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Photochemical transformation of anionic 2-nitro-4-chlorophenol in surface waters: Laboratory and model assessment of degradation kinetics and comparison with field data

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Abstract

Anionic 2-nitro-4-chlorophenol (NCP) may occur in surface waters as a nitroderivative of 4-chlorophenol, which is a transformation intermediate of the herbicide dichlorprop. Here we show that NCP would undergo efficient photochemical transformation in environmental waters, mainly by direct photolysis and reaction with $\bullet\text{OH}$. NCP has a polychromatic photolysis quantum yield $\Phi_{\text{NCP}} = (1.27 \pm 0.22) \cdot 10^{-5}$, a rate constant with $\bullet\text{OH}$ $k_{\text{NCP},\bullet\text{OH}} = (1.09 \pm 0.09) \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, a rate constant with $^1\text{O}_2$ $k_{\text{NCP},^1\text{O}_2} = (2.15 \pm 0.38) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$, a rate constant with the triplet state of anthraquinone-2-sulphonate $k_{\text{NCP},^3\text{AQ2S}^*} = (5.90 \pm 0.43) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and is poorly reactive toward $\text{CO}_3^{\bullet-}$. The $k_{\text{NCP},^3\text{AQ2S}^*}$ value is representative of reaction with the triplet states of chromophoric dissolved organic matter. The inclusion of photochemical reactivity data into a model of surface-water photochemistry allowed the NCP transformation kinetics to be predicted as a function of water chemical composition and column depth. Very good agreement between model predictions and field data was obtained for the shallow lagoons of the Rhône delta (Southern France).

Keywords: Pesticides; Sensitised photolysis; Photosensitisers; 2-Nitro-4-chlorophenol; Nitrated phenols.

1. Introduction

The occurrence of nitroaromatic compounds in the environment, and particularly in surface waters is a matter of concern because of their toxicity and potential mutagenicity. Nitrated phenols can cause gene mutations, chromosomal aberrations as well as oxidative damage to DNA (Massey et al., 1994; Heng et al., 1996; Chiron et al., 2007). They can act as inhibitors of phenol sulphotransferase (Wang and James, 2006; Kollock et al., 2009) that plays an important role in the detoxification of xenobiotics (Guangping, 2004). As far as the mode of toxic action is concerned, nitrophenols are variously classified as respiratory uncouplers or soft electrophiles (Aptula et al., 2002).

In particular, 2-nitro-4-chlorophenol (NCP) is used in resins, plastics and as a dye intermediate. It is also commonly detected in wastewater from the production of pharmaceuticals and pesticides (Saritha et al., 2007; Gharbani et al., 2010). Recently, it has been found that NCP can be formed in the environment starting from dichlorprop ((R)-2-(2,4-dichlorophenoxy)propanoic acid), which is used as post-emergent herbicide in several cultivations including flooded rice farming (Maddigapu et al., 2010). Dichlorprop would undergo fast transformation into 4-chlorophenol (Meunier et al., 2002) that can be nitrated to NCP by $\bullet\text{NO}_2$, produced upon nitrate photolysis and nitrite photooxidation (Maddigapu et al., 2010). Toxicity data of NCP are available for the inhibition of growth of the ciliate *Tetrahymena pyriformis*, and a 50% growth inhibition has been observed in the presence of 8.9 μM NCP. Such a result ranks NCP among the phenols that exhibit the highest toxicity toward *Tetrahymena pyriformis* (Aptula et al., 2002).

Photochemistry plays an important role in the transformation of xenobiotics in surface waters (Packer et al., 2003; Bartels and von Tuempling, 2008; Vulliet et al., 2010). The main processes involved are the direct photolysis and the reaction with $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and the triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$) (Richard et al., 2007). The radical $\bullet\text{OH}$ is produced by irradiation of nitrate, nitrite and CDOM (Vione et al., 2009a; Page et al., 2011; Sur et al., 2011), $\text{CO}_3^{\bullet-}$ by reaction between $\bullet\text{OH}$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$ and upon oxidation of CO_3^{2-} by $^3\text{CDOM}^*$ (Huang and Mabury, 2000; Canonica et al., 2005), while $^1\text{O}_2$ and $^3\text{CDOM}^*$ are generated by irradiation of CDOM (Al Housari et al., 2010; Coelho et al., 2011).

A major problem in the assessment of phototransformation kinetics and pathways of xenobiotics is the difficulty to reproduce environmental conditions in the laboratory. In particular, the high variability of the environment (*e.g.* chemical composition and column depth of surface waters) makes it difficult to generalise the experimental results to the conditions that can be found in natural systems.

To overcome the cited problem, we have recently proposed a very different approach for the assessment of the photochemical transformation kinetics of organic pollutants in surface waters. It is based on laboratory measurement of photochemical reactivity, namely direct photolysis quantum yield and reaction rate constants with $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and the triplet state of anthraquinone-2-sulphonate, adopted as a proxy of $^3\text{CDOM}^*$. In this case, the adopted laboratory systems are intended to measure the kinetic parameters rather than try to mimic the environment. The reactivity data are then used as input for a model of surface-water photochemistry, which takes the environmental variability into account. The model predicts phototransformation kinetics in the field as a function of water chemical composition and column depth (Albinet et al., 2010a; Hatipoglu et al., 2010). When the photochemical processes are the main attenuation pathways for xenobiotics, the cited approach produces a good agreement with field data (Maddigapu et al., 2011).

In this paper, we apply the above-described methodology to the assessment of the phototransformation kinetics of NCP, and compare the model predictions with field data. The latter are available for the time evolution of the parent compound 4-chlorophenol and of NCP in the shallow lagoons of the Rhône delta (Southern France) (Maddigapu et al., 2010).

2. Materials and methods

2.1. Chemicals. 2-Nitro-4-chlorophenol (NCP, purity grade 97%), anthraquinone-2-sulphonic acid, sodium salt (AQ2S, 97%), furfuryl alcohol (FFA, 98%), NaNO_3 (>99%), NaHCO_3 (98%), and H_3PO_4 (85%) were purchased from Aldrich, NaOH (99%), methanol and 2-propanol (both LiChrosolv gradient grade) from VWR Int., Rose Bengal (RB) from Alfa Aesar. Water used was of Milli-Q quality.

2.2. Irradiation experiments. The choice of the different adopted irradiation conditions was intended to maximise the excitation of photoactive compounds (nitrate, RB, AQ2S) to derive the kinetic parameters. Here the main goal is to obtain the production of the desired reactive transient, rather than simulate the solar spectrum. The important issues connected with the sunlight spectrum

and its attenuation with water depth, which affects phototransformation kinetics are all taken into account in the photochemical model (Vione et al., 2011a). Solutions to be irradiated (5 mL) were placed inside Pyrex glass cells (4.0 cm diameter, 2.3 cm height) and magnetically stirred during irradiation.

Irradiation of NCP + nitrate to study reactions with $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ was carried out under a Philips TL 01 lamp, with emission maximum at 313 nm and $3.0\pm 0.2 \text{ W m}^{-2}$ UV irradiance in the 300-400 nm range, measured with a power meter by CO.FO.ME.GRA. (Milan, Italy) equipped with a UV-sensitive probe. The incident photon flux in solution was actinometrically determined using the ferrioxalate method (Kuhn et al., 2004). Given $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ radiation absorption data, the quantum yield of Fe^{2+} photoproduction and the Pyrex transmittance, one can use the Fe^{2+} formation rate to normalise the incident spectral photon flux density $p^\circ(\lambda)$ that was measured with an Ocean Optics SD 2000 CCD spectrophotometer (Albinet et al., 2010b). The incident photon flux of the TL 01 lamp was $P_o = \int_{\lambda} p^\circ(\lambda) d\lambda = 2.0 \cdot 10^{-6} \text{ Einstein L}^{-1} \text{ s}^{-1}$.

The photodegradation of NCP sensitised by Rose Bengal (RB) via $^1\text{O}_2$ was studied under a Philips TL D 18W/16 yellow lamp, with emission maximum at 545 nm and 11 W m^{-2} irradiance in the visible, measured with the power meter and a model 4038 probe. The direct photolysis of NCP and its transformation photosensitised by AQ2S were studied under a Philips TL K05 lamp, with emission maximum at 365 nm, 28 W m^{-2} UV irradiance (300-400 nm), and $2.1 \cdot 10^{-5} \text{ Einstein L}^{-1} \text{ s}^{-1}$ incident photon flux.

The absorption spectra were taken with a Varian Cary 100 Scan UV-Vis spectrophotometer. Emission and absorption spectra are reported in Figure 1(a-c).

2.3. Monitoring of NCP transformation. The irradiated solutions were analysed by high-performance liquid chromatography (HPLC-UV). The adopted Merck-Hitachi instrument was equipped with an autosampler AS2000A (100 μL sample volume), pumps L-6200 and L-6000 for high-pressure gradients, a reverse-phase column Merck LiChrocart RP-C18 packed with LiChrospher 100 RP-18 (125 mm \times 4.6 mm \times 5 μm), and a UV-Vis detector L-4200 (detection wavelength 220 nm). It was adopted an isocratic elution with a 50:50 mixture of CH_3OH :aqueous H_3PO_4 (pH 2.8), at a flow rate of 1.0 mL min^{-1} . The retention time of NCP was 6.8 min, the column dead time 0.9 min.

The time evolution of FFA to quantify the formation rate of $^1\text{O}_2$ under the yellow lamp was also monitored by HPLC-UV, as reported previously (Minella et al., 2011a).

2.4. Kinetic data treatment. Reaction rates were determined by fitting the time evolution data of NCP with pseudo-first order equations of the form $C_t = C_o \exp(-k t)$, where C_t is the concentration of NCP at the irradiation time t , C_o its initial concentration and k the pseudo-first order degradation rate constant. The initial degradation rate is $Rate_{NCP} = k C_o$. The reported errors on the rates ($\pm\sigma$) were derived by curve fitting and depend on the scattering of the experimental data around the fitting curve. The reproducibility of repeated runs was around 10-15%.

3. Results and Discussion

NCP has $pK_a = 6.48$ (Aptula et al., 2002). It is expected that both the neutral and the anionic form would be present in surface waters, but the anionic one would usually prevail. For this reason and to enable comparison with the field data collected in the Rhône delta, irradiation experiments were carried out at pH 8 (adjusted with NaOH) that is representative of that environment. Therefore, the results are referred to the anionic NCP form.

The kinetic parameters relevant to the main photochemical processes that would involve anionic NCP in surface waters (direct photolysis and reaction with $\bullet OH$, $CO_3^{\bullet-}$, 1O_2 and $^3CDOM^*$) were determined by laboratory measurements. They allowed the modelling of NCP lifetime as a function of the environmental variables and the comparison of model predictions with field data.

3.1. Direct photolysis. NCP (initial concentration 20 μM) was irradiated under the TL K05 lamp (Figure 1a). Under the adopted conditions, NCP followed a pseudo-first order transformation kinetics with initial $Rate_{NCP} = (1.09 \pm 0.19) \cdot 10^{-11} \text{ M s}^{-1}$. The photon flux initially absorbed by NCP can be expressed as:

$$P_a^{NCP} = \int_{\lambda} p^{\circ}(\lambda) [1 - 10^{-\epsilon_{NCP}(\lambda)b[NCP]}] d\lambda = 8.58 \cdot 10^{-7} \text{ Einstein L}^{-1} \text{ s}^{-1},$$

where $p^{\circ}(\lambda)$ is the incident spectral photon flux density of the lamp, $\epsilon_{NCP}(\lambda)$ the molar absorption coefficient of NCP (see Figure 1a), $b = 0.4 \text{ cm}$ the optical path length in solution and $[NCP] = 20 \mu M$. From these data it is possible to obtain the polychromatic photolysis quantum yield of NCP between 300 and 540 nm, where the spectra of the lamp and NCP overlap, as $\Phi_{NCP} = Rate_{NCP} (P_a^{NCP})^{-1} = (1.27 \pm 0.22) \cdot 10^{-5}$.

3.2. Reaction with $\bullet OH$. The reaction rate constant between NCP and $\bullet OH$ was determined by competition kinetics with 2-propanol, using nitrate photolysis as the $\bullet OH$ source. The main

reactions that are expected to take place in the system are the following ones (Buxton et al., 1988; Mack and Bolton, 1999):

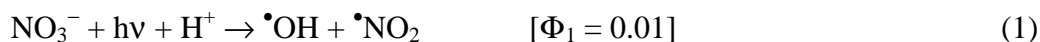


Figure 2 reports $Rate_{\text{NCP}}$ as a function of the concentration of 2-propanol, upon UVB irradiation of 10 mM NaNO_3 + 20 μM NCP. The choice of the initial nitrate concentration was motivated by the need of obtaining fast phototransformation of NCP, so that one can neglect the direct photolysis that would be a confounding factor in this context. The high adopted nitrate concentration is thus aimed at obtaining the reaction rate constant between NCP and $\bullet\text{OH}$ rather than at reproducing the environmental conditions. Such conditions will be taken into account in the photochemical model.

It is evident from Figure 2 that the alcohol inhibits the transformation of NCP, coherently with the scavenging of $\bullet\text{OH}$ in reaction (2). However, $Rate_{\text{NCP}}$ reaches a plateau at elevated concentration of 2-propanol. Such an effect, which has already been observed in the case of 2,4-dinitrophenol (Albinet et al., 2010b), is most likely accounted for by reactions between NCP and radical species produced by 2-propanol and $\bullet\text{OH}$. An alternative explanation (reaction with photogenerated $\bullet\text{NO}_2$) is little likely for NCP due to the electron-withdrawing character of the nitro group, which decreases the reactivity with electrophilic transients (Vione et al., 2009b).

A kinetic treatment including the additional reactions is reported as Supplementary Material (hereafter SM). One obtains the following equation for $Rate_{\text{NCP}}$:

$$Rate_{\text{NCP}} = R_{\text{OH}} \frac{(k_3 \cdot [\text{NCP}] + \alpha \cdot k_2 \cdot [\text{2-Propanol}])}{k_3 \cdot [\text{NCP}] + k_2 \cdot [\text{2-Propanol}]} \quad (4)$$

where $\alpha = 0.54 \pm 0.02$ is the ratio between $Rate_{\text{NCP}}$ without 2-propanol and the plateau value of $Rate_{\text{NCP}}$ (derived from experimental data, see SM). The fit of the experimental rate data with equation (4) is reported in Figure 2, with excellent agreement, and yielded $k_3 = (1.09 \pm 0.09) \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ as the reaction rate constant between NCP and $\bullet\text{OH}$.

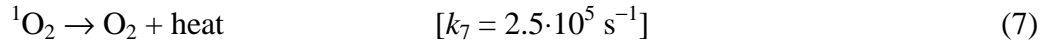
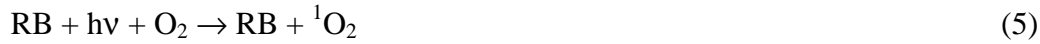
3.3. Reaction with $\text{CO}_3^{\bullet-}$. The assessment of the reactivity between organic compounds and $\text{CO}_3^{\bullet-}$ can be carried out with a semi-quantitative screening method, which makes use of nitrate and bicarbonate under irradiation (Vione et al., 2009c). The rationale of the method is that the

photolysis of nitrate yields photogenerated fragments inside a solvent cage ($[\bullet\text{O}^- + \bullet\text{NO}_2]_{\text{cage}}$) that can either recombine back to nitrate or diffuse in the solution bulk. Here $\bullet\text{O}^-$ would be protonated to $\bullet\text{OH}$ and react with dissolved substrates (Mark et al., 1996; Bouillon and Miller, 2005; Nissenson et al., 2010; Vione et al., 2011b). The ions HCO_3^- and CO_3^{2-} can react with bulk $\bullet\text{OH}$ to yield $\text{CO}_3^{\bullet-}$, which is considerably less reactive than the hydroxyl radical. Furthermore, HCO_3^- and CO_3^{2-} could also react with cage $\bullet\text{O}^-$, producing $\text{CO}_3^{\bullet-}$ and inhibiting photofragment recombination to nitrate. The final result is that the photogeneration rate of $\text{CO}_3^{\bullet-}$ in the presence of nitrate + bicarbonate would be significantly higher than that of $\bullet\text{OH}$ with nitrate alone (Vione et al., 2009c). The formation of a higher amount of a less reactive species has variable effects depending on the reactivity of a dissolved substrate with $\text{CO}_3^{\bullet-}$ vs. $\bullet\text{OH}$. Bicarbonate would inhibit the degradation of compounds that are poorly reactive toward $\text{CO}_3^{\bullet-}$. Such compounds would also undergo insignificant transformation by $\text{CO}_3^{\bullet-}$ in surface waters. Conversely, bicarbonate would enhance the degradation of compounds that react with $\text{CO}_3^{\bullet-}$ at a significant extent (Vione et al., 2009c). Bicarbonate addition to nitrate also modifies the solution pH. For this reason, the effect of bicarbonate should be compared to the behaviour of the substrate in the presence of a phosphate buffer ($\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$), at the same concentration as NaHCO_3 (comparable ionic strength) and same pH.

Figure 3 reports the initial transformation rate of 20 μM NCP upon irradiation in the presence of: (i) variable NaHCO_3 concentrations; (ii) 10 mM NaNO_3 and variable NaHCO_3 concentrations (addition of 10 mM bicarbonate increased for instance the solution pH from 5.5 to 8.5); (iii) 10 mM NaNO_3 and a phosphate buffer, at the same concentration as NaHCO_3 and same pH (within ± 0.1 units). The experimental data allow the following inferences to be made: (a) NCP degradation was very slow in the absence of nitrate and it was further inhibited by addition of bicarbonate, suggesting a negligible direct photolysis of NCP under the adopted conditions (irradiation time up to 4 h); (b) compared to phosphate at equal pH, bicarbonate inhibited the transformation of NCP.

The inhibition by bicarbonate, compared to phosphate, of NCP transformation upon nitrate photolysis suggests that NCP is little reactive toward $\text{CO}_3^{\bullet-}$. Therefore, reaction with $\text{CO}_3^{\bullet-}$ is expected to be a minor transformation pathway of NCP in surface waters.

3.4. Reaction with $^1\text{O}_2$. Figure 4 reports the initial transformation rate of NCP, as a function of its initial concentration, upon irradiation of 10 μM Rose Bengal (RB) adopted as a source of $^1\text{O}_2$ (reaction 5). The reaction (6) between NCP and $^1\text{O}_2$ would be in competition with the thermal deactivation of singlet oxygen (reaction 7; Rodgers and Snowden, 1982):



Upon application of the steady-state approximation to ${}^1\text{O}_2$ one gets the following expression for the initial transformation rate of NCP ($Rate_{\text{NCP}}$):

$$Rate_{\text{NCP}} = \frac{R_{1\text{O}_2} \cdot k_6 \cdot [\text{NCP}]}{k_7 + k_6 \cdot [\text{NCP}]} \quad (8)$$

where $R_{1\text{O}_2}$ is the formation rate of ${}^1\text{O}_2$ by 10 μM RB under the adopted irradiation device. For low $[\text{NCP}]$ one gets ($k_6 [\text{NCP}] \ll k_7$):

$$\lim_{[\text{NCP}] \rightarrow 0} \{Rate_{\text{NCP}}\} = R_{1\text{O}_2} \cdot k_6 \cdot k_7^{-1} \cdot [\text{NCP}] \quad (9)$$

The measurement of $R_{1\text{O}_2}$ was carried out upon irradiation of 10 μM RB + 0.1 mM furfuryl alcohol (FFA), which reacts with ${}^1\text{O}_2$ with a rate constant $k_{\text{FFA}} = 1.2 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Wilkinson and Brummer, 1981). The initial transformation rate of FFA under the adopted conditions was $Rate_{\text{FFA}} = (1.26 \pm 0.06) \cdot 10^{-7} \text{ M s}^{-1}$. Photogenerated ${}^1\text{O}_2$ could undergo deactivation or reaction with FFA, and upon application of the steady-state approximation to $[{}^1\text{O}_2]$ one obtains:

$$R_{1\text{O}_2} = Rate_{\text{FFA}} \cdot \frac{k_7 + k_{\text{FFA}} \cdot [\text{FFA}]}{k_{\text{FFA}} \cdot [\text{FFA}]} \quad (10)$$

From equation (10) one gets $R_{1\text{O}_2} = (2.75 \pm 0.13) \cdot 10^{-6} \text{ M s}^{-1}$. From the initial slope of the fitting curve of Figure 4 ($[\text{NCP}] \rightarrow 0$) one derives $\lim_{[\text{NCP}] \rightarrow 0} \{Rate_{\text{NCP}} [\text{NCP}]^{-1}\} = R_{1\text{O}_2} \cdot k_6 \cdot k_7^{-1} = (2.48 \pm 0.62) \cdot 10^{-4} \text{ s}^{-1}$. From the known values of $R_{1\text{O}_2}$ and k_7 one gets $k_6 = (2.25 \pm 0.67) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ as the reaction rate constant between NCP and ${}^1\text{O}_2$. This finding confirms that the hypothesis $k_6 [\text{NCP}] \ll k_7$ was reasonable.

3.5. Reaction with irradiated AQ2S. Figure 5 reports the initial transformation rate of NCP as a function of its initial concentration, upon irradiation of 0.1 mM AQ2S. The direct photolysis of

NCP was negligible at the adopted irradiation time scale (up to 4h). From the linear trend of the plot of Figure 5 one gets $Rate_{NCP} = (1.94 \pm 0.14) \cdot 10^{-5} [NCP]$. Under the adopted conditions, AQ2S would be by far the main radiation absorber. From the absorption spectra (Figure 1) one gets that at 330 nm the absorbance of 0.1 mM AQ2S would be about 60 times higher than that of 20 μ M NCP, the highest adopted NCP concentration. Therefore, it is possible to determine with excellent approximation the photon flux absorbed by 0.1 mM AQ2S as $P_a^{AQ2S} \cong \int_{\lambda} p^{\circ}(\lambda) [1 - 10^{-\varepsilon_{AQ2S}(\lambda)b[AQ2S]}] d\lambda = 2.01 \cdot 10^{-6} \text{ Einstein L}^{-1} \text{ s}^{-1}$ ($p^{\circ}(\lambda)$ is the spectral photon flux density of the TL K05 lamp, $b = 0.4 \text{ cm}$). The polychromatic quantum yield of NCP phototransformation by AQ2S would thus be $\Phi_{NCP,AQ2S} = Rate_{NCP} (P_a^{AQ2S})^{-1} = (9.65 \pm 0.70) [NCP]$.

The triplet state $^3AQ2S^*$, which is the main reactive species of AQ2S under irradiation, has a formation quantum yield $\Phi_{^3AQ2S^*} = 0.18$ and a deactivation rate constant $k_{^3AQ2S^*} = 1.1 \cdot 10^7 \text{ s}^{-1}$ (Loeff et al., 1983; Alegría et al., 1999). The formation rate of $^3AQ2S^*$ would be $R_{^3AQ2S^*} = \Phi_{^3AQ2S^*} P_a^{AQ2S}$ and its deactivation would be in competition with the reaction with NCP (with rate constant $k_{^3AQ2S^*,NCP}$). Upon application of the steady-state approximation to $^3AQ2S^*$, the transformation rate of NCP by irradiated AQ2S can be expressed as follows:

$$Rate_{NCP} = \Phi_{^3AQ2S^*} \cdot P_a^{AQ2S} \cdot \frac{k_{^3AQ2S^*,NCP} \cdot [NCP]}{k_{^3AQ2S^*} + k_{^3AQ2S^*,NCP} \cdot [NCP]} \quad (11)$$

Under the hypothesis that $k_{^3AQ2S^*,NCP} [NCP] \ll k_{^3AQ2S^*}$, one gets $Rate_{NCP} = \Phi_{^3AQ2S^*} P_a^{AQ2S} k_{^3AQ2S^*,NCP} (k_{^3AQ2S^*})^{-1} [NCP]$, which is compatible with the linear trend reported in Figure 5. It is also $\Phi_{NCP,AQ2S} = Rate_{NCP} (P_a^{AQ2S})^{-1} = \Phi_{^3AQ2S^*} k_{^3AQ2S^*,NCP} (k_{^3AQ2S^*})^{-1} [NCP]$. By comparison with the experimental trend $\Phi_{NCP,AQ2S} = (9.65 \pm 0.70) [NCP]$, one gets $k_{^3AQ2S^*,NCP} = (9.65 \pm 0.70) k_{^3AQ2S^*} (\Phi_{^3AQ2S^*})^{-1} = (5.90 \pm 0.43) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This finding confirms that the hypothesis $k_{^3AQ2S^*,NCP} [NCP] \ll k_{^3AQ2S^*}$ was correct. Hereafter it will be hypothesised that the value of $k_{^3AQ2S^*,NCP}$ is representative of the reaction rate constant(s) between NCP and the excited triplet states of CDOM.

3.6. Modelling the photochemical transformation kinetics of NCP in surface waters. The photochemical reactivity data obtained so far, combined with a model of surface-water photochemistry (Albinet et al., 2010a; Maddigapu et al., 2011) allow the prediction of the environmental persistence of NCP as a function of environmental variables, such as water chemical composition and column depth. Our model takes into account: (i) the production of $\bullet\text{OH}$ upon irradiation of nitrate, nitrite and CDOM; (ii) the production of $\text{CO}_3^{\bullet-}$ upon reaction of HCO_3^- and

CO₃²⁻ with •OH and of CO₃²⁻ with ³CDOM*; (iii) the production of ¹O₂ and ³CDOM* by irradiated CDOM; (iv) the scavenging of •OH by DOM, carbonate and bicarbonate; (v) the scavenging of CO₃^{•-} by DOM; (vi) the lifetime of ¹O₂ and ³CDOM* in aqueous solution; (vii) the absorption of radiation by CDOM and the penetration of sunlight into the water column. The photochemical production of the relevant reactive species and their scavenging depend on water depth and on concentration of nitrate, nitrite, dissolved organic matter (dissolved organic carbon, DOC, which is usually measured as non-purgeable organic carbon, NPOC), carbonate and bicarbonate (Minella et al., 2011b). Calculations are initially carried out based on an incident sunlight spectrum having 22 W m⁻² irradiance between 290 and 400 nm (Figure SM1; Frank and Klöpffer, 1988), but one should take into account the fact that sunlight irradiance is not constant in the environment. A standard summer sunny day (SSD) has been defined, considering that the sunlight UV energy reaching the ground on a fair-weather 15 July at 45°N is equivalent to 10-h steady irradiation at 22 W m⁻² UV irradiance (Maddigapu et al., 2011). Therefore, the SSD time unit adopted in the model is equivalent to a fair-weather 15 July at 45°N. The photochemical model yields the pseudo-first order rate constants of NCP phototransformation *via* the different processes in SSD⁻¹ units.

Model calculations show that NCP photochemical transformation in typical surface waters would mainly take place upon reaction with •OH and direct photolysis. Reaction with ³CDOM* would play a secondary role, and the other processes would be unimportant. Photochemical processes would be more important in shallow water bodies, where the water column can be thoroughly illuminated (Bracchini et al., 2005). The Rhône delta lagoons where NCP has been detected have an average water depth of 1 m (Chiron et al., 2009) and are a very good example of an environment where photochemistry can be important in pollutant attenuation/modification (Al Housari et al., 2011). Therefore, the model trends reported below are referred to water bodies with limited depth.

Figure 6 reports the overall pseudo-first order transformation rate constant of NCP (k_{tot} in SSD⁻¹ units, 6a) as a function of nitrite and NPOC that is a measure of DOC/DOM and, in the model, of CDOM as well. The other parameters have been kept constant (1 m depth, 5.1 µM nitrate, 26 µM carbonate and 1 mM bicarbonate). It can be seen that nitrite (•OH source) favours NCP degradation. In contrast, DOM inhibits it as an •OH scavenger and because of competition for sunlight between CDOM and NCP, which inhibits the NCP direct photolysis. The figure also reports the pseudo-first order rate constants for reaction with •OH and for the direct photolysis (respectively k_{OH} , 6b, and k_{Phot} , 6c, where $k_{\text{tot}} \approx k_{\text{OH}} + k_{\text{Phot}}$). The rate constant k_{OH} decreases with increasing NPOC at relatively low NPOC values and reaches a plateau at around 3-5 mg C L⁻¹ NPOC. The initial

decrease is mainly due to $\bullet\text{OH}$ scavenging by DOM. The plateau reached by k_{OH} at high NPOC is referred to conditions where CDOM would be the prevailing $\bullet\text{OH}$ source and DOM the main sink, the two effects compensating for each other. The almost linear decrease of k_{Phot} vs. NPOC is due to competition for irradiance between NCP and CDOM, which inhibits the direct photolysis of NCP. Note that CDOM is the chromophoric fraction of DOM, the latter including both chromophoric and non-chromophoric compounds, with possibly varying ratios in different environments due to the budget of formation-transformation processes (Osburn et al., 2011).

Figure 7 reports k_{tot} , k_{OH} , and k_{Phot} as a function of water depth and nitrate concentration, with constant $0.1 \mu\text{M}$ nitrite, 2 mg C L^{-1} NPOC, $26 \mu\text{M}$ carbonate and 1 mM bicarbonate. Nitrate as an $\bullet\text{OH}$ source enhances k_{OH} , and k_{tot} as a consequence. Increasing depth inhibits all the photochemical processes, because the bottom layers of a deeper water body would be poorly illuminated. The negligible effect on k_{Phot} of both nitrite (Figure 6c) and nitrate (Figure 7c) is accounted for by their negligible radiation absorption compared to CDOM, which is the main radiation absorber below 500 nm in most surface waters (Bracchini et al., 2005).

The values of k_{tot} , the overall transformation rate constant, are included in the range $0.04\text{-}0.18 \text{ SSD}^{-1}$ under the conditions adopted in the calculations. Considering that the half-life time $\tau_{\text{NCP}} = \ln 2 k_{\text{tot}}^{-1}$, one gets that τ_{NCP} would vary from 4 to 17 SSD. Therefore, it is suggested that photochemical transformation could be a very important sink of NCP in shallow water bodies.

3.7. Comparison with field data. In the paddy fields and shallow lagoons of the Rhône delta (Southern France), a reaction sequence applies that transforms the herbicide dichlorprop into 4-chlorophenol (4CP), which then undergoes nitration (probably photochemical) to NCP (Maddigapu et al., 2010). In 2005, 4CP reached a peak in the 2nd half of June, soon after the application of dichlorprop on the rice fields, after which its concentration decreased. The concentration of NCP peaked a couple of weeks later and decreased afterwards. Figure SM2 shows the time trend of 4CP and NCP in a lagoon, after the 4CP maximum (Maddigapu et al., 2010). Interestingly, 4CP showed pseudo-first order decay. The residence time of water in the lagoon would give half-life times of around a year (Al Housari et al., 2011), thus flushing is too slow to affect the time evolution of the compounds under consideration.

Scheme 1 depicts the transformation of 4CP into NCP, under the hypothesis of pseudo-first order kinetics. The following equations apply to the rates of 4CP and NCP:

$$-\frac{d[4CP]}{dt} = k_{4CP} [4CP] \quad (12)$$

$$\frac{d[NCP]}{dt} = k'[4CP] - k_{NCP}[NCP] \quad (13)$$

where k_{4CP} is the pseudo-first order degradation rate constant of 4CP, k' the pseudo-first order rate constant of 4CP transformation into NCP, and k_{NCP} the pseudo-first order rate constant of NCP degradation. The differential equations (12,13) constitute a system that can be solved as follows:

$$[4CP] = C_{4CP}^o e^{-k_{4CP} t} \quad (14)$$

$$[NCP] = C_{NCP}^o e^{-k_{NCP} t} + \frac{k' C_{4CP}^o}{k_{NCP} - k_{4CP}} (e^{-k_{4CP} t} - e^{-k_{NCP} t}) \quad (15)$$

where $C_{4CP}^o = 1.71$ nM is the concentration of 4CP at $t = 0$ (21 June, 4CP concentration maximum) and $C_{NCP}^o = 0.22$ nM is the corresponding initial concentration of NCP. The fit of the field data of 4CP and NCP with equations (14) and (15), respectively, yielded $k_{4CP} = (6.79 \pm 0.82) \cdot 10^{-2} \text{ day}^{-1}$, $k' = (8.69 \pm 1.66) \cdot 10^{-2} \text{ day}^{-1}$, and $k_{NCP} = (1.09 \pm 0.02) \cdot 10^{-1} \text{ day}^{-1}$ ($\mu \pm \sigma$). Within the experimental errors $k_{4CP} \approx k'$, indicating that there is a practically quantitative transformation of 4CP into NCP. It is thus suggested that (photo)nitration is quite important in the studied environment, an issue that has already been reported for other pesticide intermediates in the Rhône delta (Chiron et al., 2009). In contrast, it should be pointed out that (photo)nitration of a nitrophenol such as NCP is expected to be ineffective because of the electron-withdrawing character of the nitro group (Vione et al., 2009b). The fact that $k_{4CP} \approx k'$ also confirms that processes such as outflow, sedimentation and biodegradation, which would increase k_{4CP} and decrease k' , would be much slower than the observed transformation kinetics and could, therefore, be neglected (Al Housari et al., 2011). Interestingly, NCP undergoes slightly faster transformation compared to 4CP ($k_{NCP} > k_{4CP}$). This finding deserves some comment because the direct photolysis quantum yield of 4CP is about four orders of magnitude higher compared to NCP (Czaplicka, 2006). However, under environmental conditions the elevated quantum yield of 4CP phototransformation would be largely offset by the very limited absorption of sunlight. The combination of elevated photolysis quantum yield and poor sunlight absorption, which is usually accounted for by an absorption band with a maximum in the UVC region, is not unusual and has for instance recently been reported for ibuprofen and the herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA; Vione et al., 2010 and 2011a), the latter having some structural analogy with 4CP.

The value $k_{NCP} = (1.09 \pm 0.02) \cdot 10^{-1} \text{ day}^{-1}$ derived from the field data (which corresponds to a half-life time of 6.36 ± 0.12 days) can be compared with the results of the photochemical model

described in the previous section, applied to the relevant environmental conditions. They are 51 μM nitrate, 3.2 μM nitrite, 2.0 mg C L^{-1} NPOC, 26 μM carbonate, 2.1 mM bicarbonate and 1.0 m water depth (Maddigapu et al., 2010). As anticipated in the previous section, direct photolysis and reaction with $\bullet\text{OH}$ are expected to be the main transformation processes of NCP, with a smaller contribution from ${}^3\text{CDOM}^*$. The radical $\bullet\text{OH}$ would mainly be generated by nitrite photolysis (over 80%). Other contributions would be from CDOM (over 10%) and nitrate (around 5%). The model yielded the following results for the pseudo-first order NCP rate constants referred to the relevant processes ($\bullet\text{OH}$, direct photolysis and ${}^3\text{CDOM}^*$, respectively): $k_{\text{OH}} = (5.6 \pm 1.4) \cdot 10^{-2} \text{ SSD}^{-1}$, $k_{\text{Phot}} = (6.0 \pm 1.8) \cdot 10^{-2} \text{ SSD}^{-1}$, and $k_{3\text{CDOM}^*} = (0.9 \pm 0.1) \cdot 10^{-2} \text{ SSD}^{-1}$. The reported errors are derived from those on experimental rate constants and quantum yield as well as from model-related incertitude. The overall rate constant of NCP phototransformation would be $k_{\text{tot}} = k_{\text{OH}} + k_{\text{Phot}} + k_{3\text{CDOM}^*} = (1.25 \pm 0.33) \cdot 10^{-1} \text{ SSD}^{-1}$. Under the hypothesis that 1 day = 1 SSD, which is not unreasonable considering that the field transformation process took place in the summer season, one gets a very good agreement between model predictions and field data. One can thus conclude that photochemical transformation, mostly upon direct photolysis and $\bullet\text{OH}$ reaction, would play a key role in the attenuation of NCP in the lagoon water of the Rhône delta.

4. Conclusions

The nitroaromatic compound 2-nitro-4-chlorophenol (NCP) in its anionic form is expected to undergo significant photodegradation in surface waters, the main processes being direct photolysis and reaction with $\bullet\text{OH}$. The relevant photochemical kinetic parameters are: $\Phi_{\text{NCP}} = (1.27 \pm 0.22) \cdot 10^{-5}$ (polychromatic, 300-540 nm); $k_{\text{NCP},\bullet\text{OH}} = (1.09 \pm 0.09) \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{NCP},\text{IO}_2} = (2.15 \pm 0.38) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{\text{NCP},3\text{AQ2S}^*} = (5.90 \pm 0.43) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$. AQ2S has been used here as CDOM proxy. The incorporation of the data into a model of surface-water photochemistry allowed the photochemical persistence of NCP in surface waters to be foreseen. For the Rhône delta lagoons the model yielded a half-life time of 5-6 days, which is in very good agreement with the field data. Therefore, it is suggested that photochemistry plays a significant role in the attenuation of NCP in the lagoon water.

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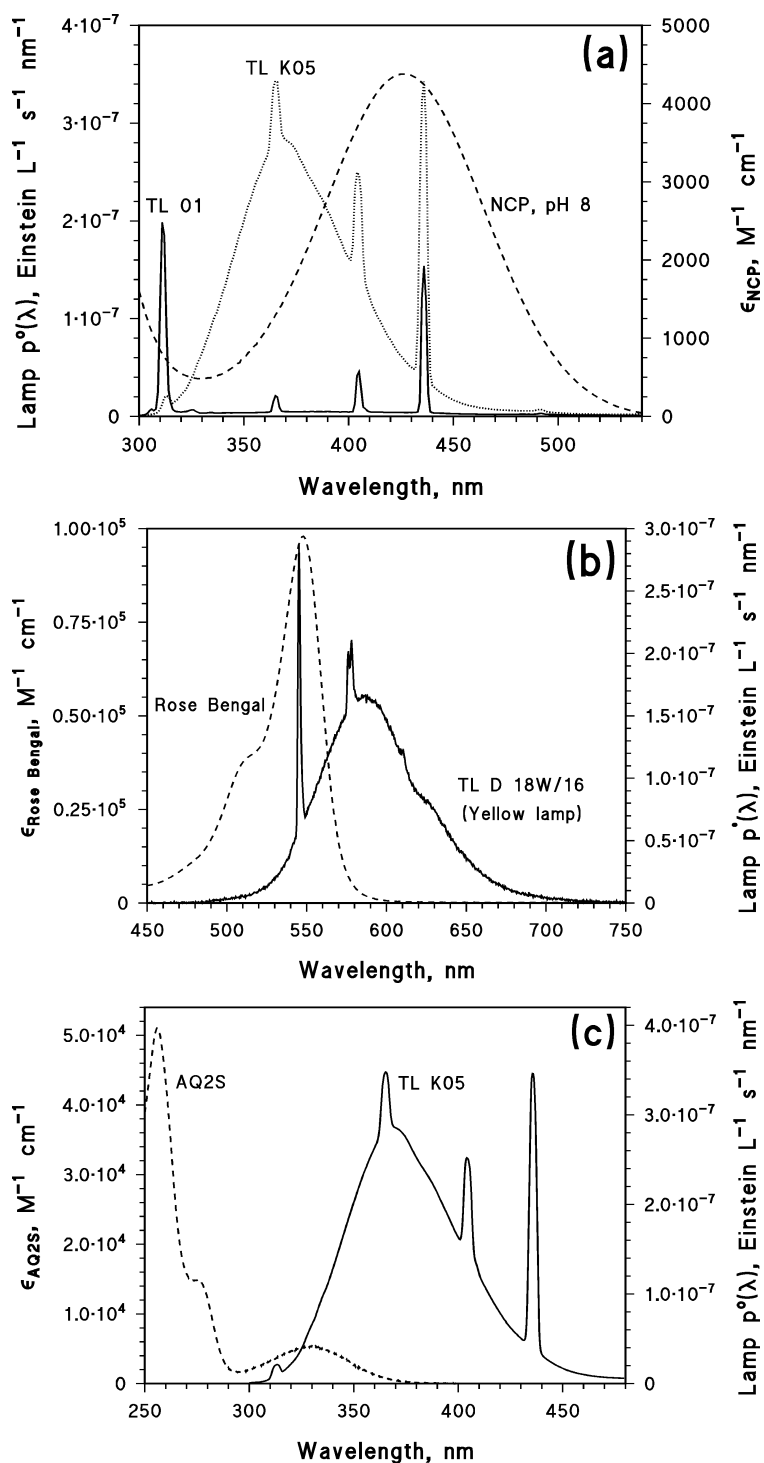


Figure 1. a) Absorption spectrum of NCP. Incident spectral photon flux density of the adopted TL K05 (emission maximum at 365 nm) and TL 01 (emission maximum at 313 nm) lamps. b) Absorption spectrum of Rose Bengal (RB). Incident spectral photon flux density of the lamp (TL D 18W/16 Yellow). c) Absorption spectrum of antraquinone-2-sulphonate (AQ2S). Incident spectral photon flux density of the TL K05 lamp.

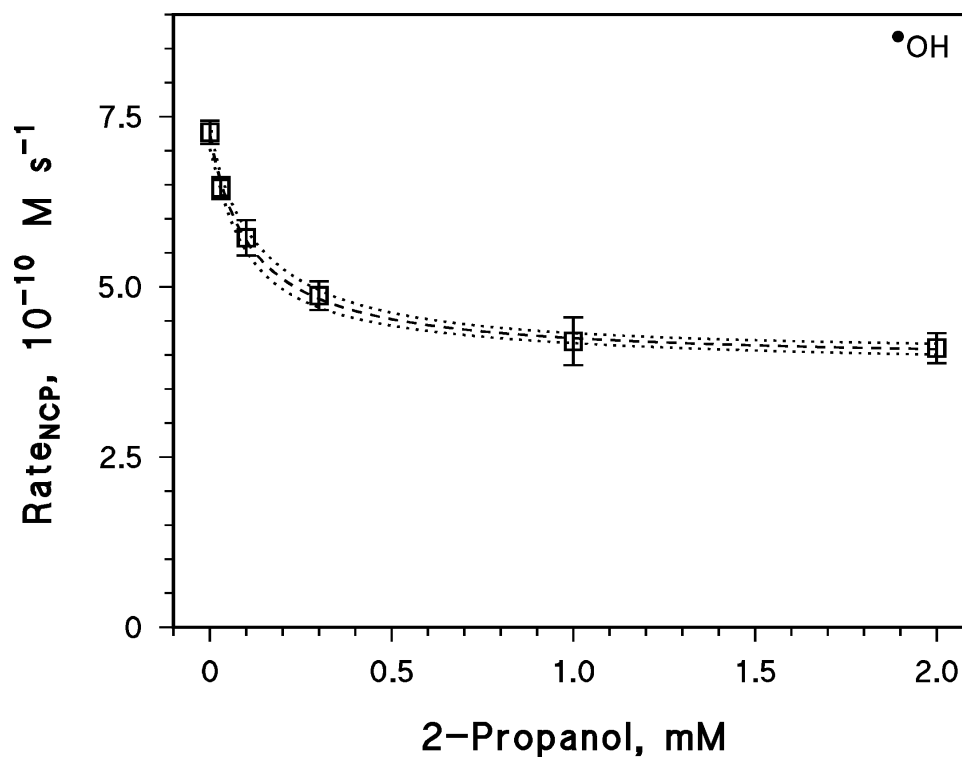


Figure 2. Initial transformation rates of 20 μM NCP upon irradiation of 10 mM NaNO_3 (TL 01 lamp), as a function of the concentration of 2-propanol. The solution pH was 8, adjusted with NaOH. The dashed curve is the fit function (equation 4), the dotted ones represent the 95% confidence limits of the fit.

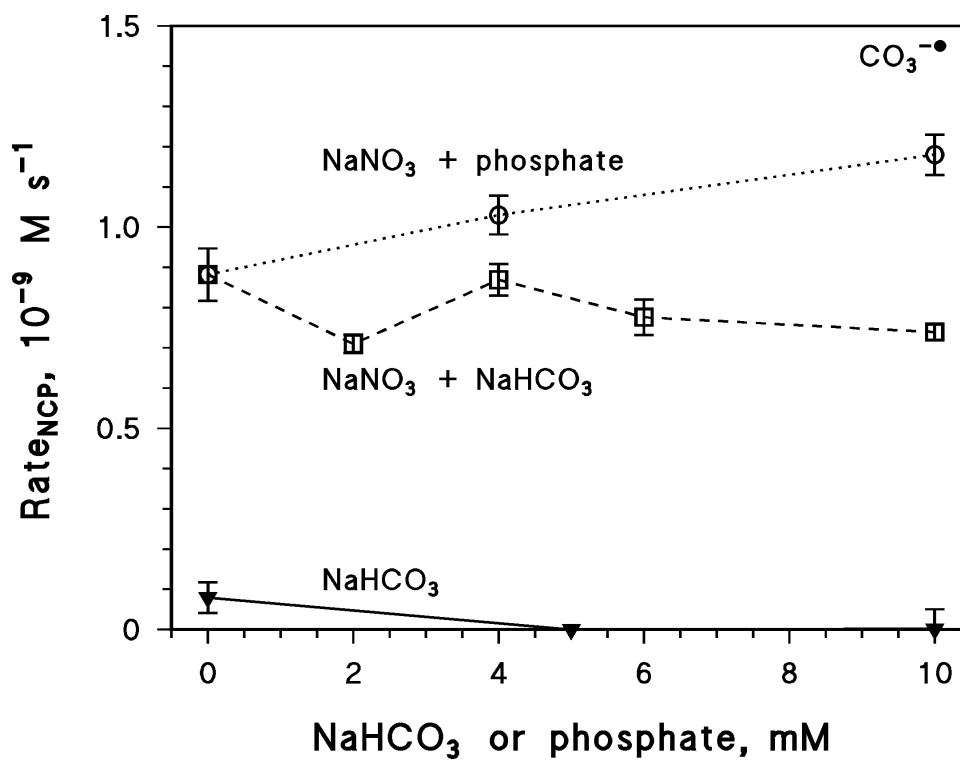


Figure 3. Initial transformation rates under irradiation (TL 01 lamp) of (\square) 20 μM NCP and 10 mM NaNO_3 , as a function of the concentration of NaHCO_3 ; (Δ) 20 μM NCP and 10 mM NaNO_3 , as a function of the concentration of phosphate buffer (same concentration as NaHCO_3 and same pH, within 0.1 units); (\diamond) 20 μM NCP, without nitrate, as a function of NaHCO_3 concentration.

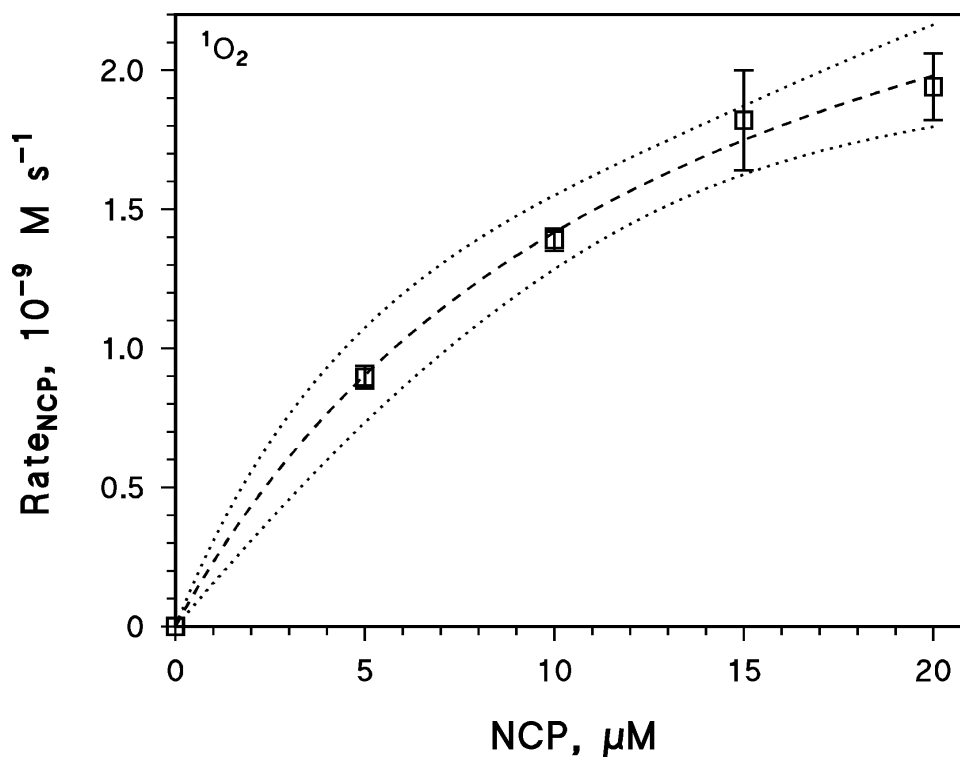


Figure 4. Initial transformation rates of NCP upon irradiation of 10 μM Rose Bengal (RB) under the yellow lamp (Philips TL D 18W/16), as a function of the NCP concentration. The solution pH was 8, adjusted with NaOH. The fit function has the form $\text{Rate}_{\text{NCP}} = a [\text{NCP}] ([\text{NCP}] + b)^{-1}$, with $a = (3.28 \pm 0.27) \cdot 10^{-9}$ and $b = (1.32 \pm 0.22) \cdot 10^{-5}$, and is reported as a dashed curve on the plot. The dotted curves represent the 95% confidence limits.

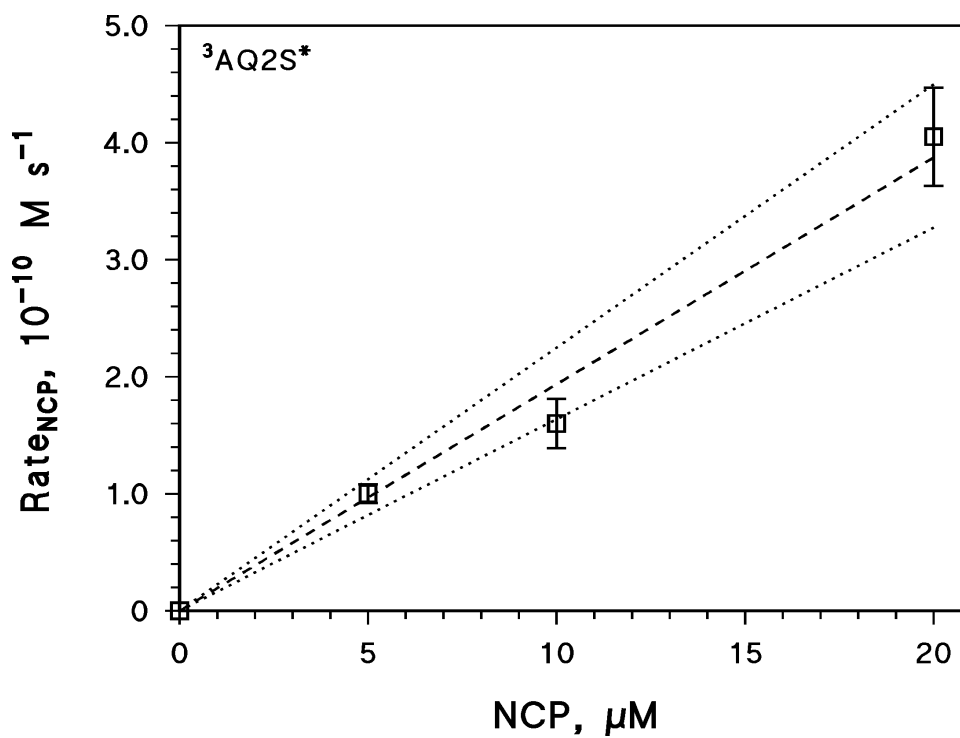


Figure 5. Initial transformation rates of NCP upon irradiation of 0.1 mM AQ2S (TL K05 lamp), as a function of NCP concentration. The solution pH was 8, adjusted with NaOH. The fit line is dashed, the dotted ones represent the 95% confidence limits.

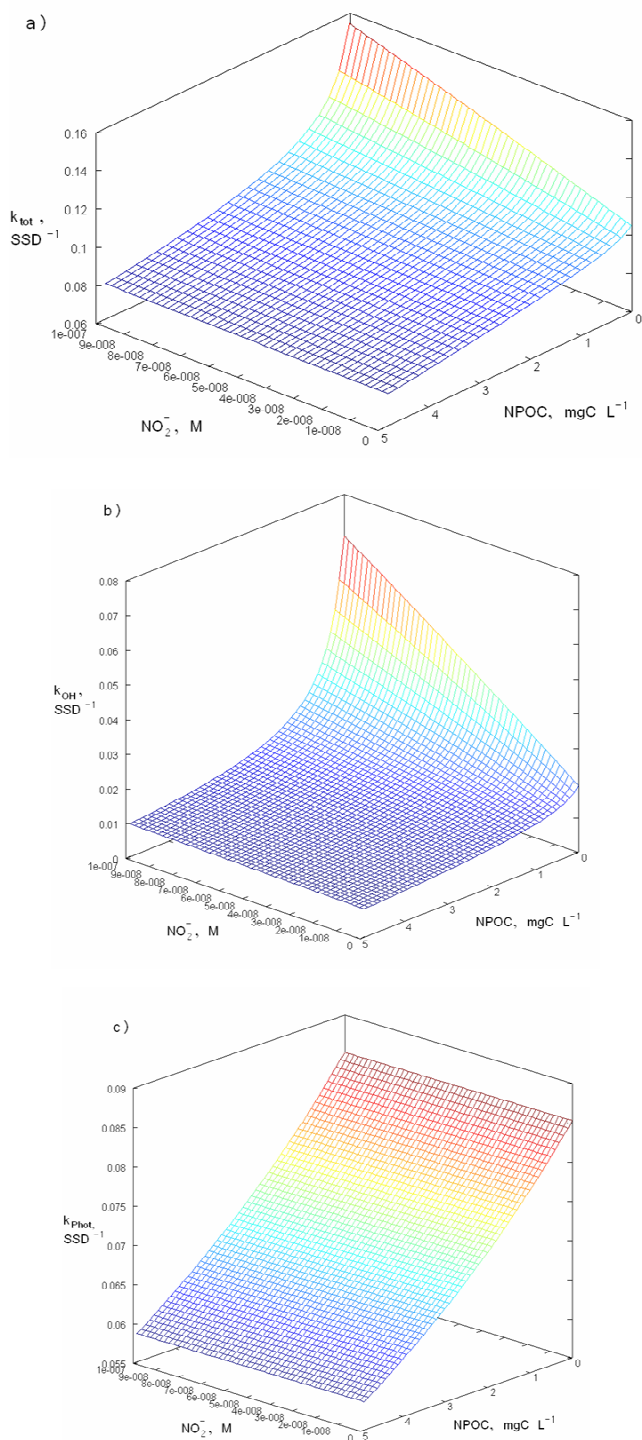


Figure 6. Modelled pseudo-first order degradation rate constants of NCP in surface waters as a function of nitrite and NPOC: the total rate constant (k_{tot} , 6a), the rate constant for transformation by $\bullet\text{OH}$ (k_{OH} , 6b) and the rate constant for the direct photolysis (k_{Photo} , 6c). The other water parameters are: depth 1 m, 5.1 μM nitrate, 26 μM carbonate, 1 mM bicarbonate.

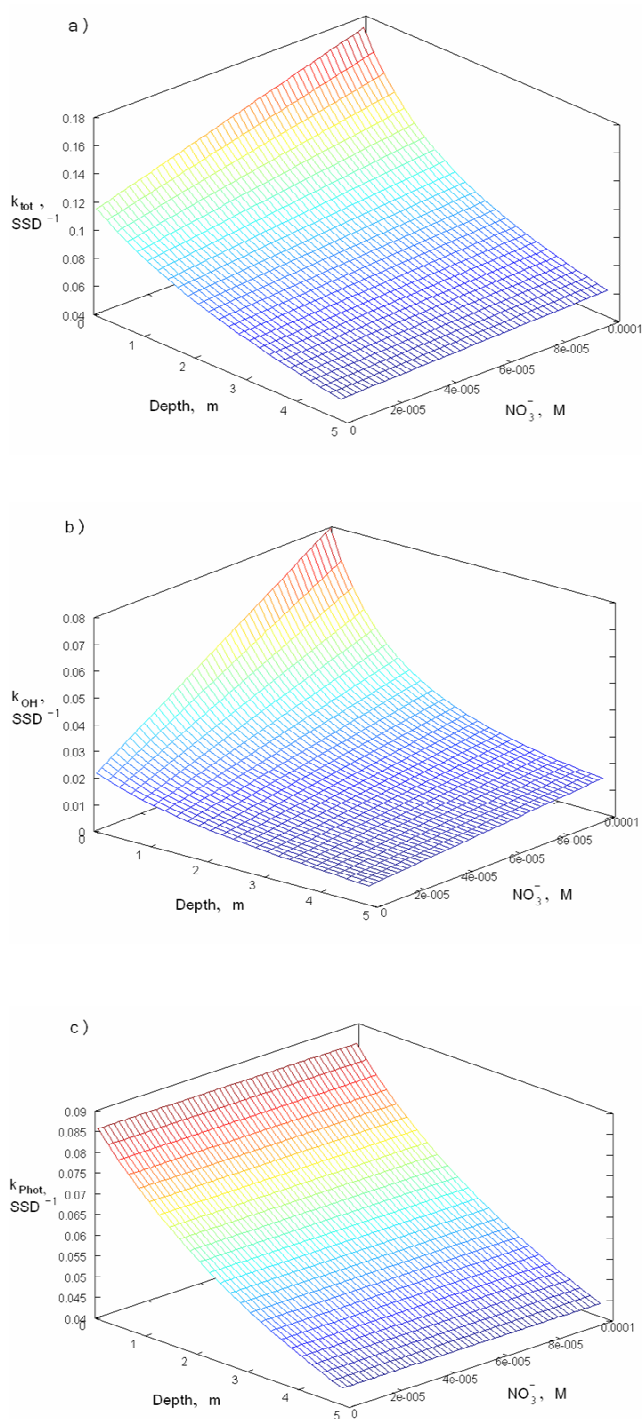
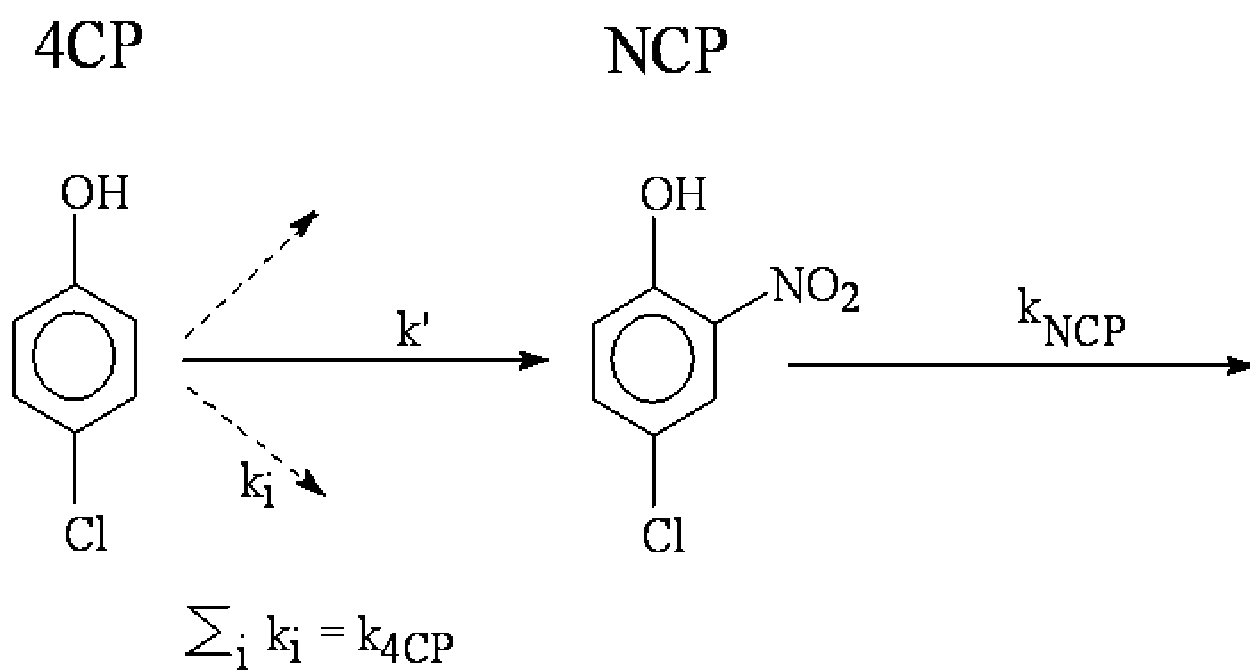


Figure 7. Modelled pseudo-first order degradation rate constants of NCP in surface waters as a function of nitrate and water depth: the total rate constant (k_{tot} , 7a), the rate constant for transformation by $\bullet\text{OH}$ (k_{OH} , 7b) and the rate constant for the direct photolysis (k_{Phot} , 7c). The other water parameters are: $0.1 \mu\text{M}$ nitrite, 2 mg C L^{-1} NPOC, $26 \mu\text{M}$ carbonate, 1 mM bicarbonate.



Scheme 1. Kinetic reaction scheme to account for the time evolution of 4CP into NCP in the Rhône delta lagoons.