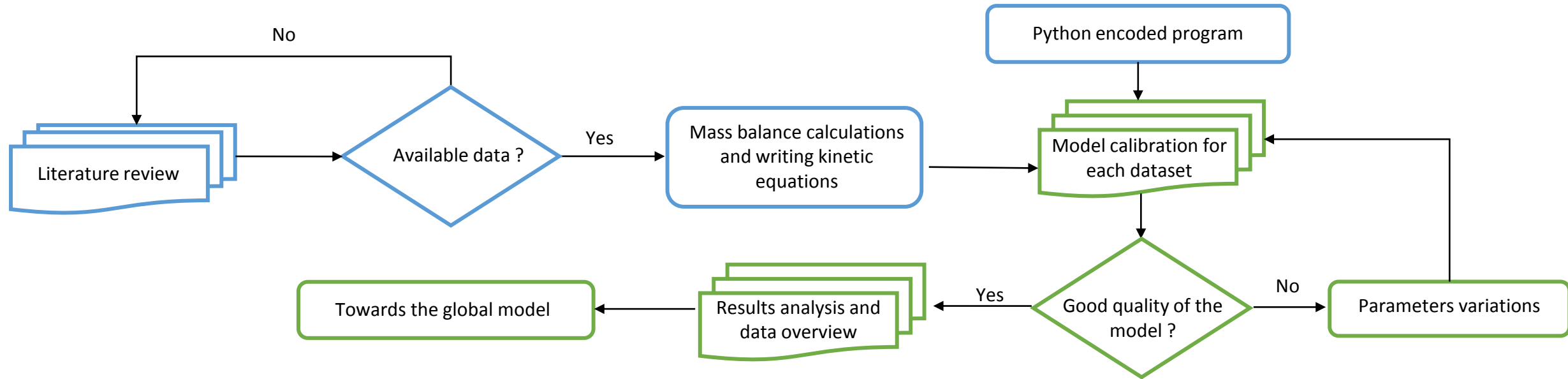
Source of data	Process	[CBZ] ₀ (μM)	[oxidant]	Time	Data for the TPs	Reaction scheme
Jelic et al., 2013	UV/TiO ₂	42.3	100 mg.L ⁻¹	120 min	Normalized peak area (A _{TPs} /A _{CBZ})	
Suara et al., 2022	UV/Cl	42.3	10 mg.L ⁻¹	10 min	[TPs]	
Pan et al., 2017	UV/Cl	2.1	5 mg.L ⁻¹	15 min	[TPs]	
Lu & Hu, 2019	UV/H ₂ O ₂	169	3 g.L ⁻¹	30 min	Normalized [TPs]/[CBZ] ₀	

- 3 different processes
- Diversity of operational conditions



Challenge : experimental [TPs]

Scientific approach: development of individual models



$$dCBZ/dt = -k_{CBZ} * [CBZ] \quad (1)$$

$$dTP/dt = \underbrace{k_{stoi\ TP} * k_{parent\ molecule} * [parent\ molecule]}_{\text{formation}} - \underbrace{k_{TP} * [TP]}_{\text{degradation}} \quad (2)$$

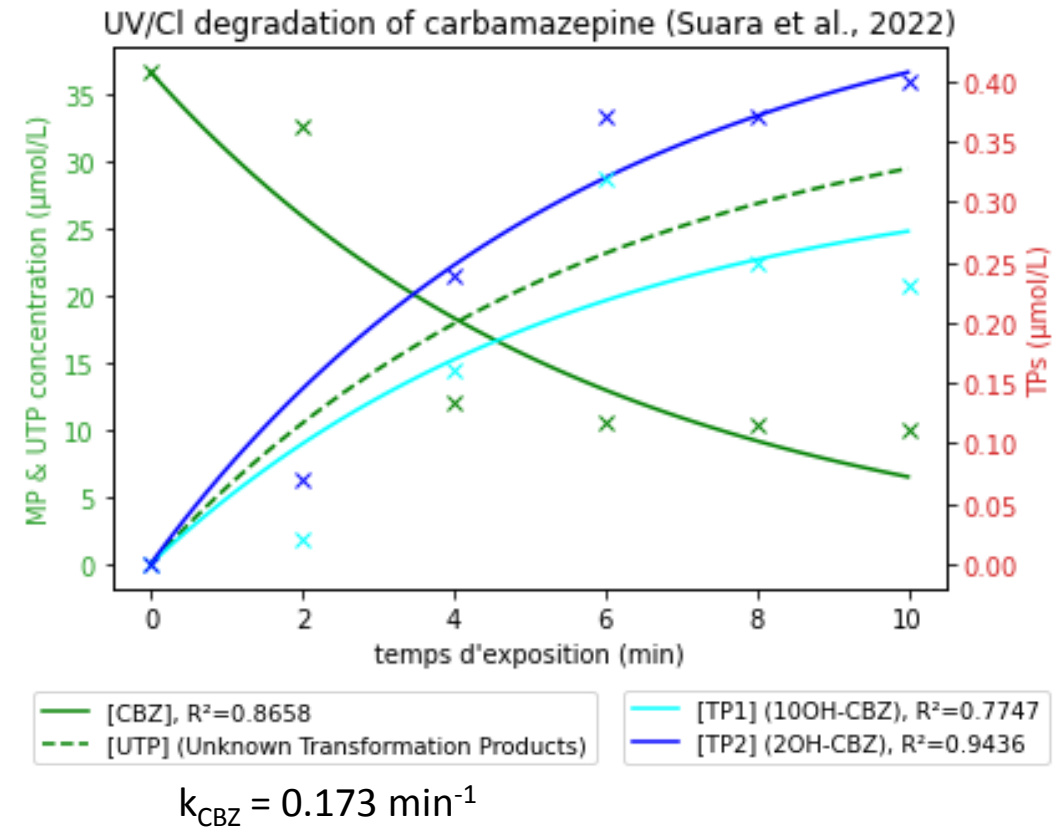
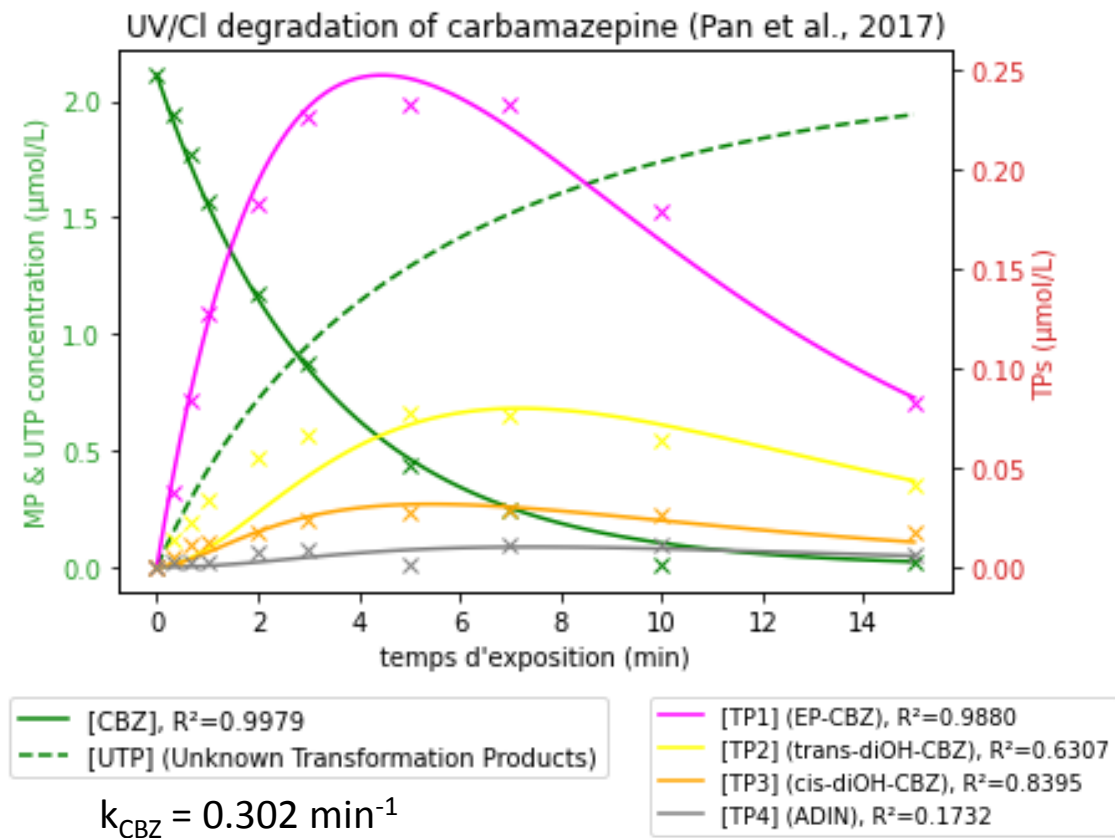
$$dUTP/dt = |dCBZ/dt| - |\Sigma(dTP/dt)| \quad (3)$$

Model parameters:

k_{stoi}: stoichiometric coefficients

k: kinetic constant for degradation

Results: modelling of CBZ degradation

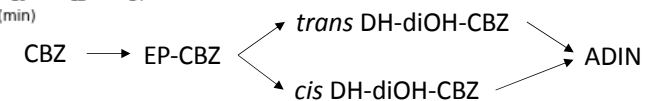
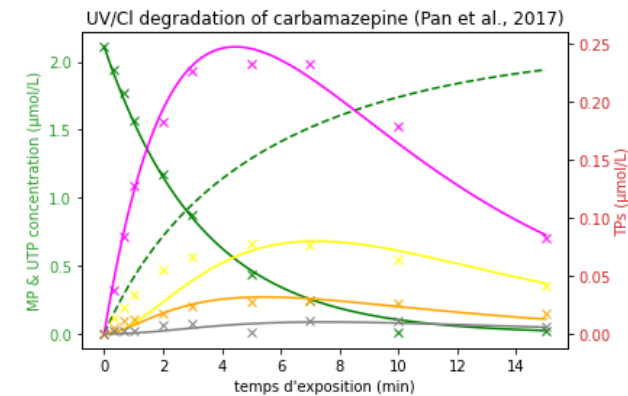


- good adequation between predicted and experimental data ($R^2 > 86\%$)
- k_{CBZ} resulting from model and k_{CBZ} originally calculated in datasets are comparable
- Pseudo-first order equation appropriate for $\frac{3}{4}$ datasets

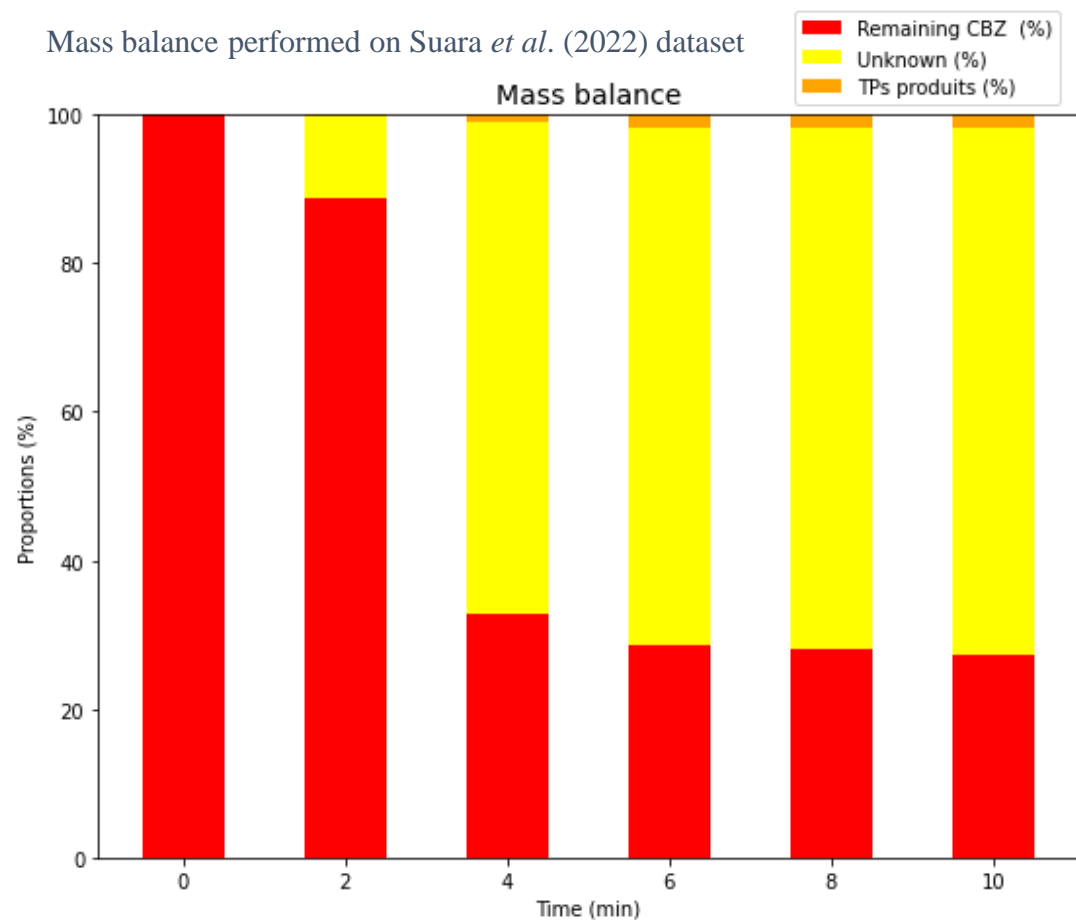
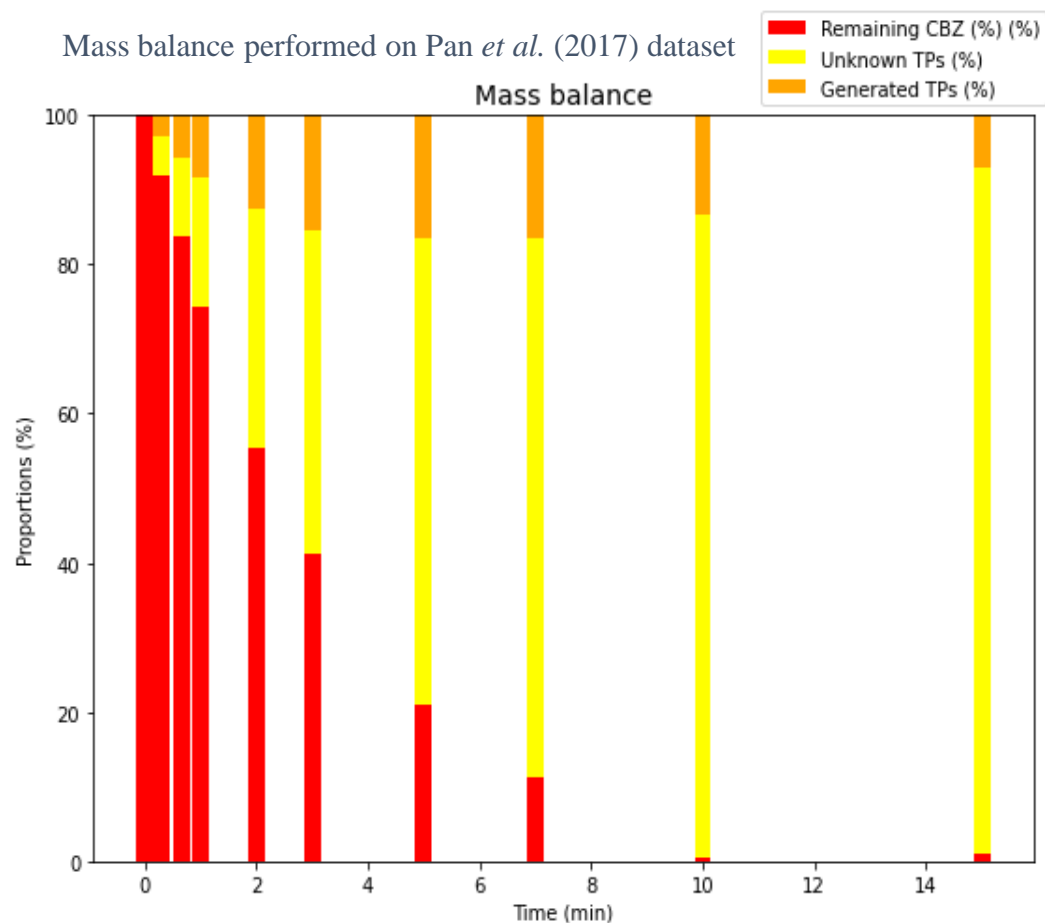
Results: modelling of TPs formation/degradation

Reference	TPs	R ² _{TPs} (%)	k _{TPs} (min ⁻¹)	k _{stoi}
Jelic et al., 2013	DH-diOH-CBZ	94.2	0.134	0.54
	2OH-CBZ	99.9	0.071	0.24
	3OH-CBZ	90.3	0.053	0.29
Suara et al., 2022	CBZ-10.11-dione	86.0	0.025	0.12
	10OH-CBZ	77.5	0.003	0.009
	2OH-CBZ	94.3	0.001	0.013
	EP-CBZ	98.8	0.161	0.24
Pan et al., 2017	trans-diOH-CBZ	63.1	0.439	1.00
	cis-diOH-CBZ	83.9	1.230	1.00
	ADIN	17.3	1.110	0.19
	EP-CBZ	18.5	1.001	0.12
Lu & Hu, 2019	9CHO-CBZ	42.8	2.060	0.05
	DH-diOH-CBZ	96.1	0.302	1.00
	2/3OH-9CHO-ADIN	85.5	0.152	0.96
	ADIN	22.9	2.312	0.32

- 11/15 TPs predicted and experimental data fit-well ($R^2 > 63\%$)
- Quality of the fit decreases for secondary and final TPs (*reaction scheme*) or lowest concentrations
- Predicted concentrations consistent with the reaction pathway



Results: mass balance calculations



- Studied TPs represents 2 % to 17% of the transformed CBZ
- Major proportion of unknown TPs



Choice of molecules of interest



Lack of reference standards

Scientific approach: development of a global model

Literature review and data collected from individual models

Overall reaction scheme design

Global model, implemented to each dataset

Good quality of the model ?

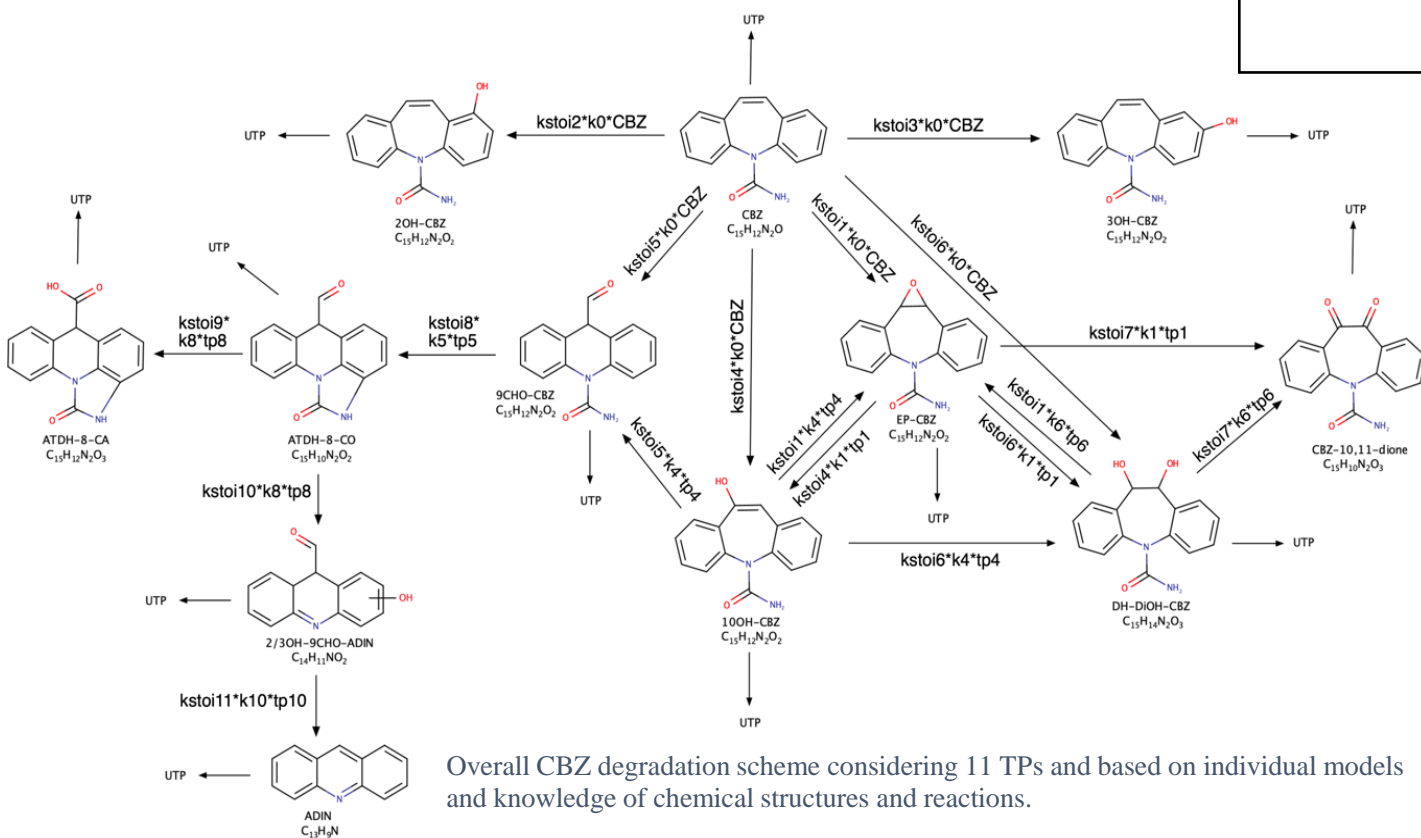
Yes

Sensitivity analysis of the parameters

No

Parameters variations

Conclusions on relevant TPs and parameters



Overall CBZ degradation scheme considering 11 TPs and based on individual models and knowledge of chemical structures and reactions.

12 molecules

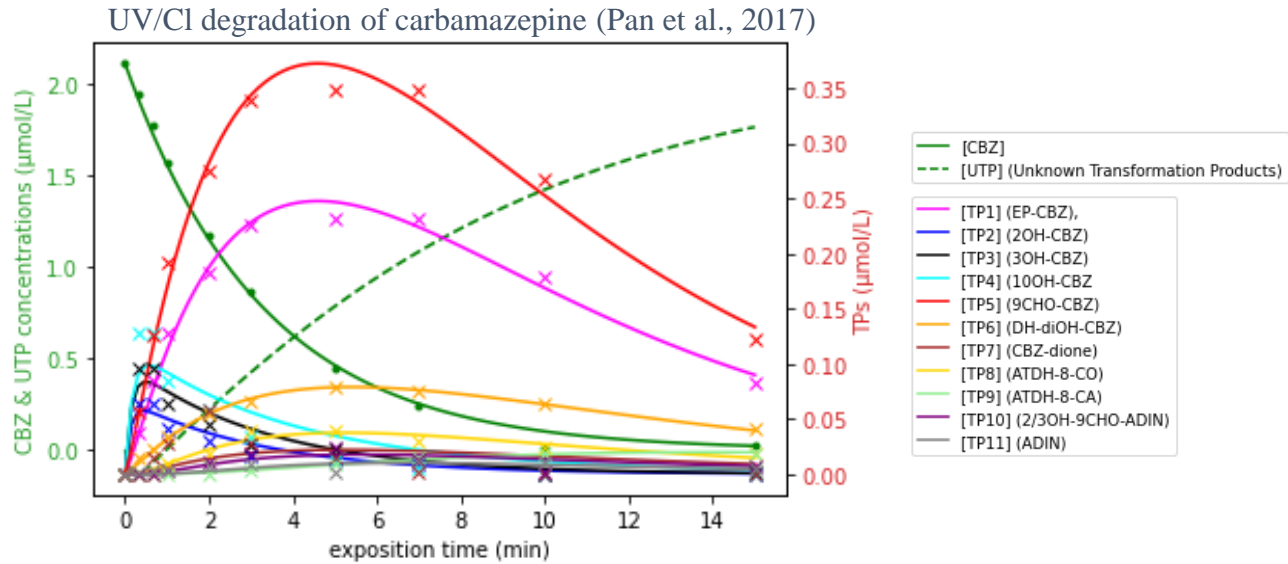
23 parameters:

11 *kstoi*

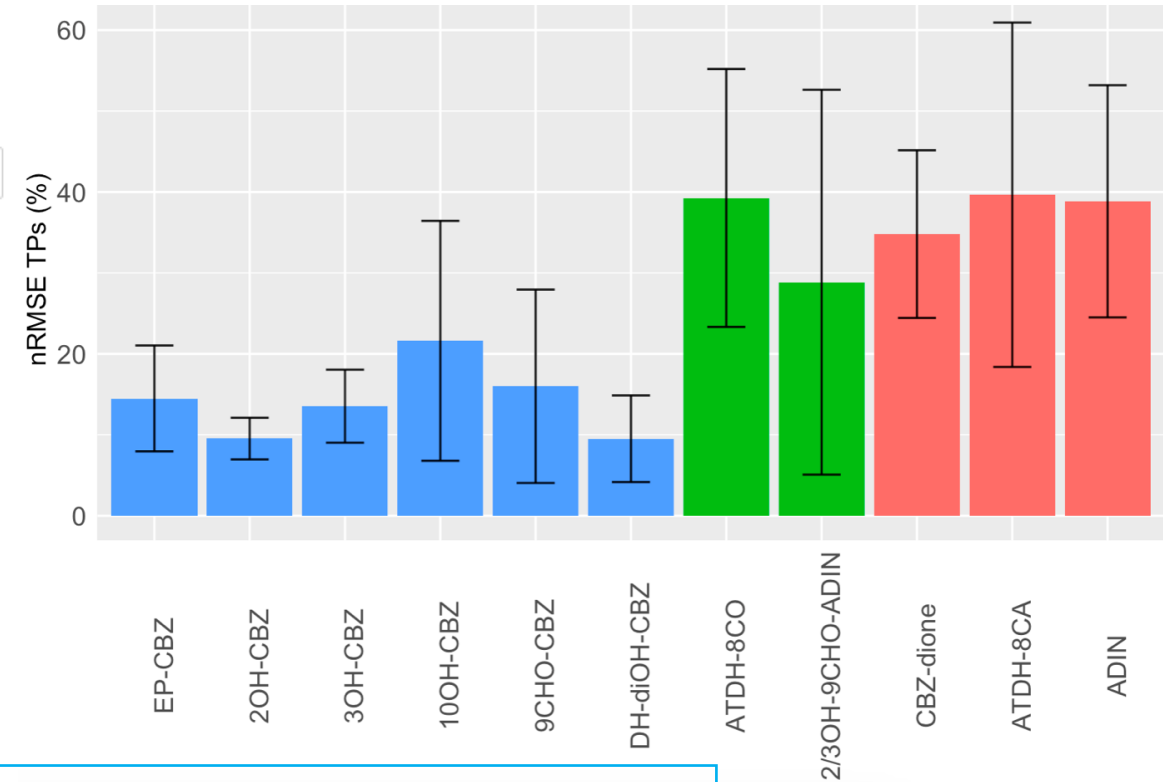
12 *k*

Results: modelling of CBZ and TPs

Global model based on an overall reaction scheme – CBZ and TPs results



Mean nRMSE (%) of each TP, calculated using data from all four datasets. Primary, intermediate and final TPs are represented in blue, green and pink, respectively.



- Good adequation between predicted and experimental data ($R^2 > 80\%$, data not shown)
- Modelling error for primary TPs < 22% ; Modelling error for intermediate and final TPs > 35%

nRMSE : normalized root mean squared error

Results: modelling of CBZ and TPs

Global model based on an overall reaction scheme – sensitivity analysis

Global model = 12 molecules, 13 differential equations, 23 parameters (k_{stoi} , k)

Which TPs ? Which parameters ?

Help future calibration

TPs parameters

Quality of the
model prediction



Observing the changes in the CBZ and primary TPs prediction upon variations of their parameters

For each parameter studied, 5 different values were used:

0.1, 0.3, 0.5, 0.7 and 0.9 for k_{stoi} ,
 10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} and 10^0 for k

Results: modelling of CBZ and TPs

Global model based on an overall reaction scheme – sensitivity analysis

		Global Model Quality	R ² TPs	
<i>k_{stoj}</i>	EP-CBZ	+++	++	
	2OH-CBZ	+++	++	
	3OH-CBZ	++	+	
	10OH-CBZ	+++	++	
	9CHO-CBZ	+++	+	+++ Strong influence
	DH-diOH-CBZ	++	+	++ Moderated influence
<i>k (min⁻¹)</i>	CBZ	+	+	+ Low influence
	EP-CBZ	++	++	
	2OH-CBZ	-	++	- No influence
	3OH-CBZ	-	+	
	10OH-CBZ	-	+	
	9CHO-CBZ	++	+	
	DH-diOH-CBZ	-	++	

- *k_{stoj}* have more influence on the model quality than *k*
- 4 Primary TPs appear as important for the overall quality of the model (EP-CBZ, 9CHO-CBZ, 2OH-CBZ and 10OH-CBZ)

Conclusions & Outlooks

- Development of a **model resolving ordinary differential equations** (ODEs) based on formation/degradation kinetic equations and mass balance approach
- **Overall reaction scheme**
- Promising results with **good correlation** between the model predictions and the experimental data for both CBZ and TPs and for both the individual and the global model
- **4 primary TPs** are instrumental for the quality of the predictions: EP-CBZ, 9CHO-CBZ, 2OH-CBZ and 10OH-CBZ. Future model calibrations should focus on the **stoichiometric k_{stoi} parameters**, rather than the kinetic constants k .

Outlooks:

Model **validation**

Investigation of the **UTP** fraction

Add more **parameters** in the model such as macroscopic properties of the TPs (hydrophobicity, ...)

Thank you for your attention !