Supporting Information for the Environmental Science and Technology article:

Degradation of chlorotriazine pesticides by sulfate radical anions and influence of organic matter

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Ten pages of Supporting Information, including 6 narratives and 4 figures:

Text S1 Competition kinetics

Principle

Second order reaction rate constants of sulfate radicals ($SO_4^{\bullet-}$) were determined by competition kinetics in analogy to Peter and von Gunten [1]. Thereby, the observed degradation rate of a probe compound under study (P) is related to the observed degradation rate of a reference compound (R) (note that both compounds have to experience the same exposure of the oxidant, e.g., by their simultaneous degradation in one reaction system). The second order rate constant of a probe compound P can be derived from Equation S1 $\ln\left(\frac{P}{P_0}\right) = \ln\left(\frac{R}{R_0}\right) \cdot \frac{k(P+SO_4^{\bullet-})}{k(R+SO_4^{\bullet-})}$ by plotting $\ln\left(\frac{P}{P_0}\right)$ against the degradation of a reference compound $\ln\left(\frac{R}{R_0}\right)$, revealing a linear function (cf. Figure S1). The reaction rate of the probe compound can be calculated from the slope of this function multiplied by the reaction rate of the competitor. 5 µM of both, the competitor and the probe compound were added in the present study. Further detailed information about competition kinetics is provided by von Sonntag and von Gunten [2].

Competition kinetics at elevated temperatures

$SO_4^{\bullet-}$ were generated by thermolysis of $S_2O_8^{2-}$ at 60°C. It is important to point out that the reaction rate determined by competition kinetics (see above) under such condition corresponds to the temperature at which the reaction rate of the competitor has been determined (typically 20-25°C). This is due to the fact that the activation energies in the reaction with radicals such as $SO_4^{\bullet-}$ and $^{\bullet}OH$ hardly differ between different reaction partners. This has been verified by conducting competition kinetics experiments with atrazine and 4-chlorobenzoic acid in presence of $SO_4^{\bullet-}$ generated by thermal activation of $S_2O_8^{2-}$ at

different temperatures. This couple of compounds (pCBA and atrazine) is suited well for this kind of test, since their reaction rates differ by nearly one order of magnitude, thus, representing a worst case scenario with regard to difference in activation energies. Figure S1 shows a double logarithmic plot of pCBA vs. atrazine according to Equation S1 during thermal activation of $S_2O_8^{2-}$ at 40, 50, and 60°C.

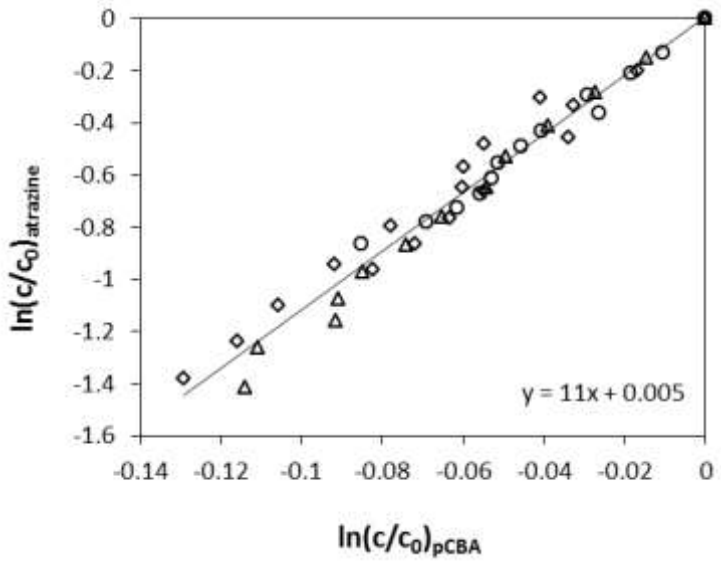

Figure S1: Degradation of pCBA vs. atrazine during thermal activation of $S_2O_8^{2-}$ at 40 °C (circles), 50 °C (triangles) and 60 °C (diamonds); $[pCBA]_0$ = 4.71 ± 0.02 µM, $[atrazine]_0$ = 4.63 ± 0.12 µM; $[S_2O_8^{2-}]_0$ = 1 mM; initial pH: 7-8

It can be seen, that data obtained from thermal activation at all temperatures lie on one line indicating that differences in activation energy can be neglected. From this plot a reaction rate for atrazine of 4.0×10^9 M^{-1} s^{-1} can be obtained which fairly well matches the value of Manoj determined by laser flash photolysis (3×10^9 M^{-1} s^{-1} [3]).

Text S2 Calculation of fractions reacting with an oxidant

The fraction of an oxidant (or other reactive species) reacting with a certain compound in competition with other solutes can be calculated if the corresponding concentrations and

78 reaction rate constants are known. The fraction corresponds to the concentration times the rate
79 constant of the compound under study, divided by the sum of concentration times rate
80 constants of all compounds reacting with the oxidant. Equation 2 gives an example for the
81 fraction of hydroxyl radicals ($^{\bullet}$OH) reacting with atrazine (f(atrazine)) in presence of para-
82 chlorobenzoic acid (pCBA) ([atrazine] and [pCBA] = concentration of atrazine and pCBA in
83 M, k($^{\bullet}$OH + atrazine), k($^{\bullet}$OH + pCBA) = second order reaction rate constant of the reaction
84 of $^{\bullet}$OH with atrazine and pCBA, respectively in M^{-1} s^{-1}).

85 Equation S2 $$f(atrazine) = \frac{[atrazine] \times k(^{\bullet}OH + atrazine)}{[atrazine] \times k(^{\bullet}OH + atrazine) + [pCBA] \times k(^{\bullet}OH + pCBA)}$$

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87 **Text S3 Radiation source**

88 For photochemical experiments a merry-go-round apparatus has been purchased from Hans
89 und Thomas Schneider Glasapparatebau in Kreuzwertheim. This apparatus was equipped with
90 a low pressure mercury arc from Heraeus Noble Light (GPH303T5L/4, 15 W). This radiation
91 source emits nearly monochromatic light at 254 nm. The quartz glass of this radiation source
92 is not transparent for the minor emission at 185 nm. A water filter with an optical path length
93 of ca. 1 cm served as an additional safeguard. Thus, effects by 185 nm radiation can be
94 neglected.

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96 **Text S4 Use of buffers in presence of humic acids**

97 For preventing speciation of the humic acids, which could cause changes in the reactivity
98 towards $SO_4^{\bullet-}$ and $^{\bullet}$OH, buffering of pH was necessary (pH = 7.2). Therefore 1.25-2.5 mM
99 phosphate was added. Due to the high concentration of humic acids (7.5-15 mgC L^{-1}) only a
100 minor fraction of $SO_4^{\bullet-}$ is expected to react with the phosphate species and interferences by
101 phosphate radicals can be neglected as will be explained below. The second order reaction
102 rate constants of $SO_4^{\bullet-}$ with phosphate species are small (k(HPO_4^{2-} + $SO_4^{\bullet-}$) = 1.2×10^6 M^{-1}

s^{-1} [4] $k(H_2PO_4^- + SO_4^{\bullet-}) \leq 7.4 \times 10^4$ M^{-1} s^{-1} [5]). Due to the high DOC concentration, the reaction rate of $SO_4^{\bullet-}$ plus DOC has to be below 1000 L $mg^{-1}C$ s^{-1} for enabling a > 10% fraction of $SO_4^{\bullet-}$ reacting with phosphate (calculations done using the principle explained in Text S2). Yet, for the $SO_4^{\bullet-}$ being similar reactive as $^{\bullet}OH$ a reaction rate < 1000 L $mg^{-1}C$ s^{-1} is unlikely (average reaction rate $k(^{\bullet}OH + DOC) = 2.5 \times 10^4$ L $mg^{-1}C$ s^{-1} [6, 7], note that a reaction rate of the reaction $SO_4^{\bullet-}$ with humic acids was determined in the present study to be $6.8 \pm 0.3 \times 10^3$ L mgC^{-1} s^{-1}). Hence, the above assumption is justified.

Text S5 Determination of $SO_4^{\bullet-}$ and $^{\bullet}OH$ rate constants with dissolved organic matter

The reaction rate constants of DOC plus $SO_4^{\bullet-}$ and $^{\bullet}OH$ have been determined as will be described in the following. It has to be mentioned, that the photochemical calculations below are in analogy to Katsoyiannis et al. [8].

In the present system $SO_4^{\bullet-}$ and $^{\bullet}OH$ are mainly scavenged by DOC competing for the degradation of atrazine. Since $k(SO_4^{\bullet-})$ and $k(^{\bullet}OH)$ of atrazine are known, the reaction rates of $^{\bullet}OH$ and $SO_4^{\bullet-}$ plus DOC can be calculated on basis of the fluence rate and first order degradation of atrazine. The corresponding relationship is shown in Equation S3.

Equation S3

$$k' = \frac{2.303 \times \varepsilon_{peroxide} \times \phi_{peroxide} \times H \times [peroxide] \times k(atrazine + radical)}{[DOC] \times k(DOC + radical)} + k(photolysis\ of\ atrazine)$$

$k'(atrazine)$: First order degradation rate of atrazine / s^{-1}

$\varepsilon_{peroxide}$: Molar absorption coefficient of H_2O_2 or $S_2O_8^{2-}$ / $m^2\ mol^{-1}$

$\phi_{peroxide}$: Quantum yield of H_2O_2 or $S_2O_8^{2-}$ / mol $Einstein^{-1}$

H : Fluence rate / Einstein $m^{-2}\ s^{-1}$

$[peroxide]$: Concentration of H_2O_2 or $S_2O_8^{2-}$ / M

$k(atrazine + radical)$: Second order rate constant of atrazine plus $^{\bullet}OH$ or $SO_4^{\bullet-}$/ $M^{-1}\ s^{-1}$

$k(photolysis\ of\ atrazine)$: Rate of atrazine photolysis / s^{-1}

$[DOC]$: Concentration of DOC / mgC L^{-1}

$k(DOC + radical)$: Rate constant of the reaction $^{\bullet}OH$ or $SO_4^{\bullet-}$ plus DOC / $LmgC^{-1}\ s^{-1}$

As the only unknown, *k* (DOC + radical) can either be derived by calculating the first order degradation rate of atrazine (experimental data) and solving the above Equation 3 for *k*(DOC + radical), or by adjusting *k*(DOC + radical) arriving at the best fit for the experimentally determined degradation of atrazine. The latter method has been used in the present study for different DOC and peroxide concentrations.

Following reaction parameters have been applied:

- quantum yield of H_2O_2 (254 nm, radical formation) : 1 mol $Einstein^{-1}$ [9]
- quantum yield of $S_2O_8^{2-}$ (254 & 248 nm, radical formation) : 1.4 mol $Einstein^{-1}$ [10, 11]
- molar absorption of H_2O_2 at 254 nm :1.86 $m^2\ mol^{-1}$ [8]
- molar absorption of $S_2O_8^{2-}$ at 254 nm : 2.2 $m^2\ mol^{-1}$ [12]
- second order rate constant of atrazine plus $SO_4^{\bullet-}$ and $^{\bullet}OH$: $3 \times 10^9\ M^{-1}\ s^{-1}$

The small fraction of radicals scavenged by the phosphate buffer ($H_2PO_4^-$ and HPO_4^{2-}) and by the corresponding peroxide (H_2O_2 or $S_2O_8^{2-}$) was also considered. Therefore the following terms have to be included in the denominator in Equation S3:

$[H_2PO_4^-] \times k(H_2PO_4^- + \text{radical}) + [HPO_4^{2-}] \times k(HPO_4^{2-} + \text{radical}) + [\text{peroxide}] \times k(\text{peroxide} + \text{radical})$

With:

$[H_2PO_4^-]$: Concentration of dihydrogen phosphate / M

$[HPO_4^{2-}]$: Concentration of hydrogen phosphate / M

[peroxide] : Concentration of corresponding peroxide (H_2O_2 or $S_2O_8^{2-}$) / M

$k(H_2PO_4^- + \text{radical})$: Second order reaction rate constant of $H_2PO_4^-$ plus $^{\bullet}OH$ or $SO_4^{\bullet-}$ / M^{-1} s^{-1}

$k(HPO_4^{2-} + \text{radical})$: Second order reaction rate constant of HPO_4^{2-} plus $^{\bullet}OH$ or $SO_4^{\bullet-}$ / M^{-1} s^{-1}

k(peroxide + radical) : Second order reaction rate constant of corresponding peroxide (H_2O_2 or $S_2O_8^{2-}$) plus $^{\bullet}OH$ or $SO_4^{\bullet-}$ / M^{-1} s^{-1}

The concentrations of the phosphate species result from the total phosphate buffer concentration and the corresponding pH (i.e., pH 7.2)

The corresponding rate constants for the phosphate species can be obtained from Maruthamuthu and Neta [5]. The reaction rates for the reaction of $^{\bullet}OH$ with H_2O_2 can be obtained from Buxton et al.,[13] and the reaction rate of the reaction of $SO_4^{\bullet-}$ with $S_2O_8^{2-}$ can be found in Herrmann et al.,[14].

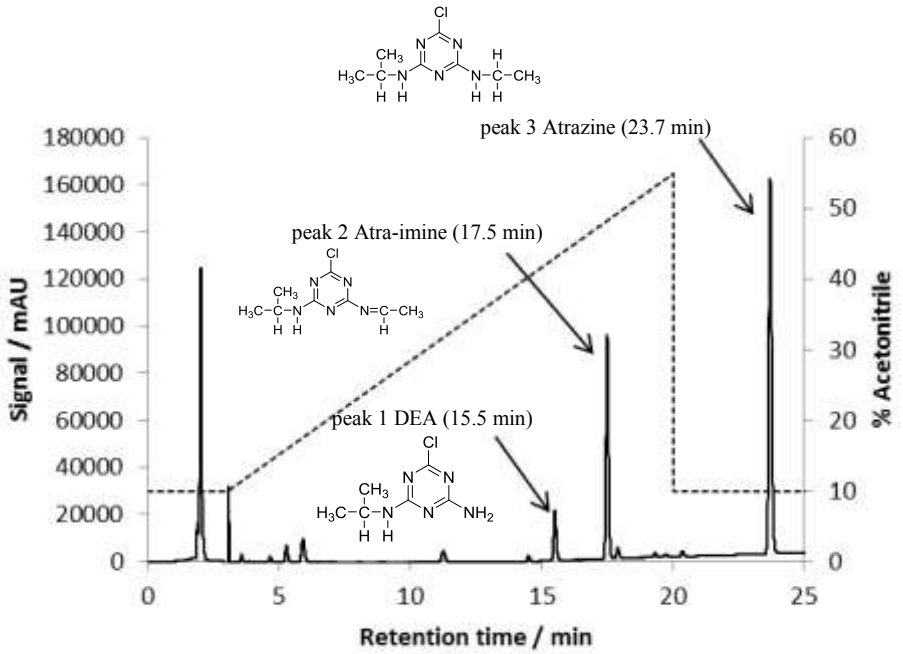
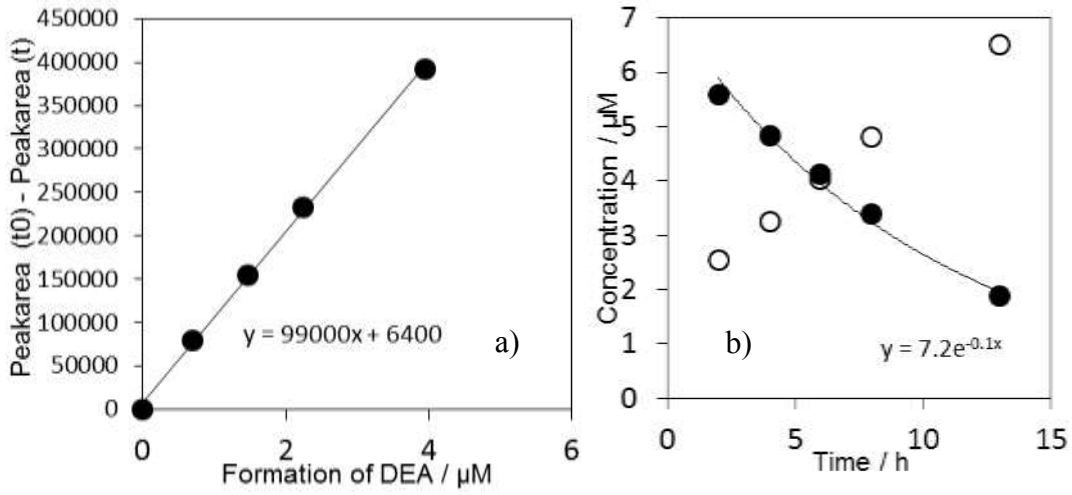


Figure S2 Chromatogram of atrazine degradation by $SO_4^{\bullet-}$ generated in thermal activation of $S_2O_8^{2-}$ (60°C, $[atrazine]_0$ = 21 µM, $[S_2O_8^{2-}]_0$ = 1 mM, reaction time = 8 min, initial pH = 7; eluent acetonitrile/water (pH6-7)); DEA: Desethylatrazine, chemical structures are shown in the figure.

Text S6 Determination of response factors of atra-imine in HPLC-DAD measurements

Atra-imine was calibrated in an experiment whereupon hydrolysis of atra-imine DEA formation was monitored over time (half-life time of atra-imine was ≈ 7 h (Figure S3)). Atra-imine was formed at experimental conditions given in the caption of Figure S2. Assuming a 100% yield of DEA arising from hydrolysis of atra-imine, the DEA formation corresponds to the amount of the hydrolyzed atra-imine. Thus, a plot of the atra-imine peak area vs. concentration of formed DEA, yields the required response factor of atra-imine (≈ 99000 mAU × min μM^{-1} (213 nm)) (Figure S3). This response is very similar compared to DEA (≈ 91000 mAU × min μM^{-1}, 213 nm). Furthermore, the UV-spectra of atrazine, atra-imine and DEA obtained from the DAD hardly differ (Figure S4). Thus, calibration of DEA fairly works for atra-imine in the spectral range where DEA gives a fair response (i.e., 210 and 240 nm).



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196 **Figure S3** a) Calibration of atra-imine; b) hydrolysis of atra-imine: closed symbols atra-

197 imine, open symbols DEA; pH ≈ 7, T = 20-25°C

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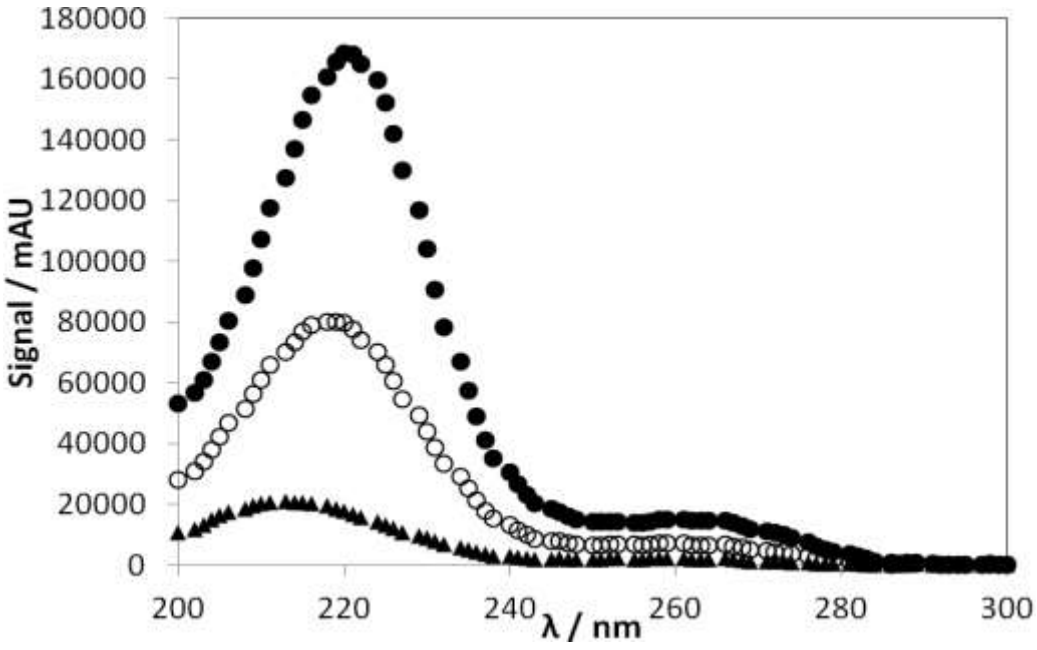

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200 **Figure S4:** Spectra of atrazine (closed circles), Schiff base (N-ethyl side chain) (open circles)

201 and DEA (triangles) obtained from the HPLC-DAD-measurement.

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Literature

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