Impact of variable Parameters on the Formation of possible Transformation Products during Drinking Water Treatment Simulation

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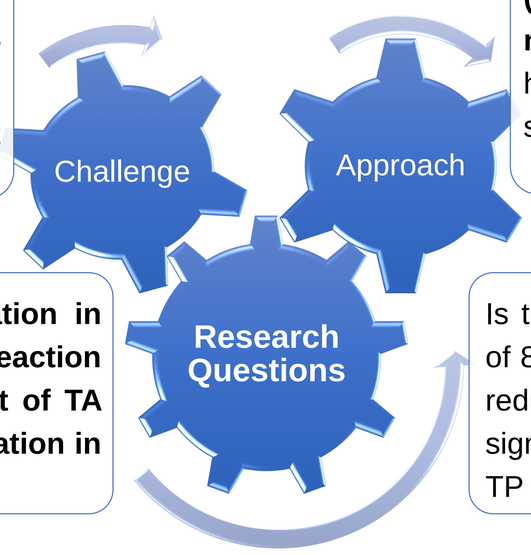
Introduction

Raw water used for drinking water often contains plant protection products and biocides from various sources such as agriculture[1] and urban infrastructure[2]. Consequently, those **micropollutants are exposed to disinfection treatments potentially leading to formation of transformation products (TPs)**, which might not be monitored and could possess toxic properties[3].

The aim of the **"Guidance document on the impact of water treatment processes on residues of active substances or their metabolites in water abstracted for the production of drinking water",** published by EFSA (2023)[4], is to provide a comprehensive account of experiments that **simulate potential drinking water treatments and assess the resulting TPs.**

Guidance document only specifies minimum and/ or maximum values for process parameters, e.g. amount of **treatment agent (TA)** and reaction time

Design of Experiment (DoE) coupled with **nontarget analytics** and high-resolution mass spectrometry (HRMS)



Does the potential variation in parameters such as reaction time, pH and the amount of TA impact a significant alteration in the number of TPs?

Is the large sample volume of 800 mL necessary or is a reduction possible without significant influence on the TP formation?

Figure 1: Overview on challenge, following research questions and chosen approach

Methods

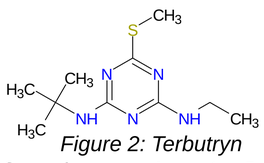


Figure 2: Terbutryn

Model active substance (AS): Terbutryn (biocide and former pesticide; part of Water Framework Directive and detected in surface/ground water[5]

Test system: CIPAC C Standard Water (500 ppm hardness) + 3 mg·L^{-1} DOC

DoE: Definitive Screening Design with 17 trials per TA (see Table 1 for details on tested parameters and levels)

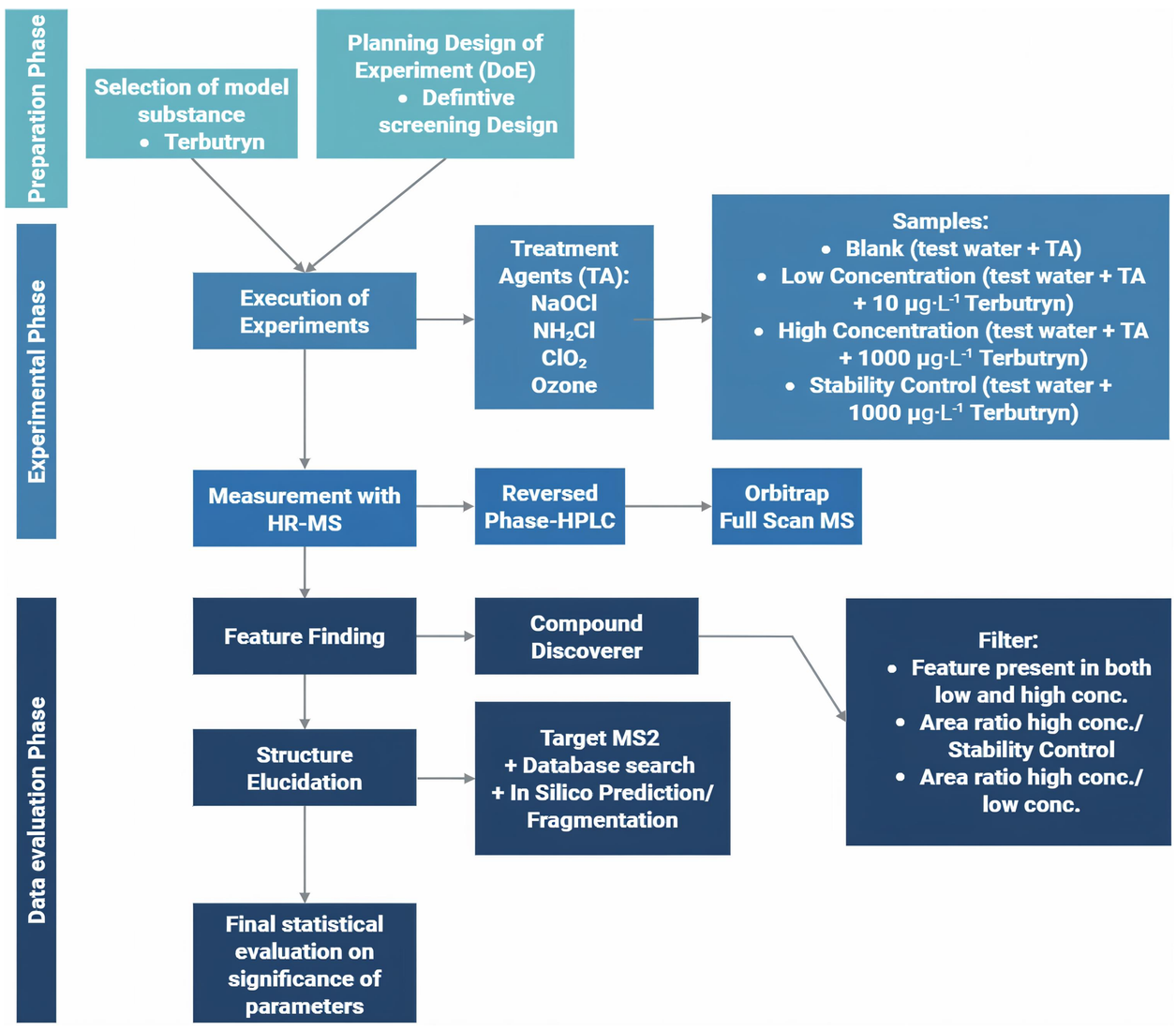


Figure 3: Three stage workflow with detailed information for each phase

Results – Statistics

- **Sample volume and reaction time** had **no significant effect** on the number of TPs formed in all treatments
- **Amount of TA in 3 out of 4 treatments significant for TP formation**
- **Critical Parameters** are **molar ratio of TA/Terbutryn within NaOCl and NH_2Cl** since the **variation given by guideline results in significant altered number of TP**

Table 1: Comparison of possible parameter values according to the guidance document and the experimentally tested ranges including p-values indicating significance ($p < 0.05$)

Treatment	Parameter	Guideline value	Tested values	Number of TPs	p-value (Power)
Chlorination NaOCl	**pH Value**	**6.5; 7.5; 8.5**	**6.5; 7.5; 8.5**	3-12	**0.0020*** (0.9192)
	Reaction time	12-24h	15; 19.5; 24 h		0.5265
	Molar Ratio free Cl_2/AS	**> 10**	**11; 20.5; 30**		**0.0008*** (0.8004)
Chlorination NH_2Cl	Reaction time	≥ 24h	20; 24; 28 h	1-4	0.4952
	Molar Ratio NH_2Cl/AS	**5-10**	**5; 7.5; 10**		**0.0207*** (0.7863)
Oxidation ClO_2	Reaction time	≥ 12h	15; 19.5; 24 h	2-6	0.2710
	Molar Ratio ClO_2/AS	≥ 2.5	2.5; 6.25; 10		0.5667
Ozonation	pH Value	6.5; 9.5	6.5; 8; 9.5	1-15	0.0577
	Concentration O_3	**1.5 mg·L^{-1}**	**1.5; 2.5; 3.5 mg·L^{-1}**		**0.0071*** (0.9360)

Results – Transformation products

- **High variety in number of TPs for chlorination with NaOCl and ozonation**
- Less NH_2Cl conc was followed with higher number of TPs
- **Higher amounts of TA led to both reduced** (A) and **increased (B) formation** of certain TPs
- **TPs** were identified whose formation was **dependent on both TA and pH** (C)

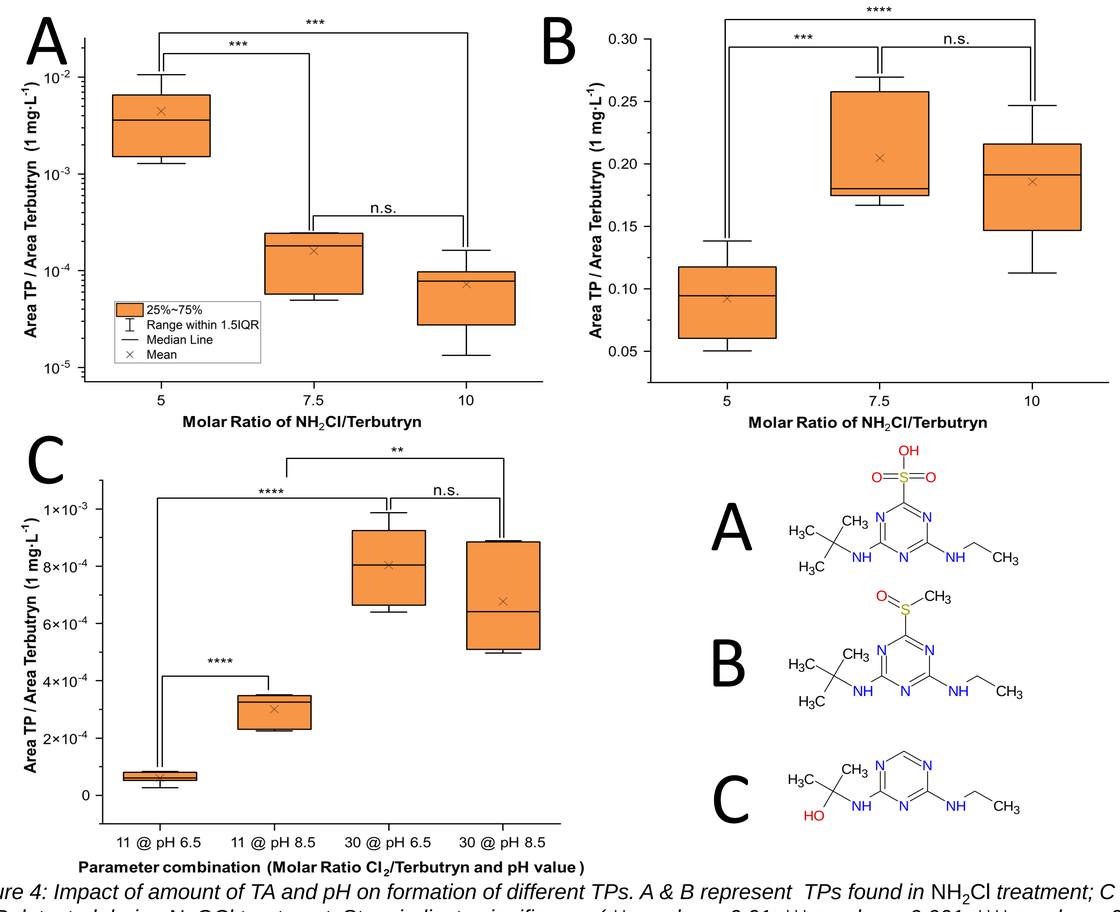


*Figure 4: Impact of amount of TA and pH on formation of different TPs. A & B represent TPs found in NH_2Cl treatment; C shows a TP detected during NaOCl treatment. Stars indicate significance (** p-value < 0.01; *** p-value < 0.001; **** p-value < 0.0001)*

Conclusion

- **pH and amount of TA significantly influenced TP formation**
- Sample volume und reaction time did not have a significant effect
- Large Range in number of TPs for NaOCl and ozone treatment (high real effect size)
- **Ranges for amount of TA given for NaOCl and NH_2Cl by guideline are critical**

References

[1] Sjerps et al. (2019): Occurrence of pesticides in Dutch drinking water sources. *Chemosphere* 235, S. 510–518. DOI: 10.1016/j.chemosphere.2019.06.207.
[2] Hensen et al. (2018): Entry of biocides and their transformation products into groundwater via urban stormwater infiltration systems. *Water Research* 144, S. 413–423. DOI: 10.1016/j.watres.2018.07.046.
[3] Brix et al. (2009): Identification of disinfection by-products of selected triazines in drinking water by LC-Q-ToF-MS/MS and evaluation of their toxicity. *Journal of Mass Spectrometry* 44 (3), S. 330–337. DOI: 10.1002/jms.1509
[4] European Food Safety Authority (2023): Guidance document on the impact of water treatment processes on residues of active substances or their metabolites in water abstracted for the production of drinking water, 28.08.2023.
[5] Carabias-Martínez et al. (2003): Evolution over time of the agricultural pollution of waters in an area of Salamanca and Zamora (Spain). In: *Water Research* 37 (4), S. 928–938. DOI: 10.1016/S0043-1354(02)00366-4.

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