Sources and Environmental Fate of Organic UV filters

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Outline

Organic UV filter structures and physico-chemical properties and biodegradation

Structures

Solubility/Biodegradation

Source of Organic UV filters in the Environment

Wastewater

Consumer Products

Photochemical Fate of Organic UV filters in the Environment

Photochemical degradation

Research gaps

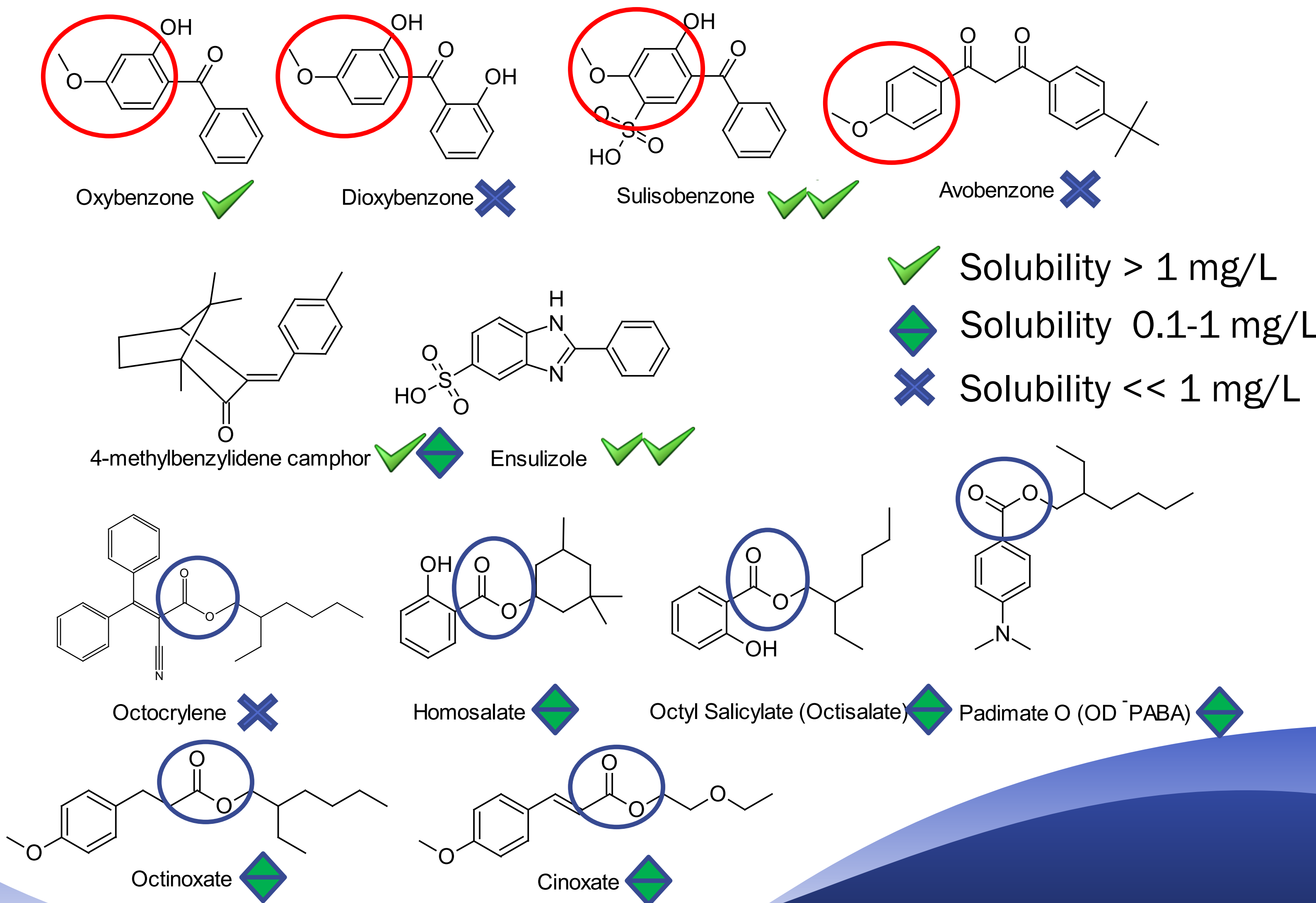
<u>Organic UV filter structures, physico-chemical properties and biodegradation</u>

Structures

Solubility/Biodegradation

Hydrolysis potential

Major Organic UV filters and their Structures



Major Organic UV filters: Solubility and Biodegradation

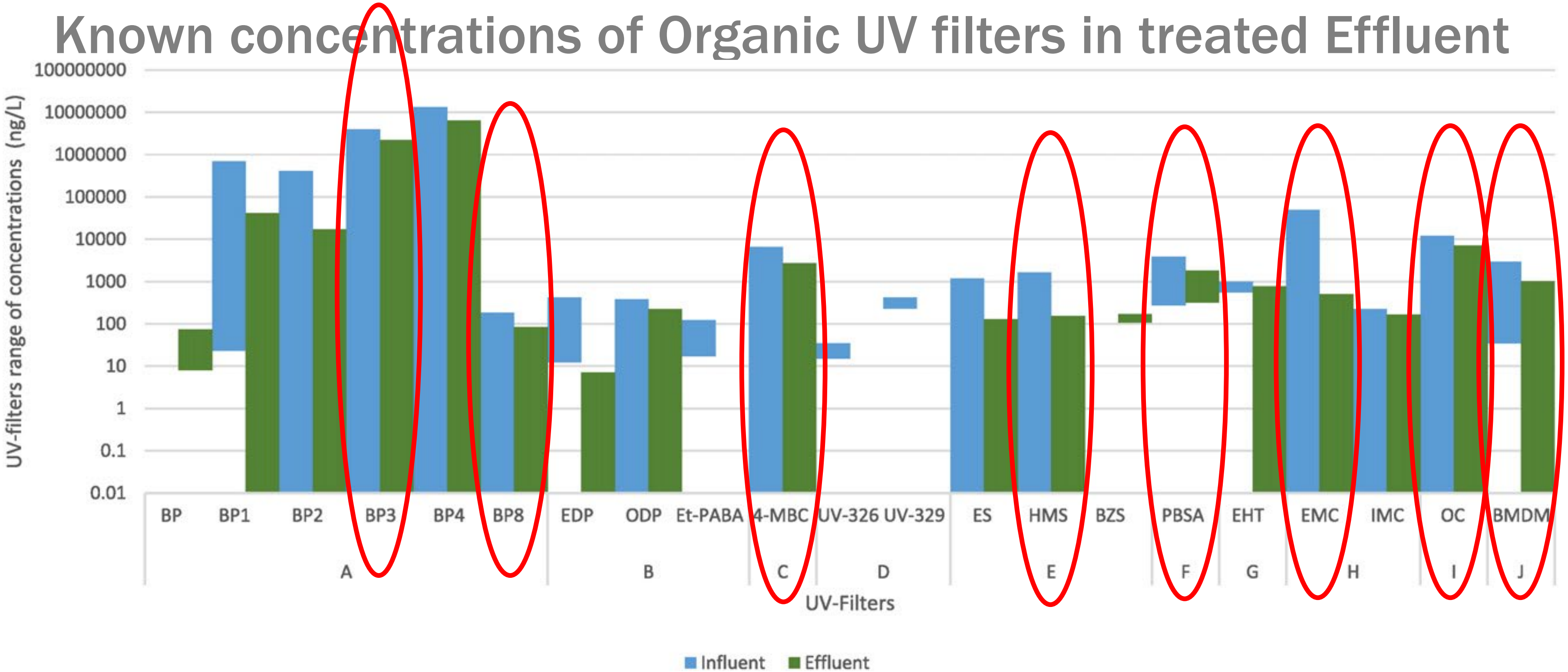
Chemical	Water solubility (mg/L) (freshwater)	Biodegradation	source
Oxybenzone (BP3)	3 /6	62% in 28 days (not reliable), biodegradable	https://echa.europa.eu/registration-dossier/-/registered-dossier/5515/5/3/2
Dioxybenzone (BP8)	0.013	0% in 28 days (not biodegradable)	https://echa.europa.eu/registration-dossier/-/registered-dossier/23375/5/3/2
Sulisobenzone (SSB, BP4)	300,000	44% in 7 days (readily bioavailable)	https://echa.europa.eu/registration-dossier/-/registered-dossier/10063/5/3/2
Avobenzone (BMDM, BMDBM)	0.027	No biodegradation observed	https://echa.europa.eu/registration-dossier/-/registered-dossier/14835
4-methylbenzylidine campher (4-MBC)	1.08	No biodegradation observed	https://echa.europa.eu/registration-dossier/-/registered-dossier/25426/5/3/2
Ensulizole (PBSA)	109	No biodegradation observed	https://echa.europa.eu/registration-dossier/-/registered-dossier/5464/5/3/2
Octocrylene (OC)	0.019- 0.054	Poorly biodegradable (0-10% after 28 d)	https://echa.europa.eu/registration-dossier/-/registered-dossier/14858/5/3/2
Homosalate (HMS)	0.4	70% in 28 days (ultimately biodegradable)	https://echa.europa.eu/registration-dossier/-/registered-dossier/13246/5/3/2
Octisalate (OS)	<0.5	89% in 28 days (readily biodegradable)	https://echa.europa.eu/registration-dossier/-/registered-dossier/14203/5/3/2
Padimate O (OD-PABA)	0.1	14 (readily bioavailable)	https://echa.europa.eu/registration-dossier/-/registered-dossier/24214/4/9
Octinoxate (EMC)	0.04	78% in 28 days (readily biodegradable)	https://echa.europa.eu/registration-dossier/-/registered-dossier/15876/5/3/2
Cinoxate	unknown	unknown	

Source of Organic UV filters in the Environment

Wastewater

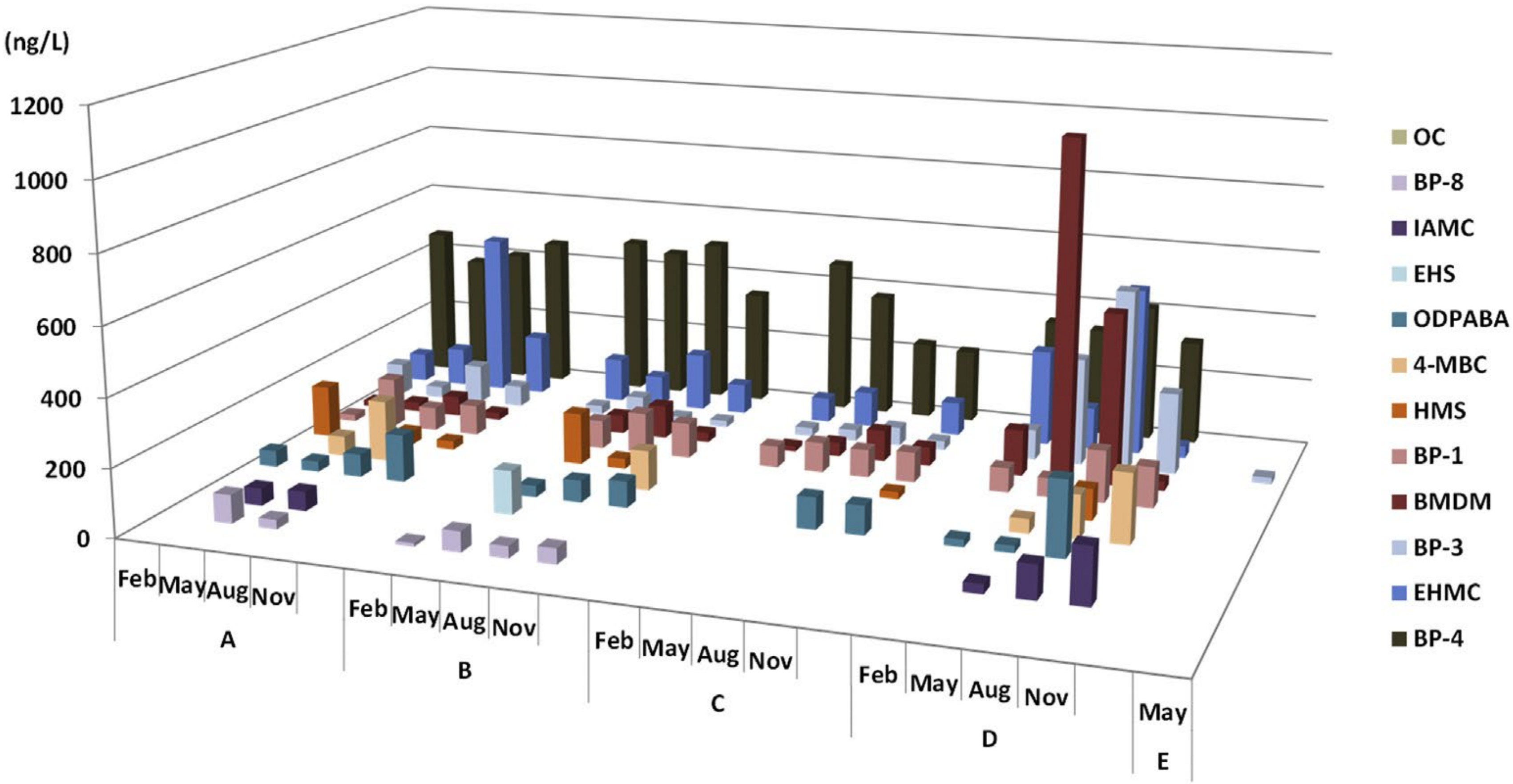
Consumer Products

Known concentrations of Organic UV filters in treated Effluent



Ramos, S.; Homem, V.; Alves, A.; Santos, L., A review of organic UV-filters in wastewater treatment plants. *Environment International* **2016,** *86*, 24-44.

Known concentrations of Organic UV filters in treated Effluent



Tsui, M. M. P.; Leung, H. W.; Lam, P. K. S.; Murphy, M. B., Seasonal occurrence, removal efficiencies and preliminary risk assessment of multiple classes of organic UV filters in wastewater treatment plants. *Water Research* **2014,** *53*, 58-67.

Organic UV filter in Consumer Products

Substance	CAS	Found in sunscreens	Found in other cosmetics*	Textiles	Plastics	Toys	Paint, varnishes, adhesives, fillers	Food packaging	Printing inks for food packaging	Printing inks, other	Cleaning products and detergents	Found in biomonitoring	Found in drinking water	Found in the aquatic environment and biota
BP-3	131-57-7	B	B, L		L W		L	L				L	L	L
OC	6197-30-4	B	B,L,M		L							L	L	L
4-MBC	36861-47-9	W	L									L	L	L
OD-PABA	21245-02-3	B	B				M		L	M		L	L	L
BMDBM	70356-09-1	B	B,M,L			M							L	
OS (Ethylhexyl salicylate)	118-60-5	B	B,M					L						
EMC (OMC)	5466-77-3	B	B,L,M									L	L	L
HMS	118-56-9	B	B,L,M					L				L		L

*L = found in the literature, B = found in the shop visits in 11 selected stores, M = identified as being used by questioned market players and W = information from the producers' and suppliers' websites.

Source: Survey and health assessment of UV filters, Survey of chemical substances in consumer products No. 142, 2015. Ministry of Environment and Food, The Danish Environmental Protection Agency. Note: red letters are added from literature.

Organic UV filter in Consumer Products

Substance	CAS	Intended Use	Reference
BP-3	131-57-7	Cosmetics, personal care products, cleaning products (shoes), coatings, inks, adhesives, manufacturing of plastic products	https://comptox.epa.gov/dashboard/dsstoxdb/results?search=oxybenzone#product-use-categories https://echa.europa.eu/registration-dossier/-/registered-dossier/5515/3/1/6
OC	6197-30-4	Cosmetics, personal care products, surface sealer, perfumes, photochemicals, manufacturing of plastic products	https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID9025299#exposure
4-MBC	36861-47-9	Cosmetics, personal care products	https://echa.europa.eu/registration-dossier/-/registered-dossier/25426/3/1/6
OD-PABA	21245-02-3	Cosmetics, personal care products, coatings and paints, thinners, paint removers, Ink and toners, plant protection products	https://echa.europa.eu/registration-dossier/-/registered-dossier/24214/3/1/6
BMDBM	70356-09-1	Cosmetics, personal care products,	https://echa.europa.eu/registration-dossier/-/registered-dossier/14835/3/1/5
OS (Ethylhexyl salicylate)	118-60-5	Cosmetics, personal care products,	https://echa.europa.eu/registration-dossier/-/registered-dossier/14203/3/1/5
EMC (OMC)	5466-77-3		
HMS	118-56-9	Cosmetics, personal care products	https://echa.europa.eu/registration-dossier/-/registered-dossier/13246/3/1/4
Ensulizole (PBSA)	27503-81-7	Cosmetics, personal care products	https://echa.europa.eu/registration-dossier/-/registered-dossier/5464/3/1/6
Sulisobenzone (SSB, BP4)	4065-45-6	Cosmetics, personal care products, washing and cleaning products, leather treatment, coatings, paint, thinners, air care products, etc.	https://echa.europa.eu/registration-dossier/-/registered-dossier/10063/3/1/6
Cinoxate	104-28-9	Cosmetics, personal care products,	
Dioxybenzone (BP8)	131-53-3	Cosmetics, personal care products, manufacturing of plastic products	https://echa.europa.eu/registration-dossier/-/registered-dossier/23375/3/1/4

Photochemical Fate of Organic UV filters in the Environment

Photochemical degradation

Research gaps

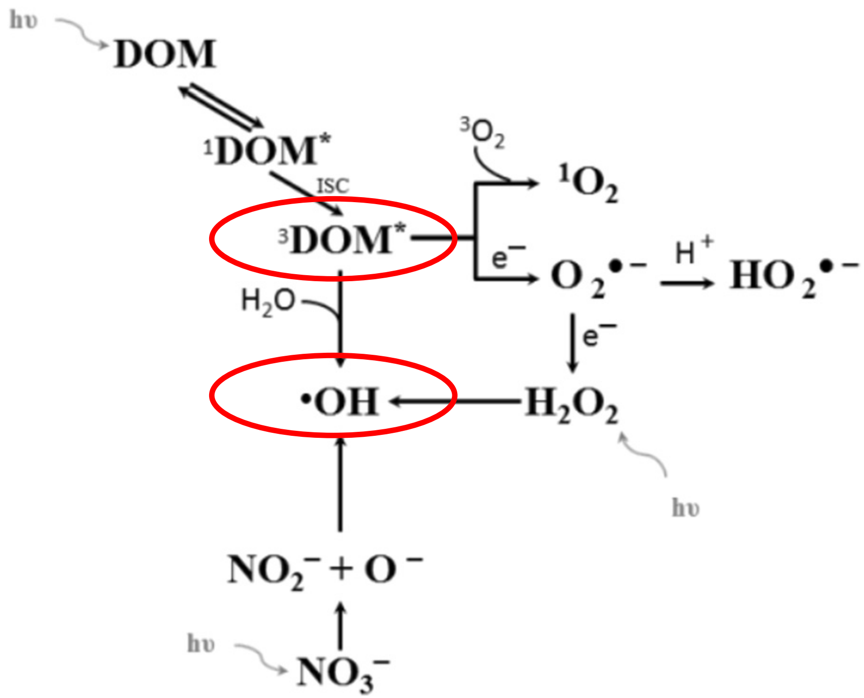
Photochemistry Background and Importance

- Photochemistry is expected to be a <u>**major sink**</u> for organic UV filters in aquatic environments, especially in the sunlit coastal ocean.

- Photo-products are in general <u>**more water soluble**</u> and hydroxylation of aromatic compounds may increase toxicity.

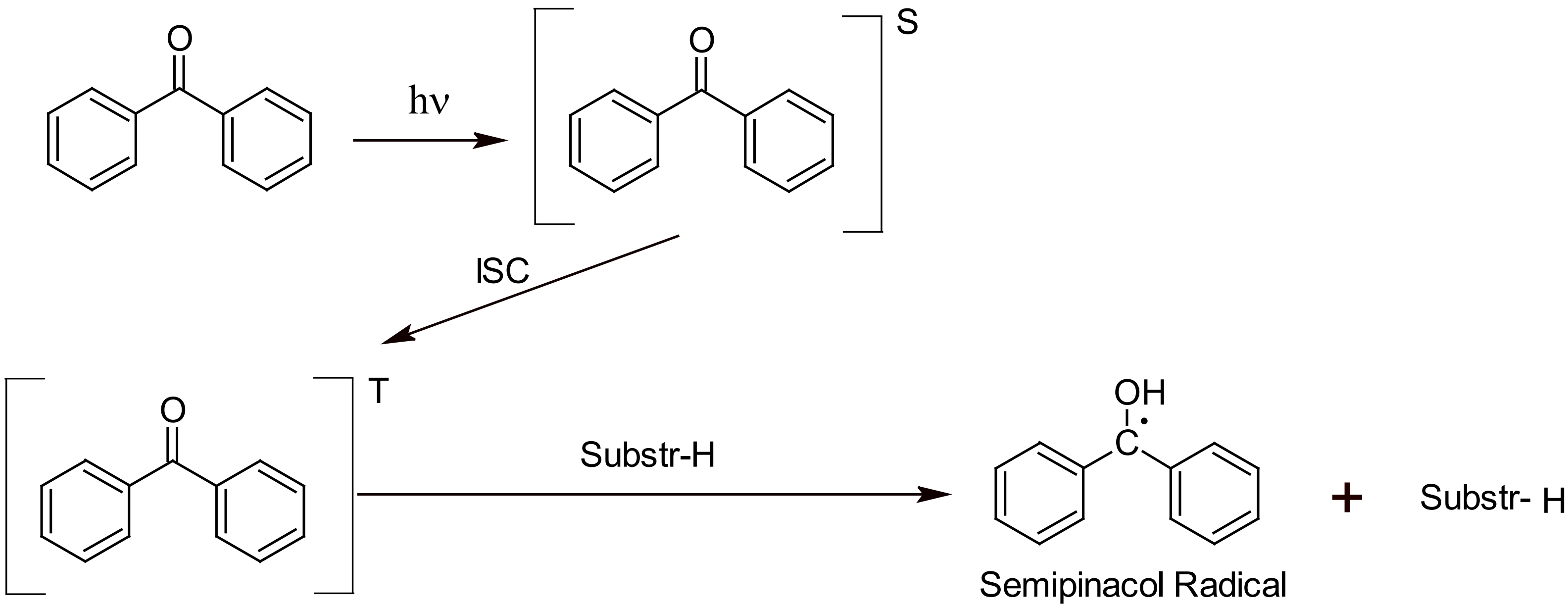
- Interplay between photochemical activation for further microbial degradation

Photochemistry Background Reactive Oxygen Species



Gmurek, M.; Olak-Kucharczyk, M.; Ledakowicz, S., Influence of dissolved organic matter in natural and simulated water on the photochemical decomposition of butylparaben. *Journal of Environmental Health Science and Engineering* **2015,** *13*, (1), 28.

Photochemistry Background on Benzophenone



Benzophenone is one of the best photosensitizer known in photochemistry. The yield of the excited state is almost 100%.

Photochemistry Background on Aromatic Esters

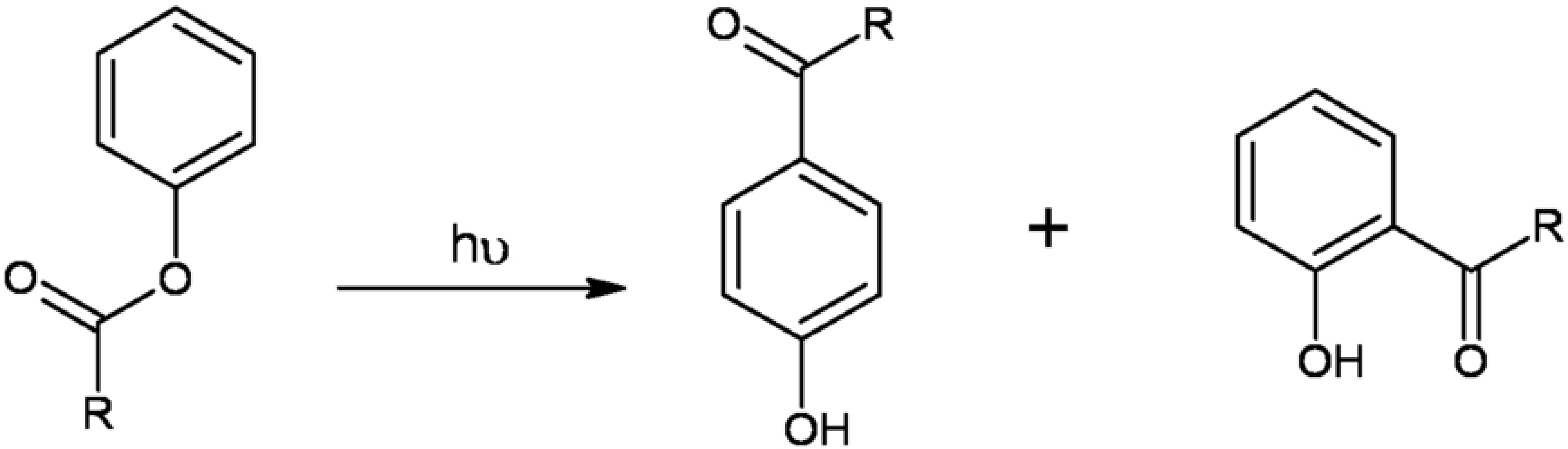
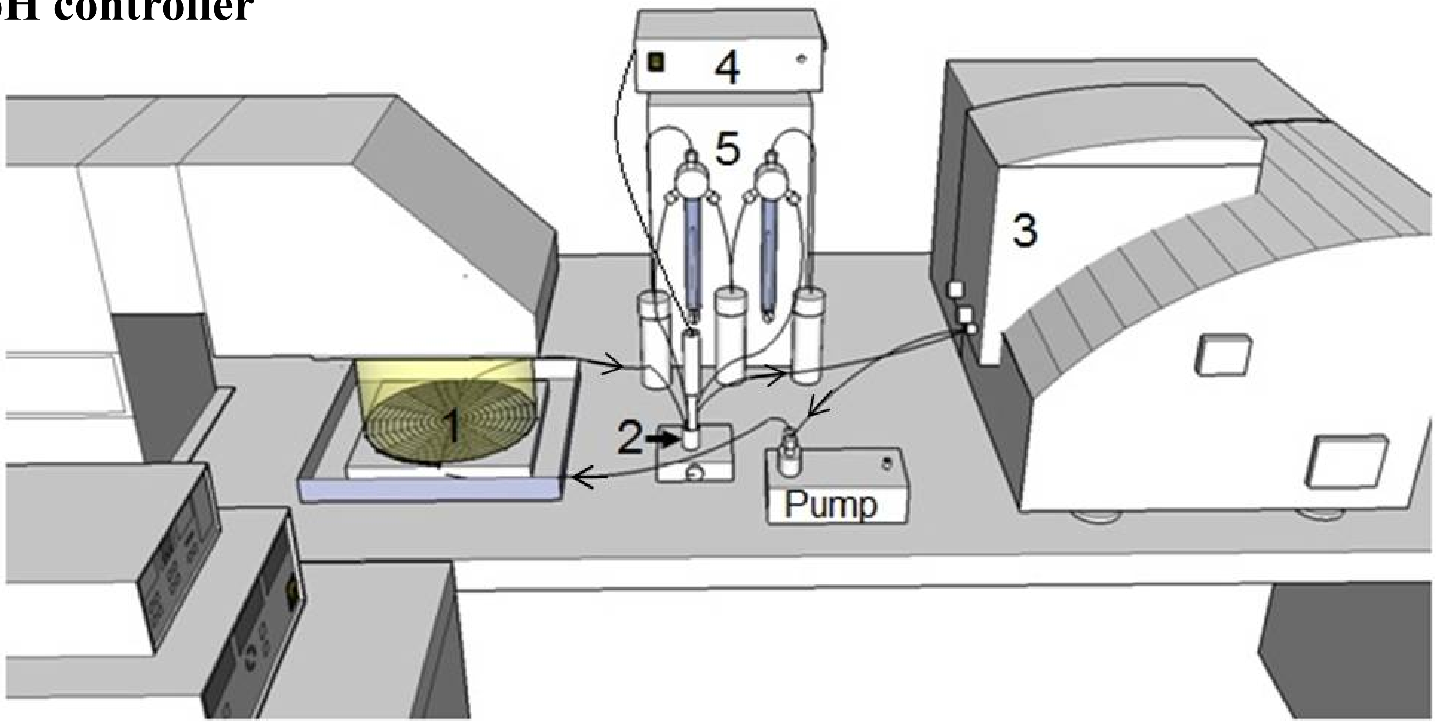


Photo-Fries Rearrangement pathway

Coppinger, G. M.; Bell, E. R., Photo-Fries Rearrangement of Aromatic Esters. Role of Steric and Electronic Factors. *The Journal of Physical Chemistry* **1966,** *70*, (11), 3479-3489.

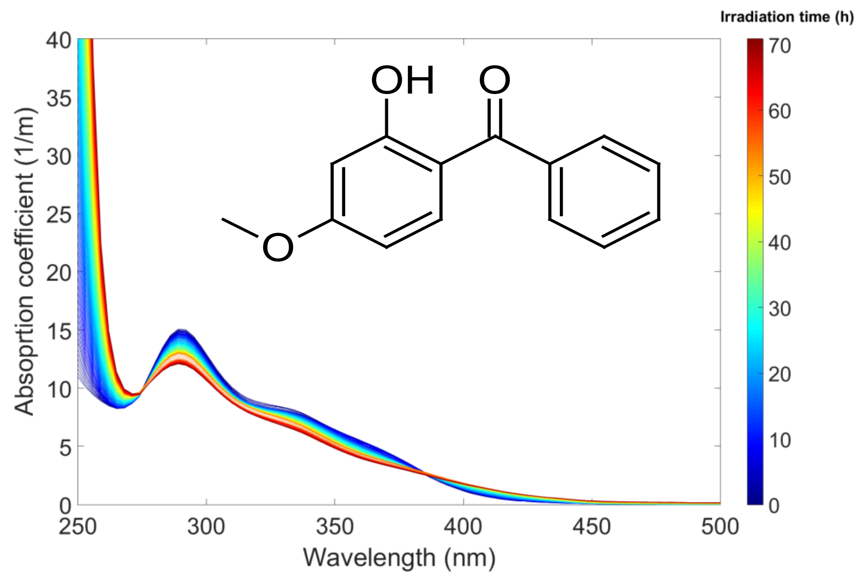
Aquatic Photochemistry Instrumentation

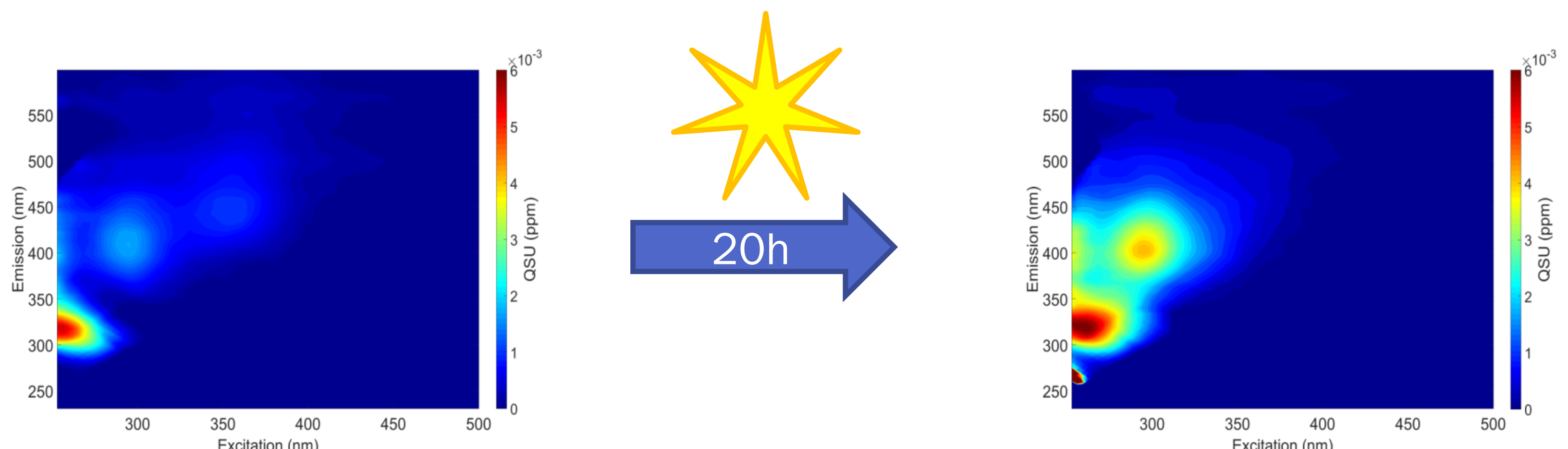
1. **Custom-built irradiation cell (1 mm pathlength to avoid inner filtering)**
2. **Equilibrator vial (to allow oxygen equilibration with atmosphere)**
3. **Horiba Aqualog Fluorometer (EEM and UV-Vis simultaneously)**
4. **pH electrode**
5. **pH controller**



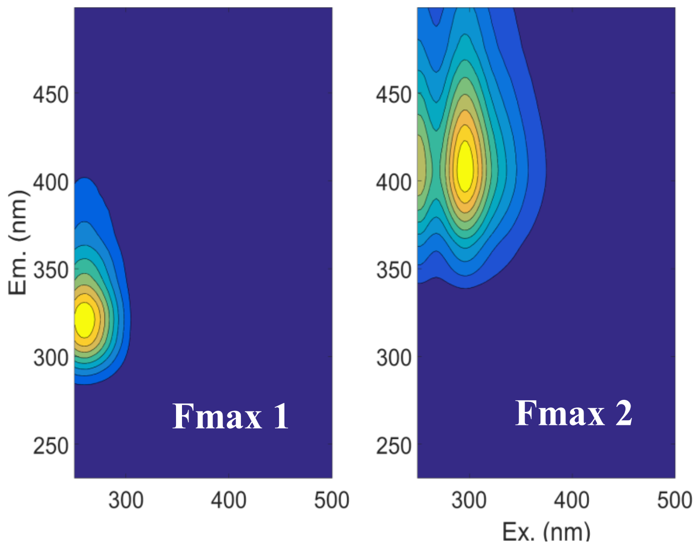
Oxybenzone Photochemistry

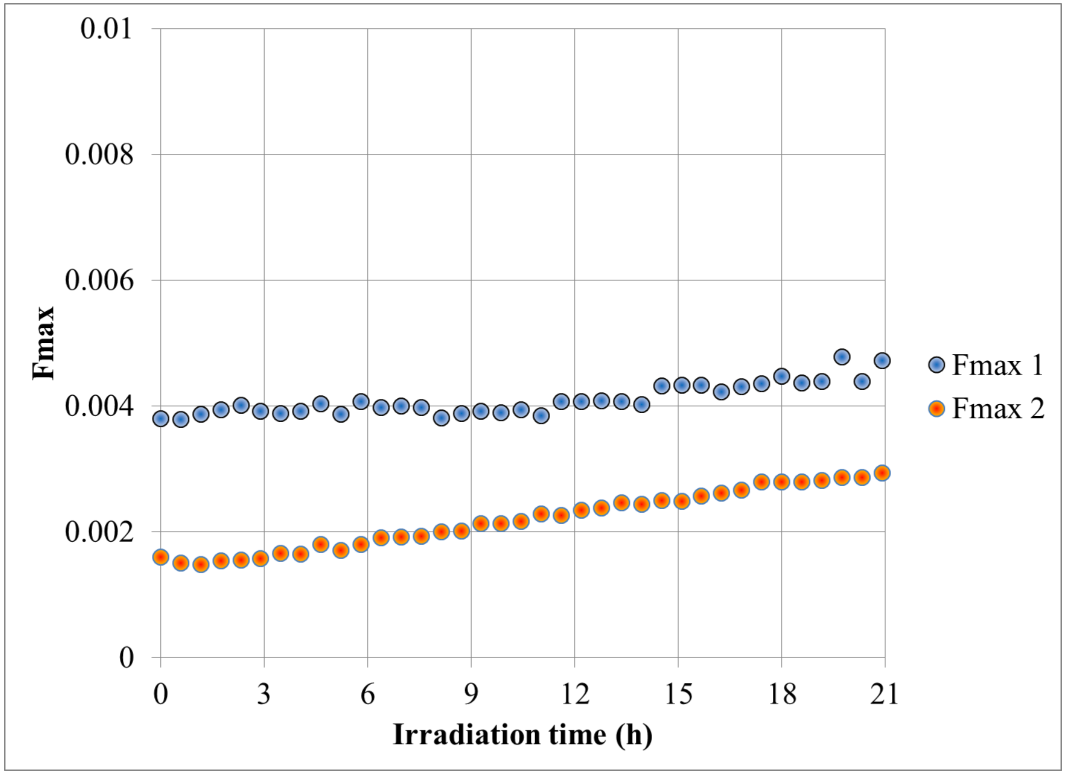
Seawater





Oxybenzone Photochemistry PARAFAC Model

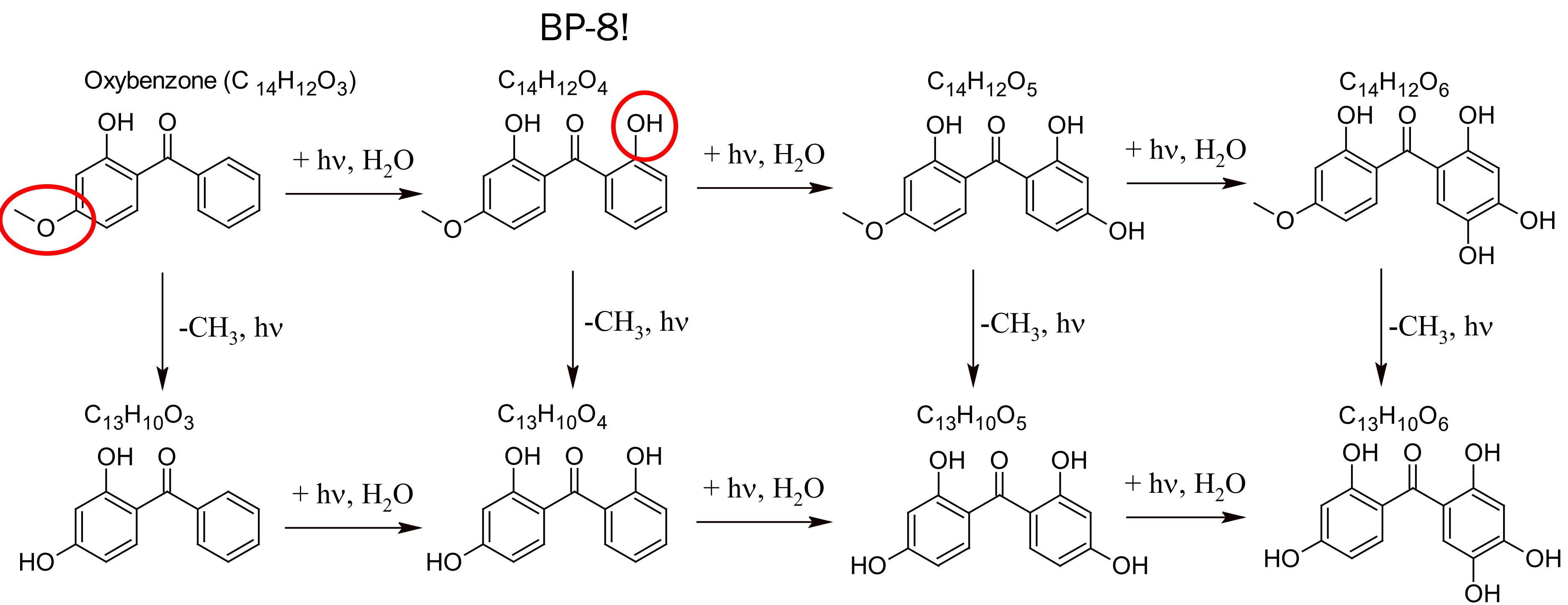




Additional degradation kinetics in the literature:

Li, Y. J.; Qiao, X. L.; Zhou, C. Z.; Zhang, Y. N.; Fu, Z. Q.; Chen, J. W., Photochemical transformation of sunscreen agent benzophenone-3 and its metabolite in surface freshwater and seawater. *Chemosphere* 2016, *153*, 494-499.

Oxybenzone Photochemistry Non-targeted FT-ICR MS

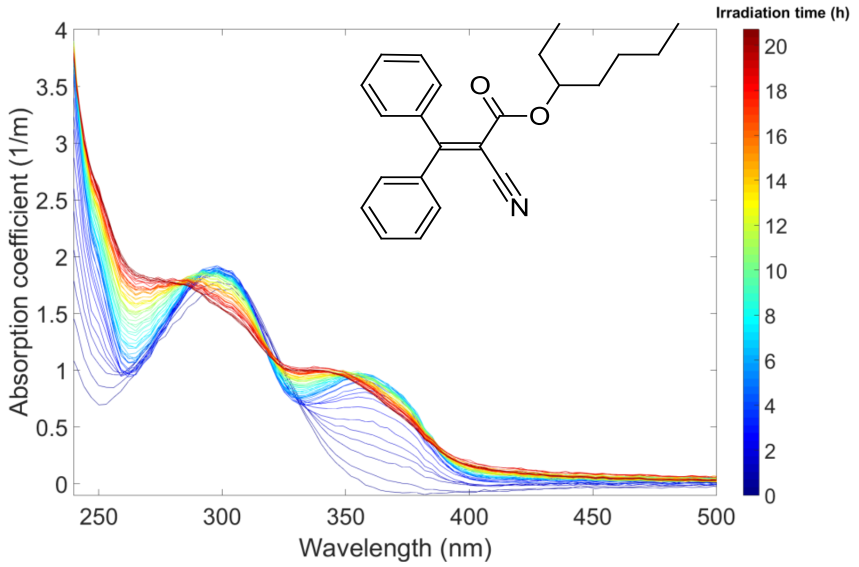


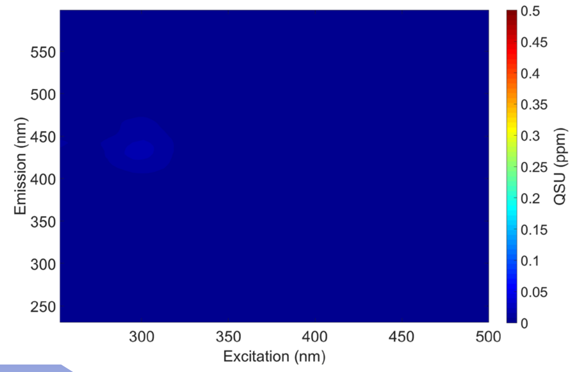
Hydroxylated photo-products have also been described previously:

Zúñiga-Benítez, H.; Aristizábal-Ciro, C.; Peñuela, G. A., Heterogeneous photocatalytic degradation of the endocrine-disrupting chemical Benzophenone-3: Parameters optimization and by-products identification. Journal of Environmental Management 2016, 167, 246-258.

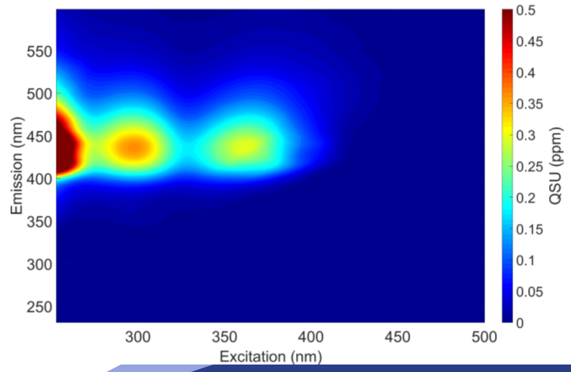
Octocrylene Photochemistry

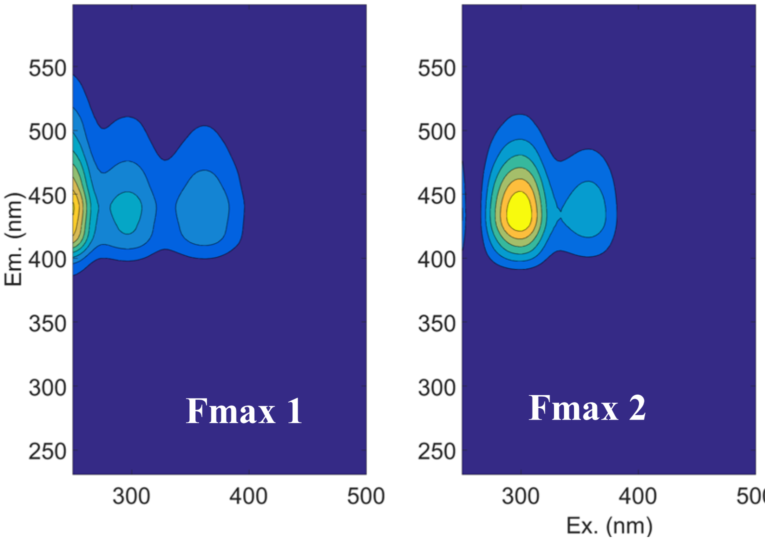
Seawater

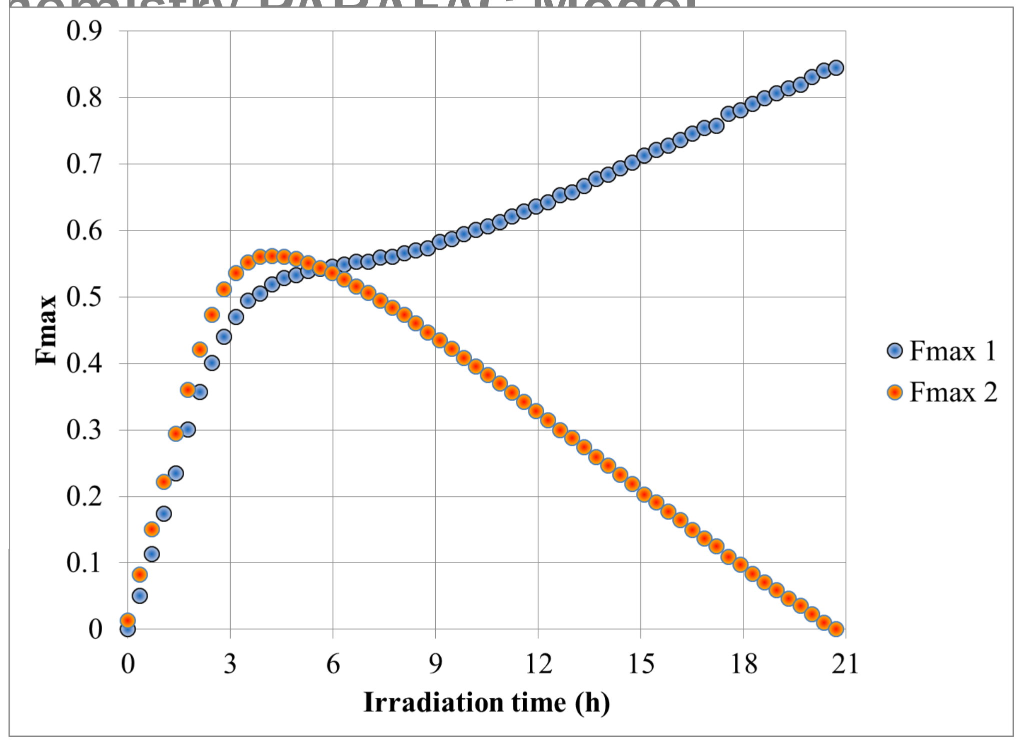




20h




Fmax 1
Fmax 2
Em. (nm)
550
500
450
400
350
300
250
300
400
500
Ex. (nm)

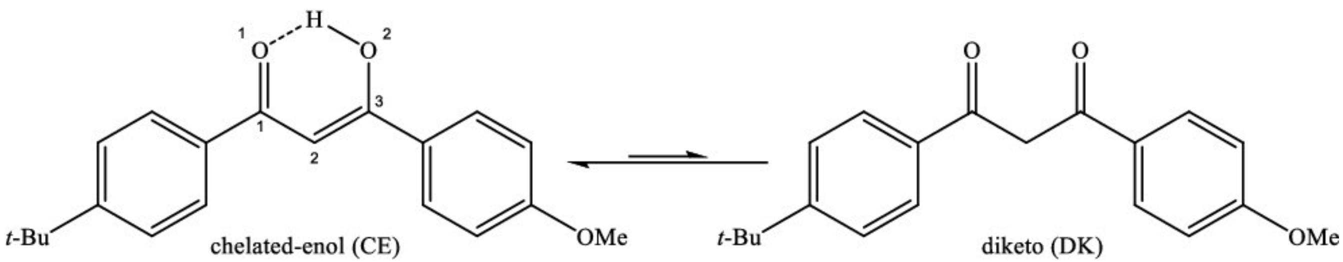

Fmax
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
3
6
9
12
15
18
21
Irradiation time (h)
Fmax 1
Fmax 2

Avobenzone Photochemistry

Solubility is very low in seawater and results were inconsistent with very minimal photodegradation

This is consistent with literature that showed minimal if any photodegradation in polar solvents.

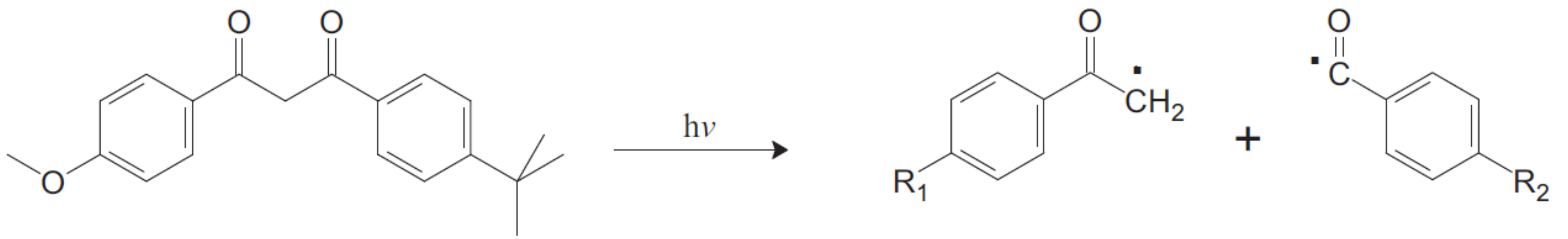
However, avobenzone is often combined with octocrylene, because of the photoprotection of avobenzone by octocrylene in unpolar “solvents’ or “oils”. Avobenzone is considered to be photochemically labile in formulations. Hence, photochemical behavior in the microlayer is likely to be fundamentally different to the observed behavior in water.



Schematic Diagram Illustrating the UVA Active Chelated-Enol (CE) and UVB Active Diketo (DK) Tautomer of Avobenzone. Irradiation of the DK Tautomer Causes Photoinitiated α-Cleavage

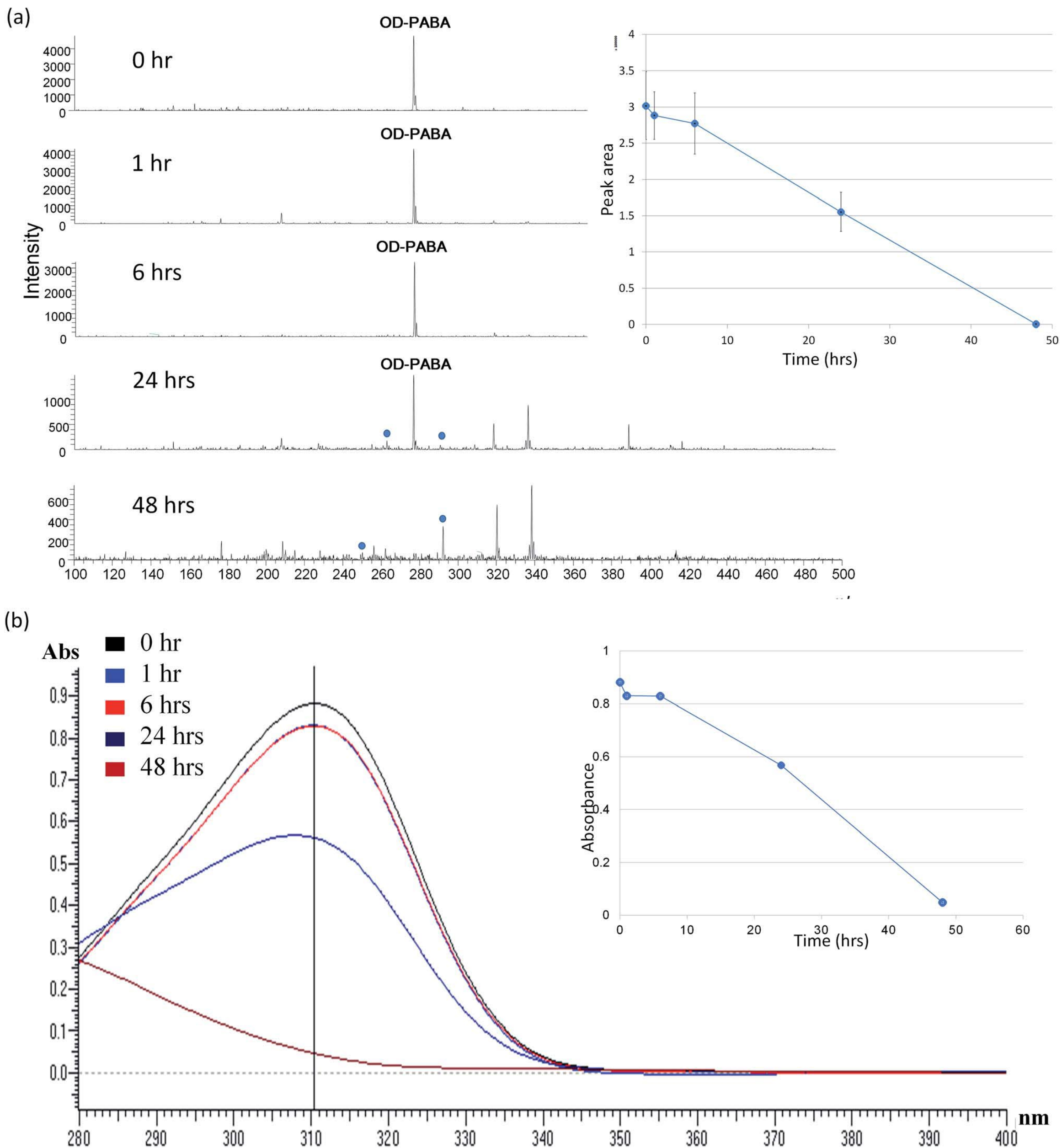
Berenbeim, J. A.; Wong, N. G. K.; Cockett, M. C. R.; Berden, G.; Oomens, J.; Rijs, A. M.; Dessent, C. E. H., Unravelling the Keto–Enol Tautomer Dependent Photochemistry and Degradation Pathways of the Protonated UVA Filter Avobenzone. *The Journal of Physical Chemistry A* **2020,** *124*, (15), 2919-2930.

Avobenzone Photochemistry



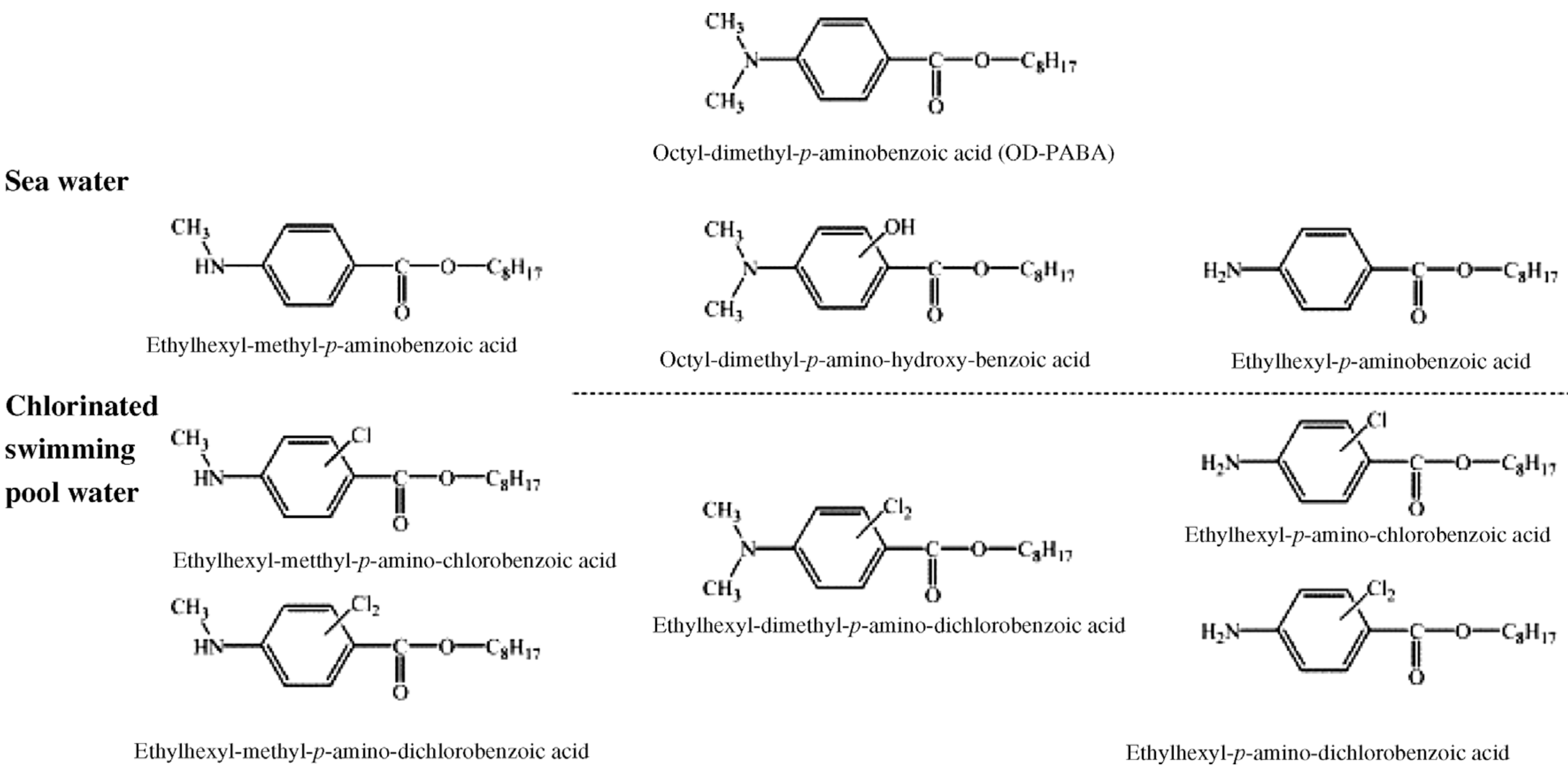
Kockler, J.; Oelgemöller, M.; Robertson, S.; Glass, B. D., Photostability of sunscreens. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2012,** *13*, (1), 91-110. **Note: This is also an excellent review paper to show the controversy of UV filter photochemistry and the contradicting results in the literature.)**

OD-PABA Photochemistry



Cho, Y.-T.; Su, H.; Huang, I. C.; Lai, C.-Y.; Tsai, Y.-D., Rapid characterization of organic UV filters and their photoproducts in sunscreens by thermal desorption electrospray ionization mass spectrometry for the photostability study. *Analytical Methods* **2019,** *11*, (47), 6013-6022.

OD-PABA Photochemistry



Silvia Díaz-Cruz, M.; Llorca, M.; Barceló, D.; Barceló, D., Organic UV filters and their photodegradates, metabolites and disinfection by-products in the aquatic environment. *TrAC Trends in Analytical Chemistry* **2008,** *27*, (10), 873-887.

Sulisobenzone (BP-4) Photochemistry

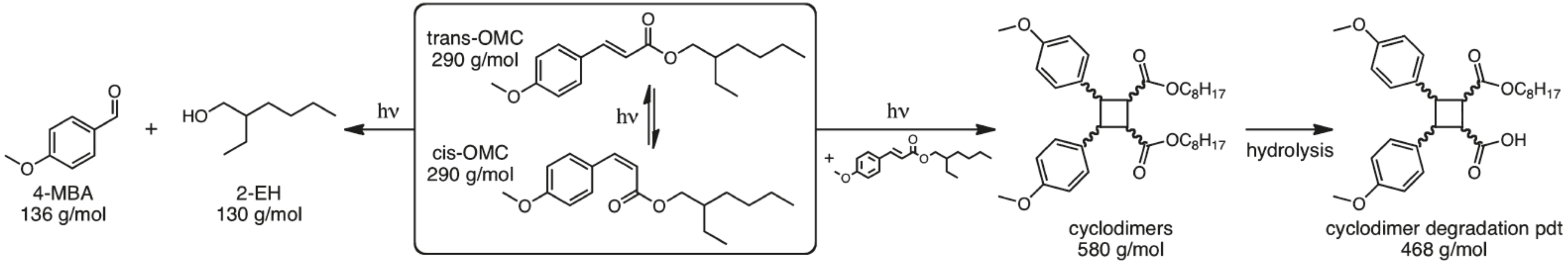
1) Major photodegradation pathway is expected to be by hydroxyl radicals and $^{3}DOM^{*}$
2) Hydroxylation of the aromatic rings are likely.
3) To the best of my knowledge no photo-products in natural waters have been described.

Ensulizole Photochemistry

No data on aquatic photochemistry and degradation products are known to date

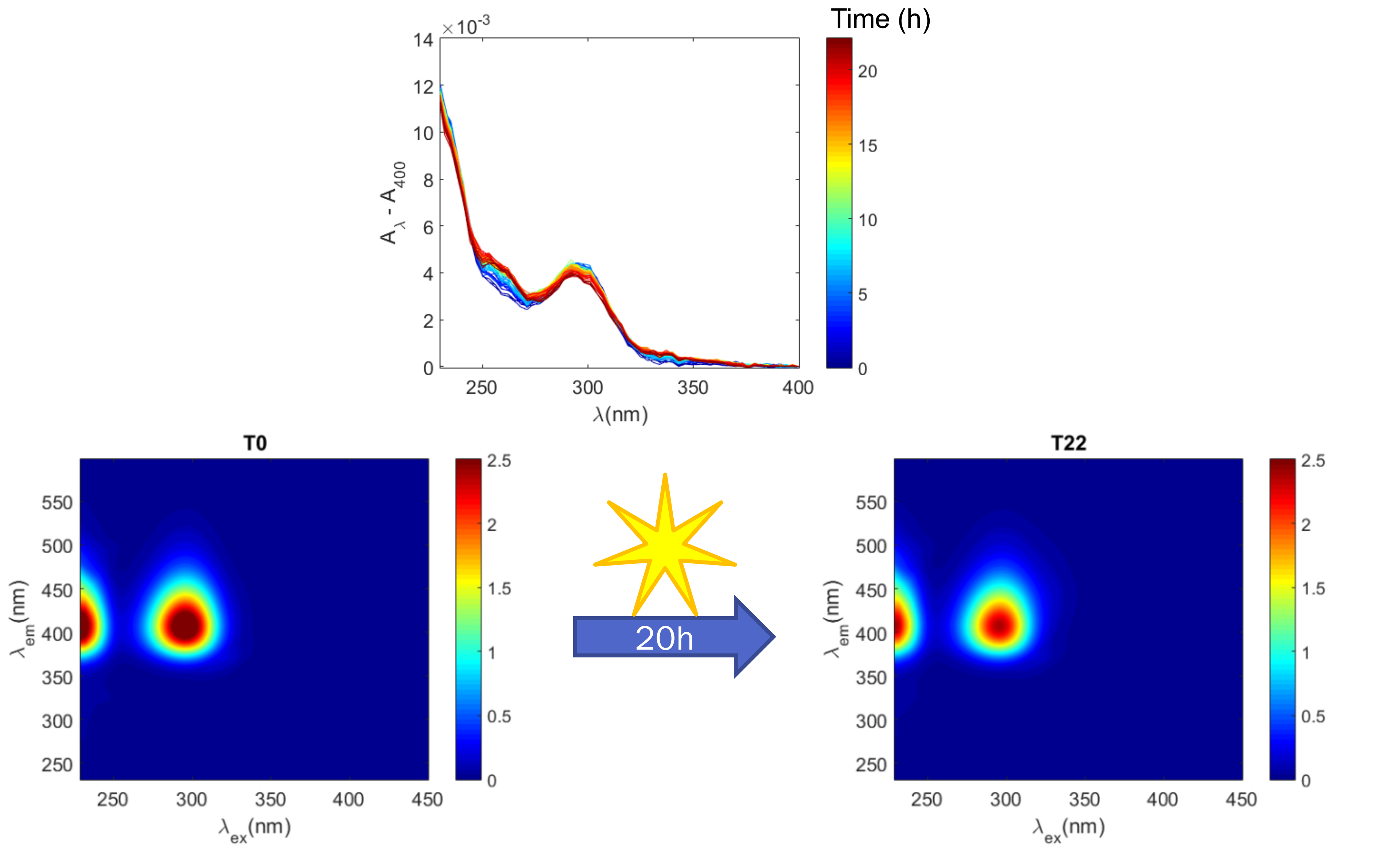
Octinoxate Photochemistry

Scheme 1. Upon Direct Photolysis, OMC Undergoes Photoisomerization, Followed by Photodegradation and Photodimerization to Yield 4-Methoxybenzaldehyde, 2-Ethylhexanol, and Several Dimer Isomers

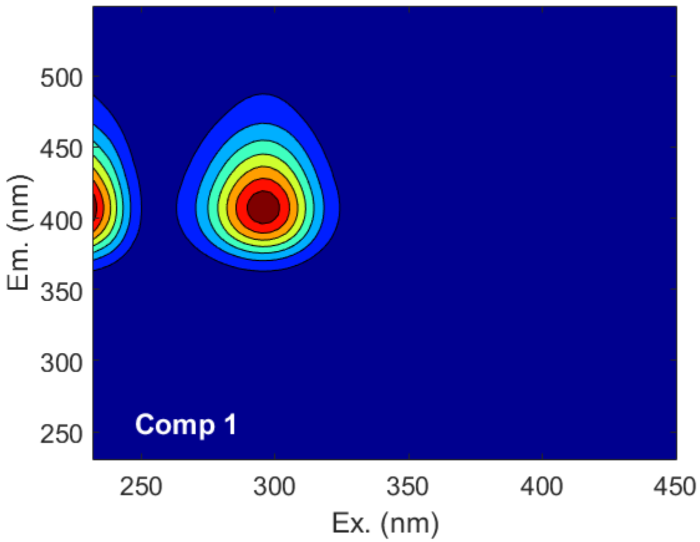


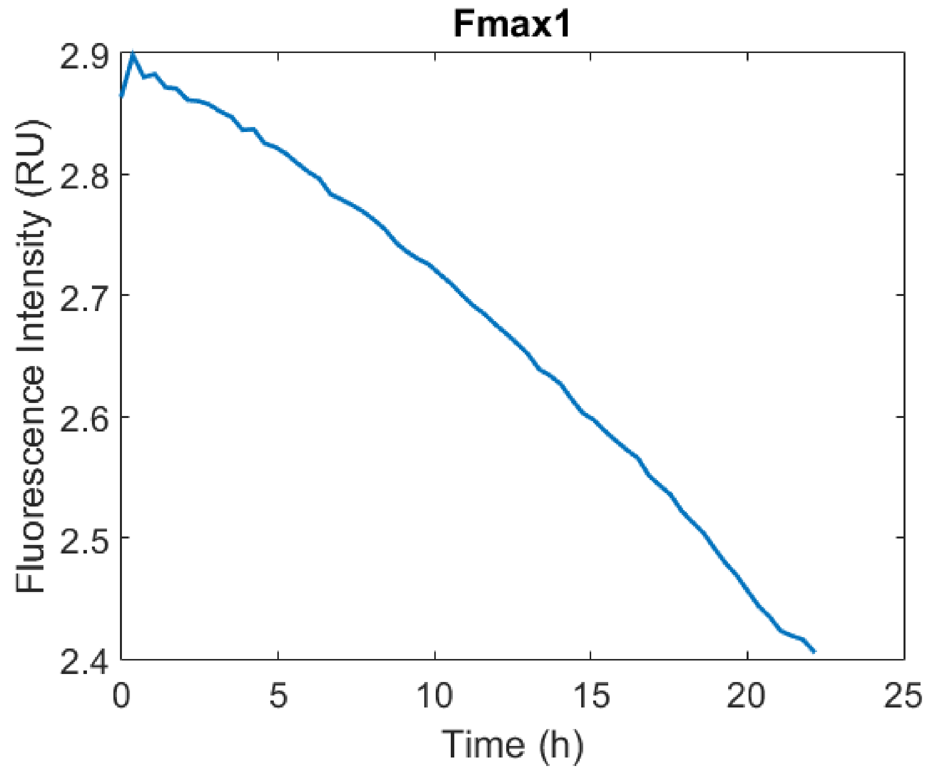
MacManus-Spencer, L. A.; Tse, M. L.; Klein, J. L.; Kracunas, A. E., Aqueous Photolysis of the Organic Ultraviolet Filter Chemical Octyl Methoxycinnamate. *Environ. Sci. Technol.* **2011,** *45*, (9), 3931-3937.

Homosalate Photochemistry



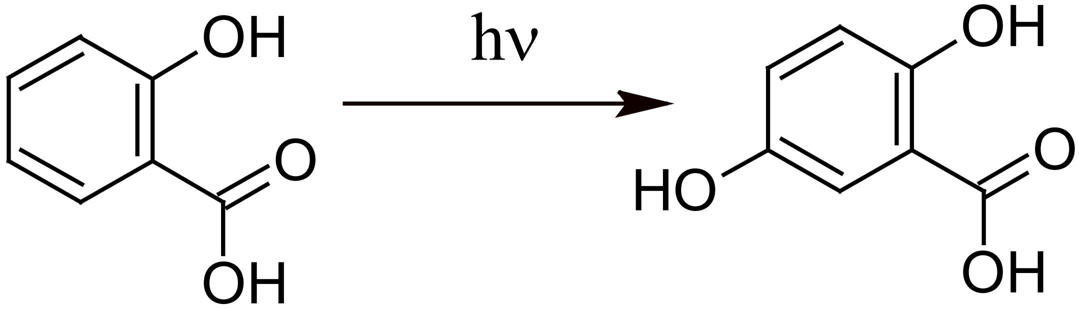
Homosalate Photochemistry PARAFAC Model





Octisalate Photochemistry

1) Octisalate contains the same chromophore as Homosalate: Salicylic acid!
2) Absorbance and fluorescence of Homosalate, Octisalate and Salicylic acid are indistinguishable
3) Perhaps the photochemistry of salicylic acid can give some clues:



4) Hydroxylation of salicylic acid was confirmed in the literature and several hydroxylated photoproducts of Homosalate and Octisalate are expected.

Take Home Messages

- Organic UV filters that have a reasonable solubility in water are frequently detected in treated effluent and aquatic systems
- Diverse sources of organic UV filters are known and production indicates widespread usage.
- Photochemistry of organic UV filters in aquatic systems is severely understudied and the determination of photo-products is rare
- When photo-products are determined, hydroxylation of aromatic rings yield the most likely photo-products, and hydoxyl radicals and $^3DOM^*$ are the major players
- The photochemistry of organic UV filters in the aquatic environment is fundamentally different when compared to evaluation of photochemical effects on the skin and in unpolar solvents.
- Naturally occurring dissolved organic matter ($^3DOM^*$) seems to accelerate the photo-degradation of some UV filters, similar to published rates on pharmaceuticals.

Research Gaps

- Structural elucidation of UV-filter photo-products in seawater and freshwater are missing for most UV filters.
- Photochemical degradation pathways are fundamentally different in different natural waters and data is largely missing, especially in seawater.
- Photochemical reactions in water surface microlayers are unknown, but the production of more water-soluble photo-products is expected, here similarities to crude oil degradation can be made.
- Persistence of UV-filters in different aquatic systems remain largely undefined.
- The interplay between photochemical degradation and activation for further microbial degradation remains unknown.
- Evaluation of synergistic photochemical effects of hydrophobic UV filters in varying aquatic systems remain rare.
- The role of esterase enzymes on hydrolysis of UV-filter esters remain largely unknown.
- Photo-Fries rearrangements of organic UV-filter esters will likely yield more complex photo-products, beside hydroxylation, but no evaluation of this mechanism exists to date.

Questions?

More Information?

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