Photochemical degradation of bisphenols in aqueous solution: Degradation kinetics and identification of transformation products

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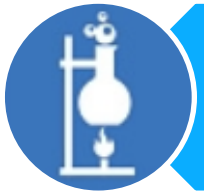
Introduction

Setup of the experiment

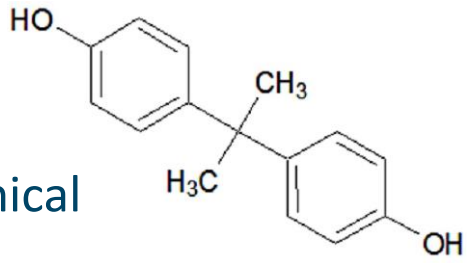


Kinetics of degradation

Identification of transformation products

Conclusions

Introduction



Bisphenol A (BPA) = high production volume industrial chemical

- In production of polycarbonate, epoxy resins

- As developer in thermal paper

- Endocrine disruptive compound

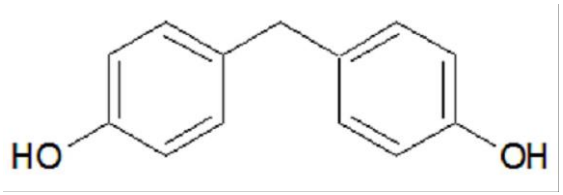
Introduction

BPA analogues – **bisphenols** (BPs):

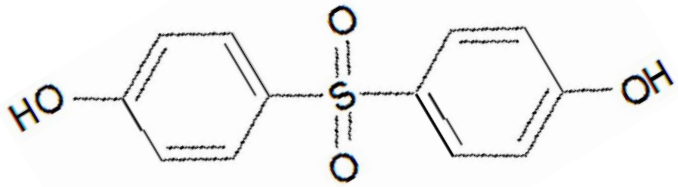
- Structural similarity
- Detected in humans and environment
- Potentially similar toxic effects

Study occurrence and fate of BPs in the environment

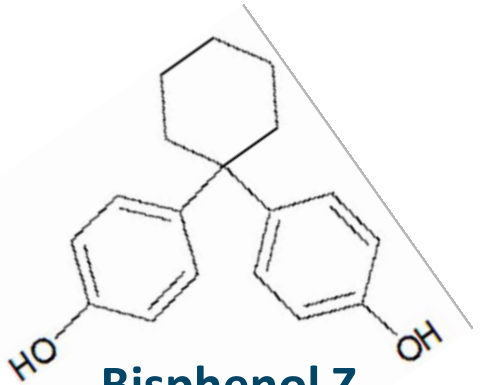
Removal through photochemical methods



Bisphenol F
BPF



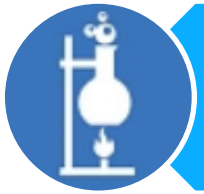
Bisphenol S
BPS



Bisphenol Z
BPZ

Introduction

Setup of the experiment



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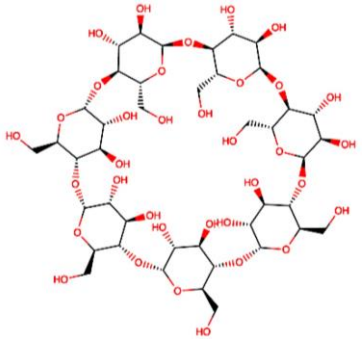
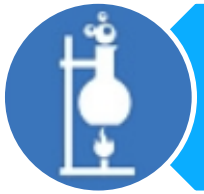
Photochemical degradation

- **BPF/BPS/BPZ in aqueous solution**
  MilliQ water
- **Monochromatic UV light λ_{max} = 254 nm**
  by 6 watt low pressure Hg lamp
- **Three treatments:**
  1. **UV**
     UV light only
  2. **Cyclodextrin**
     UV with added ß-cyclodextrin (ß-CD)
  3. **Photo-Fenton**
     UV with added Fenton's reagent
     $H_2O_2 + FeSO_4 + H_2SO_4$



Introduction

Setup of the experiment



Kinetics of degradation

Identification of transformation products

Conclusions

Kinetics of degradation

Experiment

- **Initial concentration = 200 ng/L**
- 350 mL sample in duplicate
  at t = 0 min → 2 h
- Labeled internal standards added
  $^{13}C_{12}$-BPF, $^{13}C_{12}$-BPS and $^{13}C_{12}$-BPB

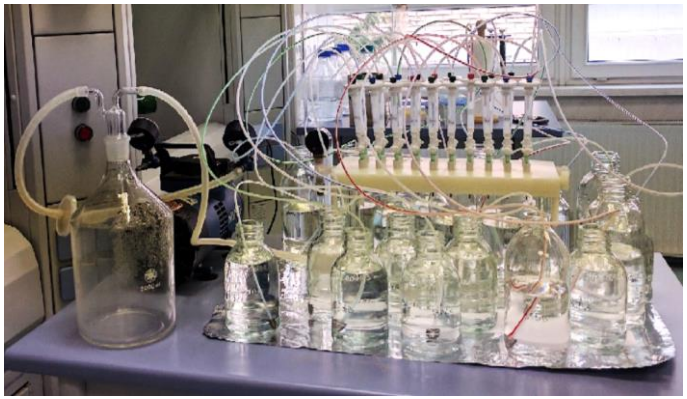
Objectives

- What is the kinetic profile of the degradation of the BPs?
- What is the degradation efficiency of the three treatments?

Kinetics of degradation

Sample preparation

- SPE with Oasis HLB cartridges
- Derivatisation with BSTFA



Analysis

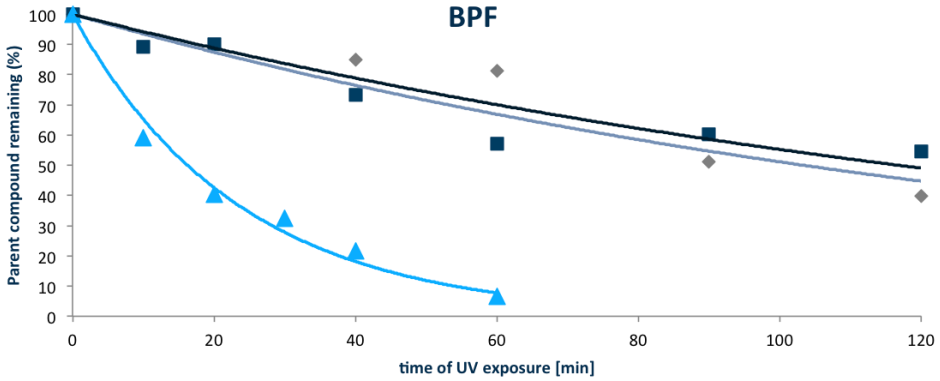
- GC-EI-MS
- Column: Agilent DB 5-MS
  30 m x 0.25 mm x 0.25 µm
- SIM method

Compound	*m/z*	RT (min)
BPF-TMS	344	8.61
	329	
$^{13}C_{12}$-BPF-TMS	356	8.61
	341	
BPS-TMS	394	13.20
	379	
$^{13}C_{12}$-BPS-TMS	406	13.20
	391	
BPZ-TMS	412	12.49
	397	
$^{13}C_{12}$-BPB-TMS	383	9.83
	398	

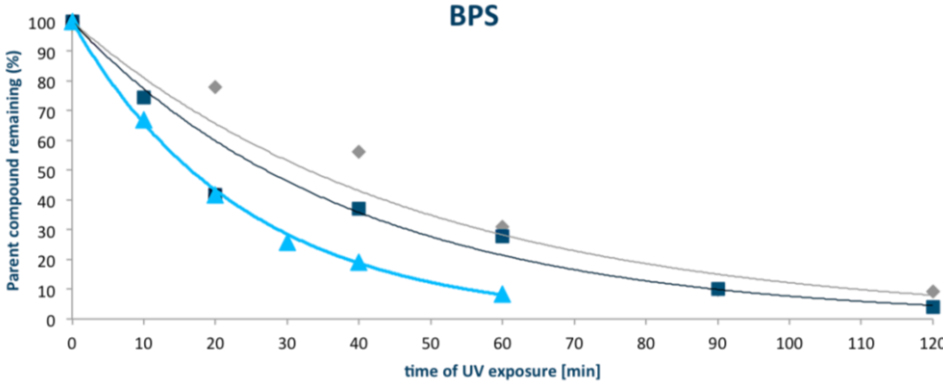
Kinetics of degradation

Results

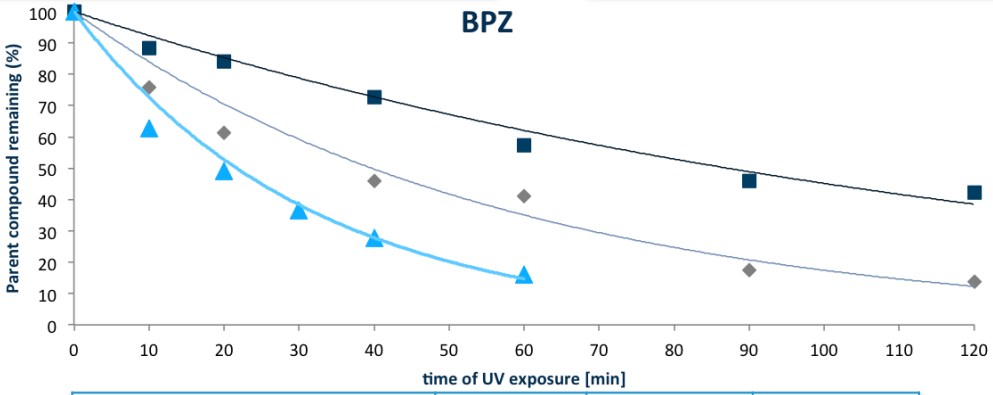
➢ **What is the kinetic profile of the degradation of the BPs?** → **Pseudo first-order**



treatment	UV	ß-CD	PF
rate constant k (min^{-1})	0.005	0.006	0.043



treatment	UV	ß-CD	PF
rate constant k (min^{-1})	0.021	0.026	0.042



treatment	UV	ß-CD	PF
rate constant k (min^{-1})	0.017	0.008	0.052

Kinetics of degradation

Results

➢ **What is the degradation efficiency of the three treatments?**

- Shortest half-lives for all three BPs with Photo-Fenton reaction
  → enhanced degradation due to generation of reactive OH•

- **BPF**

treatment	UV	ß-CD	PF
$t_{1/2}$ (min)	139	116	16

- **BPS**

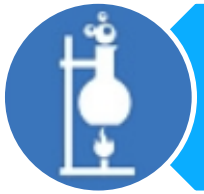
treatment	UV	ß-CD	PF
$t_{1/2}$ (min)	33	27	17

- **BPZ**

treatment	UV	ß-CD	PF
$t_{1/2}$ (min)	41	87	22

Introduction

Setup of the experiment



Kinetics of degradation

Identification of transformation products

Conclusions

Identification of transformation products

Experiments

- **Initial concentration = 5 mg/L**
- 1 mL sample in triplicate
  at same time intervals as kinetic experiment
- Labeled internal standards added
  $^{13}C_{12}$-BPF, $^{13}C_{12}$-BPS and $^{13}C_{12}$-BPB

Objective

➢ What are the major transformation products (TPs)?

Identification of transformation products

Analysis

- LC-ESI-QTOFMS
- Column: Agilent Poroshell 120 EC-C18 3.0 x 50mm 2.7µm
- Mobile phase: A = 100 % MilliQ water, B = 100 % methanol
- ESI +/-

Time (min)	% B
0.00	10
1.00	10
5.00	50
10.00	85
11.00	95
15.00	95
15.10	10
20.00	10

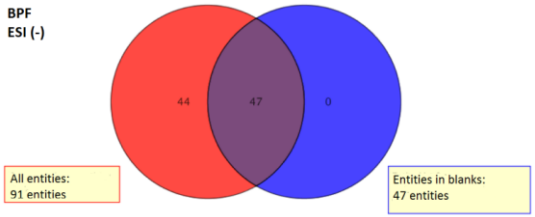
1. **Auto-MS/MS** (data dependent acquisition)
   CE = 10 and 20 V

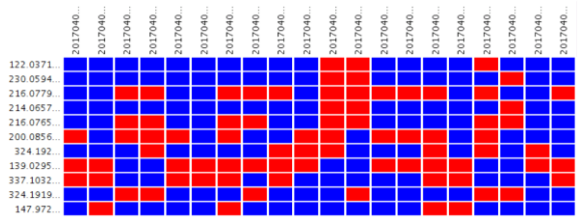
2. **Targeted MS/MS** reinjection
   CE = 10 and 20 V
   Target list *m/z*

Identification of transformation products

Workflow data analysis

1. Auto-MS/MS → Molecular Feature Extraction
2. List of entities → filter out possible false positives





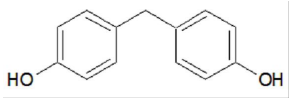
3. Heatmap of molecular masses of possible transformation products
4. Identification
   Comparison with suspect list based on literature
5. Target list *m/z* → reinjection targeted MS/MS

Confidence level of identification
Schymanski E. et al. – Environ. Sci. Technol. 2014, 48 (4): 2097-2098

Identification confidence	*Minimum data requirements*
***Level 1:** **Confirmed** structure* by reference standard	MS, MS^2, RT, Reference Std.
***Level 2:** **Probable** structure* a) by library spectrum match b) by diagnostic evidence	MS, MS^2, Library MS^2 MS, MS^2, Exp. data
Level 3:** **Tentative candidate(s) structure, substituent, class	MS, MS^2, Exp. data
Level 4:** **Unequivocal molecular formula	MS isotope/adduct
Level 5:** **Exact mass of interest	MS

Identification of transformation products

Results



BPF

M = 200.0837 Da

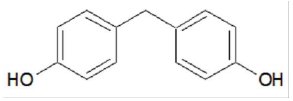
➢ **What are the major transformation products?**

Accurate mass (Da)	*m/z*	RT (min)	Formula	Diff (ppm)	Score	Treatment	Literature	Confidence level
230.0570	229.0497	4.512	$C_{13}H_{10}O_4$	6.50	86.37	PF		L3
216.0794	215.0721	5.266	$C_{13}H_{12}O_3$	7.59	91.93	UV/CD/PF	✔	L3
216.0786	215.0714	6.255	$C_{13}H_{12}O_3$	7.73	89.16	UV/CD/PF	✔	L3
214.0650	213.0535	6.034	$C_{13}H_{10}O_3$	8.09	81.47	PF	✔	L3
139.0295	138.0200	5.147	-	-	-	UV/CD		L5
122.0368	121.0294	4.556	$C_7H_6O_2$	5.33	95.53	PF	✔	L3

- Hydroxylation and cleavage products
- New and previously detected products

Identification of transformation products

Results

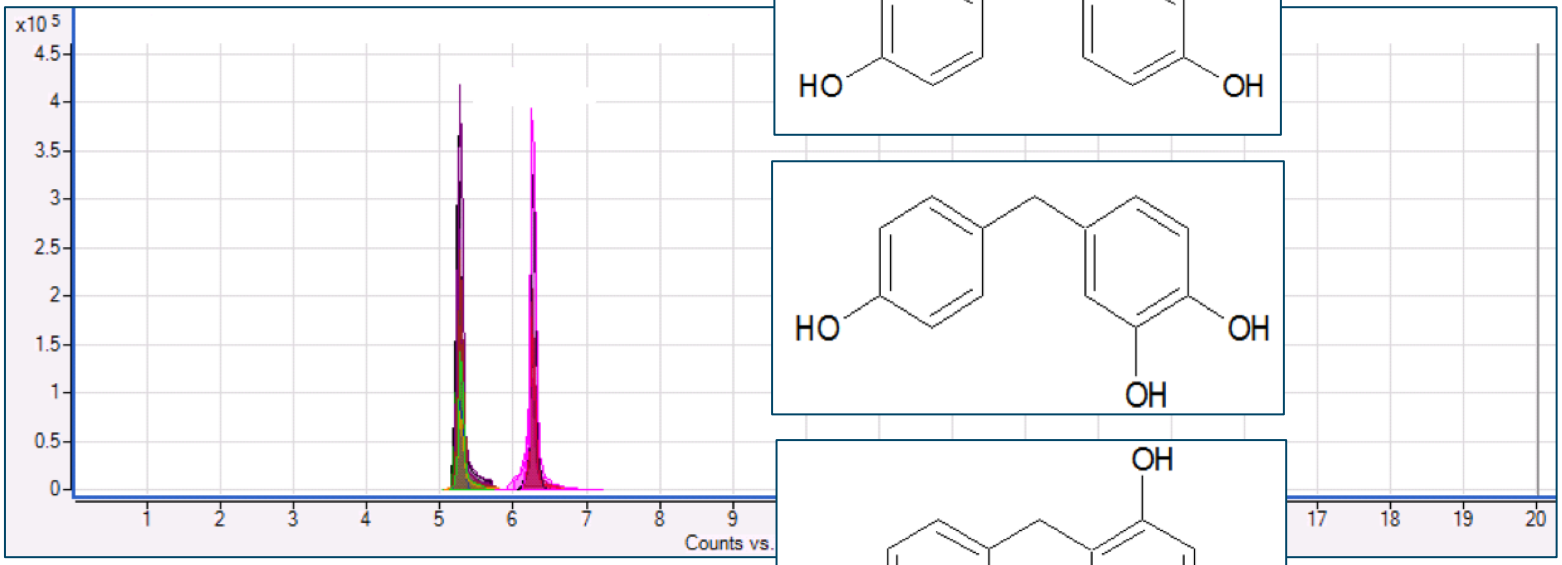


BPF

M = 216.0786 Da

M = 200.0837 Da

➢ **What are the major transformation products?**

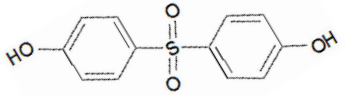


L3

- ESI (-)
- RT ~ 5.2 min and RT ~ 6.2 min
- $C_{13}H_{12}O_3$ → positional isomers

Identification of transformation products

Results



BPS

M = 250.0300 Da

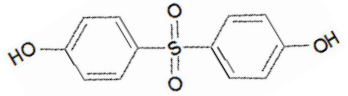
➢ **What are the major transformation products?**

Accurate mass (Da)	*m/z*	RT (min)	Formula	Diff (ppm)	Score	Treatment	Literature	Confidence level
266.0247	265.0176	4.674	$C_{12}H_{10}O_5S$	4.57	88.39	UV/CD/PF		L3
218.0222	217.0147	4.518	-	-	-	CD		L5
173.9973	172.9907	0.647	$C_6H_6O_4S$	4.98	94.56	UV/CD	✔	L2b
124.0142	123.0070	0.763	$C_6H_4O_3$	14.44	81.82	CD		L4

- Hydroxylation and cleavage products
- New and previously detected products

Identification of transformation products

Results

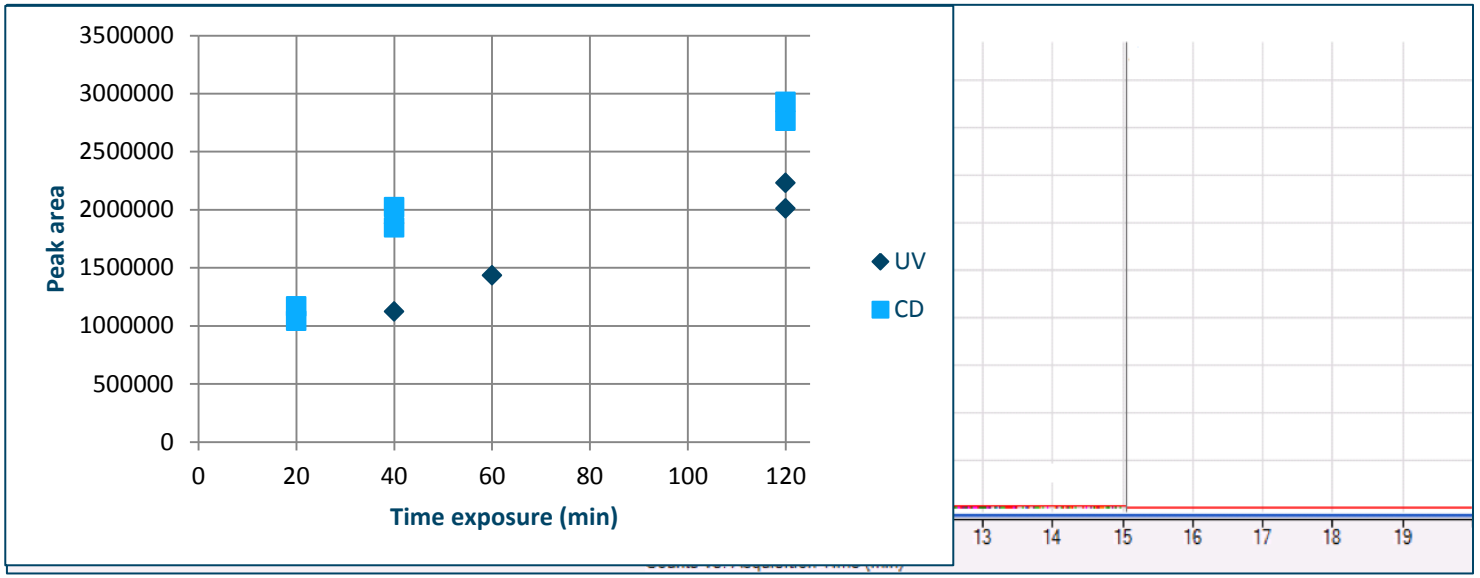


BPS

M = 250.0300 Da

➢ **What are the major transformation products?**

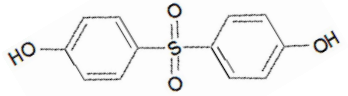
M = 173.9986 Da



- ESI (-)

Identification of transformation products

Results



BPS

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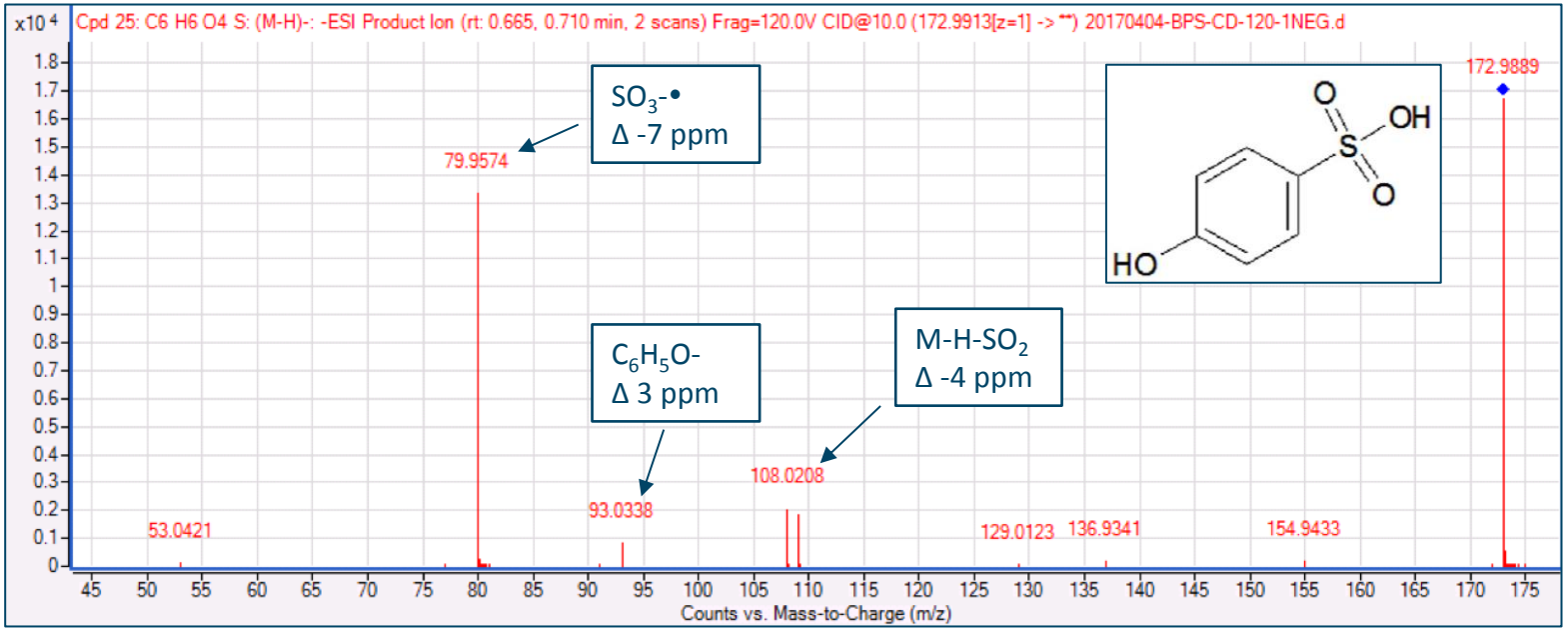


L2b

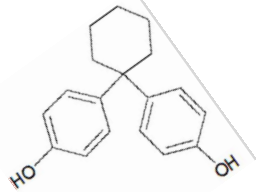
- Same product ions at CE 20 V
- Same fragmentation pattern in other samples
- Also detected by Wang X. et al. – Water Sci. Technol. 2014, 70.3: 540-547

Identification of transformation products

Results

➢ **What are the major transformation products?**

BPZ



M = 268.1463 Da

Accurate mass (Da)	*m/z*	RT (min)	Formula	Diff (ppm)	Score	Treatment	Literature	Confidence level
156.0788	155.0716	3.672	-	-	-	UV/CD		L5
192.0416	191.0344	1.580	$C_{10}H_8O_4$	3.35	97.25	CD		L3
192.0410	191.0337	2.345	$C_{10}H_8O_4$	6.76	95.41	PF		L4
284.1418	283.1351	5.571	$C_{18}H_{20}O_3$	2.25	85.16	PF	✔	L3
284.1421	283.1358	6.511	$C_{18}H_{20}O_3$	3.13	83.88	PF	✔	L3
284.1424	283.1350	8.757	$C_{18}H_{20}O_3$	8.19	79.42	PF	✔	L3
284.1418	283.1341	9.222	$C_{18}H_{20}O_3$	2.01	89.10	PF	✔	L3
304.1703	303.1634	7.577	$C_{18}H_{24}O_4$	3.65	86.54	UV/CD		L4

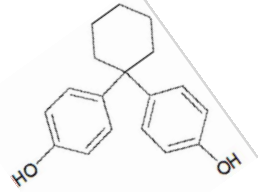
- Hydroxylation and cleavage products
- New and previously detected products

Identification of transformation products

Results

➢ **What are the major transformation products?**

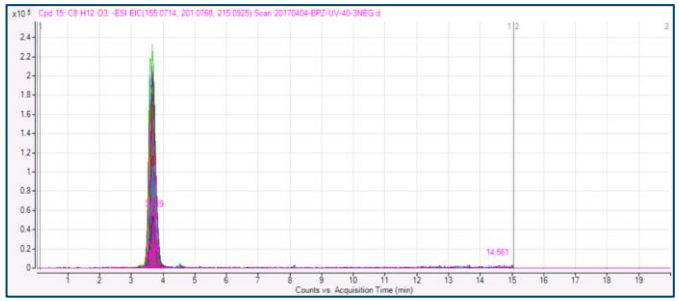
BPZ



M = 268.1463 Da

M = 156.0781 Da

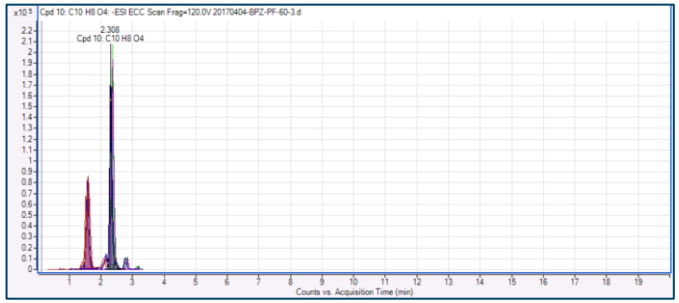
- ESI (-)



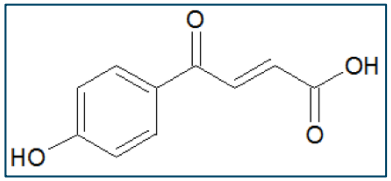
L5

M = 192.0422 Da

- ESI (-)
- $C_{10}H_8O_4$

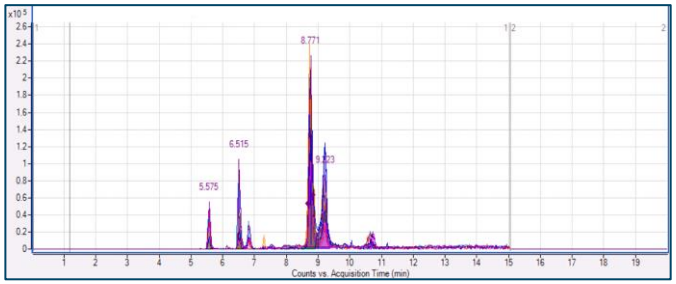


L3



M = 284.14 Da

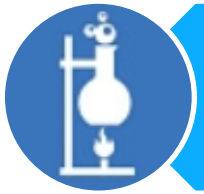
- ESI (-)
- $C_{18}H_{20}O_3$



L3

Introduction

Setup of the experiment



Kinetics of degradation

Identification of transformation products

Conclusions

Conclusions

Degradation kinetics

- **Kinetic profile: pseudo first order**
- **Degradation efficiency: shortest $t_{1/2}$ for PF**

Identification of transformation products

- **Hydroxylation and cleavage products detected**
- **Identification at different levels of confidence L5 – L2b**
- **New and previously detected products**

To do

- **Targeted MS/MS**
- **Confirmation of identification**
- **Proposal degradation pathway**

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FWO

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Opening new horizons

ARSS

Slovenian Research Agency

MASSTWIN

mass twin