Feasibility of UV AOP with optimized DOC removal at the Andijk III WTW, the Netherlands

Bram Martijn, PWNT

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UV AOP

- Why? Barrier for micropollutants
- How: UV photons on H_2O_2 generate OH-radicals
- What happens:
  - Targets double bonds, unsaterated sites, hydrogen abstraction
  - conversion rather that mineralisation (metabolites)

- Common type of UV technologies
  - LP UV AOP vs MP UV AOP

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Background

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UV for organic contaminant control

- physical-chemical process
- based on degradation of compounds by UV absorption; photolysis
- advanced processes use H_2O_2 to generate OH-radicals
- OH-radicals oxidize compounds

photolysis and OH-radical oxidation

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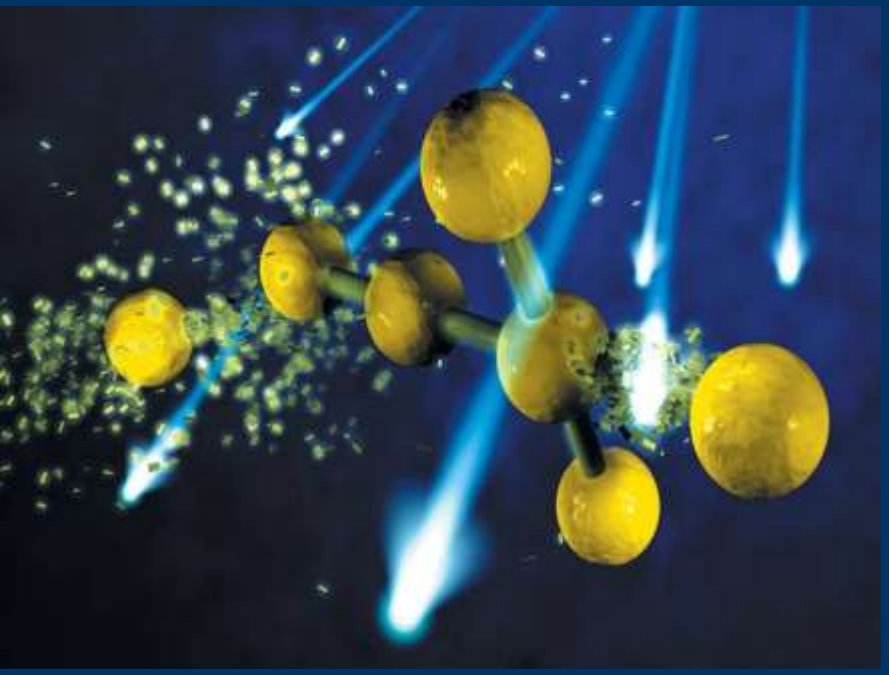
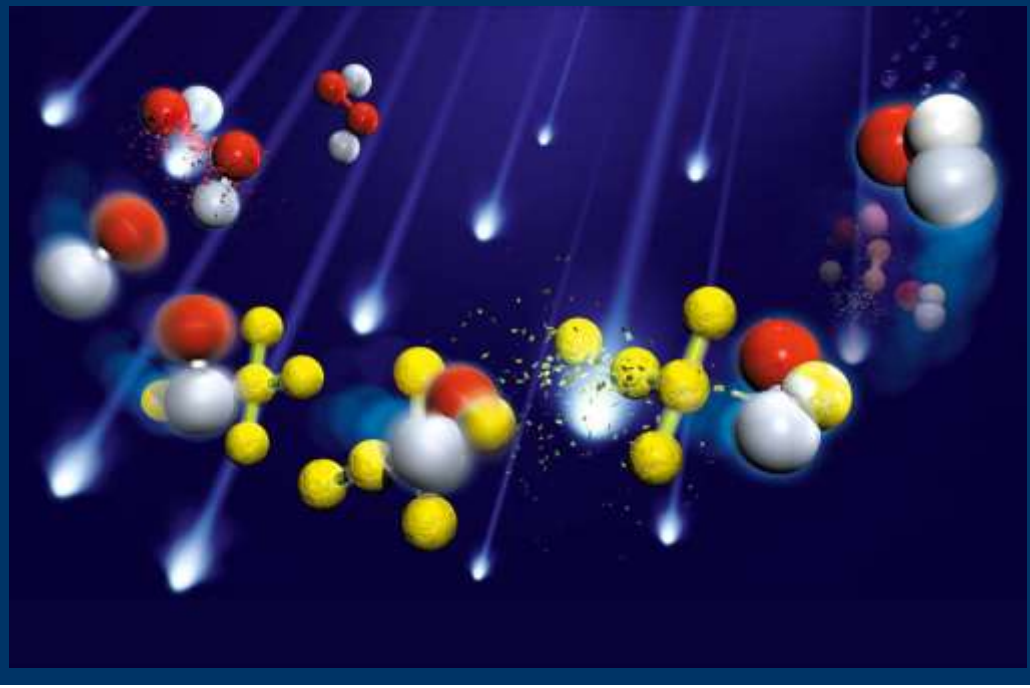
Artist impression photolysis and OH radical oxidation





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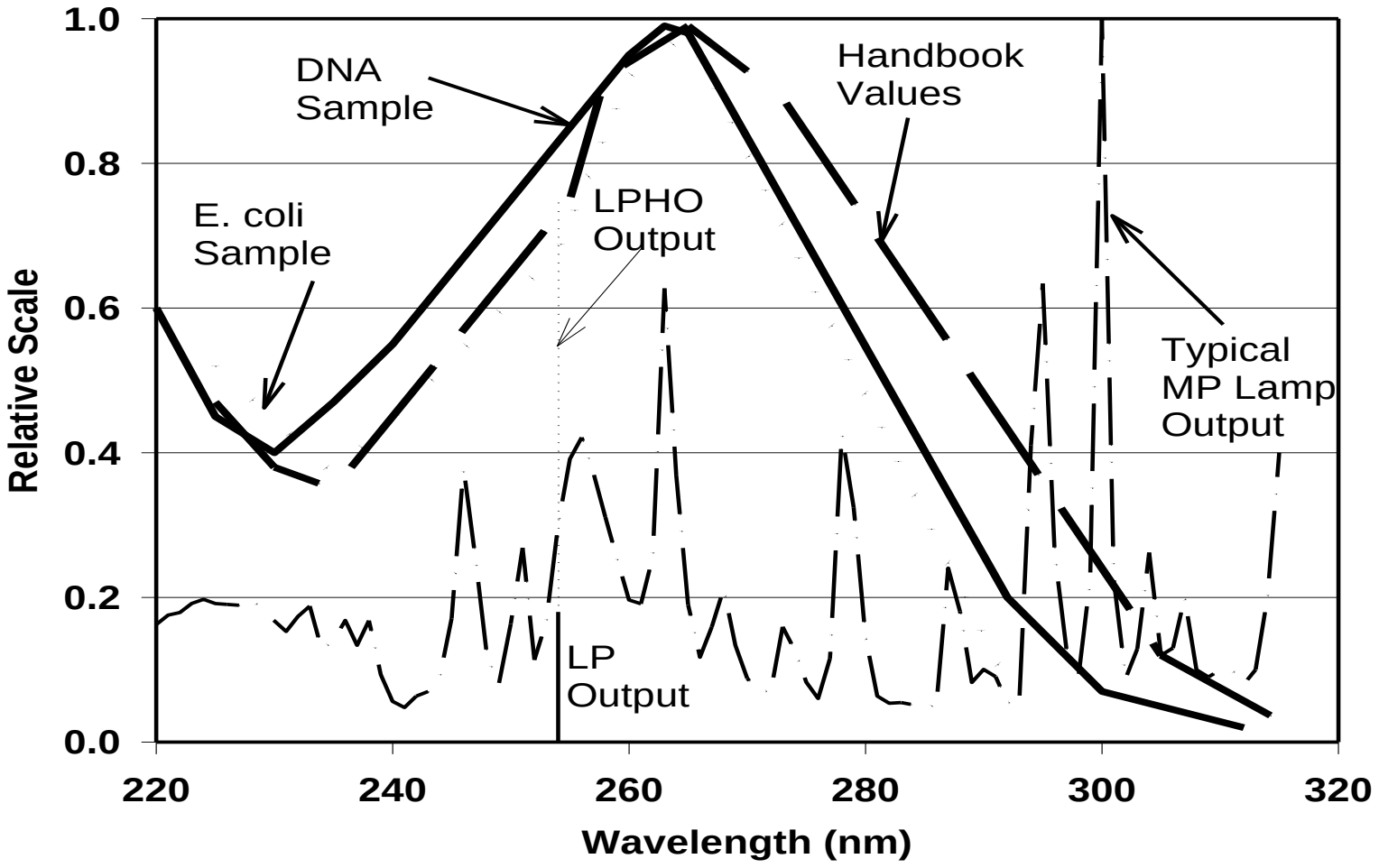

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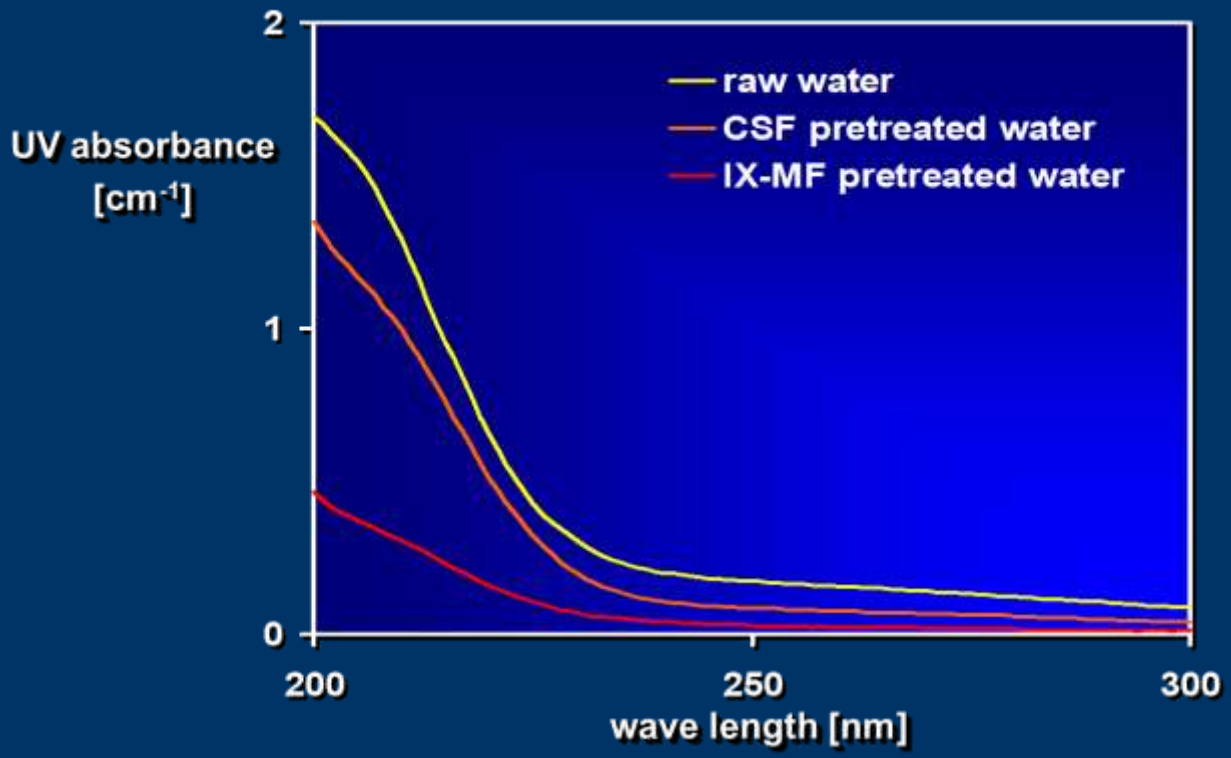
UV absorbance of raw, CSF and IX-MF pretreated water



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Percentage photon flow absorbed by 6 mg/L H_2O_2 to generate OH radicals

MP UV AOP

	254 nm	240 nm
UF	2.6%	4.5%
CSF	5.3%	8.2%
IX-UF	14.7%	19.4%

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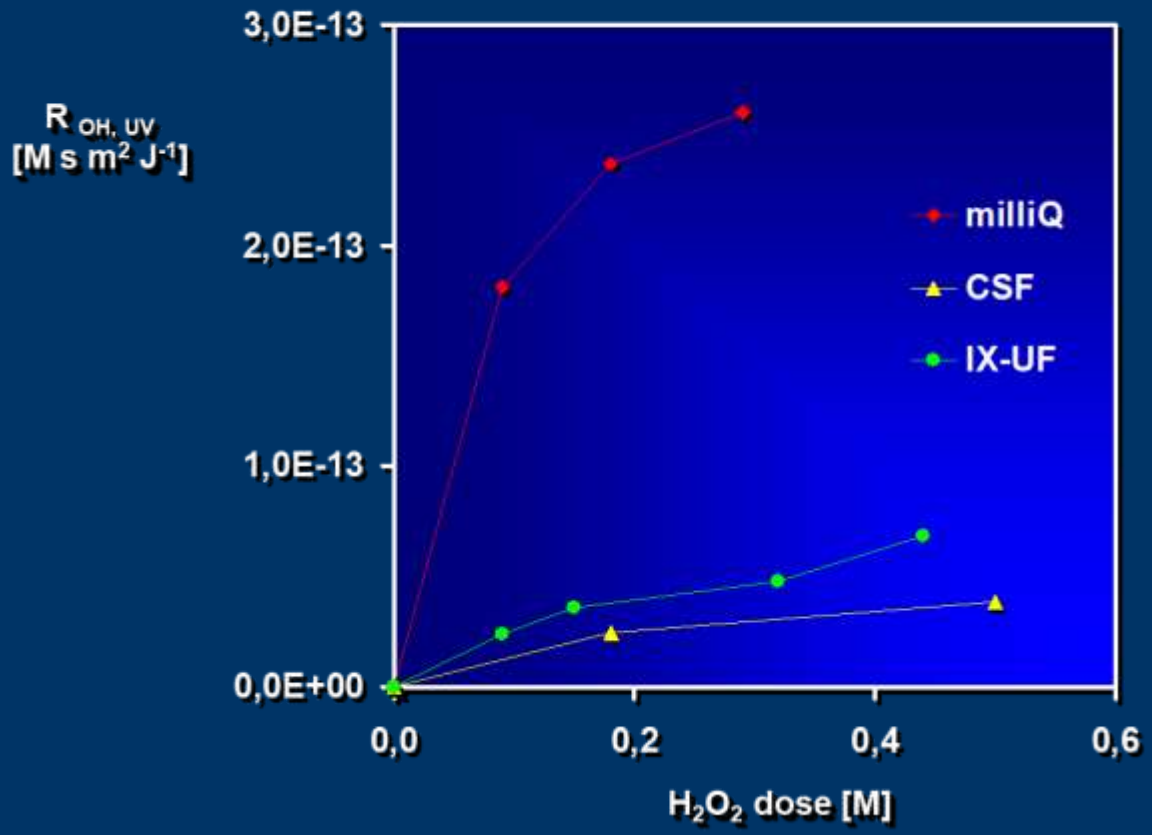
Radical exposure as a function of H_2O_2 dose for milliQ, CSF and IX-UF treated IJssel Lake water



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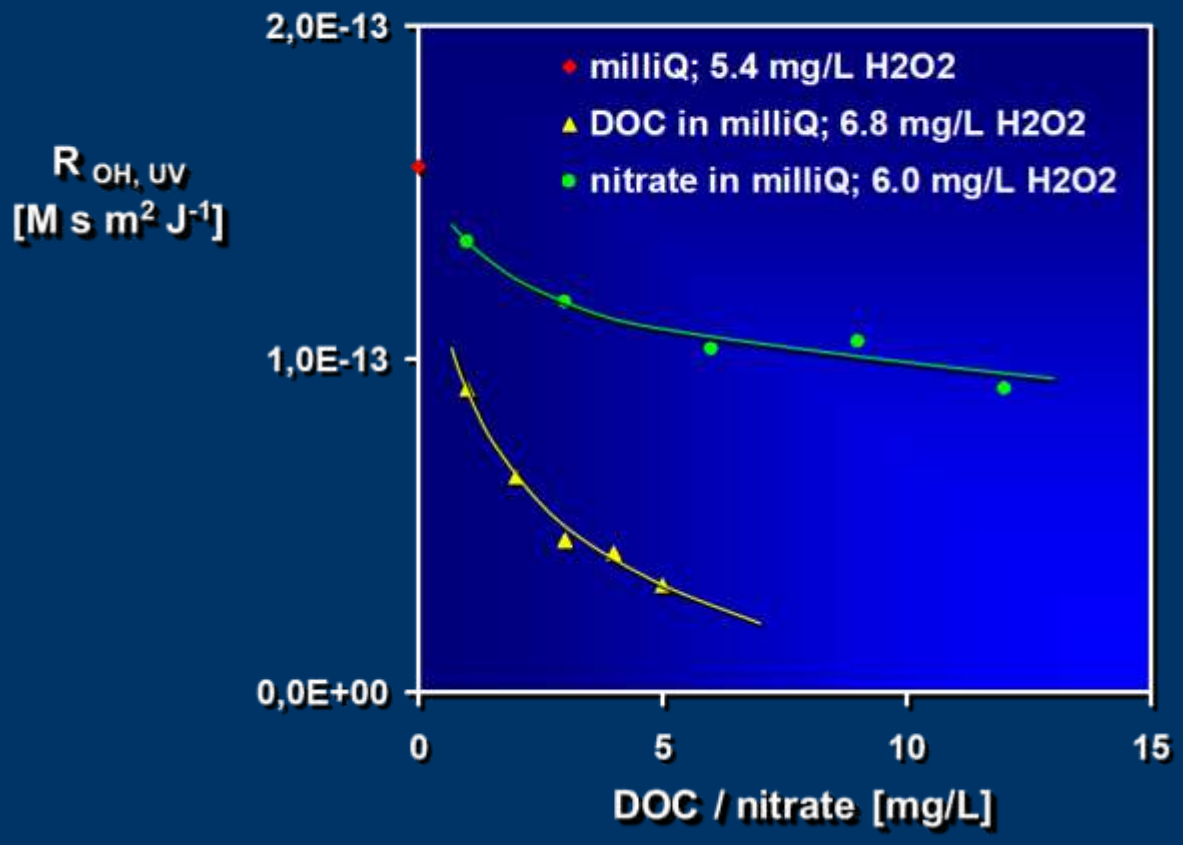
Impact DOC and nitrate on efficiency OH-radical oxidation



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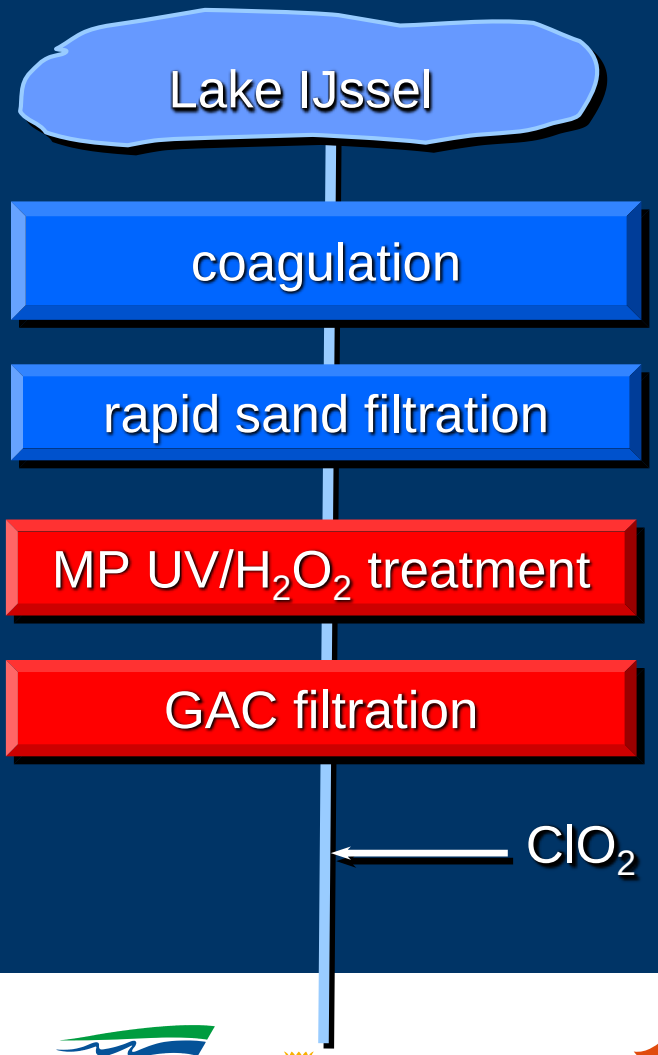
surface water treatment at PWN



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Some results

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‘Robustness’ test 2017 - 2018

- process conditions MP UV/H_2O_2-GAC pilot
  - UV/H_2O_2 0.54 kWh/m^3; 6 mg H_2O_2/L
  - GAC Norit ROW 0.8, EBCT 20 min
- CSF-UF-RO at PWN as well
- selection priority compounds
  - pharmaceuticals
  - perfluorated compounds

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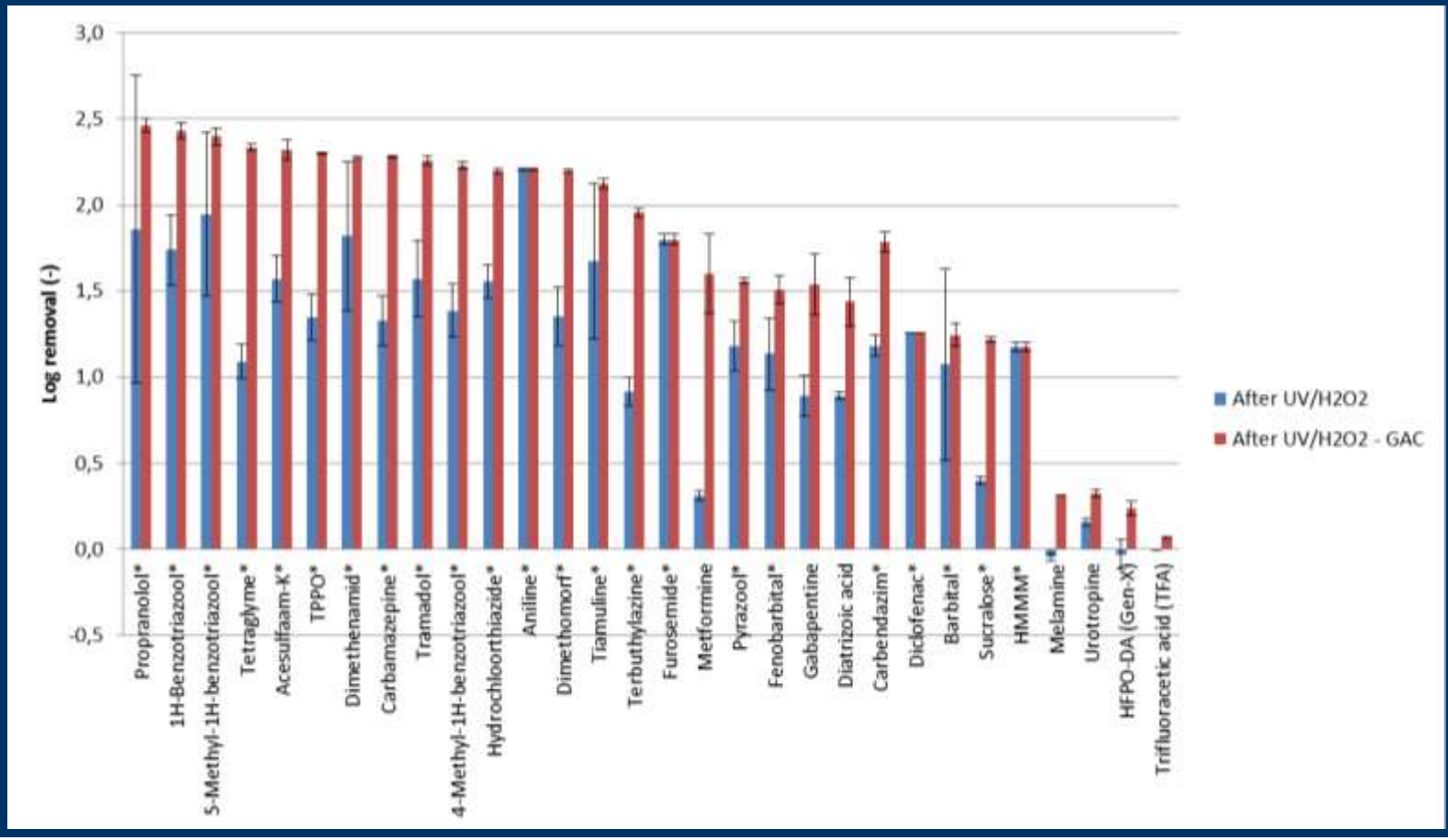
Degradation by MP UV AOP GAC



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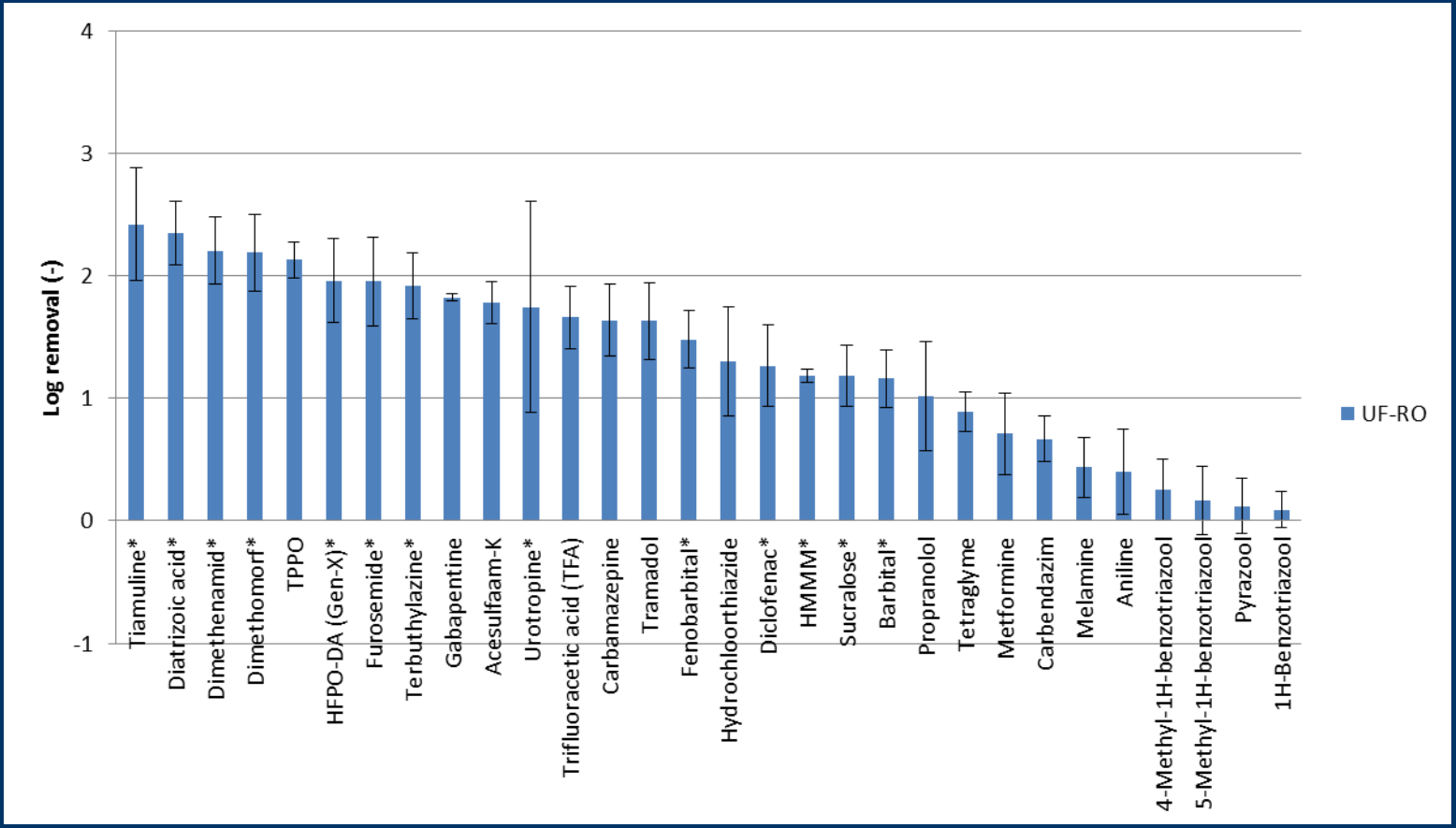
Retention by RO



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UV AOP vs other technologies for the removal of org micro's

- Combination UV-AOP GAC proves to be very robust
  - Designed for herbicides
  - Performs good for CeC
  - Non degradable non adsorbable compounds pass through
- Alternative AOP's such as LP UV O3 H2O2 perform similar
- RO as the reference performs similar
  - Pyrazole is a 'nice' case compound

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Observations

- Water matrix constituents reduce efficiency
  - NOM and nitrate
- Trade off between pretreatment and efficiency of the UV AOP
- Performs well under current conditions
- Would alternative UV system improve efficiency?
  - Evaluate feasibilty LP UV AOP

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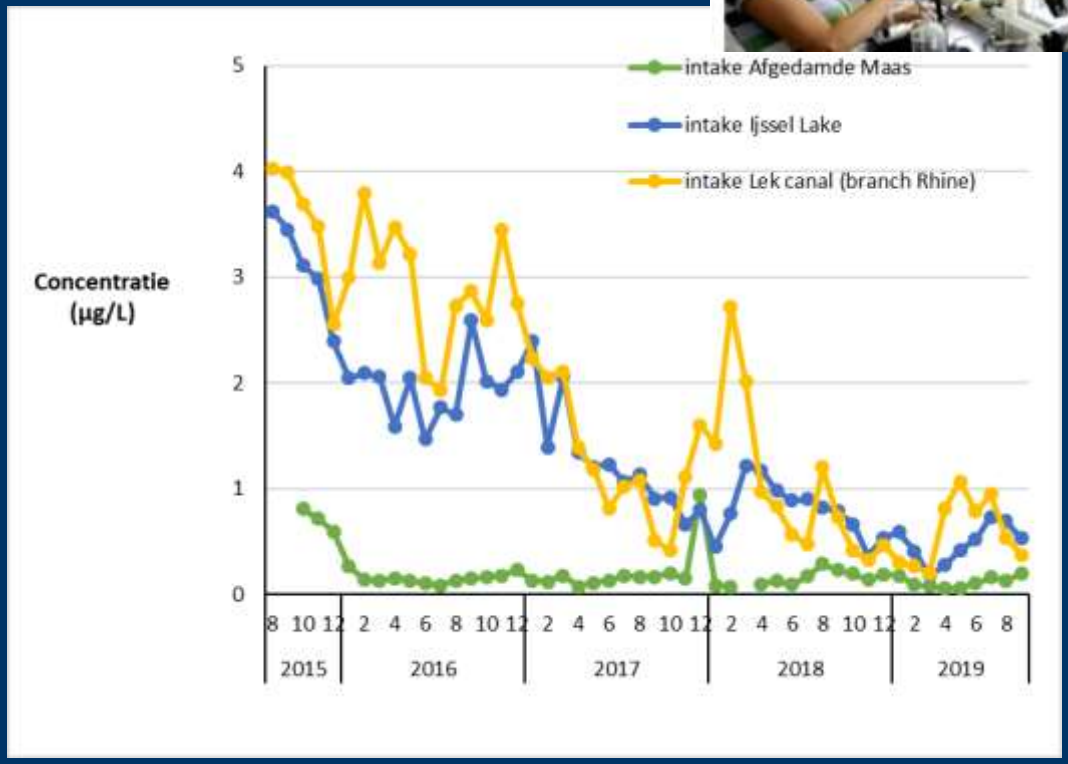
Pyrazole case

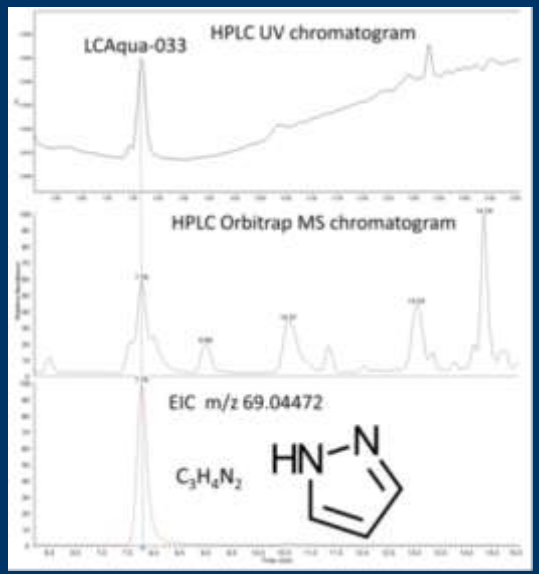
Ineos darf weniger Pyrazol in den Rhein leiten

Von Stefan Schneider

Laut einer neuen amtlichen Bewertung könnte die Chemikalie trinkwassergefährdend sein.

Dormagen. Das Petrochemie-Unternehmen Ineos muss bei der Einleitung seiner Abwässer in den Rhein nachbessern. Das hat die Bezirksregierung Köln dem Konzern auferlegt. Hintergrund sind Funde der Chemikalie Pyrazol im Rhein, die das Landesumweltamt (LANUV) auf den Plan





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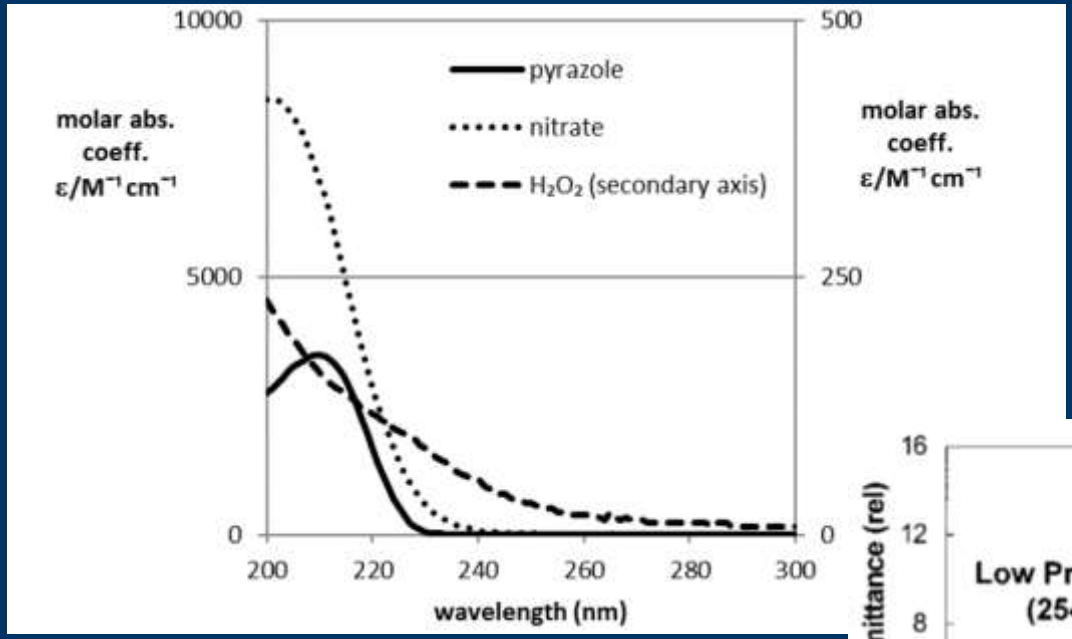
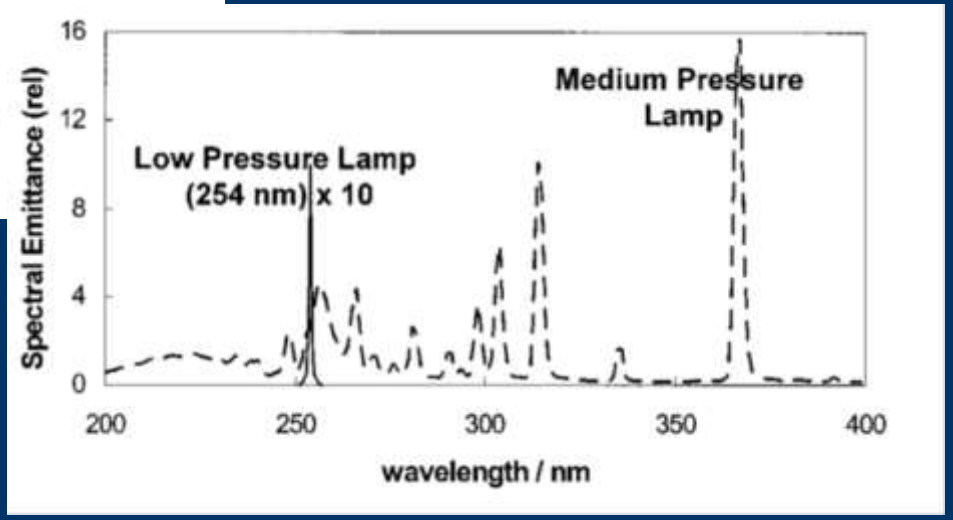
Absorption and emmission spectra





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investigation

- Operational observations:
  - Poor removal by RO
  - Good degradadation by UV AOP, but to what extend

- Mechanistic undertanding
  - Contribution of photolysis; LP UV vs MP UV
  - Impact of the water matrix on efficiency
    - Wavelength specific inner filter?
    - Impact of H_2O_2 dose

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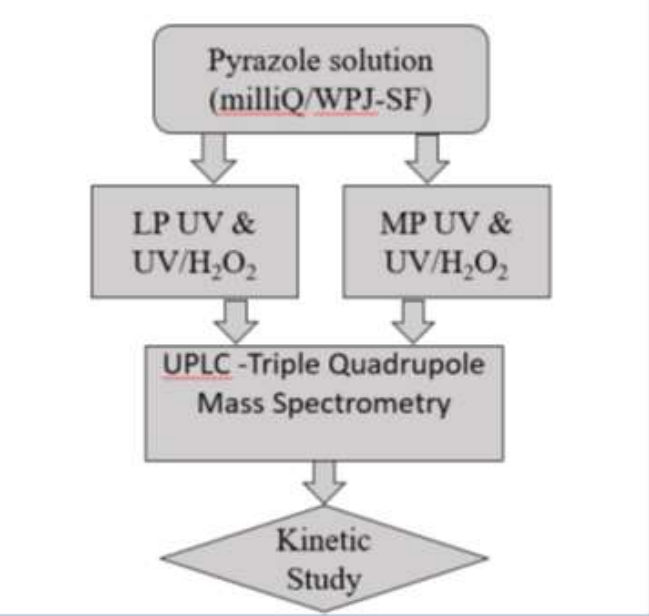
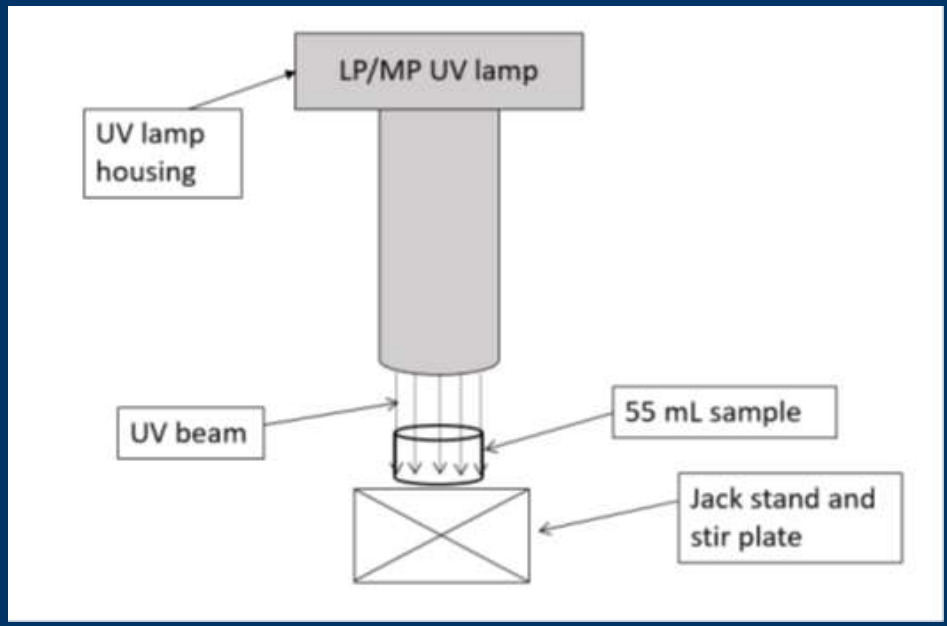
Experimental set-up





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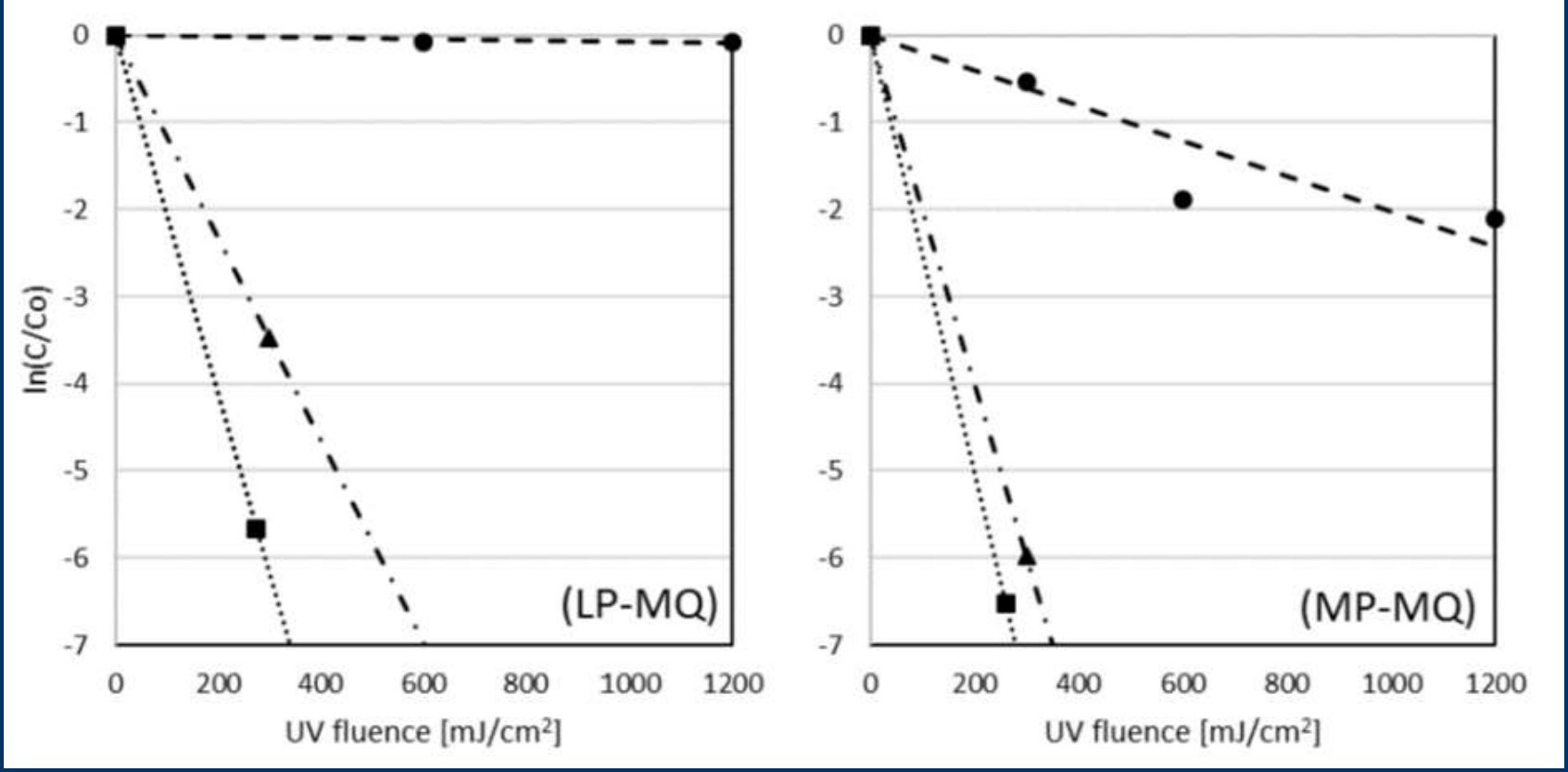
Pyrazole degradation as a function of the fluence without and with a dosage of 6 and 50 mg/L H_2O_2

milliQ



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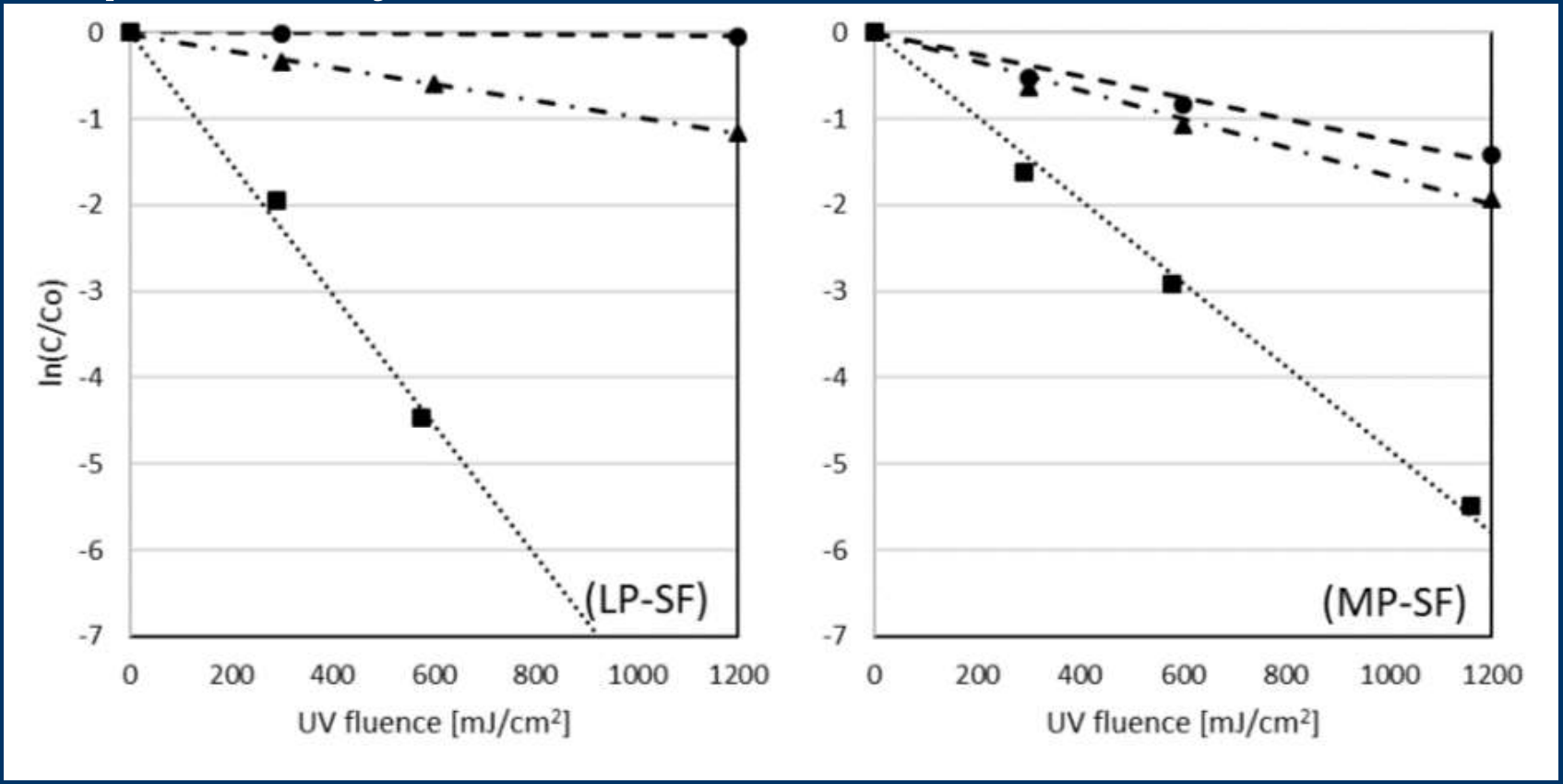
Pyrazole degradation as a function of the fluence without and with a dosage of 6 and 50 mg/L H_2O_2

CSF pretreated Ijssel Lake water



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Fluence based pseudo first order reaction rate constants (k x 10^{-4}/cm^2/mJ)

		0 mg/L H_2O_2	6 mg/L H_2O_2	50 mg/L H_2O_2
LP UV	milliQ	--	142	206
	Pretreated IJssel Lake water	--	9.51	62.9
MP UV	milliQ	18.4	200	250
	Pretreated IJssel Lake water	11.4	15.7	46.8

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Observations degradation

- Pyrazole was degraded by MP UV photolysis but not by LP UV photolysis.

- In pretreated IJssel Lake water:
  - MP UV/H_2O_2 treatment with 6 mg/L H_2O_2 showed a higher degradation rate than LP UV/H_2O_2 treatment
  - For 50 mg/L H_2O_2 degradation rate achieved by LP UV/H_2O_2 treatment was slightly higher.

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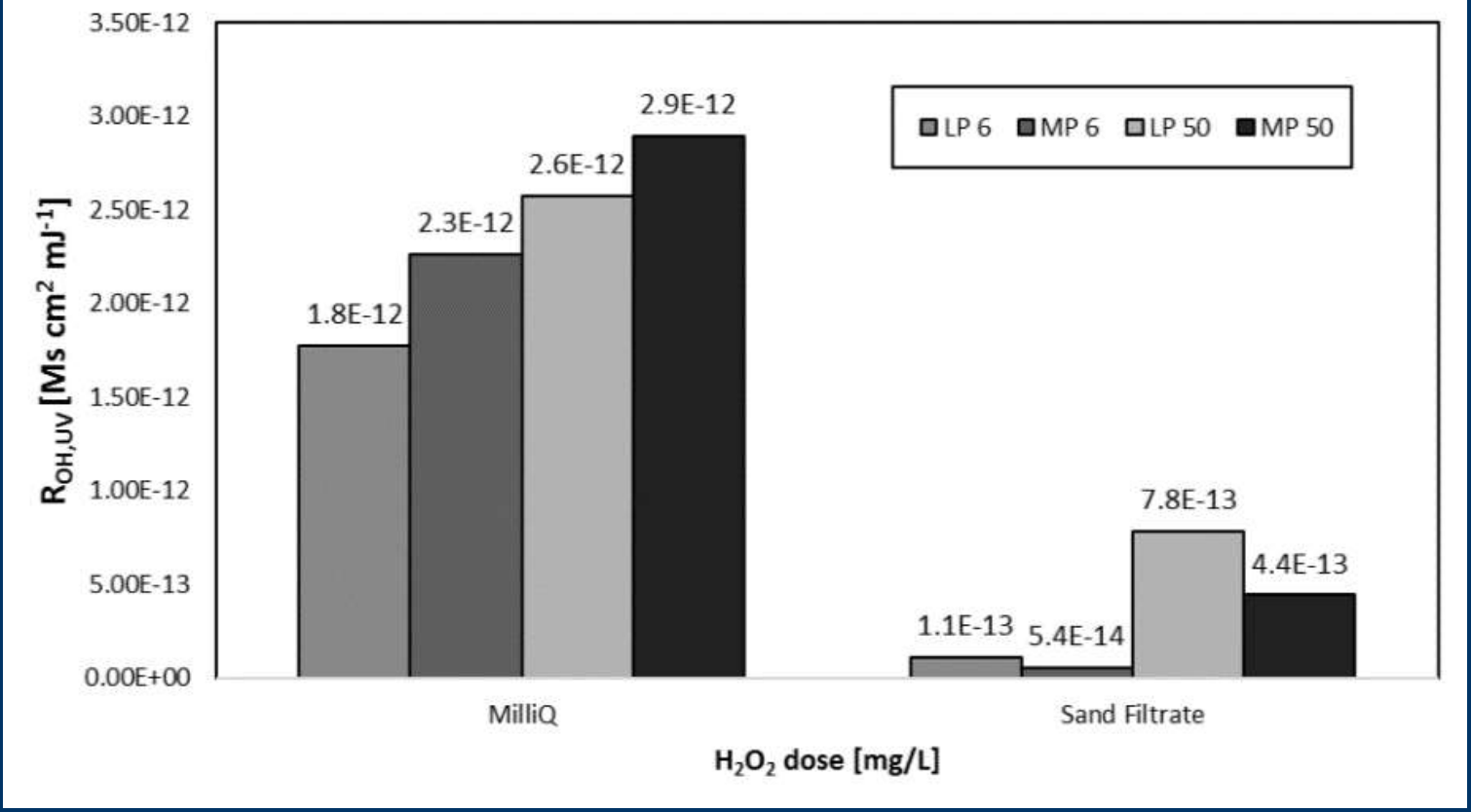
Radical exposure $R_{OH,UV}$ (Ms cm^2 mJ^{-1}) for pyrazole degradation



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Observations radical exposure

- Radical exposure
  - In milliQ radical exposure was greater for MP UV/H_2O_2 treatment than for LP UV/H_2O_2 treatment.
  - In pretreated IJssel Lake water radical exposure of MP UV/H_2O_2 treatment and LP UV/H_2O_2 treatment was not significantly different for 6 mg/L H_2O_2
  - For 50 mg/L H_2O_2 dose LP UV/H_2O_2 treatment caused a larger $R_{OH,UV}$.

- Both MP UV/H_2O_2 treatment and LP UV/H_2O_2 treatment can achieve the required pyrazole degradation under economically feasible conditions.

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Conclusions pyrazole

- MP UV treatment is slightly more attractive by the contribution from UV photolysis
- Also in extensive pretreated water MP UV/H_2O_2 treatment is more favorable
- In heavily polluted water LP UV/H_2O_2 treatment may be more attractive
- A business case was made for full scale implementation of LP UV AOP at some locations of PWN

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Metabolites and byproducts

- Nitrite
- AOC and biological stability
- Amino acis related nitrated byproducts
- Amestest / bioassays

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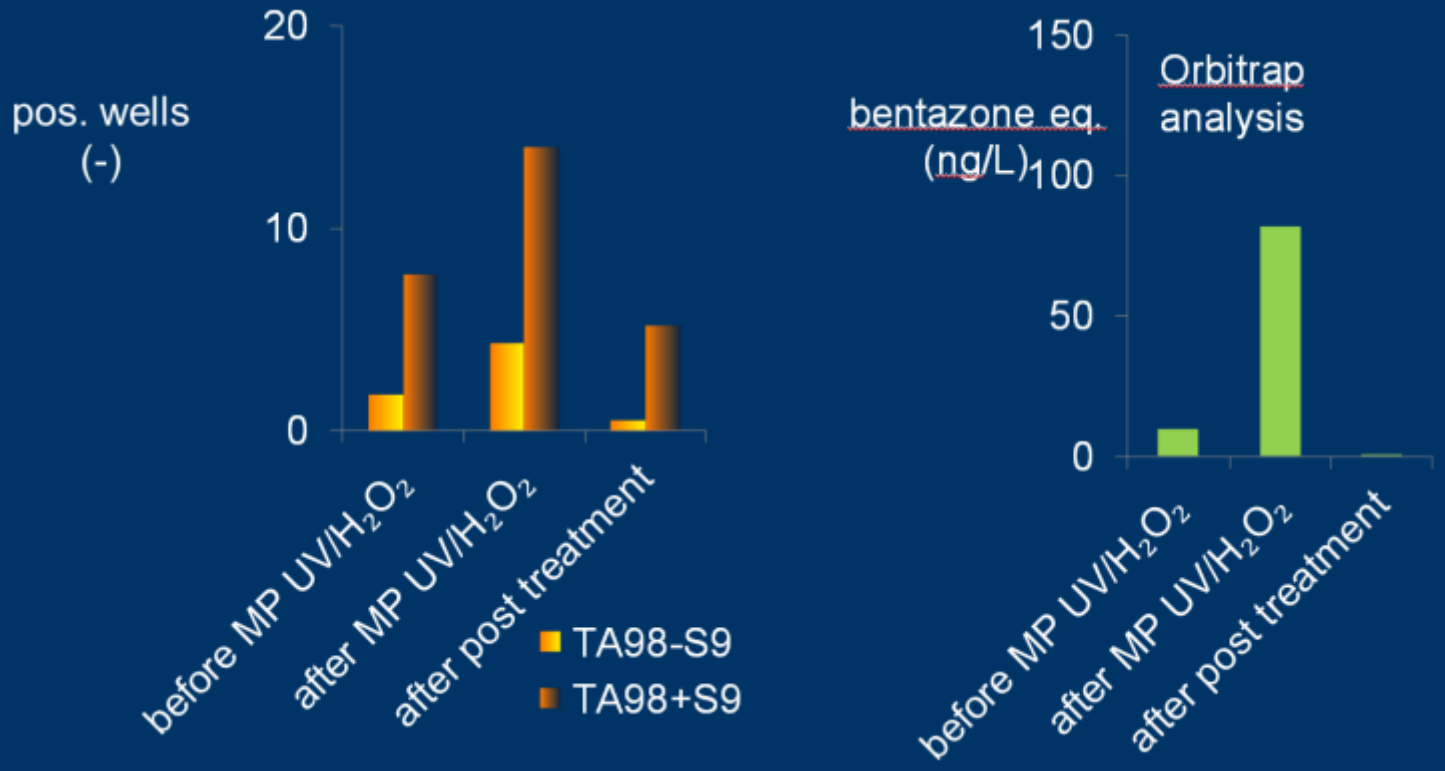
full scale water treatment; bioassay results versus chemical identification



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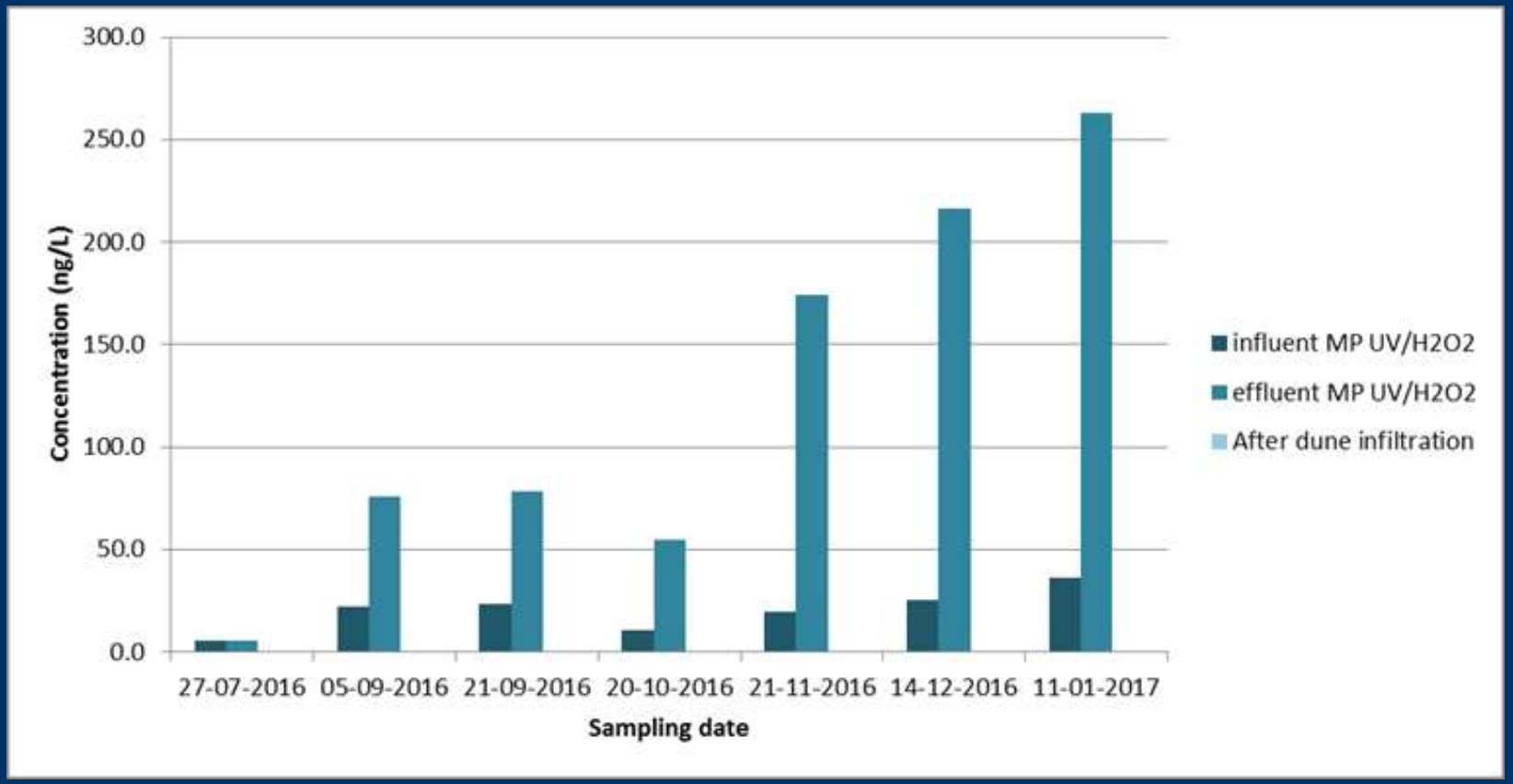
by-products MP UV/H_2O_2 and after dune infiltration water by QToF N-DBP



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Bioassays and byproducts robustness

Monsterneming	Code
voor doseren (controle influent)	A
na doseren, vóór behandeling (gedoseerd influent)	B
na UV/H_2O_2 behandeling	C
na buffervat opslag, vóór GAC behandeling	D
na GAC behandeling	E

	>LOQ					>ecologische trigger value				
	A	B	C	D	E	A	B	C	D	E
anti-androgene activiteit	+ +	+ +	- -	- -	- -	- -	- -	- -	- -	- -
estrogene activiteit	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
PAKs activiteit	- -	+ -	+ +	- -	- -	- -	- -	- -	- -	- -
oxidative stress	- -	- -	+ +	+ +	- -	- -	- -	+ +	+ +	- -

	A	B	C	D	E
TA98 geen metabolisme	++	++	++	++	+ -
TA98 + S9 metabolisme	- -	- +	++	++	- -
TA100 geen metabolisme	- -	++	+ -	++	+ -
TA100 + S9 metabolisme	- -	- -	- -	++	- -
Test resultaat	+	+	+	+	-

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Overall results

DOC removal effect UV AOP

- Energy
  - Reduced energy demand for same treatment target due to NOM removal
- Environment
  - Improved efficiency feasible by improved pretreatment
- Health
  - Byproducts; response Ames test, known mechanism with more insight in precursor; relates to ilca biopolymers; mitigation vs prevention in formation
- Savings
  - Same installation suitable for more production; confidence in the technology maintained and improved
- Chemicals
  - Choice to balance H_2O_2 dosage vs energy input

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