Oxidative treatment of pharmaceutical residues using thermal plasma activation

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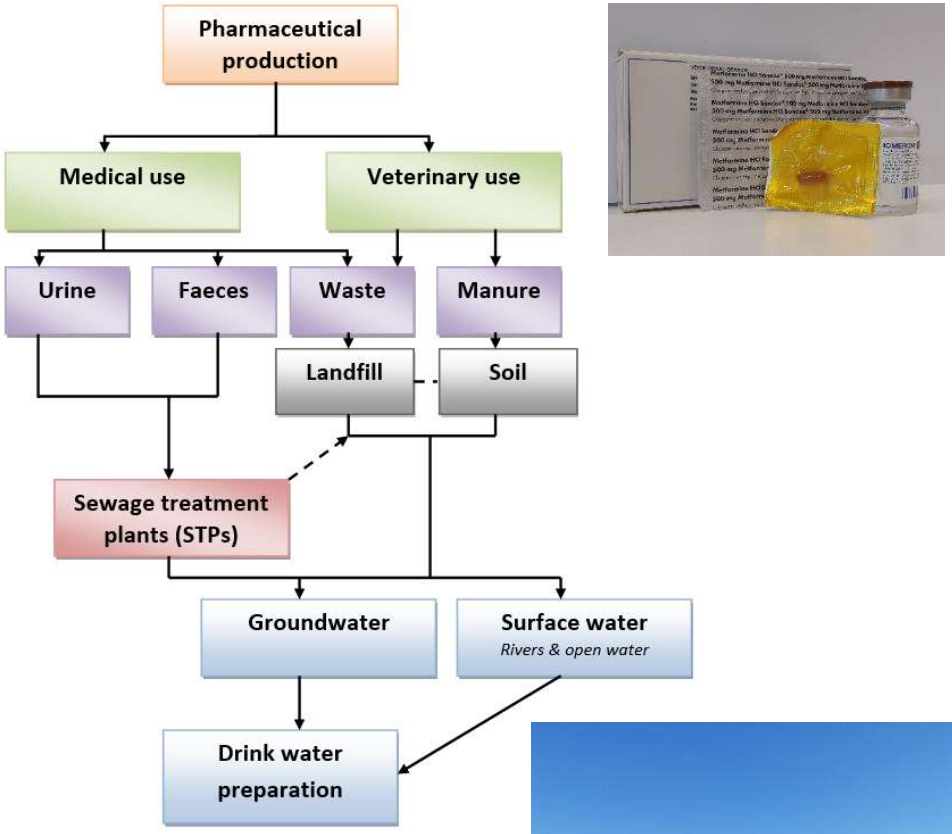
Introduction

- **Widespread usage of pharmaceuticals**
  - *Veterinary and human use*
- **Emission via direct and indirect routes**
- **Conventional sewage treatment plants (STPs)**
  - *Sedimentation*
  - *Biodegradation*
  - *Filtration*



Aim of the study

- **Prevention and mitigation of wastewater contamination by pharmaceuticals**

- **Onsite oxidative treatment of wastewater**
  - Plasma Activated Water (PAW)
    - Laboratory simulation on different matrices

- **Toxicity Assay**
  - Effect of formed degradation products

Selection of priority substances

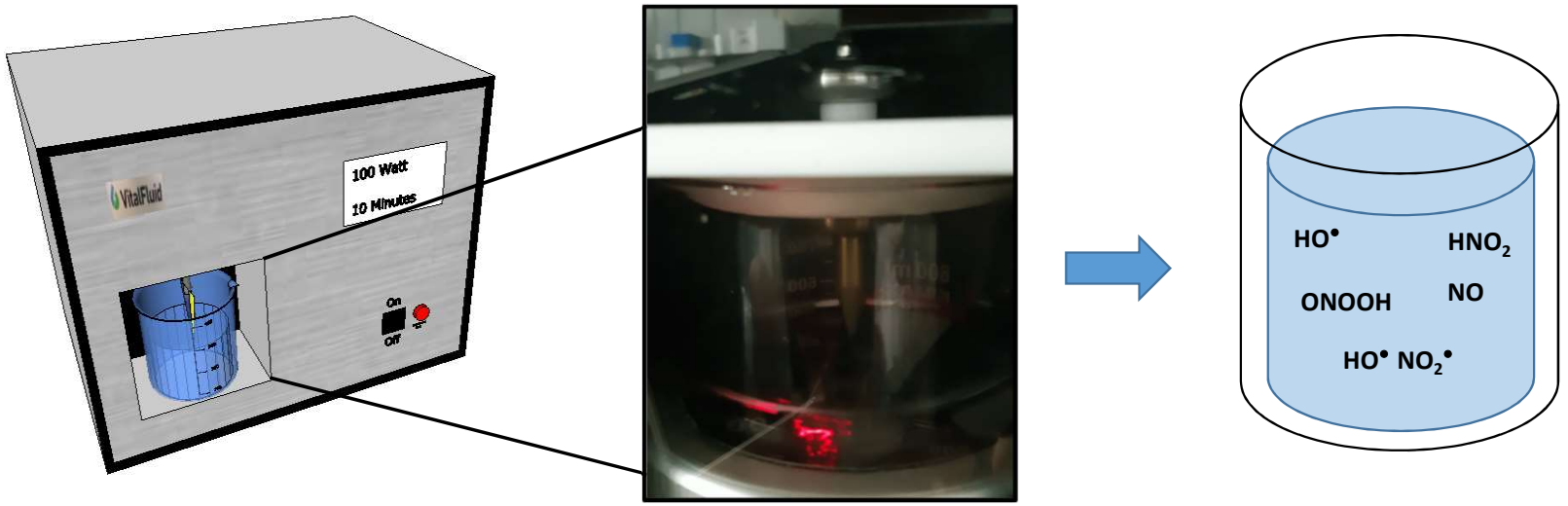
- MEDUWA consortium -> Taskforce
  - Shortlist as guidence

- Selection criteria:
  - *Measurements in Vechte basin*
  - *Consumption*
  - *Biodegradation*
  - *Toxicity*

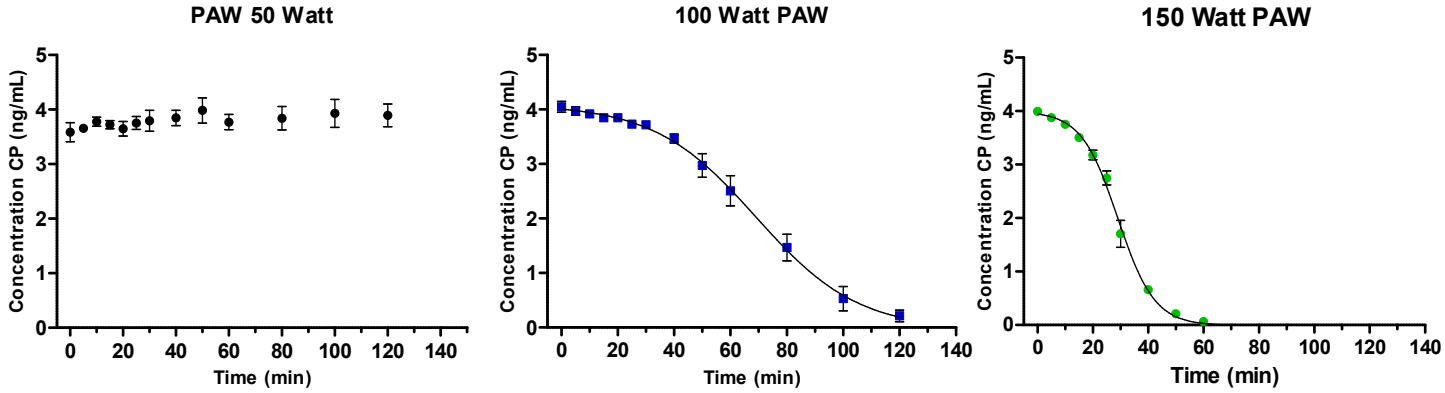
- Shortlist 14 compounds:

  Antibiotics, anti-epilepticum, cytostatic, contrast agents, analgesic and anti-diabatic

Plasma activation optimisation

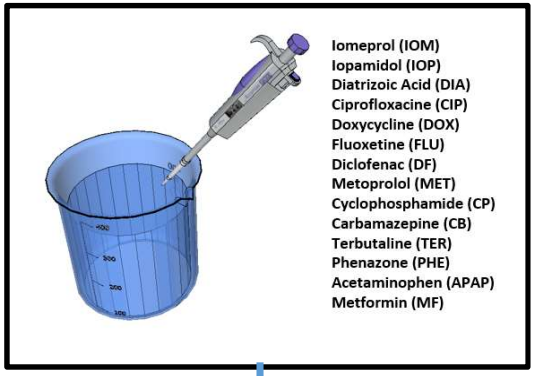


PAW Lab Unit (150 Watt)



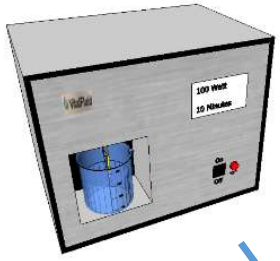
Applied laboratory methodology

1a) Simulation Matrices

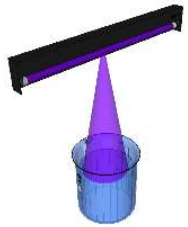


1b) Hospital sewage water

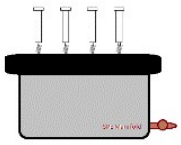
2a) PAW Treatment



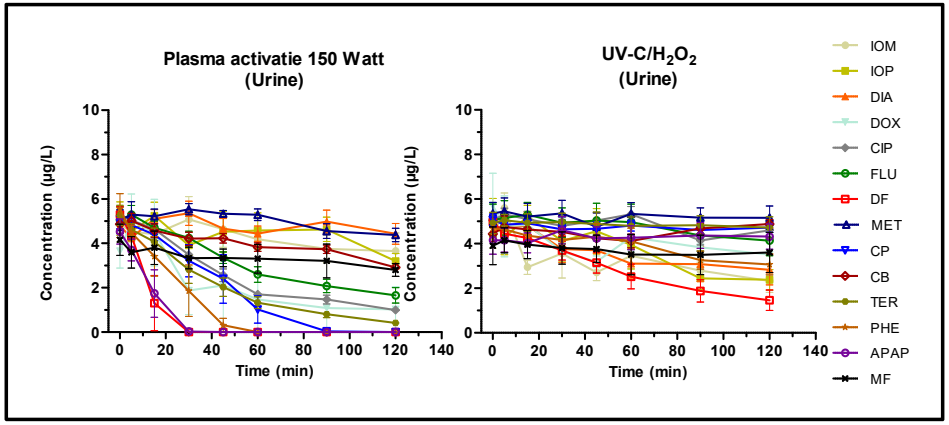
2b) UV-C/H_2O_2



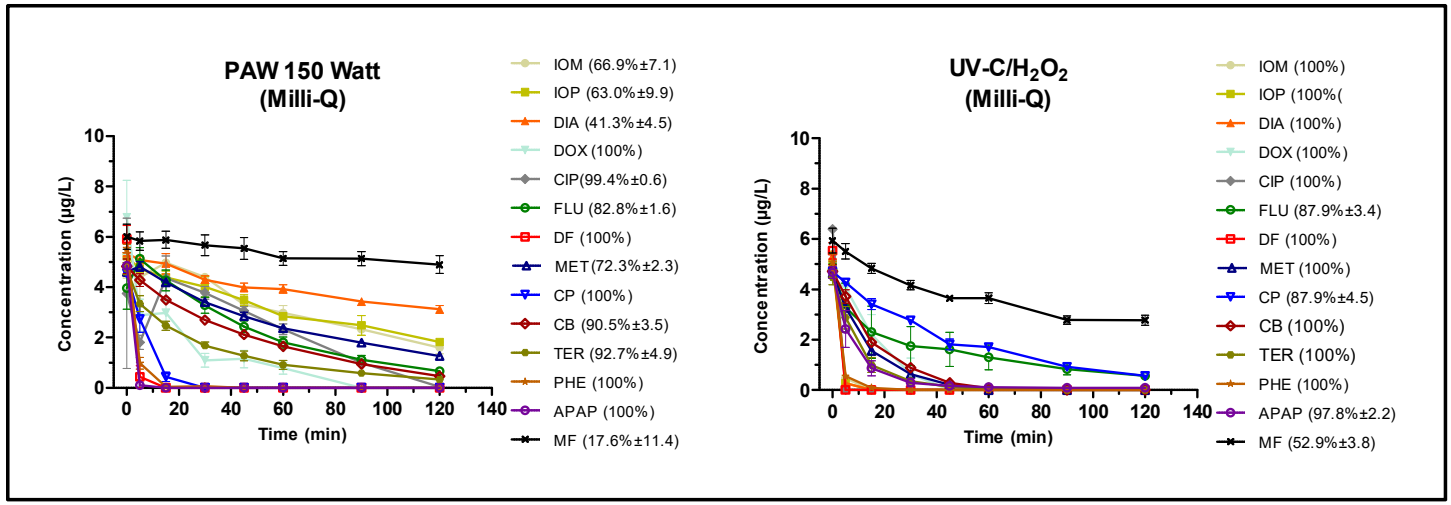
3) SPE

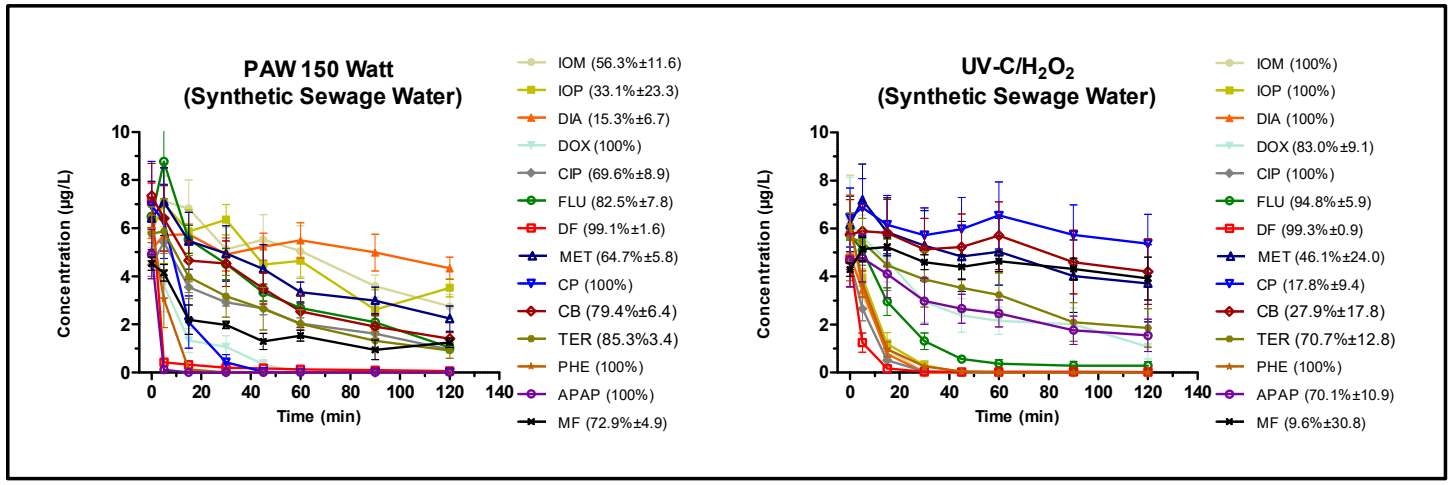


3b)LC-MS/MS analysis



Oxidative degradation simultation matrices





- Milli-Q
- Tap Water
- Synthetic Urine
- Urine
- Synthetic Sewage Water
- Hospital Sewage Water

Organic compounds => absorb UV light
Metabolites/hormones etc.

Scavenging effect (secondary radicals):

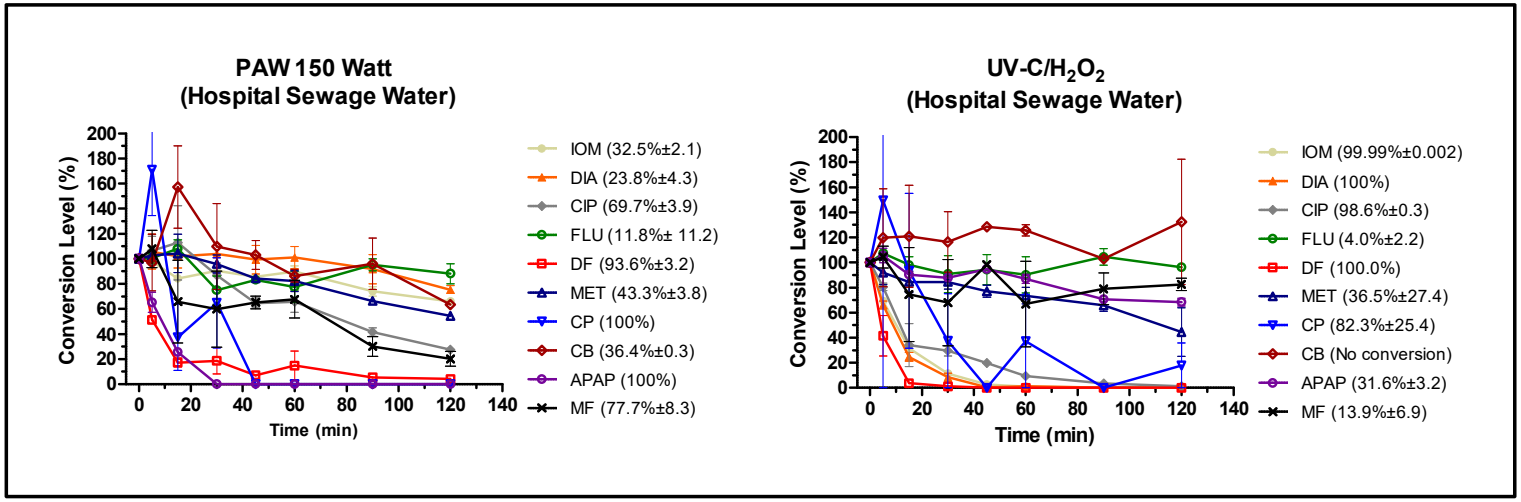
$$\bullet OH + Cl^- \rightarrow HOCl^{\bullet -}$$
$$\bullet OH + NH_3 \rightarrow NH_2 + H_2O$$

Detection of medicines in sewage water

Hospital sewage water (A) Monday – Thursday (16 - 19 Sep 2019) x̄ Concentration (µg/L) (±sd) *n* = 4									
IOM	**DIA**	**CIP**	**FLU**	**DF**	**MET**	**CP**	**CB**	**APAP**	**MF**
2425.4 (±90.3)	12.6 (±1.6)	13.2 (±2.8)	0.35 (±0.03)	1.1 (±0.5)	1.9 (±0.5)	0.2 (±0.1)	0.36	293.9 (±64.4)	33.02 (±4.2)
Domestic sewage water (B) Thursday (31 Oct 2019) x̄ Concentration (µg/L) (±sd) *n* = 4									
IOM	**DIA**	**CIP**	**FLU**	**DF**	**MET**	**CP**	**CB**	**APAP**	**MF**
n.d.	n.d.	1.1 (±0.5)	0.7 (±0.4)	5.8 (±4.7)	2.5 (±0.7)	n.d.	1.9 (±0.7)	482.9 (±286.2)	76.4 (±30.0)

Compounds used in the hospital Prescription drugs Over-the-counter drugs

Oxidative degradation hospital sewage water matrix



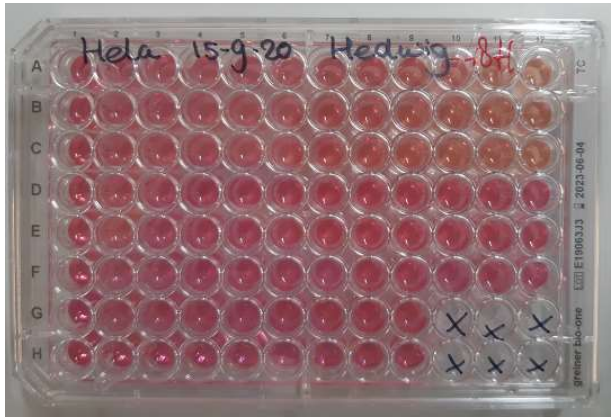
AOP	Total Conc. (µg/L)	Total R̄ (%)	Total Conc. w/o X-ray	Total R̄ (%) w/o X-ray
PAW $150W_{Start}$	2782.1	-	344.1	
$End_{120\ min}$	1624.7	41.6	11.2	96.7
$UV\text{-}C/H_2O_2$ Start	2881.9	-	371.8	
$End_{120\ min}$	248.5	91.4	248.3	33.2

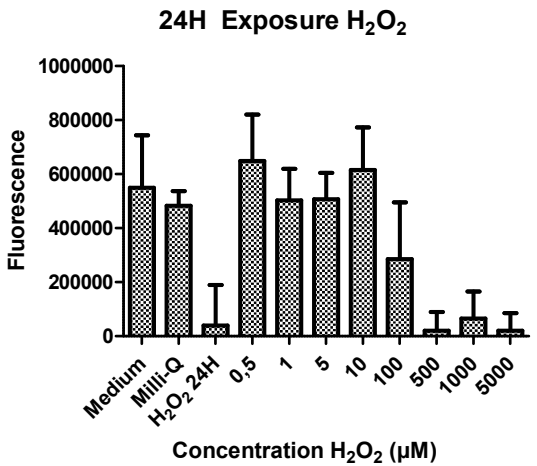
- **Complex matrix**
  - *Presence of soaps, detergents, metabolites and hormones*
- **Non-detected conversion products**
  - *Reformed into pristine structures*
- **RONS are continuously produced (With Plasma)**
  - *Contrast Agents are light sensitive*
  - *Iodine functional groups hinder the availability of unsaturated C-atoms during radical attack*

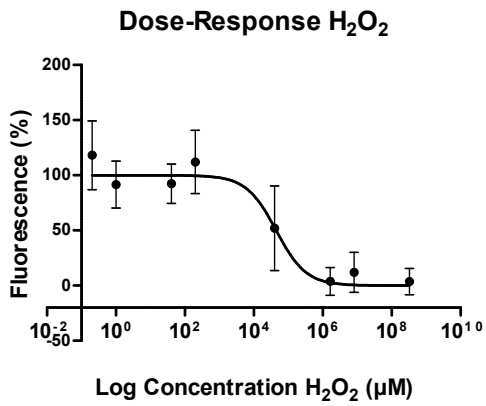
Cytotoxicity-Assay

- HELA-cell line -> Epithelial uterus cells

- 20 µL oxidative treated sample in 180 µL medium
  - Cells were 24H and 48H exposed
- CM-H_2DCFDA (Fluorescence) → Oxidative stress
- 0.5% (v/v) Crystalviolet → Biomass
- Positive control with Hydrogen Peroxide
  - 500 µM = appropiate

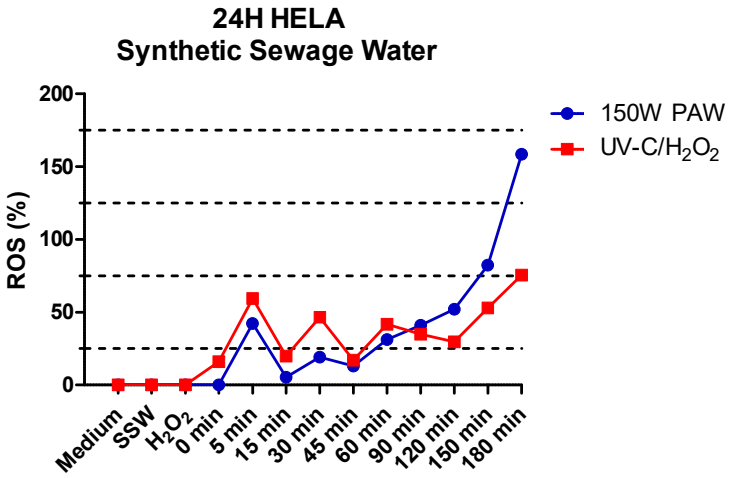


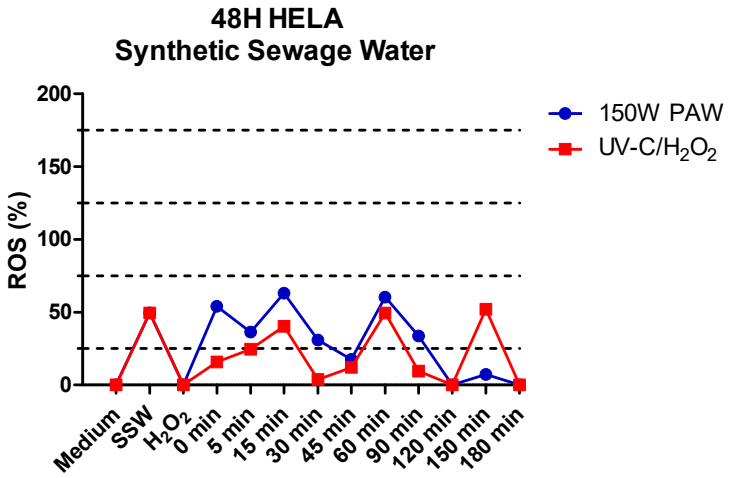




Treated synthetic sewage water

- Hospital sewage water simulation
  - 10 compounds
  - 150 W plasma
  - UV-C/H_2O_2
- No HELA-cell death was observed after oxidative treatment applications
- Cell recovery





Conclusions

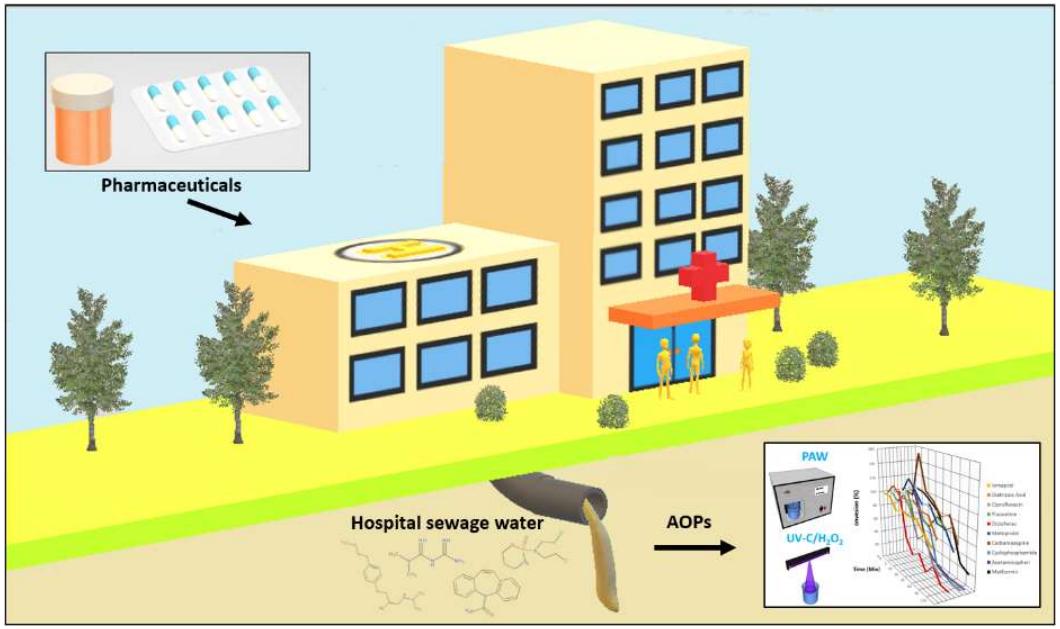
- **Distinct efficiency between oxidative treatment techniques**

- **Certain molecules are completely removed with PAW other with UV-C/H_2O_2**
  - *Oxidation by hydroxyl radicals or degradation with reactive nitrogen species*

- **Complexity of the matrix influences the degradation**

- **Current cell toxicity assay set-up works technically well**
  - *No signficant toxicity observed compared*

- **Additional oxidation technique**
  - *To complement wastewater treatment*



Acknowlegdements

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