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Transformation products generated by oxidation of carbamazepine during wastewater treatment processes - Review and Modelling -

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Introduction – Context

Carbamazepine (CBZ) is an anticonvulsant drug, used for the treatment of epilepsy, bipolar disorder and trigeminal neuralgia.

- Global consumption > 1000 t/year [1].
- Poorly removed (< 25%) by conventional secondary processes (500-1000 ng.L⁻¹ in WWTP effluents [2])

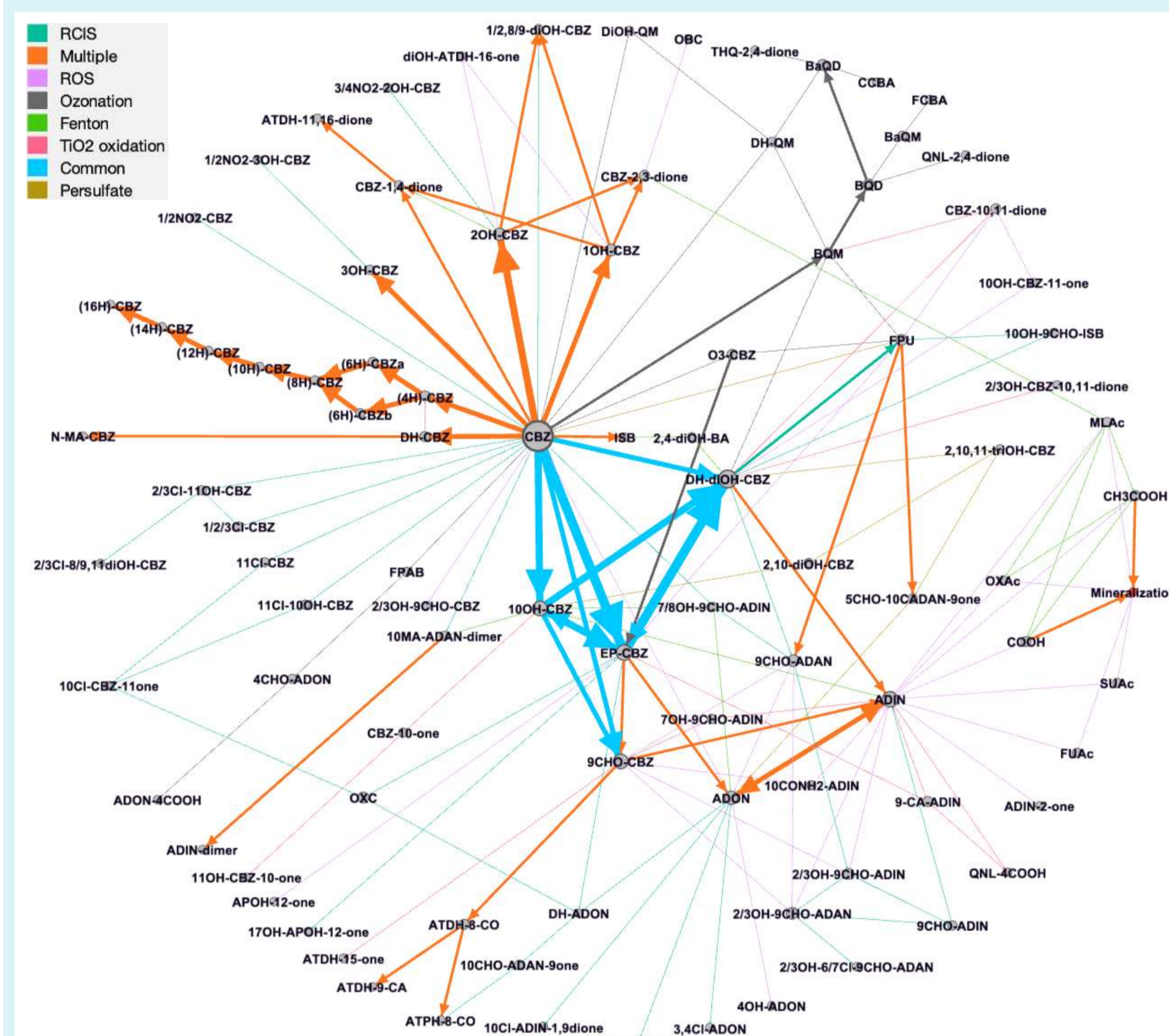
CBZ can be eliminated by polishing treatment processes, such as ozonation or advanced oxidation processes (AOP), known to be responsible for transformation products (TPs) generation [3, 4].

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

computer-based modelling as a promising tool to predict the fate of TPs and their TPs [5, 6].

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

1- TPs generation from CBZ oxidation



> 100 TPs identified:
4 TPs common to all processes

Key intermediary TPs emerge (ADIN, ADON)

Various, complex reaction pathways:

TPs generated from different processes and pathways

Inverse reactions

Diversity of structures and characteristics (hydrophobicity, permeability, ionization state)

Reaction pathways of TPs generated from CBZ oxidation (Drawn with Gephi software 0.9.5, review of n= 34 papers, between 2000 and 2022)

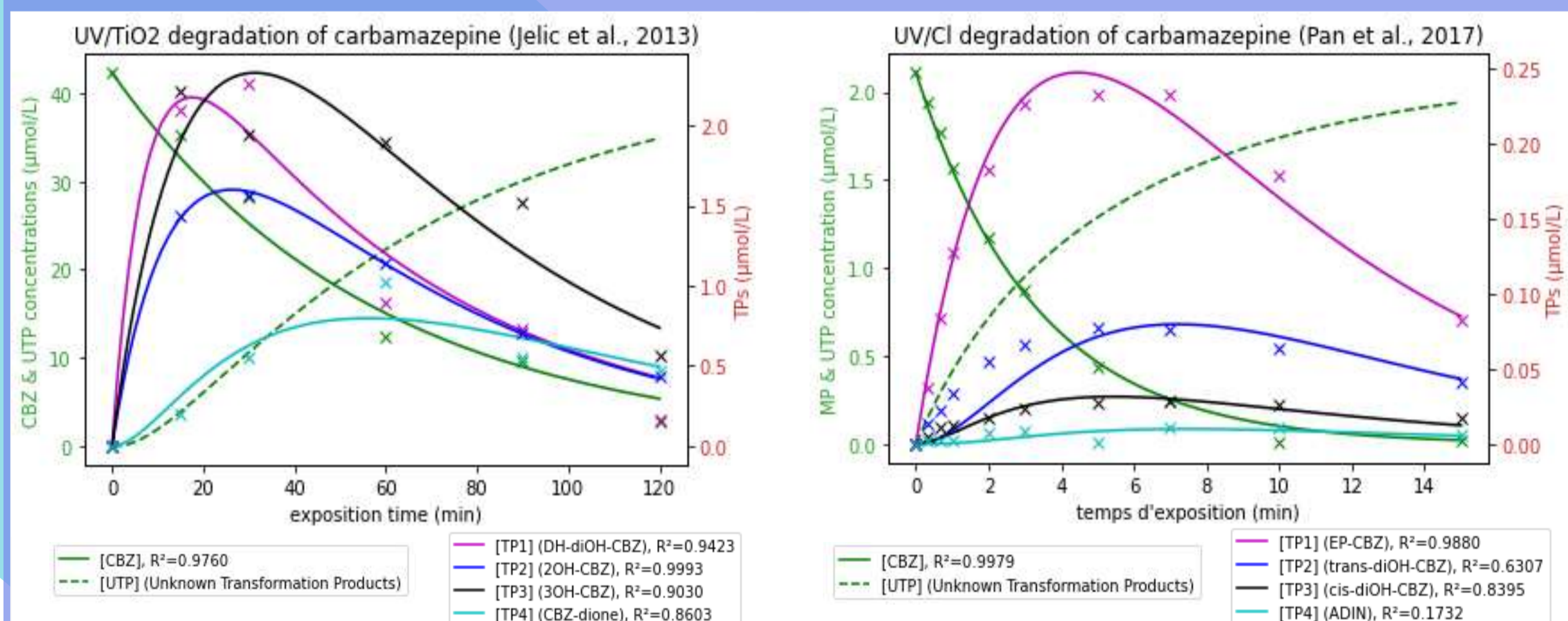
2- Numerical model calibration

Python program => Resolution of ordinary differential equations (ODE) based on formation and degradation kinetic equations:

$$\text{For CBZ} \rightarrow \text{TP} : d(\text{TP}, t) = k_{\text{stoi TP}} * k_{\text{CBZ}} * [\text{CBZ}] (\text{TP formation}) - k_{\text{TP}} * [\text{TP}] (\text{TP degradation})$$

5 datasets: TiO₂ photocatalysis (n = 2), UV/Cl (n = 2), UV/H₂O₂ (n = 1)

- (1) Franz et al., *Catalyst*, 2020; 2) Jelic et al., *Journal of Hazardous Materials*, 2013; 3) Lu & Hu, *Sciences of the Total Environment*, 2019; 4) Pan et al., *Water Research*, 2017; 5) Suara et al., *Environmental Science and Pollution Research*, 2022)



2 examples of CBZ degradation modelling by UV/TiO₂ and UV/Cl

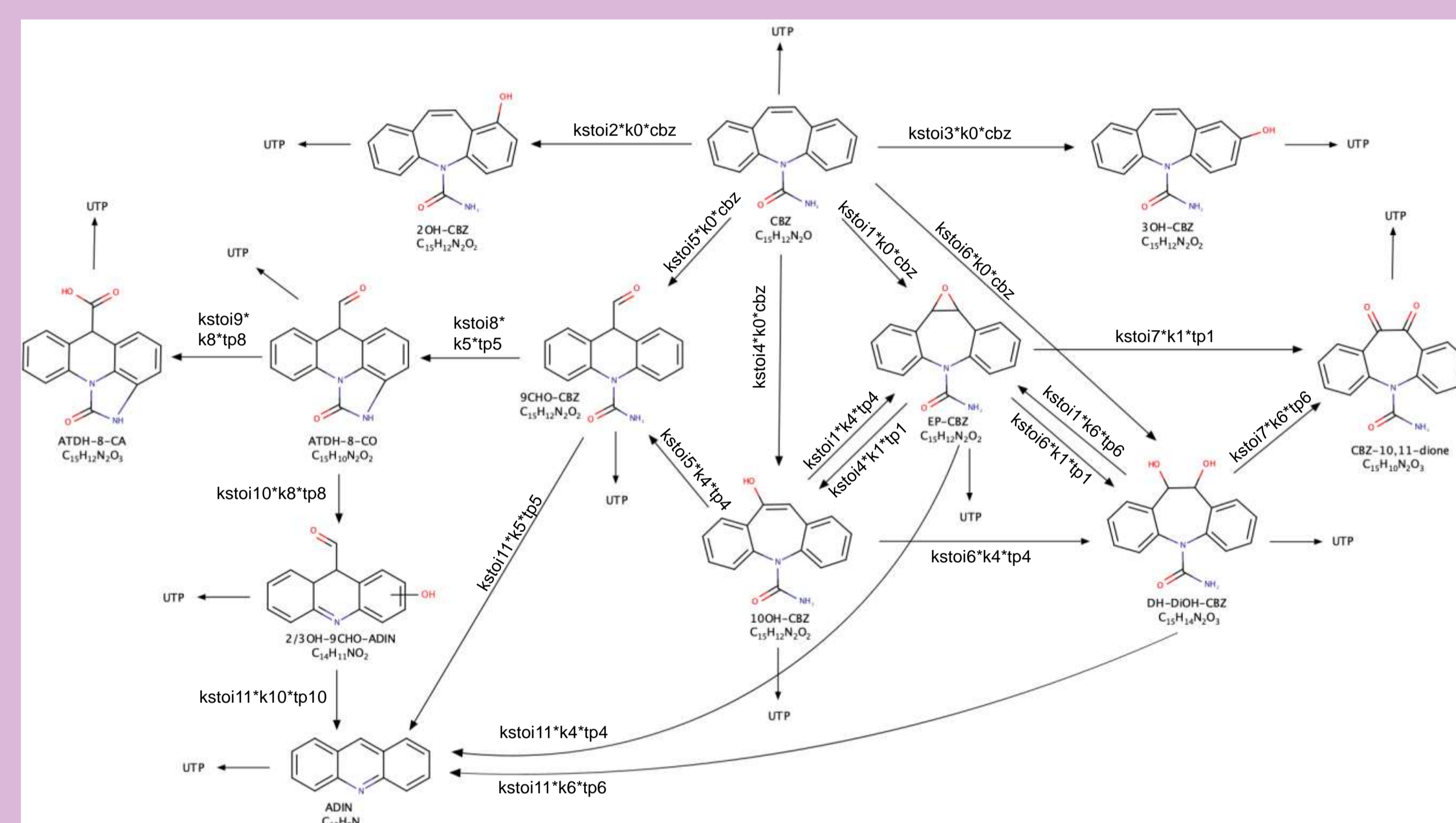
Parameters values calibrated for each studied dataset

Ref	R ² _{CBZ} (%)	k _{CBZ} (min ⁻¹)	Mean R ² _{TPs} (%)	Mean nRMSE of the model
1)	93,0	5.155 x 10 ⁻²	81 +/- 9% (n=2)	13,97%
2)	97,6	1.723 x 10 ⁻²	93 +/- 6% (n=4)	7,76%
3)	99,3	1.876 x 10 ⁻¹	53 +/- 36% (n=5)	19,08%
4)	99,8	3.027 x 10 ⁻¹	66 +/- 35% (n=4)	14,17%
5)	86,6	1.730 x 10 ⁻¹	86 +/- 12% (n=2)	14,12%

- Good fit for CBZ degradation
- Resulting k_{CBZ} ≈ k literature
- Overall, good quality of TPs modeling

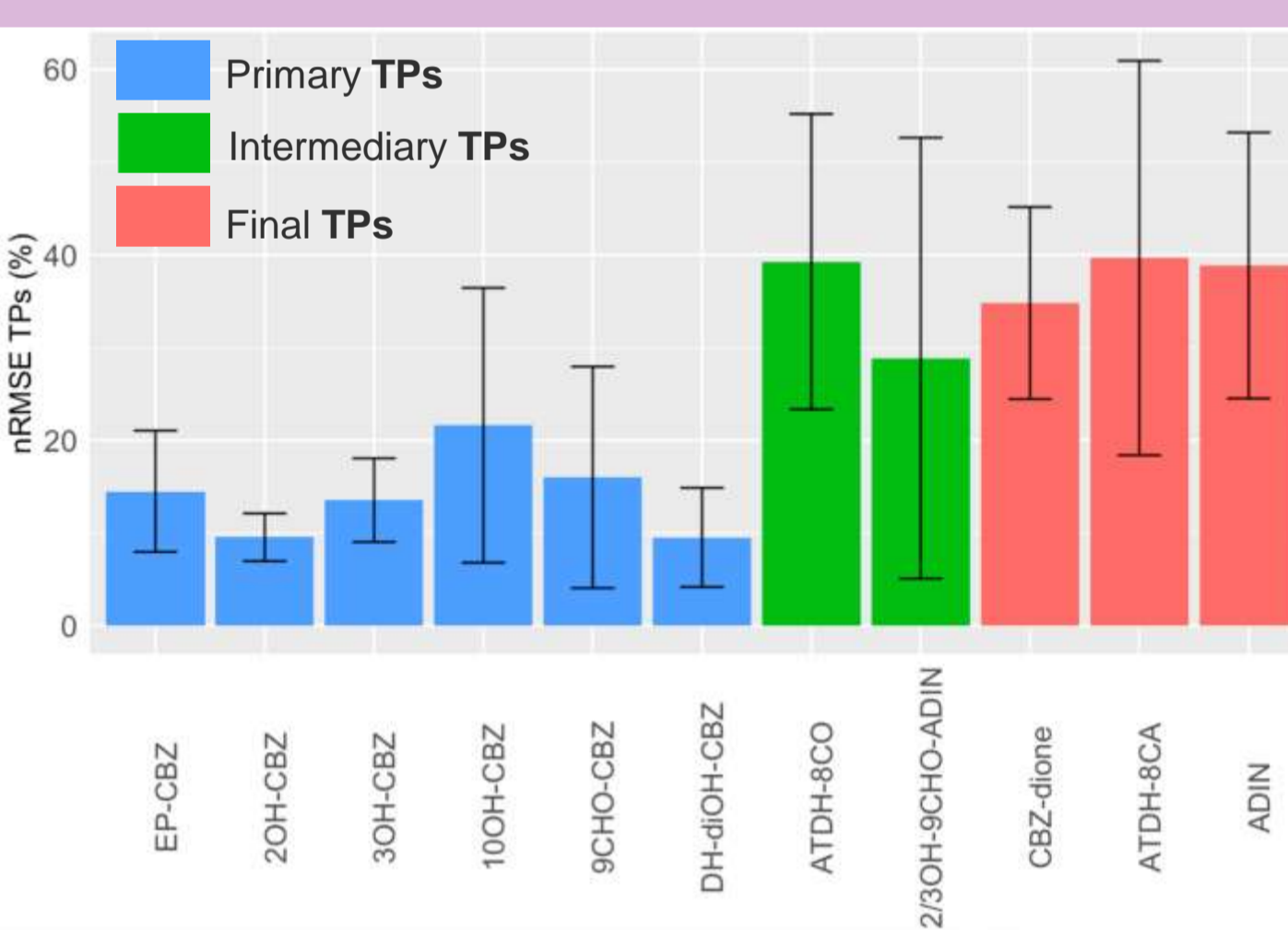
3- Unique degradation scheme

- ➔ One reaction pathway by compiling the 5 datasets
- New formation and degradation kinetic equations
- Unique model applied for all datasets



Unique reaction scheme. Obtained by compilation of the 5 studied datasets and knowledge from literature (Drawn with MarvinSketch [v22.13], UTP = unknown transformation product)

Modelling the 5 experiments with the unique pathway



Main results obtained for the compiled model, for the 5 studied datasets

Ref	nRMSE _{CBZ} (%)	k _{CBZ} (min ⁻¹)	Mean nRMSE of the model (%)
1)	9,8	5.156 x 10 ⁻²	20,3
2)	5,6	1.723 x 10 ⁻²	24,9
3)	3,1	1.876 x 10 ⁻¹	35,9
4)	1,7	3.036 x 10 ⁻¹	12,2
5)	15,6	1.730 x 10 ⁻¹	31,8

mean nRMSE (%) of each TPs, calculated from all dataset.

- nRMSE_{primary TPs} < 22% & 30% < nRMSE_{other TPs} < 40%

➔ The further the molecule is from CBZ in the reaction pathway, the harder it is to predict.

- Mean nRMSE of the model ≤ 35% → acceptable fit

Sensitivity analysis on k_{stoi} and k (min⁻¹) parameters:

- Model more sensitive towards k_{stoi} (rather than k (min⁻¹))
- Not sensitive to 3OH-CBZ and DiOH-CBZ parameters variations

CONCLUSION

- Modeling TPs fate through a unique degradation scheme was successful
- Good CBZ degradation modeling and prediction of TPs formation and degradation
- Sensitivity allows to choose the most interesting data to focus on and help for future model calibration
- Perspective: model validation by experimental data on CBZ degradation & TPs formation

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