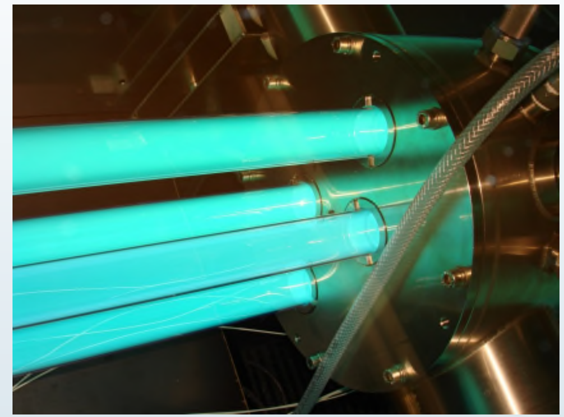
UV/H_2O_2 processes for removal of organic micropollutants

optimization of process conditions and reactor geometry

KWR Watercycle Research Institute

Contents

- Introduction
- Modeling of UV/H_2O_2 processes
- Optimization of reactor geometry
- Pilot experiments at drinking water utilities
  - Comparison of performance (E_{EO})
  - Effect of pretreatment
  - Transformation products
- Conclusions



Introduction

- Increasing amounts and concentrations of organic micropollutants in surface water (e.g. personal care products, pesticides, pharmaceuticals)
- Total concentrations up to ± 30 µg/L
- How to remove in order to produce drinking water?

- Membrane filtration: concentrate?
- (Advanced) oxidation processes:
  - O_3: bromide is turned into bromate
  - UV/H_2O_2: “high” energy demand

Introduction

Organic micropollutants

Increasing contents of (polar) organic micropollutants like

- Pesticides
- Personal care products
- Pharmaceuticals

Due to

- Aging
- Climate change
- REACH

Surface water (e.g. river Meuse) contains up to ± 30 μg pharmaceuticals and metabolites/L

Expected: 40% increase within next 35 years

Dutch Situation,

Advanced oxidation processes:

No O_3 because of high bromide levels

→ UV/H_2O_2 process.

UV/H_2O_2 processes
Modeling

UV:

- Photolysis of micropollutants
- Disinfection

Oxidation:

- Photolysis of H_2O_2 ⟶ •OH
- Oxidation of micropollutants by •OH

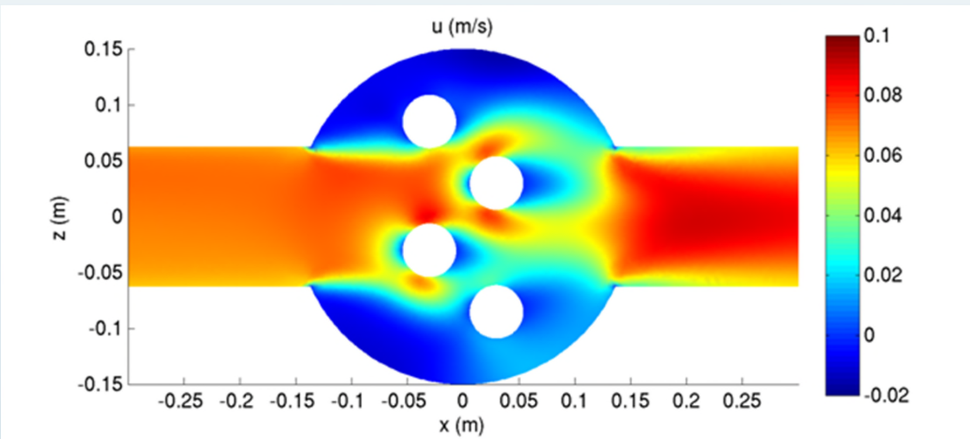
Kinetic model:

- Describing conversion of compound as a function of UV dose
- Key factors photolysis: quantum yield and molecular absorption
- Key factors oxidation: reaction rate constant
- Simultaneous calculation of total reaction scheme

UV/H_2O_2 processes
Modeling

CFD model:

Describing UV dose distribution through reaction vessel



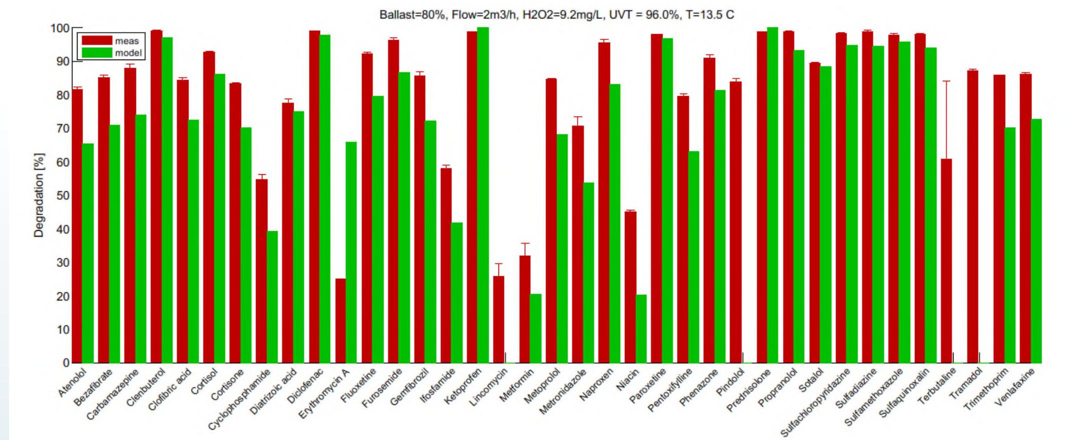
1. **Kinetic model:**
   Conversion as a function of UV dose
2. **CFD:**
   UV dose distribution
3. **Combination:**
   Conversion in the UV reactor

UV/H_2O_2 processes
Modeling

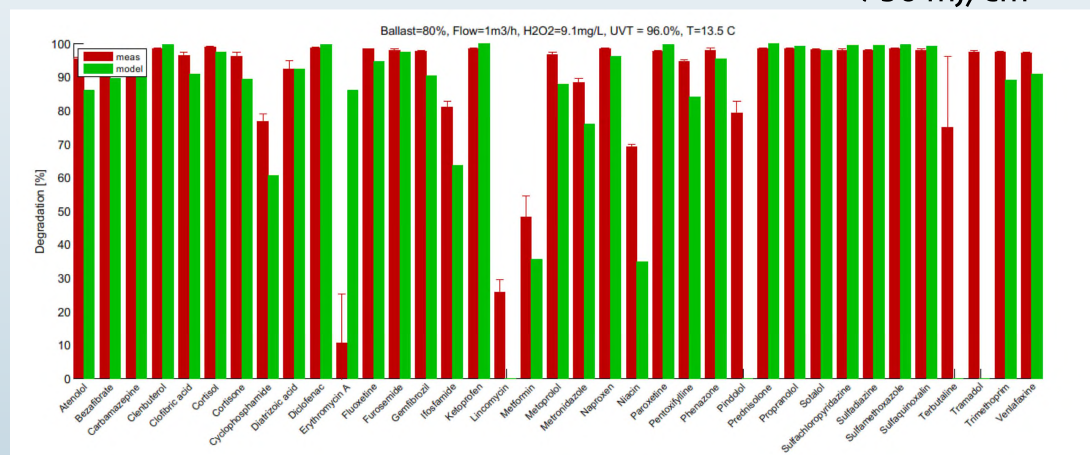
Model:

- Accurate prediction of conversion in reactor
- **Different doses**
- Different H_2O_2 concentrations
- Differents water matrices.
- Various types of reactors

365 mJ/cm²



730 mJ/cm²



UV/H_2O_2 processes
Modeling

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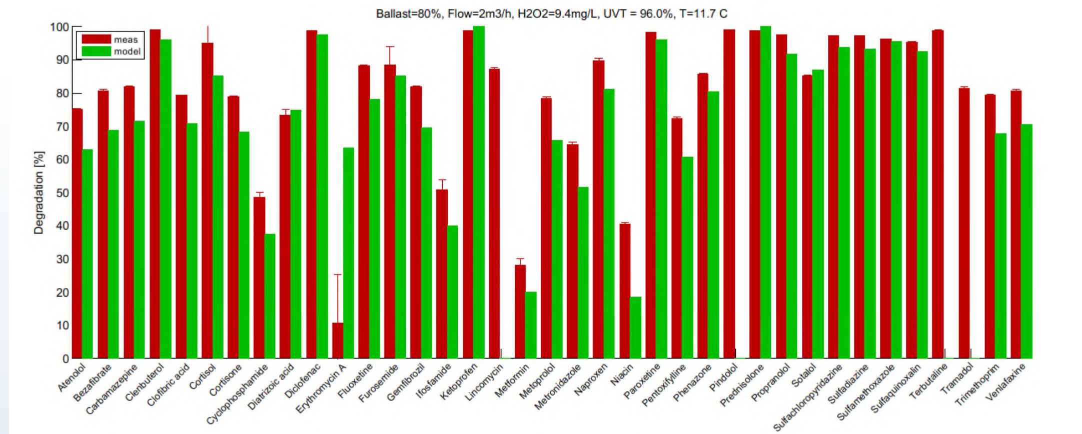
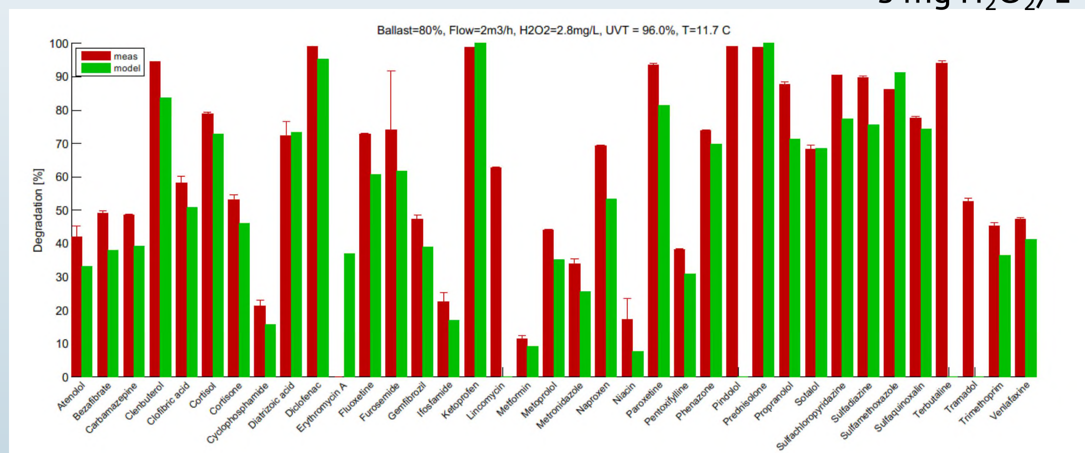
10 mg H_2O_2/L



3 mg H_2O_2/L



UV/H_2O_2 processes
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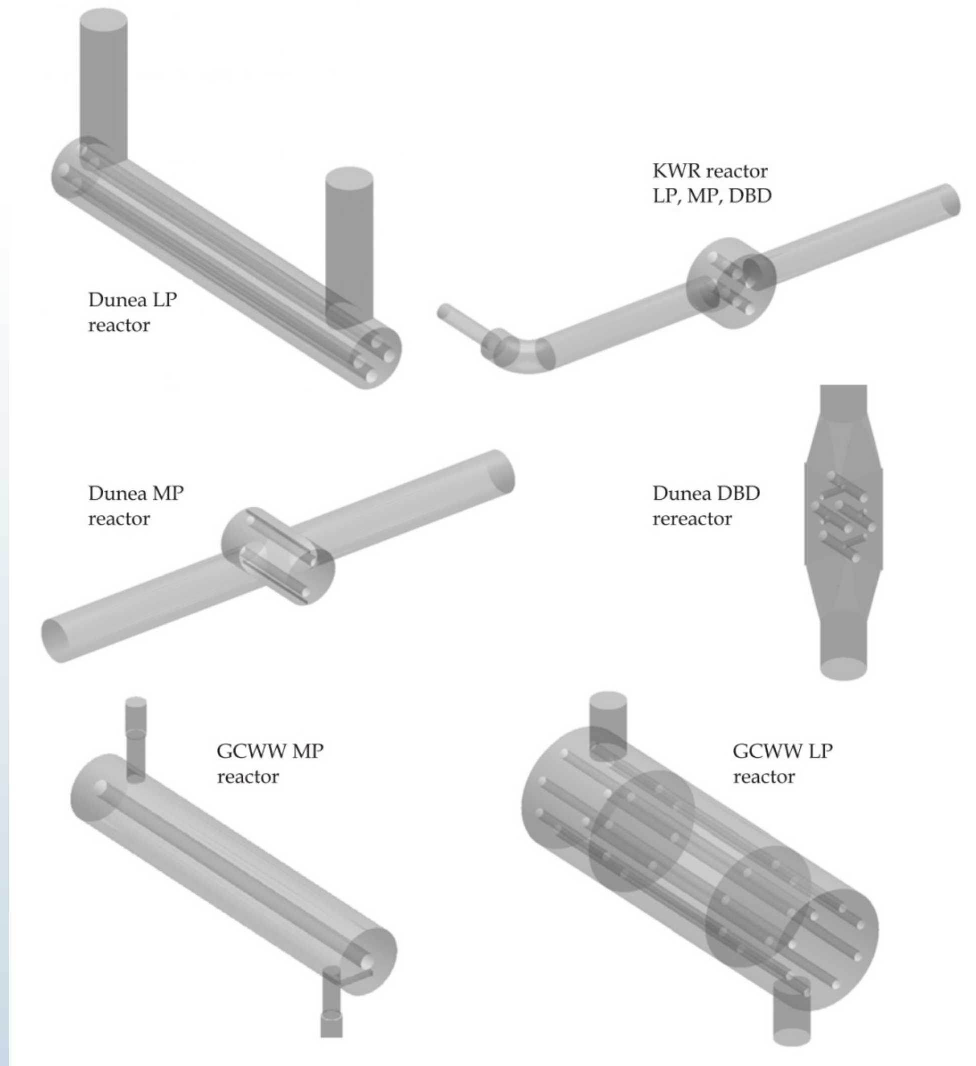


UV/H_2O_2 processes
Modeling

Other applications of modeling:

- Optimization of reaction conditions
- Optimization of reactor geometry

Regular UV disinfection reactor

Decrease flow by a factor of about 10 to obtain UV dose of about 500 mJ/cm^2

Regular reactor vessel has been optimized for disinfection, not for AOP.

Design and construction of new UV-reactors

Tested at van Remmen UV Technology and at two Dutch drinking water companies (Dunea and WML)

Wols et al. (2012), Chem.Eng.J. 210, 289-297
Wols and Hofman-Caris (2012), Wat.Res., 46(9), 2815-2827
Wols et al.(2012), Oz.Sci.Eng. 34(2), 81-91
Wols and Hofman-Caris (2013), Wat.Res. 47(15), 5876-5888
Wols et al. (2014), Chem.Eng.J. 255, 334-343
Wols et al. (2015). Chem.Eng.J. 263, 336-345
Wols et al. (2015). Wat.Res. 75, 11-24

Optimization of reactor geometry

Five different reactors tested

Conventional disinfection reactor D130

Optimized reactor D200

- one or two flow plates
- one 120 W LP lamp
- 1-2.5 m^3/hour

NEW

- Four 300 W LP lamps
- 10 m^3/hour
- UV-T >85%

Chaos

- Ten 120 W LP lamps
- 10 m^3/hour
- Longer residence time
- Broader UV-dose distribution, higher mean UV dose.

Process optimization

Experiments at van Remmen UV Technology; three new types of reactors

D130: Original disinfection reactor

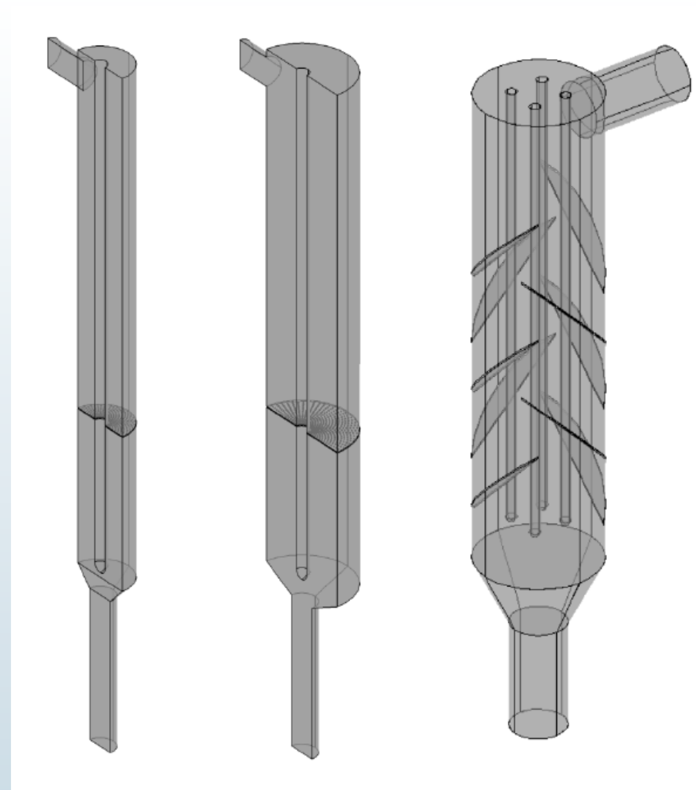
D200 with one flow plate:

20-30% higher removal of pharmaceuticals compared to D130 (conventional)

NEW

At UV-T = 85-90% 5-15% higher removal of pharmaceuticals, compared to D200

UV-T = 75%



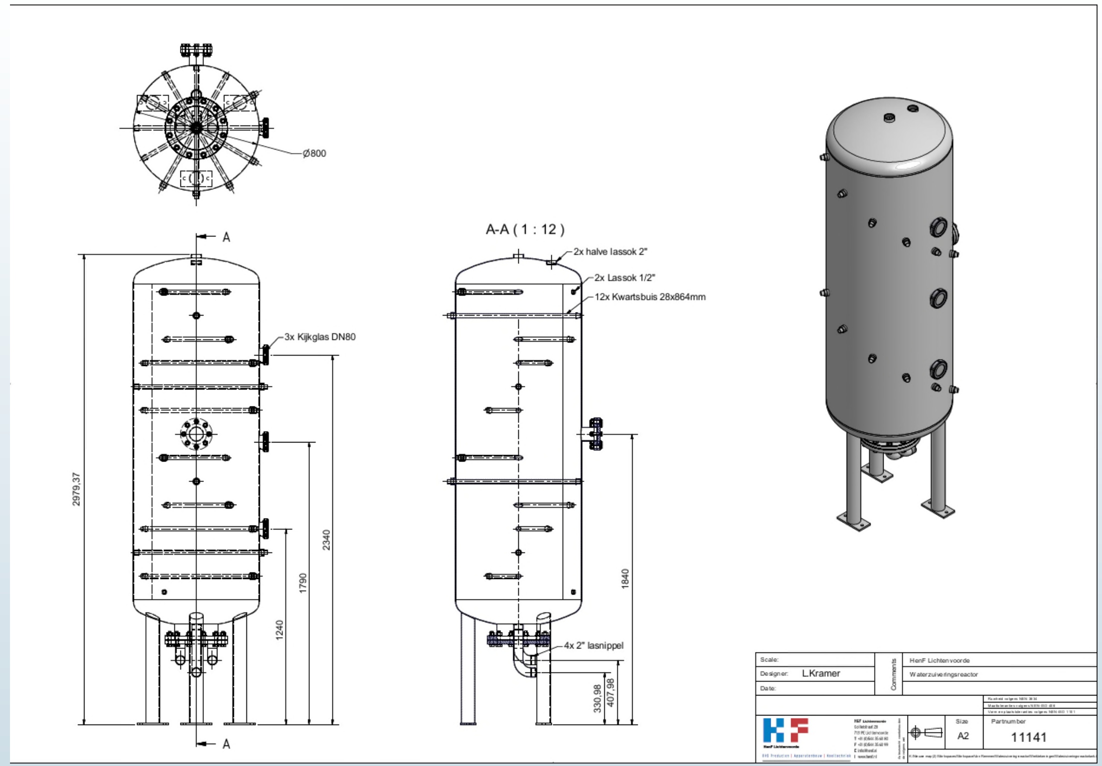
D130 D200 NEW

Process optimization

Experiments at van Remmen UV Technology; three types of reactors

CHAOS

Wider UV-dose distribution; lower degradation for compounds with high removal rates (5-10% compared to D200), higher conversion for compounds with low removal rates



Degradation of micropollutants

Comparison by means of E_{EO}

$$E_{EO} = \frac{P}{F * \log \frac{c_i}{c_f}}$$

E_{EO} = electrical energy per order

P = electrical power

F = flow

C_i = concentration influent

C_f = concentration effluent

For comparison of:

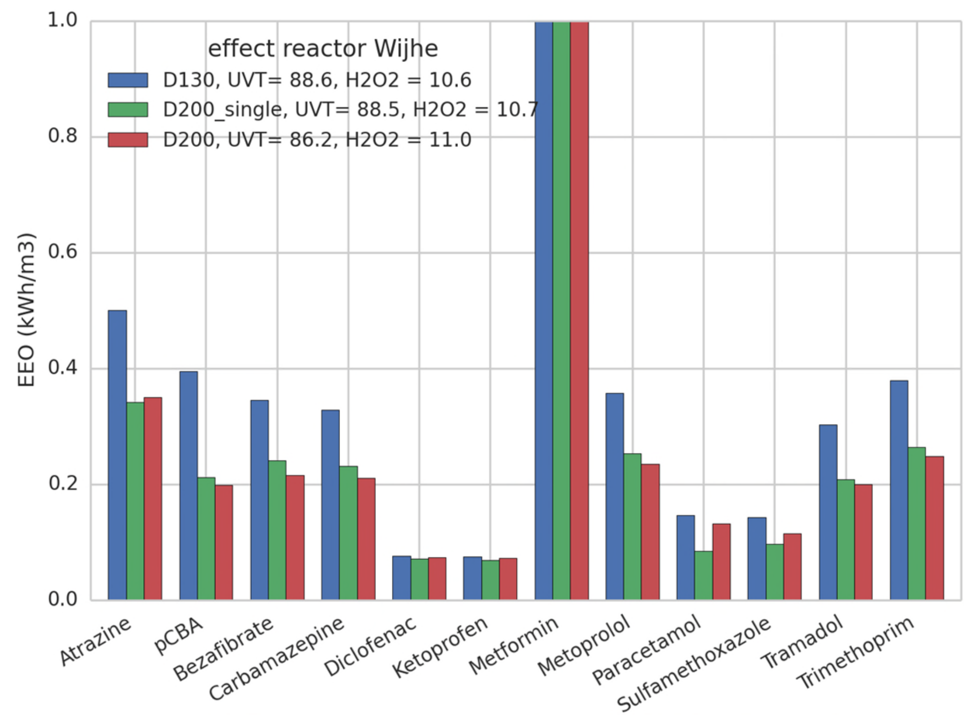
- Effectivity for various compounds under identical conditions and in the same reactor
- Effectivity of different reactors for the same compound(s) under identical conditions
- Influence of conditions for the same compound(s) in the same reactor.

Effect of reactor geometry
Experiments at van Remmen UV Technology

Blue bar: "conventional disinfection reactor" (D130)

Green bar: D200, one flow plate

Red bar: D200: two flow plates



Process optimization

Experiments at Dunea Drinking Water company

Three types of reactors tested:

D200 with two flow plates, NEW and CHAOS

UV-T = 75%

Increase process efficiency by water pre-treatment: removal of NOM and part of micropollutants:

O_3/H_2O_2 or GAC filtration: higher UV-T (≈ 87%)

30-70% decrease in energy demand; most efficient for NEW reactor.

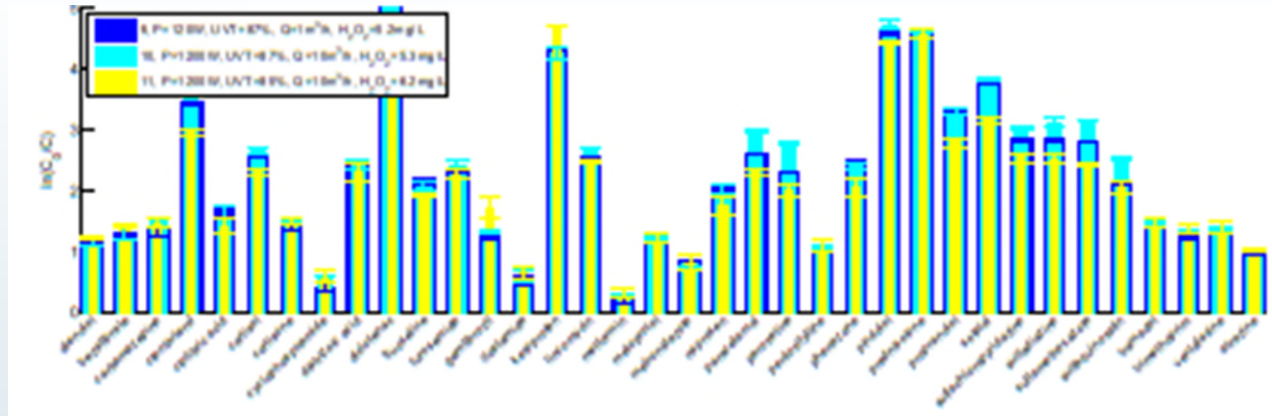
Different circumstances

Dunea

UV-T = 75%, improved by pretreatment

Accurate model predictions

In general relatively high conversions



WML

UV-T = 94%

Actual conversion higher than predicted values:

Reflection at reactor wall has to be taken into account: >20% higher UV dose

UV-T improves further to 96% during reaction

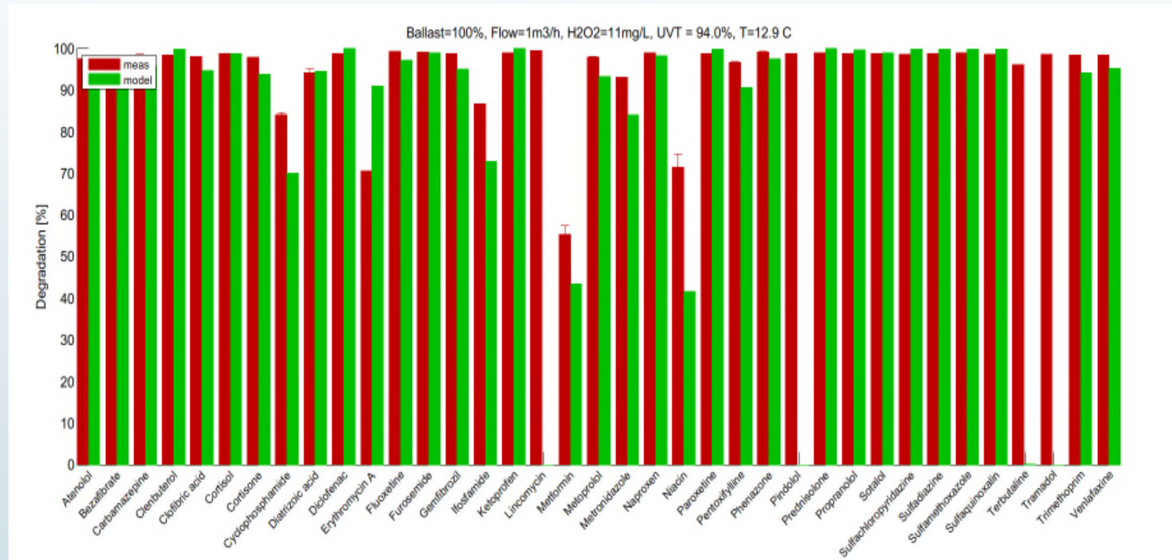
Degradation of micropollutants at WML
Model versus measurements

Taking reflection into account:

Good correlation between predicted

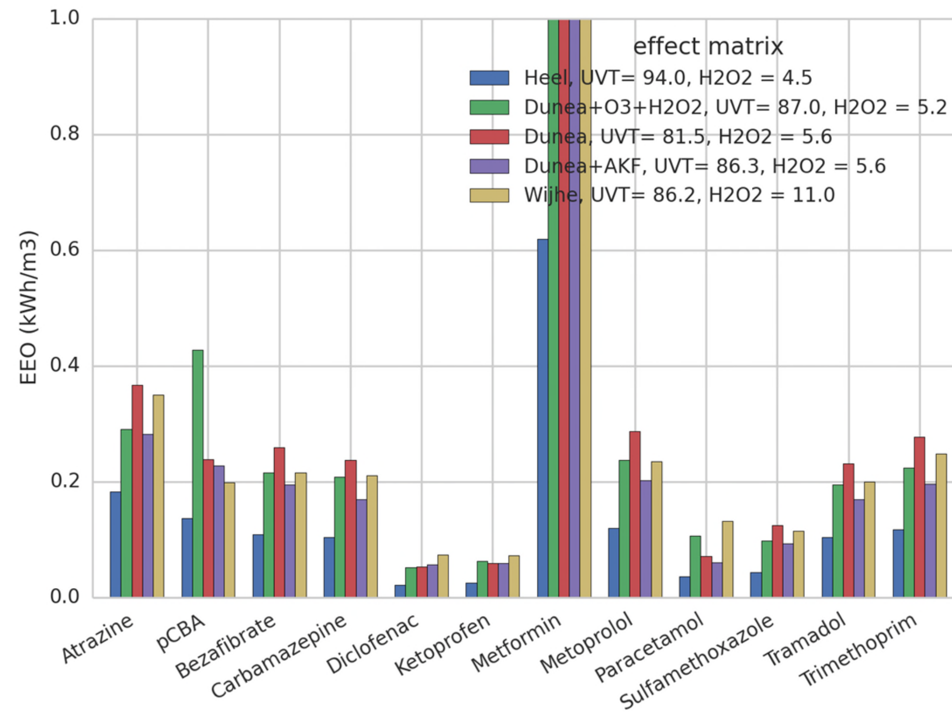
(green bars) and measured (red bars)

conversions



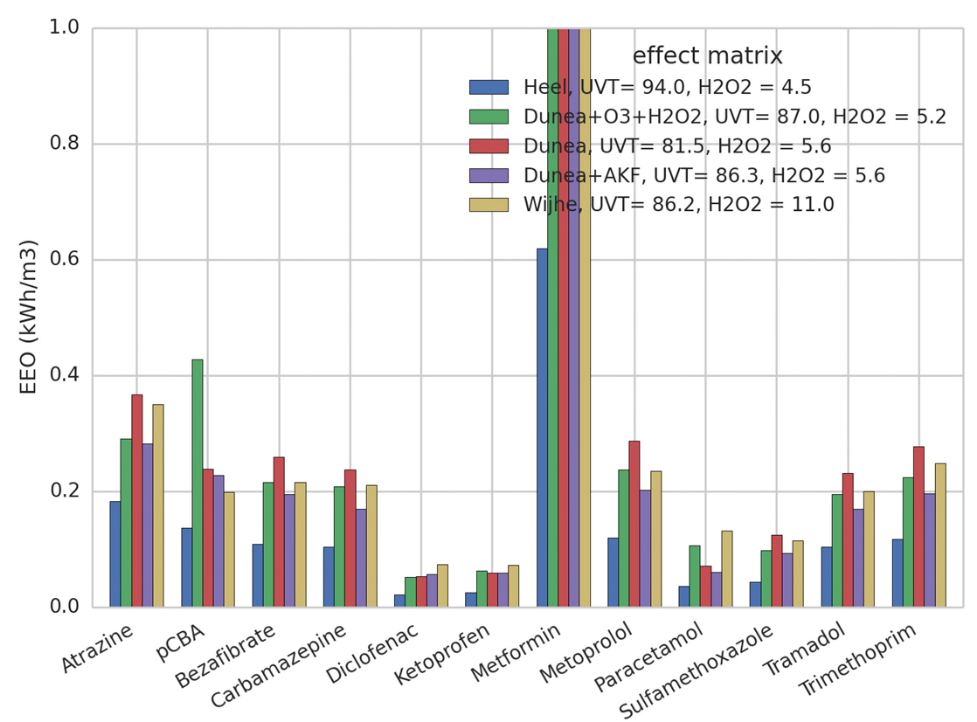
Effect of water matrix
D200

- **Blue bars: WML**
- **Green bars: Dunea, O_3/H_2O_2 pretreatment**
- **Red bars: Dunea, no pretreatment**
- **Purple bars: Dunea, ACF pretreatment**
- **Yellow bars: Van Remmen UV Technology**



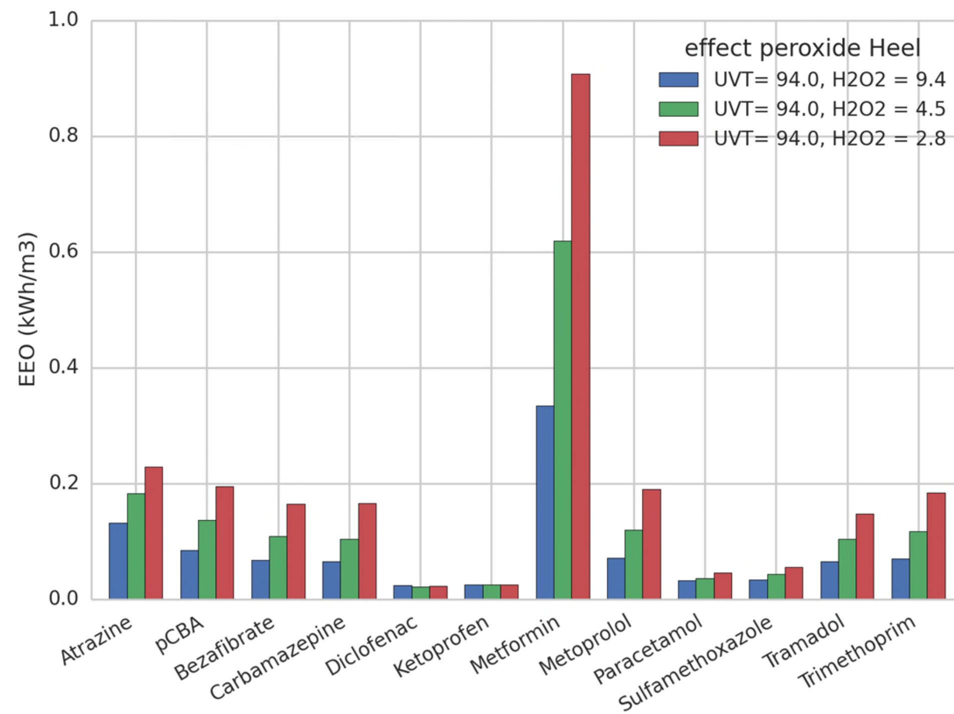
Effect of water matrix
D200

Type of Water	Additional pretreatment	UV-T (%)	TOC (mg C/L)
Wijhe	--	86	1.4
Dunea	--	82	3.3
Dunea	ACF	86	2.4
Dunea	O_3/H_2O_2	87	3.4
WML	--	94	1.4



Effect H_2O_2 concentration
Experiments at WML

The lower the H_2O_2 concentration the more energy will be required.

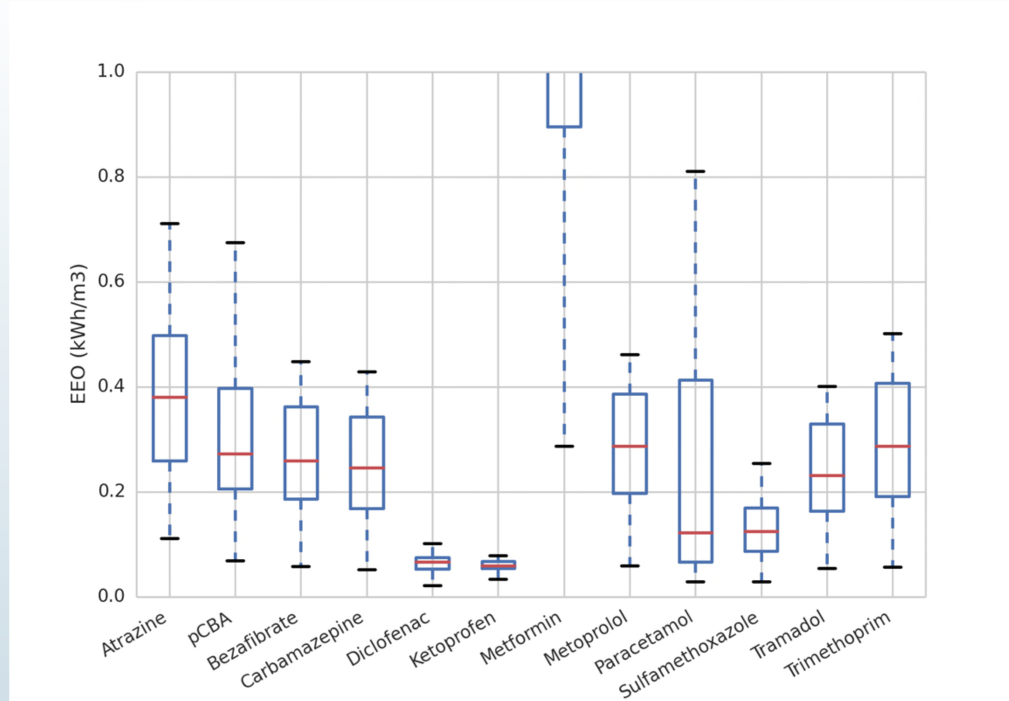


E_{EO} for different compounds

Large differences in susceptibility of compounds for UV/H_2O_2

Some compounds show large influence of conditions/reactor

Degradability of some compounds hardly affected by conditions/reactor



Process optimization

Dunea:

pretreatment gives better results (less energy required)

WML:

Optimization in UV-dose and H_2O_2 concentration

Formation of transformation products?

UV-dose (mJ/cm^2)	Average conversion (%)
730	90
487	85
365	81

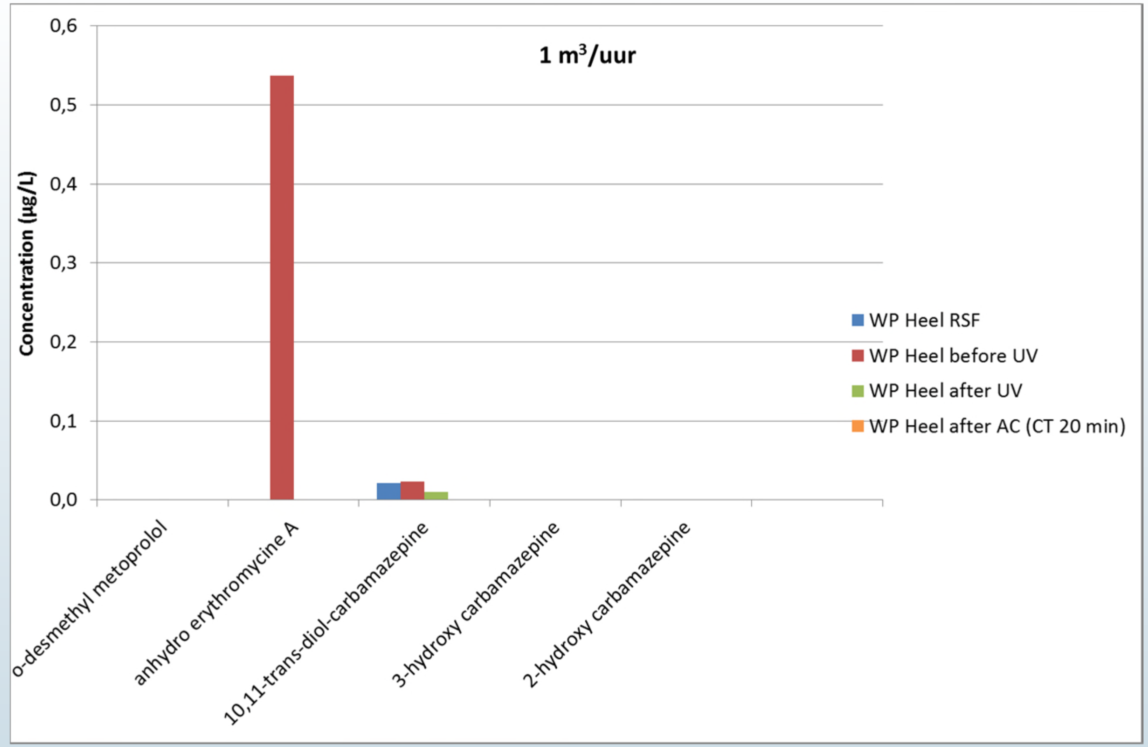
H_2O_2 conc. (mg/L)	Average conversion (%)
9.4	78
4.5	69
2.8	56

Process optimization
Where to look at?

730 mJ/cm²

For sufficient conversion of mother compounds lower UV dose and/or H_2O_2 concentration can be applied.

However: higher concentrations of transformation products observed



Process optimization
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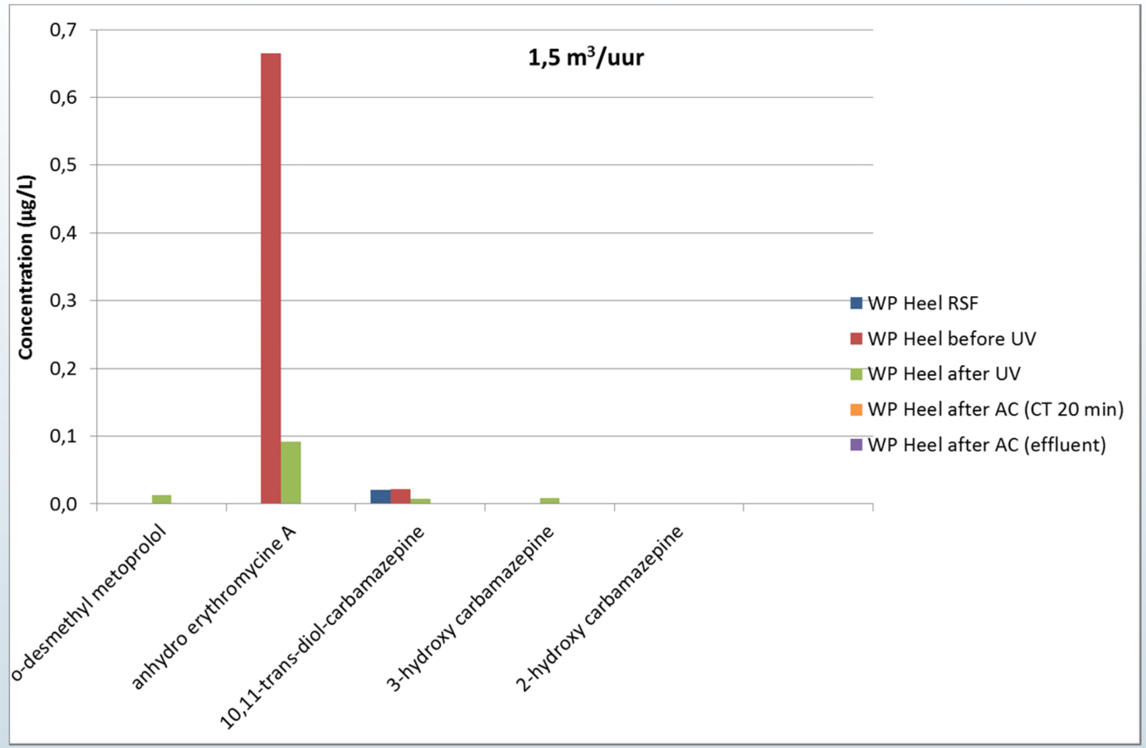
487 mJ/cm²



Process optimization
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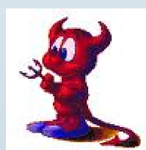

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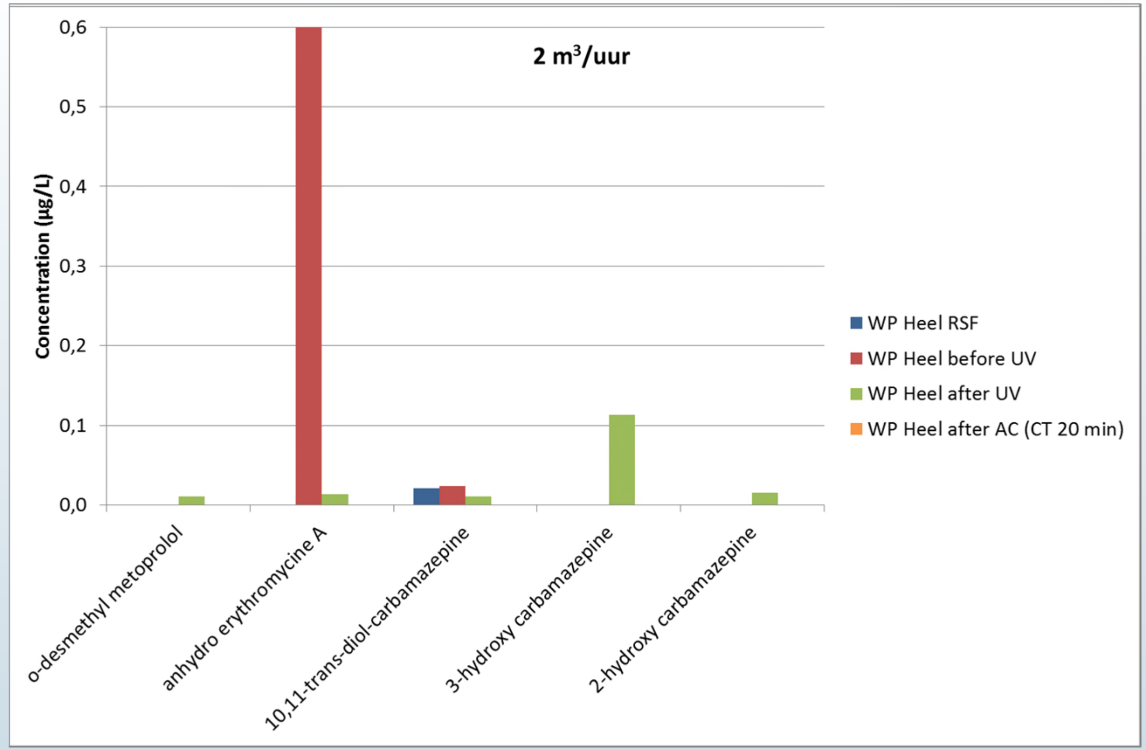

Conclusions

1. UV/H_2O_2 processes very effective for degradation of a broad range of organic micropollutants
2. Modeling gives good prediction of conversions
3. Modeling can be used to improve process conditions and reactor geometry.
4. Pre-treatment can result in 30-70% energy savings
5. Improved reactor geometry results in 30-40% energy savings
6. Large differences in E_{EO} values, depending on reactor geometry, conditions (H_2O_2 concentration, water matrix) and type of compounds
7. Degradability of some compounds strongly depends on conditions and/or UV reactor
8. Optimization: higher concentrations of transformation products may occur

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Questions?