2nd AOP PhD SUMMER SCHOOL

EFFECT OF AOPS ON THE TOXICITY OF EMERGING CONTAMINANTS AND THEIR DEGRADATION PRODUCTS

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WHY DO WE NEED ADVANCED TREATMENT TECHNOLOGIES

- Conventional treatment plants are generally not designed for the removal of «problematic pollutants».
- Ground-and surface waters serve as raw water resources for drinking water supply and have to be treated properly.
- Advanced water treatment technologies are used for the efficient removal of these «problematic pollutants» in water treatment facilities.
- Advanced treatment processes including membrane filtration, activated carbon adsorption, ozonation and AOPs are applied to achieve the ever stricter becoming regulative requirements.

INTEGRATION OF CONVENTIONAL TREATMENT TECHNOLOGIES WITH AOPS

- Conventional physical, chemical and biological treatment methods are economically/technically more attractive/feasible and hence cannot be fully replaced by advanced methods including AOPs.
- In water treatment, not the total oxidation (mineralization), but the removal of the «problematic pollutant» and toxicity reduction are mainly targeted.
- AOPs can be coupled with conventional wastewater treatment processes and operations to remove the «problematic pollutants», improve the overall treatment efficiency and satisfy the legislative demands.

APPLICATIONS OF AOPs

- During treatment applications, AOPs usually form more polar, hydrophilic, low-molecular-weight degradation products and hence reduce the toxicity and/or improve biodegradability of the treated effluent
- Application of AOPs may reduce the estrogenic/mutagenic effects of the problematic pollutants
- However, their application also carries the risk to produce more toxic, less bioamenable, more estrogenic or mutagenic products
- **It is important to follow-up performancde parameters with bioassays to safeguard AOP applications**

EMERGING CONTAMINANTS OF CONCERN

- **Priority Substances**: Pollutants exhibiting a significant risk to the aquatic ecosystem at low concentrations; **«micropollutants»**
- **Emerging Contaminants** that are not included in the Priority Substances List: Some **Pharmaceuticals and Personal Care Products (PPCPs)**, X-ray contrast chemicals, some additives/stabilizers (parabens),etc.
- **Endocrine Disrupting Compounds (EDCs)** such as estradiol, estrone, alkyl phenols, phythalates, bisphenol A are listed and categorized
- Recently, the inlucison of some emerging contaminants including 17α-ethinylestradiol (EE2), dicloflenac and carbamazepine, has been recommended by the EU

NATURE AND TOXICITY OF ADVANCED OXIDATION PRODUCTS

- Example: Ozonation/enhanced ozonation products are typically aldehydes (formaldehyde, glyoxal, acetaldehyde), carboxylic acids (acetic, formic, succinic, phythalic), ketones and brominated organic compounds
- More complex, early-stage degradation (dimerization, hydroxylation, etc.) products with unknown toxicological properties are also expected
- Their identification can sometimes be difficult (advanced instrumental methods and techniques are required)
- **Hence, biodegradability, toxicity, genotoxicity and estrogenic activitiy are important follow-up parameters for AOPs (to validate their ecotoxicological safety)**

TREATMENT OF MICROPOLLUTANTS WITH AOPS: DETOXIFICATION OR TOXICATION?

- Assessment of degradation products and their toxicity has demonstrated that oxidation products can in some cases be more inhibitory, estrogenic, toxic, and/or mutagenic than the original target target contaminant (pollutatant).
- **For example, ozonation of the widely used fungicide tolylfluanide resulted in its conversion into the carcinogen N-nitrosodimethylamine**
- **Biodegradability, toxicity and estrogenic activitiy are important follow-up parameters for AOPs**

BIOASSAYS

- The development of economic and sensitive bioassays is important for cost-effective environmental monitoring and feasibility evaluation of AOPs
- Bioassays are important tools to safeguard the applicability of AOPs
- **A cost-benefit analysis should be accompanied with toxicological studies on ecologically relevant organisms**

BIOASSAYS

- Traditional bioasssays are time-consuming and require specialized facilities to host a large number of organisms under specific environmental conditions
- High costs, huge sample volumes and long feeding/testing periods make the bioassays unfeasible
- When using **toxicity test kits**, the sample volume, amount of employed chemicals, testing time and hence the overall costs of bioassays are significantly reduced
- The development of more cost-effective, sensitive and reliable bioassays with increased biological and ecological relevance is important

BIOASSAYS

Bioassays should preferrably be...

- Inexpensive
- Biologically and ecologically relevant
- Sensitive
- Simple (user-friendly)
- Allow high sample throughput (the use of microplates and low-volume samples)
- Used for both toxicity screening and monitoring

«POPULAR» TEST ORGANISMS

- Photobacteria (*Vibrio fischeri* bioluminescence inhibition test)-are extremely sensitive but have a lack of ecological relevance compared to other toxicity tests
- *Daphnia magna* (freshwater crustacean, water flea)
- *Phaeodactylum tricornutum* (marine diatoms)
- *Pseudokirchneriella subcapitata* (freshwater microalgae)
- *Scenedesmus subspicatus (*freshwater green algae)
- *Lemna minor* (duckweed)
- Rotifiers, fish and mussels

When assessing impacts on freshwater and marine environments, the use of higher test organisms is also recommended.....

TOXICITY TEST PROTOCOLS

- ***Vibrio fischeri*** are by far the most popular, widely used test organisms
- Provided in test kits
- A simple test completed in a short period of time (5-15-30 min)
- The procedure is supported by the ISO 11348 Standard; increasing its reliability
- Extrapolation of toxicity results to higher organisms is frequently questioned
- High sensitivity does not allow to work at higher concentrations of the tested chemicals
- The use of lab cultures provides less sensitive but more realistic response in toxicity results

BIOASSAYS

- In-vitro bioassays cover different modes of toxic action including mutagenicity, teratogenicity, immunotoxicity, estrogenicity and neurotoxicity (acetylcholine esterase activity) in concentrated effluent samples
- They are not designed to replace chronic in-vivo bioassays of the entire effluent samples
- In-vivo bioassays are more realistic, comprehensive and integrative tools for toxicity assessment

SOME IMPORTANT BIOASSAYS

- Fish Early Life Stage Toxicity Test (**FELST**)
- In-Vivo Vitellogenin (**VTG**) Detection in Fish
- Enzyme Linked Immunosorbent Assay (**ELISA**)
- In-Vitro Yeast Estrogen Screen (**YES**) Assay
- The Ability To Disrupt Gap Junctional Intercellular Communication (**GJIC**) - Indicator for Tumor Promoting Properties
- Salmonella / E-coli Mutagenicity Test (**Ames Mutation Test**)
- Genotoxicity with the Umu Chromotest (**UmuC**)

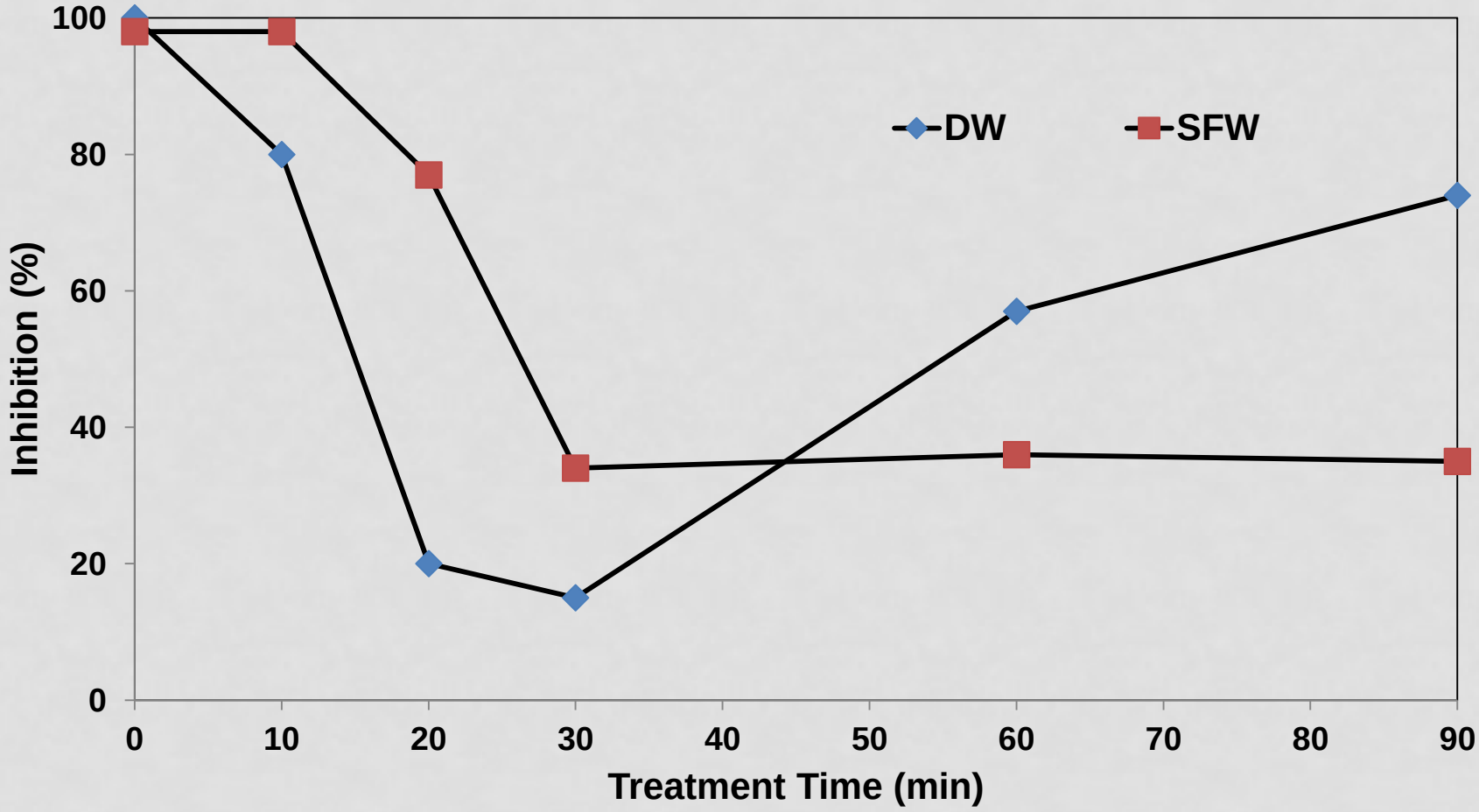
FACTORS AFFECTING TOXICITY RESULTS DURING APPLICATION OF AOPs

- Single and combined effects of micropollutants
- Type of test (acute, sub-chronic, etc.)
- Concentration of the model pollutant
- Water/effluent characteristics (its chemical composition, type of pretreatment applied prior to AOPs)
- **Sensitivity of the test organism to the micropollutant and its degradation products**

CASE STUDIES: H_2O_2/UV-C TREATMENT OF 2,4-DCP IN DISTILLED WATER (DW) AND SYNHTETIC FRESH WATER (SFW)

- 20 mg/L 2,4-DCP (120 μM); pH7.0; 2.5 mM H_2O_2
- Results (DW):
  - Complete 2,4-DCP removal in 10 min
  - 90% DOC removal in 35-40 min
- Results (SFW):
  - Complete 2,4-DCP removal in 20 min
  - 70% DOC removal in 45-50 min
  - 90% DOC removal in 60-70 min

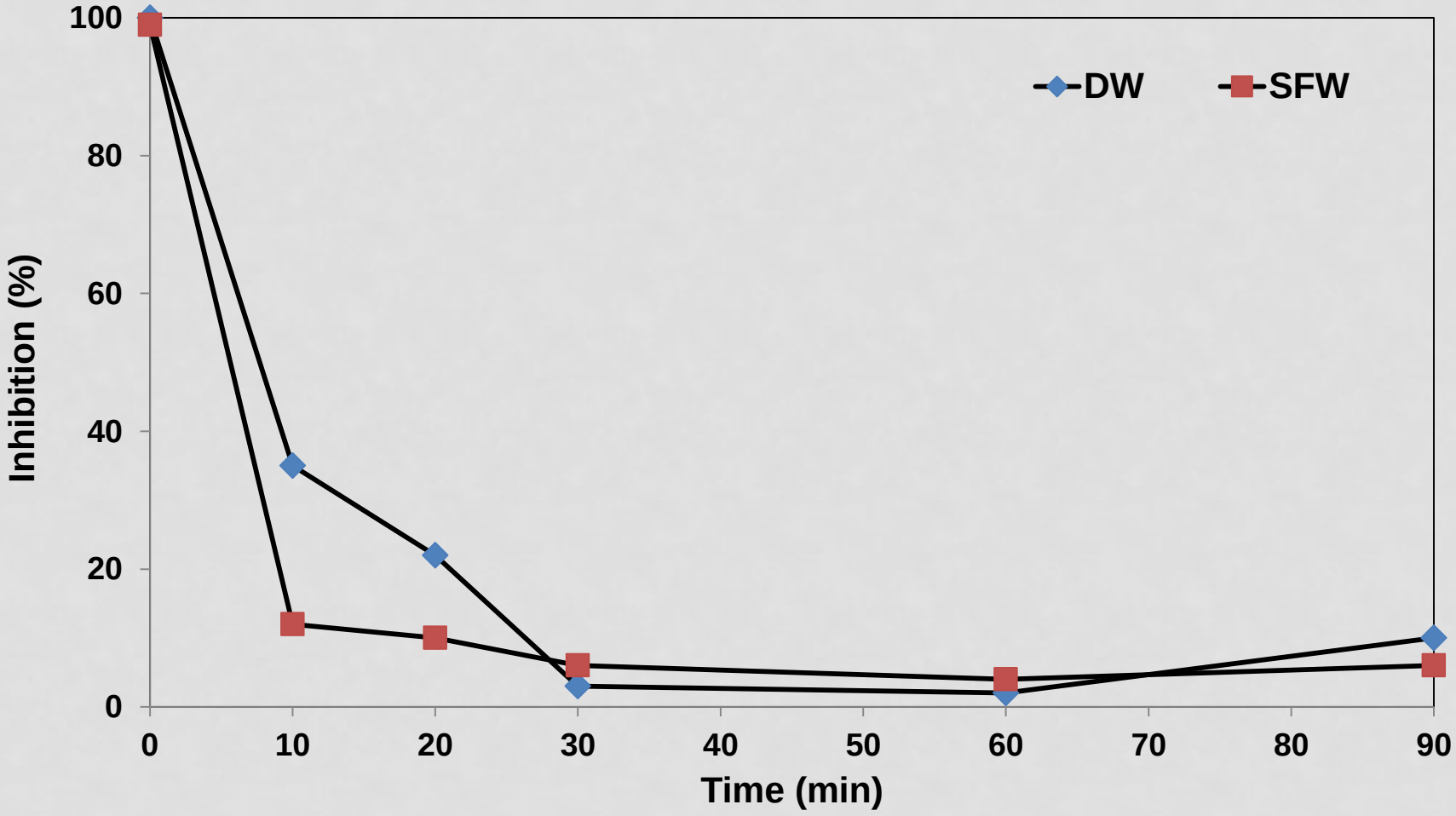
H_2O_2/UV-C TREATMENT OF 2,4-DCP IN DW AND SFW



CASE STUDIES: PHOTO-FENTON TREATMENT OF 2,4-DCP IN DW AND SFW

- 20 mg/L 2,4-DCP (120 μM); pH3.0; 2.0 mM H_2O_2; 0.1 mM Fe(II)
- Results (DW):
  - Complete 2,4-DCP removal in 5 min
  - 90% DOC removal in 20-25 min (stops)
- Results (SFW):
  - Complete 2,4-DCP removal in 10-15 min
  - 80% DOC removal in 30-35 min (stops)

PHOTO-FENTON TREATMENT OF 2,4-DCP IN DW AND SFW



TRANSFORMATION PRODUCTS (2,4-DCP)

- Degradation products were chlorinated and non-chlorinated carboxylic acids as well as formaldehyde
- **Common degradation products of H_2O_2/UV-C and Photo-Fenton treatment**;
  - Hydroquinone, chlorohydroquinone, dichlorohydroquinone, chlorobenzendiol, dichlororesorcinol
- **Possible causes of the higher toxicity for H_2O_2/UV-C oxidation of 2,4-DCP removal could be degradation products which were not observed during Photo-Fenton treatment;**
  - Chloromethanediol, chlorocyclohexenedione, chloromaleic acid, dichloromonohydroxy benzoquinone, 2,4-dichlorohexanedioic acid

TRANSFORMATION PRODUCTS (2,4-DCP)

- **H_2O_2/UV-C and Photo-Fenton** treatment of 2,4-DCP was accompanied with the formation of chlorinated and hydroxylated (dechlorination) aromatic intermediates;
  - 3,5-dichloro-2-hydroxybenzaldehyde, 4-CP, chlorohydroquinone, phenol, 2,5-dichlorohydroquinone (**common products**)
  - Acetic acid (**Photo-Fenton**) and formic acid (**common product**) were identified during 2,4-DCP treatment.

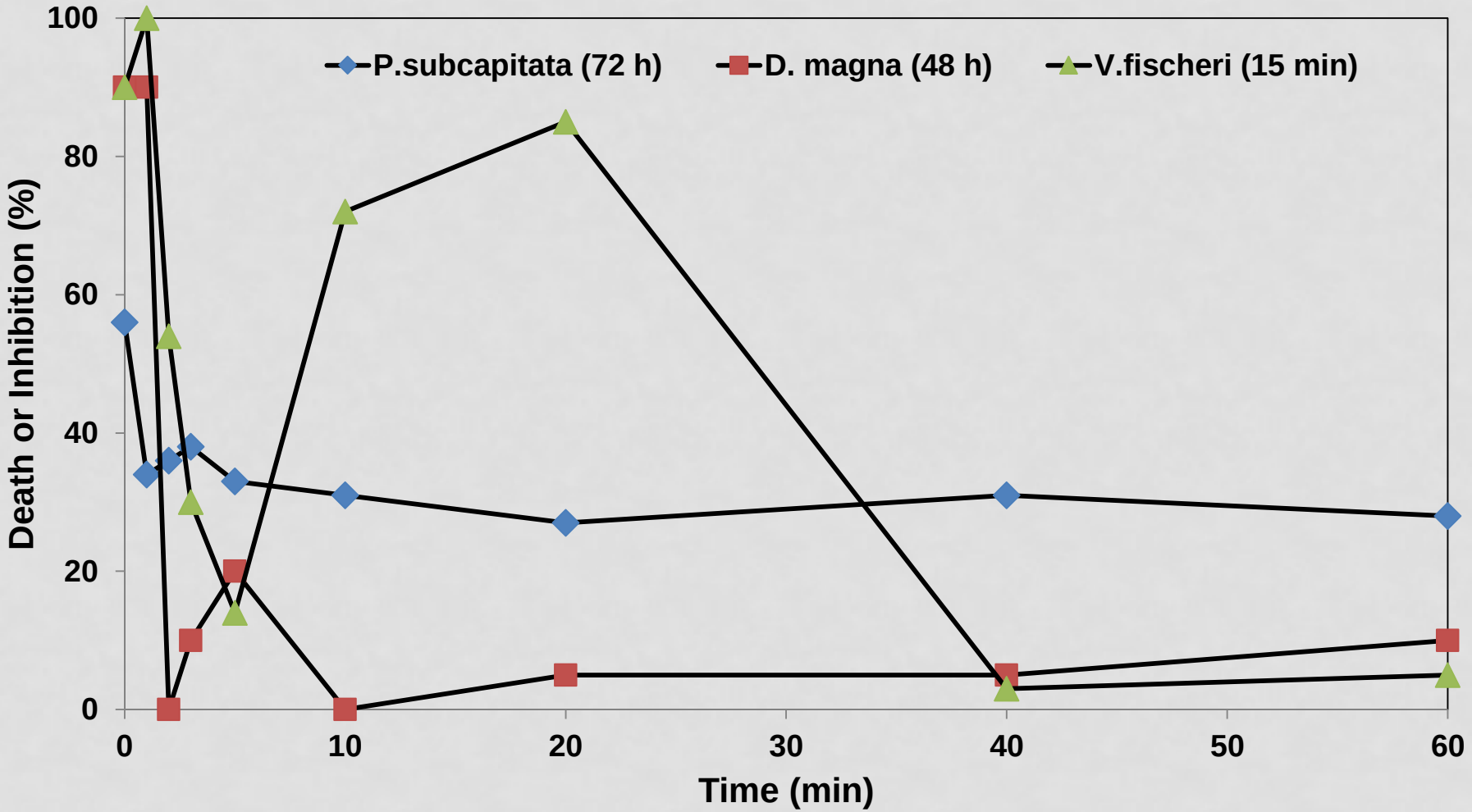
TRANSFORMATION PRODUCTS (2,4-DCP)

- Products of **H_2O_2/UV-C and Photo-Fenton** treatment of 2,4-DCP;
  - Hydroquinone and formic acid were found to be the common oxidation products of **H_2O_2/UV-C and Photo-Fenton** procsesses.
  - Their formation and subsequent abatement was appreciably faster during **Photo-Fenton** treatment.

CASE STUDIES: H_2O_2/UV-C TREATMENT OF BPA IN DW

- 20 mg/L BPA (88 μM); pH7.0; 2.5 mM H_2O_2
- **Results (DW):**
  - Complete BPA removal in 5-10 min
  - 90% DOC removal in 40-50 min

H_2O_2/UV-C TREATMENT OF BPA IN DW



TRANSFORMATION PRODUCTS (BPA)

- Acetic, succinic and fumaric acids were identified for H_2O_2/UV-C treatment of BPA.
- Oxalic acid was not identified during H_2O_2/UV-C treatment of BPA.

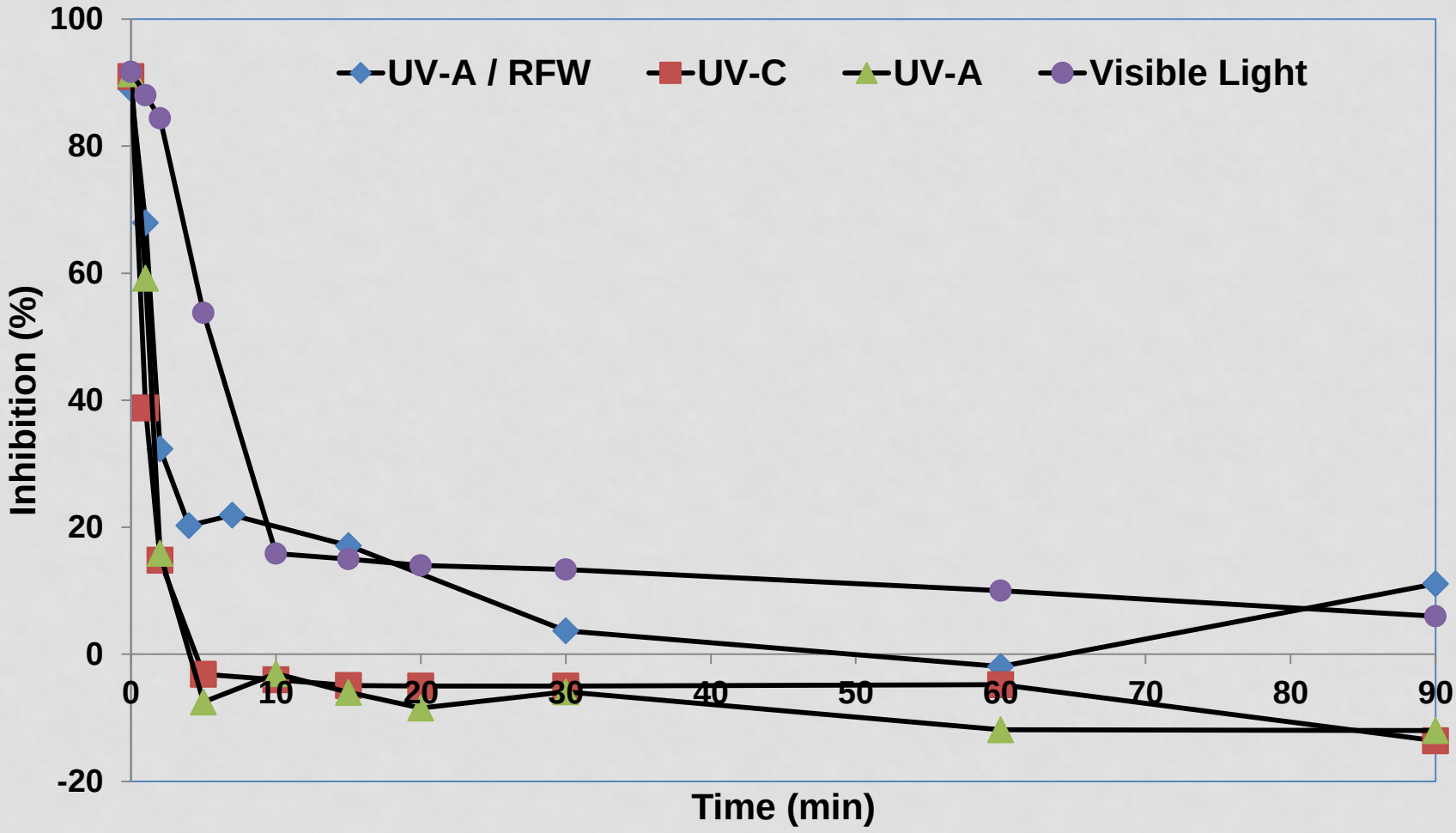
TRANSFORMATION PRODUCTS (BPA)

- Phenol, hydroquinone, benzaldehyde, isopropenyl phenol and 4,4,'-hydroxy benzophenone were common transformation products for the studied AOPs
- 4-(1-hydroxy-1- methyl ethyl)phenol, 2- hydroxy -1-(4- hydroxy phenyl)ethanone, glutaric acid and 1-(4 cyclohexyl phenyl)ethanone **were only identified for H_2O_2/UV-C treatment**

CASE STUDIES: PHOTO-FENTON TREATMENT OF BPA IN PURE WATER (DW) AND REAL FRESHWATER (RFW)

- 20 mg/L BPA (88 μM); pH5.0; 2.0 mM H_2O_2; 0.1 mM Fe(II)
- DOC of the RFW sample: 6.9 mg/L
- **Results (DW):**
  - Complete BPA removal in < 2 min
  - Complete DOC removal in 35-40 min
- **Results (RFW):**
  - Complete BPA removal in 5 min
  - 50% DOC removal in 90 min

PHOTO-FENTON-LIKE TREATMENT OF BPA IN DW AND RFW



TRANSFORMATION PRODUCTS (BPA)

- Ring opening products including hexanoic, fumaric, succinic and oxalic acids
- Hydroxylated phenolic compounds;
  - hydroquinone
  - 4-isopropenylphenol
  - 4-4'-dihydroxy-acetophenone
  - 4-isopropylenecatechol
  - 4-4'-dihydroxybenzophenone
  - 4-ethyl,1,3-benzenediol

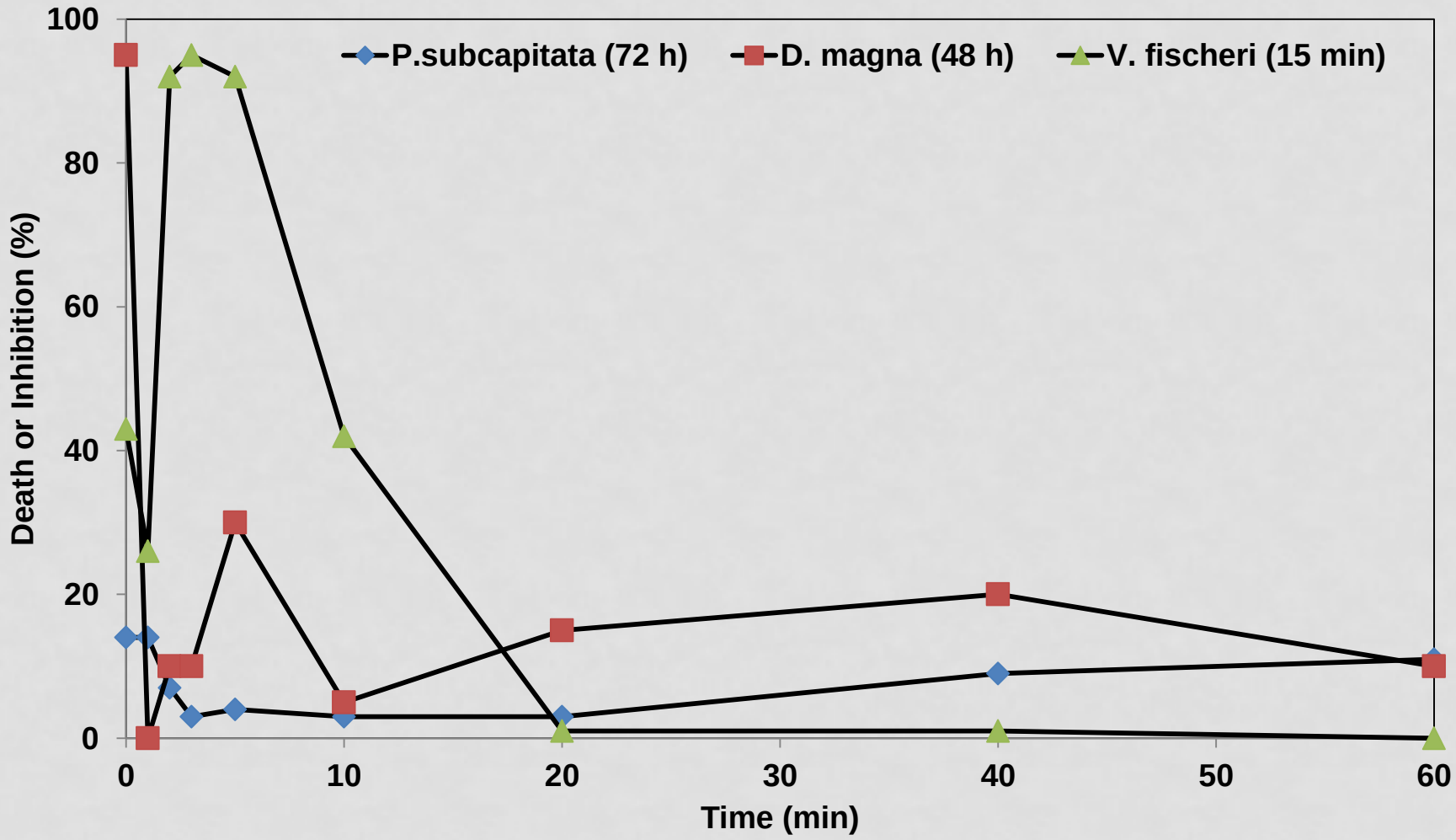
CASE STUDIES: H_2O_2/UV-C TREATMENT OF AN OCTYLPHENOL POLYETHOXYLATE (TX-45) IN DW

- 20 mg/L TX-45 (97 μM); pH7.0; 2.5 mM H_2O_2

Results:

- Complete TX-45 removal in 4-5 min
- 90% DOC removal in 40-50 min

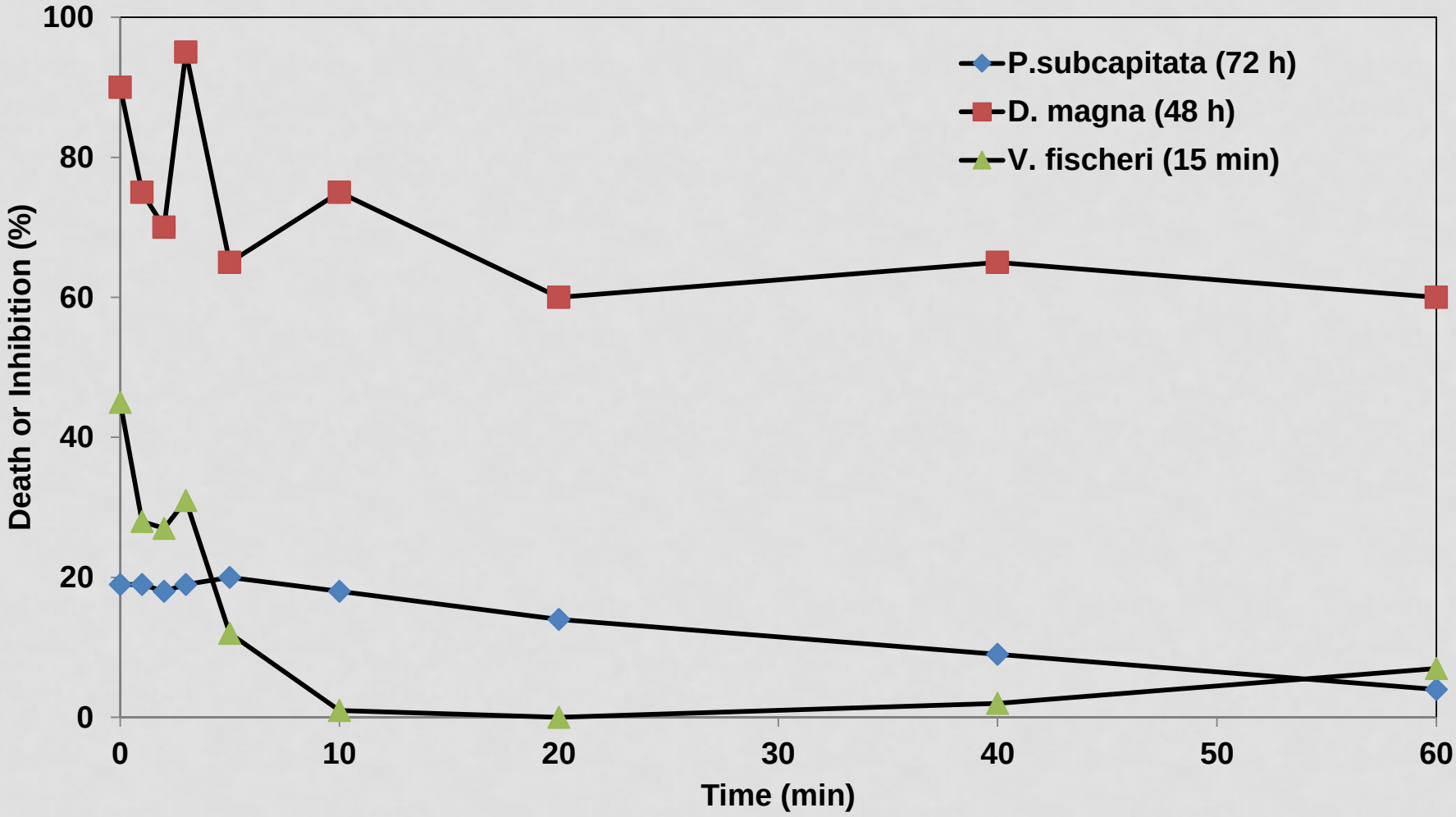
H_2O_2/UV-C TREATMENT OF TX-45 IN DW



CASE STUDIES: PS/UV-C TREATMENT OF TX-45 IN DW

- 20 mg/L TX-45 (97 μM); pH7.0; 2.5 mM PS
- **Results:**
  - Complete TX-45 removal in 2-3 min
  - 90% DOC removal in 30-40 min

PS/UV-C TREATMENT OF TX-45 IN DW



TRANSFORMATION PRODUCTS (TX-45)

- Acetic and succinic acids were identified for **both H_2O_2/UV-C and PS/UV-C proceses**
- Oxalic and fumaric acids were additionally identified during **H_2O_2/UV-C** treatment

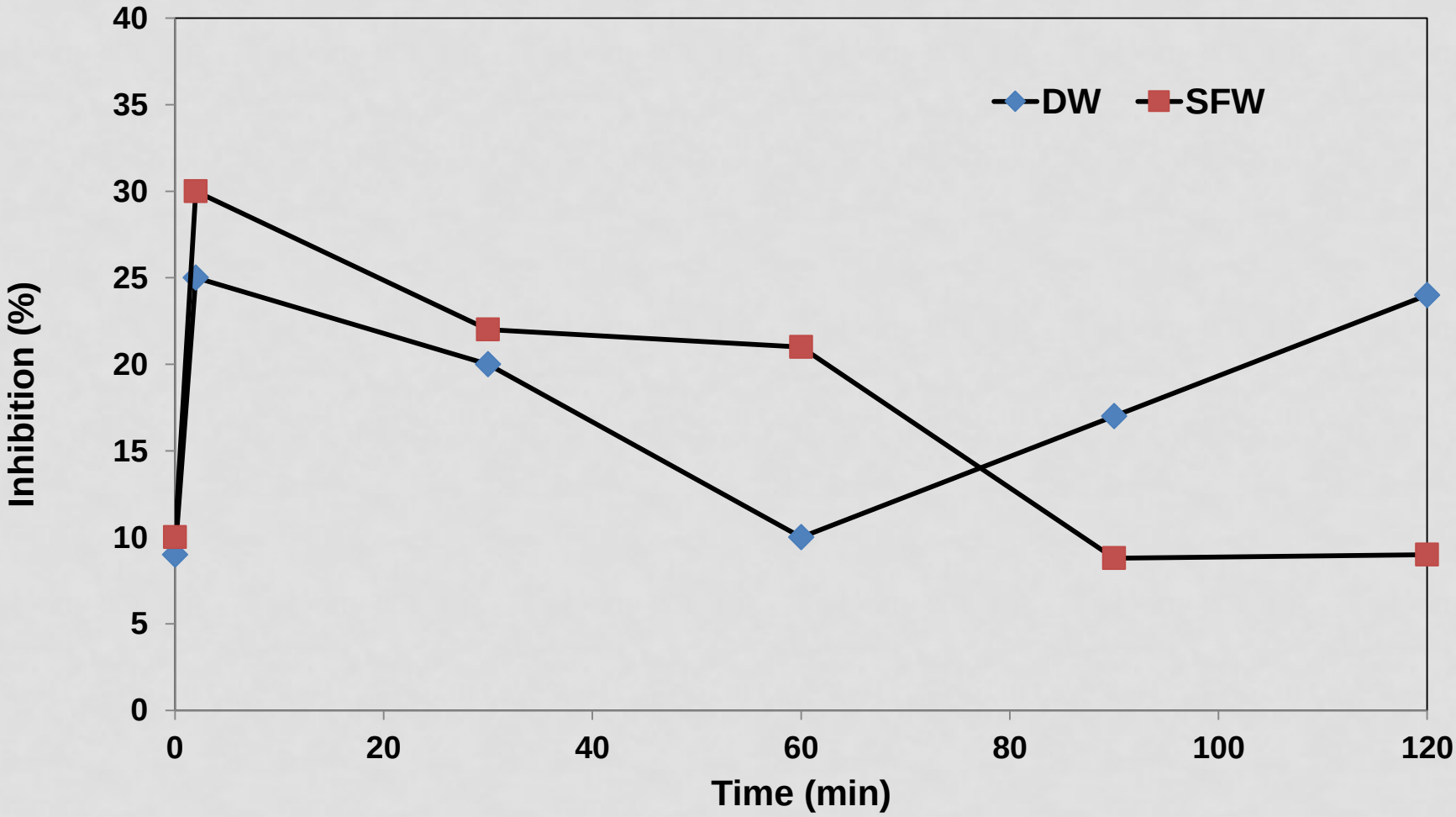
TRANSFORMATION PRODUCTS (TX-45)

- 1-6 ethoxylated PEG; 1-4 ethoxylated PEG mono carboxylic acid; 1-3 ethoxylated PEG dicarboxylic acid, 1-2 ethoxylated octyl phenol and 4-tert- octyl phenol formation was evidenced **during both H_2O_2/UV-C and PS/UV-C treatments.**
- In addition to the above products, 7-8 ethoxylated PEG, PEG monocarboxylic acid, 5 ethoxylated PEG monocarboxylic acid, 4-5 ethoxylated PEG monocarboxylic acid and 1-3 ethoxylated octyl phenol monocarboxylic acid, octyl phenol 3 ethoxylate and octyl phenol 4 ethoxylate **were identified during PS/UV-C treatment.**

CASE STUDIES: H_2O_2/UV-C TREATMENT OF A NONYL PHENOL POLYEHTOXYLATE (NP-10) IN DW AND SFW

- 20 mg/L NP-10 (30 μM); pH7.0; 2.5 mM H_2O_2
- **Results (DW):**
  - Complete NP-10 removal in 4-5 min
  - 80% DOC removal in 80 min
- **Results (SFW):**
  - Complete 2,4 NP-10 removal in 7-8 min
  - 70% DOC removal in 90 min

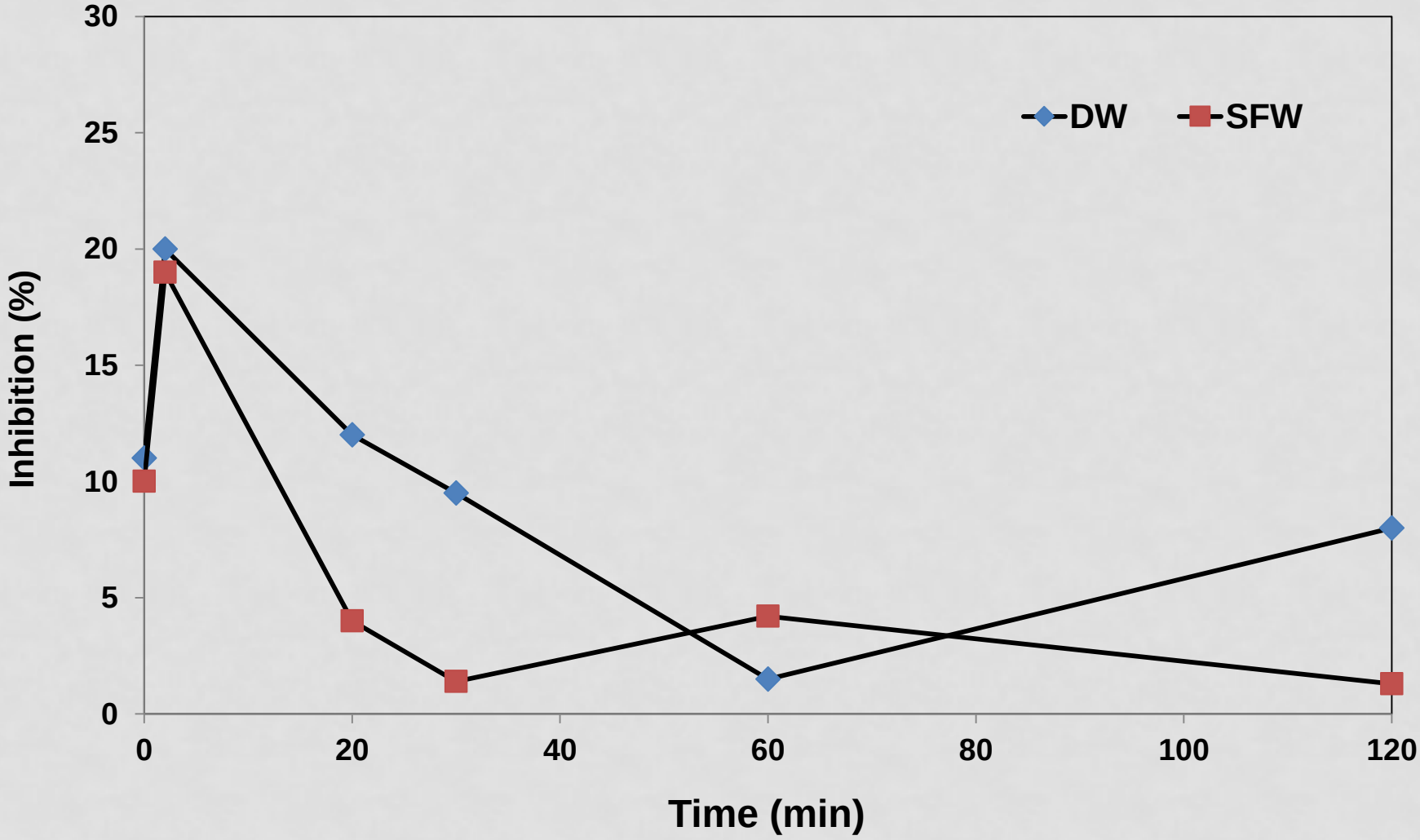
H_2O_2/UV-C TREATMENT OF NP-10 IN DW AND SFW



CASE STUDIES: PHOTO-FENTON TREATMENT OF NP-10 IN DW AND SFW

- 20 mg/L NP-10 (30 μM); pH3.0; 2.0 mM H_2O_2; 0.1 mM Fe(II)
- **Results (DW):**
  - Complete NP-10 removal in 2-3 min
  - 70% DOC removal in 25-30 min
- **Results (SFW):**
  - Complete 2,4 NP-10 removal in 5-10 min
  - 70% DOC removal in 40 min

PHOTO-FENTON TREATMENT OF NP-10 IN DW AND SFW



TRANSFORMATION PRODUCTS (NP-10)

- Short polyethoxy-chain nonyl phenol polyethoxylates, PEG (**H_2O_2/UV-C and Photo-Fenton Treatment**)
- Monocarboxylated PEGs (**H_2O_2/UV-C treatment**)
- Formic and acetic acid, formaldehyde (**H_2O_2/UV-C and Photo-Fenton Treatment**)
- Oxalic and acetic acid as well as aldehyde formation was more pronounced **during H_2O_2/UV-C** treatment
- **Acetic acid** was identified as the most resistant oxidation end product and accumulated in the SFW.

TRANSFORMATION PRODUCTS (NP-10)

- A degradation product resulting from the hydroxyl radical attack of the tertiary alkyl chain and the aromatic ring was detected during **Photo-Fenton treatment**.
- Higher toxicity was attributable to the higher concentration and number of degradation products observed **during H_2O_2/UV-C** treatment of NP-10
  - PEG and NP formation speaks for de-ethoxylatio which could be the main **reason of the acute toxicity increase during treatment**

CONCLUSIONS AND RECOMMENDATIONS

- AOPs are not always toxicologically safe.....
- According to the acute toxicity test results, some degradation products of AOPs can be more toxic / inhibitory than the original (parent) pollutant
- In parallel to the complete and rapid degradation of the originally toxic micropollutant (emerging contaminant), a reduction in its toxic response can be observed
- A re-increase in toxicity parallel to the formation of more inhibitory degradation products has also been evidenced
- This profile is usually followed by a decrease in toxicty at the later/final stages of oxidation corresponding to complete/increased oxidation/mineralization rates

CONCLUSIONS AND RECOMMENDATIONS

- When assessing the toxicity of pollutants, the water/wastewater matrix should be considered
- The synergistic/antagonistic effects of oxidation products in a complex mixture should be considered
- Some chemicals that are used to stop the oxidation process or remove the oxidizing agent may also contribute to the toxicity

CONCLUSIONS AND RECOMMENDATIONS

- **A single bioassay does not always reflect the actual ecotoxicological profile of a micropollutant and should be supported by a battery test for comparative purposes**

- **In bioassays, all major trophic levels should be represented, if possible**
- **Toxicity (acute, chronic, sub-chronic, etc.) should be evaluated separately from biodegradability (BOD_5, Zahn Wellens test, OUR measurements, etc.)**
- **Cytotoxicity, immunotoxicity, genotoxicity and estrogenicity should also be considered during cost-benefit analysis assessment of AOPs**

THANK YOU….
QUESTIONS?