



Modeling the fate of UV filters in subsurface: Co-metabolic degradation and the role of biomass in sorption processes

P. Rodríguez-Escales ^{a, b, *}, X. Sanchez-Vila ^{a, b}

^a Dept. of Civil and Environmental Engineering, Universitat Politècnica de Catalunya, Jordi Girona 1-3, 08034, Barcelona, Spain

^b Associated Unit: Hydrogeology Group (UPC-CSIC), Spain

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ABSTRACT

Ultraviolet filters (UVFs) are emerging organic compounds found in most water systems. They are constituents of personal care products, as well as industrial ones. The concentration of UVFs in the water bodies in space and time is mostly determined by degradation and sorption, both processes being determinant of their bioavailability and toxicity to ecosystems and humans. UVFs are a wide group of compounds, with different sorption behavior expected depending on the individual chemical properties (pK_a , K_{oc} , K_{ow}). The goal of this work is framed in the context of improving our understanding of the sorption processes of UVFs occurring in the aquifer; that is, to evaluate the role of biomass growth, solid organic matter (SOM) and redox conditions in the characterization of sorption of a set of UVFs. We constructed a conceptual and a numerical model to evaluate the fate of selected UV filters, focused on both sorption and degradation. The models were validated with published data by Liu et al. (2013), consisting in a suite of batch experiments evaluating the fate of a cocktail of UVs under different redox conditions. The compounds evaluated included ionic UV filters (Benzophenone-3; 2-(3-*t*-butyl-2-hydroxy-5-methylphenyl)5-chloro-benzotriazole; 2-(2'-hydroxy-5'-octylphenyl)-benzotriazole) and neutral ones (octyl 4-methoxycinnamate; and octocrylene).

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1. Introduction

Ultraviolet filters (UVFs) are emerging organic compounds (EOCs) commonly found in water systems (Jurado et al., 2014). They are found worldwide as they are constituents of a large number of widely used personal care products (e.g., sunscreens, perfumes, creams, body lotions or shampoos), but also of a number of industrial applications (furniture varnishes, paints). UVFs form a wide group of organic compounds with different chemical properties; the most common ones found are Benzophenone-3 (BP-3), plus a number of its derivatives, 3-(4-methylbenzylidene) camphor (4-MBC), octyl 4-methoxycinnamate (OMC), octocrylene (OC), 2-(3-*t*-butyl-2-hydroxy-5-methylphenyl)5-chloro-benzotriazole (UV-326), and 2-(2'-hydroxy-5'-octylphenyl)-benzotriazole (UV-329). Some of them (4-MBC and OMC) have been reported in the literature as endocrine disruptors (Calafat et al., 2008; Fent et al., 2006; Schlumpf et al., 2004). Human exposure to benzophenone

derivatives has been associated with estrogen-dependent diseases such as women endometriosis (Kunisue et al., 2012).

UVFs can enter the water systems either directly through recreational activities (swimming and bathing), runoff from rainfall in contact with construction sites or garden furniture, but also indirectly, by the supply of untreated (raw effluent), insufficiently treated (primary effluent), or partially treated (secondary effluent) sewage waters. Consequently, they have been detected in all types of water bodies: surface waters (Giokas et al., 2004; Kawaguchi et al., 2006), seawater (Kawaguchi et al., 2006), wastewater (Giokas et al., 2004; Li et al., 2007), and groundwater (Jurado et al., 2014). Furthermore, UVFs have also been found sorbed in a number of environmental matrices: sewage sludge (Gago-Ferrero et al., 2011b; Nieto et al., 2009), sediments (Baron et al., 2013; Gago-Ferrero et al., 2011a), and biota – fish and invertebrates (Balmer et al., 2005; Fent et al., 2010; Gago-Ferrero et al., 2013), altogether suggesting that, aside from degradation, sorption is arguably the most determinant factor governing the concentration of UVFs in the water bodies, and thus their bioavailability and toxicity to ecosystems and humans.

The extent of sorption partitioning –defined as the distribution

* Corresponding author. Dept. of Civil and Environmental Engineering, Universitat Politècnica de Catalunya, Jordi Girona 1-3, 08034, Barcelona, Spain.

E-mail address: paula.rodriguez.escales@upc.edu (P. Rodríguez-Escales).

of an organic compound between the solid and the aqueous phase of a given EOC is compound-dependent, and it is governed either by its affinity for organic phases (hydrophobic partitioning) or by electrostatic and similar interactions between ionized molecules and charged solid surfaces (non-hydrophobic partitioning) (Franco et al., 2009; Polesel et al., 2015; Torresi et al., 2017). At equilibrium, sorption and desorption rates are equal. Then, the ratio of concentrations of sorbed C_s^* -mass per unit of mass of solids [MM⁻¹]- and dissolved C_w^* -mass per volume of water [ML⁻³]- species is characterized by the solid-liquid partitioning coefficient, $K_d = C_s^*/C_w^*$. K_d [L³M⁻¹] is a lumped sorption coefficient, being the sum of different species-specific partitioning coefficients (Franco et al., 2009) use the term “apparent coefficient”).

As a general rule, neutral organic compounds have a quite limited water solubility, mainly because water molecules change their overall H-bonding to their surroundings when forced to interact with nonpolar compounds. On the other hand, organic matter minimizes the hydrophobic surface area, because it exists in large part as organic chains coiled into globular units, much like globular proteins, and occurs in somewhat isolated patches coating mineral solids. Consequently, neutral organic compounds can physically penetrate between the chains and find themselves “dissolved” in the non-aqueous medium (Schwarzenbach et al., 1993). This type of sorption of neutral compounds is termed “absorption”, and it is mainly related to the partitioning between the organic matter and water (K_{oc} , [L³M⁻¹], tabulated in many chemical databases), and to the amount of organic matter (f_{oc} , [-]). Then, sorption partitioning is given as:

$$K_d = K_{oc} \cdot f_{oc} \quad (1)$$

When an organic compound includes ionized structural components ($-COO^-$, $-NH_3^+$, $-SO_3^-$, ...), a variety of processes become significant for sorption: (1) the electrostatic interactions with charged sites on the sorbent, and (2) exchange reactions with ligands previously bound to the solid. Note that the extent of solid association of ionic compounds also varies as a function of external factors like the pH of the solution, since pH governs both the presence of charges on mineral surfaces and the fraction of organic compound present in ionized form (through pK_a) (Franco et al., 2009; Schaffer et al., 2012). Solution ionic strength and ionic composition also affect the sorption of charged organic chemicals, especially if inorganic and organic ions compete for the binding sites. The mineral surface composition of the sorbent is also key; for example, oxides and hydroxides - like quartz or goethite mineral surfaces - present ionic radicals in their surfaces. Besides this, the age of organic matter also plays an important role in sorption properties, implying a distributed reactivity and increasing the heterogeneity of the environment (Kleineidam et al., 2002; Weber et al., 1992)(Kleineidam et al., 2002; Weber et al., 1992).

Traditionally, in natural environments, sorption of organic compounds is characterized by only regarding the properties of the compounds (K_{oc}), and a somewhat static sorption environment, considering only the fraction of organic carbon (f_{oc}), leading to an individual K_d value if equilibrium conditions are assumed. Then, when sorption is introduced in the advection-dispersion equation, the storage term becomes multiplied by a constant retardation factor (R [-]) given by:

$$R = 1 + \frac{\rho}{n} K_d, \quad (2)$$

where ρ [ML⁻³] denotes the bulk density and n [-] the effective porosity of the soil. Although, most of the reviewed literature considers this simple model (Burke et al., 2013; Henzler et al., 2014; Schaffer et al., 2015), the assumption of constant R is only realistic

when the environment is static, meaning the simultaneous verification of three conditions: 1) no changes in hydrochemistry (constant pH and ionic strength); 2) the organic compounds being always neutral; and 3) the amount and the properties of sorbent being kept constant. As an example, all three conditions are met in a sterile environment (e.g., Burke et al., 2013).

Therefore, considering a constant retardation factor in dynamic environments could lead to making mistakes in predicting the fate of organic compounds, mainly the ionic ones. Knowing the actual relevance of this simplification remains a challenge in most environments, but would be definitely an issue in those with active redox reactions, such as biodegradation, for several reasons. First, redox reactions in groundwater can vary pH, typically in the 6 to 8 range (Brun and Engesgaard, 2002); this could be relevant in sorption of ionic compounds that have pK_a 's values in that same range, such as a number of benzophenones (pK_a 's values being 7.07 for Benzophenone-3; 7.09 for Benzophenone-1; 6.75 for Benzophenone-2, and 7.85 for 4-Benzophenone (estimated by Chemaxon)). Second, in active redox systems, organic carbon sediments could be oxidized, thus changing some sorbent properties; this includes its potential complete disappearance by dissolution or mineralization, or the reappearance of other organic sediment surfaces with different sorption properties. Last, in redox active zones, there is a growth of microorganisms due to the oxidation of organic matter, implying the production of solid biological compounds, like extracellular polymeric substances (EPS), and the formation of biofilms. Both microorganisms and biological material can act as sorbents of organic compounds. Although in wastewater treatment, sorption of organic compounds in active sludge has been observed (Torresi et al., 2017), this assumption has not yet been addressed in the groundwater literature.

All the three mentioned issues are quite relevant in Managed Aquifer Recharge (MAR) facilities, hyporheic zones and bioremediation applications. In all cases, the biological processes are very active and many redox reactions are occurring simultaneously (Greskowiak et al., 2006). This phenomenon is enhanced in recharge applications, e.g., by the presence of a reactive layer of organic matter (Beganskas et al., 2018; Grau-Martínez et al., 2017; Valhondo et al., 2014), that could lead to biomass growth and bioclogging (Barba et al., 2019; Massmann et al., 2006; Perujo et al., 2018). Besides this, recharge processes are a relevant source of EOCs (here including UVFs) into aquifer systems (Kim et al., 2017; Laws et al., 2011; Maeng et al., 2011; Park and Lee, 2018).

As stated above, the chemical properties (pK_a , K_{oc}) of the different UVFs govern the individual expected sorption behavior. This work aims at improving the understanding of sorption processes occurring in the aquifer of a set of UVFs, with emphasis in the specific role of biomass growth, organic sediment, redox conditions and pH. In section 2 we present a conceptual model to evaluate the fate of selected UV filters, mainly focused on sorption processes but also on degradation, plus the development of the corresponding numerical model. The models were validated with data published in the literature, consisting in batch experiments evaluating the fate of a cocktail of UVFs (both ionic and neutral) under different redox conditions. Section 3 provides the results of the modeling process followed by a discussion on the role and significance of the different processes in the fate of UV filters. This is followed by a concluding section.

2. Model development

2.1. Experimental data description and conceptualization of the fate of UV filters

To frame the conceptual and the numerical models, we start by

introducing the experimental data from Liu et al. (2013), involving a set of batch experiments targeting on the biodegradation of five UVFs in aquifer materials. Both the groundwater and the sediments (mainly composed by carbonates), were obtained from an aquifer at Bolivar (South Australia). The physicochemical properties of the UVFs are shown in Table 1. The experiments were performed under different redox conditions (aerobic and anaerobic-nitrate, sulfate and iron reducing conditions), all in triplicate, plus sterile controls. Each batch test included 5 g of aquifer material and 5 mL of groundwater, and spiked with 50 μ L of UVF mixture stock solution, prepared in methanol. The experiments were incubated at 20 °C and sampled at days 0, 7, 14, 21, 28, 35, 49, 63, and 77. The sterile control was autoclaved and the metabolic activity was inhibited by adding sodium azide (NaN_3). In the aerobic experiment, this condition was maintained by opening the caps three times a day inside a laminar flow chamber. For the anaerobic ones, all the preparations were carried out under an $\text{N}_{2(g)}$ atmosphere. The anaerobic microcosms were constructed using Hungate tubes, flushed with nitrogen gas and sterilized, and then either un-amended with the electron acceptors as the anaerobic control sulfate in the case of sulfate-reducing conditions. Liu et al. (2013) analyzed both the aqueous and the solid concentrations of the five UVFs; from those results and considering that sorption was in equilibrium, we calculated the K_d values. Different authors concluded that considering sorption in equilibrium compared to degradation is quite plausible, especially when dealing with recalcitrant organic compounds, like UVFs (Barret et al., 2011; Joss et al., 2006; Rodríguez-Escales et al., 2013).

2.2. Model conceptualization

Any conceptual model on the fate of UVFs should include all the relevant processes that influence either degradation or sorption, sketched in Fig. 1. Degradation was conceptualized as co-metabolic (process 4 in Fig. 1) occurring due to the oxidation of labile and

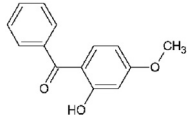
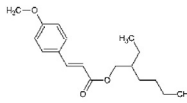
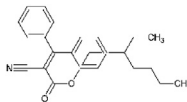
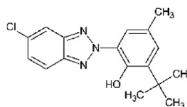
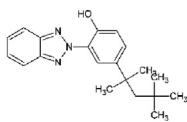
dissolved organic carbon (DOC) (process 3) by the relevant electron acceptor (oxygen, nitrate, or sulfate), and mediated by microorganisms (biomass). Consequently, besides the production of inorganic carbon (process 3.2), there is a growth of heterotrophic biomass (process 3.1), eventually decaying and being oxidized to inorganic carbon. We hypothesized that biomass also acted as a sorbent of UVF. At this point, biomass was treated as a pool of organic carbon from the oxidation of DOC, thus, we did not distinguish where the sorption occurred (e.g. surface of wall cells, EPS's of biofilm). In the experiments, the labile organic carbon was added externally, but it could be also produced by the hydrolysis of sedimentary organic matter (SOM) (process 2).

Several factors, such as pH, temperature and oxidant concentrations, affect the reactivity of SOM towards oxidants and environmental conditions (Hartog et al., 2004; van Bergen et al., 1998). As the experiments were amended with high concentration of oxidants, it is also reasonable to believe that SOM reacted to become labile organic carbon. At this point, we introduced the possibility that SOM was not degraded directly into dissolved organic carbon and we tested a second scenario considering the creation of a secondary SOM (SOM_{sec}) (see process 2.1 in Fig. 1). Thus, we proposed two possibilities of conceptual model: 1) with two organic surfaces as sorbents: SOM and biomass material (surface of microbes or EPS); and 2) with three surfaces as sorbents (SOM, SOM_{sec} and biomass material).

2.3. Numerical model

The conceptual model was turned into a set of equations to reproduce all the processes mentioned, then described in the following subsections. Similarly as Rodríguez-Escales and Sanchez-Vila (2016), the kinetic reactions postulated were introduced into the geochemical code PHREEQC (Parkhurst and Appelo, 1999), thus coupling the processes affecting the fate of UVFs with the more common hydrochemical reactions. PHREEQC calculates the

Table 1
Physicochemical properties of the UV-filters included in this study. (1) Estimated by using EPIWEB (PCKOCWIN v1.66); (2) Estimated by ChemAxon; (*) Neutral compound.

| Compound and CAS number | Structure | Properties | | | |
|---|---|------------------|---------------------|---------------------|----------------|
| | | Molecular Weight | $\log K_{oc}^{(1)}$ | $\text{pK}_a^{(2)}$ | $\log P^{(2)}$ |
| Benzophenone-3 (BP-3) 131-57-7 |  | 228.25 | 3.10 | 7.07 | 3.62 |
| octyl 4-methoxycinnamate (OMC) 5466-77-3 |  | 290.41 | 4.09 | NC | 5.38 |
| Octocrylene (OC) 6197-30-4 |  | 361.49 | 5.61 | NC | 6.78 |
| 2-(3- <i>t</i> -butyl-2-hydroxy-5-methylphenyl)5-chloro benzotriazole (UV-326) 3896-11-5 |  | 315.5 | 6.07 | 10.08 | 5.33 |
| 2-(2'-hydroxy-5'-octylphenyl)-benzotriazole (UV-329) 3147-75-9 |  | 323 | 6.55 | 9.30 | 5.96 |

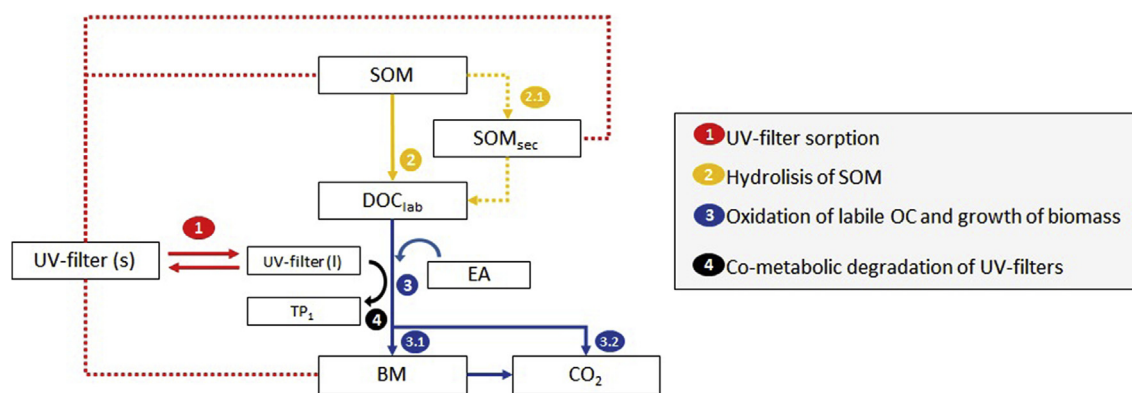


Fig. 1. Processes affecting the fate of UV filters in aquifers and soils. DOC Dissolved Organic Carbon; sed – sediment; lab – labile; SOM- Sedimentary Organic Matter; BM – biomass; EA - Electron Acceptor; TP – Transformation Product.

equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces by applying the law of mass action complemented by the thermodynamic parameters present in a geochemical database that can be modified or extended by the modeler.

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

We incorporated into the PHREEQC geochemical database the speciation of three ionic UVFs: BP-3, UV-326 and UV-329. As complex organic molecules, the acidity and the basicity depend on the functional groups that have either proton donor or proton acceptor properties, leading consequently to different pK_a values. In Table 2, we list the reactions involving UVFs that were incorporated into the database. In this case, the three compounds could behave as organic acids due to the hydroxyl group bounded to aromatic

rings, with a pK_a of 7.07 for BP-3, 10.08 for UV-326 and 9.3 for UV-329. The $\log K$ introduced in the database was taken as equivalent to the pK_a . Note that, in the case of BP-3, the potential formation of the ionic compound is relevant at pH values typical of natural aquifers (on the range 6–8). In fact, the fraction of the neutral compound (α_{UV_0}) is a function of pH (e.g., Schwarzenbach et al., 1993), by:

$$\alpha_{UV_0} = \frac{1}{1 + K_a/[H^+]}, \quad (3a)$$

while, similarly, the fraction of the ionic compound (α_{UV_a}) is given by

$$\alpha_{UV_a} = \frac{K_a}{[H^+] + K_a}. \quad (3b)$$

Both the pK_a and the different ionic molecular forms were extracted from Chemicalize, <https://chemicalize.com/developed> by

Table 2

Set of reactions added to the database concerning the formation of the ionic compounds of UV-filters.

| Reaction | logK |
|--|-------|
| Speciation reactions of organic acids and the formation of the corresponding ionic UV filters | |
| Speciation of BP-3 (as an organic acid) and formation of BP-3 ⁻ | |
| | 7.07 |
| Speciation of UVA-326 and formation of UVA-326 ⁻ | |
| | 10.08 |
| Speciation of UVA-329 and formation of UVA-329 ⁻ | |
| | 9.3 |

ChemAxon (<http://www.chemaxon.com>). UV-326 and UV-329 have also a basic pK_a equal to -0.96 and 0.84 , respectively, in the nitrogen atoms of the benzotriazole rings. We did not include them, as significant formation of the ionic form is not expected for the pH values typical of natural aquifers.

2.3.2. Sorption model between the active surfaces (SOM and biomass) and UV-filters

Sorption and desorption were modeled as surface complexation reactions between the two active surfaces (SOM and biomass) and the different UVFs (both ionic and neutral forms). We assumed that sorption was always in equilibrium, thus characterized by K_d . In Table 3, there are the sorption reactions we defined in the PHREEQC database with the corresponding values of $\log K$ (from K_{oc} , see equation (1)). As Liu et al. (2013) performed control and abiotic experiments, considering only sorption (no degradation), we determined the corresponding experimental K_{oc} and K_d values taking into account the amount of organic carbon (f_{oc} equal to 0.004). As there were different sorbents and some of the UV filters were ionizable, the total K_d , denoted $K_{d_{UV,TOT}}$, is defined as the sum of the K_d values in the different media and in the different forms (neutral and ionic):

$$K_{d_{UV,TOT}} = \sum_{j=1}^2 \sum_{i=1}^3 K_{d_{ij}} \quad (4)$$

where “i” is referred to the different sorbents (1 = SOM, 2 = SOM_{sec} and 3 = biomass), and “j” to the different form of the UVFs (1 = neutral and 2 = ionic form).

SOM can sorb both to the neutral and the ionic forms of organic compounds (Schwarzenbach et al., 1993). Since the concept of SOM is very large and global – it covers multiples of molecules (cellulose, lignin, fulvic acids or humic acids) - there are several sorption mechanisms involved: H-bonding, ionic interactions, van der Waal forces, and absorption. If an ionic form of a UV molecule is present, Schwarzenbach et al. (1993) defines $K_{d_{UV,SOM}}$ as:

$$K_{d_{UV,SOM}} = \frac{K_{oc,UV_0} + K_{oc,UV_a} K_a / [H^+]}{1 + K_a / [H^+]} f_{oc} \quad (5)$$

where K_{oc,UV_0} and K_{oc,UV_a} are referred to the organic carbon partition of the UVF at neutral and at ionic forms, respectively, which in this work were considered equal for simplicity and lack of additional data. This expression is equivalent to the K_{oc} definition of Franco et al. (2009) and Schaffer et al. (2012). The neutral form is relevant for low pH values, equivalent to $K_a / [H^+] \ll 1$. In this case, expression (5) can be approximated as:

$$K_{d_{UV,SOM}} = K_{oc,UV_0} f_{oc} \quad (6)$$

Table 3

Set of reactions added to the database in order to consider the sorption of UV-filters into SOM and biomass (X). (1) $\log K$ was related to K_{oc} , determined by $\log K_{d,PHREEQC} = \log K_{oc} - \log m_{org} = \log K_{oc} - \log(10^{100})$. The $\log K_{oc}$ values were determined from the control experiments without degradation of Liu et al. (2013).

| Reaction | $\log K$ ($\log K_{oc}$) |
|---|----------------------------|
| Sorption of UV filters to SOM | |
| BP-3 + \equiv SOM \leftrightarrow BP-3 \equiv SOM | -97.4736 (2.53) |
| OMC + \equiv SOM \leftrightarrow OMC \equiv SOM | -96.6744 (3.33) |
| OC+ \equiv SOM \leftrightarrow OC \equiv SOM | -96.4540 (3.55) |
| UVA-326 + \equiv SOM \leftrightarrow UVA-326 \equiv SOM | -96.6803 (3.32) |
| UVA-329 + \equiv SOM \leftrightarrow UVA-329 \equiv SOM | -96.6187 (3.38) |
| Sorption of ionic UV filters to Biomass (X) | |
| BP-3 ⁻ + \equiv X \leftrightarrow BP-3 ⁻ \equiv X | Fitted |
| UVA-326 ⁻ + \equiv X \leftrightarrow UVA-326 ⁻ \equiv X | Fitted |
| UVA-329 ⁻ + \equiv SOM \leftrightarrow UVA-329 ⁻ \equiv SOM | Fitted |

Contrarily, the ionic form is only quantitatively relevant when the pH is close to pK_a , i.e., $1 \ll K_a / [H^+] \ll 1000$. If this is not occurring, expression (5) can be approximated as:

$$K_{d_{UV,SOM}} \approx \frac{K_{oc,UV_0} f_{oc}}{1 + \frac{K_a}{[H^+]}} \quad (7)$$

This is the case of UV-326 and UV-329 with pK_a 's of 10.08 and 9.3, respectively. But, using only this statement for simplifying (5) to (7) was not valid for BP3, since the pK_a is 7.07, quite close to the working pH's. Nevertheless, we also simplified the expression. Our reason, also followed by Schwarzenbach et al. (1993), was that the formation of the conjugate acid of BP-3 was in the phenolic ring, forming phenolate. As $K_{oc,BP3_a}$ is completely unknown, we looked at the K_{ow} of the BP-3 fragments following Lyman et al. (1992). The K_{ow} of the phenolic ring was more than three orders of magnitude higher than that of the phenolate (Lyman et al., 1992; Schwarzenbach et al., 1993), indicating that phenolate was much more soluble with less interaction to the solid surfaces. Consequently, we hypothesized that $K_{oc,BP3_a} \ll K_{oc,BP3_0}$, so that the simplification of (7) could be used.

The sorption of organic compounds into biomass (X) has been only related to ionic compounds (Flemming, 1995; Franco et al., 2009; Torresi et al., 2017). In porous media, biomass is organized in biofilms, which contains living organisms and also other biological materials such as EPS. In biofilms, sorption can act upon different regions (Flemming, 1995): i) EPS with cationic groups in amino sugars and proteins, and anionic groups in uronic acids and proteins; ii) outer membrane and lipopolysaccharides of gram-negative cells with their lipid membranes, the lipoteichoic acids in gram positive cells; iii) cell walls consisting of N-acetylglucosamine and N-acetylmuramic acid, offering more cationic and anionic sites. Although cation sorption in biofilms has been widely reported in the literature (Franco et al., 2009; Torresi et al., 2017), e.g., a wide variety of metal ions bound to EPS (Flemming et al., 1996), anionic sorption is also physically possible, due to the positive charges in amino groups in sugars, sugar acids and proteins. The literature on sorption of organic compounds in biofilms is poor and contradictory; for example, Torresi et al. (2017) only observed sorption into biofilm of 9 of 23 compounds, being the cationic ones. On the other hand, Späth et al. (1998) observed that BTEX sorbed to biomass, mainly to EPS. This was surprising, even for the authors, because EPS are mainly formed by water (Brangari et al., 2018) and sorption should be preferentially for polar compounds. As literature is not conclusive, we followed the hypothesis that sorption into biomass only occurred with polar compounds, thus, with ionic forms of UVs. Then, $K_{d_{UV,X}}$ was defined as follows:

$$K_{d_{UV,X}} = \frac{K_{X,UV_a} K_a / [H^+]}{1 + K_a / [H^+]} f_{sites} \quad (8)$$

where f_{sites} is related to the available sites for sorption of biomass and it is conceptually equivalent to the f_{oc} defined in (5); K_{X,UV_a} is the partitioning coefficient of ionic UVFs into biomass ($[UV_x^-]_{eq} / [UV_w]_{eq}$). This parameter is directly related to the $\log K$ values displayed in Table 2, fitted from experimental data.

2.3.3. Organic matter and co-metabolic degradation model

UVFs degradation was driven by co-metabolism, with the oxidation of labile organic matter as the main process, and, consequently, the broken up of the UVF molecules. The oxidation was conducted by electron acceptors (oxygen and sulfate) in a separate way, and coupled with the biomass growth/decay and with the degradation of UVFs. The degradation of the labile dissolved organic carbon and the growth of biomass were modeled

using equations (9)–(11), which were set up in previous works (Rodríguez-Escales et al., 2014, 2016):

$$r_{ED} = -k_{\max} \frac{[ED]}{[ED] + K_{S,ED}} \frac{[EA]}{[EA] + K_{S,EA}} [X] \quad (9)$$

$$r_{EA} = Qr_{ED} - Sb[X] \quad (10)$$

$$r_X = -Y_h r_{ED} - b[X] \quad (11)$$

where [ED] is the concentration of the electron donor (organic carbon, methanol); [EA] that of the electron acceptor (oxygen, nitrate or sulfate depending on the experiment), and [X] the biomass concentration (aerobic or sulfate-reducing, respectively), all in [ML⁻³]; k_{\max} [T⁻¹] is the consumption rate of electron donor per unit value of biomass; $K_{S,ED}$ and $K_{S,EA}$ [ML⁻³] the half saturation constants of electron donor and acceptor, respectively; b [T⁻¹] a biomass decay constant; Y_h the microbial yield [C biomass/C organic matter], and Q [EA/ED] and S [EA/C endogenous] are stoichiometric coefficients. The values of Q and S are 2.92 and 0.4 for aerobic conditions and 3.62 and 0.1 for sulfate-reducing ones. We did not consider an inhibition process due to the co-existence of different electron acceptors (typical in some Monod kinetics models, (Rodríguez-Escales et al., 2017)), since the different experiments involved only one electron acceptor each. The calibration process is described in Section 2.3.4.

Note that in the experiments of Liu et al. (2013), as it is also the case in most aquifers, there was a little amount of sedimentary organic carbon. The literature reports that, if a certain activity of oxidants is occurring, SOM can be hydrolyzed, releasing dissolved organic carbon into the system (Hartog et al., 2004). As the experiments were amended with a high quantity of oxidants, we incorporated the release of DOC from SOM as:

$$r_{DOC} = -k_{\text{prim}}[SOM] \quad (12)$$

Note that (11) has to be added to (8) to have the overall rate of DOC. As pointed out in the conceptual model, we also tested the possibility of the creation of a secondary SOM from the primary one, understood as an intermediate step until the formation of dissolved organic carbon. Then, the rate of SOM_{sec} was conceptualized as:

$$r_{SOMsec} = k_{\text{prim}}[SOM] - k_{\text{sec}}[SOM_{\text{sec}}] \quad (13)$$

On the other hand, the degradation rates of UVFs were assumed to depend on redox conditions as described by Liu et al. (2013), and simulated using the following first-order kinetic reaction:

$$r_j = -C_j \sum_{i=1}^n k_{j,i} F_i \quad (14)$$

where j represents the actual UVF, i represents the redox condition, up to the n ones where UVFs degradation were studied, and $k_{j,i}$ [T⁻¹] the first-order degradation constant for each species j at a specific redox state i . Since different redox conditions occurred simultaneously in the aquifer material during the simulations, we incorporated in (13) the activation factor F_i [–], which activated the degradation rate of UVF when oxidation of organic carbon occurred; it is defined as:

$$F_i = \frac{p}{p + q_i} \quad (15)$$

where p [ML³T⁻¹] is the rate of organic carbon degradation and q_i

[ML³T⁻¹] a constant which was related to the rate at degradation of UVF was activated. If $p \geq q_i$ degradation occurred without any problem, but if $p < q_i$ degradation was limited. The $k_{j,i}$ values were calibrated by fitting the model results with the experimental observations of UVFs in both aqueous and solid phases.

2.3.4. Initial conditions of the model and calibration process

Table 4 shows the initial concentration of the compounds considered in the biogeochemical model. The calcium concentration of Table 4 was calculated assuming equilibrium with calcite, acknowledging the sediment was composed of 10% calcite (Liu et al., 2013). On the other hand, as the solution in Liu et al. (2013) was not chemically balanced, we added enough sodium into the model to keep the electrostatic balance equal to 0. The organic carbon source was the methanol (2.47×10^{-1} M) added with the UVF mixture stock solution. For the sulfate-reducing condition, lactate (1×10^{-2} M) was considered the electron donor. The initial concentrations of UVFs were approximately 1 µg/g aquifer. The aerobic conditions were simulated by assuming equilibrium with the atmospheric oxygen. The sulfate-reducing conditions were kept by adding 20 mM of NaSO₄ and Na₂S as a reducing agent.

Regarding model parameters, the biogeochemical kinetic ones (k_{\max} , $K_{S,ED}$, $K_{S,EA}$, b) for the aerobic oxidation model and for the sulfate reduction model; the kinetic parameters of co-metabolic degradation of UVF (k_{ij} and F_i); and the sorption constant for ionic UVFs (K_{X,UV_i}) were first calibrated by hand and then refined automatically using code PEST (Doherty, 2005). PEST allowed computing the sensitivities, correlations, and confidence intervals for the optimized model parameters using the Levenberg-Marquardt algorithm. The weights of each chemical species associated to the measurement errors were applied using the inverse of the standard deviation of the confidence interval of measurements (95%). For calibration, we used the experimental information from Liu et al., (2013) (aerobic biomass, sulfate reducing biomass, sulfate, mass of UVFs in the aqueous and in the solid phases, and K_d 's of ionic UVFs). Finally, we evaluated the likelihood of the two conceptual models proposed regarding the formation of a secondary SOM comparing to different Information Criteria values calculated by PEST.

3. Results and discussion

3.1. Coupling degradation model of UVs with sorption

Fig. 2 shows the results of the co-metabolic degradation model of UVFs coupled to sorption processes considering both SOM and biomass as active surfaces. In the Figure, the two tested scenarios of conceptual models are shown: the first one, considering only one step between the SOM hydrolysis and the DOC formation, and the second one, considering the formation of a secondary SOM before the DOC formation (see Fig. 1). Besides this, we also added to the plot the results of the K_d without considering the role of the

Table 4

Initial concentrations considered in the biogeochemical model. In the sulfate-reducing scenario, Sulfate concentration was 20 mM.

| Compound | Concentration (M) | UV-filter | Concentration (M) |
|-------------------------|-----------------------|---------------|-----------------------|
| pH | 7.5 | BP-3 | 4.32×10^{-6} |
| Oxygen | 1.25×10^{-5} | OC | 2.81×10^{-6} |
| Nitrate | 1.43×10^{-6} | OMC | 3.33×10^{-6} |
| Sulfate | 2.65×10^{-3} | UV-326 | 3.04×10^{-6} |
| Inorganic carbon | 4.5×10^{-3} | UV-329 | 2.84×10^{-6} |
| Sodium | 7×10^{-3} | | |
| Calcium | 1.27×10^{-3} | | |

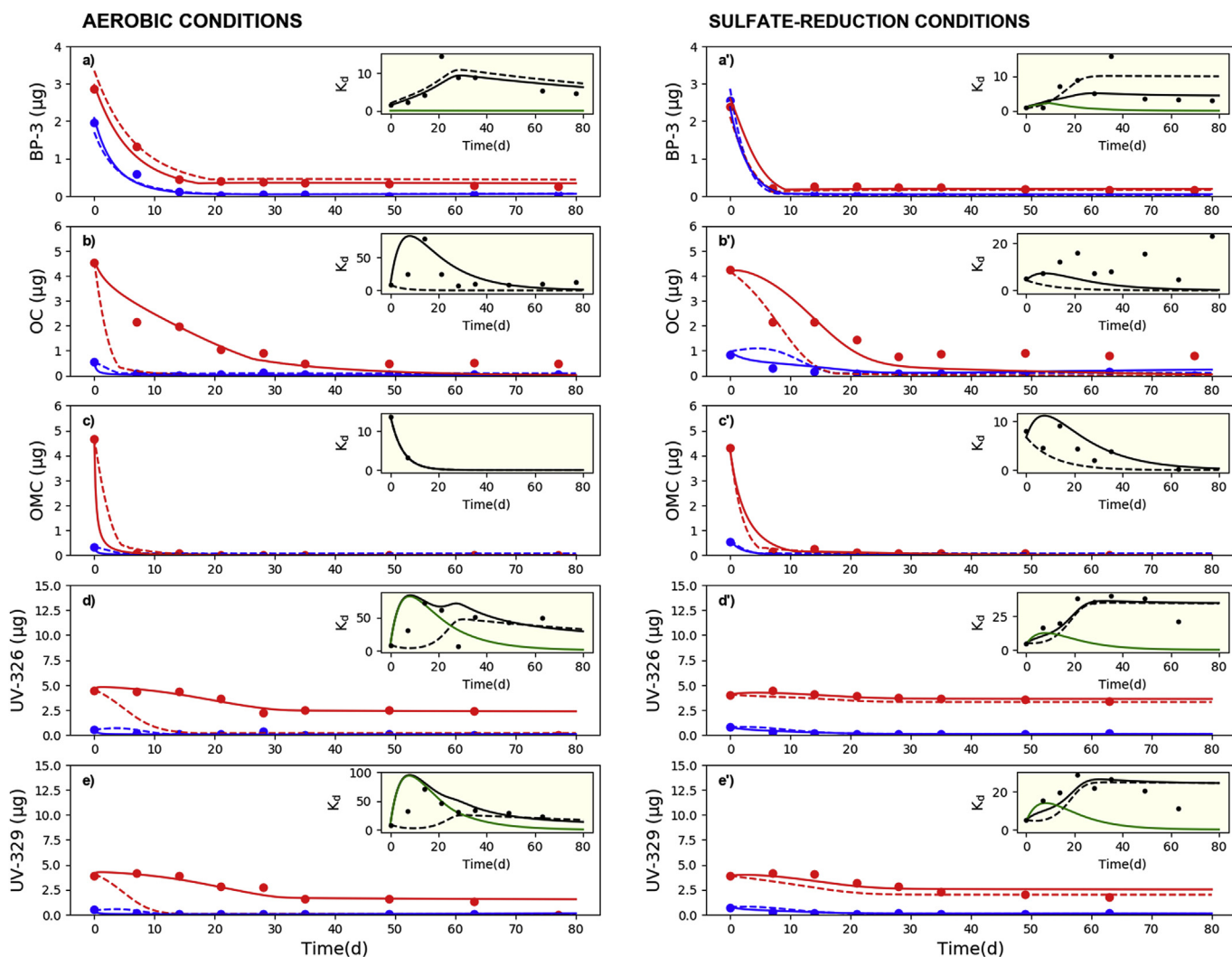


Fig. 2. Results of the model in terms of mass of UV filters as a function of time in both dissolved (blue) and solid (red) phases. Left: aerobic conditions, Right: sulfate-reduction conditions). Dashed lines correspond to first scenario model and the solid ones to the second one, where a transitional appearance of a secondary surface for sorption, being formed from SOM. Green solid line in the insert plot, showing the evolution of lumped K_d as a function of time, was obtained using a model without considering the biomass sorption. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

biomass as a sorbent. The model was developed for aerobic conditions (subplots a–e), and for sulfate-reducing ones (subplots a'–e'). Table 5 shows the constant parameters for all conditions and for different UVs.

Note that whereas the first conceptual model of SOM (dashed lines) fitted quite acceptably the experimental data of UVFs mass as a function of time in both dissolved (blue) and solid (red) phases, the corresponding fittings of K_d values were not good enough (solid black lines of side plots), especially for OC, UV-326 and UV-329. This indicated that the model did not consider all the processes involved and the formation of a secondary SOM was a reasonable hypothesis; actually, at around days 15–20 a peak in sorption was observed (large values of lumped K_d), followed by a decay with time. As this transition was not coincident with the time evolution of biomass and SOM (see Fig. 3), it could indicate that a transitional appearance of a secondary sorbing surface. The reasoning behind this assumption is that the degradation of SOM to DOC does not take place in just one single metabolic step, but rather a complex degradation pathway is always associated to the presence of recalcitrant organic matter (Hartog et al., 2004). The addition of this secondary sorption process helped improving the fitting of the

Table 5

Model parameters for each redox condition. (1) It was determined considering that the whole surface of biomass was suitable to sorb. (2) Sulfate concentrations were as high that sulfate Monod term (Eq (9)) was equivalent to 1.

| Parameter | Units | Aerobic conditions | Sulfate-reducing conditions |
|--|--------------|----------------------------------|----------------------------------|
| UVs Sorption parameters | | | |
| $K_{X,BP-3}$ (1) | $L\ kg^{-1}$ | $(1.52 \pm 0.37) \times 10^0$ | $(1.71 \pm 0.30) \times 10^0$ |
| $K_{X,UV-326}$ (1) | $L\ kg^{-1}$ | $(2.96 \pm 1.11) \times 10^{-1}$ | $(1.71 \pm 0.29) \times 10^0$ |
| $K_{X,UV-329}$ (1) | $L\ kg^{-1}$ | $(2.15 \pm 1.04) \times 10^{-1}$ | $(9.38 \pm 2.63) \times 10^{-1}$ |
| Organic matter degradation | | | |
| k_{max} | d^{-1} | $(1.78 \pm 6.20) \times 10^{-1}$ | $(2.95 \pm 0.08) \times 10^2$ |
| $K_{S,ED}$ | M | $(5.60 \pm 0.08) \times 10^{-4}$ | $[-]^{(2)}$ |
| $K_{S,EA}$ | M | $(5.52 \pm 3.79) \times 10^{-2}$ | $(8.42 \pm 0.39) \times 10^{-3}$ |
| Y_h | $[-]$ | 4.0×10^{-2} | 1.2×10^{-3} |
| b | d^{-1} | $(8.50 \pm 5.80) \times 10^{-3}$ | $(2.13 \pm 9.8) \times 10^{-4}$ |
| SOM release | | | |
| K_{prim} | d^{-1} | $(1.50 \pm 0.49) \times 10^{-1}$ | $(5.6 \pm 5.4) \times 10^{-2}$ |
| K_{sec} | d^{-1} | $(8.00 \pm 2.00) \times 10^{-2}$ | $(1.5 \pm 1.3) \times 10^{-1}$ |
| UV degradation by co-metabolism | | | |
| k_{BP-3} | d^{-1} | $(3.50 \pm 0.40) \times 10^{-1}$ | $(2.36 \pm 1.06) \times 10^0$ |
| k_{OC} | d^{-1} | $(2.93 \pm 0.27) \times 10^0$ | $(2.00 \pm 1.78) \times 10^0$ |
| k_{OMC} | d^{-1} | $(4.53 \pm 0.45) \times 10^0$ | $(3.20 \pm 0.75) \times 10^0$ |
| k_{UV-326} | d^{-1} | $(1.05 \pm 0.22) \times 10^0$ | $(7.50 \pm 6.75) \times 10^{-1}$ |
| k_{UV-329} | d^{-1} | $(1.42 \pm 0.21) \times 10^0$ | $(1.58 \pm 0.54) \times 10^0$ |

experimental lumped K_d value (solid line in Fig. 2). The plausibility of this hypothesis was verified using several information criteria (Akaike's, AIC, corrected Akaike's, AICc, Bayesian, BIC, and Kashap's, KIC). Regardless the criteria used, plausibility was larger for the second scenario (formation of a secondary surface) rather than for the first one (aerobic and sulfate-reducing conditions), see Table 1 of Supporting information.

The importance of biomass as a sorbent in ionic compounds is clearly shown in Fig. 2 (grey line in the insert plot), most particularly for BP-3, in agreement with the literature on the sorption of BP-3 onto biological matrices (fish and crustaceans) (Mao et al., 2019). In the case of the neutral compounds (OC and OMC), the best fit was obtained by assuming no sorption to the biomass (results not shown). Both the experimental results and the model parameters show that the most degraded UVF was OMC followed in descending order by UV-329, UV-326, BP-3, and OC. The constants of activation factors for aerobic and anaerobic conditions (Equation (15)) were 1×10^{-4} mol/Ls for BP-3, OC and OMC, and 2×10^{-3} mol/Ls for UV-326 and UV-329. It is noted that the results and the constant parameters did not vary considerable from different redox conditions, as already reported by Liu et al. (2013). The extreme values were BP-3, showing the largest amount of degradation in sulfate-reducing conditions, and OC, with the fastest overall degradation observed for aerobic conditions. This could indicate that degradation pathways were governed by the redox state. For BP-3, the first degradation step is the o-demethylation to produce 2,4-hydroxybenzophenone (BP-1) in both aerobic and anaerobic conditions (Liu et al., 2012). Nevertheless, under anoxic conditions, the relatively long half-life of BP-3 in nitrate reducing conditions could indicate that these processes were inhibited by nitrate (Liu et al., 2012; Milligan and Häggblom, 1999), justifying that redox conditions could affect the disappearance rate of BP-3.

Interestingly, biomass sorption constants did not differ more than one order of magnitude amongst the different redox conditions (see Table 3). Note that the fitted K_d values were corrected considering the amount of biomass, quite different in the two conditions (see Fig. 3). Note that K_X of BP-3 was comparable to $K_{d,SOM}$ (equal to 1.35, considering f_{oc} of 0.004), but its relevance was lower in the cases of UV-326 and UV-329 ($K_{d,SOM}$ equal to 8.35 and 9.62, respectively). We want to highlight that, to our knowledge, this is the first time these parameters were determined, so it was not possible to compare them to the literature. In the case of K_{oc} for BP-3, our results (339 L/kg, Table 3) were in the same order of

magnitude of those reported by Cao et al. (2014) for natural organic matter formed mainly by humic acids.

Finally, we remark that the values of K_{oc} 's fitted from the abiotic experiments of Liu et al. (2013) (reported in Table 3) differ considerably from the theoretical values, determined by EPI-SUITE (Table 1). On the other hand, empirical approximations considering logP provide values of K_{oc} close to the theoretical ones. The best expression for BP-3 was the empirical expression of Sabljic et al. (1995): $K_{oc} = 10^{0.6 \log P + 0.32}$, predicting a log value of 2.49 (the experimental one was 2.53). On the other hand, in the cases of UV-326 and UV-329, the best fit was obtained using the expression of Franco et al. (2009): $K_{oc} = \frac{10^{0.54 \log P + 0.11}}{1 + 10^{(pH_{soil} - 0.6 - pK_a)}} + \frac{10^{0.11 \log P + 1.54}}{1 + 10^{(pK_a - pH_{soil} + 0.6)}}$, which predicted log K_{oc} values of 2.98 and 3.32 (the experimental ones were 3.32 and 3.38, respectively).

3.2. Evaluating the effect of pH in sorption of ionic UV-filters

Besides biomass, pH plays a significant role in sorption processes of ionic compounds (Schaffer et al., 2012). Subsurface water pH is commonly governed by calcite equilibrium. Then, we tested the effect of different scenarios of calcite equilibrium in the K_d values of UVFs (Fig. 4). We evaluated scenarios of calcite subsaturation (saturation indexes, SI, from -2 to -1), and scenarios of over-saturation (SI from $+2$ to $+1$). These scenarios are realistic in aquifers, representative of different mineralogy. For example, $SI = -2$ was observed in granitic geologies, whereas $SI = +2$ can represent carbonate geologies (Folch et al., 2011). From the modeling effort, the UVF most affected by these changes was BP-3, especially in aerobic conditions, that we associated to: 1) pK_a of BP-3 (7.07) was quite close to working pH values (plots d, and d' in Fig. 4), and 2) aerobic conditions implied a wider range of pHs (that itself controls the fate of BP-3) compared to sulfate reducing conditions (Barry et al., 2002). Note that K_d spans two orders of magnitude between the two extreme cases, with direct consequences in BP-3 mobility and, consequently, in risk assessment. Besides, in a calcareous hyporheic zone or a recharge facility, the mobility of BP-3 will be conditioned to carbonate equilibrium. It would be expected than in the first centimeters, generally in aerobic conditions, the mobility of BP-3 will be larger than in depth (and reduced conditions). For the two other ionic compounds, UV-326 and UV-329, the effects of changes in calcite saturation was not that important as compared to BP-3.

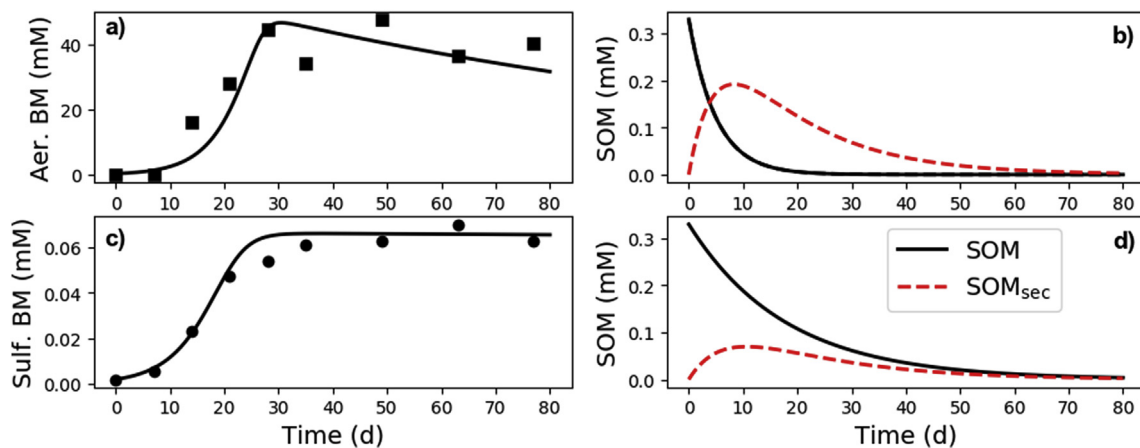


Fig. 3. Evolution of the different sorbents in the experiments. The circles in a) and c) represent the experimental data of aerobic and sulfate reducer biomass, respectively, b) and d) evolution of SOM; solid lines correspond to the one-step model; red dashed lines model including a secondary sorption surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

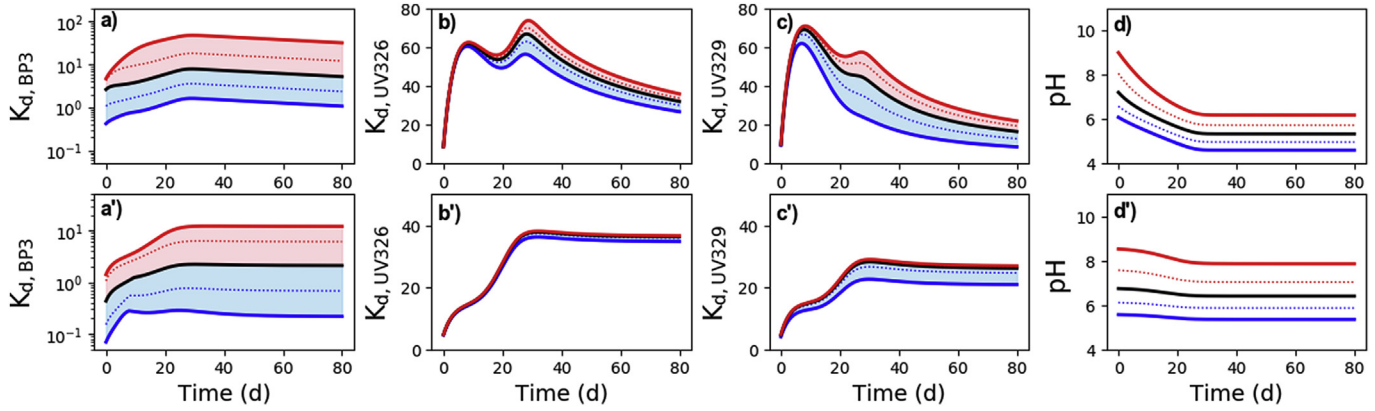


Fig. 4. Effect in K_d of ionic UV-filters at different saturation index –SI– values of calcite at different redox conditions, aerobic ones (a–d) and sulfate-reducing ones (a'–d'). Black line represents calcite equilibrium, red lines represent different scenarios of calcite saturation (SI = 2, solid; SI = 1, dotted), blue lines represent scenarios of calcite sub-saturation (SI = –2, solid; SI = –1, dotted). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

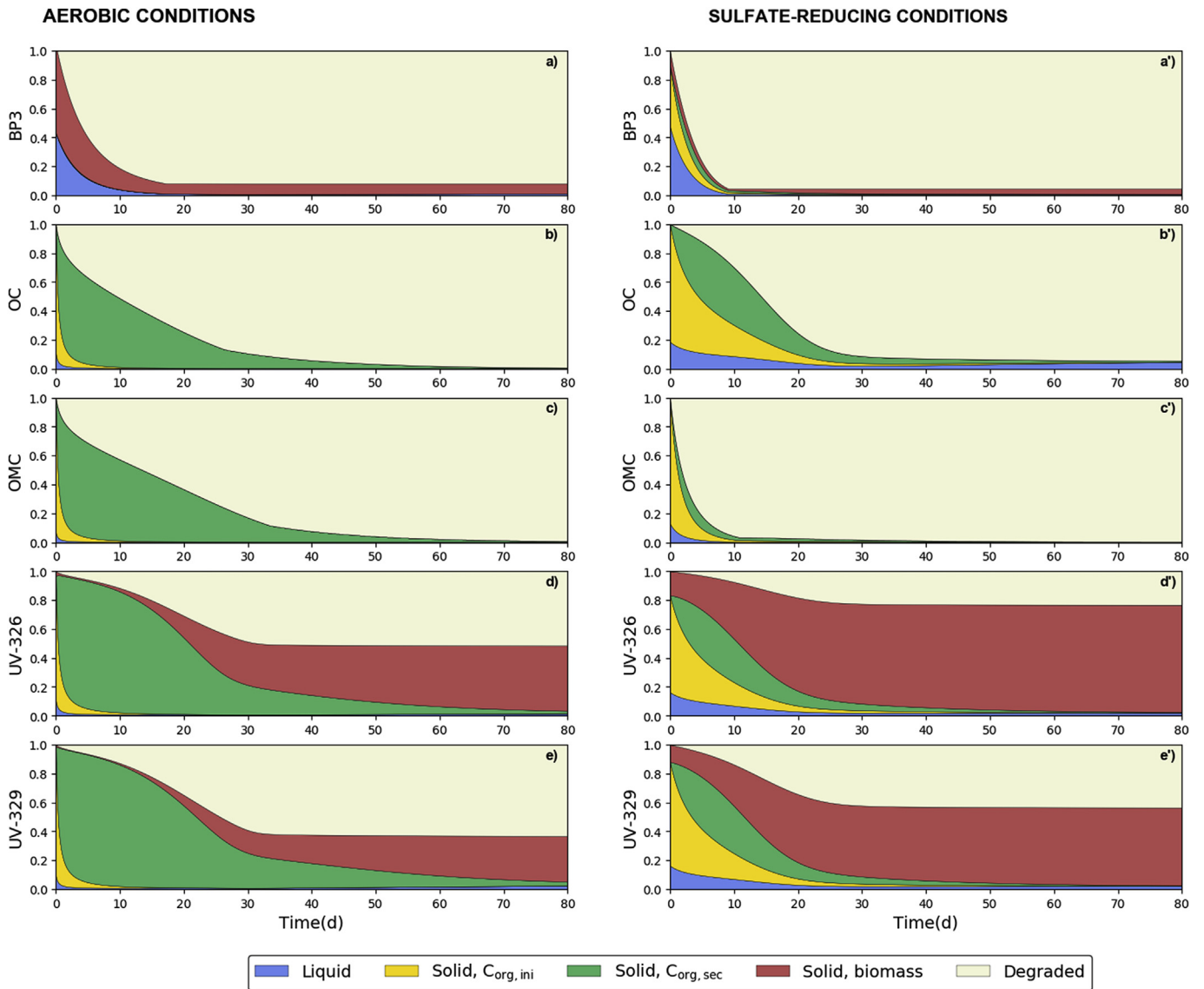


Fig. 5. Temporal evolution of the relative importance of the processes involved in the fate of UV filters under aerobic (left) and sulfate-reducing (right) redox conditions.

3.3. The role and significance of the different processes in the fate of UV-filters

Fig. 5 presents the results of a simulation for the relative importance of the different pools on the fate of UVFs: liquid phase, organic carbon solid phase (SOM and SOM_{sec}), biomass, and degradation as a function of time, for two different redox conditions and assuming a two-step conceptual SOM.

Regarding the fate of ionic UVFs, BP-3 was mostly degraded in less than 20 days, with a remaining fraction in biomass pool, more significant under aerobic conditions, probably due to large production of aerobic biomass. The fate of UV-326 and UV-329 did not differ much between the two conditions (similar sorption parameters, see Tables 1 and 5); these compounds had more affinity to SOM than BP-3, explained by the values of $\log K_{oc}$ (3.32 for UV-326, 3.38 for UV-329, and 2.53 for BP-3). For UV-326 and UV-329, SOM_{sec} was the main pool in aerobic conditions, indicating that these two compounds have more affinity to SOM than to biomass. This is quite logical since their pK_a 's are 9.30 and 10.08 and pH oscillated from 7.9 to 5.3 in the aerobic experiment and 7.9 to 6.4 in the anaerobic ones, indicating that the formation of ionic compound was not quantitatively important.

Regarding the fate of neutral compounds (OC and OMC), they were fast degraded, especially OMC with a half-life time of 5 days. In the case of OC, SOM was a more important pool compared to OMC, again responding to the K_{oc} values, higher for OC (3.55) than for OMC (3.33).

Our results show that UVFs fate will depend on the environmental conditions, especially on the activity of biogeochemical processes. If such processes are not occurring, e.g., in a groundwater poor of labile organic carbon, co-metabolic degradation would not occur, and the fate of UVFs will be conditioned by sorption and the presence of SOM. As typically the SOM content in groundwater is low, most of the compounds will be found in dissolved (water) phase. On the other hand, in active biogeochemical environments (e.g., in managed aquifer recharge surface facilities), UVFs would be degraded because other biogeochemical processes are occurring and also they would be sorbed into biomass. In these cases, biofilms will grow in warm seasons from carbon fixation (Barba, 2018; Massmann et al., 2006); moreover, if the origin of the recharge water is treated wastewater, it might contain a significant amount of UVFs (Biel-Maeso et al., 2019). Thus, in these cases, biomass sorption and co-metabolic degradation should be incorporated into the conceptual model in order to have a good picture of the processes governing the fate of UVFs.

4. Conclusions

In this work, we explored the relevance of biomass to act as an important sorbent for ionic UVFs (BP-3, UV-326 and UV-329) in porous media. To our knowledge, this is the first work indicating that biomass can be an important sorbent capable of retaining UVFs in the subsurface. Furthermore, our work improves the understanding of the UVs fate in the subsurface.

We have developed a geochemical model for UVF sorption, that considers co-metabolic degradation and sorption to two different pools of sedimentary organic carbon, being the sediment and the biomass formed during the process. This coupling was based in an extension of a geochemical database, incorporating the speciation and sorption reactions of UVFs. In this way, this work opens the door to use the capabilities for allowing editable and customizable geochemical databases to incorporate a great extension of organic pollutants to allow evaluating their fate in relation to all the hydrogeochemical reactions occurring in an aquifer.

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. Thus, redox conditions modify the sorption properties of the media, which condition the fate of the studied UVFs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2019.115192>.

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