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# Review of photochemical reaction constants of organic micropollutants required for UV advanced oxidation processes in water

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## ABSTRACT

Emerging organic contaminants (pharmaceutical compounds, personal care products, pesticides, hormones, surfactants, fire retardants, fuel additives etc.) are increasingly found in water sources and therefore need to be controlled by water treatment technology. UV advanced oxidation technologies are often used as an effective barrier against organic contaminants. The combined operation of direct photolysis and reaction with hydroxyl radicals ensures good results for a wide range of contaminants. In this review, an overview is provided of the photochemical reaction parameters (quantum yield, molar absorption, OH radical reaction rate constant) of more than 100 organic micropollutants. These parameters allow for a prediction of organic contaminant removal by UV advanced oxidation systems. An example of contaminant degradation is elaborated for a simplified UV/H<sub>2</sub>O<sub>2</sub> system.

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## 1. Introduction

There is a growing concern about the occurrence of organic micropollutants in source waters for drinking water supply (Pal et al., 2010). These so-called emerging organic contaminants are continuously released into the environment as a result of their use in industry, medical care, agriculture, consumer goods and household activity (Gros et al., 2008). These compounds can be, amongst others, pharmaceuticals, personal care products, pesticides, endocrine disruptors, surfactants, fire retardants, fuel additives (Pal et al., 2010; Gros et al., 2008). Moreover, new compounds are continuously being developed and manufactured, and therefore released into the environment. Some studies even report on emerging organic contaminants found in drinking water (Heberer, 2002; Benotti et al., 2009). In addition, analytical techniques are rapidly advancing, reducing detection limits and allowing the analysis of more and more contaminants (Kuster et al., 2008; Snyder, 2008). These developments give rise to higher demands of water treatment technology to remove all the pollutants found in water sources.

UV advanced oxidation processes (AOPs) are often used as an effective barrier against micropollutants (Yuan et al., 2009). The combination of UV photolysis and hydroxyl (OH) radical reactions ensures the removal of a wide range of compounds. Common techniques are (De Laat et al., 1999; Esplugas et al., 2007; Lau et al., 2007; Cooper et al., 2008; Vilhunen and Sillanpaa, 2010): UV alone, UV/H<sub>2</sub>O<sub>2</sub>, UV/Fe<sup>3+</sup>, UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>, UV/O<sub>3</sub>, UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, UV/TiO<sub>2</sub>, UV/chlorine and UV in combination with other photocatalysts. One of the major issues is the removal efficiency of specific target contaminants by the UV advanced oxidation processes. The variations in molecular structures of contaminants induce variations in removal rates of UV AOPs, both with respect to direct photolysis and radical reactions. In addition, water matrix effects have an important impact on removal rates. So, for an optimal organic micropollutant control, each UV AOP system has to be specifically operated in accordance with its water matrix and targeted contaminant removal. So, (model) predictions of the performance of UV AOP systems applicable to a wide range of compounds would be very beneficial for the design and operation of these systems. Such models have to account for the hydraulics, UV radiation, photochemical reaction and spreading of contaminants. These kinds of models were developed in the last decade (Sozzi and Taghipour, 2007; Alpert et al., 2010; Santoro et al., 2010) and are still being improved. The photochemical reaction part of such models describes the photolysis and OH radical reactions of various target compounds. These models require physicochemical

parameters for each target compound, namely quantum yield, molar absorption and OH radical reaction rate constant. These physicochemical constants are reported in literature for various compounds. Usually, these constants are determined from dedicated small-scale experiments for a few compounds under specific experimental conditions. An overview of reported constants is only provided for OH radical rate constants (Buxton et al., 1988), which have a much wider application area than UV AOPs. However, these data do not contain many emerging pollutants that are of interest nowadays. In addition, an overview of both UV photolysis and oxidation constants for a wide range of chemical compounds has not been found in literature. This review therefore represents an unprecedented overview of 254 nm quantum yields and absorption coefficients, as well as an update on a previous review of Buxton et al. (1988) regarding the OH radical rate constants. These photochemical reaction data are essential for the prediction of contaminant removal by UV AOPs.

The kinetic rate constants presented in this review can also assist in selecting contaminants for regulatory purposes. For example, the California Department of Public Health has recently released the new ‘Title 22’ guidelines for ground water replenishment and reuse that addresses trace organic contaminants and advanced oxidation (CDPH, 2011). From an occurrence study of their municipal wastewaters, agencies have to select different indicator compounds that represent nine different groups depending on their chemical structure. Agencies must demonstrate that their AOP system achieves a certain degradation for each group of contaminants. The kinetic constants in this review may assist in selecting the appropriate compounds: contaminants that will be easily removed as well as compounds that are expected to be critical.

## 2. Materials and methods

### 2.1. Kinetics

For UV AOP systems, most important pathways to degradation are direct photolysis and hydroxyl radical reactions. These processes can be captured in the following parameters: quantum yield, molar absorption and OH radical reaction rate constant. This will be demonstrated for the kinetics of the UV/H<sub>2</sub>O<sub>2</sub> process using a monochromatic UV source.

The direct photolysis of a compound M is described by the following photochemical reaction:



The local photolysis rate inside a (small) volume becomes (Zepp, 1978; Beltran et al., 1995):

$$r_M^{\text{photo}} = -\Phi_M f_M \left( \frac{E'_a \Delta A}{\Delta V} \right), \quad (2)$$

where  $\Phi_M$  the quantum yield of a compound [mol/Einstein], which is defined as the fraction of photons that decompose the compound over the total number of photons absorbed by the compound.  $E'_a$  is the absorbed photon fluence rate [Einstein/m<sup>2</sup>/s] irradiated at surface  $\Delta A$  in the volume  $\Delta V$ , and the factor  $f_M$  represents the fraction of photons absorbed by the compound over all the photons absorbed in the volume. So,  $f_M = \epsilon_M [M]/a$ , where  $a$  represents the total absorption of the water [1/m] and  $\epsilon_M$  the molar extinction of compound  $M$  [m<sup>2</sup>/mol] and  $[M]$  the (local) concentration of compound  $M$  [mol/L]. The total absorption at 254 nm can be measured by spectrophotometry or calculated from the summation over all compounds ( $S_j$ ) in the water matrix:  $a = \sum \epsilon_j S_j$ . For natural waters, the major contributors of the total absorption above 250 nm is the chromophoric dissolved organic matter (CDOM), which can be empirically related to the adsorption (Vione et al., 2010). Using Beer–Lambert law, the absorbed fluence rate over the path length  $\Delta x (= \Delta V/\Delta A)$  in the small volume  $\Delta V$  can be expressed as:

$$E'_a = a \ln(10) E'_p(\mathbf{x}) \Delta x, \quad (3)$$

where  $E'_p(\mathbf{x})$  is the photon fluence rate at position  $\mathbf{x}$ . The local photolysis rate then becomes:

$$r_M^{\text{photo}} = -\ln(10) \Phi_M \epsilon_M [M] E'_p(\mathbf{x}), \quad (4)$$

Physicochemical constants of compounds are often measured in dedicated bench-scale experimental set-ups. These set-ups are therefore often (well-stirred) batch reactor systems, for which we can use a volume-averaged concentration  $\overline{[M]}$ , resulting in the following rate equation (Beltran et al., 1995; Benitez et al., 1995):

$$\frac{d\overline{[M]}}{dt} = \frac{1}{V_0} \int r_M^{\text{photo}} dV, \quad (5)$$

where  $V_0$  is the total volume of the system.

For a collimated beam, an analytical solution of the compound degradation in the volume  $V_0$  [m<sup>3</sup>] can be obtained. In such a system, the fluence rate only changes over the depth coordinate ( $z$ ) of the water sample in the Petri dish. Neglecting the divergence of the light beam, the fluence rate can be written according to the Lambert–Beer law:  $E'_p(z) = E'_p(0)10^{-az}$ . Here is  $E'_p(0)$  the incident fluence rate entering the water surface in the Petri dish. Since the collimated beam is a well-stirred system, it is assumed that the local concentration  $[M]$  is equal to the average concentration  $\overline{[M]}$ . Using this assumption and substituting the expression for  $E'_p(z)$  into Eq. (4), an expression for the degradation is obtained by solving Eq. (5) (De Laat et al., 1999; Beltran et al., 1993; Sharpless and Linden, 2003; Lopez et al., 2003):

$$\ln\left(\frac{\overline{[M]}_T}{\overline{[M]}_0}\right) = -\Phi_M \epsilon_M E'_p(0) \frac{1 - 10^{-aL}}{aL} T, \quad (6)$$

where  $L$  is the depth of the collimated beam [m] and  $T$  the irradiation time [s].

When hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is added to the water that is irradiated by UV, hydroxyl radicals (OH<sup>•</sup>) are formed due to the photolysis of the –O–O– peroxidic bond (Lopez et al., 2003):



The hydroxyl radicals selectively react with substances ( $S_j$ ) in the water:



The rate equation for hydroxyl radicals becomes:

$$r_{\text{OH}} = 2 \ln(10) \Phi_H \epsilon_H [\text{H}_2\text{O}_2] E'_p(x) - \sum_{j=1}^J k_j [S_j] [\text{OH}^\bullet], \quad (9)$$

where  $\Phi_H$ ,  $\epsilon_H$  and  $[\text{H}_2\text{O}_2]$  are the quantum yield, molar absorption and concentration of H<sub>2</sub>O<sub>2</sub>, respectively, and  $[S_j]$  the concentration of background substance  $S_j$ . The first term accounts for formation of OH radicals by photolysis of hydrogen peroxide and the second term accounts for the reaction of hydroxyl radicals with all compounds  $J$  in the solution. The constant  $k_j$  is the OH radical reaction rate constant (L/mol/s). The rate equation for a compound  $M$  now consists of a photolysis and an oxidation part:

$$r_M = -\ln(10) \Phi_M \epsilon_M [M] E'_p(x) - k_M [M] [\text{OH}^\bullet], \quad (10)$$

which requires the concentration of hydroxyl radicals [OH<sup>•</sup>] from Eq. (9). Since compounds react very fast with hydroxyl radicals, a steady-state concentration is often assumed for the hydroxyl radical concentration (De Laat et al., 1999; Sharpless and Linden, 2003), so that  $r_{\text{OH}} = 0$ , resulting in:

$$[\text{OH}^\bullet]^{\text{ss}} = \frac{2 \ln(10) \Phi_H \epsilon_H [\text{H}_2\text{O}_2] E'_p(x)}{\sum_j k_j [S_j]}. \quad (11)$$

For the steady-state OH radical concentration, an analytical solution for the degradation in a collimated beam apparatus can be obtained (under the above-mentioned assumptions of the collimated beam and the assumption that  $[\text{H}_2\text{O}_2]$  and  $\sum k_j [S_j]$  are stationary):

$$\ln\left(\frac{\overline{[M]}_T}{\overline{[M]}_0}\right) = -E'_p(0) \frac{1 - 10^{-aL}}{aL} T \left( \Phi_M \epsilon_M + 2 \Phi_H \epsilon_H \overline{[\text{H}_2\text{O}_2]} \frac{k_M}{\sum_j k_j [S_j]} \right), \quad (12)$$

where the term  $E'_p(0)(1 - 10^{-aL})/aL T$  multiplied with the energy of a photon ( $U_{254}$  [J/Einstein]) is equal to the UV dose [J/m<sup>2</sup>] (Bolton and Stefan, 2002). For predicting removal rates of organic compounds, most important physicochemical parameters thus are: quantum yield ( $\Phi_M$ ), molar absorption ( $\epsilon_M$ ) and OH radical reaction rate ( $k_M$ ). The same holds for other UV AOPs, they only differ on how the hydroxyl radicals are generated. An exception must be made for UV/TiO<sub>2</sub> slurries, where a Lambert–Beer approach would not be valid due to the effect of radiation scattering (Cabrera et al., 1996; Satuf et al., 2005).

## 2.2. Selection of studies and compounds

In this work, UV AOP studies were selected, in which quantum yields or OH radical reaction rate constants were measured,

and the reported parameters were listed for several compounds. The compound's quantum yield is least reported in literature, because it is only used in UV specific studies, whereas OH radical reaction rate constants are also used in other oxidation studies (for example ozonation). The quantum yield is therefore regarded as the principal parameter for determining the list of compounds. In addition, quantum yields are also wavelength dependent. Quantum yields as a function of wavelength are rarely reported in literature, usually the 254 nm quantum yield (used for monochromatic low pressure UV sources) or a 200–300 nm wavelength averaged quantum yield (used for polychromatic medium-pressure UV sources) or an average quantum yield of sunlight radiation is reported. In this work the 254 nm quantum yield is considered and compounds were selected for which this particular quantum yield is reported.

The OH radical reaction rate constants are reported for some well-known compounds by Buxton et al. (1988), but also in online databases (NIST, 2002). However, for less-known or new emerging contaminants, specific bench-scale studies have to be performed to determine OH radical reaction rate constants. The molar absorption (or molar extinction) is most easily obtained, since it is widely reported in literature, but can also be measured fairly simply by spectrophotometry (Inczedy et al., 1997).

### 2.3. Experimental conditions and water matrix

In the direct photolysis process, water samples with target compounds were irradiated by low pressure UV sources. For the most of the 254 nm quantum yields were fitted from the measured compound's degradation. Either the degradation rate, according to Eq. (6), or the time integrated degradation is then determined to estimate the quantum yield value. The photon fluence rate is measured by actinometry, or, depending on the type of UV system, calculated by emission models (for example: for a collimated beam, see Bolton and Stefan (2002), and an axial system, see Benitez et al. (1995)). In some other cases the quantum yields were determined using a competition method with a reference compound.

The molar extinction can be measured by spectrophotometry, using Beer–Lambert law to determine the molar extinction from the measured absorption and compound's concentration (Inczedy et al., 1997).

In the advanced oxidation process, hydroxyl radicals can be generated in several ways. Among them, the following methods were used in the studies described in this work: UV photolysis of hydrogen peroxide, UV photolysis of titanium dioxide, UV photolysis of sodium nitrate, reaction of ozone with hydrogen peroxide, Fenton's process (reaction of ferrous iron with hydrogen peroxide), photo-Fenton's process,  $\gamma$ -radiolysis (ionization of water) and pulse radiolysis of water (short pulse of high energy electrons that lead to the formation of hydroxyl radicals). The UV sources can be monochromatic (low pressure) lamps, polychromatic (medium or high pressure) lamps and sunlight. The most well-known technique to measure OH radical rate constants is the competition method (CM) (Haag and David Yao, 1992), which has been used in most studies. In this method a target compound and a reference compound with a known reaction

rate constant are degraded in the same experimental batch. Both compounds can thus be compared to each other: the ratio of the degradation rates of both compounds is equal to the ratio of reaction rate constants. Different reference compounds were used in the studies: chlorobenzene, nitrobenzene, 4-nitrobenzoate (ion), benzoic acid, acetophenone, 2-bromoethanol, pCBA (para-chlorobenzoic acid), PCE (tetrachloroethylene), DMPO (5,5-dimethylpyrroline-N-oxide) 2-propanol, SCN<sup>-</sup> (thiocyanic acid) and accelerine (N,N-dimethyl-4-nitroso-benzenamine).

In most studies, compounds were added to MilliQ water, and buffered to adjust the pH to a desired value. In some studies, the quantum yields and molar absorptions are measured as a function of pH, for which the values of pH around 7 are reported in this work. In addition, some studies show the temperature dependence of quantum yields, which follow an Arrhenius type of relation. Again, the most commonly used temperature between 20 and 25 °C is selected from these studies.

## 3. Results

The physicochemical constants (quantum yield at 254 nm, molar absorption at 254 nm and OH radical reaction rate constant) are shown in Table LABEL:app\_mean for a pH range of 5.5–9, where the averages are taken for compounds with more than one reported value. Table S1 in the supporting information shows the experimental details (if reported): the process that is used in each study to generate photons at 254 nm or hydroxyl radicals; the method that is employed to measure the physicochemical constant; and under which pH and temperature the experiment has been performed.

Measured quantum yields are all but one (triphenyltin hydroxide) smaller than 1 and vary between  $1.3 \cdot 10^{-5}$  and  $1.25 \text{ mol E}^{-1}$  with an average of  $0.129 \text{ mol E}^{-1}$ . Molar extinctions vary between 14.7 and  $69,381 \text{ M}^{-1}\text{cm}^{-1}$  with an average of  $6260 \text{ M}^{-1}\text{cm}^{-1}$ . OH radical reaction rate constants vary between  $5 \cdot 10^7$  and  $5.6 \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1}$  with an average of  $7.7 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ . Some of the reported OH radical reaction rate constants approach diffusion-control limits ( $\sim 1\text{--}2 \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1}$ ). Sanchez-Polo et al. (2008) report rate constants of nitroimidazoles that even exceed diffusion-control limits, but they do not discuss these high values. A possible but unverified explanation is a Grotthus like mechanism of hydroxyl radicals in water (Kochany and Bolton, 1992).

The same compounds that were reported in more than one study may show differences in reported constants. Some differences between the same compounds can be attributed to pH: these differences may change the compound's and/or radical's conjugate acid or base concentration, which may affect the degradation rate. Other dissimilarities reveal that in separate studies both the quantum yield and hydroxyl radical rate constant differ in the same order of magnitude for the same compound, which can be related to systematic differences, such as experimental set-up, chemical supplier, chemical analysis method, or water matrix effects. Chemical analysis methods have evolved over time, resulting in more accurate solutions. Differences in water matrix may lead to involvement of other radicals that degrade compounds, which

**Table 1 – Summary of photochemical constants of various organic compounds, details and references are provided in Table S1. Range of pH is between 5.5 and 9. For compounds with more than one reported constant, averages are taken and standard deviation is given in parentheses.**

Name (CAS)	$\Phi_{254}$ ( $10^{-2}$ ) mol/Einstein	$\epsilon_{254}$ ( $10^3$ ) L/mol/cm	$k_{OH}$ ( $10^9$ ) L/mol/s
1,2,3-trichlorobenzene (87-61-6)	19.0	0.308	6.10
1,4-dichlorobenzene (106-46-7)	60.0	0.118	7.95 ( $\pm 3.61$ )
2,4-Dichlorophenoxyacetic acid (94-75-7)	0.950	0.173	3.24 ( $\pm 1.61$ )
2,6-Dinitrotoluene (606-20-2)	2.20	6.64	0.750
4-t-Octylphenol (140-66-9)	1.60	0.675	4.20
Acenaphthene (83-32-9)	5.20	1.33	8.80
Acetovanillone (498-02-2)	2.33	–	–
Alachlor (15972-60-8)	14.8 ( $\pm 5.8$ )	0.479 ( $\pm 0.059$ )	5.20 ( $\pm 0.28$ )
Amoxicillin (26787-78-0)	37.2 ( $\pm 28.1$ )	1.20	5.43 ( $\pm 2.13$ )
Anthracene (120-12-7)	14.9 ( $\pm 7.4$ )	1.07 ( $\pm 0.04$ )	–
Atrazine (1912-24-9)	4.77 ( $\pm 1.37$ )	3.40 ( $\pm 0.66$ )	2.30 ( $\pm 0.14$ )
Benzene (71-43-2)	88.0	0.250	6.72 ( $\pm 1.71$ )
Benzo[a]anthracene (56-55-3)	0.121	69.4	–
Benzo[a]pyrene (50-32-8)	16.4 ( $\pm 21.2$ )	1.08	25.1 ( $\pm 0.2$ )
Bisphenol A (80-05-7)	0.655 ( $\pm 0.276$ )	0.750	8.00 ( $\pm 3.11$ )
Boldenone (846-48-0)	61.0	14.6	–
Bromoxynil (1689-84-5)	4.00	4.97	–
Butachlor (23184-66-9)	82.0	0.410	7.40
Caffeine (58-08-2)	0.180	3.92	6.40 ( $\pm 0.71$ )
Carbamazepine (298-46-4)	0.060	6.07 ( $\pm 0.00$ )	8.02 ( $\pm 1.90$ )
Carbendazime (10605-21-7)	0.230	4.47	2.20
Carbofuran (1563-66-2)	1.66	0.800	2.46 ( $\pm 1.04$ )
Carbomethoxyfenitrothion (54812-31-6)	0.084	5.02	–
Chloramphenicol (56-75-7)	8.40	4.33	5.80
Chlorfenvinphos (470-90-6)	7.25 ( $\pm 2.33$ )	7.97 ( $\pm 0.97$ )	10.9 ( $\pm 10.8$ )
Chlorotetracycline (57-62-5)	2.95	16.8 ( $\pm 2.9$ )	–
Chlorotoluron (15545-48-9)	3.19	6.08	4.30
Chlorpyrifos (2921-88-2)	1.60	0.650	4.54 ( $\pm 0.52$ )
Chrysene (218-01-9)	0.315	–	9.82
Ciprofloxacin (85721-33-1)	1.18 ( $\pm 0.22$ )	17.2 ( $\pm 6.8$ )	5.94 ( $\pm 1.72$ )
Clofibric acid (882-09-7)	27.5 ( $\pm 37.3$ )	0.927 ( $\pm 0.930$ )	5.03 ( $\pm 2.38$ )
Coumaphos (56-72-4)	0.270	2.40	–
DBCP (96-12-8)	49.0	0.015	0.150
DNOC (534-52-1)	0.048	6.83	–
Desethylatrazine (6190-65-4)	5.90	3.44	1.20
Desethyldeisopropylatrazine (3397-62-4)	1.80	2.20	0.050
Desisopropylatrazine (1007-28-9)	5.90	3.60	1.80
Diatrizoic acid (737-31-5)	3.50	31.2	0.540
Diazinon (333-41-5)	6.53 ( $\pm 3.24$ )	2.94 ( $\pm 1.34$ )	8.75 ( $\pm 0.35$ )
Dibenz[a,h]anthracene (53-70-3)	0.222	12.6	–
Diclofenac (15307-86-5)	29.2 ( $\pm 8.6$ )	4.77 ( $\pm 1.16$ )	8.38 ( $\pm 1.24$ )
Dimetridazole (551-92-8)	0.320	2.24	56.0
Diphenhydramine (147-24-0)	12.5	0.388	5.42
Disulfoton (298-04-4)	16.0	0.160	–
Diuron (330-54-1)	1.43 ( $\pm 0.41$ )	16.1 ( $\pm 0.4$ )	4.60
Doxycycline (564-25-0)	1.15 ( $\pm 1.47$ )	49.9 ( $\pm 65.1$ )	7.74
EPN (2104-64-5)	0.810	4.36	–
Estradiol (50-28-2)	5.50 ( $\pm 1.70$ )	0.403 ( $\pm 0.024$ )	14.1
Ethinylestradiol (57-63-6)	4.83 ( $\pm 1.95$ )	1.04 ( $\pm 1.35$ )	10.3 ( $\pm 0.7$ )
Etridiazole (2593-15-9)	46.0	0.720	–
Fenchlorfos (299-84-3)	71.0	0.635	–
Fenitrothion (122-14-5)	0.910	4.66	–
Fensulfothion (115-90-2)	4.90	1.74	–
Fenthion (55-38-9)	9.20	10.3	–
Fluoranthene (206-44-0)	44.7	0.311	–
Fluorene (86-73-7)	0.565 ( $\pm 0.262$ )	16.7	6.34 ( $\pm 5.04$ )
Hydrochlorothiazide (58-93-5)	4.10	6.65	5.70
Ibuprofen (15687-27-1)	19.2	0.256	7.04 ( $\pm 0.52$ )
Iohexol (66108-95-0)	4.03	27.6	3.81
Iopromide (73334-07-3)	3.90	21.0	3.30
Isazofos (42509-80-8)	2.70	0.070	–

(continued on next page)

**Table 1 – (continued)**

Name (CAS)	$\Phi_{254}$ ( $10^{-2}$ ) mol/Einstein	$\epsilon_{254}$ ( $10^3$ ) L/mol/cm	$k'_{OH}$ ( $10^9$ ) L/mol/s
Isofenfos (25311-71-1)	4.95 ( $\pm 2.62$ )	1.05 ( $\pm 0.29$ )	–
Isoprotruron (34123-59-6)	0.285 ( $\pm 0.120$ )	6.01 ( $\pm 0.09$ )	3.00 ( $\pm 3.11$ )
Ketoprofen (22071-15-4)	29.8 ( $\pm 8.7$ )	15.3 ( $\pm 0.2$ )	6.89 ( $\pm 2.14$ )
Ketorolac (74103-06-3)	0.600	6.54	–
Linuron (330-55-2)	3.60	13.4	4.30
MCPA (94-74-6)	15.0	0.352	4.55 ( $\pm 2.90$ )
Mefenamic acid (61-68-7)	–	4.63	–
Methyl chlorpyrifos (5598-13-0)	1.30	0.610	–
Methyl parathion (298-00-0)	0.043	4.58	–
Metolachlor (51218-45-2)	45.5 ( $\pm 21.9$ )	0.564 ( $\pm 0.086$ )	6.96 ( $\pm 2.00$ )
Metoprolol (51384-51-1)	3.47 ( $\pm 4.12$ )	0.565 ( $\pm 0.333$ )	7.84 ( $\pm 0.77$ )
Metoxuron (19937-59-8)	2.00	–	–
Metronidazole (443-48-1)	0.340 ( $\pm 0.014$ )	2.10	17.9 ( $\pm 22.6$ )
NDMA (62-75-9)	24.8 ( $\pm 10.2$ )	1.65	0.380 ( $\pm 0.071$ )
Naproxen (22204-53-1)	2.78 ( $\pm 2.06$ )	4.00 ( $\pm 0.70$ )	8.61
Nitrobenzene (98-95-3)	0.700	5.56	3.40 ( $\pm 0.71$ )
Norfloracin (70458-96-7)	0.340	15.4	1.000
Oxamyl (23135-22-0)	55.0	5.32	–
Oxytetracycline (79-57-2)	1.15 ( $\pm 1.03$ )	15.8 ( $\pm 3.5$ )	6.96
PFOA (335-67-1)	0.001	–	–
PFOS (1763-23-1)	0.017	–	–
Paracetamol (103-90-2)	0.180	6.64 ( $\pm 2.14$ )	5.85 ( $\pm 4.51$ )
Parathion (56-38-2)	0.060	–	9.70
Pentachlorophenol (87-86-5)	2.50	7.40	9.00
Phenacetin (62-44-2)	0.460	9.10	–
Phenanthrene (85-01–8)	0.690	40.5	13.4
Phenazone (60-80-0)	3.37 ( $\pm 4.18$ )	8.60 ( $\pm 0.43$ )	7.93 ( $\pm 4.34$ )
Phenol (108-95-2)	2.55 ( $\pm 0.64$ )	0.750 ( $\pm 0.325$ )	10.3 ( $\pm 5.2$ )
Phenytoin (57-41-0)	27.9	1.26	6.28
Primidone (125-33-7)	8.20	0.220	6.70
Profenofos (41198-08-7)	2.60	0.460	–
Progesterone (57-83-0)	2.20	17.0	–
Propachlor (1918-16-7)	12.7	0.421	4.45 ( $\pm 0.21$ )
Propazine (139-40-2)	9.90	3.37	1.65 ( $\pm 0.21$ )
Prothiofos (34643-46-4)	110	0.121	–
Pyrene (129-00-0)	0.385	18.2	–
Pyridaphenthion (119-12-0)	0.032	1.87	–
Ronidazole (7681-76-7)	0.221	2.26	13.9
Simazine (122-34-9)	8.30	3.33	2.90 ( $\pm 0.28$ )
Sulfadiazine (68-35-9)	0.581	20.1	4.50 ( $\pm 1.13$ )
Sulfadimidine (57-68-1)	0.870	14.0 ( $\pm 6.4$ )	6.32 ( $\pm 1.75$ )
Sulfamethoxazole (723-46-6)	3.79 ( $\pm 1.15$ )	13.2 ( $\pm 4.5$ )	5.82 ( $\pm 1.99$ )
Terbutylazine (5915-41-3)	9.40	3.83	2.80
Testosterone (58-22-0)	3.30	15.1	–
Tetracycline (60-54-8)	0.380	8.82 ( $\pm 6.66$ )	7.70
Tinidazole (19387-91-8)	0.196	2.34	45.0
Tolclofos (57018-04–9)	1.70	0.774	–
Trenbolone (10161-33-8)	0.290	6.30	4.30
Trichloroethylene (79-01–6)	35.4	–	3.30
Trifluralin (1582-09-8)	60.0	4.97	–
Trimethoprim (738-70-5)	0.118	2.94	6.30 ( $\pm 0.85$ )
Triphenyl phosphite (115-86-6)	29.0	0.644	–
Triphenyltin hydroxide (76-87-9)	125	0.582	9.40
m-cresol (203-39-4)	5.70	0.302	–
m-nitrophenol (554-84-7)	0.019	3.41	–
n-Butylparaben (94-26-8)	0.330	15.4	4.80
o-nitrophenol (88-75-5)	0.200	4.31	–
pCBA (74-11-3)	1.30	2.37	5.00

have not accounted for in the research. For example, Miller and Olejnik (2001) report different quantum yields for mixtures of benzo[a]pyrene, chrysene and fluorene than for the sole compound. Also, differences in molar adsorption may

result in differences in quantum yields, since the product of both is used in the fitting of quantum yield from measured degradation data (compare for example, doxycycline data of Yuan et al. (2011a) and Rivas et al. (2010) in Table S1). Or, in

some research, the fitted quantum yields are also used in the fitting of the hydroxyl radical rate constant, so that higher quantum yields may be accompanied with lower hydroxyl radical rate constants or vice versa (see for example, amoxicillin data of [Andreozzi et al. \(2005\)](#) compared to the data of [Benitez et al. \(2009\)](#) in Table S1).

### 3.1. Cluster analysis

Cluster analysis is performed on the reported data by means of self-organizing maps (SOM). SOM analysis is a technique to visualize high-dimensional data onto a regular low-dimensional grid ([Kohonen, 1990](#)). The map consists of nodes or neurons in a hexagonal grid. Each node is associated with a weight vector, a vector with a length equal to the number of input data variables. Nodes with similar weight vectors are mapped close together and dissimilar far apart. For each node, compound(s) are associated with that particular node that matches best. Each node may therefore represent zero, one or several compounds. In addition, closely related chemicals can be found in the same region of the self-organizing map.

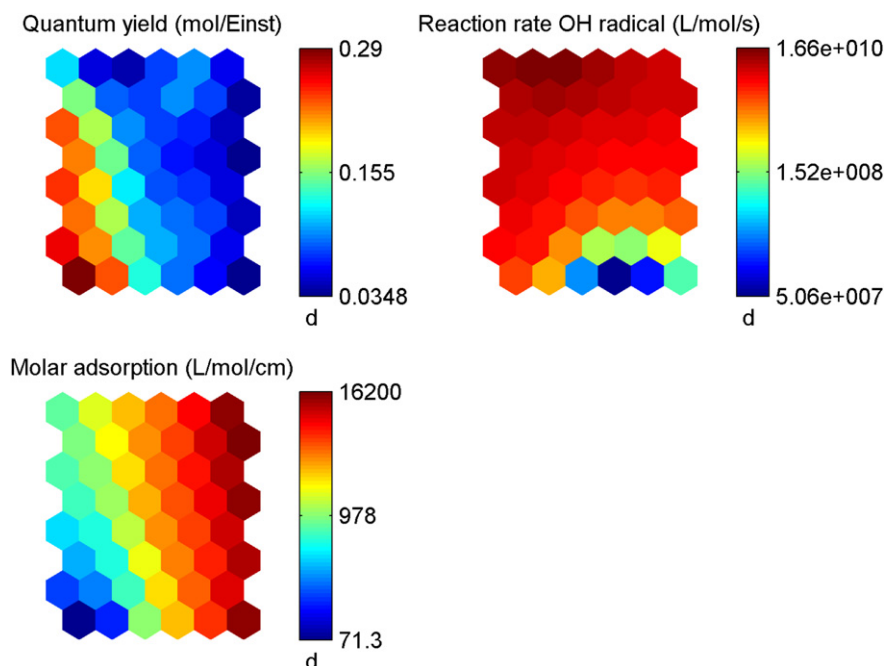
A self-organizing map is constructed using the three physicochemical parameters (reaction rate OH radical, quantum yield and molar absorption, Table 1) as input data. The resulting SOM shows the UV photolysis and oxidation behaviour of these compounds. The values of the weight vectors are shown in Fig. 1, which represent the physicochemical constants at each node. The map demonstrates that similar values of each of the three constants are grouped together. Also, high quantum yield values correspond with low molar absorption values and vice versa. The quantum yields and molar absorptions mainly differ in horizontal direction, so that the highest compound's removal is expected

at the right (the molar adsorption shows the largest differences). The hydroxyl radical rate constants mainly differ in vertical direction, so that the highest compound's removal is expected at the top. In Fig. 2, each compound is depicted in its best matching node. Some nodes are associated with several compounds, for example a node with dimetridazole, metronidazole, ronidazole and tinidazole, which are all nitroimidazole antibiotic medications. These compounds behave very similar during UV/H<sub>2</sub>O<sub>2</sub> treatment. Also, closely related compounds can be found in the same region of the SOM (for example compounds that look similar according to their nomenclature: parts with \*zole, \*zine, \*chlor, etc in their name). NDMA deviates clearly from the other compounds due to its much lower OH radical reaction rate than the other compounds. Therefore, some empty nodes are surrounding this compound.

## 4. Discussions

### 4.1. Hydroxyl radical scavenging

The hydroxyl radicals react nonselectively with different compounds in the water. The amount of hydroxyl radicals formed is the limiting factor in these reactions, and there is a competition between compounds for the hydroxyl radicals. As a wide variation of background substances can be present in the water matrix, scavenging of hydroxyl radicals may significantly reduce the degradation rate of target compounds. The main scavengers therefore need to be included to obtain a proper prediction of compound degradation in water matrices. So, knowledge on the OH radical rate constants of background substances is required to use Eqs. (9) and (10), where the total scavenging rate is given by:  $\sum_j k_j [S_j]$  with unit



**Fig. 1 – Self-organizing maps analysis. Quantum yields, molar absorption and OH radical reaction rate constants are shown for the nodes.**

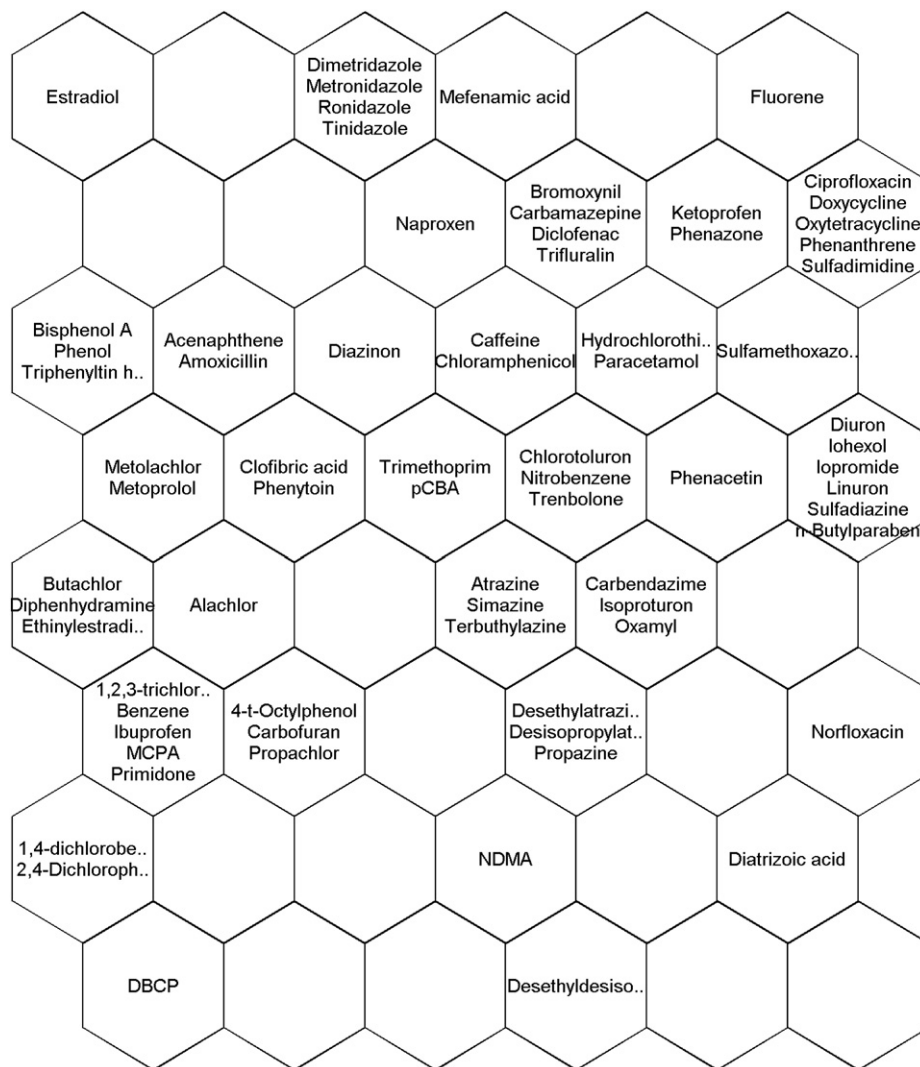


Fig. 2 – Self-organizing maps analysis. Compounds with similar behaviour towards UV/H<sub>2</sub>O<sub>2</sub> treatment are clustered.

[1/s]. These rate constants are given in Table 2 for the most important scavengers in water, including studies on (natural) organic matter. For (natural) organic matter, differences in OH radical rate constants can be found due to the variation in organic matter content and composition. Generally, river and lake waters have rate constants of about  $2\text{--}3 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$ , whereas wastewater effluents have higher values.

#### 4.2. Role of other radicals

The hydroxyl radicals react with all background compounds in the water and may create other radicals, resulting in a complex reaction scheme. Some studies (Glaze et al., 1995; Crittenden et al., 1999; Mazellier et al., 2002a; Wu and Linden, 2010) provide an overview of hydroxyl radical reactions with hydrogen peroxide, (bi)carbonate, phosphate and interacting radicals. Photolysis of free chlorine (HOCl and OCl<sup>-</sup>) results in the formation of hydroxyl radicals and chlorine radicals (Watts and Linden, 2007; Jin et al., 2011). The chlorine radicals may induce a chain of reactions producing other chlorine related radicals (De Laat et al., 2004; Grebel et al., 2010; Yuan

et al., 2011b). So, the target compound *M* may not only be destructed by hydroxyl radicals, but also by other radicals, for example perhydroxyl radicals (HO<sub>2</sub>), superoxide radicals (O<sub>2</sub><sup>-</sup>), carbonate radicals (CO<sub>3</sub><sup>-</sup>), phosphate radicals (HPO<sub>4</sub><sup>-</sup>), sulfate radicals (SO<sub>4</sub><sup>-</sup>), chlorine radicals (Cl<sup>\*</sup>), dichloride radicals (Cl<sub>2</sub><sup>-</sup>) or Br<sub>2</sub><sup>-</sup>. Reaction rate constants of these and other inorganic radicals are reviewed by Neta et al. (1988). Recently, the importance of the carbonate radical has been highlighted (Mazellier et al., 2002a; Wu and Linden, 2010; Djebbar et al., 2003). Carbonate radicals are formed when hydroxyl radicals react with carbonate or bicarbonate. The carbonate radicals selectively react with organic compounds and reaction rates can be substantial for aromatic or sulfur-containing molecules (Mazellier et al., 2002a). Second order rate constants are reported for some pesticides (Table 3). The values are usually around two or three orders of magnitude smaller than the OH radical rate constants. Nevertheless, when hydrogen carbonate concentrations are high, more hydroxyl radicals are consumed to form carbonate radicals, so that the destruction of target compounds by carbonate radicals may become important (Wu and Linden, 2010).



**Table 2 – Main hydroxyl radical scavengers.**

Name	Reference	$k_{OH}$
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	Buxton et al. (1988)	$2.7 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$
Hydrogen peroxide anion (HO <sub>2</sub> <sup>-</sup> )	Christensen et al. (1982)	$7.5 \cdot \text{M}^{-1} \text{ s}^{-1}$
Carbonate (CO <sub>3</sub> <sup>2-</sup> )	Buxton et al. (1988)	$3.9 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	Buxton et al. (1988)	$8.5 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$
Hydrogen phosphate ion (HPO <sub>4</sub> <sup>2-</sup> )	Maruthamuthu and Neta (1978)	$1.5 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$
Dihydrogen phosphate ion (H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> )	Maruthamuthu and Neta (1978)	$2.0 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$
Nitrite (NO <sub>2</sub> <sup>-</sup> )	Coddington et al. (1999)	$1.0 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
Bromide ion (Br <sup>-</sup> )	Zehavi and Rabani (1972)	$1.06 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
DOC	Larson and Zepp (1988)	$3.0 \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
DOC (lake and river water)	Brezonik and Fulkerson-Brekken (1998)	$2.9 (\pm 1.0) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
NPOC (ground water)	Vione et al. (2006)	$9.8 \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
NPOC (surface water)	Vione et al. (2006)	$6.0 \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
Suwannee River fulvic acid	Westerhoff et al. (2007)	$1.6 (\pm 0.24) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
Saguaro Lake	Westerhoff et al. (2007)	$1.79 (\pm 0.37) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
Elliot soil humic acid	McKay et al. (2011)	$1.21 (\pm 0.09) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
Pony Lake fulvic acid	McKay et al. (2011)	$6.90 (\pm 0.53) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
Suwannee River standard fulvic acid	McKay et al. (2011)	$2.06 (\pm 0.09) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
DOC (Lake Zurich)	Katsoyiannis et al. (2011)	$2.7 (\pm 1.2) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
DOC (Lake Jonsvatnet)	Katsoyiannis et al. (2011)	$2.0 (\pm 0.2) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
DOC (Lake Greifensee)	Katsoyiannis et al. (2011)	$2.1 (\pm 0.8) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
Tap water	Nagarnaik and Boulanger (2011)	$8.5 (\pm 1.0) \cdot 10^7 \text{ M}_C^{-1} \text{ s}^{-1}$
Hospital effluent	Nagarnaik and Boulanger (2011)	$7.3 (\pm 0.2) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
DOC (WWTP)	Westerhoff et al. (2007)	$3.3 (\pm 1.4) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
WWTP effluent	Nagarnaik and Boulanger (2011)	$5.8 (\pm 0.2) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
WWTP influent	Nagarnaik and Boulanger (2011)	$6.8 (\pm 1.0) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
Effluent organic matter	Katsoyiannis et al. (2011)	$3.5 (\pm 0.2) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$
Effluent organic matter	McKay et al. (2011)	$7.85 (\pm 1.35) \cdot 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$

#### 4.3. Formation of byproducts

In principle, complete mineralization of organic micro-pollutants may be achieved by means of UV oxidation processes. However, as this would require extended UV irradiation times and large amounts of energy, in general byproducts, with a higher polarity and water solubility than the parent compounds, will be formed (Chen et al., 2008; Rosenfeldt and Linden, 2004). These byproducts may be more problematic from a toxicological point of view, like in the case

of hydroxylamines (Huber et al., 2003), phenols, quinones carboxylic acids and aldehydes (Shemer and Linden, 2007a, b; Toor and Mohseni, 2007). Other examples are the formation of the mutagenic acridine from direct photolysis of carbamazepine (Chiron et al., 2006), or dibenzodioxin from triclosan (Latch et al., 2005). If the UV dose applied and/or the H<sub>2</sub>O<sub>2</sub> concentration will be high enough, eventually these byproducts may be degraded as well as their parent compounds (Shemer and Linden, 2007a, b). In water with appreciable levels of chloride ions, chlorinated compounds may be formed, which are known for their toxicity (Yuan et al., 2011b). Similar effects may be encountered with bromide ions, which are present in much lower concentrations than chloride, but which have to be taken into account, as brominated compounds are generally more cytotoxic and genotoxic (Gebel et al., 2010). Recently, a model was developed which predicts the pathway of contaminant degradation and byproduct formation during advanced oxidation (Li and Crittenden, 2009). This model may be used to predict whether or not toxic byproducts are to be expected. UV oxidation of NOM can result in the formation of genotoxic compounds (Heringa et al., 2011), free metal ions (Parkinson et al., 2001) and chlorine compounds (Bond et al., 2009). In order to cover all possible effects some authors state that chemical analysis (to determine the decay of the target compounds) should always be complemented by the application of bioassays that provide an integrated measure of toxicity, covering the effects of byproducts and antagonistic or synergistic interactions (Shemer and Linden, 2007a, b).

**Table 3 – Second order reaction rate constants with carbonate radicals.**

Name	Reference	$k_{CO_3^{\cdot-}}$ (M <sup>-1</sup> s <sup>-1</sup> )
Atrazine (1912-24-9)	Huang and Mabury (2000)	$4.0 \cdot 10^6$
Carbendazime (10605-21-7)	Mazellier et al. (2002b)	$6.0 (\pm 2.0) \cdot 10^6$
Chlorpyrifos (2921-88-2)	Wu and Linden (2010)	$8.8 (\pm 0.4) \cdot 10^6$
Diuron (330-54-1)	Djebbar et al. (2003)	$5.0 \cdot 10^6$
Methyl parathion (298-00-0)	Huang and Mabury (2000)	$2.0 \cdot 10^5$
Parathion (56-38-2)	Wu and Linden (2010)	$2.8 (\pm 0.2) \cdot 10^6$
Phenol (108-95-2)	Busset et al. (2007)	$1.6 \cdot 10^7$
Thiobencarb (28249-77-6)	Huang and Mabury (2000)	$2.8 \cdot 10^5$

#### 4.4. Expected removal during drinking water treatment

Using Eq. (12), an estimate of the degradation during UV/H<sub>2</sub>O<sub>2</sub> treatment (low pressure lamps) has been made for all the compounds with known physicochemical parameters (Fig. 3). In this estimate, OH radical scavenging by hydrogen peroxide, (bi)carbonate and DOC has been considered. The average water quality of Nieuwegein water (pumping station Tull and 't Waal) has been used. Large variations in compound degradation from ~5% to ~99% were predicted, caused by the differences in chemical structures. Some compounds are well removed by direct photolysis, some by hydroxyl radical reactions, and some by both processes. Recalling the cluster

analysis (Figs. 1 and 2), compounds with highest removal rates are expected at the upper right position of the SOM, and the lowest at the lower left position. These trends can be observed in estimated degradation. Compounds in the same nodes of the SOM show comparable degradation results and should be found close together in Fig. 3. This is apparently not always the case, since the nodes in the SOM also reveal another property: compounds in the same nodes show a similar ratio of the three photochemical constants, and therefore in some extent a similar ratio between photolysis and oxidation degradation, which can be observed from the ratio of the red and yellow bars in Fig. 3. This example confirms the effectiveness of the combination of both processes, and explains

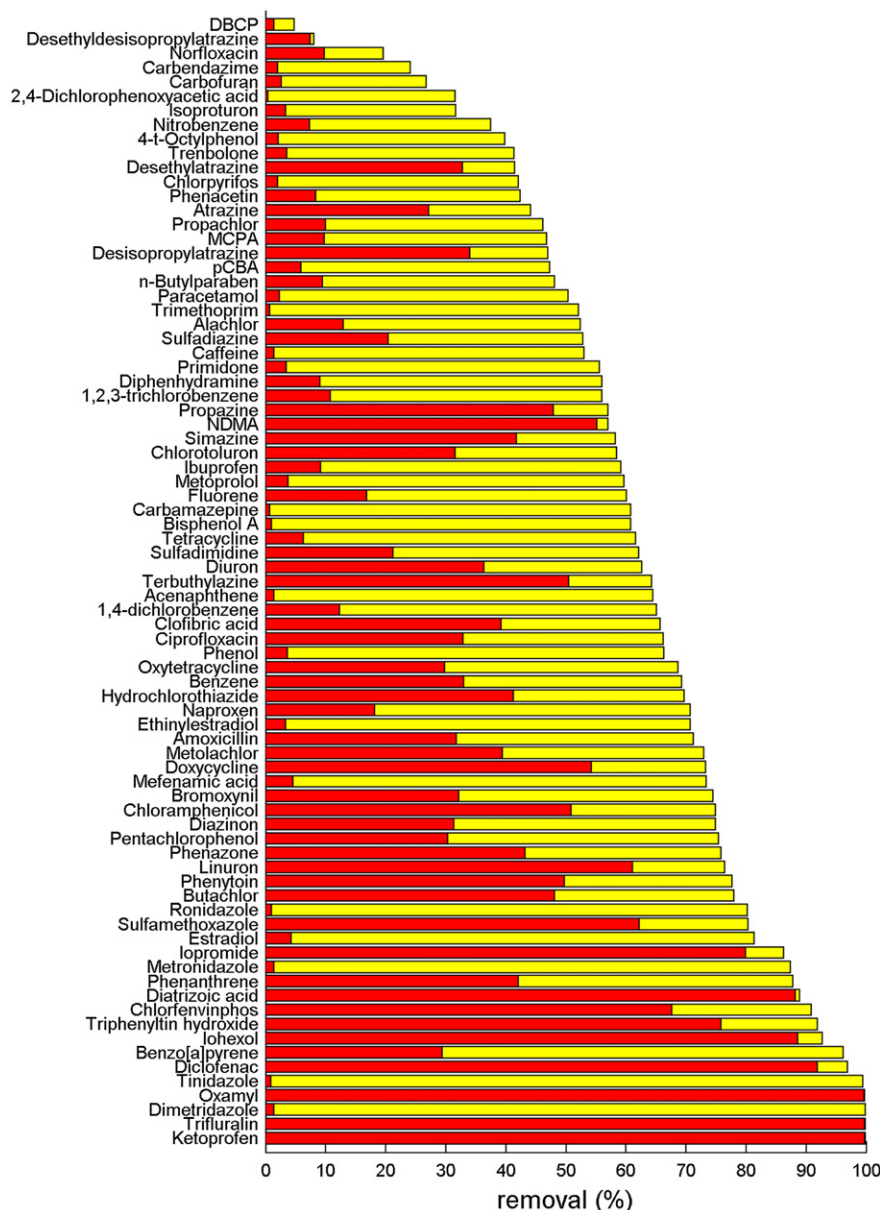


Fig. 3 – Predictions of compound degradation during UV/H<sub>2</sub>O<sub>2</sub> treatment (low pressure lamps, 400 mJ/cm<sup>2</sup>) for a typical water matrix (Nieuwegein water – pumping station Tull and 't Waal: 250 mg/L HCO<sub>3</sub><sup>-</sup>, 1.7 mg/L DOC, pH 8). The effect of direct photolysis is in red, and OH radical reactions in yellow. The compounds are shown in the order of low removal to high removal. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

why UV AOPs are successful water treatment technologies for a wide range of applications.

## 5. Conclusions

The present work provides an unprecedented overview of photochemical reaction parameters for a wide range of organic contaminants in UV AOPs. For more than 100 pharmaceuticals, hormones, pesticides, fuel additives and other industrial compounds, the reported values of quantum yields, molar absorption and OH radical reaction rate constants are provided. Also, the scavenging of hydroxyl radical by water matrix constituents is considered. Knowledge on these physicochemical constants and water matrix effects allows for the prediction of contaminant removal by UV AOPs. This was shown in this work for the degradation of compounds in a collimated beam, but these constants can also be used in more advanced (CFD) models to predict the performance of different UV AOP systems. Since more and more contaminants are being detected in source waters, these predictions contribute to the improvement of contaminant control by UV AOP systems.

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## Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.watres.2012.03.036](https://doi.org/10.1016/j.watres.2012.03.036).

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