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Prediction of organic micropollutant removal in drinking water treatment processes, based on QSPR modelling

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Joint Research Programme

KWR

Bridging Science to Practice



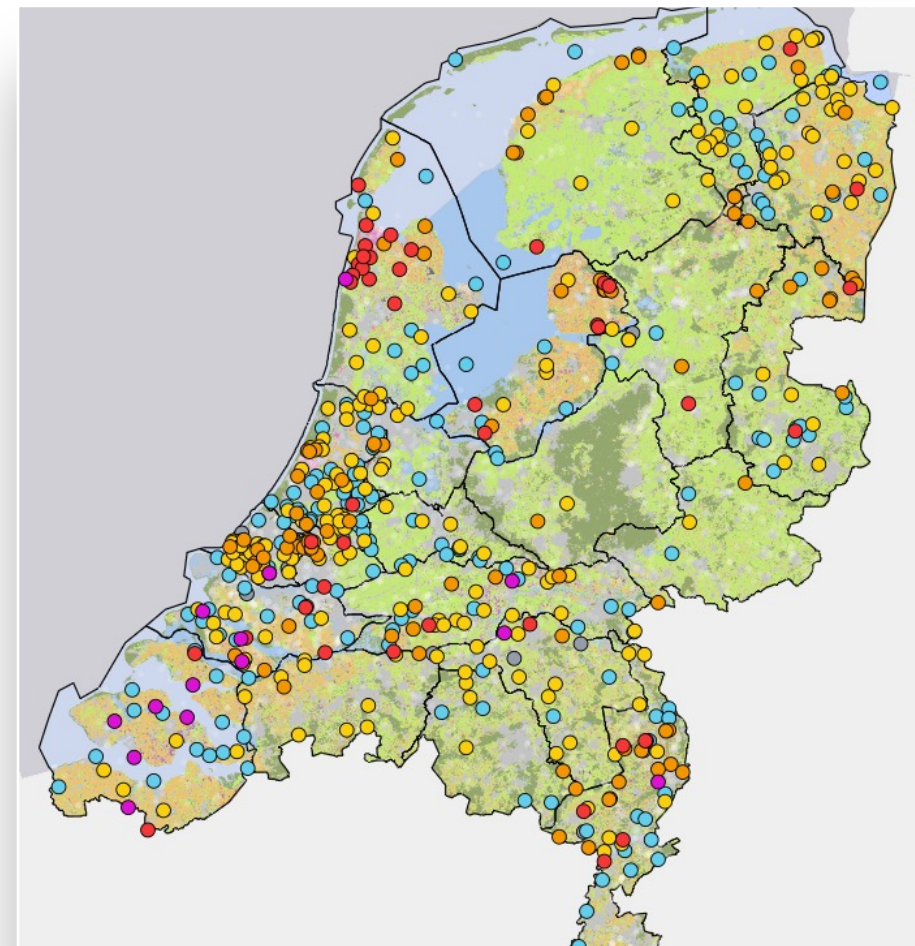
Problem

Occurrence of organic micropollutants (OMPs):

- Increasing amount of chemicals (>114M in pubchem)
- Also in drinking water sources (>400 in Dutch surface water)
 - Pesticides
 - Pharmaceuticals
 - Industrial compounds (e.g. PFAS)

Yielding

- Greater uncertainty in risk assessment (legislation)

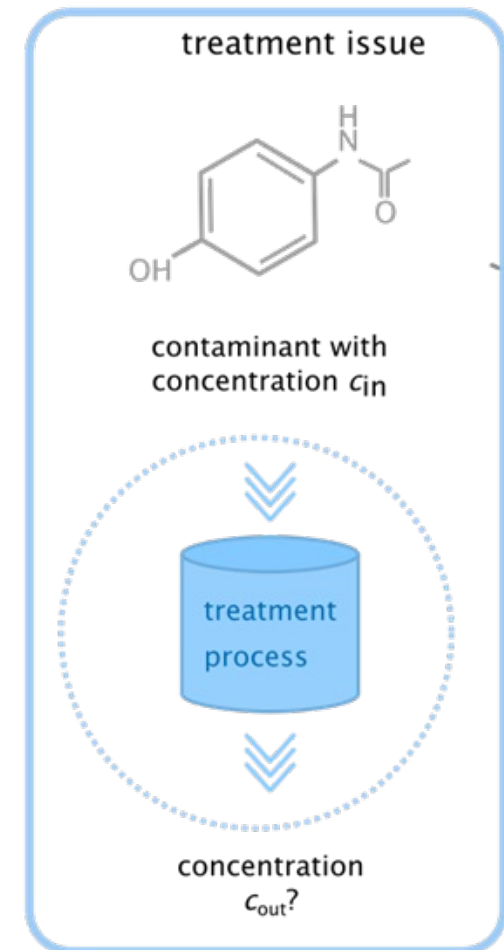


A priori knowledge on removal of OMP

To assess

- risk of substance upstream
- robustness of water treatment
- most effective (extra) treatment step

Requires regular, time-intensive and expensive experiments



Approach: model estimations (hybrid modelling)

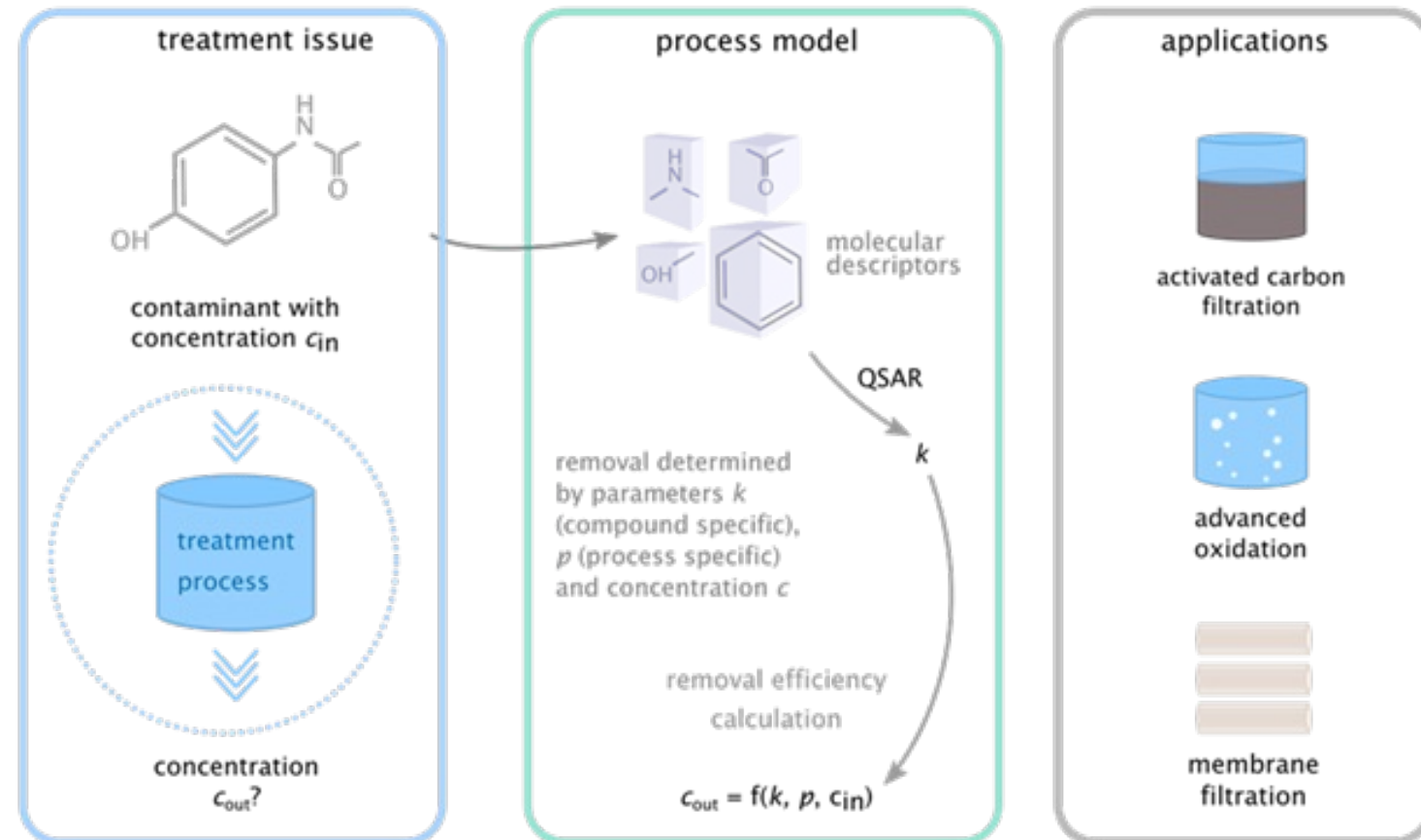
Predict removal for (new) organic compounds

Development steps:

1. Process model
2. Statistical model (QSPR)
3. Validation

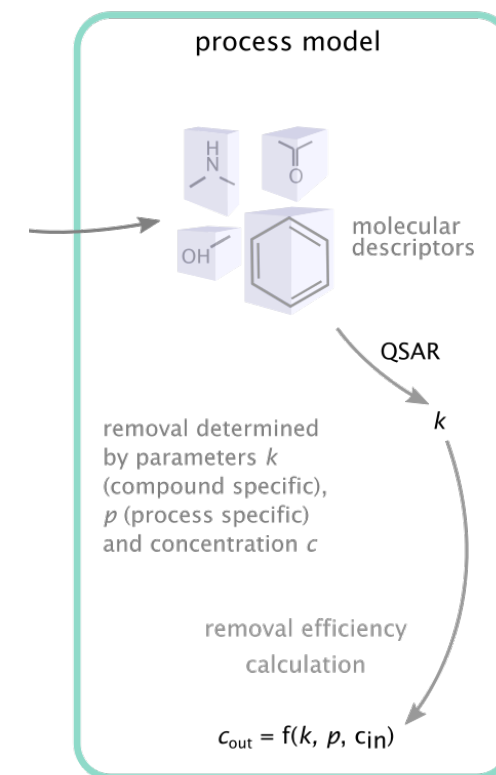
Three water treatment processes:

- Activated carbon filtration
- Reverse osmosis filtration
- Advanced oxidation



QSAR/QSPR approach

- Molecular properties of compounds determined from **molecular descriptor software** → >1000 descriptors
- **Statistical model** links descriptors to property/reaction constant from process model of water treatment process (QSAR/QSPR)
- Train statistical model with **data** from measurements/literature.
- **New** compounds:
 - Calculate molecular properties
 - Calculate process model property/reaction constant
 - Use this in process model to calculate **removal**





Need for data

- Training of QSPRs
- Validation of models (other data)

Data from:

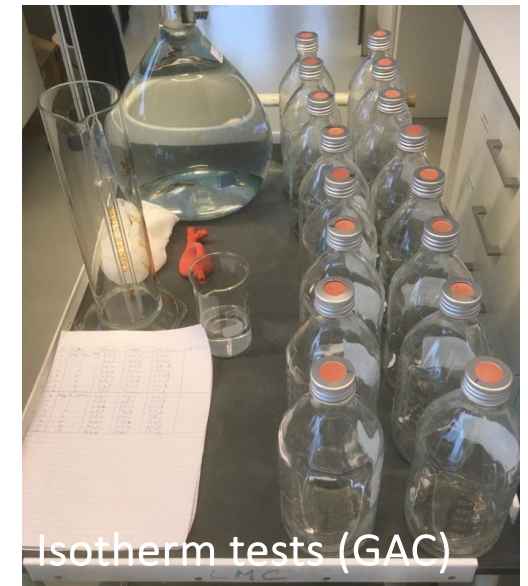
- Lab-scale experiments
- Pilot experiments
- Full-scale

Data collected with (Dutch/Flemisch) drinking water companies:

- ~20 years of OMP measurements
- >100 individual OMPs tested



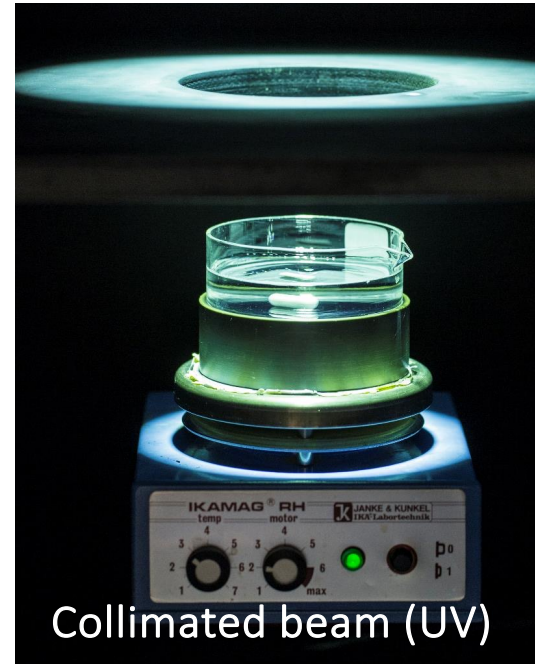
Pilot tests (GAC)



Isotherm tests (GAC)



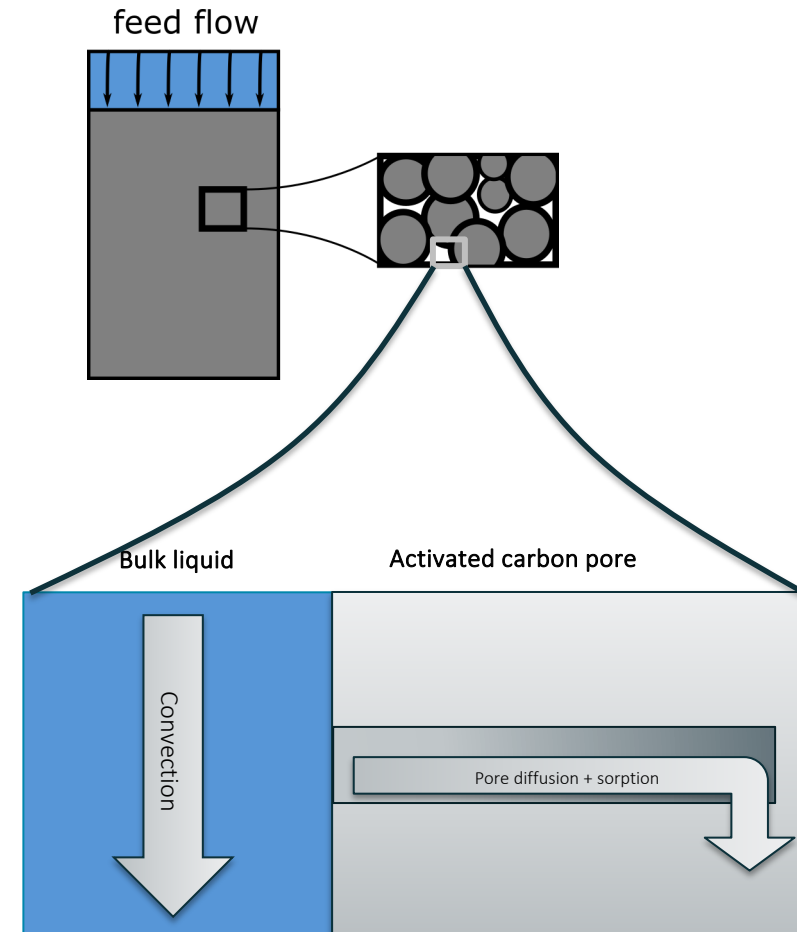
Pilot tests (RO)



Collimated beam (UV)

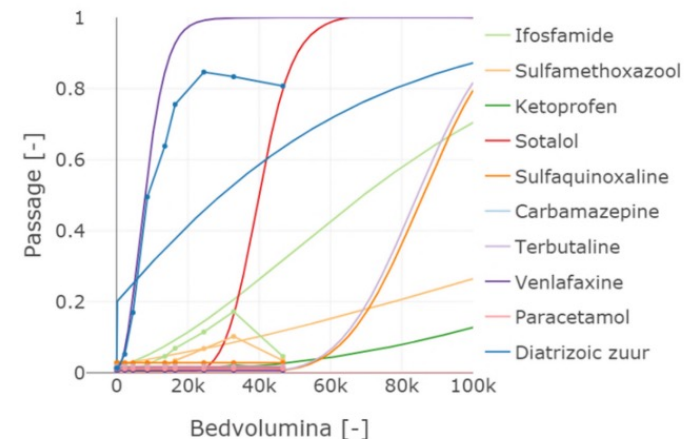
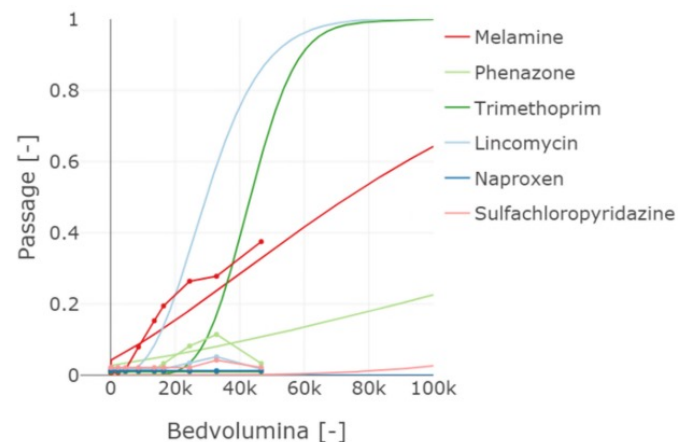
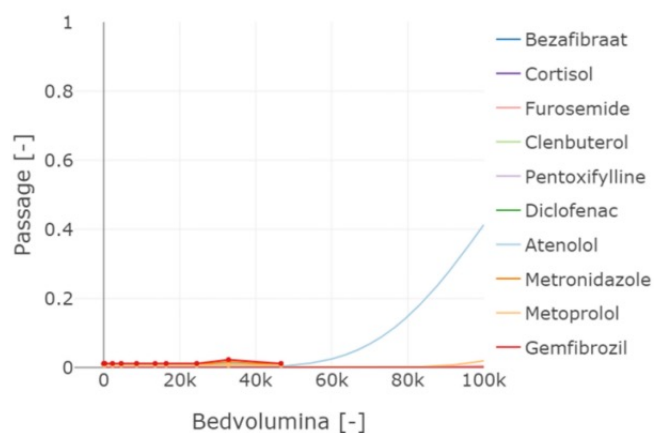
Granular activated carbon (GAC)

- 1D convection-adsorption model
- Pore diffusion
 - Pore diffusion constant
- Adsorption
 - QSPR predicted Freundlich isotherm
- Competition with DOC (challenge!)
 - Equivalent background component



Validation of granular activated carbon

- Competition with DOC (differs per OMP or group of OMPs)
- (unknown) diffusion limitations



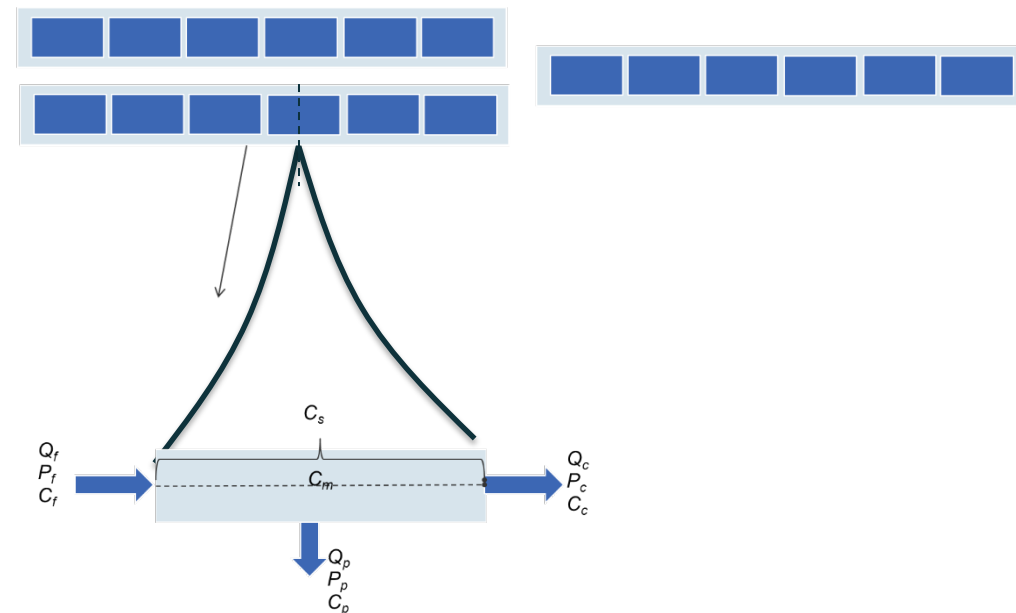
Reverse osmosis (RO)

- Solution-diffusion model (on a slice)
- Mass balances over configurations
- Parameters:
 - Membrane supplier provided properties (area, salt retention)
 - Configuration
 - Pressure/recovery/flow
 - **OMP retention based on QSPR (solute diffusion, B)**
 - QSPR fitted from ~80 OMP measured data

Spiegler, Kedem, Katchalsky equations:

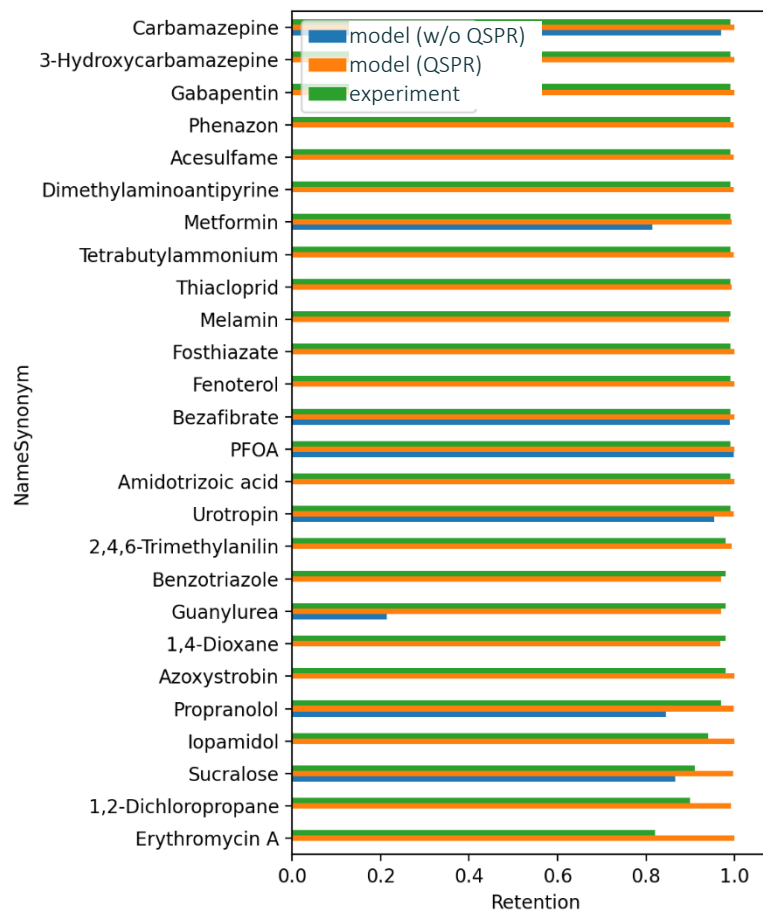
$$J_s = B(C_m - C_p) + (1 - \sigma)C_m J_w$$

$$J_w = A\{(P_f - P_p) - \sigma(\pi_f - \pi_p)\}$$

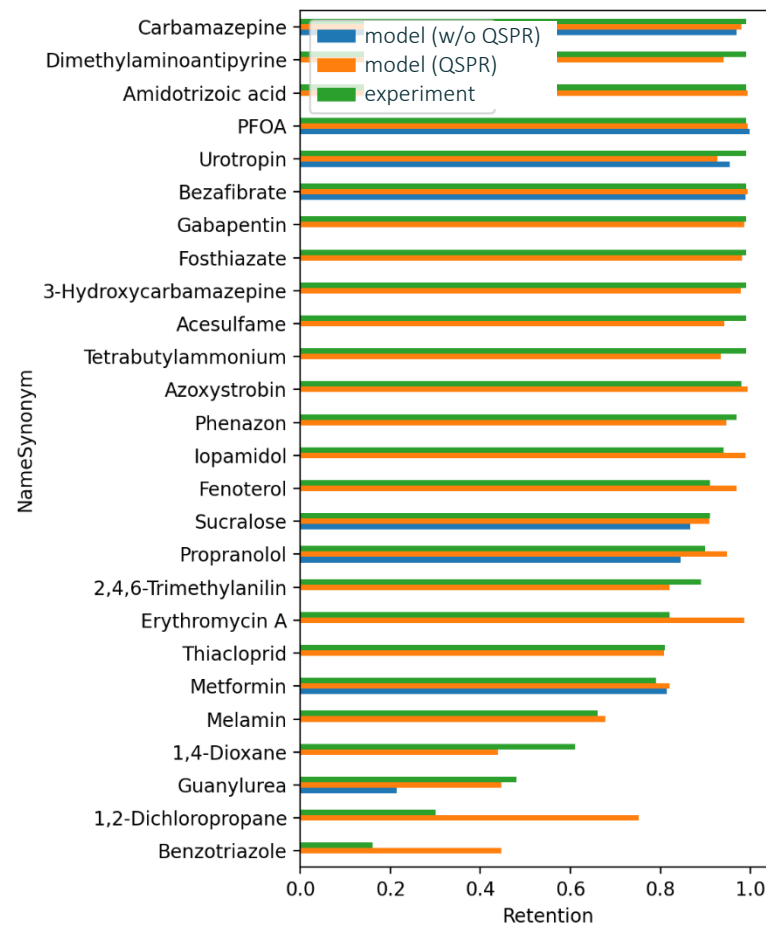


Validation RO (/NF)

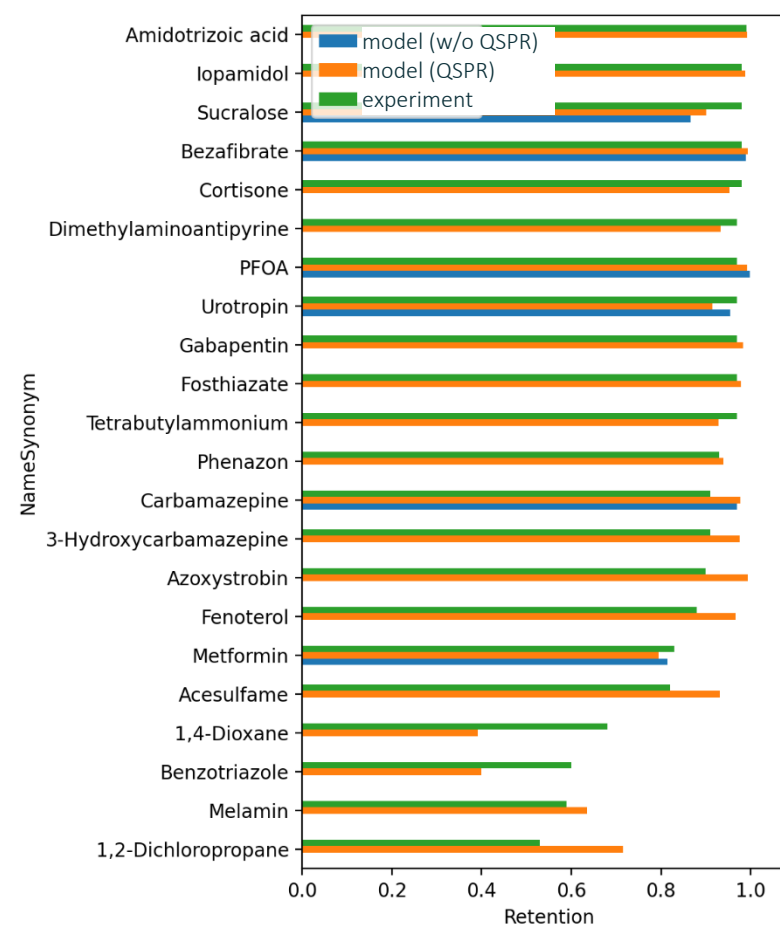
SWC5



ESNA1



dNF40



Advanced oxidation model: UV, UV/H₂O₂, O₃, O₃/H₂O₂, UV/O₃

1. Kinetic model

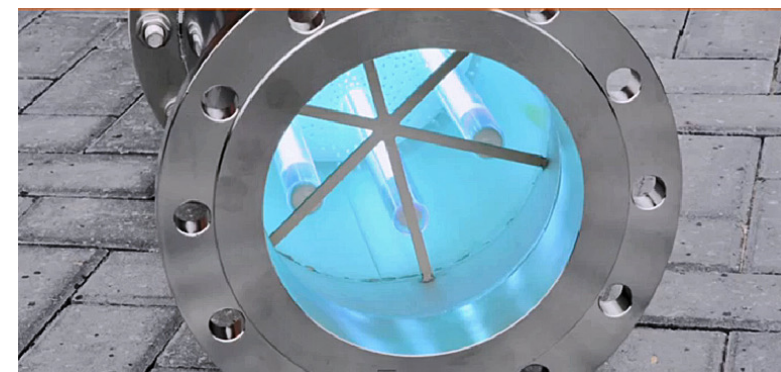
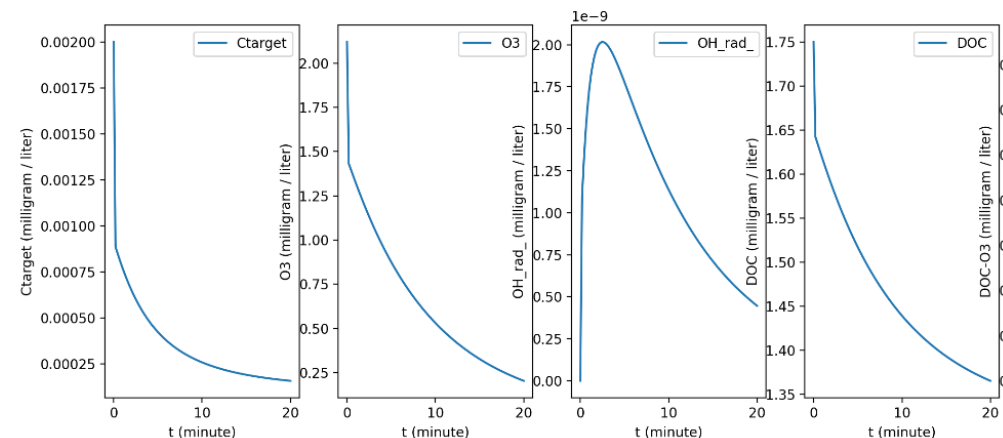
- List of (photo)chemical reactions

2. Photochemical constants: from literature data or calculated by QSPR:

- OH radical reaction rate constants
- O₃ reaction rate constants
- Direct photolysis constants (QY and molar absorption)

3. Validation from measurements

- E.g. collimated beam experiments or pilot results





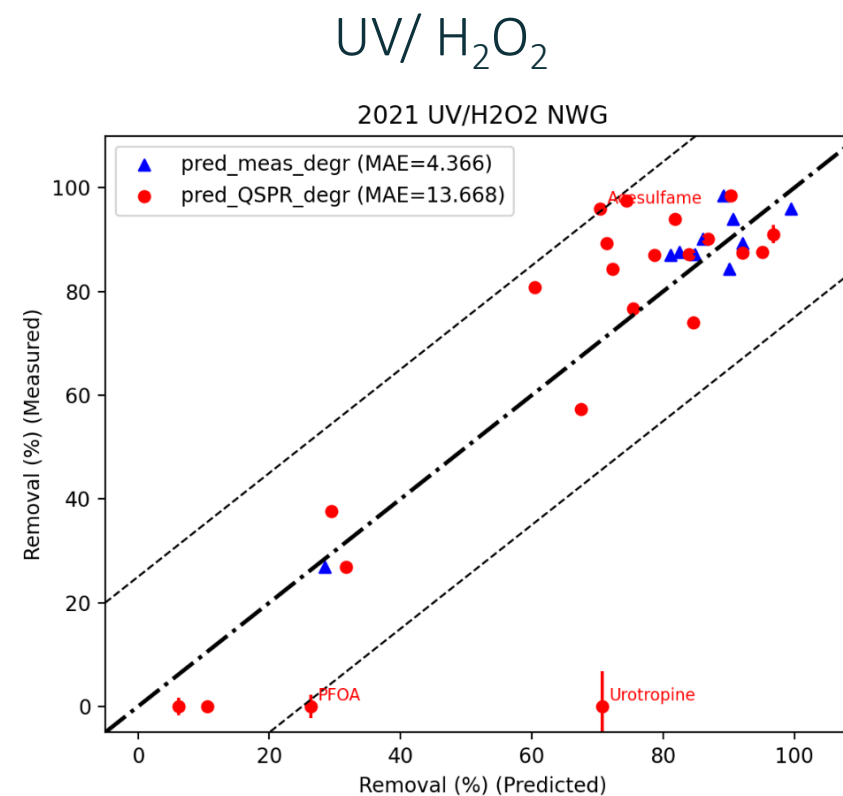
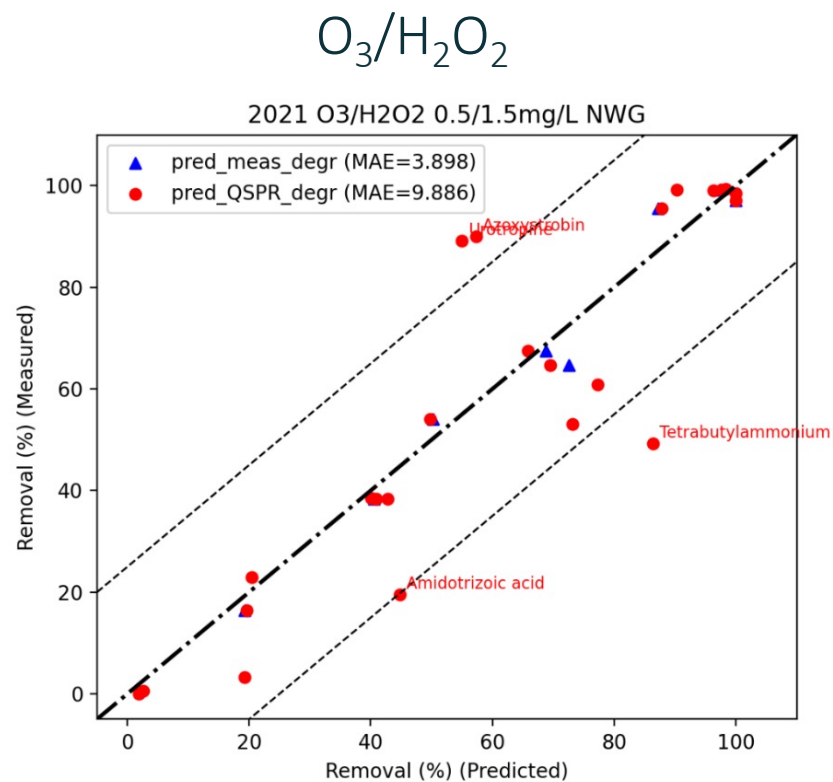
Kinetic model

- Photolysis: H_2O_2 , OMV
- Reactions with H_2O_2
- Background reactions (other radicals)
- Components in water matrix:
 - (bi)carbonaat
 - DOC
 - Phosphate
- Equilibrium reactions
- Solved by mathematical differential equations

name	rn1	r1	rp1	rn2	r2	rtype	pn1	p1	pn2	p2	pn3	p3	rate	unit
kphoto_p		1 H2O2				f>		2 OH_rad_						
kphoto_o		1 O3	+		1 H2O	f>		1 H2O2	+	1 O2				
kphoto_C		1 Ctarget				f>								
target_O3		1 O3	+		1 Ctarget	>		1					0.00E+00	M-1s-1
target_OH		1 OH_rad_	+		1 Ctarget	>		1					0.00E+00	M-1s-1
target_CC		1 CO3_rad_	+		1 Ctarget	>		1					0.00E+00	M-1s-1
O3_gas		1 O3g				>		1 O3					0.00E+00	s-1
O3_gas		1 O3				>							0.00E+00	s-1
		1 O3	+		1 OH-	>		1 HO2-	+	1 O2			120	M-1s-1
		1 O3	+		1 HO2-	>		1 O3_rad_-	+	1 HO2_rad_-			2.20E+06	M-1s-1
		1 HO2_rad_				>		1 O2_rad_-	+	1 H+			1.58E+05	s-1
		1 O2_rad_	+		1 H+	>		1 HO2_rad_-					1.00E+10	M-1s-1
		1 O3	+		1 O2_rad_-	>		1 O2_rad_-	+	1 O2			3.00E+09	M-1s-1
		1 O3_rad_	+		1 H2O	>		1 O2	+	1 OH_rad_	+	1 OH-	1.50E+01	s-1
		1 O3_rad_	+		1 OH_rad_	>		1 HO2_rad_	+	1 O2_rad_-			3.00E+09	M-1s-1
		1 O3	+		1 OH_rad_	>		1 HO2_rad_	+	1 O2			1.10E+08	M-1s-1
		1 O3_rad_	+		1 OH_rad_	>		1 O3	+	1 OH-			1.00E+10	M-1s-1
		1 O3	+		1 DOC	>		1					1.00E+01	M-1s-1
		1 O3	+		1 DOC-O3	>	0.7	O3_rad_-					5.00E+04	M-1s-1
		1 OH_rad_	+		1 DOC-O3	>		1					2.00E+08	M-1s-1
		1 OH_rad_	+		1 DOC	>		1					2.00E+08	M-1s-1
		1 CO3_rad_	+		1 DOC	>		1					5.00E+06	M-1s-1
		1 HO2-	+		1 OH_rad_	>		1 O2_rad_-	+	1 H2O			7.50E+09	M-1s-1
		1 H2O2	+		1 OH_rad_	>		1 O2_rad_-	+	1 H2O	+	1 H+	2.70E+07	M-1s-1
		1 H2O2	+		1 HO2_rad_	>		1 OH_rad_	+	1 H2O	+	1 O2	3.00E+00	M-1s-1
		1 H2O2	+		1 O2_rad_-	>		1 OH_rad_	+	1 OH-	+	1 O2	1.30E-01	M-1s-1
		1 OH_rad_	+		1 O2_rad_-	>		1 OH-	+	1 O2			9.40E+09	M-1s-1
		2 OH_rad_				>		1 H2O2					5.50E+09	M-1s-1
		1 OH_rad_	+		1 HO2_rad_	>		1 H2O	+	1 O2			6.60E+09	M-1s-1
		2 HO2_rad_				>		1 H2O2	+	1 O2			8.30E+05	M-1s-1
		1 HO2_rad_			1 O2_rad_-	>		1 HO2-	+	1 O2			9.70E+07	M-1s-1
		1 H+	+		1 OH-	>		1 H2O					1.00E+10	
		1 H2O				>		1 H+	+	1 OH-			1.90E-06	
		1 H2CO3				>		1 H+	+	1 HCO3-			4.50E+03	
		1 H+	+		1 HCO3-	>		1 H2CO3					1.00E+10	
		1 HCO3-				>		1 H+	+	1 CO3-2			4.50E-01	
		1 H+	+		1 CO3-2	>		1 HCO3-					1.00E+10	
		1 H+	+		1 HO2-	>		1 H2O2					2.00E+10	M-1s-1
		1 H2O2				>		1 H+	+	1 HO2-			4.50E-02	s-1
		1 HCO3-	+		1 O3	>							1.00E-03	
		1 CO3-2	+		1 O3	>							1.00E-02	
		1 HCO3-	+		1 OH_rad_	>		1 H2O	+	1 CO3_rad_-			8.50E+06	
		1 CO3-2	+		1 OH_rad_	>		1 OH-	+	1 CO3_rad_-			3.90E+08	
		1 CO3_rad_	+		1 H2O2	>		1 HCO3-	+	1 HO2_rad_			8.00E+05	
		1 CO3_rad_	+		1 HO2-	>		1 CO3-2	+	1 HO2_rad_			5.60E+07	
		2 CO3_rad_-				>							8.00E+05	
		1 CO3_rad_	+		1 O3_rad_-	>		1 CO3-2	+	1 O3			6.00E+07	
		1 CO3_rad_	+		1 OH_rad_	>		1 HO2-					3.00E+09	
		1 CO3_rad_	+		1 O2_rad_-	>		1 CO3-2	+	1 O2			4.00E+08	
		1 H3PO4	+		1 OH_rad_	>		1 H2O	+	1 H2PO4_rad_			2.60E+06	
		1 H2PO4-	+		1 OH_rad_	>		1 OH-	+	1 H2PO4_rad_			2.20E+07	
		1 HPO4-2	+		1 OH_rad_	>		1 OH-	+	1 HPO4_rad_-			7.90E+05	
		1 H3PO4				>		1 H+	+	1 H2PO4-			6.31E+07	
		1 H+	+		1 H2PO4-	>		1 H3PO4					1.00E+10	
		1 H2PO4-				>		1 H+	+	1 HPO4-2			6.31E+02	
		1 H+	+		1 HPO4-2	>		1 H2PO4-					1.00E+10	
		1 HPO4-2				>		1 H+	+	1 PO4-3			5.01E-03	
		1 H+	+		1 PO4-3	>		1 HPO4-2					1.00E+10	

Validation AOP

- Compared with measured removal



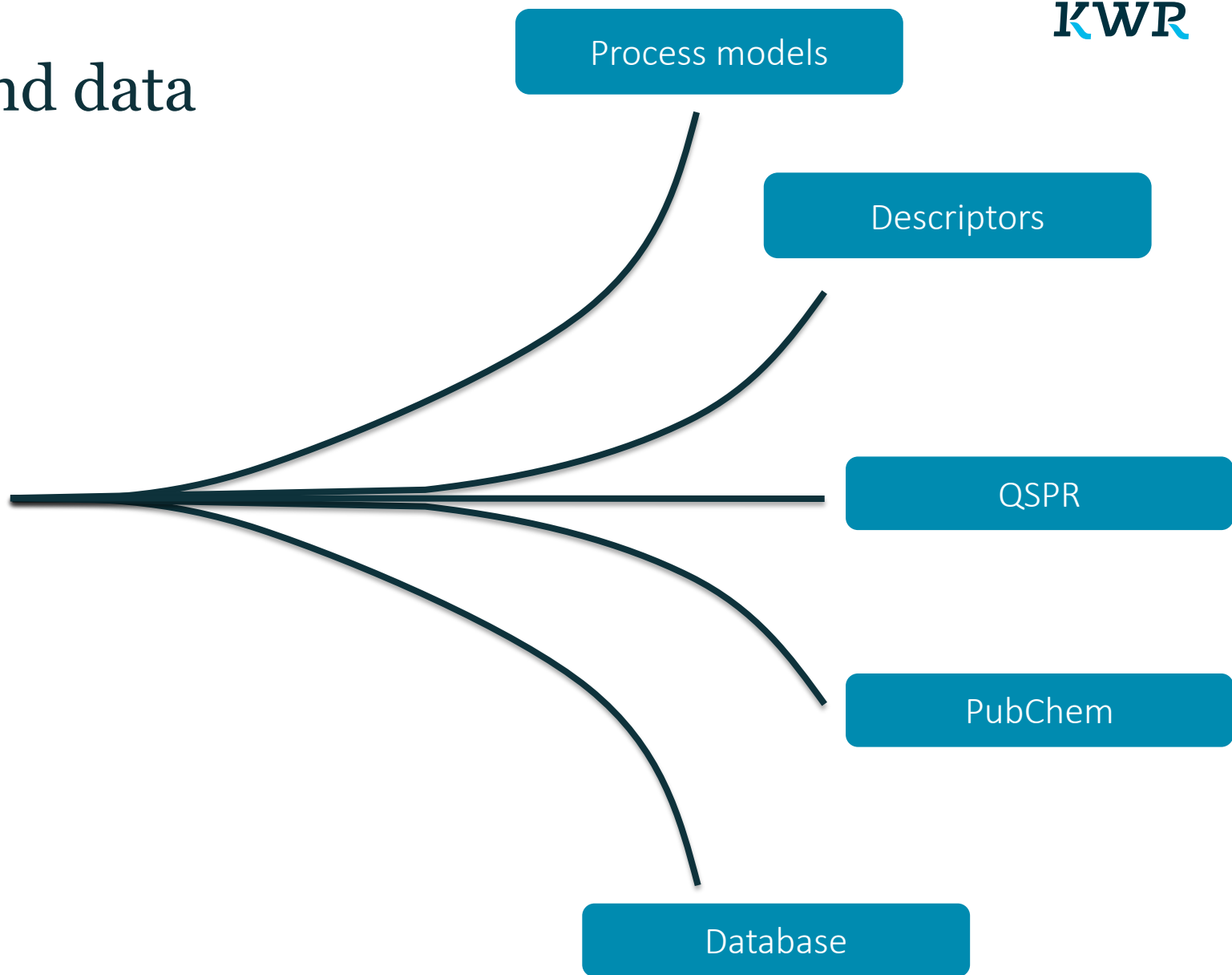
Accessing models and data

AquaPriori webtool

The screenshot shows the AquaPriori webtool interface. At the top, there is a navigation bar with 'Simulations' and 'Profile' tabs. Below the navigation bar is a toolbar with icons for '+ New', 'Edit', 'Delete', 'Export', and 'Results'. The main content is a table with the following columns: Name, Date Created, Process, and Compound. The table contains six rows of simulation data.

Name	Date Created	Process	Compound
Soil Passage Example	9/26/2022	Soil Passage	ATP;5957
Reverse Osmosis Example 2	2/17/2023	Reverse Osmosis	atrazine;2256
Reverse Osmosis Example	12/9/2022	Reverse Osmosis	Atenolol;2249
Activated Carbon Example-Copy	2/17/2023	Activated Carbon	Diatrizoic acid;2140
Activated Carbon Example 2	2/17/2023	Activated Carbon	ketoprofen;3825
Activated Carbon Example	11/1/2022	Activated Carbon	aspirin;2244

Page 1 of 1 (6 items) | Page size: 15





Conclusions

- Models developed for OMP removal in water treatment processes (process models + QSPRs)
- Access to data and models via AquaPriori webtool
- Quick assessment of treatment of new OMP possible

Future improvements:

- Other water treatment processes (e.g. nanofiltration)
- Soil passage
- Toxicity assessment
- Uncertainty assessment



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