EVALUATING THE ROLE OF BIOMASS IN THE SORPTION OF FOUR UV-FILTERS

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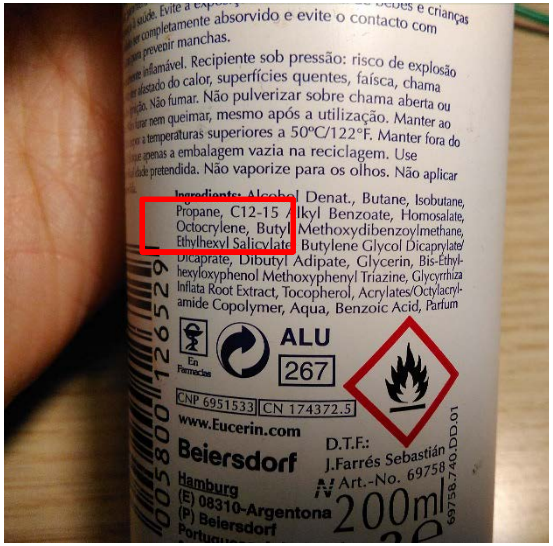
INTRODUCTION

Why do we have to study UV filters?

UV filters are used as **personal and care products** like sunscreens and cosmetics (perfumes, creams or shampoos), and in **a number of industrial** applications



Some of them are <u>endocrine disruptors</u> and have estrogenic activity

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We're killing the world's coral reefs with SUNCREAM and mascara

SLAPPING on the sunscreen is killing off one of the planet's greatest natural spectacles.

By STUART WINTER
PUBLISHED: 12:27, Wed, Oct 21, 2015 | UPDATED: 13:46, Wed, Oct 21, 2015

They are also destroying coral reefs...

INTRODUCTION

... and what is conditioning their fate in the subsurface?

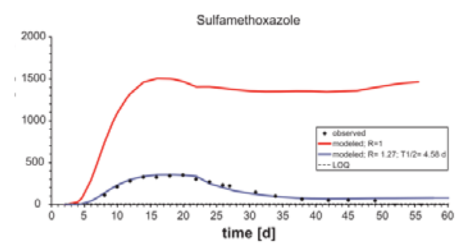
The fate of UV filters in subsurface is governed by **degradation** and **sorption** processes

Degradation processes:

UV-filters are **recalcitrant compounds** that are degraded under **co-metabolic** processes in the presence of more labile compounds. Most of current models of **degradation of EOCs** only focus on apparent processes

Shaffer et al. 2014. Water Research

$$\boxed{\frac{\partial C}{\partial t} = -kC \;\Rightarrow\; T_{1/2} = \frac{\ln K}{2}}$$



$\boxed{T_{1/2}\ 4.58\ \text{d}}$ Shaffer et al. 2015

Complex processess (like-cometabolism) needs more complex rates...

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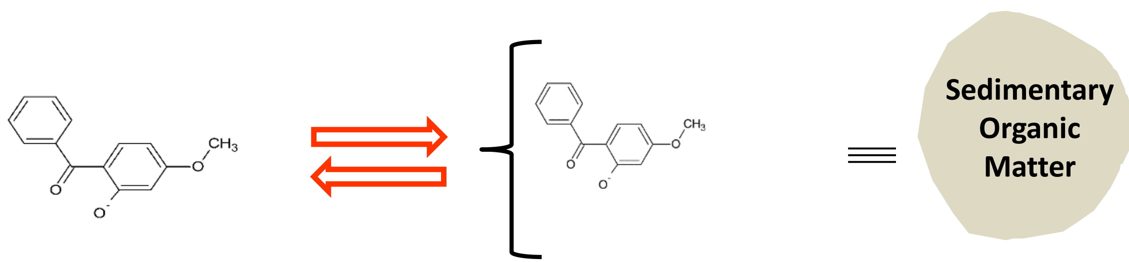
Sorption processes:

Sorption is also modelled as a phenomenological process...



$$K_{d,i} = \frac{C_{i,s}}{C_{i,w}} = \frac{C_{i,om} f_{oc}}{C_{i,w}} = K_{oc,i} f_{oc}$$

It is not as simple....

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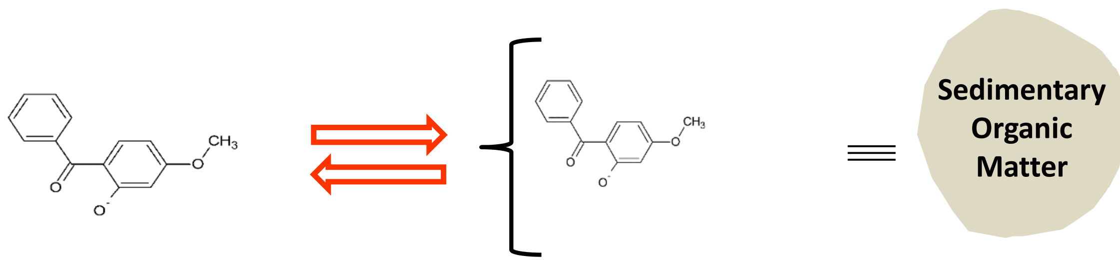
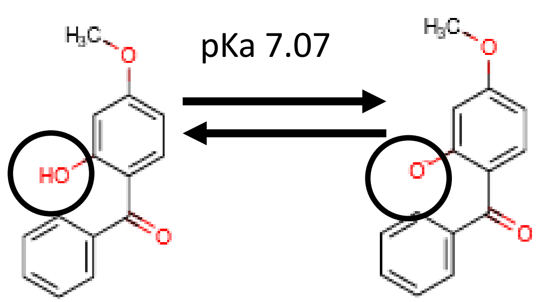
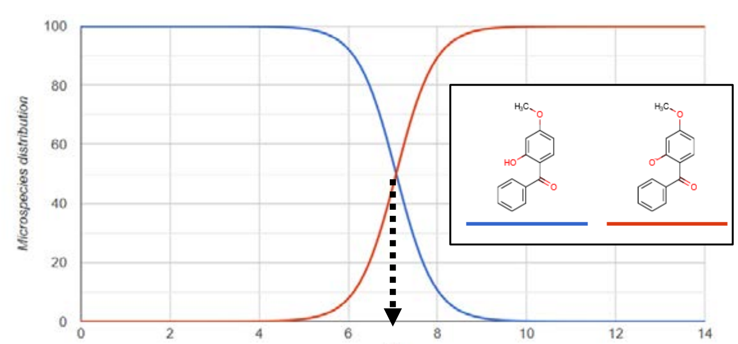


Sorbate





- Not all EOCs are neutral.
- Ionics EOCs can form ionic forms at certain pH.

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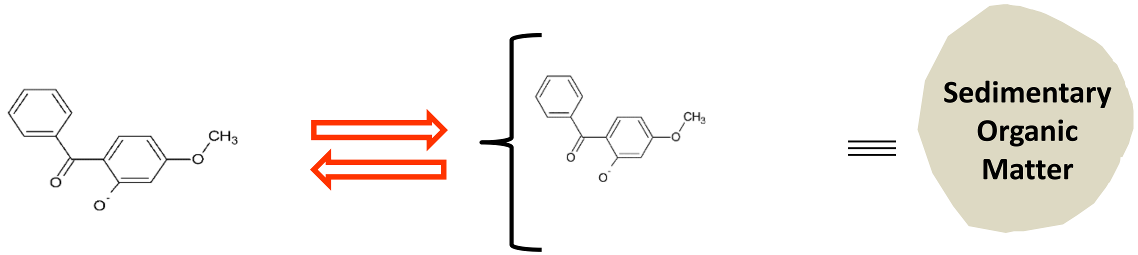

Sorbent

- **Organic matter** is the most important surface, but not the only one… mineral surfaces can act as sorbents
- What are the real processes or sorption?

INTRODUCTION

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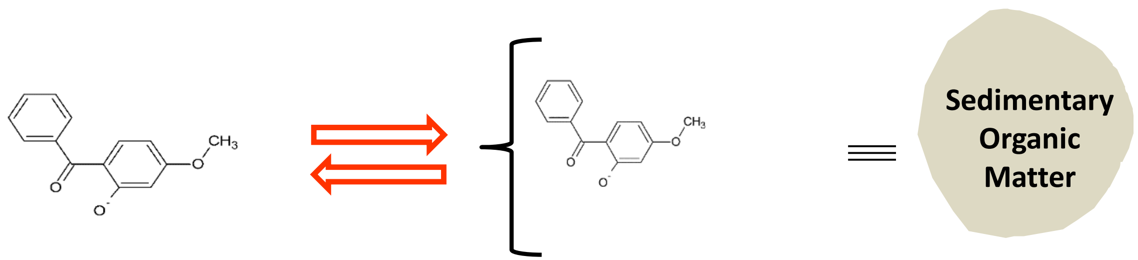


$$K_d = \frac{C_s}{C_w}$$

$$K_d = \frac{C_{om} f_{om} + C_{min} A + C_{ie} \sigma_{ie} + C_{rxn} \sigma_{rxn} A}{C_{w,neut} + C_{w,ion}}$$

INTRODUCTION

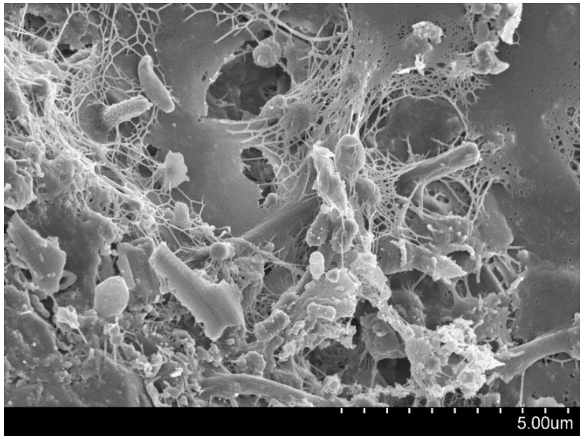
...what is **solid organic matter** in an aquifer?

Sedimentary organic matter

- It is the traditional SOM (0.01-0.1)
- Normally, it is recalcitrant.

Biomass

- Not important if aquifers are not biologically active
- Biomass can be an important sorbent → biofilm formation (e.g. during Managed Aquifer Recharge, bioremediation...)



MOTIVATION

The goal of this work is to evaluate the effect of redox conditions in the fate of a cocktail of UV-filters and to evaluate the effect of biomass in sorption processes.

↓

Developing a conceptual and a numerical model of sorption and degradation of UV-filters

↓

Validating the model with experimental data of Liu et al. 2013

EXPERIMENTS

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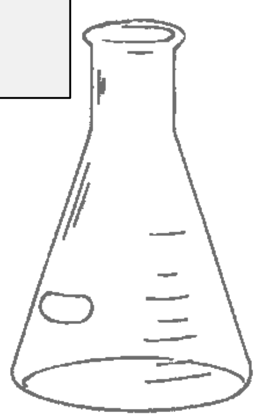
Liu et al (2013) performed a set of experiments evaluating the **degradation of a cocktail of UV-filters** in different redox conditions. They measured the temporal evolution of water and solid concentrations.

Organic matter (acetate)
Electron acceptor
UV-filter cocktail
Groundwater
Sediment (mainly carbonates)

Total time: 80 d



AEROBIC CONDITIONS

ANAEROBIC CONDITIONS

Sulfate-reducing conditions

EXPERIMENTS

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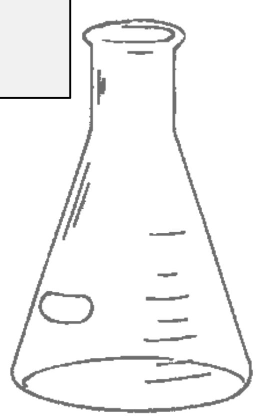

		pKa	$logD_{ow}$
Benzophenone-3	BP3	7.07	3.13
Octyl 4-methoxycinnamatte	OMC	Neutral	5.38
Octocrylene	OC	Neutral	6.78
2-(3-t-butyl-2-hydroxy-5-methylphenyl)5-chloro benzotriazole	UVA-326	10.08	5.33
2-(2'-hydroxy-5'-octylphenyl)-benzotriazole	UVA-329	9.30	5.9

CONCEPTUAL AND NUMERICAL MODELS

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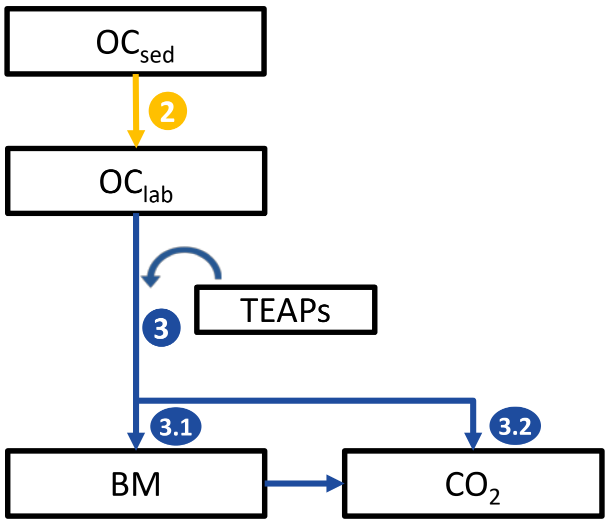
CONCEPTUAL MODEL



1 UV-filter sorption

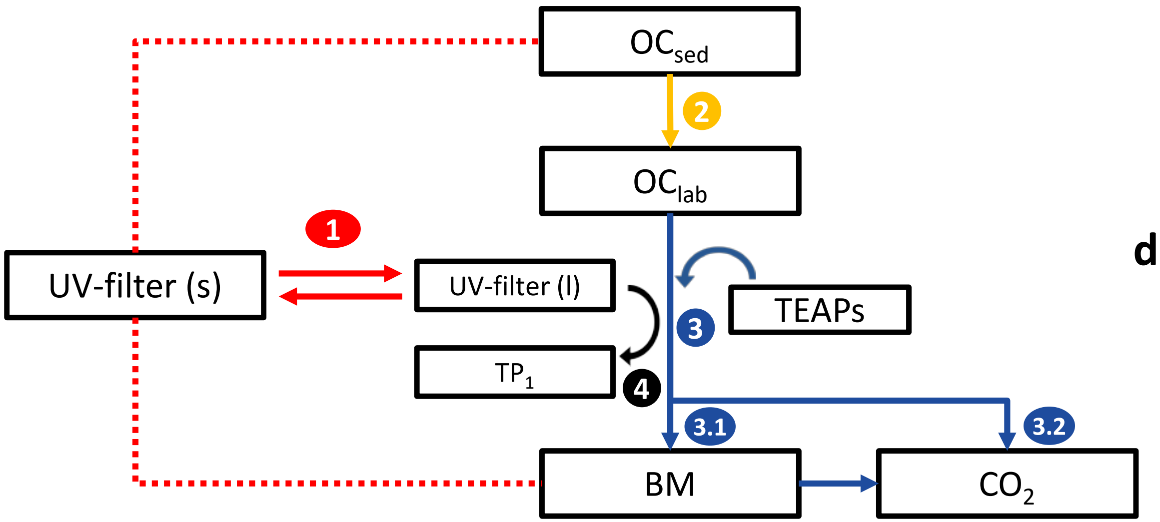
2 Hydrolisis of OC_{sed}

3 Oxidation of labile OC and growth of biomass

4 Co-metabolic degradation of UV-filters

OC_{sed} Sedimentary organic carbon
OC_{lab} Labile organic carbón
TP Transformation product
TEAPs Electron Acceptor
BM Biomass

CONCEPTUAL MODEL



UV-filter's fate depends on biogeochemical processes

⇩

Coupling sorption and degradation of UV filters with geochemical models

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OC_{sed} Sedimentary organic carbon
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NUMERICAL MODEL

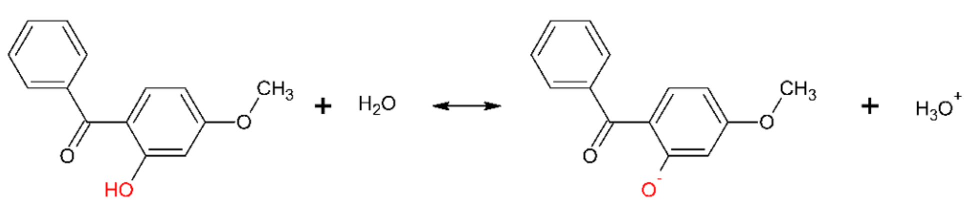
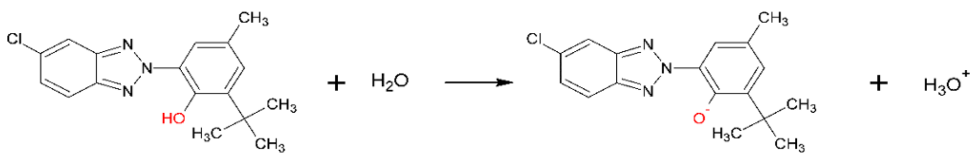
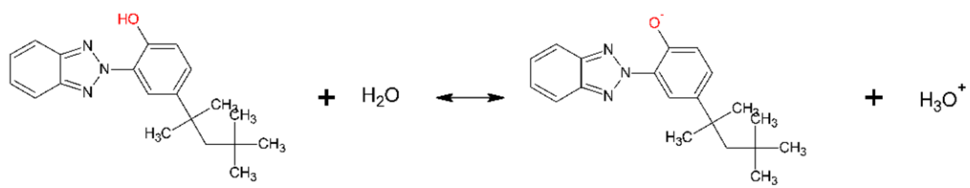
1. **Extension of the geochemical database**:
    1. incorporation of the ionic UV-filters into the geochemical speciation and interaction with pH
    2. incorporation of sorption reactions with SOM and with biomass

2. **Construction of biogeochemical modeling**

3. **Construction of co-metabolic degradation model coupled to biogeochemical processes**

NUMERICAL MODEL

Extension of the geochemical database: incorporation of the ionic UV-filters into the geochemical speciation and interaction with pH

Reaction	logK
Speciation reactions of ionic UV filters [1]	
Speciation of BP3 (as an organic acid) and formation of $BP3^-$ 	7.07
Speciation of UVA-326 (as an organic acid) and formation of UVA-326$^-$ 	10.08
Speciation of UVA-329 (as an organic acid) and formation of UVA-329$^-$ 	9.3

NUMERICAL MODEL

Extension of the geochemical database: incorporation of sorption reactions with SOM and with biomass

$$K_{d_{UV,TOT}} = \sum_{j=1}^{j} \sum_{i=1}^{i} K_{d_{i,j}}$$

where "i" is referred to the different sorbents (1=SOM and 2=biomass), and "j" to the different form of the UVs (1=neutral and 2=ionic form).

Sedimentary Organic Matter:

$$K_{d_{UV,SOM}} = \frac{[K_{oc,UV_0} + K_{oc,UV_{[-]}} K_a / [H^+]] f_{oc}}{1 + \frac{K_a}{[H^+]}} \xrightarrow[K_{OC_{UV[-]}} \ll K_{OC_{UV[0]}}]{K_a / [H^+] << 1000} K_{d\,UV,SOM} \sim \frac{K_{oc_{UV_0}} f_{oc}}{1 + \frac{K_a}{[H^+]}}$$

Biomass:

$$K_{d_{UV,X}} = \frac{[K_{X,UV_{[-]}} K_a / [H^+]] f_{sites}}{1 + \frac{K_a}{[H^+]}}$$

Only ionic compounds interact with biomass

NUMERICAL MODEL

Extension of the geochemical database: incorporation of sorption reactions with SOM and with biomass

Reaction	logK[1]
Sorption of ionic UV filters to SOM [2]	
BP3 + ≡SOM ↔ BP3≡SOM	-97.4736
OMC + ≡SOM ↔ OMC≡SOM	-96.6744
OC+ ≡SOM ↔ OC ≡SOM	-96.4540
UVA-326 + ≡SOM ↔ UVA-326≡SOM	-96.6803
UVA-329 + ≡SOM ↔ UVA-329≡SOM	-96.6187
Sorption of ionic UV filters to Biomass (X) [3]	
$BP3^{-}$+ ≡X ↔ $BP3^{-}$ ≡X	Fitted
UVA-326^{-}+ ≡X ↔ UVA-326^{-} ≡X	Fitted
UVA-329^{-}+ ≡SOM ↔ UVA-329^{-} ≡SOM	Fitted

Experimentally determined in abiotic experiments (only SOM)

$$K_{d_{UV,X}} = \frac{[K_{x,UV_{[-]}} K_a / [H^+]] f_{sites}}{1 + \frac{K_a}{[H^+]}}$$

It was assumed 1 (all biomass surface acts as a sorbent)

NUMERICAL MODEL

Co-metabolic degradation: coupling geochemical processes with UV filters degradation

Degradation of labile organic carbon:

$$r_{ED} = -k_{max} \frac{[ED]}{[ED]+K_{S,ED}} \frac{[EA]}{[EA]+K_{S,EA}} [X]$$

$$r_{EA} = Q r_{ED} - Sb[X]$$

$$r_X = -Y_h r_{ED} - b[X]$$

Release of labile organic carbon from Sedimentary Organic Matter:

$$r_{DOC} = -k_{max} [SOM]$$

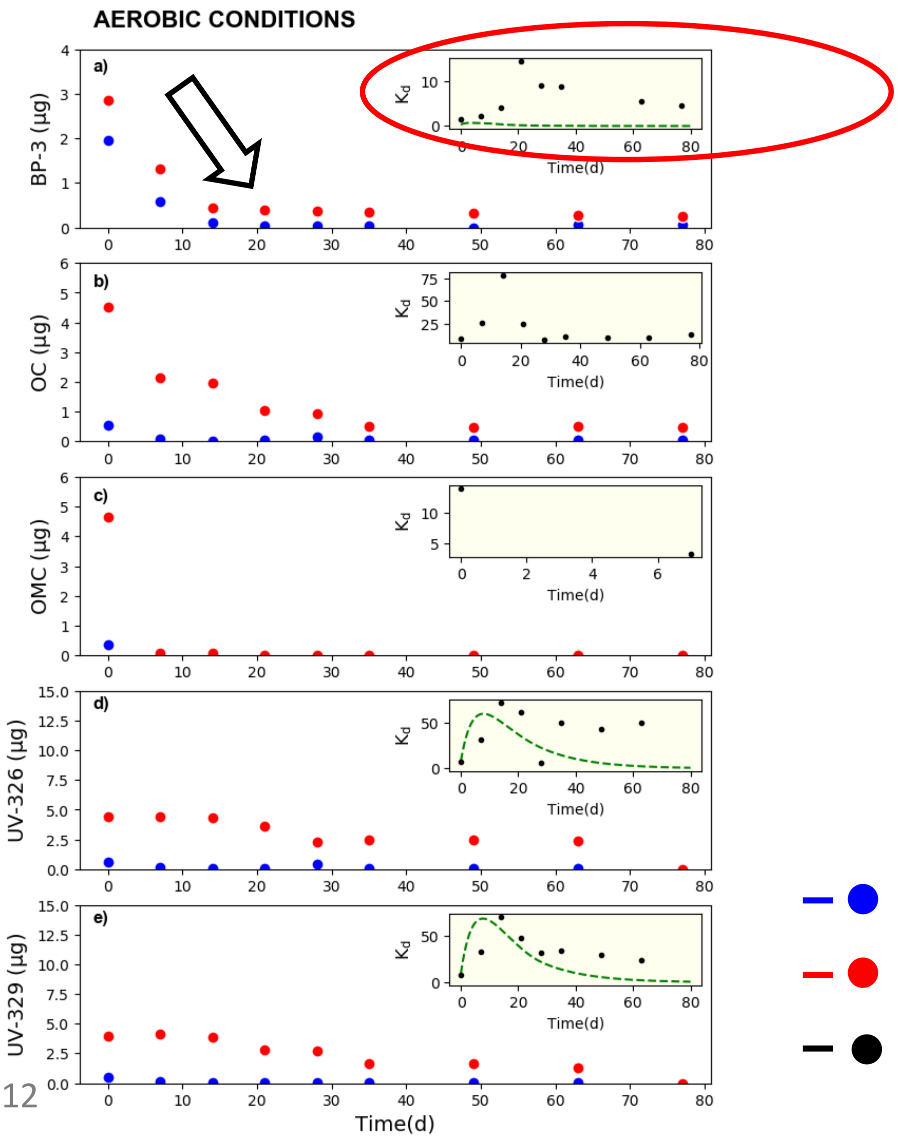
UV filter degradation coupled to oxidation of organic carbon:

$$r_j = -C_j k_{j,i} F_i \qquad j = BP3, OMC, OC, UV326, UV329$$

RESULTS

RESULTS

Modeling results: evolutoin of UV filters in water and solid surfaces



— ● Aqueous mass

— ● Solid mass

— ● K_d (full model)

— K_d without biomass as a sorbent

Rodríguez-Escales and Sanchez-Vila, Water Research 2020

RESULTS

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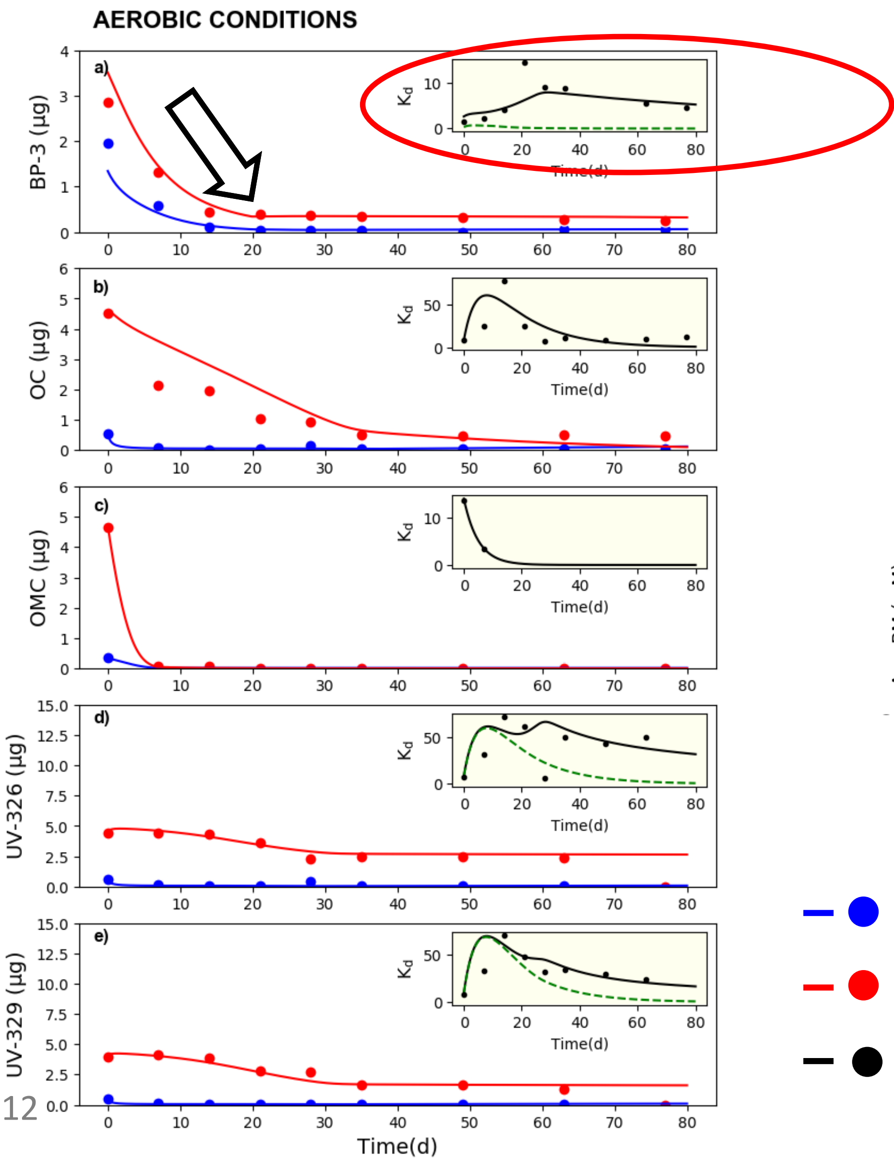

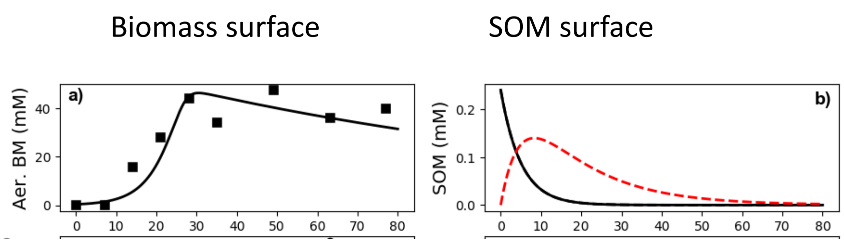

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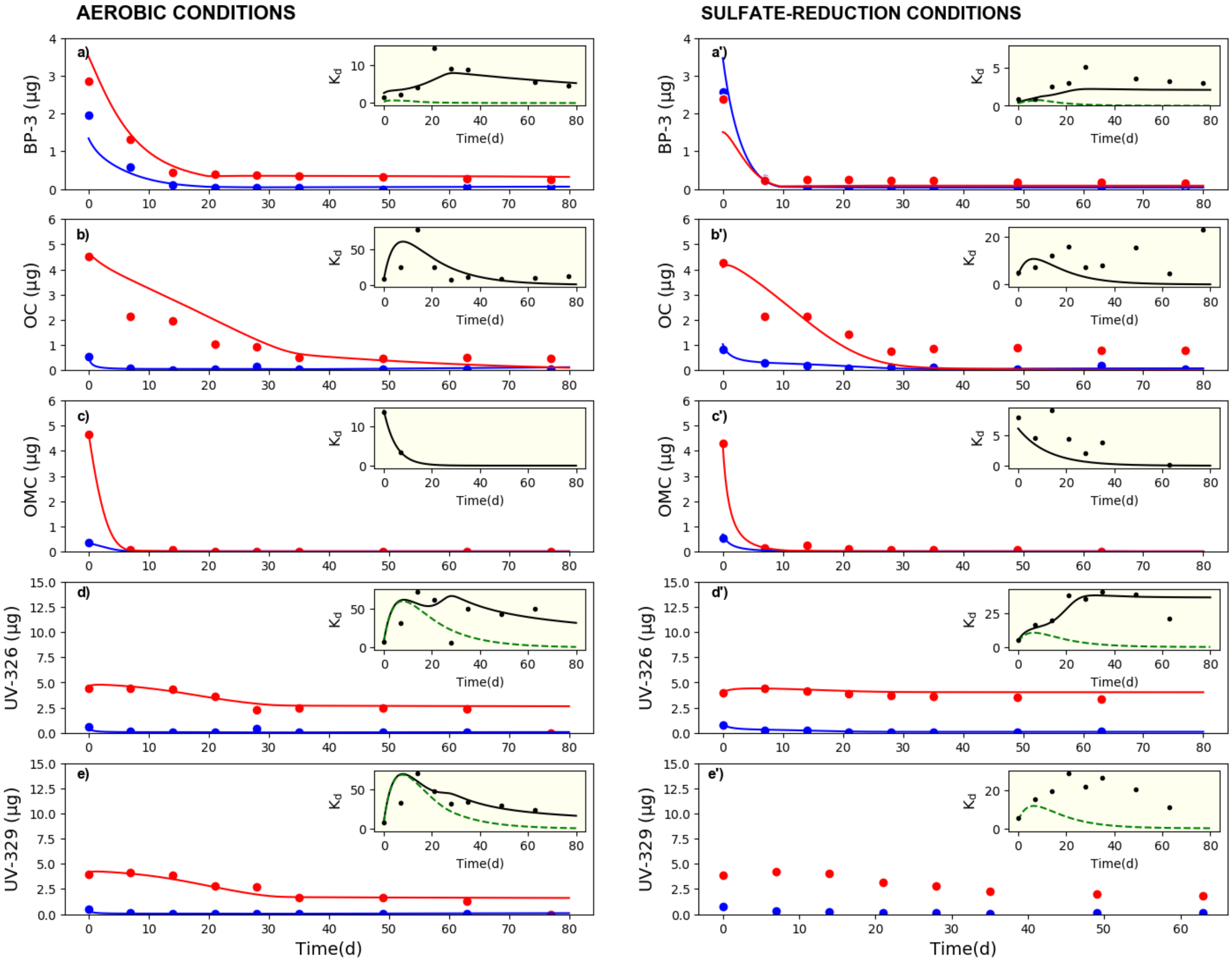
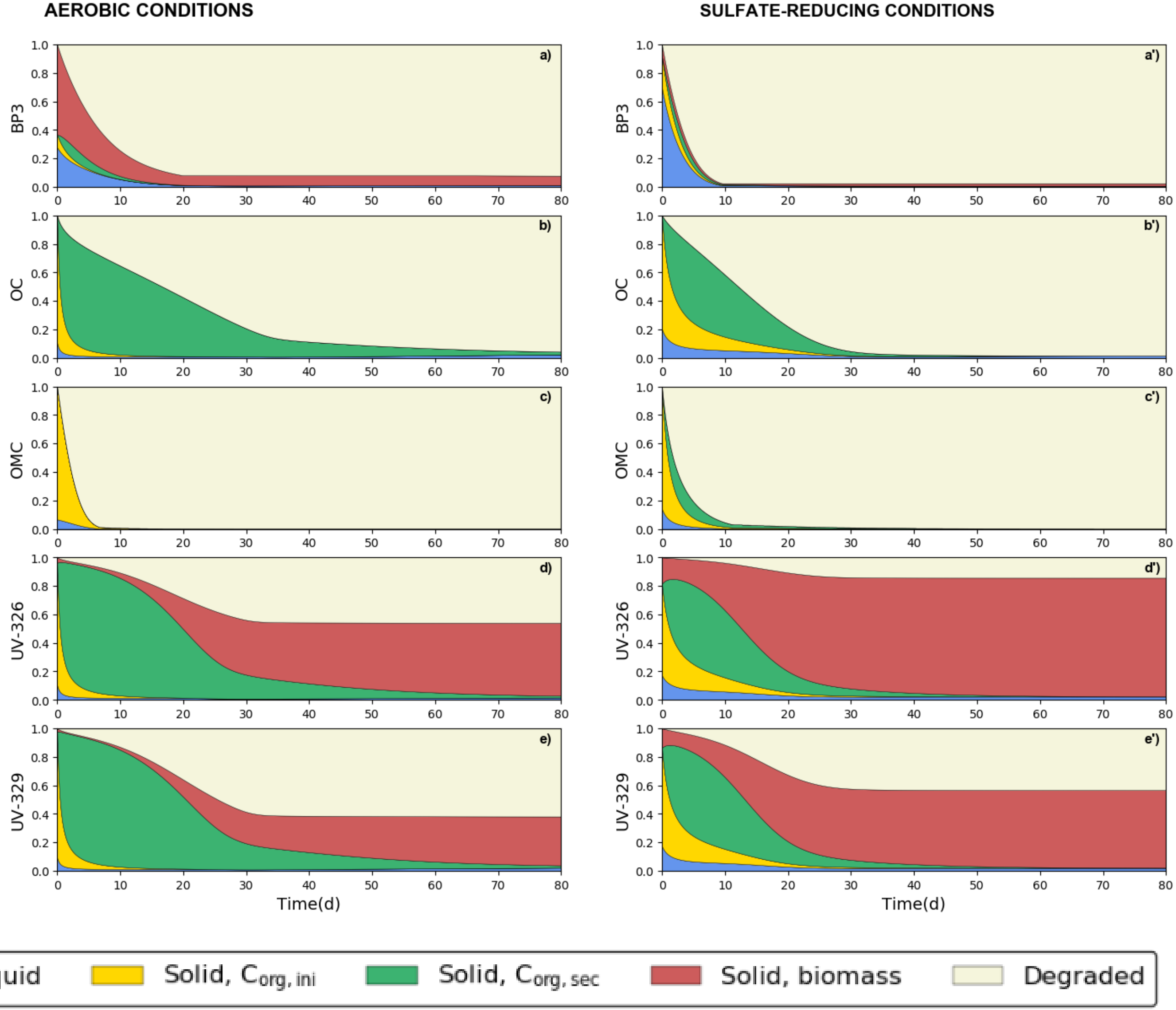


Rodríguez-Escales and Sanchez-Vila, Water Research 2020

RESULTS

Effect of redox conditions in the fate of UV filters



[Rodríguez-Escales and Sanchez-Vila, Water Research 2020]

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CONCLUSIONS

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1. We have developed a geochemical model for UV filters, that considers co-metabolic degradation and sorption to two different pools of sorbents: sedimentary organic carbon and biomass.

2. In this work we have demonstrated that **biomass can act as an important sorbent for ionic UV filters** (BP-3, UV-326 and UV-329) in porous media.

3. We further conclude that redox conditions, by themselves, do not condition the fate of UV filters (similar degradation constants). Nevertheless, **redox conditions affect the biomass growth, showing a much higher growth of aerobic biomass than anaerobic one, and also modifying the pH.**

More information is available in [Rodríguez-Escales et al. 2020]

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