Sunlight-induced transformation of sulfadiazine and sulfamethoxazole in surface waters and wastewater effluents

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Abstract

Sulfadiazine (SD) and sulfamethoxazole (SMX) are widely used sulfonamide antibiotics, which are present as contaminants in surface waters and are known to undergo phototransformation. This kinetic study was conducted to identify the processes responsible for their phototransformation in sunlit surface waters. Water samples from the Thur River (Switzerland) and from a pilot wastewater treatment plant, as well as aqueous solutions of two well-characterized natural dissolved organic matter (DOM) extracts, namely Suwannee River and Pony Lake fulvic acids (SRFA, PLFA), were examined. Both sulfonamides were found to undergo direct and indirect phototransformation, with contributions of excited triplet states of DOM and of effluent organic matter (EfOM) and possibly of hydroxyl radical and other unidentified reactive species. Under simulated sunlight, SMX mainly reacted through direct phototransformation, with a certain contribution of indirect phototransformation occurring for a wastewater effluent. The behavior of SD was found to be more diverse. For river waters, wastewater effluents and PLFA solutions, indirect phototransformation was predominant, while for SRFA solutions direct phototransformation prevailed. The rates of phototransformation of SD were interpreted as the result of a complex interplay between the photosensitizing and the inhibitory effect of DOM/EfOM, with an additional component related to the nitrite ion as a source of photoproduced hydroxyl radical. For typical conditions found in surface waters comparable to the Thur River, phototransformation half-lives on the order of 3–13 d were estimated for the two studied sulfonamides.

Keywords: Phototransformation; DOM; Excited triplet states; Hydroxyl radical; Sulfonamide antibiotics; Antioxidants.

1. Introduction

Pharmaceuticals and personal care products have been identified as contaminants of concern owing to their ubiquitous occurrence and the risk that they might cause to the aquatic environment (Boxall et al., 2003, Daughton and Ternes, 1999, Kolpin et al., 2002). Among the pharmaceuticals, sulfonamide antibiotics are antibacterial compounds widely used in human and veterinary medicine (Hirsch et al., 1999). Depending on their application, they may enter the aquatic environment through wastewater effluents (Götz et al., 2010), leaching from manure (Sukul et al., 2008), or direct use in aquaculture ponds (Guerard et al., 2009a). Sulfonamide antibiotics, including the two title compounds, are frequently encountered at concentrations of 0.01–2 μg/L in surface waters (Hirsch et al., 1999, Hollender et al., 2009, Kolpin et al., 2002). Besides the possible risks connected to the presence of a low-concentration cocktail of pharmaceuticals (Pomati et al., 2006), the main concern is that bacteria in the environment might develop resistance against these antibiotics in spite of the low exposure levels (Dodd et al., 2009, Dodd, 2012, Gilliver et al., 1999, Witte, 1998).

The fate of sulfonamide antibiotics in the aquatic environment has been the subject of various studies in recent years. Although the capability of certain bacterial strains to degrade sulfonamide antibiotics has been newly demonstrated (Bouju et al., 2012, Zhang et al., 2012), investigations in an aquatic outdoor field microcosm lead to the conclusion that biodegradation was not an important loss process for sulfamethoxazole (SMX) and suggested photodegradation as the main depletion pathway (Lam et al., 2004). Boreen and co-workers characterized the phototransformation of ten sulfonamides containing five-membered (Boreen et al., 2004) and six-membered (Boreen et al., 2005) heterocyclic groups. While compounds of the first class were shown to undergo uniquely direct phototransformation under sunlight, the sulfonamides with the

six-membered substituents were subject to both direct and indirect phototransformation, the latter apparently initiated by excited triplet states of dissolved organic matter (DOM), denoted hereafter as $^{3}DOM^{*}$. The photochemical kinetic behavior of sulfonamide antibiotics is complicated by the acid–base speciation of these compounds, which exhibit two pK_as, typically in the range of ≈1.5–3 and ≈5–8, respectively (Boreen et al., 2004, 2005). The direct phototransformation kinetics could be described satisfactorily by considering the distinct species involved (protonated, neutral, anionic) and assigning them a constant quantum yield (Boreen et al., 2004, 2005), a method which was also applied to describe UVC-induced phototransformation of SMX (Canonica et al., 2008). At neutral pH, direct phototransformation half-lives (for mid-latitude, mid-summer, surface of water body conditions) were on the order of ≈3–30 h, which should translate into half-lives of a few days to weeks if one considers the attenuation of light in a water body, daily and seasonal cycles, and meteorological variability of solar irradiance (Zepp and Cline, 1977). For SMX, an average half-life of 19 d was found in the mentioned microcosm study (Lam et al., 2004), compatible with the just mentioned rough estimation. The indirect phototransformation was studied in more detail for SMX (Lam and Mabury, 2005), sulfadimethoxine (Guerard et al., 2009a, Guerard et al., 2009b) and sulfadiazine (SD) (Sukul et al., 2008). The transformation of sulfadimethoxine induced by simulated sunlight was found to be accelerated in the presence of autochthonous (phytoplankton-derived) DOM, while allochthonous (from soil runoff) DOM did not enhance the transformation (Guerard et al., 2009a, Guerard et al., 2009b). The study on SD also showed an accelerating effect on the phototransformation rate induced by fulvic and humic acid. By contrast, the phototransformation of SMX was slowed down by DOM, which was attributed to the light screening effect. A recent study (Ryan et al., 2011) showed that SMX may indeed undergo indirect phototransformation in wastewater effluent,

and excited triplet states of effluent organic matter (EfOM), denoted hereafter as $^{3}EfOM^{*}$, as well as the hydroxyl radical were proposed to be the key species involved.

Besides the just mentioned investigations, the inhibiting effects of DOM on triplet-induced phototransformation of aquatic contaminants have to be considered as well (Canonica and Laubscher, 2008, Wenk et al., 2011, Wenk and Canonica, 2012). Along with several other contaminants and model aromatic compounds, sulfonamides were shown to be importantly affected by such an inhibition. Allochthonous DOM was found to be a better inhibitor than autochthonous DOM, meaning that indirect phototransformation rates were lower in the presence of allochthonous DOM, in striking coincidence with the results by Guerard and coworkers on sulfadimethoxine (Guerard et al., 2009a, Guerard et al., 2009b). To date such an inhibiting effect of DOM on the indirect phototransformation of sulfonamides, induced by the chromophoric components of DOM itself, has only been studied under laboratory conditions using the UV-A and visible emission of a medium-pressure mercury lamp (Wenk and Canonica, 2012). An important result of the latter study was that phenolic antioxidants were successfully used to mimic the inhibiting effect caused by DOM, and phenol was able to inhibit the transformation of SMX and SD initiated by $^{3}DOM^{*}$. However, the validity of such a method still has to be demonstrated for the case of irradiation using (simulated) sunlight.

The present study was conceived to identify the various factors that affect the rates of sunlight-induced transformation of sulfonamide antibiotics in surface freshwaters, with a particular focus on DOM and EfOM. SMX and SD were selected as representative compounds of the mentioned two categories of sulfonamides identified by Boreen and coworkers (Boreen et al., 2004, 2005). In the pH range investigated in this study (7.9–8.7), no influence of pH on transformation rates of both sulfonamide antibiotics is expected, since both compounds are present almost exclusively

(>96%) in their anionic form (p$K_{a,2}$=5.7 for SMX and 6.4 for SD (Boreen et al., 2004, 2005)). The photochemical transformation kinetics of SMX and SD was investigated under simulated sunlight for solutions of two well-characterized fulvic acids, in surface waters and wastewaters, and in a number of water samples taken along the course of the Thur River (North-East Switzerland). Additional mechanistic tests were performed by adding, to the irradiation experiments, isopropanol and phenol to scavenge hydroxyl radical and oxidation intermediates of the sulfonamides, respectively.

2. Experimental Section

2.1. Chemicals

The organic compounds sulfadiazine (SD, Sigma-Aldrich, >99%), sulfamethoxazole (SMX, Sigma-Aldrich >99%), 2,4,6-trimethylphenol (TMP, EGA-Chemie, 99%), isopropanol (Sigma-Aldrich, >99%) and phenol (Fluka, ≥99.5%) were used without further purification. All inorganic chemicals were analytical grade from common commercial sources. Ultrapure water was produced by the "barnstead nanopure" water purification system from Thermo Scientific. Stock solutions of SD, SMX and TMP were made in ultrapure water at pH 8 with 5 mM phosphate (Na_2HPO_4/NaH_2PO_4). Pony Lake fulvic acid (PLFA) and Suwannee River fulvic acid (SRFA) were used as standard DOMs and obtained from the International Humic Substances Society. Stock solutions of standard DOMs were made in ultrapure water with an approximate concentration of 100 mgC L^{-1}, the exact DOM concentration was measured after preparation of the stock solutions.

2.2. River water and wastewater effluent samples

River water samples were taken from the Thur River, a tributary of the Rhine River located in North-East Switzerland. The Thur River valley has no natural or artificial lake in its course. The annual average discharge (1904–2011) is about 47 m^3 s^{-1}. The catchment is characterized by its rural environment and agricultural activity. If not further specified, Thur River water samples were taken at a single sampling point near Niederneunforn (47° 35′ 60″ N, 8° 46′ 60″ E). A detailed description of the field site is given elsewhere (Diem et al., 2013, Schneider et al., 2011). Sampling points of a one-day field campaign along the course of the Thur River are described in detail in the Supplementary Information (SI), Text S1. Wastewater effluent was taken from a wastewater pilot plant of Eawag, receiving municipal wastewater of the city of Dübendorf, Switzerland (mixed household and industrial origin). Selected water quality parameters of the sampled river waters and wastewaters, which are relevant for the phototransformation studies, are given in Table 1. All sampled river waters and wastewaters were directly filtered under vacuum by using pre-rinsed cellulose nitrate membrane filters of 0.45 μm pore size. The filtered samples were stored in glass bottles in the dark at 4 °C. A fraction of the filtered wastewater sample A1 was treated by electrodialysis (PCCell GmbH, Heusweiler, Germany) to remove salts, in particular nitrate and nitrite, and the filtrate is termed as wastewater A2 (Table 1). More water quality parameters of river and wastewater samples, and river water samples of the one-day field campaign are listed in the SI, Tables S1 and S2, respectively. Note that in all used water samples iron was below the limit of detection (< 10 μg L^{-1}) as measured by ICP-OES.

(Table 1)

2.3. Irradiation experiments

Steady state irradiations were performed in glass-stoppered quartz tubes (external diameter 18 mm, internal diameter 15 mm) using primarily a solar simulator (Heraeus model Suntest CPS+). In brief, the sample tubes were exposed to the simulated solar light in a temperature-controlled ultrapure water bath (25.0±0.5 °C) located under the solar simulator. A detailed description of the experimental set up is given elsewhere (Huntscha et al., 2008). Alternatively, a DEMA 125 merry-go-round photoreactor (Hans Mangels GmbH, Bornheim-Roisdorf, Germany) equipped with a Heraeus Noblelight TQ 718 medium-pressure mercury lamp (MP Hg lamp) was employed. It was operated with a borosilicate glass cooling jacket and a 0.15 M sodium nitrate filter solution (permitting only transmission of wavelengths, $\lambda > 320$ nm) (Wegelin et al., 1994), a typical configuration used to study photosensitized reactions and reduce the contribution of direct phototransformation to the total photoinduced transformation (Canonica et al., 1995). For both irradiation setups, light screening effects caused by absorption of light in the irradiated samples, in particular by the DOM or EfOM present in the aqueous solutions and real water samples, were neglected because smaller than the typical relative experimental error of ≈15% for the determination of phototransformation rate constants. For the solar simulator, they were estimated to be <7.6% for SRFA solutions and <5.0% for all other waters, based on the absorption coefficients of these samples at 310 nm, while for the merry-go-round photoreactor they were even lower (calculations performed using the method described in Wenk et al. (2011)).

During irradiation experiments, 400 µL samples were withdrawn from each tube at six equidistant time intervals during irradiation. With the solar simulator, water samples containing SD, SMX and TMP were irradiated for a total time of 6, 8 and 2 hours, respectively. With the merry-go-round photoreactor, overall irradiation times were 2 hours, 4 hours and 18 min,

185 respectively. Solutions containing standard DOM were buffered at pH 8.0 with 5 mM phosphate
186 (Na_2HPO_4/NaH_2PO_4). The pH of filtered river water and wastewater samples was in the range of
187 7.5–8.5 (Table 1) and was not modified for the experiments. Each tube was filled with 16 mL
188 either with ultrapure water, river water, wastewater or standard DOM and spiked with an
189 appropriate amount of stock solution of a single target compound (SD, SMX or TMP) yielding a
190 concentration of 1–5 μM. To assess the photosensitizing capacity of DOM, TMP was used as a
191 reference compound since the phototransformation of TMP is not inhibited by DOM (Canonica
192 and Laubscher, 2008). Isopropanol (10 mM) was used as a hydroxyl radical scavenger. Phenol
193 (10 μM) was applied as a model compound to investigate the triplet-induced transformation of
194 SD and SMX and to gain information about the antioxidant or inhibitive potential of DOM/EfOM
195 in the water samples.
196 Actinometry was performed using an aqueous solution containing *p*-nitroanisol (10 μM) and
197 pyridine (600 μM) as described elsewhere (Dulin and Mill, 1982, Kari et al., 1995). The photon
198 fluence rate in the range of 300–400 nm was calculated according to the method described in
199 Canonica et al. (2008), using a wavelength-independent quantum yield of 0.000544 mol $einstein^{-1}$
200 for the depletion of *p*-nitroanisol and spectral data that are given in the SI (Text S2, Table S3).
201
202 **2.4. Analyses**
203 High-performance liquid chromatography (HPLC) using UV absorbance and fluorescence
204 detection was employed to quantify the concentration of SD, SMX and TMP over the course of
205 the irradiations. Both an Agilent 1100 HPLC system equipped with a diode array detector and a
206 fluorescence detector or an equivalent Dionex Ultimate 3000 HPLC system were employed.
207 Compounds were analyzed with isocratic programs at a flow rate of 1 mL min^{-1} on a reverse-

phase column (Nucleosil C18-5 μm, 125 × 3 mm Macherey-Nagel, Düren, Germany) at room temperature. The mobile phase consisted of a mixture of acetonitrile (ACN)/10mM phosphoric acid (pH 2.1) and was run at a proportion of 10/90 for SD, 20/80 for SMX and 50/50 for TMP, respectively. SD and SMX were detected by UV absorption at a wavelength of 270 nm, and TMP was detected by fluorescence at an excitation wavelength of 225 nm and an emission wavelength of 316 nm. Pseudo-first-order depletion rate constants of the target compounds, termed in the following as phototransformation rate constants (k_p), were obtained by linear regression of the logarithmic concentration values at each sampling time.

DOM concentrations of all filtered (0.45 μm) water samples and fulvic acid solutions were measured as dissolved organic carbon (DOC) using a Shimadzu model TOC-V CPH analyzer (Shimadzu Corporation, Kyoto, Japan). Carbonate/bicarbonate concentrations were measured as alkalinity by titration with 0.1 M hydrochloric acid (endpoint pH 4.5) using a Titrando 809 potentiometric titrator (Metrohm, Zofingen, Switzerland). Nitrite was analyzed colorimetrically by addition of a reagent composed of aminobenzenesulphonamide and N-(1-Naphthyl)-ethylendiaminhydrochloride. The absorbance of the resulting red azo dye was measured at 543 nm using a Cary 100 spectrophotometer (Varian AG, Zug, Switzerland). Ammonium concentrations were measured based on the reaction of ammonium with hypochlorite under alkaline conditions to give chloramine. This further reacts with salicylic acid to a blue dye complex (dichlorophenolindophenol), whose absorbance is measured at 690 nm. Nitrate concentrations were measured with a Metrohm model 761 Compact ion chromatograph (Metrohm Schweiz AG, Zofingen, Switzerland).

3. Results and Discussion

3.1. Phototransformation rate constants of sulfadiazine and sulfamethoxazole in various waters and aqueous solutions

3.1.1. Irradiation with simulated sunlight (λ > 290 nm)

The UV photon fluence rate (determined for the wavelength range of 300–400 nm) in the experiments performed in the solar simulator was ≈135 μeinstein m^{-2} s^{-1} (±15%), corresponding to a half-life of *p*-nitroanisol of ≈4.5 h. This value compares well with previous studies (Dulin and Mill, 1982) for irradiations under genuine sunlight and indicates an irradiation intensity equivalent to the strength of sunlight between summer and autumn at 40° N latitude on a cloud-free day. The results of simulated sunlight-induced phototransformation rate constants of SD and SMX for various water samples and aqueous solutions are displayed in Figure 1.

(Figure 1)

Figure 1. Solar simulator experiments (λ > 290 nm): Phototransformation rate constants of (a) SD and (b) SMX (initial concentration: 1 μM for SD and 5 μM for SMX) in selected water samples in the presence and absence of scavengers (isopropanol: hydroxyl radical scavenger; phenol: inhibitor for triplet-induced oxidation). The DOM concentration is given in brackets as mgC L^{-1}. Error bars indicate 95% confidence intervals obtained from linear regression.

For SD (Figure 1a) phototransformation rate constants for all water samples and DOM solutions, in the presence and absence of scavengers, are significantly higher than for ultrapure water solution, indicating that indirect phototransformation is likely to be a significant process. In the

absence of scavengers, the phototransformation rate constants for spring water (0.09 h^{-1}) and river water A (0.13 h^{-1}) are enhanced by a factor of 2.4 and 3.5, respectively, compared to the rate obtained for ultrapure water (0.037 h^{-1}), which is assumed to correspond to the rate constant for direct phototransformation. Interestingly, the phototransformation rate constants in DOM-containing waters do not seem to strongly depend on the DOM concentration. Wastewater B exhibits the highest rate (0.22 h^{-1}), although its DOM concentration is in the same range as for the other wastewaters. The increased rate is possibly related to the high nitrite concentration of this wastewater (Table 1, see also discussion below). Regarding the solutions of the two DOM extracts, PLFA shows a rate similar to those for the river waters, while the rate for SRFA is clearly lower, but still higher than the one for ultrapure water.

To identify the factors controlling the phototransformation rate constants of SD, experiments using isopropanol as a scavenger of the hydroxyl radical and phenol as an inhibitor of the triplet-induced transformation of sulfonamides were performed. The addition of 10 mM isopropanol (second-order rate constant for the reaction with the hydroxyl radical: $k_{\cdot OH,isopropanol}=1.9\times10^{9}$ $M^{-1}s^{-1}$ (Buxton et al., 1988)) results in an increment of the (first-order) hydroxyl radical scavenging rate constant by 1.9×10^{7} s^{-1}. Using the total scavenging rate constants of hydroxyl radical given in Table S4 ($0.8–3.1\times10^{5}$ s^{-1}), we calculated that isopropanol scavenged 98.4–99.6% of the hydroxyl radical for the waters considered in this study. Isopropanol addition significantly affected only the phototransformation rate constant for wastewater B, causing a 36% decrease. This is an indication that the hydroxyl radical, which is generated by photolysis of nitrate, nitrite and other water components, may be an important photooxidant initiating the transformation of SD in this wastewater (see below). With the addition of 10 μM phenol two effects are anticipated: First, triplet-induced oxidation of SD is expected to be reduced at an extent varying upon

277 DOM/EfOM composition (Wenk and Canonica, 2012); second, phenol is also a hydroxyl radical
278 scavenger ($k_{\cdot OH,phenol}$=1.3×10^{10} M^{-1}s^{-1}, average of three values from (Buxton et al., 1988)),
279 resulting in an increase of the hydroxyl radical scavenging rate constant by 1.3×10^{5} s^{-1}. Thus, for
280 the studied waters a significant fraction (46%–62%) of the hydroxyl radical is scavenged in the
281 presence of 10 μM phenol. Figure 1a shows that the presence of phenol significantly reduced the
282 phototransformation rate constants of SD for all waters, though at a variable extent. The
283 reduction for the spring water and river water was similar to the sample containing PLFA. With
284 the assumption that indirect phototransformation rate constants can be calculated by subtraction
285 of the rate obtained for ultrapure water from the overall rate, one obtains reductions in indirect
286 phototransformation of about 60% (±6%) upon phenol addition, very much in line with the
287 previous observations with PLFA and several surface water samples irradiated using the merry-
288 go-round photoreactor (λ > 320 nm) (Wenk and Canonica, 2012). Such a strong reduction was
289 attributed to the relatively low concentration of antioxidant moieties in PLFA and the studied
290 surface waters. By contrast, the reduction of phototransformation rate constant upon phenol
291 addition was minor for the SRFA solution and the wastewaters A1 and A2, probably indicating a
292 higher concentration of antioxidant moieties in these waters. For wastewater B the rate constant
293 reduction upon phenol addition was quite substantial and larger than the reduction obtained upon
294 isopropanol addition (see above). Therefore, both inhibition of triplet-induced oxidation and
295 hydroxyl radical scavenging appear to be responsible for the observed reduction of the rate
296 constant. Finally, it has to be noted that even for ultrapure water phenol addition causes a slight
297 reduction of the phototransformation rate constant, possibly indicating that direct
298 phototransformation involves reaction intermediates that may be reduced by antioxidants such as
299 phenol.

Figure 1b displays the phototransformation rate constants of SMX obtained for various water samples under simulated sunlight. Except for wastewater C, the rates are essentially constant and unaffected by the presence of isopropanol or phenol, indicating that the depletion of SMX is dominated by direct phototransformation. However, in wastewater C a significantly higher phototransformation rate constant was observed, which was reduced by the addition of isopropanol or phenol to the values typical for direct phototransformation. The enhanced depletion of SMX in wastewater C is possibly caused by the presence of photogenerated hydroxyl radical or by excited triplet states of the EfOM, as proposed elsewhere (Ryan et al., 2011). For a further discussion of the role of the hydroxyl radical, see below.

3.1.2. Irradiation with UV-A and visible light (λ>320 nm)

The results of irradiation experiments performed with the merry-go-round photoreactor (Figure 2) confirm on the one hand some trends observed for SD under simulated sunlight but yield on the other hand a completely new picture concerning the phototransformation of SMX. For SD (Figure 2a) the enhancement of phototransformation with PLFA, river water A and wastewater B with respect to the other waters is higher than for simulated sunlight (Figure 1a), suggesting, for these three water samples, a higher proportion of photo-active chromophores under these irradiation conditions than under simulated sunlight. The effects of scavenger addition are overall very similar for both types of irradiation, in agreement with the assumption that the phototransformation mechanisms should essentially be the same. For SMX (Figure 2b) direct phototransformation appears to be largely suppressed, in agreement with the observation that SMX barely absorbs any light above 320 nm (see Figure S4 for its electronic absorption spectrum). In contrast, indirect phototransformation is clearly observed for all water samples, with the highest rate for wastewater C. The relative phototransformation rate constants of SMX

follow the same order and approximate magnitude as for SD, and the effect of scavenger addition is also very similar. In wastewater B for SD and wastewater C for SMX, the contribution of hydroxyl radical to phototransformation is indicated by the significant rate reduction upon isopropanol addition, and the even greater reduction observed upon addition of phenol points to an important contribution of triplet-induced phototransformation.

(Figure 2)

Figure 2. Merry-go-round photoreactor experiments (λ >320 nm): Phototransformation rate constants of (a) SD and (b) SMX (initial concentration: 1 μM for SD and 5 μM for SMX) in different water samples in the presence and absence of scavengers. The DOM concentration is given in brackets as mgC L^{-1}. Error bars indicate the 95% confidence intervals obtained from linear regression.

The results for SMX obtained under UV-A and visible irradiation may be relevant to its phototransformation in surface waters. At the surface of sunlit natural waters, direct phototransformation of SMX is very dominant in most cases, as can be concluded from solar simulator experiments (Figure 1b). However, the relative contribution of indirect phototransformation is expected to increase with depth in a water body, since the spectrum of solar light at increasing depth becomes more and more red-shifted due to the wavelength-dependent absorption caused by DOM/EfOM. This is expected to reduce the rate of light absorption by SMX (see Figure S4) more strongly than the rate of light absorption by DOM/EfOM (which extends largely in the UV-A spectral range), and consequently direct

phototransformation should undergo a stronger reduction than indirect phototransformation. Thus, indirect phototransformation possibly plays a more important role in the fate of SMX in surface waters than can be deducted from the present solar simulator experiments.

3.1.3. Estimating the contribution of the hydroxyl radical

To understand the role of the hydroxyl radical in the phototransformation of SD in wastewater B and of SMX in wastewater C, calculations of hydroxyl radical photoproduction rates under solar simulator conditions and of hydroxyl radical steady-state concentrations in the various waters were performed considering the various sources, namely nitrate, nitrite and EfOM (see SI, Text S3 and Table S4). The contribution of nitrate as a hydroxyl radical precursor was found to be negligible, which is backed by the absence of reduction in SD phototransformation rate constant upon isopropanol addition for wastewater A1 (which has the highest nitrate concentration of all studied samples, see Figure 1a and Table 1). Nitrite and EfOM, as sources of photoproduced hydroxyl radical, were estimated to be responsible for only part of the phototransformation rate constant reductions observed upon addition of isopropanol (which scavenges >99% of the hydroxyl radical in the studied water samples). Besides a possible inaccuracy in the determination of nitrite concentrations (see SI, Text S3), these results may be explained by the presence of an additional reactive species that is efficiently scavenged by isopropanol. A plausible hypothesis is that the wastewaters B and C might have contained industrially-derived photochemical sources of strong oxidizing species, such as aromatic quinones, whose excited triplet states have very high reduction potentials (Loeff et al., 1993) and thus act as strong oxidants (Bedini et al., 2012). The strong reduction in the rate constant for SMX observed upon addition of phenol (Figures 1b and 2b) concurs with an excited triplet-induced transformation pathway. Further hints on the origin of the enhanced phototransformation of SMX in wastewater

C were obtained by performing irradiation experiments using a dilution series of this wastewater (SI, Figure S2). The phototransformation rate constants of SMX increased linearly (R^2=0.947) with the concentration of wastewater. This trend is consistent with the assumption of a linear increase in concentration of photosensitizers (in this case all photoactive components of the wastewater). One should also consider a possible inhibiting effect by antioxidant components in the water, which would diminish upon dilution, but the net effect on the phototransformation rate constant could be in favor of an increase with concentration, as observed for the SD in PLFA solutions (see Section 3.2.). If hydroxyl radical was the main reactive species involved in the observed indirect phototransformation, one would expect no decrease in rate constant with decreasing concentration of wastewater, because a decrease in photosensitizer concentration would be counterbalanced by a proportional decrease in the concentration of scavengers, and consequently in first-order scavenging rate constant, thus leaving the steady–state concentration of hydroxyl radical unchanged. A similar experimental dilution series using river water B revealed no significant change in the rate constant of SMX phototransformation, consistent with the conclusions from Figure 1 that the dominant reaction pathway for SMX in river water is direct phototransformation.

3.2. Effect of concentration and type of DOM

To investigate the effect of DOM on the phototransformation rate constants of SD and SMX, buffered solutions with various concentrations of two well-characterized DOM extracts, SRFA and PLFA, were irradiated using the solar simulator. These fulvic acids were selected because they can be considered as representatives of two different types of aquatic DOM, the first of mainly allochthonous character and the second of pure autochthonous character, and therefore

394 they should be able to reflect to a great extent the variability of effects to be expected from
395 surface water DOM.
396
397 (Figure 3)
398
399 **Figure 3.** Solar simulator experiments: Dependence of the phototransformation rate constants of
400 SD, SMX and TMP (inset), all at 1 μM initial concentration, on the concentration of dissolved
401 SRFA and PLFA in buffered aqueous solution (pH 8.0). Error bars indicate the 95% confidence
402 intervals obtained from linear regression.
403
404 From Figure 3, two very distinct trends of SD phototransformation rate constants with respect to
405 DOM concentration are observed for the two fulvic acids. Upon SRFA addition (0.1–3.0 mgC L^{-1})
406 the phototransformation rate constant of SD becomes on average slightly higher than the rate of
407 direct phototransformation (at 0 mgC L^{-1} of SRFA), with a ≈30% increase at low DOM
408 concentration (0.1–0.2 mgC L^{-1}) followed by a slight decrease at higher concentrations. For
409 PLFA a marked, non-linear increase in the phototransformation rate constant is observed with
410 increasing DOM concentration. The enhancement of the rate with respect to direct
411 phototransformation reaches a factor of ≈3.6 at [DOM] = 1.9–2.5 mgC L^{-1}. The differential
412 trends in phototransformation rate constants of SD in the presence of autochthonous versus
413 allochthonous DOM are analogous to the results obtained for sulfadimethoxine in various waters
414 and DOM solutions (Guerard et al., 2009a, Guerard et al., 2009b). We suggest that the higher
415 inhibiting capacity of SRFA with respect to triplet-induced oxidation (Wenk et al., 2011, Wenk
416 and Canonica, 2012), which correlates with its higher electron donating capacity (Aeschbacher et

al., 2012), is responsible for the efficient suppression of the indirect phototransformation of SD in the presence of SRFA. In the investigated concentration range the role of PLFA as a photosensitizer prevails over its role as an inhibitor of SD phototransformation.

In contrast to SD and in line with previous studies (see Introduction), the depletion rate constant of SMX is almost independent of DOM concentration for both fulvic acids (Figure 3). The main transformation pathway of SMX is attributed to direct phototransformation (0.048 h^{-1}) and indirect phototransformation seems to play a minor role. Indeed, the average increase of the phototransformation rate constant in the presence of PLFA (0.055 h^{-1}) and SRFA (0.057 h^{-1}) is less than 20% relative to the direct phototransformation rate constant.

TMP was used as a reference compound to assess the photosensitizing capacity of DOM (mainly by excited triplet sates of DOM), since TMP is mainly degraded by DOM-induced phototransformation (Canonica et al., 1995, Faust and Hoigné, 1987), and its triplet-induced phototransformation is not inhibited by the presence of DOM (Canonica and Laubscher, 2008). For TMP (inset of Figure 3) the phototransformation rate constant is, as expected, directly proportional to DOM concentration for both fulvic acids, PLFA being a better photosensitizer than SRFA (when normalized to the carbon concentration). The behavior of TMP is in sharp contrast with that of SD and SMX, and stresses the importance of DOM-induced inhibition in the case of the phototransformation of SD.

3.3. Effect of river water composition on the phototransformation of sulfadiazine (SD) and 2,4,6-trimethylphenol (TMP)

Phototransformation rate constants of SD and TMP (reference compound) were measured in water samples that were collected during a one-day sampling campaign along the course of the Thur River, from its source to 80 km downstream. Eight different sampling points were chosen,

441 to consider in particular the possible impact of effluents from municipal wastewater treatment
442 plants (see Experimental Section).
443
444 (Figure 4)
445
446 **Figure 4.** Solar simulator experiments ($\lambda > 290$ nm): Phototransformation rate constants of SD
447 and TMP (both at 1μM initial concentration) in water samples taken along the course of the Thur
448 River. The DOM concentration is given in brackets as mgC L^{-1}, while pH varies in the range of
449 7.9–8.7 for the river water samples (see SI, Table S2) and is 8.0 for the ultrapure water solution.
450 Error bars indicate the 95% confidence intervals obtained from linear regression.
451
452 Figure 4 shows that the concentration of DOM in the Thur River increases from the source
453 downwards, and so does the rate constant for TMP phototransformation (hatched bars). The pH
454 of the river water samples also increases with distance from the river source (see SI, Table S2),
455 however this change is believed to be of minor importance for the phototransformation kinetics
456 of TMP and SD, since their speciation remains basically unchanged in the pH range under
457 consideration (7.9–8.7). The increase in TMP phototransformation rate constant correlates well
458 with the DOM concentration ($R^2 = 0.87$) (see SI, Figure S3). In contrast, the phototransformation
459 of SD does not seem to strongly depend on the DOM concentration in river water samples, i.e. in
460 a concentration range of 0.4–2.5 mgC L^{-1}. However, the phototransformation rate constants of
461 SD are on average significantly higher (by a factor of ≈2.7) than in pure water, clearly indicating
462 that indirect phototransformation takes place. These results for SD show an intermediate behavior
463 with respect to the phototransformation rate constants in the presence of PLFA and SRFA,

464 respectively (Figure 3). For the lowest DOM concentration (river source: 0.4 mgC L^{-1}) the
465 enhancement in the phototransformation rate constant is significant and approaches the effect of
466 PLFA, however, at higher DOM concentrations the rate constants level off. A possible
467 explanation is that, with increasing distance from the source, the fraction of antioxidant moieties
468 in DOM increases. Probable sources of antioxidant moieties are runoff of agricultural areas, rich
469 in allochthonous material, whose composition is expected to be more similar to that of SRFA,
470 and input from wastewater treatment plants, whose EfOM apparently has a higher antioxidant
471 capacity than the DOM of river water (see discussion of the results for wastewaters A1 and A2,
472 Figure 1a).
473

474 ## 4. Environmental Implications

475 As shown in previous studies and in the present paper, the photochemical transformation of
476 sulfonamide antibiotics in surface waters and wastewaters is controlled by several processes,
477 which are illustrated in Scheme 1.
478

479 (Scheme 1)
480

481 **Scheme 1.** Photochemical pathways for the transformation of a sulfonamide antibiotic (SA) in
482 surface waters and wastewaters. Abbreviations: DOM_{ox}/$EfOM_{ox}$ are oxidized forms of
483 DOM/EfOM; PS are photoactive precursors and RS are their corresponding reactive species;
484 SA'_2, SA'_3 are transformation intermediates of SA; $SA_{1,phot}$, $SA_{2,ox}$ and $SA_{3,ox}$ are final reaction
485 products of SA. Dashed arrows indicate reaction pathways that may be operative, depending on
486 the specific RS.

A given sulfonamide antibiotic (SA) can undergo simultaneously direct phototransformation (process #1) and indirect (oxidative) phototransformation through excited triplet states of DOM/EfOM (process #2) or other reactive species (RS, process #3). RS is a collective term to describe any reactive species other than $^3DOM^*/^3EfOM^*$, such as hydroxyl radical, singlet oxygen, or oxidizing radicals derived from DOM/EfOM, and PS is the corresponding collective term to designate their precursors. Each of these three processes leads to a group of final products termed $SA_{1,phot}$, $SA_{2,ox}$ and $SA_{3,ox}$, respectively. For processes #2 and #3, DOM/EfOM can interfere in the route of product formation by reacting with transformation intermediates, SA'_2 and SA'_3 (process #4), leading to re-formation of the parent sulfonamide, SA (in principle, interference with process #1 is also possible, but it has been neglected in the scheme to keep it simple). In process #4, DOM/EfOM is assumed to function as an antioxidant (or electron donor) and thus reacts to give $DOM_{ox}/EfOM_{ox}$. For some RS, e.g. hydroxyl radical, DOM/EfOM can be effective scavengers, which is represented by process #5.

Despite their markedly different photochemical behavior, the phototransformation of SD and SMX can be explained in terms of Scheme 1. While the sunlight-induced transformation of SMX is generally dominated by direct phototransformation (process #1), SD undergoes both direct (process #1) and indirect phototransformation (processes #2 and #3), the latter being favored in waters containing DOM with a low antioxidant capacity (weak back-reaction through process #4). The photochemical fate of SD and SMX in surface waters is probably typical for the two classes of sulfonamide antibiotics identified by Boreen and coworkers (Boreen et al., 2004, 2005), namely the one containing a five-membered and six-membered heterocyclic ring substituent, respectively. However, SMX was also shown to be potentially affected by DOM/EfOM-induced photosensitized transformation, a process which may become important at increasing depth

511 below the surface of a water body, and this effect is expected to concern the analogous
512 compounds of the same sulfonamide class. A quantitative assessment of such an effect is planned.
513 For both sulfonamides half-lives for conditions corresponding to the surface of a water body,
514 mid-latitude, clear-sky midday conditions and season intermediate between summer and fall were
515 in the range of 5–18 h. Considering the diurnal variation of sunlight intensity (including night
516 time, factor of ≈4), partial cloud cover (factor of ≈1.4) and reduction of sunlight intensity by the
517 screening effect in a water depth of 1 m (factor of ≈3 for averaged half-life in a well-mixed water
518 layer), one comes up with estimated half-lives in the order of 3–13 d. In rivers and creeks such
519 half-lives may be further increased by the shadow caused by the presence of trees near the stream
520 and water plants in the stream (Kari and Giger, 1995).
521

522 ## 5. Conclusions

523 Sulfamethoxazole (SMX) and sulfadiazine (SD), as representatives of sulfonamide antibiotics,
524 were shown to undergo both direct and indirect phototransformation in river waters, solutions of
525 DOM extracts, and secondary effluents of wastewater treatment plants. The relative importance
526 of direct and indirect phototransformation depends on the target compound, the type and
527 concentration of DOM, and the spectrum of light used to induce the photochemical reaction.
528 Under solar-simulated irradiation, direct phototransformation of SMX was largely predominant,
529 and significant indirect phototransformation was only detected in a sample of a wastewater
530 effluent. The reactive species responsible for this indirect pathway was possibly the hydroxyl
531 radical, but its photochemical sources could not be identified with certainty. However, SMX was
532 shown to also undergo DOM/EfOM-photosensitized transformation when UVA light from a

533 medium-pressure mercury arc lamp was used for irradiations. This process might become
534 important with increasing depth in a water body.
535 In river waters, wastewater effluents and solutions of PLFA (an authochtonous aquatic DOM),
536 SD phototransformation occurred mainly by DOM/EfOM photosensitization at DOM
537 concentrations >0.4 mgC L^{-1}. However, in solutions of SRFA, an allochtonous DOM with strong
538 antioxidant capacity, indirect phototransformation of SD appeared to be much less important than
539 direct phototransformation. SD constitutes an example of water contaminant whose
540 photochemical fate is affected by both photosensitizing and antioxidant properties of
541 DOM/EfOM (Wenk et al., 2011, Wenk and Canonica, 2012). Moreover, 2,4,6-trimethylphenol
542 (TMP) was employed as a useful reference compound to assess the photosensitizing strength of
543 DOM/EfOM, since its transformation is not affected by the presence of antioxidants (Canonica
544 and Laubscher, 2008).
545 Phenol was successfully employed as a diagnostic compound to selectively inhibit the
546 transformation of the sulfonamides photosensitized by DOM/EfOM (oxidation reaction attributed
547 to their excited triplet states). Since phenol also scavenges hydroxyl radical, the combined use of
548 a second hydroxyl radical scavenger, such as isopropanol, is recommended if the presence of
549 hydroxyl radical in the irradiated solution cannot be *a priori* excluded.
550

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555

Appendix A. Supplementary Data

Supplementary data related to this article can be found at

References

Aeschbacher, M., Graf, C., Schwarzenbach, R.P., Sander, M., 2012. Antioxidant properties of humic substances. Environmental Science & Technology 46(9), 4916-4925.

Bedini, A., De Laurentiis, E., Sur, B., Maurino, V., Minero, C., Brigante, M., Mailhot, G., Vione, D., 2012. Phototransformation of anthraquinone-2-sulphonate in aqueous solution. Photochemical & Photobiological Sciences 11(9), 1445-1453.

Boreen, A.L., Arnold, W.A., McNeill, K., 2004. Photochemical fate of sulfa drugs in the aquatic environment: Sulfa drugs containing five-membered heterocyclic groups. Environmental Science & Technology 38(14), 3933-3940.

Boreen, A.L., Arnold, W.A., McNeill, K., 2005. Triplet-sensitized photodegradation of sulfa drugs containing six-membered heterocyclic groups: Identification of an SO2 extrusion photoproduct. Environmental Science & Technology 39(10), 3630-3638.

Bouju, H., Ricken, B., Beffa, T., Corvini, P.F.X., Kolvenbach, B.A., 2012. Isolation of bacterial strains capable of sulfamethoxazole mineralization from an acclimated membrane bioreactor. Applied and Environmental Microbiology 78(1), 277-279.

Boxall, A.B.A., Kolpin, D.W., Halling-Sorensen, B., Tolls, J., 2003. Are veterinary medicines causing environmental risks? Environmental Science & Technology 37(15), 286A-294A.

Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot OH/\cdot O^-$) in aqueous solution. J. Phys. Chem. Ref. Data 17(2), 513-886.

Canonica, S., Jans, U., Stemmler, K., Hoigne, J., 1995. Transformation kinetics of phenols in water: Photosensitization by dissolved natural organic material and aromatic ketones. Environmental Science & Technology 29(7), 1822-1831.

Canonica, S., Laubscher, H.-U., 2008. Inhibitory effect of dissolved organic matter on triplet-induced oxidation of aquatic contaminants. Photochemical & Photobiological Sciences 7(5), 547-551.

Canonica, S., Meunier, L., Von Gunten, U., 2008. Phototransformation of selected pharmaceuticals during UV treatment of drinking water. Water Research 42(1-2), 121-128.

Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environmental Health Perspectives 107, 907-938.

Diem, S., Rudolf von Rohr, M., Hering, J.G., Kohler, H.P.E., Schirmer, M., Von Gunten, U., 2013. NOM degradation during river infiltration: Effects of the climate variables temperature and discharge. Water Research 47(17), 6585-6595.

592 Dodd, M.C., Kohler, H.P.E., Von Gunten, U., 2009. Oxidation of antibacterial compounds by
593 ozone and hydroxyl radical: Elimination of biological activity during aqueous ozonation
594 processes. Environmental Science & Technology 43(7), 2498-2504.

595 Dodd, M.C., 2012. Potential impacts of disinfection processes on elimination and deactivation of
596 antibiotic resistance genes during water and wastewater treatment. Journal of Environmental
597 Monitoring 14(7), 1754-1771.

598 Dulin, D., Mill, T., 1982. Development and evaluation of sunlight actinometers. Environmental
599 Science & Technology 16(11), 815-820.

600 Faust, B.C., Hoigné, J., 1987. Sensitized photooxidation of phenols by fulvic acid and in natural
601 waters. Environmental Science & Technology 21(10), 957-964.

602 Gilliver, M.A., Bennett, M., Begon, M., Hazel, S.M., Hart, C.A., 1999. Enterobacteria -
603 Antibiotic resistance found in wild rodents. Nature 401(6750), 233-234.

604 Götz, C.W., Abegglen, C., McArdell, C.S., Koller, M., Siegrist, H., Hollender, J., Schärer, M.,
605 2010. Micropollutants. Evaluation of advanced treatment steps using indicator-substances. Gas
606 Wasser Abwasser (4), 325-333.

607 Guerard, J.J., Chin, Y.P., Mash, H., Hadad, C.M., 2009a. Photochemical fate of sulfadimethoxine
608 in aquaculture waters. Environmental Science & Technology 43(22), 8587-8592.

609 Guerard, J.J., Miller, P.L., Trouts, T.D., Chin, Y.P., 2009b. The role of fulvic acid composition in
610 the photosensitized degradation of aquatic contaminants. Aquatic Sciences 71(2), 160-169.

611 Hirsch, R., Ternes, T., Haberer, K., Kratz, K.L., 1999. Occurrence of antibiotics in the aquatic
612 environment. Science of the Total Environment 225(1-2), 109-118.

613 Hollender, J., Zimmermann, S.G., Koepke, S., Krauss, M., McArdell, C.S., Ort, C., Singer, H.,
614 von Gunten, U., Siegrist, H., 2009. Elimination of organic micropollutants in a municipal
615 wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration.
616 Environmental Science & Technology 43(20), 7862-7869.

617 Huntscha, S., Singer, H., Canonica, S., Schwarzenbach, R.P., Fenner, K., 2008. Input dynamics
618 and fate in surface water of the herbicide metolachlor and of its highly mobile transformation
619 product metolachlor ESA. Environmental Science & Technology 42(15), 5507-5513.

620 Kari, F.G., Giger, W., 1995. Modeling the photochemical degradation of
621 ethylenediaminetetraacetate in the River Glatt. Environmental Science & Technology 29(11),
622 2814-2827.

623 Kari, F.G., Hilger, S., Canonica, S., 1995. Determination of the reaction quantum yield for the
624 photochemical degradation of Fe(III)-EDTA: Implications for the environmental fate of EDTA in
625 surface waters. Environmental Science & Technology 29(4), 1008-1017.

626 Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton,
627 H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US
628 streams, 1999-2000: A national reconnaissance. Environmental Science & Technology 36(6),
629 1202-1211.

630 Lam, M.W., Young, C.J., Brain, R.A., Johnson, D.J., Hanson, M.A., Wilson, C.J., Richards, S.M.,
631 Solomon, K.R., Mabury, S.A., 2004. Aquatic persistence of eight pharmaceuticals in a
632 microcosm study. Environmental Toxicology and Chemistry 23(6), 1431-1440.

633 Lam, M.W., Mabury, S.A., 2005. Photodegradation of the pharmaceuticals atorvastatin,
634 carbamazepine, levofloxacin, and sulfamethoxazole in natural waters. Aquatic Sciences 67(2),
635 177-188.

636 Loeff, I., Rabani, J., Treinin, A., Linschitz, H., 1993. Charge-transfer and reactivity of nπ* and
637 ππ* organic triplets, including anthraquinonesulfonates, in interactions with inorganic anions: A
638 comparative study based on classical Marcus theory. Journal of the American Chemical Society
639 115(20), 8933-8942.

640 Pomati, F., Castiglioni, S., Zuccato, E., Fanelli, R., Vigetti, D., Rossetti, C., Calamari, D., 2006.
641 Effects of a complex mixture of therapeutic drugs at environmental levels on human embryonic
642 cells. Environmental Science & Technology 40(7), 2442-2447.

643 Ryan, C.C., Tan, D.T., Arnold, W.A., 2011. Direct and indirect photolysis of sulfamethoxazole
644 and trimethoprim in wastewater treatment plant effluent. Water Research 45(3), 1280-1286.

645 Schneider, P., Vogt, T., Schirmer, M., Doetsch, J., Linde, N., Pasquale, N., Perona, P., Cirpka,
646 O.A., 2011. Towards improved instrumentation for assessing river-groundwater interactions in a
647 restored river corridor. Hydrology and Earth System Sciences 15(8), 2531-2549.

648 Sukul, P., Lamshoft, M., Zuhlke, S., Spiteller, M., 2008. Photolysis of C-14-sulfadiazine in water
649 and manure. Chemosphere 71(4), 717-725.

650 Wegelin, M., Canonica, S., Mechsner, K., Fleischmann, T., Pesaro, F., Metzler, A., 1994. Solar
651 water disinfection: Scope of the process and analysis of radiation experiments. J. Water Supply
652 Res. Technol. - Aqua 43(3), 154-169.

653 Wenk, J., von Gunten, U., Canonica, S., 2011. Effect of dissolved organic matter on the
654 transformation of contaminants induced by excited triplet states and the hydroxyl radical.
655 Environmental Science & Technology 45(4), 1334-1340.

656 Wenk, J., Canonica, S., 2012. Phenolic antioxidants inhibit the triplet-induced transformation of
657 anilines and sulfonamide antibiotics in aqueous solution. Environmental Science & Technology
658 46(10), 5455-5462.

659 Witte, W., 1998. Medical consequences of antibiotic use in agriculture. Science 279(5353), 996-
660 997.

661 Zepp, R.G., Cline, D.M., 1977. Rates of direct photolysis in aquatic environment. Environmental
662 Science & Technology 11(4), 359-366.

663 Zhang, W.W., Wen, Y.Y., Niu, Z.L., Yin, K., Xu, D.X., Chen, L.X., 2012. Isolation and
664 characterization of sulfonamide-degrading bacteria Escherichia sp HS21 and Acinetobacter sp
665 HS51. World Journal of Microbiology & Biotechnology 28(2), 447-452.

666

667

Table 1
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Table 1: Sampled river waters and wastewaters with selected water quality parameters.

Water samples	DOC ($mgC\ L^{-1}$)	Nitrate ($mgN\ L^{-1}$)	Nitrite ($\mu gN\ L^{-1}$)	Ammonium ($\mu gN\ L^{-1}$)	Alkalinity (mM)	pH
Spring water	0.4	0.3	< 0.25	7.3	1.65	7.9
River water A	3.8	1.1	< 0.25	-	4.40	8.1
River water B	2.5	2.8	11.2	12.7	4.99	8.5
Wastewater A1	6.6	13.9	106	79.6	6.21	8.0
Wastewater A2 [a]	5.8	< 0.25	1.7	17.7	1.18	7.5
Wastewater B	5.5	6.2	509	133	6.89	8.3
Wastewater C	5.6	2.7	25	191	8.37	8.0

Note: [a] Wastewater A2 was derived from wastewater A1 by electrodialysis treatment.

Figure 1

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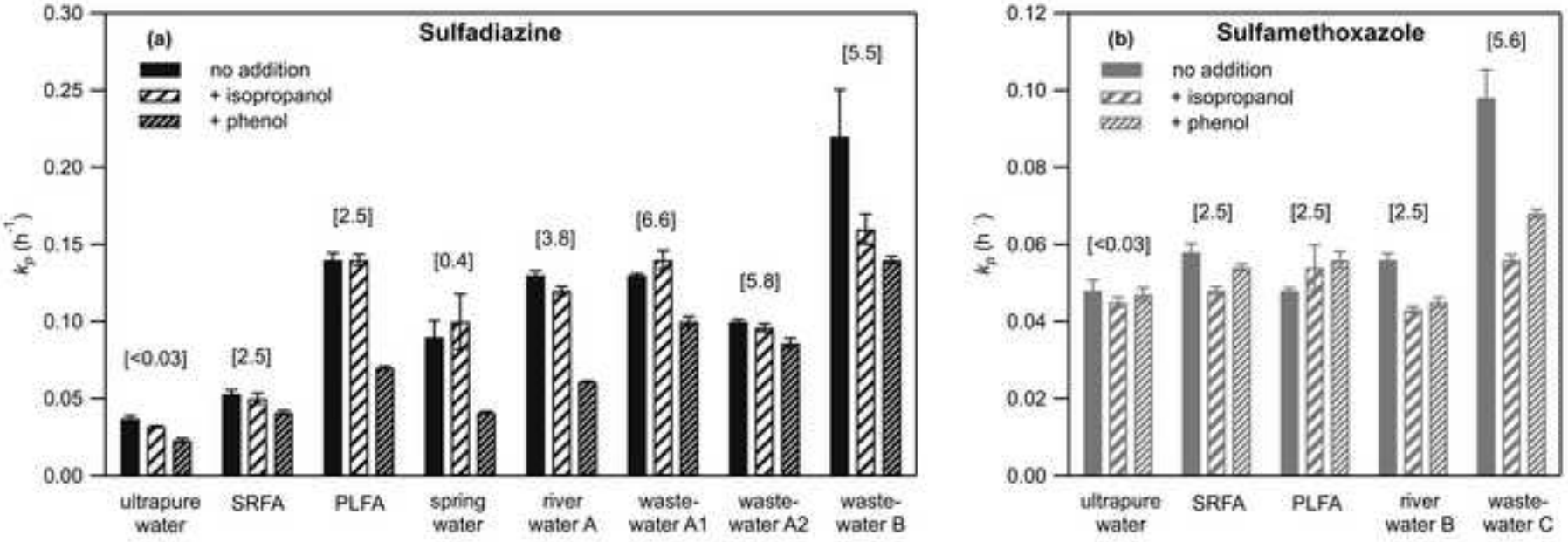

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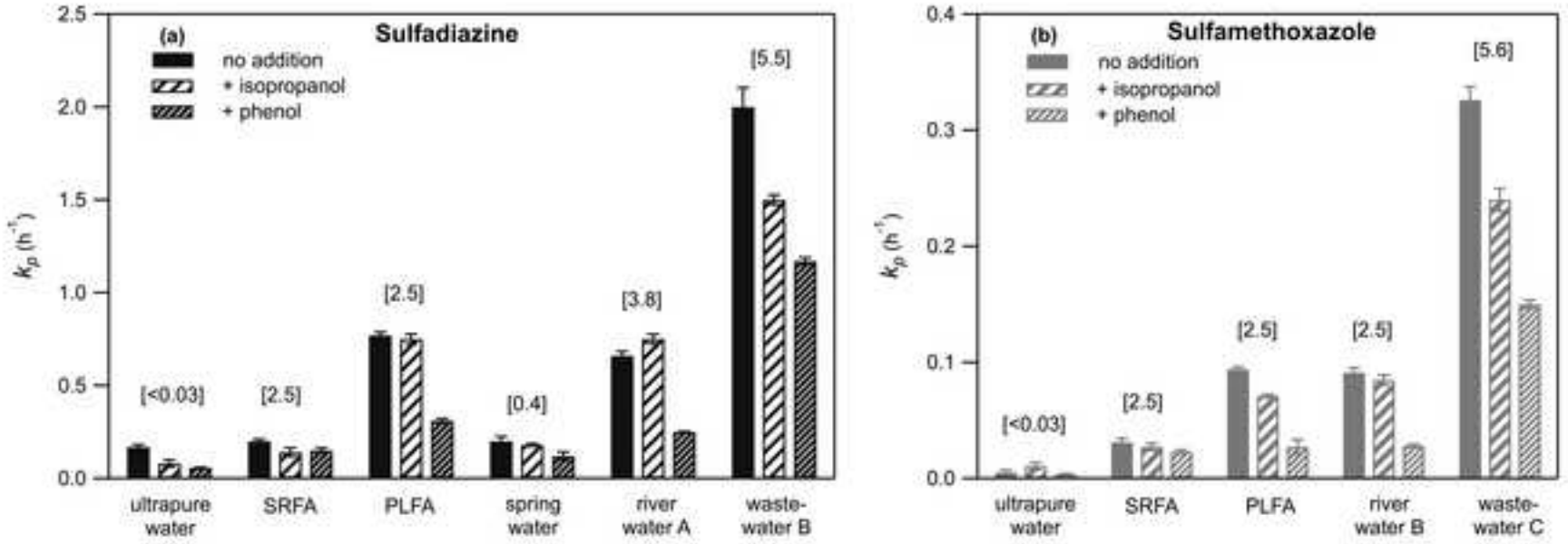

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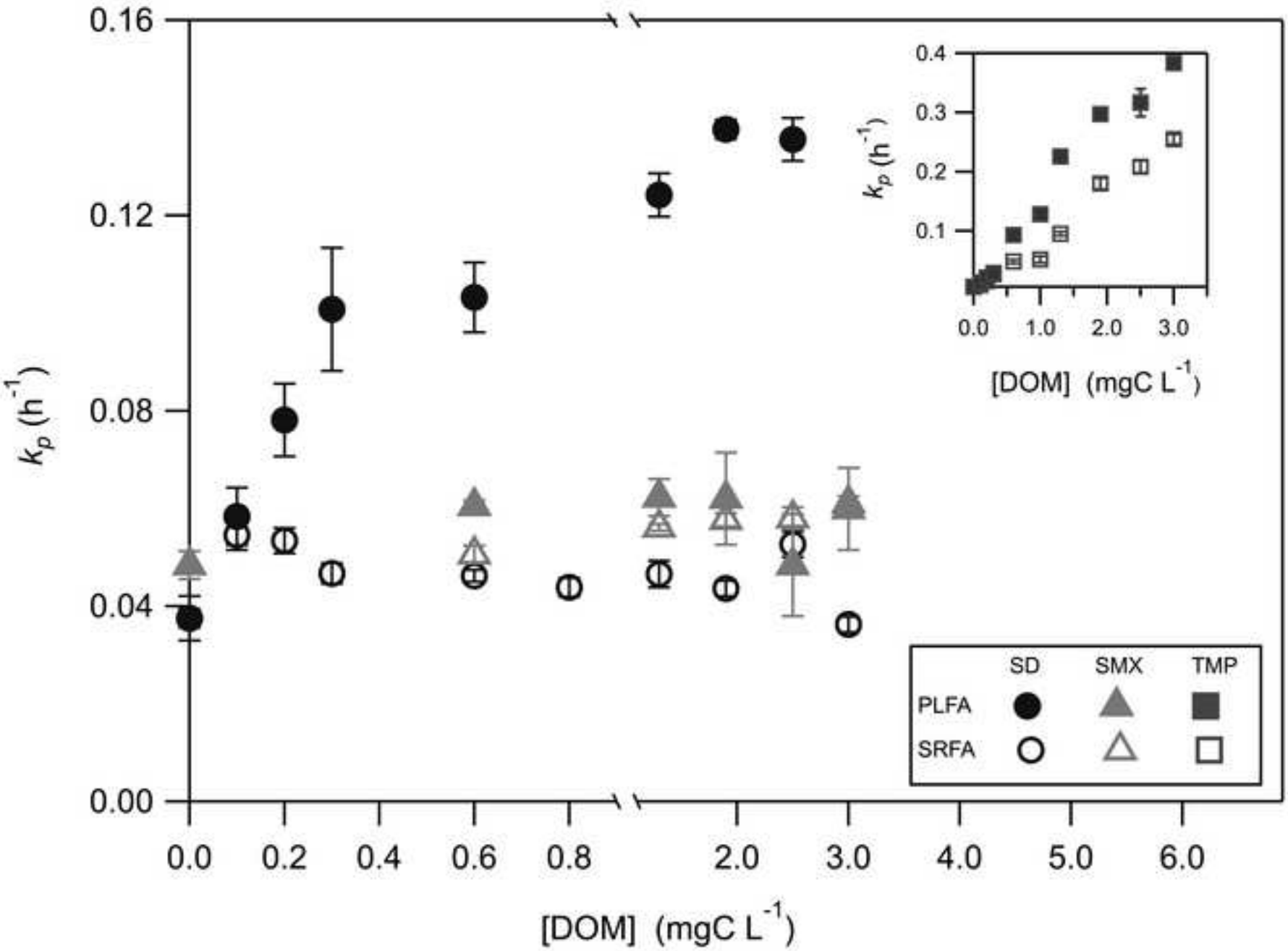

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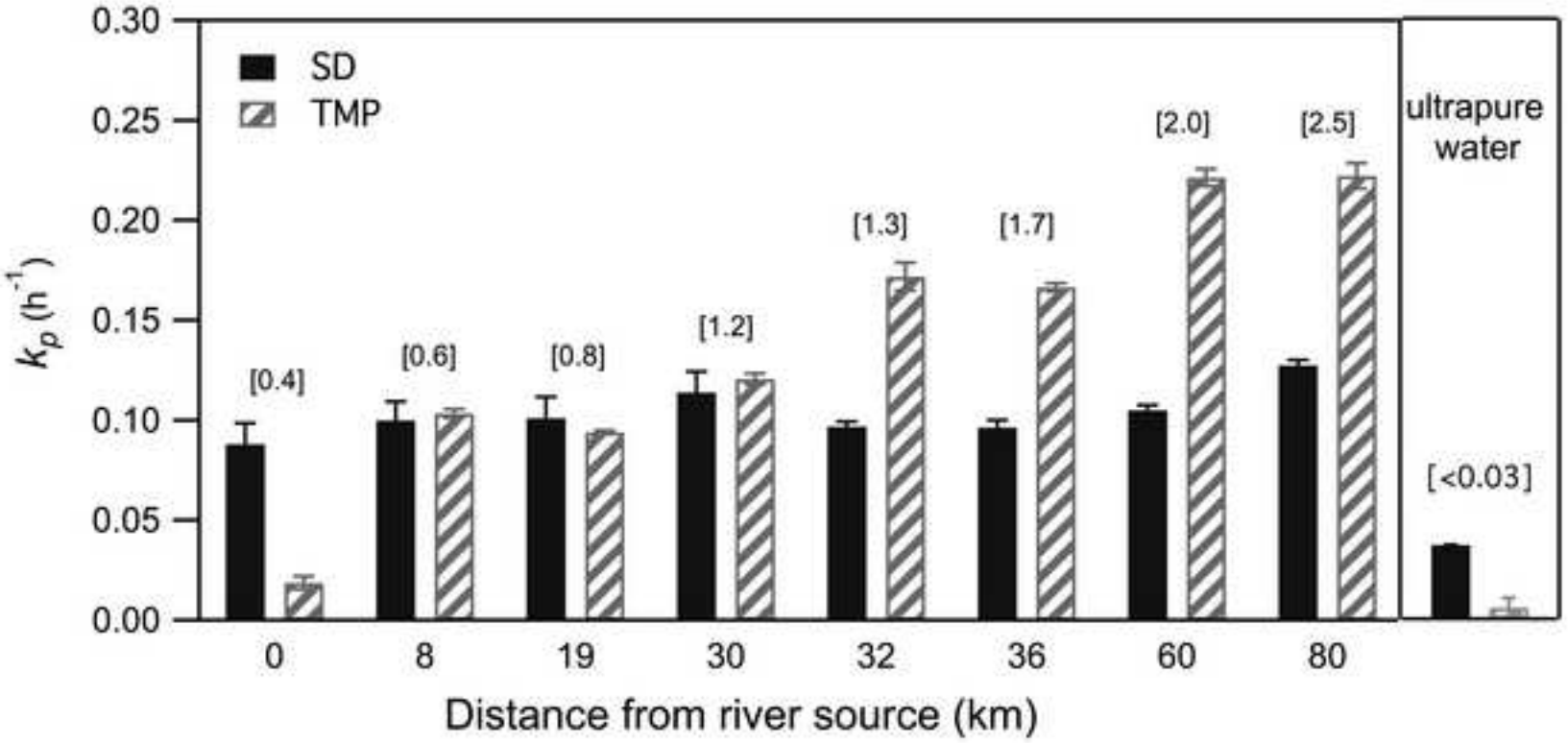
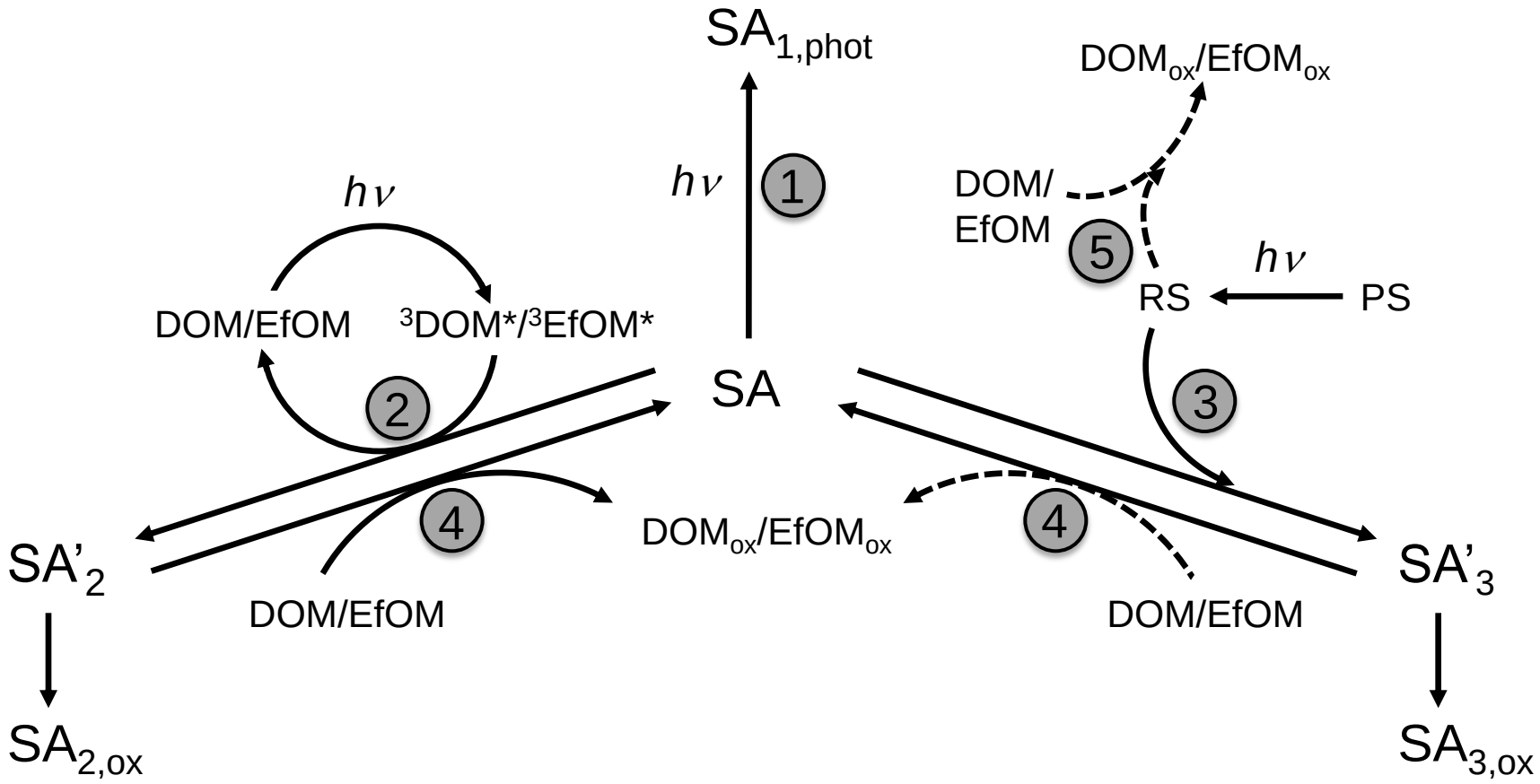


Scheme 1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