Norway grants

STÁTNÍ FOND ŽIVOTNÍHO PROSTŘEDÍ ČESKÉ REPUBLIKY

VALIDATION TESTING OF ADVANCED OXIDATION PROCESSES FOR THE REMOVAL OF PHARMACEUTICALS FROM WWTP EFFLUENT

Trace & Treat

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ALS

NIVA Norwegian Institute for Water Research

Ing. Tomáš Macsek, Ph.D.

Prague, 05. 06. 2024

Content

01 Project summary

- Demonstrate the use of ozonation in combination with nature-based solutions (NBS) for pharmaceuticals and their metabolites removal from wastewater treatment plant (WWTP) effluents and concentrated point sources (medical facilities, pharmaceutical industry, etc.).

- Partners of the project

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- Duration of the project: 4/2022 – 4/2024

01 Project summary

- Demonstration project

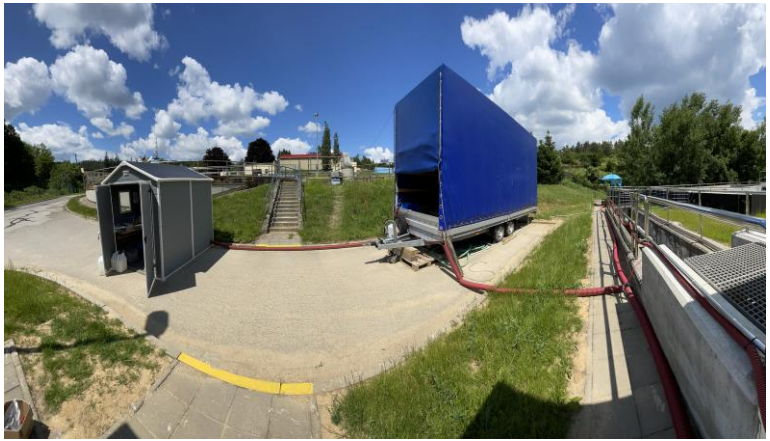
- 2 demonstration sites
  1. Veterinary university Brno (ozonation only)
     – effluent of WWTP VETUNI
     – WW of VETUNI campus
     – WW from breeding and treatment of animals (horses, cattle, pigs, poultry, etc.).
  2. WWTP Blansko (ozonation + NBS)
     – 29 400 PE
     – mechanical-biological WWTP with biological nitrogen removal and chemical precipitation of phosphorus

01

Demonstration site – WWTP VETUNI

01

Demonstration site – WWTP Blansko



01

Monitored pharmaceuticals and metabolites

- Main focus on the Indicative list of SEF CR (IND)
  - ❑ 33 pharmaceuticals and metabolites
  - ❑ 28 were monitored in the project

- Proposal for a Directive of the European Parliament and of the Council concerning urban wastewater treatment:
  - ❑ Carbamazepin, citalopram, clarithromycin, diklofenac, hydrochlorothiazid, metoprolol, venlafaxin, irbesartan, ~~telmisartan~~ (8/12)
- In total 141 substances were monitored

		název	popis
léčiva	1	acebutulol	beta blokátor
	2	atenolol	beta blokátor
	3	azithromycin	antibiotikum
	4	carbamazepine	antiepileptikum
	5	clarithromycin	antibiotikum
	6	diclofenac-4'-hydroxy	metabolit
	7	diclofenac	nesteroidní antiflogistikum
	8	furosemid	diuretikum
	9	gabapentin	antiepileptikum
	10	hydrochlorthiazide	diuretikum
	11	ibuprofen	nesteroidní antiflogistikum
	12	ibuprofen-2-hydroxy	metabolit
	13	ibuprofen-carboxy	metabolit
	14	iopromid	rentgenkontrastní látka
	15	ketoprofen	nesteroidní antiflogistikum
	16	metformin	lék proti cukrovce
	17	metoprolol	beta blokátor
	18	naproxen	nesteroidní antiflogistikum
	19	naproxen-o-desmethyl	metabolit
	20	oxypurinol	purin (proti dně)
	21	paracetamol	lék proti bolesti
	22	paraxanthine	metabolit caffeinu
	23	ranitidine	antiulcerosum (léčba žal. vředů)
	24	sotalol	beta blokátor
	25	sulfamethoxazol	antibiotikum
	26	sulfapyridin	antibiotikum
	27	telmisartan	antihypertensivum
	28	tramadol	lék proti bolesti
	29	trimethoprim	antibiotikum
	30	venlafaxine	antidepresivum
hormony	31	17-alpha-estradiol	estrogenní steroidní hormon
	32	17-alpha-ethinylestradiol (EE2)	estrogenní steroidní hormon
	33	17-beta-estradiol (E2)	estrogenní steroidní hormon

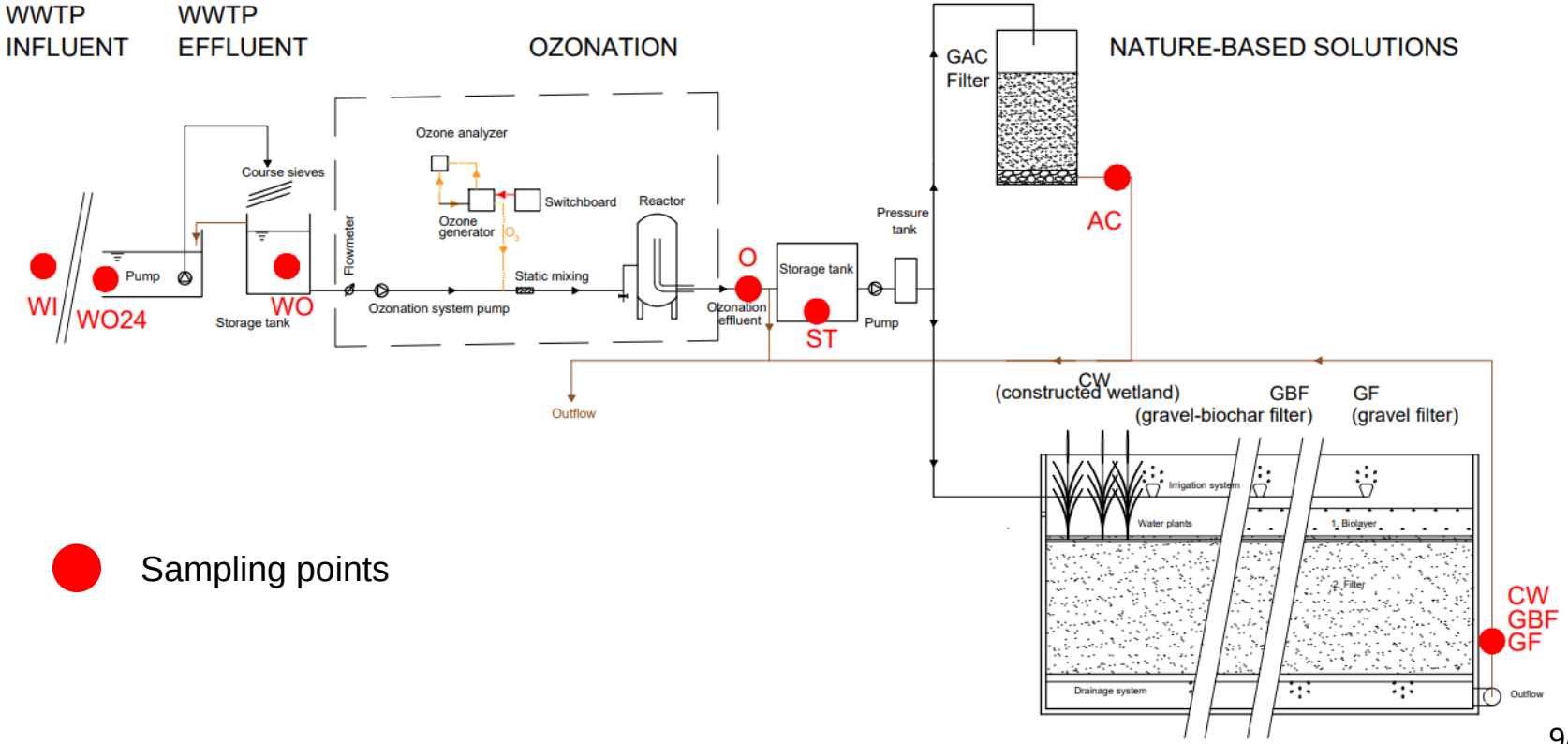
01 Demonstration site – WWTP Blansko

- Ozonation was used as a quartery step of treatment – treating current WWTP effluent

- Used nature–based solutions:
  - ❑ Constructed wetland with a gravel–biochar filter (CW)
  - ❑ Gravel–biochar biofilter (GBF)
  - ❑ Gravel biofilter (GF)
  - ❑ Granular activated carbon filter (reference)

01

Demonstration site – WWTP Blansko



Sampling points

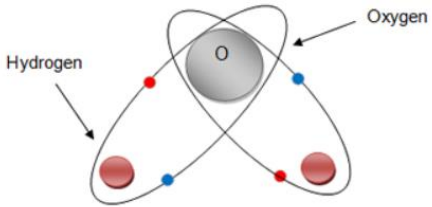
01 Main goals of the project

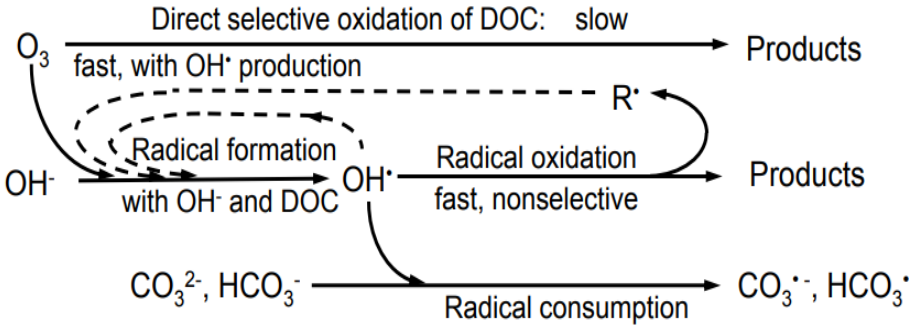
The main purpose of the project was to answer the following questions:

- How do current WWTP technologies remove contaminants of emerging concern (CECs)?
- Is ozonation an effective technology for removing CECs? (target removal: 80% overall reduction)
- Is the UV absorbance at a wavelenght of 254nm an effective surrogate parameter to track actual CECs removal?
- What are the advantages of nature based solutions as a posttreatment for ozonated effluent?

02

Investigated processes: Ozonation



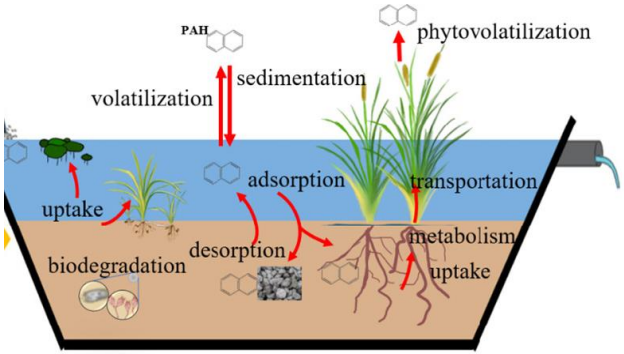


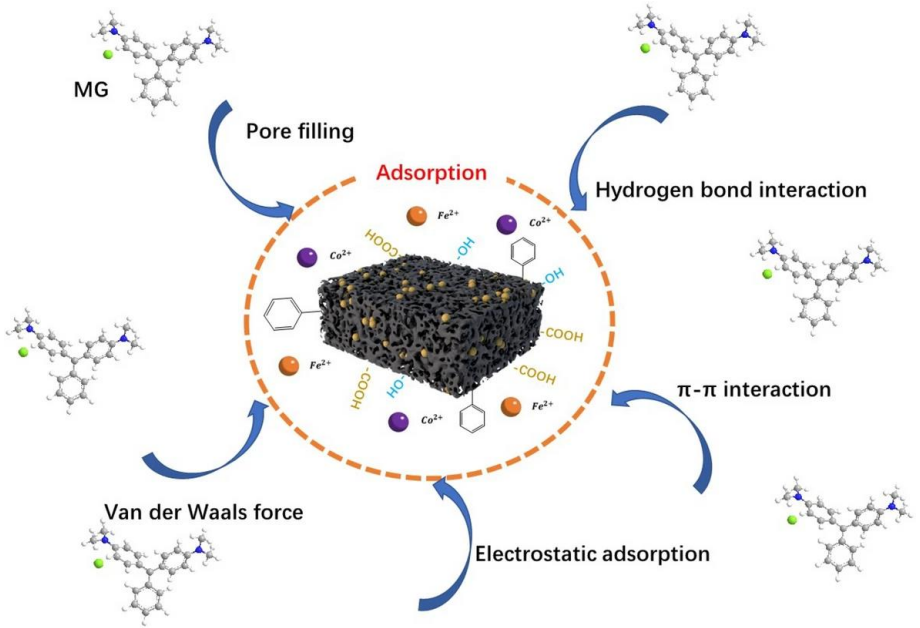
Oxidizing agent	Oxidation potential
Hydroxyl radical	2,8 V
Ozone	2,1 V
Hydrogen peroxide	1,8 V
Potassium permanganate	1,7 V
Chlorine	1,4 V
Oxygen	1,2 V

SIEGRIST, Hansruedi. et al. *Advanced treatment processes for micropollutant removal*. In: . NEPTUNE Workshop, 21/22 April, Koblenz, Germany, 2009.

02

Investigated processes: NBS





Congcong Zhao, Jingtao Xu, Dawei Shang, Yanmeng Zhang, Jian Zhang, Huijun Xie, Qiang Kong, Qian Wang,
Application of constructed wetlands in the PAH remediation of surface water: A review, Science of The Total Environment,Volume 780,2021,146605,ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2021.146605.

YANG, Mengyuan; CUI, Ce; DAI, Lanling; JIANG, Shan; LAN, Jianwu et al. Removal of malachite green by cobalt@iron-doped porous carbon composite derived from CoFe-MOF and bamboo pulp black liquor. Online. *Journal of Materials Science: Materials in Electronics*. 2023, roč. 34, č. 14. ISSN 0957-4522

02

Surrogate indicator for CECs removal

How to evaluate/track CECs removal

Direct method → analytically

+ Exact determination of individual and overall CECs concentrations
+ Exact determination of individual and average CECs removal

- Duration of analysis (days)
- Costs

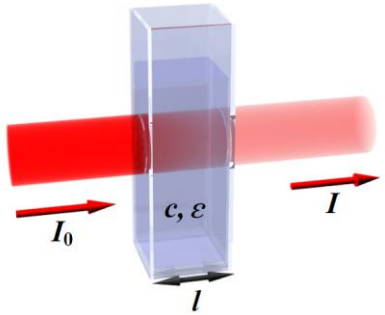
Indirect method → Surrogate parameter

+ Real-time monitoring

- Limited accuracy
- Individual concentrations cannot be determined

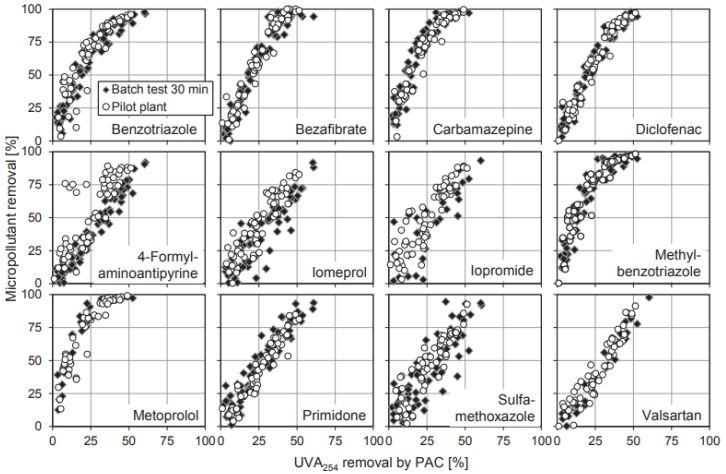
02 Surrogate indicator for CECs removal

- Absorbance at wavelenght 254 nm
- It indicates how much light was absorbed by the measured sample
- Absorbance is proportional to the concentration of the absorbing (organic) substances
- $A = - log \frac{Io}{I}$



- **Relative decrease in absorbance λ=254 nm**

$$\Delta \text{ UV 254 [\%]} = \frac{Abs\ UV254_{before\ treatment} - Abs\ UV254_{after\ treatment}}{Abs\ UV254_{before\ treatment}} \cdot 100$$

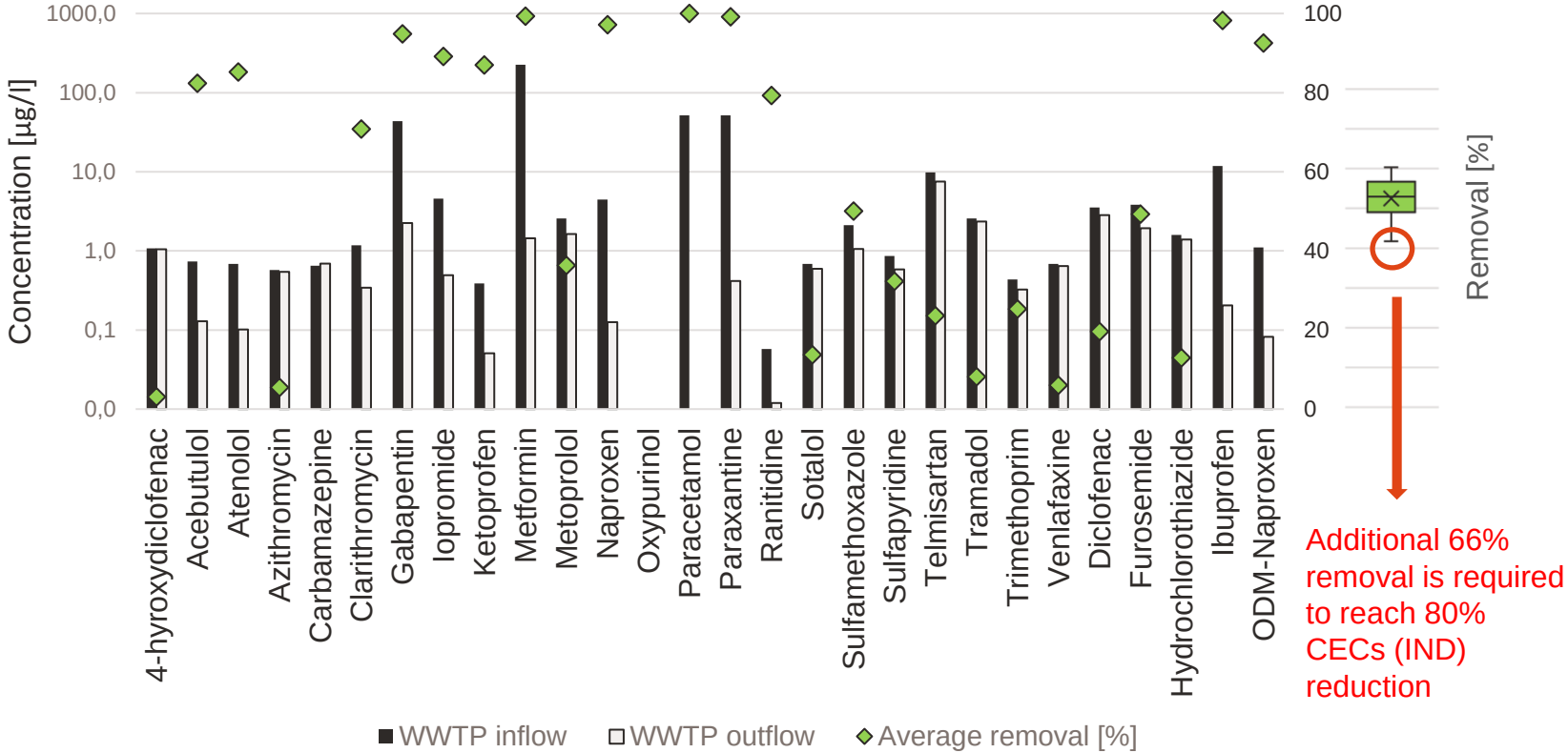


ALTMANN, Johannes, Lukas MASSA, Alexander SPERLICH, Regina GNIRSS a Martin JEKEL, 2016. UV 254 absorbance as real-time monitoring and control parameter for micropollutant removal in advanced wastewater treatment with powdered activated carbon. *Water Research*. **94**, 240-245. ISSN 00431354. doi:10.1016/j.watres.2016.03.001

03 Results – CECs removal at WWTP

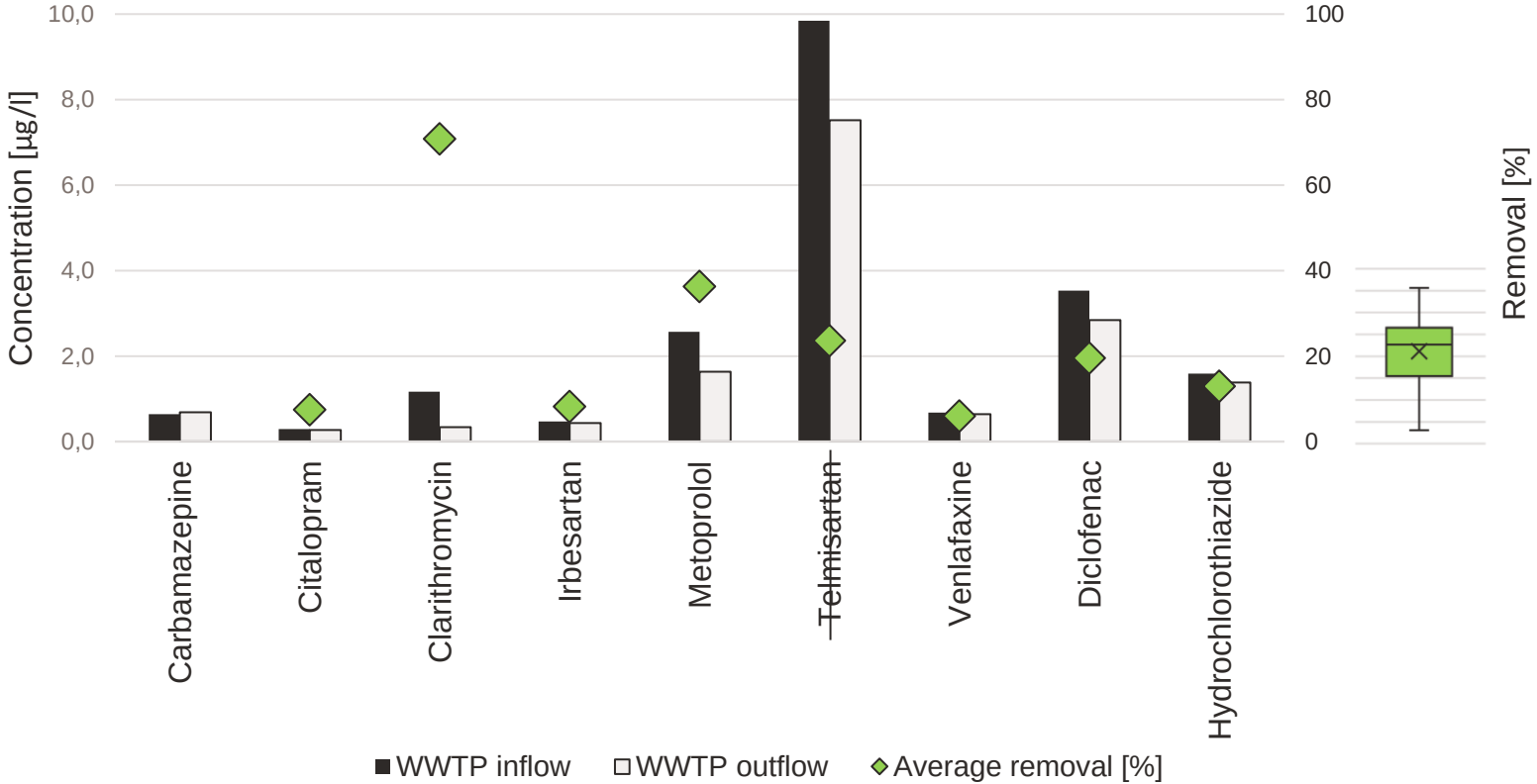
03

CECs (IND) at WWTP Blansko



Additional 66% removal is required to reach 80% CECs (IND) reduction

03 CECs in upcoming EU directive



03

Results – CECs removal by ozonation + NBS

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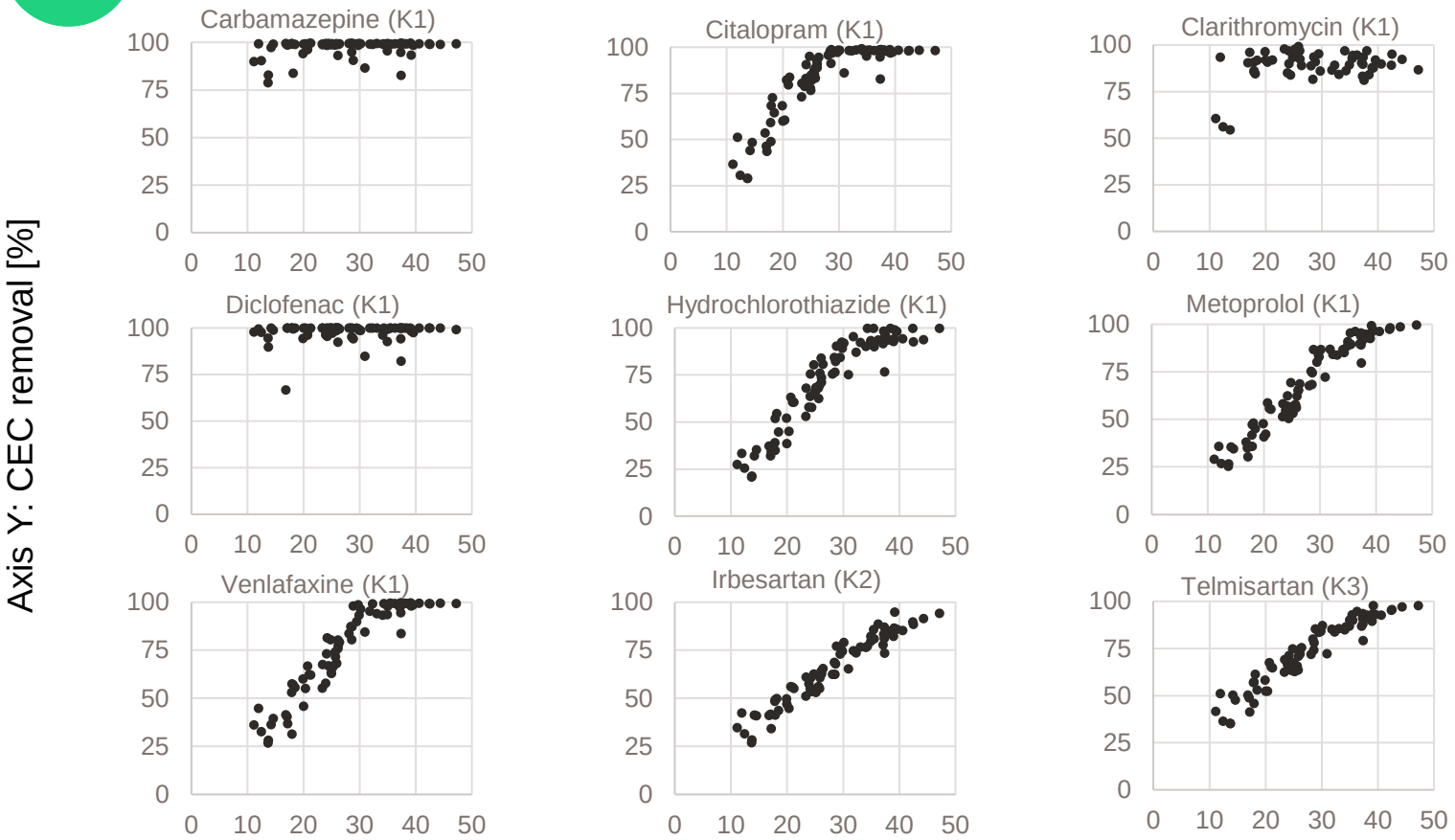
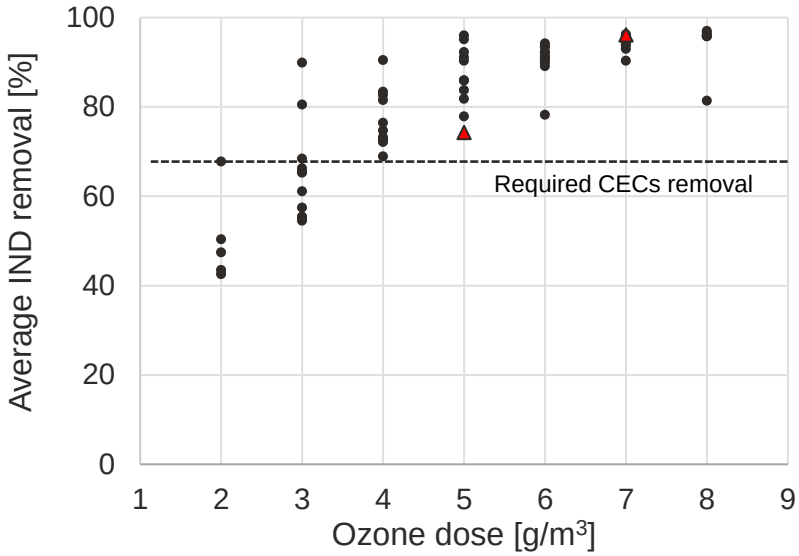
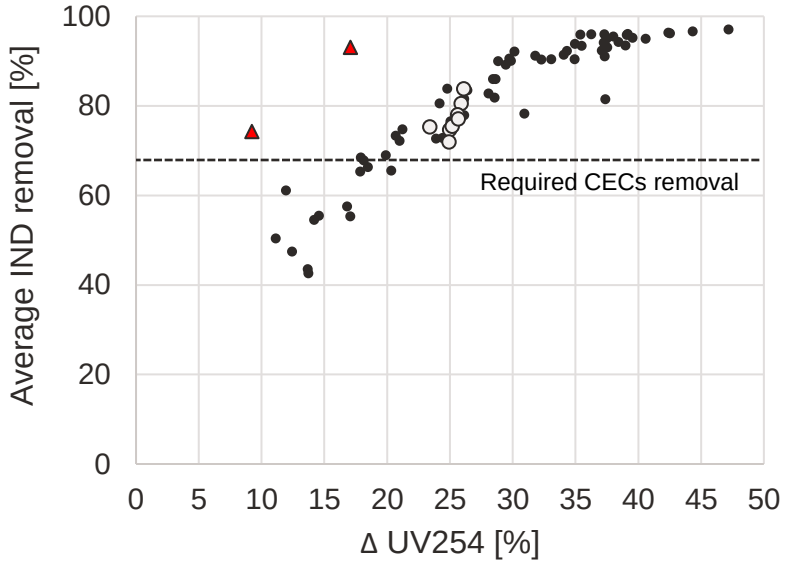
CECs removal vs ΔUV254



03 Average CECs (IND) removal with O_3

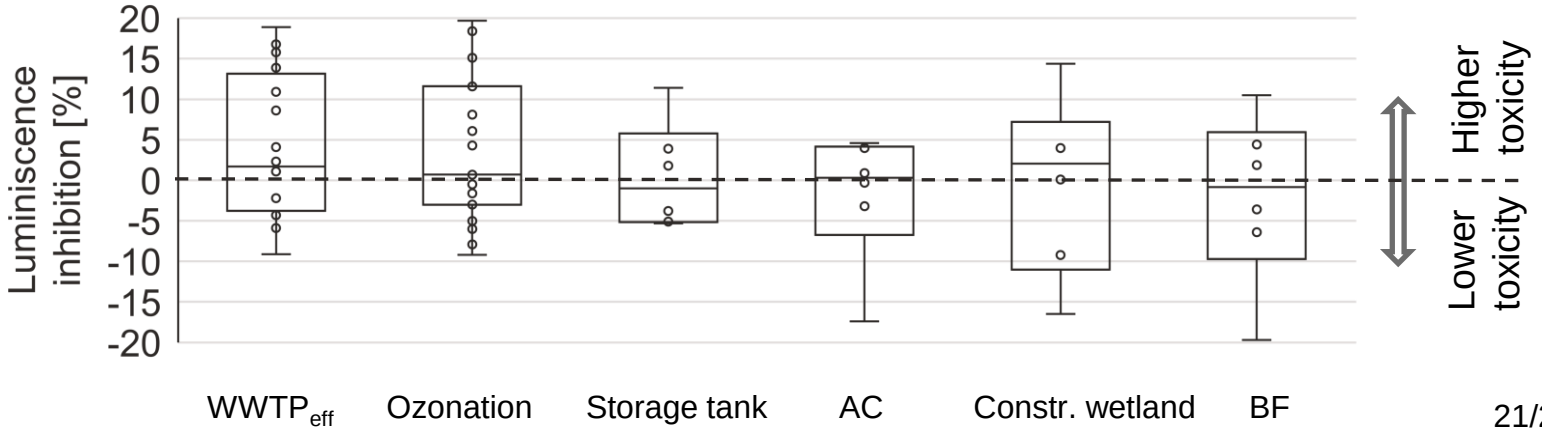


X

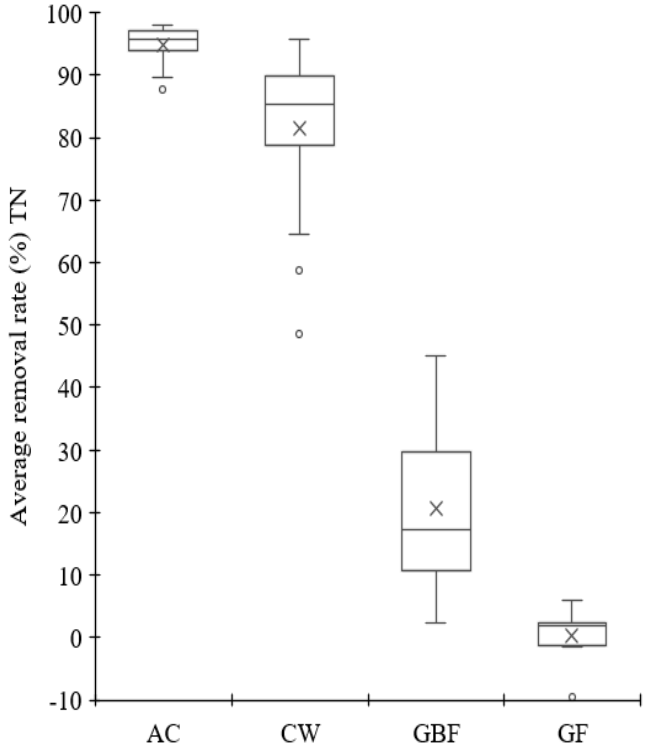


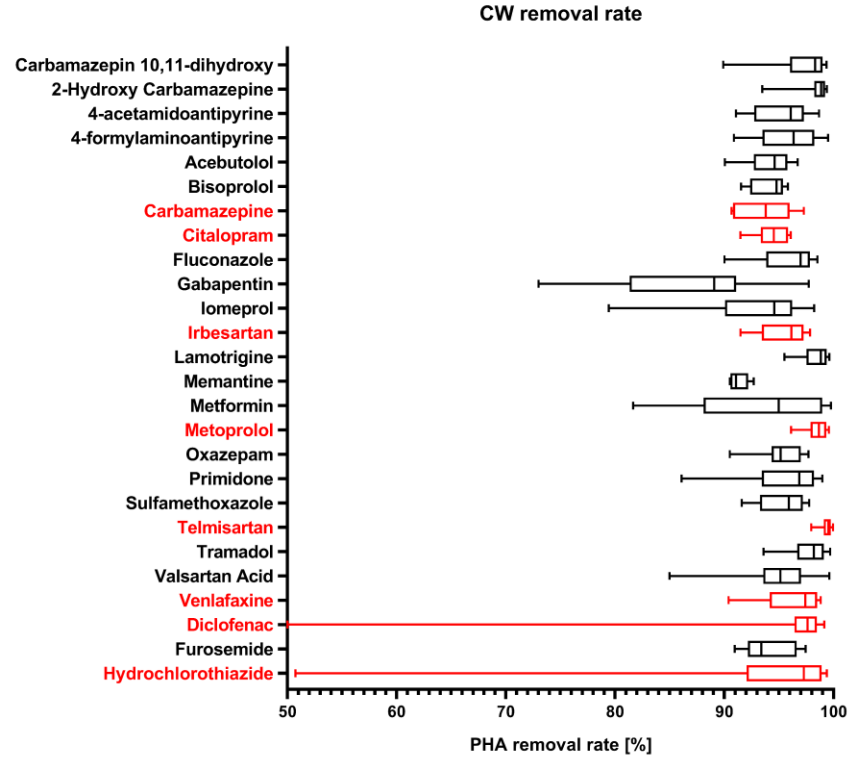
03 Ecotoxicity – *Vibrio fisheri* luminiscence

- *Vibrio fisheri* is a marine gram-negative, non-pathogenic bacterium that naturally luminesces under optimal environmental conditions. When exposed to a toxic substance, the metabolic process is disrupted, and light output is reduced. The reduction in light intensity measurement directly correlates with the degree of toxicity.



03 NBS additional benefits





04 Conclusion

- Current WWTP technologies are not designed to remove CECs
- Ozonation as a quartery step of treatment is effective in CECs reduction
- Advanced ozone dose strategies lead to stable CECs removal
- NBS as a post ozonation treatment secured the final ecotoxicity, enhanced further removal of CECs and removed additional nitrogen pollution

Norway grants

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Thank you for your attention

Ing. Tomáš Macsek, Ph.D.
Tomas.Macsek@vutbr.cz

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