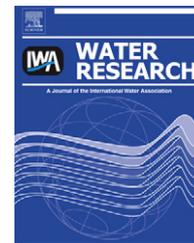


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Effect of dissolved organic compounds on the photodegradation of the herbicide MCPA in aqueous solution

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ABSTRACT

This work shows that the addition of phenol and 2-propanol as model organic compounds significantly decreases the direct photolysis quantum yield of 4-chloro-2-methylphenoxyacetic acid (MCPA) upon UVB irradiation in aqueous solution. Laser flash photolysis data suggest that 2-propanol is able to decrease the formation of the MCPA excited states under irradiation. A decrease from 0.54 to 0.34 of the photolysis quantum yield of the anionic form of MCPA (which prevails over the undissociated one in surface waters) could have a considerable impact on the MCPA lifetime in ecosystems where the direct photolysis is the main phototransformation pathway. In surface water bodies where the direct photolysis has comparable kinetics as the reaction with $\cdot\text{OH}$, a decrease of the quantum yield would enhance the relative importance of the $\cdot\text{OH}$ pathway, which yields considerably less toxic intermediates than the direct photolysis.

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1. Introduction

The 4-chloro-2-methylphenoxyacetic acid (MCPA) is extensively used as a herbicide against broad-leaf weeds; for this reason, like other phenoxyacid compounds (Rugge et al., 2002), it is environmentally widespread and has been detected in agricultural drainage water (Tran et al., 2007), ground-water (Spliid and Koppen, 1998; Harrison et al., 1998), and sometimes even in water supplies intended for human use (Henriksen et al., 2001). It is an acid with $\text{pK}_a \approx 3.1$ (Martell et al., 1997) and, therefore, it is mainly present in environmental waters as the anionic form. Interestingly, the

undissociated form that is more lipid-soluble shows the highest toxicity (Cabral et al., 2003). MCPA absorbs UV radiation with a maximum around 280 nm, and the ability of both the anionic and the undissociated forms to absorb sunlight is quite limited. However, the low sunlight absorption is compensated for by the rather elevated quantum yield of direct photolysis, around 0.6 for the anionic form and 0.35 for the neutral one (Zertal et al., 2001).

The main intermediate that is produced upon direct photolysis of MCPA is 4-chloro-2-methylphenol (Zertal et al., 2001, 2005). The latter compound has been detected in the Rhône delta waters, where MCPA is extensively used as

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post-emergent herbicide in flooded rice farming. The concentration levels of 4-chloro-2-methylphenol (some $\mu\text{g L}^{-1}$) were comparable to those of the parent herbicide. Interestingly, 4-chloro-2-methylphenol undergoes efficient photonitration to 4-chloro-2-methyl-6-nitrophenol in the delta waters (Chiron et al., 2009). Therefore, the photo-transformation of MCPA can lead to toxic and potentially mutagenic secondary (and tertiary) pollutants in the environment. Field data are further supported by the laboratory finding that the intermediates of MCPA direct photolysis are more toxic than the parent compound (Zertal et al., 2001).

Interestingly, the phototransformation rate of MCPA was over twice higher in ultra-pure than in river water (Chiron et al., 2007), which suggests that the direct photolysis of MCPA could be a very important transformation pathway. River water contains compounds that would compete with MCPA for radiation absorption, but some of them could photosensitise the degradation of MCPA itself. From the experimental set-up adopted by Chiron et al. (2007), it can be inferred that the presence of light-absorbing species could decrease the radiation absorption of MCPA by at most 30%. However, some of the light-absorbing components of river water have a photosensitising activity that would induce indirect MCPA transformation. Accordingly, the observed >50% inhibition of MCPA photodegradation in river vs. ultra-pure water cannot only be explained by competition for irradiance. Similar results have been observed for the phototransformation of phenanthrene and carbofuran, and have been tentatively attributed to a decrease of the quantum yield of direct photolysis in the presence of dissolved organic compounds (Bachman and Patterson, 1999; Bertilsson and Widenfalk, 2002; Richard and Canonica, 2005). Moreover, antioxidant compounds present in dissolved organic matter have been shown to inhibit the transformation of aquatic contaminants, photosensitised by the triplet states of Coloured Dissolved Organic Matter (CDOM) (Cannonica and Laubscher, 2008). Unfortunately the reasons of the quantum yield decreases were not thoroughly investigated in previous studies, and the implications for the lifetime of the relevant compounds were only marginally dealt with.

The purpose of the present paper is to investigate on the effect of dissolved organic compounds on the direct photolysis of MCPA, combining steady-state irradiation and laser flash photolysis experiments. The direct photolysis of MCPA upon UVB irradiation was studied in the presence of variable concentrations of phenol and 2-propanol as model organic compounds. The effect of the organic substrates on the excited states of MCPA was assessed by laser flash photolysis.

To compare the direct photolysis and the reaction with $\cdot\text{OH}$ as MCPA transformation pathways in natural ecosystems, the results of the irradiation experiments were coupled with models of surface-water photochemistry that have been developed recently by the authors (Vione et al., 2009a,b,c, 2010). This approach has allowed, for the first time to our knowledge, a general modelling of the lifetime of a compound that undergoes inhibition of the direct photolysis quantum yield by DOM. The approach outlined in the present study could open up new perspectives in the complex issue of the environmental effects on the photolysis quantum yields, by allowing the photo-fate of the relevant substances to be

properly assessed and quantified. Indeed, the very limited number of studies into the effect of DOM on the direct photolysis quantum yields can be explained by the fact that it is difficult to make use of the experimental data for environmental predictions. However, the direct photolysis processes in surface water bodies are occurring in the presence of DOM, and the possible effects on the quantum yields would be of paramount importance. The methodology presented here overcomes most of the past difficulties and allows for the quantum yield to be considered as an environment-dependent as well as a substrate-dependent property, not only in theory but also as far as the actual consequences are concerned.

2. Experimental

2.1. Reagents and materials

4-Chloro-2-methylphenoxyacetic acid (MCPA, purity grade >95%), phenol (>99%), 2,4-dinitrophenylhydrazine (97%), acetone (99.8%), HCl (37%) and HClO_4 (70%) were purchased from Aldrich, H_3PO_4 (85%), NaOH (99%), 2-propanol (LiChrosolv gradient grade) and acetonitrile (LiChrosolv gradient grade) from VWR Int. All reagents were used as received, without further purification. Water used was of Milli-Q quality (18 $\text{M}\Omega\text{ cm}^{-1}$ resistivity, 2 ppb total organic carbon concentration, Millipore).

2.2. Irradiation experiments

Aqueous solutions (total volume 5.0 mL) of MCPA (up to 0.50 mM) and phenol (up to 0.50 mM) or 2-propanol (up to 1.0 M) were placed into Pyrex glass cells (4.0 cm diameter, 2.3 cm height), tightly closed with a screw cap. The pH value was adjusted with HClO_4 or NaOH and did not vary significantly during irradiation. The choice of the concentration values was mainly motivated by experimental convenience. In the case of phenol, the adopted concentration range was not dissimilar from the dissolved organic carbon levels that are found in surface waters (Al Housari et al., 2010).

The cells were irradiated under magnetic stirring with a Philips TL01 lamp, with emission maximum at 313 nm. The UV lamp irradiance (290–400 nm) was $5.6 \pm 0.3\text{ W m}^{-2}$ ($\mu \pm \sigma$), measured with a CO.FO.ME.GRA. (Milan, Italy) power meter. The incident photon flux in solution was 3.1×10^{-6} Einstein $\text{L}^{-1}\text{ s}^{-1}$, measured by ferrioxalate actinometry (Kuhn et al., 2004). Fig. 1 reports: (i) the emission spectrum of the lamp, measured with an Ocean Optics SD 2000 CCD spectrophotometer and normalised to the actinometry results, and (ii) the absorption spectrum of MCPA at two different pH values, taken with a Varian Cary 100 Scan UV–Vis spectrophotometer. The lamp spectrum takes into account the transmittance of the Pyrex glass of the cells adopted for irradiation. Since MCPA has $\text{pK}_a \approx 3.1$ (Martell et al., 1997), the absorption spectra at pH 1.8 and 7.7 are referred to the undissociated and dissociated forms, respectively. The choice of the lamp was a compromise between the need of adopting environmentally significant radiation and that of achieving the excitation of MCPA. The irradiation temperature was around 30 °C. Dark

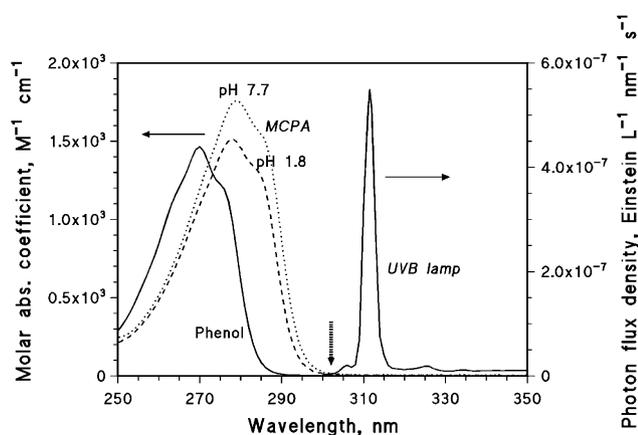


Fig. 1 – Absorption spectra (molar absorption coefficients ϵ) of MCPA at pH 1.8 and 7.7, adjusted by addition of HClO_4 and NaOH , respectively. The absorption spectrum of phenol is also reported (independent of pH in the relevant range). Emission spectrum (spectral photon flux density incident in solution) of the adopted UVB lamp. The vertical arrow shows the (limited) overlap between the spectrum of the lamp and that of MCPA. MCPA would show the highest absorption of lamp radiation around 300 nm.

experiments at the same temperature were also carried out, by putting cells wrapped in aluminium foil under the same lamp.

After irradiation, the solutions were allowed to cool at 4 °C in the dark for 15 min, and then analysed by High Performance Liquid Chromatography coupled with Diode Array Detection (HPLC-DAD). The instrument used (VWR-Hitachi, Elite series) was equipped with L-2200 autosampler (sample volume 60 μL), L-2130 quaternary pump for low-pressure gradients, L-2300 column oven (40 °C), and L-2455 Diode Array Detector. It was used a column Merck Hibar RT 250-4, packed with LiChrospher 100 CH-18/2 (250 mm \times 4 mm \times 10 μm). The eluent was a 50:50 mixture of acetonitrile (A) and aqueous H_3PO_4 (pH 2.5) (B), at 1.0 mL min^{-1} flow rate. The DAD signal was acquired between 200 and 300 nm, and 220 nm was adopted as the quantification wavelength for both MCPA and phenol. Under the adopted elution conditions the retention times were (min): phenol (3.60) and MCPA (5.55), the column dead time being 1.90 min. Acetone was determined by pre-column derivatisation with 2,4-dinitrophenylhydrazine (Warneck and Wurzinger, 1988), followed by elution with 60:40 A:B at 1.0 mL min^{-1} flow rate. The hydrazone derivative of acetone had a retention time of 7.20 min and the quantification wavelength was 368 nm.

2.3. Calculations and data treatment

The irradiation time was up to 24 h, and a total of six concentration vs. time data points were collected for each run (including $t = 0$). Fig. 2 shows as an example the data concerning MCPA transformation at pH 7.7 (2a) and 1.8 (2b). No degradation of MCPA was observed in the dark. The time evolution data for the disappearance of MCPA and phenol were fitted with equations of the form $C_t = C_0 \exp(-kt)$, where

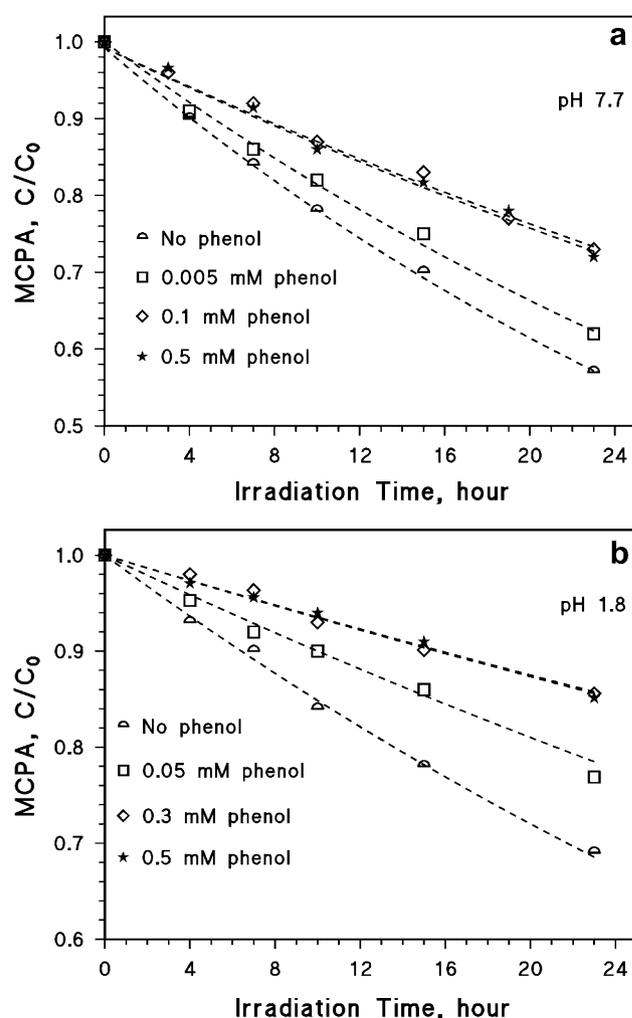


Fig. 2 – Time evolution of 0.2 mM MCPA upon UVB irradiation, for different concentration values of phenol. a) pH 7.7 and b) pH 1.8.

C_t is the concentration of the substrate at the time t , C_0 the initial concentration, and k the pseudo-first order degradation rate constant. The initial transformation rate of the substrate is $R = k C_0$. Note that very similar results (with differences much below the experimental errors) would be obtained by fitting the experimental data with straight lines. The reported errors on the rates ($\pm\sigma$) were derived from the scattering of the experimental data around the fitting curves (intra-series variability). The reproducibility of repeated runs (inter-series variability) was around 10–15%.

The photodegradation quantum yields of phenol and MCPA were obtained upon division of the relevant initial transformation rates by the photon flux absorbed by MCPA (P_a^{MCPA}). Therefore, it is $\Phi_{\text{Substrate}} = R_{\text{Substrate}} (P_a^{\text{MCPA}})^{-1}$. The absorbed photon flux can be calculated from the spectral data, considering that $P_a^{\text{MCPA}} = \int p^\circ(\lambda) \cdot [1 - 10^{-\epsilon_{\text{MCPA}}(\lambda) \cdot b \cdot [\text{MCPA}]}] d\lambda$ (Braslavsky, 2007), where $p^\circ(\lambda)$ is the incident spectral photon flux density (it is reported as the lamp emission spectrum in Fig. 1), $\epsilon_{\text{MCPA}}(\lambda)$ the molar absorption coefficient of MCPA, $b = 0.4$ cm the optical path length inside the cells, and $[\text{MCPA}]$ the initial concentration of the substrate.

The importance of the direct photolysis and of the reaction with $\cdot\text{OH}$ for the degradation of MCPA in surface waters were compared by means of a modelling approach. Based on recently developed models (Vione et al., 2009a,b), the half-life time of MCPA upon direct photolysis would be:

$$\tau_{\text{MCPA,Phot}}^{\text{SSD}} = \frac{1.9 \cdot 10^{-8} d}{\Phi_{\text{MCPA}} \int_{\lambda} p^{\circ}(\lambda) \cdot \left[1 - 10^{-A_1(\lambda) \cdot d}\right]_{A_1(\lambda)}^{\tau_{\text{MCPA}}(\lambda)} d\lambda} \quad (1)$$

The measure unit of τ_{MCPA} is summer sunny days (SSD), corresponding to 15 July at 45°N latitude under fair-weather conditions. Furthermore, $p^{\circ}(\lambda)$ is the spectrum of sunlight (in Einstein $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$, corresponding to 22 W m^{-2} UV irradiance; see Figure A-SM, where SM = Supplementary Material), $A_1(\lambda)$ the specific absorbance of surface water (in cm^{-1}), and d (in cm) the water column depth. Note that d could be the average depth of thoroughly mixed water bodies, or the mixing layer depth of stratified lakes (in which case the half-life time would be referred to the mixing layer). The absorption spectrum $A_1(\lambda)$ should be referred to the surface water layer, where sunlight irradiance is maximum and the photochemical reactions are, therefore, most favoured. A more complete description of the direct photolysis model is reported as Supplementary Material (hereafter SM). Note that the model takes into account the competition for sunlight irradiance between MCPA and the other water components. Also note that a sunlight UV irradiance of 22 W m^{-2} can be observed in a fair-weather 15 July at 45°N latitude, at 10 am or at 2 pm.

In the case of $\cdot\text{OH}$, the half-life time of MCPA (always in SSD units) would be (Vione et al., 2009c, 2010):

$$\tau_{\text{MCPA},\cdot\text{OH}}^{\text{SSD}} = 1.9 \cdot 10^{-5} \cdot \frac{\sum_i k_{\text{Si}} \cdot [\text{S}_i]}{R_{\cdot\text{OH}}^{\text{tot}} \cdot k_{\text{MCPA},\cdot\text{OH}}} \quad (2)$$

where $\sum_i k_{\text{Si}} [\text{S}_i]$ is the rate constant of the natural $\cdot\text{OH}$ scavengers in the surface water layer (in s^{-1}), $R_{\cdot\text{OH}}^{\text{tot}}$ (in M s^{-1}) is the formation rate of $\cdot\text{OH}$ under 22 W m^{-2} sunlight irradiance, and $k_{\text{MCPA},\cdot\text{OH}} = 6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is the second-order reaction rate constant between $\cdot\text{OH}$ and MCPA (anionic form; Benitez et al., 2004). Further information on the adopted model of $\cdot\text{OH}$ formation and reactivity in surface waters is reported as SM.

2.4. Laser flash photolysis experiments

Laser flash photolysis experiments were carried out using the fourth harmonic (266 nm) of a Quanta Ray GCR 130-01 Nd:YAG laser. This laser produces a pulse of 9 ns in duration and, during these experiments, operated with an output of 30 mJ per pulse. Transient species produced upon 266 nm irradiation of the samples inside a quartz cuvette (3 mL volume) were monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator and a photomultiplier (1P28). A spectrometer control unit was used for synchronising the pulsed light source and programmable shutters with the laser output. The signal from the photomultiplier was digitised by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyse the digitised signal. After each laser shot a peristaltic pump system was used in order to replace the solution before a new experiment. The absorbance and disappearance of the

transient species were investigated as a function of pH and of the concentration of 2-propanol.

Before each experiment, an appropriate volume of quencher (i.e. 2-propanol) was added to the MCPA solution and the pH was adjusted using HClO_4 or NaOH . All the experiments were performed at ambient temperature ($295 \pm 2 \text{ K}$) and in aerated solution. The choice of 2-propanol as quencher was motivated by its elevated reactivity, as shown for instance by its reaction rate constant with $\cdot\text{OH}$ ($2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; Buxton et al., 1988). Although it is not the case of MCPA (*vide infra*), the excited states of some organic substrates are able to oxidise water to $\cdot\text{OH}$, which is then involved into the direct photo-transformation processes (Brigante et al., 2010). Accordingly, the ability of 2-propanol to effectively scavenge $\cdot\text{OH}$ would be potentially important in these studies.

2.5. Phosphorescence measurements

Phosphorescence experiments were carried out by freezing at 77 K with liquid N_2 a glycerol/water (50/50 v/v) solution of MCPA, in order to obtain an appropriate experimental resolution. The phosphorescence spectrum was recorded on a Horiba Jobin-Yvon SPEX Fluorog 3-22 spectrometer, equipped with a 1934 D phosphorimeter accessory. The excitation wavelength (280 nm) corresponds to the MCPA maximum absorption.

3. Results and discussion

3.1. Irradiation of MCPA in the presence of other organic compounds

Fig. 3 reports the initial photodegradation rates of 0.20 mM MCPA and of phenol (R_{MCPA} and R_{phenol} , respectively), as a function of the initial phenol concentration, at pH 7.7 where

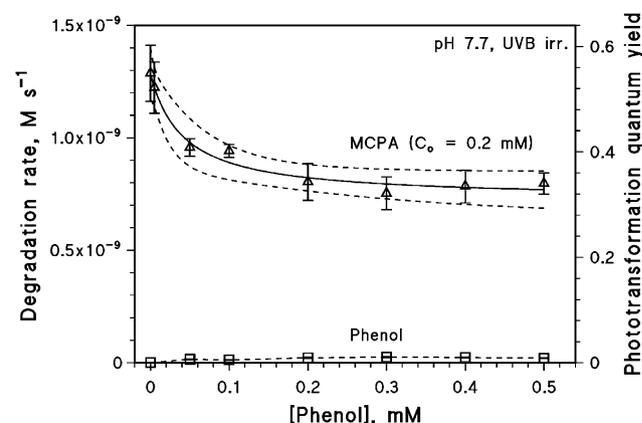


Fig. 3 – Initial transformation rates of 0.2 mM MCPA and of phenol under UVB irradiation at pH 7.7, as a function of the initial phenol concentration. The right Y-axis also reports the phototransformation quantum yields, calculated as $\Phi_i = \text{Rate}_i (P_a^{\text{MCPA}})^{-1}$ ($i = \text{MCPA}$ or phenol). The fit of the Φ_{MCPA} values with equation (3) is also reported (solid curve), together with the 95% confidence bands (dashed curves).

the anionic form of MCPA prevails. It is apparent that phenol inhibited the photodegradation of MCPA, which was decreased by about 40% with 0.20–0.50 mM phenol compared to MCPA alone.

While inhibiting the MCPA photodegradation, phenol underwent in turn a slight degradation in the presence of MCPA. The transformation rate of phenol was always below $3.0 \times 10^{-11} \text{ M s}^{-1}$, and it was considerably lower than the corresponding decrease of the MCPA degradation rate. Also note that no phenol was formed upon photodegradation of MCPA alone, and that phenol underwent insignificant photodegradation without MCPA under the adopted irradiation device. Phenol is not able to absorb radiation above 300 nm, like that emitted by the irradiation device used in the present work (see Fig. 1), thus the decrease of the MCPA degradation rate cannot be attributed to competition with phenol for radiation absorption. Moreover, negligible transformation of either phenol or MCPA took place in the dark. This allows exclusion of hydrolysis or thermal decomposition reactions at the adopted time scale, and indicates that the combination of irradiation at 30 °C and cooling at 4 °C for 15 min prevented volatilisation of the relevant substrates.

Fig. 4 shows the trends of R_{MCPA} and of R_{Phenol} as a function of phenol concentration, at pH 1.8 where there is prevalence of the undissociated form of MCPA. Also in this case, the phototransformation of MCPA was inhibited by phenol and the sum $R_{\text{Phenol}} + R_{\text{MCPA}}$ decreased with [Phenol]. In other words, the increase of R_{Phenol} could not compensate for the decrease of R_{MCPA} . This finding suggests that, at the two studied pH values, the effect of phenol was not just a competition with MCPA for the reactive species that may be responsible for the degradation of the two substrates. Indeed, considering that MCPA is the only compound that absorbs radiation in the system, it should be the photosensitiser for phenol degradation. The latter would thus take place upon reaction with light-excited MCPA or with possible photo-generated radical species. The same species/photoreactive transients would be involved into the transformation of MCPA in the absence of phenol. This scenario is reasonable but cannot account for the rate trends reported in Figs. 3 and

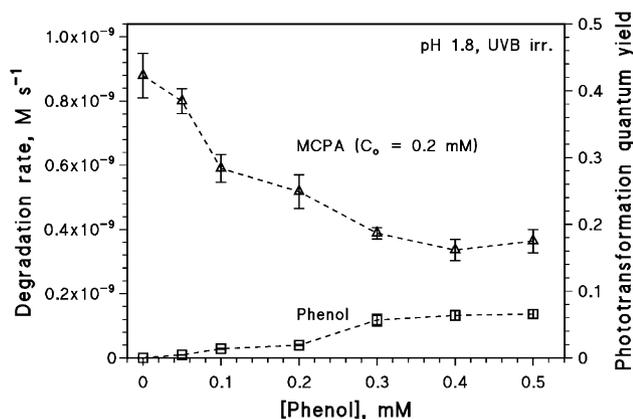


Fig. 4 – Initial transformation rates of 0.2 mM MCPA and of phenol under UVB irradiation at pH 1.8, as a function of the initial phenol concentration. The right Y-axis also reports $\Phi_i = \text{Rate}_i (P_a^{\text{MCPA}})^{-1}$ ($i = \text{MCPA or phenol}$).

4. Phenol could be more reactive than, less reactive than or as reactive as MCPA towards the photogenerated species/transients. If it is less or as reactive, the degradation of a phenol molecule would replace that of an MCPA molecule: R_{MCPA} would be decreased and R_{Phenol} increased with increasing [Phenol], but the sum $R_{\text{Phenol}} + R_{\text{MCPA}}$ would remain constant. This is not in agreement with the experimental data. If phenol is more reactive than MCPA, it could also scavenge specie/transients that in its absence would undergo deactivation processes rather than react with MCPA. In this case the sum $R_{\text{Phenol}} + R_{\text{MCPA}}$ should increase with [Phenol], and the increase would be more marked if the difference in reactivity between phenol and MCPA is larger. The experimental data do not agree with any of the proposed scenarios. The sum $R_{\text{Phenol}} + R_{\text{MCPA}}$ would decrease with increasing [Phenol], as observed, if the main effect of phenol was a physical quenching of radiation-excited MCPA. In this case, the photoreactivity of MCPA as well as its degradation rate would be decreased without inducing the transformation of phenol. The limited transformation rate of phenol with irradiated MCPA would be alternatively explained by: (i) a minor fraction of phenol interacting with radiation-excited MCPA and undergoing chemical reactivity, the larger fraction causing physical quenching, or (ii) phenol reacting with radical species produced by MCPA under irradiation, in addition to causing physical quenching.

The second Y axis of Figs. 3 and 4 reports the photodegradation quantum yields of MCPA and phenol. Interestingly, Φ_{MCPA} did not change much between pH 1.8 and 7.7. At pH 7.7, which is most significant for surface waters, the quantum yield of MCPA photodegradation without phenol was $\Phi_{\text{MCPA}} = 0.54 \pm 0.05$ ($\mu \pm \sigma$). It compares well with the value of 0.59 obtained by Zertal et al. (2001) upon irradiation of MCPA at 280 nm. The addition of phenol decreased Φ_{MCPA} down to a value of about 0.34, which was approximately constant in the phenol concentration interval of 0.20–0.50 mM. It is possible to derive the following phenomenological equation to describe the trend of Φ_{MCPA} vs. [Phenol] (the error bounds represent $\pm \sigma$, [Phenol] is in molarity):

$$\Phi_{\text{MCPA}} = \frac{(2.3 \pm 0.7) \cdot 10^{-5} + (0.31 \pm 0.01)[\text{Phenol}]}{(4.1 \pm 1.3) \cdot 10^{-5} + [\text{Phenol}]} \quad (3)$$

Fig. 3 reports the fit of equation (3) to the experimental data.

At pH 1.8 and in the absence of phenol, the quantum yield for the photolysis of the undissociated form of MCPA ($\Phi_{\text{MCPA}} = 0.42 \pm 0.03$, see Fig. 3) was not far from $\Phi_{\text{MCPA}} = 0.35$, found by Zertal et al. (2001) at 280 nm. The addition of 0.5 mM phenol yielded $\Phi_{\text{MCPA}} = 0.18 \pm 0.02$.

Fig. 5 reports R_{MCPA} and Φ_{MCPA} upon irradiation of 0.20 mM MCPA, with varying concentration values of 2-propanol. The alcohol is not able to absorb radiation at $\lambda > 230 \text{ nm}$, thus competition with MCPA for lamp irradiance is not an issue. 2-Propanol inhibited the photolysis of MCPA, but considerably higher concentration values than for phenol were required to obtain a similar effect. Compared with MCPA alone, a 35% inhibition of Φ_{MCPA} was observed with 0.10 M 2-propanol, and 48% inhibition with 1.0 M 2-propanol. Interestingly, no formation of acetone from 2-propanol was detected. Acetone is an intermediate of the reaction between 2-propanol and $\cdot\text{OH}$ (Warneck and Wurzinger, 1988), and the fact that it is not

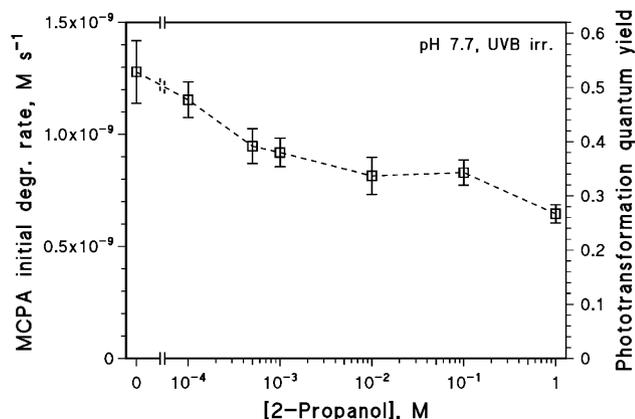


Fig. 5 – Initial transformation rates of 0.2 mM MCPA under UVB irradiation at pH 7.7, as a function of the initial concentration of added 2-propanol. The right Y-axis also reports $\Phi_{\text{MCPA}} = \text{Rate}_{\text{MCPA}} (P_a^{\text{MCPA}})^{-1}$.

being formed suggests that negligible production of $\cdot\text{OH}$ takes place with MCPA under irradiation.

3.2. Laser flash photolysis experiments

Figure B-SM (i.e. Figure B in the Supplementary Material) shows the transient absorption spectra obtained after the laser pulse of 0.50 mM MCPA at pH 1.8, 3.8 and 7.8. It is clearly shown a pH dependence of the MCPA excited states. At acidic pH, where MCPA exists in the molecular form, the absorption maximum of the transient is centred at 300 nm. In contrast, the excitation of the anionic form at pH 3.8 and 7.8 leads to a transient with maximum absorption at 290 nm. In both cases, a good fit of the absorbance decay after the laser shot was obtained with a double-exponential plot. This suggests the presence of at least two transient species absorbing between 270 and 360 nm. The first species has a fast decay (first-order rate constant $k \sim 6.0 \times 10^5 \text{ s}^{-1}$) that could be assigned to the fast decay of the MCPA triplet state. The second one, with a first-order decay constant of $\sim 2.5 \times 10^4 \text{ s}^{-1}$ could be attributed to a new transient species derived from the triplet state reaction in aqueous solution.

Note that the photolysis processes of chlorophenols take place via the early formation of a triplet state, which then evolves into a carbene (Grabner and Richard, 2005). The latter species typically has an absorption maximum around 350–400 nm, which in our case is not compatible with the 290–300 nm absorption peak of the first evolving transient. Additional evidence for the formation of a triplet state was obtained by phosphorescence measurements (see Figures C and D in SM). At 77 K the triplet state of MCPA emits phosphorescence radiation with a maximum at 410 nm.

The addition of 2-propanol to the MCPA solution did not modify significantly the decay rate constant of either transient, but the complexity of the absorption spectrum could prevent such an effect to be highlighted. However, 2-propanol affected the absorbance of the second transient species. Fig. 6 reports the maximum value of the 300 nm absorbance reached by the second species, as a function of 2-propanol

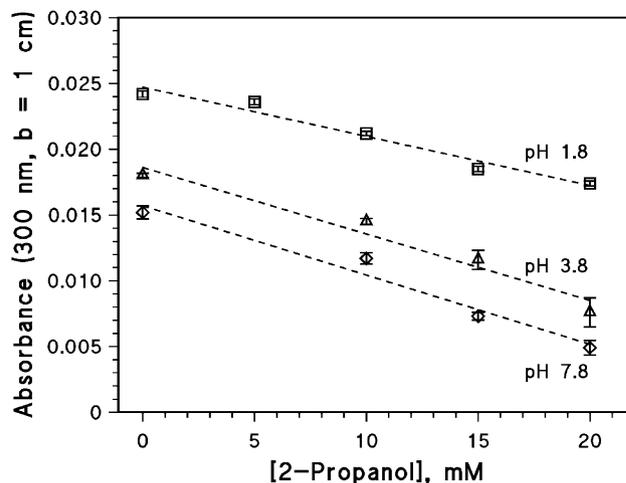


Fig. 6 – Linear dependence of the second transient species absorbance obtained after LFP excitation (266 nm, 25 mJ) of 0.5 mM MCPA solutions, as a function of 2-propanol concentration at different pH values. The error bars were derived at the 1σ level from the scattering of the experimental data. The lines show the linear regression of the experimental data.

concentration at different pH values. The decrease of the absorbance suggests an effect of 2-propanol in terms of decreasing the formation of the second transient species. Reaction with or physical quenching of the first transient species could explain such a phenomenon.

At pH 1.8, the absorbance decrease caused by 2-propanol was slightly lower (with a slope of $-0.37 \pm 0.04 \text{ M}^{-1}$) than at pH 3.8 and 7.8 (slopes of $-0.51 \pm 0.07 \text{ M}^{-1}$ and $-0.53 \pm 0.07 \text{ M}^{-1}$, respectively). The decrease by about one third of the absorbance of the MCPA transient species at 300 nm and pH 7.8, in the presence of 10 mM 2-propanol (Fig. 6), compares well with the 38–40% decrease of the rate of MCPA photodegradation at pH 7.7, with the same alcohol concentration (Fig. 5).

Overall, the experimental data suggest that 2-propanol decreases the formation of the MCPA transient species, and that such an effect is higher with the anionic form of the pesticide than with the undissociated one. It could be connected with the decrease of the rate and quantum yield of MCPA direct photolysis in the presence of 2-propanol. Unfortunately it was not possible to study the effect of phenol on the transient states of MCPA with the 266 nm laser pulse, because at that wavelength phenol competes with MCPA for radiation absorption and prevents the distinction between radiation screening and other photochemical effects. Furthermore, the third harmonic of the Nd-YAG laser (355 nm) cannot be used because at that wavelength, neither MCPA nor phenol absorb radiation.

3.3. Environmental implications

3.3.1. Implications for two water bodies with different photoreactivity (Rhône delta and Lake Candia)

The inhibition of MCPA photodegradation by organic compounds could have important consequences for the

environmental fate of the herbicide, because the direct photolysis is likely to be a major transformation pathway in natural waters (Chiron et al., 2007). An alternative route for MCPA transformation in the environment is the reaction with $\cdot\text{OH}$ (Mabury and Crosby, 1996). The goal of this section is to compare the two transformation pathways, and to assess the possible impact of the quantum yield variations. The anionic form of MCPA will be considered here because it prevails in surface waters. Phenol could be a model for the antioxidants present in the pool of surface-water dissolved organic matter, and its presence would decrease Φ_{MCPA} by up to 40% (Fig. 3). A concentration of 0.30 mM phenol would correspond to a dissolved organic carbon (DOC) content of over 20 mg C L⁻¹, while the DOC values of surface waters are often lower (Takeda et al., 2004). However, Chiron et al. (2007) have observed a ratio of the MCPA photodegradation rate (R_{MCPA}) in river compared to ultra-pure water of about 0.5, while the corresponding ratio of the photon fluxes absorbed by MCPA in the two systems was 0.7. The difference can be explained if the Φ_{MCPA} in the presence of dissolved organic matter (river water) is 0.7 times that in ultra-pure water (because $0.7 \cdot 0.7 \approx 0.5$). Moreover, the Φ_{MCPA} in river water could be even lower than 0.7 times that in ultra-pure water if additional processes, photosensitised by photoactive compounds, were also operational (in which case the rate of direct photolysis in river water would be less than 0.5 times that in ultra-pure water). Accordingly, a 30–40% decrease of Φ_{MCPA} by dissolved organic compounds could be reasonable in surface waters.

The MCPA half-life times were calculated by use of photochemical models described in SM (also see equations 1, 2). In the cases of both direct photolysis and $\cdot\text{OH}$ reaction, calculations have been referred to: (i) the Rhône delta waters, where MCPA is a precursor of phenolic compounds that can be further transformed into toxic and potentially mutagenic nitro-derivatives (Chiron et al., 2009); (ii) Lake Candia, which is a much less favourable environment than the Rhône delta for the processes induced by $\cdot\text{OH}$ (Vione et al., 2009c). Water composition data and the absorption spectra $A_1(\lambda)$ are reported in Table 1 and in Figure A-SM, respectively.

Fig. 7a reports the half-life times of MCPA (τ_{MCPA}) in the case of the Rhône delta, because of direct photolysis and reaction with $\cdot\text{OH}$, as a function of the water column depth. Different values were adopted for the quantum yield Φ_{MCPA} , all referred to the anionic form, including the Φ_{MCPA} determined in the present study without phenol (0.54) and the plateau

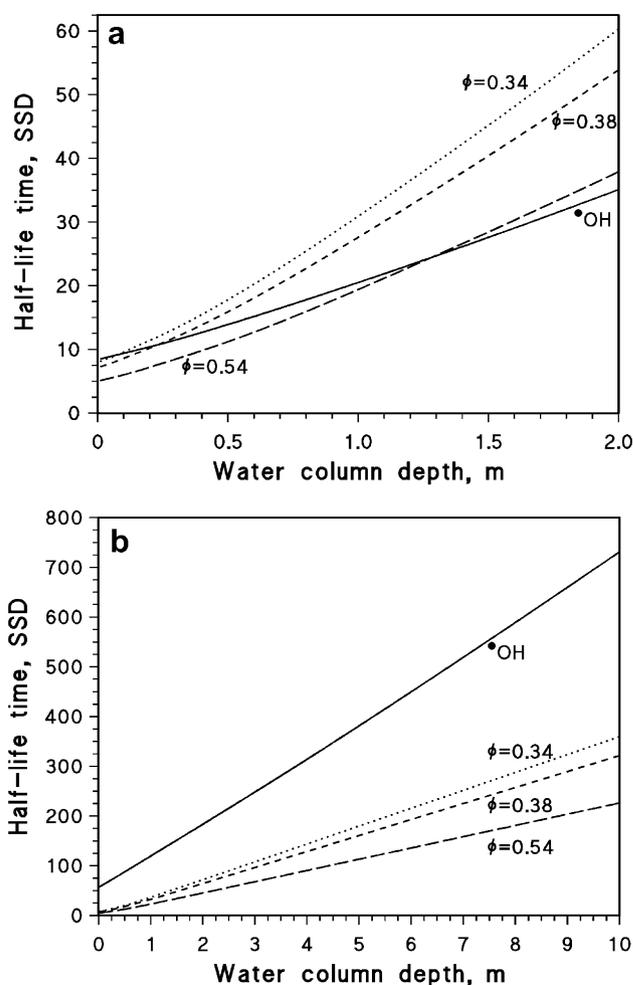


Fig. 7 – Half-life times in summer sunny days (SSD, equivalent to 15 July at 45°N latitude) of MCPA due to the reaction with $\cdot\text{OH}$ and the direct photolysis, for different values of the MCPA photolysis quantum yield ($\Phi_{\text{MCPA}} = 0.54, 0.38$ or 0.34). Conditions are referred to lagoon water of the Rhône delta (Chiron et al., 2009) (7a) and to the Lake Candia (Vione et al., 2009c) (7b). For the water composition data see Table 1; water absorption and sunlight spectra are reported in Figure A-SM. The average depth of the Rhône delta lagoons is 1 m, that of Lake Candia is 6 m.

Table 1 – Data concerning lagoon water in the Rhône delta (Chiron et al., 2007) and water in Lake Candia (Vione et al., 2009c).

| | Rhône delta (S France) | Lake Candia (NW Italy) |
|----------------------------|---------------------------|---------------------------|
| Water depth d , m | 1.0 | 6.0 |
| Nitrate, M | 5.1×10^{-5} | 1.6×10^{-6} |
| Nitrite, M | 3.2×10^{-6} | 1.5×10^{-7} |
| Bicarbonate, M | 2.1×10^{-3} | 1.1×10^{-3} |
| Carbonate, M | 2.6×10^{-5} | 6.1×10^{-6} |
| pH | 7.5 | 8.1 |
| NPOC, mg C L ⁻¹ | 4.5 | 5.4 |

value in the presence of phenol in excess (0.34, see Fig. 3). It is also reported the trend of τ_{MCPA} for $\Phi_{\text{MCPA}} = 0.38$, following the experimental results of Chiron et al. (2007) which, as reconsidered in the present work, suggest a 30% decrease of Φ_{MCPA} in river water. Depending on the water column depth and the photolysis quantum yield, τ_{MCPA} could vary from less than 10 to over 50 SSD. Additionally, the relative importance of direct photolysis vs. reaction with $\cdot\text{OH}$ would be higher in shallow waters. This is reasonable because MCPA absorbs sunlight to a lesser extent than the $\cdot\text{OH}$ sources nitrate, nitrite or CDOM, and competes better for irradiance at low depths of the water column. As shown in Fig. 7a, the value of Φ_{MCPA} determines the importance of direct photolysis vs. reaction with $\cdot\text{OH}$ in the degradation of MCPA. For a 1.0 m depth that is the average

in the Rhône delta lagoons, it appears that direct photolysis and reaction with $\cdot\text{OH}$ would be comparable if $\Phi_{\text{MCPA}} = 0.54$. In contrast, the $\cdot\text{OH}$ pathway would be more important if Φ_{MCPA} is lower (0.38 or 0.34). Therefore, the effect of organic matter on the photolysis quantum yield could control the photo-transformation processes of MCPA and, as a consequence, the formation of peculiar intermediates.

The models suggest an MCPA half-life time of about 20 days for a 1.0 m water depth, and even lower if more than one pathway is simultaneously operational. This is very near to the observed lifetime of phenoxyacid herbicides and of their phenol derivatives in the Rhône delta waters in late spring-early summer (Chiron et al., 2009).

Fig. 7b shows the corresponding case for Lake Candia (average depth 6 m, thoroughly mixed water). In Lake Candia the importance of the $\cdot\text{OH}$ pathway is much lower than for the Rhône delta. Accordingly, while in the delta waters the two pathways (direct photolysis and $\cdot\text{OH}$ reaction) could have comparable importance, in the case of Lake Candia the direct photolysis would be the main MCPA transformation process. The figure shows that τ_{MCPA} because of direct photolysis would increase by about 60% if Φ_{MCPA} is decreased from 0.54 to 0.34.

A final consideration is that the photochemical processes induced by CDOM (which would involve ${}^3\text{CDOM}^*$ or ${}^1\text{O}_2$) could also degrade MCPA in surface waters (Stangroom et al., 1998). However, the organic matter present in river water has been found to inhibit rather than enhance the phototransformation of MCPA (Chiron et al., 2007).

3.3.2. General modelling of MCPA photodegradation

Equation (3) reports the trend of Φ_{MCPA} as a function of phenol concentration. With this compound, the dissolved organic carbon or Non-Purgeable Organic Carbon (NPOC) content is $\text{NPOC} = 7.2 \times 10^4 [\text{Phenol}]$, where [Phenol] is expressed in molarity. Accordingly, equation (3) for phenol could be expressed as follows:

$$\Phi_{\text{MCPA}} = \frac{(2.3 \pm 0.7) \cdot 10^{-5} + (4.3 \pm 0.1) \cdot 10^{-6} \text{NPOC}}{(4.1 \pm 1.3) \cdot 10^{-5} + 1.4 \cdot 10^{-5} \text{NPOC}} \quad (4)$$

Under the hypothesis that the Φ_{MCPA} trend observed with phenol is also valid for surface-water DOM, one can use equation (4) to model the half-life time of MCPA as a function of the DOM content (expressed as NPOC) and of the water column depth. To this purpose, it is also necessary to model the absorption spectrum of surface water. A suitable procedure is to base the modelled spectrum on the NPOC values, because organic matter is the main sunlight absorber in the spectral region of interest (about 300–500 nm; Bracchini et al., 2010). Further details of this approach are reported as SM.

Fig. 8 shows the trend of the half-life time of MCPA ($t_{1/2}^{\text{MCPA}}$, SSD) as a function of NPOC (mg C L^{-1}) and the column depth d (m), for both direct photolysis and the reaction with $\cdot\text{OH}$. To facilitate the comparison of the two processes, the remaining water parameters (nitrate, nitrite, carbonate, bicarbonate) were fixed at the values found in the Rhône delta lagoons (Table 1), where the two pathways would have comparable importance. Note that the main transformation pathway is that associated with the lowest half-life time. It is apparent that the direct photolysis becomes most important at high

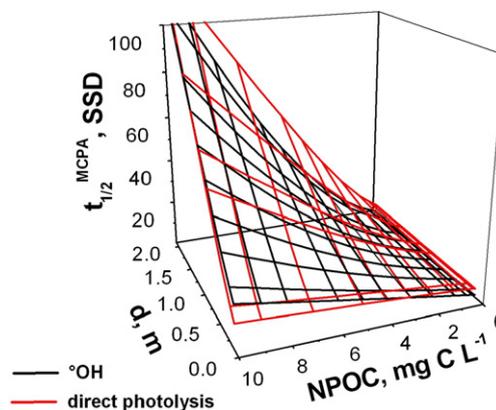


Fig. 8 – Modelled half-life times in summer sunny days (SSD, equivalent to 15 July at 45°N latitude) of MCPA due to the reaction with $\cdot\text{OH}$ and the direct photolysis, as a function of dissolved organic carbon (measured as NPOC) and water column depth. The value of Φ_{MCPA} was derived from equation (4), the water absorption spectrum was modelled based on the NPOC value as described in SM.

NPOC and low d , while the opposite conditions favour the reaction with $\cdot\text{OH}$. Shallow water favours the direct photolysis because of the very limited sunlight absorption by MCPA. Dissolved organic matter inhibits both pathways but there is a more marked effect on the $\cdot\text{OH}$ one, mostly linked to hydroxyl scavenging. However, in the absence of the inhibition of Φ_{MCPA} by DOM, the direct photolysis would be the main pathway in a much wider range of conditions.

Interestingly, equation (4) that is based on the experimental data (Fig. 3) foresees an abrupt decrease of Φ_{MCPA} for relatively low values of the NPOC, followed by a plateau at elevated NPOC. In contrast, the scavenging of $\cdot\text{OH}$ would be directly proportional to the NPOC. Fig. 9 reports in greater detail the half-life time trend of MCPA for $d = 1.4$ m. A close look at the figure suggests that, at low NPOC, the direct photolysis starts with

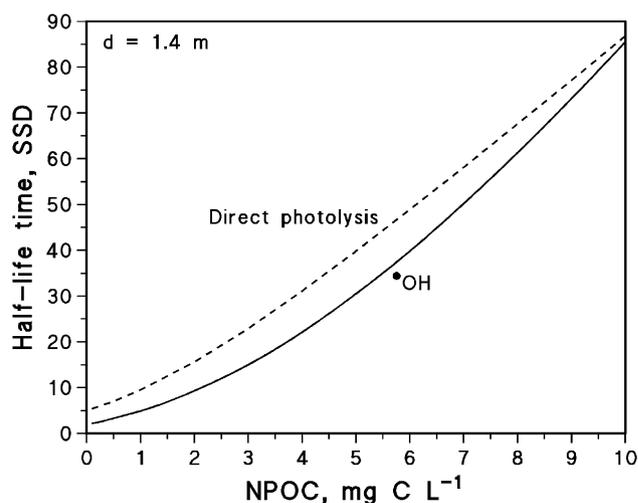


Fig. 9 – MCPA half-life time as a function of the NPOC, for $d = 1.4$ m, for both direct photolysis and the reaction with $\cdot\text{OH}$.

a higher slope than the $\cdot\text{OH}$ reaction. This would be due to the considerable, initial inhibition of Φ_{MCPA} by DOM. Above 4–5 mg C L⁻¹ NPOC, the $\cdot\text{OH}$ slope becomes higher because of the plateau reached by Φ_{MCPA} vs. NPOC.

4. Conclusions

Dissolved organic compounds such as phenol and 2-propanol are able to decrease considerably the direct photolysis quantum yield of MCPA. At equal concentration, phenol was more effective than 2-propanol in reducing Φ_{MCPA} . Under UVB irradiation, Φ_{MCPA} varied from 0.54 ± 0.05 without phenol to a plateau value of around 0.34, in the presence of 0.2–0.5 mM phenol. Interestingly, the inhibition of the MCPA photolysis by phenol was larger than could be expected from a mere competition for the same reactive species. Moreover, 2-propanol was able to inhibit the formation of the excited states of MCPA. The experimental data are compatible with a physical quenching carried out by the added organic compounds on the excited states of MCPA.

The findings of the present study are very significant to the photochemical fate of MCPA in surface waters. The decrease of Φ_{MCPA} by DOM could lead to a corresponding increase of the half-life time in ecosystems where the direct photolysis is the main MCPA transformation pathway. In contrast, in water bodies where the direct photolysis is comparable to the reaction with $\cdot\text{OH}$, the effect of DOM on Φ_{MCPA} could be critical to the photochemical fate of the herbicide. The direct photolysis intermediates of MCPA (including most notably 4-chloro-2-methylphenol; Zertal et al., 2001) are more toxic than the parent compound, while the reaction with $\cdot\text{OH}$ affords an at least partial depollution (Bojanowska-Czajka et al., 2007). Therefore, the inhibition of the direct photolysis by DOM could direct the phototransformation of MCPA toward less toxic intermediates.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.watres.2010.07.079.

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