Identification and Assessment of Photo Transformation Products of the UV Filter Ethylhexyl Methoxycinnamate Present in Grey Water Intended for Water Reuse

Conference Paper · September 2015

CITATIONS
0

READS
62

4 authors, including:

Franziska Jentzsch
Leuphana University Lüneburg
5 PUBLICATIONS **11** CITATIONS
SEE PROFILE

Christoph Leder
KWHC GmbH
61 PUBLICATIONS **1,162** CITATIONS
SEE PROFILE

Oliver Olsson
Leuphana University Lüneburg
91 PUBLICATIONS **471** CITATIONS
SEE PROFILE

Institute of Sustainable and Environmental Chemistry

Identification and Assessment of Photo Transformation Products of the UV Filter Ethylhexyl Methoxycinnamate Present in Grey Water Intended for Water Reuse

F. Jentzsch, C. Leder, K. Kuemmerer, O. Olsson

Introduction

- Classical biological treatment of grey water (GW) intended for decentralized reuse purposes is ineffective in removal of micro pollutants like UV filter substances that originate from personal care products.
- The discharge of ultraviolet (UV) filters should be prevented due to their hormonal activities [Kunz and Fent 2006] and potential of bioaccumulation [Balmer et al. 2005].
  - For this reason the UV treatment as potential post treatment method of UV filters in GW was investigated and assessed.
- As long as full mineralization is not achieved, the proposed photo-oxidation process can result in the formation of photo transformation products (TPs) that may continue to pose environmental or health concerns.

This study aims the analysis of the primary elimination of the UV filter ethylhexyl methoxycinnamate (EHMC) during photolysis at 1 mg L^{-1} via high performance liquid chromatography (HPLC) with UV detection. Moreover, a qualitative photolysis experiment with initial concentrations of 5 mg L^{-1} EHMC was performed in order to monitor and identify the TPs by LC with multistage mass spectrometry detection (LC-MSn). Finally, the suggested TPs were assessed by *in silico* quantitative structure-activity relationship (QSAR) models to indicate alterations of the toxicity during photolysis.

Materials and Methods

Photolysis: TQ 150 medium-pressure mercury vapor lamp, immersion-type reactor, filled with 800 mL of Millipore water with either 1 % (v/v) acetonitrile (ACN) or 5 % (v/v) ACN. (c_{EHMC}: 1 mg L^{-1}/ 5 mg L^{-1}).

Irradiation time: 256 min. Sampling after 0, 2, 4, 8, 16, 32, 64, 96, 128, 192 and 256 min.

HPLC-UV: chromatographic column RP 18plus; binary gradient program: Eluent A (10 mmol L^{-1} ammonium acetate in ultrapure water), Eluent B (ACN); flow rate: 0,3 mL min^{-1}. Detection: 305 nm.

LC-MSn: LC-(ESI)-MS: fullscan and auto fragmentation (MSn); LC method as described above; MS method optimized by syringe pump experiments for H^+ and NH_4^+ adducts.

QSAR model: Models of the cheminformatics tool CASE Ultra were applied to investigate the revealed TPs.

Results

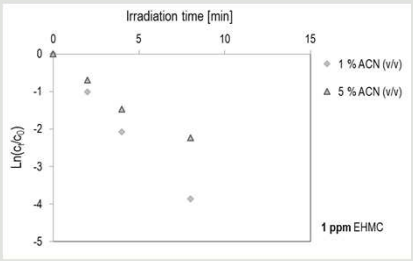

Figure 1: Elimination of EHMC (1 mg L^{-1}) during photolysis - direct comparison of the influence of the solvent composition on the degradation behavior of EHMC.

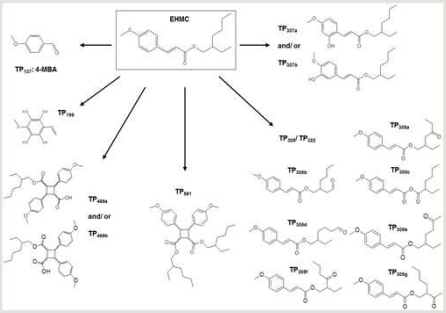

Figure 3: TPs generated by photodegradation of EHMC.

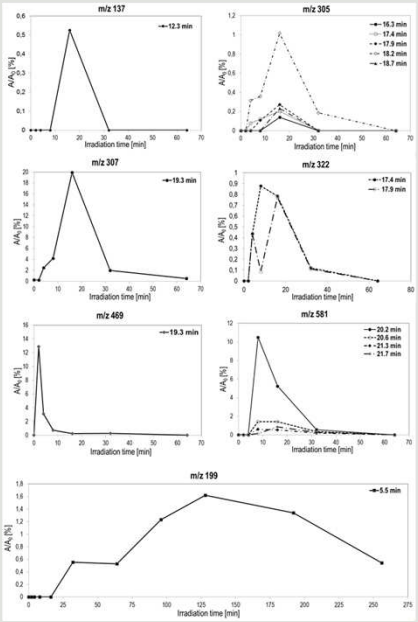

Figure 2: Relative peak area A/A_0 [%] (as A is the peak area of the TP at a defined time point, A_0 is the peak area of EHMC at 0 min) of photo-TPs LC-MS assorted by their m/z ratio and named by the corresponding retention time (RT).

Table 1: QSAR predictions for the selected endpoints of EHMC and the TPs.

$TP_{m/z}$	RT [min]	A0J	A7S	A7U	A7V
EHMC	21.2	-	-	IN	IN
TP_{137}	12.3	-	-	+	-
TP_{199}	5.5	IN	-	-	-
TP_{305a}	17.4 17.9 18.2	-	-	IN	IN
TP_{305b}		-	-	IN	IN
TP_{305c}		-	-	IN	+
TP_{305d}		IN	-	IN	IN
TP_{305e}		IN	-	IN	+
TP_{305f}		-	-	IN	IN
TP_{305g}		-	-	IN	IN
TP_{307a}	19.3	-	-	+	IN
TP_{307b}		-	-	IN	IN
TP_{469a}	19.6	OD	OD	OD	OD
TP_{469b}		OD	OD	OD	OD
TP_{581}	20.2 20.6 21.3 21.7	-	-	-	-

Human carciogenicity (A0J); Genotoxicity: A7S – micronucelous formation *in vivo* composite, A7U – chromosome aberration *in vitro* composite, A7V – chromosome aberration *in vitro* CHO.
OD – Out of Domain (the test chemical is not included in the applicability domain of the applied model); IN - Inconclusive (the molecule contained too many unknown fragments); +/- : positive/ negative prediction

Discussion

- The primary elimination of EHMC was achieved during irradiation and followed first order kinetic (Fig. 1). High co-solvent content (5 % ACN) slowed down the elimination.
- The detection of more than one signal of a m/z indicated the formation of isomers (Fig. 2 and Fig. 3).
- Some TPs described in literature were confirmed [Rodil et al. 2009, MacManus-Spencer et al. 2011] others were found the first time.
- The comparison of the alerts that lead to the inconclusive (IN) prediction of genotoxicity of EHMC (A7U, A7V, Tab. 1) and positive alerts (A7U: TP_{137}, TP_{307a}; A7V: TP_{305c}, TP_{305e}) illustrates that alternative positive or an additional alert exist. These data provide indications that the activities of various TPs on genotoxic endpoints might be altered compared with the parent compound.

Conclusion

By this work UV radiation, which is usually applied for disinfections purposes, was studied as potential post-treatment method of GW. The UV treatment proved to be highly efficient due to the fast and complete elimination of EHMC. However, the formation of several photo TPs was monitored by LC-MS. The outcomes of the *in silico* toxicity assessment of EHMC and the TPs indicated that the toxicity for some endpoints might be altered during photolysis. Therefore, further investigation should be conducted concerning the possibly modulated toxicity to confirm the *in silico* predictions.

Acknowledgment

The research leading to this results is a collective purpose of Lower Saxony and Israel and has received financial support by the State of Lower Saxony (Ministry of Science and Culture) (VWZN 2830).
The authors kindly thanks to the MultiCASE Inc., Ohio USA for providing the QSAR software (CASE Ultra) for the analysis.

References

Balmer, M. E.; Buser, H.-R.; Müller, M. D.; Poiger, T. (2005) *Environ. Sci. Technol.* 39 (4): 953–962

Kunz, P. Y.; Fent, K. (2006) *Aquat. Toxicol.* 79: 305-324

MacManus-Spencer, L. A.; Tse, M. L.; Klein, J. L.; Kracunas, A. E. (2011) *Environ. Sci. Technol.* 45: 3931-3937

Rodil, R.; Moeder, M.; Altenburger, R.;Schmitt-Jansen, M. (2009) *Anal Bioanal Chem* 395: 1513-1524

Contact

Leuphana University Lüneburg
Faculty of Sustainability
Institute of Sustainable and Environmental Chemistry

M. Sc. Franziska Jentzsch
Fon +49.4131.677-2899
Franziska.Jentzsch@leuphana.de
www.leuphana.de

LEUPHANA
UNIVERSITY OF LÜNEBURG