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MODELLING THE PHOTOCHEMICAL GENERATION KINETICS OF 2-METHYL-4-CHLOROPHENOL, AN INTERMEDIATE OF THE HERBICIDE MCPA (2-METHYL-4-CHLOROPHENOXYACETIC ACID) IN SURFACE WATERS

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Abstract

The 2-methyl-4-chlorophenol (MCP) is the main transformation intermediate of the herbicide MCPA in surface waters and it is more toxic than the parent compound. MCP is produced from MCPA by both direct photolysis and $\bullet\text{OH}$ reaction. The latter process has higher yield of MCP from MCPA: 0.5 vs. 0.3 for the direct photolysis. Our model results show that the formation rate of MCP would be higher in waters that contain low organic matter and high nitrate and nitrite. Such conditions are favourable to MCPA direct photolysis and $\bullet\text{OH}$ -induced transformation, which are both inhibited by organic matter, while $\bullet\text{OH}$ formation is enhanced by nitrate and nitrite. Good agreement is obtained between model predictions and field data of MCPA transformation in the Rhône river delta (Southern France). The field data also suggest that MCP undergoes slightly faster transformation than MCPA in that environment.

Introduction

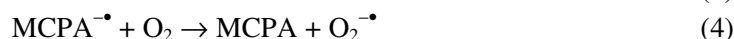
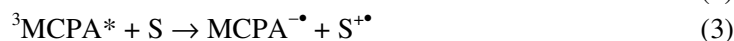
The occurrence of xenobiotic compounds depends on emission by human activities and on the transformation that these molecules undergo in the environmental compartments. Sunlight-driven processes play a considerable role in the attenuation of xenobiotics in surface waters, and they are comparatively more important when biodegradation reactions are slow (Boreen et al., 2003). Photochemical reactions in surface waters can be broadly divided into direct photolysis and indirect phototransformation. The direct photolysis is the transformation of a compound that absorbs solar radiation; it proceeds via *e.g.* bond breaking or ionisation. In some cases radiation absorption is followed by inter-system crossing (ISC) to an excited triplet state, which may undergo transformation reactions directly or upon interaction with other molecules, including the solvent. The probability of an absorbed photon to induce transformation is measured by the photolysis quantum yield (Braslavsky, 2007).

Indirect phototransformation involves reaction with transient species, produced upon absorption of solar radiation by photoactive molecules called photosensitisers. The main photosensitisers in surface waters are chromophoric dissolved organic matter (CDOM) and the ions nitrite and nitrate (Al Housari et

al., 2010). All these species can produce $\bullet\text{OH}$ radicals upon radiation absorption. In the case of CDOM, part of the $\bullet\text{OH}$ photoproduction could be accounted for by photogeneration of H_2O_2 followed by photolysis or the Fenton reaction (Richard et al., 2007; Mostofa and Sakugawa, 2009). Irradiated CDOM also yields excited triplet states ($^3\text{CDOM}^*$) and singlet oxygen ($^1\text{O}_2$). Oxidation of HCO_3^- and CO_3^{2-} by $\bullet\text{OH}$ (and to a lesser extent by $^3\text{CDOM}^*$) yields the carbonate radical (Canonica et al., 2005). In summary, the transients $\bullet\text{OH}$, $^3\text{CDOM}^*$, $^1\text{O}_2$ and $\text{CO}_3^{\bullet-}$ are key players of indirect photochemistry in surface waters.

The direct or indirect photochemical transformation yields intermediates that are often less harmful than the parent compound, but which in some cases can have higher environmental and/or health impact. Therefore, a complete assessment of the environmental attenuation of xenobiotics requires taking into account their transformation intermediates (Buth et al., 2009).

MCPA is a widely used phenoxy herbicide, active against broad-leaf weeds. It is an acid with $\text{pK}_a = 3.1$, thus its anionic form usually prevails in surface waters (Iglesias et al., 2010). The main phototransformation pathways of MCPA in the environment are the reaction with $\bullet\text{OH}$ (second-order rate constant of $6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; Benitez et al., 2004) and the direct photolysis. The limited absorption of solar radiation by MCPA is compensated for by the elevated photolysis quantum yield Φ_{MCPA} , which is around 0.5 for the anionic form (Zertal et al., 2001). It has recently been found that Φ_{MCPA} is decreased by dissolved organic compounds. MCPA photolysis proceeds via formation of the triplet state ($^3\text{MCPA}^*$) and subsequent reactions. However, $^3\text{MCPA}^*$ can oxidise dissolved organic compounds and produce $\text{MCPA}^{\bullet-}$, which can give back MCPA in the presence of oxygen (see reactions 1-4; S is a dissolved organic substrate). Reactions (3,4) would decrease the observed transformation rate of MCPA (Vione et al., 2010).



The main phototransformation intermediate of MCPA is MCP, which is formed by MCPA direct photolysis and reaction with $\bullet\text{OH}$ (Zertal et al., 2001). MCP has been detected in rice fields in the Rhône delta (S. France), after application of MCPA as post-emergent herbicide (Chiron et al., 2009). Both MCP and MCPA are ATPase inhibitors, but MCP is significantly more effective (Duchnowicz et al., 2005) and its formation might account for the observed increase of the toxicity of MCPA solutions upon irradiation (Zertal et al., 2001). As a potentially harmful intermediate of MCPA photochemical transformation, MCP should be considered as a secondary pollutant of environmental concern.

The purpose of this paper is to carry out a model assessment of MCP formation from MCPA in natural waters. It adopts a model approach based on the known data of MCPA phototransformation and on water chemical composition and depth. Model predictions are compared with the available field data.

Methods including the photochemical model

The field data of MCPA and MCP used in this work are reported in Chiron et al. (2009) and are referred to Rhône delta lagoons (S. France). The transformation of anionic MCPA in surface waters would mainly take place *via* direct photolysis and reaction with $\bullet\text{OH}$ (Vione et al., 2010) and can be quantitatively assessed by means of a photochemical model (Maddigapu et al., 2011). Model application to MCPA

yields its pseudo-first order transformation rate constants ($k_{\text{MCPA}\cdot\text{OH}}$ and $k_{\text{MCPA,DP}}$ for $\cdot\text{OH}$ reaction and direct photolysis, respectively) as a function of water chemical composition and column depth. Input data are the bimolecular reaction rate constant between MCPA and $\cdot\text{OH}$ ($6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; Benitez et al., 2004) and Φ_{MCPA} . The latter depends on the organic matter content of the solution (expressed as Dissolved Organic Carbon, DOC, or Non-Purgeable Organic Carbon, NPOC), as follows (Vione et al., 2010):

$$\Phi_{\text{MCPA}} = \frac{1.6 + 0.31 \cdot \text{NPOC}}{2.9 + \text{NPOC}} \quad (5)$$

MCP is formed from MCPA by both direct photolysis and $\cdot\text{OH}$ reaction. The respective yields are $\eta_{\text{MCP,DP}} = 0.3$ and $\eta_{\text{MCP}\cdot\text{OH}} = 0.5$ (Zertal et al., 2001). The pseudo-first order formation rate constant of MCP is $k_{\text{MCP}} = \eta_{\text{MCP}\cdot\text{OH}} k_{\text{MCPA}\cdot\text{OH}} + \eta_{\text{MCP,DP}} k_{\text{MCPA,DP}}$ and the overall yield is $\eta_{\text{MCP}} = k_{\text{MCP}} (k_{\text{MCPA}})^{-1}$, where $k_{\text{MCPA}} = k_{\text{MCPA}\cdot\text{OH}} + k_{\text{MCPA,DP}}$. The values of k_{MCP} and η_{MCP} depend on water chemical composition and depth.

The time unit adopted by the model is the SSD (Summer Sunny Day), equivalent to a fair-weather 15 July at 45°N (Maddigapu et al., 2011). The model can also give the steady-state concentrations of the reactive transients ($\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$, $^3\text{CDOM}^*$) under definite irradiation conditions (*e.g.* 22 W m⁻² UV irradiance) (Minella et al., 2011). For MCPA, [$\cdot\text{OH}$] would be the most significant concentration because the reactions with $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$ are less important than that with $\cdot\text{OH}$ (Vione et al., 2010).

Results and discussion

The concentration of the herbicide MCPA (C_{MCPA}) was reduced to one third of its initial value in 15 days in a Rhône delta lagoon, having the following features: average water depth $d = 1$ m, 51 μM nitrate, 3 μM nitrite, 2.1 mM bicarbonate, 26 μM carbonate and 4.5 mg C L⁻¹ NPOC (Chiron et al., 2009). Under the hypothesis of a first-order degradation kinetics of MCPA, one obtains a rate constant $k' = 0.07 \text{ day}^{-1}$. By comparison, the model predicts $k_{\text{MCPA}} = 0.06 \text{ SSD}^{-1}$, with good agreement if 1 day = 1 SSD, which is reasonable because field data were collected in June-July. The model also foresees that about 55% of MCPA transformation would be accounted for by reaction with $\cdot\text{OH}$ and the remaining 45% by direct photolysis. Two sample cases of the model results for MCP formation are now reported.

Figure 1a reports the modelled k_{MCP} vs. nitrite and NPOC. The other parameters are the same as for the Rhône delta lagoon described above. Dissolved organic matter (DOM and its chromophoric fraction CDOM), quantified as NPOC, would considerably inhibit MCP formation by decreasing both $k_{\text{MCPA}\cdot\text{OH}}$ and $k_{\text{MCPA,DP}}$. In fact, DOM scavenges $\cdot\text{OH}$ and decreases Φ_{MCPA} (equation 5). CDOM competes for irradiance with nitrate, nitrite and MCPA, inhibiting both $\cdot\text{OH}$ formation and MCPA direct photolysis.

The trend of [$\cdot\text{OH}$] under the conditions of Figure 1a and with a constant 22 W m⁻² UV irradiance is reported in Figure 1b. The [$\cdot\text{OH}$] trend reflects the fact that nitrite is an important $\cdot\text{OH}$ source and organic matter a key $\cdot\text{OH}$ scavenger. k_{MCP} (Figure 1a) and [$\cdot\text{OH}$] (Figure 1b) have similar trends because the $\cdot\text{OH}$ reaction is an important pathway under the reported conditions ([$\cdot\text{OH}$] = (5-20) $\times 10^{-16}$ M). Figure 1b shows a residual [$\cdot\text{OH}$] without NO_2^- . Indeed, $\cdot\text{OH}$ is also produced by CDOM (partly *via* H_2O_2 formation as already explained; Richard et al., 2007; Mostofa and Sakugawa, 2009) and, at a lesser extent, by nitrate.

Figure 2 shows the trends of k_{MCP} and [$\cdot\text{OH}$] as a function of nitrite and NPOC. The adopted values of d , bicarbonate and carbonate are the same as in Figure 1, but nitrate is lower (1 μM) and nitrite is varied in a range of lower concentrations. Under such conditions, most of $\cdot\text{OH}$ would be produced by CDOM.

Figure 2b shows that [$\bullet\text{OH}$] increases with NPOC at low nitrite and decreases at high nitrite. In this system organic matter would be both an important source and scavenger of $\bullet\text{OH}$, but at low nitrite the $\bullet\text{OH}$ production by organic matter would prevail over the scavenging, while the opposite case would occur at high nitrite. This accounts for the opposite trend of [$\bullet\text{OH}$] vs. NPOC in the two cases.

Comparing Figure 2a and Figure 2b, one sees rather different trends of k_{MCP} and [$\bullet\text{OH}$]. The main reason is that here ($[\bullet\text{OH}]=(1-6)\times 10^{-17}$ M) the direct photolysis would strongly prevail over $\bullet\text{OH}$ reaction as MCPA transformation pathway, and organic matter would always inhibit MCPA photolysis.

Figure 3 reports the yield $\eta_{\text{MCP}} = k_{\text{MCP}} (k_{\text{MCPA}})^{-1}$, for the conditions depicted in Figure 1 (3a) and Figure 2 (3b). Because $\eta_{\text{MCP,DP}} = 0.3$ and $\eta_{\text{MCP,\bullet OH}} = 0.5$, η_{MCP} is expected to vary in the 0.3-0.5 range. It would reach the lower limit when the direct photolysis is the main phototransformation pathway, the upper limit when $\bullet\text{OH}$ reaction prevails. Intermediate values mean that the two processes are both important. Figure 3 shows that η_{MCP} does not approach 0.5, implying that the direct MCPA photolysis is never negligible. Nitrite enhances η_{MCP} because of the increasing importance of the $\bullet\text{OH}$ reaction; η_{MCP} is poorly dependent of NPOC because organic matter inhibits both $\bullet\text{OH}$ reaction and direct photolysis.

In the Rhône delta lagoon (water data already reported), in 15 days the MCPA concentration (C_{MCPA}) decreased from 1.2 to 0.4 nM, MCP concentration (C_{MCP}) from 0.84 to 0.35 nM (Chiron et al., 2009). The model predicts $\eta_{\text{MCP}} = 0.41$. It is possible to elaborate a kinetic equation system for the rates of MCPA and MCP. The formation rate of MCP ($d(C_{\text{MCP}})/dt$) would be a fraction η_{MCP} of the MCPA transformation rate, $d(C_{\text{MCPA}})/dt$. MCP would also undergo degradation with rate constant k'' :

$$d(C_{\text{MCPA}})/dt = -k' C_{\text{MCPA}} \quad (6)$$

$$d(C_{\text{MCP}})/dt = \eta_{\text{MCP}} [-d(C_{\text{MCPA}})/dt] - k'' C_{\text{MCP}} \quad (7)$$

From equation (6) one gets $C_{\text{MCPA}} = C_{\text{MCPA}}^o e^{-k't}$, where C_{MCPA}^o is the initial MCPA concentration. From the field data ($C_{\text{MCPA}}^o = 1.2$ nM, $C_{\text{MCPA}} = 0.4$ nM, $t = 15$ days) one gets $k' = 0.07$ day $^{-1}$. By substituting $d(C_{\text{MCPA}})/dt = -k' C_{\text{MCPA}}^o e^{-k't}$ into (7) and by solving the differential equation one gets $C_{\text{MCP}} = \eta_{\text{MCP}} k' C_{\text{MCPA}}^o (k'' - k')^{-1} (e^{-k't} - e^{-k''t}) + C_{\text{MCP}}^o e^{-k''t}$, where $C_{\text{MCP}}^o = 0.84$ nM is the initial MCP concentration. With $C_{\text{MCPA}}^o = 1.2$ nM, $C_{\text{MCP}} = 0.35$ nM, $\eta_{\text{MCP}} = 0.41$, $k' = 0.07$ day $^{-1}$ and $t = 15$ days one gets $k'' = 0.1$ day $^{-1}$. MCP would thus undergo faster degradation in the Rhône delta lagoon than the parent MCPA ($k'' > k'$). This is reasonable because, for instance, the reaction rate constant between MCP and $\bullet\text{OH}$ is higher than that of MCPA (Bojanowska-Czajka et al., 2007).

Conclusions

In sunlit surface waters, the formation of MCP from MCPA would mainly take place upon direct photolysis and reaction with $\bullet\text{OH}$. The MCP yield from MCPA in the latter process (0.5) is higher than for the direct photolysis (0.3). By means of a model approach it is shown that the pseudo-first order formation rate constant of MCP from MCPA, k_{MCP} , is higher at low NPOC values and at elevated concentrations of nitrate and, most notably, nitrite. Indeed, dissolved organic matter inhibits MCPA transformation: CDOM competes for irradiance with MCPA, nitrate and nitrite; DOM decreases Φ_{MCPA} and consumes $\bullet\text{OH}$ that is produced by CDOM, nitrite and nitrate. The MCP yield from MCPA ($\eta_{\text{MCP}} = k_{\text{MCP}} (k_{\text{MCPA}})^{-1}$) is usually

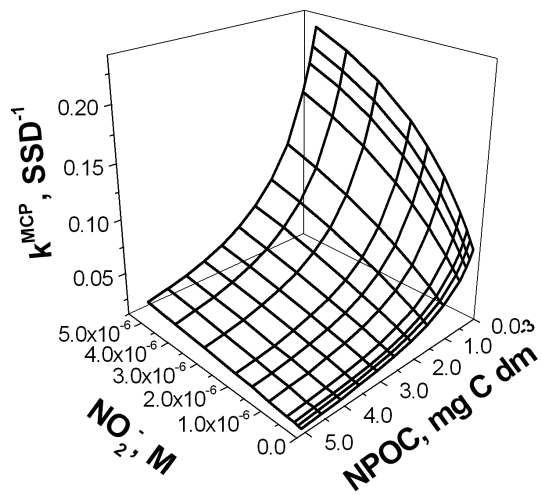
included in the 0.3-0.4 range. Very good agreement is obtained between model predictions and field data of MCPA phototransformation in the Rhône delta waters (Southern France). Field data also suggest that MCP transformation is a bit faster compared to the parent MCPA ($k'' = 0.1 \text{ day}^{-1}$ vs. $k' = 0.07 \text{ day}^{-1}$).

Acknowledgements

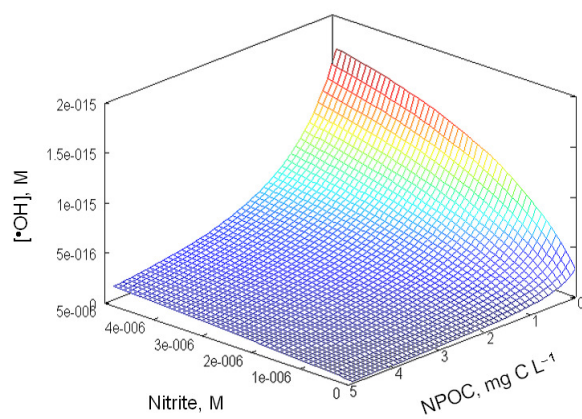
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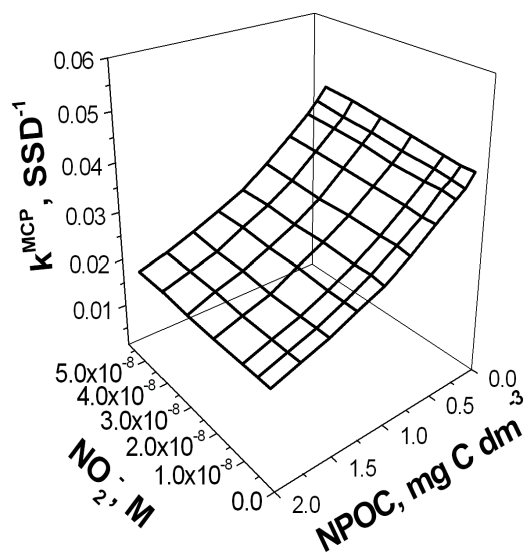


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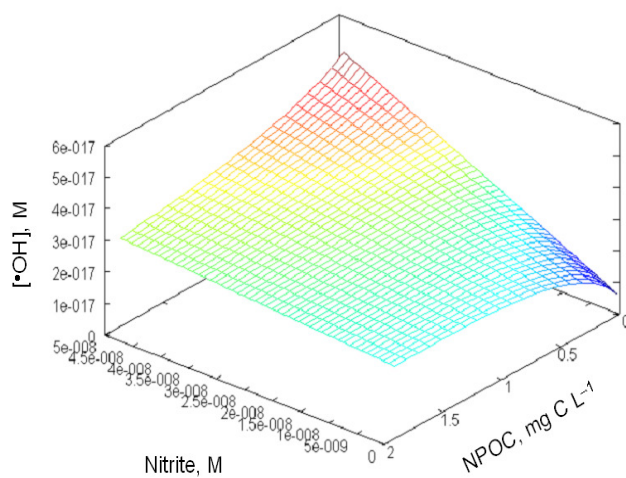


b)

Figure 1. First-order rate constant of MCP formation (1a) and steady-state $[\cdot\text{OH}]$ (1b) as a function of nitrite and NPOC. Other conditions: $d = 1$ m, $51 \mu\text{M}$ nitrate, 2.1 mM bicarbonate, $26 \mu\text{M}$ carbonate. $[\cdot\text{OH}]$ is here referred to a sunlight UV irradiance of 22 W m^{-2} and is directly proportional to the irradiance.

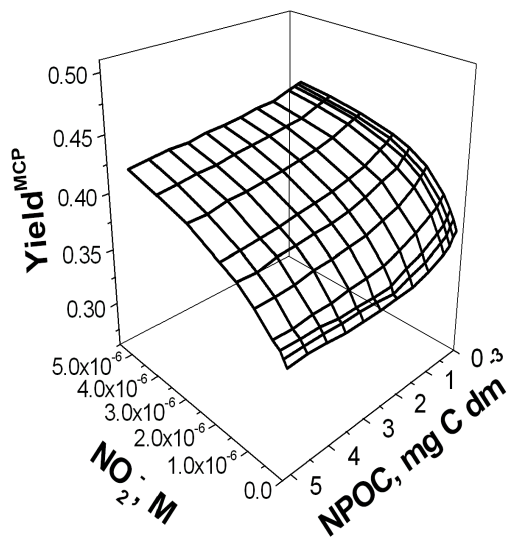


a)

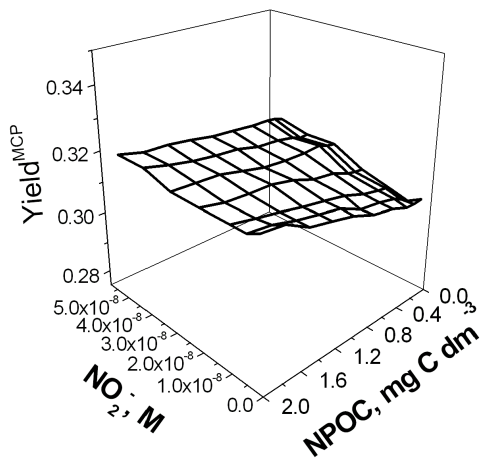


b)

Figure 2. First-order formation rate constant of MCP (2a) and steady-state $[\cdot\text{OH}]$ (2b) as a function of nitrite and NPOC. Other conditions: $d = 1$ m, $1 \mu\text{M}$ nitrate, 2.1 mM bicarbonate, $26 \mu\text{M}$ carbonate. $[\cdot\text{OH}]$ is here referred to a sunlight UV irradiance of 22 W m^{-2} .



a)



b)

Figure 3. Trend of the MCP yield from MCPA ($\eta_{MCP} = k_{MCP} (k_{MCPA})^{-1}$) as a function of nitrite and NPOC, with $d = 1$ m, 2.1 mM bicarbonate and 26 μ M carbonate. Nitrate concentration is 51 μ M (3a) or 1 μ M (3b).