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PESTICIDE BY-PRODUCTS IN THE RHÔNE DELTA (SOUTHERN FRANCE). THE CASE OF 4-CHLORO-2-METHYLPHENOL AND OF ITS NITRODERIVATIVE

Serge Chiron,^{a,*} Laetitia Comoretto,^a Elisabetta Rinaldi,^b Valter Maurino,^b Claudio Minero,^b Davide Vione^b

^a Laboratoire Chimie Provence, Aix-Marseille Universités-CNRS (UMR 6264), 3 place Victor Hugo, 13331 Marseille cedex 3, France.

^b Dipartimento di Chimica Analitica, Università di Torino, Via Pietro Giuria 5, 10125 Torino, Italy. <http://www.chimicadellambiente.unito.it>

* Corresponding author. Tel. +33 - 4 91 10 85 25 Fax +33 - 4 91 10 63 77
E-mail: serge.chiron@up.univ-mrs.fr

Abstract

A field monitoring campaign for pesticides and their transformation intermediates was carried out in the Rhône delta (Southern France). It was evidenced the following transformation sequence: MCPA → 4-chloro-2-methylphenol (CMP) → 4-chloro-2-methyl-6-nitrophenol (CMNP). Interestingly CMP disappeared about as quickly as MCPA, while CMNP was environmentally more persistent than the parent molecules. This is very relevant to the environmental risk associated with the occurrence of these compounds, because the nitration of chlorophenols reduces their acute toxicity but the nitroderivatives could have more marked long-term effects, associated with their genotoxicity.

Irradiation experiments suggested that the photonitration of CMP into CMNP involves nitrogen dioxide, generated from the photolysis of nitrate and from the photooxidation of nitrite by $\cdot\text{OH}$. The photochemistry of Fe(III) species could also play a significant role, but its contribution is still difficult to be quantified. Another important intermediate of CMP transformation is methylnitrophenol (MNP), produced via a dechlorination/ nitration pathway, with *ortho*-cresol as the most likely reaction intermediate.

Keywords: environmental photochemistry, genotoxic compounds, environmental fate, pesticide derivatives.

Introduction

The consequences of pesticide use on natural ecosystems were one of the first important issues in the field of environmental chemistry. The impact of pesticide molecules on the environment depends on several factors: their toxicity, their bioaccumulative and long-term effects, their transport between different compartments, and their persistence in the environment (Manahan, 2005). Moreover, it has recently been determined that by-products of transformation in the environment can play a significant role in defining the impact of pesticides on both human health and the natural ecosystems (Goncalves et al., 2006; Mitsou et al., 2006; Caceres et al., 2007).

Photochemical reactions in surface waters are important transformation pathways for biorefractory pollutants such as pesticides. Photochemical reactions can result from: direct photolysis (Vialaton and Richard, 2002; Lam and Mabury, 2005), transformation photosensitised by the triplet states of Dissolved Organic Matter (DOM; Canonica et al., 2006; Canonica, 2007), and reaction with radical species photogenerated by irradiation of DOM itself, nitrate, nitrite and Fe(III), sometimes upon interaction with dissolved inorganic anions (Lam et al., 2003; Canonica et al., 2005; Vione et al., 2006; Chiron et al., 2006). These processes can reduce the lifetime of pesticides in surface waters, thus reducing their concentration in aqueous systems. However, these processes can also generate harmful by-products. The latter case is true for instance of the photodegradation of the pesticides carbendazim, acetochlor, simazine, chlorpyrifos, and EPTC (S-ethyl dipropylcarbamothioate) (Virág et al., 2007).

The present paper reports on a field monitoring study of 4-chloro-2-methylphenol (CMP) and its nitroderivative 4-chloro-2-methyl-6-nitrophenol (CMNP) in the Rhône delta. CMP was chosen because it is a degradation by-product of the herbicide (4-chloro-2-methylphenoxy)-acetic acid (MCPA, Reitzel et al., 2004) and of the antimicrobial agent chlorophene (4-chloro-2-(phenylmethyl)phenol, Zhang and Huang, 2003). MCPA is extensively applied in the rice fields of the Rhône delta as a post emergent herbicide, and its transformation by-products contribute to the chlorophenol burden of the delta (Comoretto et al., 2007).

The occurrence of CMNP is interesting because in-vitro studies of the transformation of different pesticides containing aromatic rings in the presence of nitrate and nitrite under irradiation have shown the formation of various nitroderivatives (Nélieu et al., 2004; Shankar et al., 2007; Nélieu et al., 2007). Nitroaromatic compounds are of considerable concern for their genotoxicity (Heng et al., 1996; Chiron et al., 2007b). In addition, their environmental occurrence and the formation in the aromatic photonitration process have recently been shown in a field study (Chiron et al., 2007a). The cited study has shown that 2,4-dichloro-6-nitrophenol can be generated upon nitration of 2,4-dichlorophenol (another by-product of pesticide hydrolysis) by $\cdot\text{NO}_2$ in the water of the paddy fields of the delta. Nitrogen dioxide is formed in surface waters by irradiation of nitrate and nitrite (Mack and Bolton, 1999; Minero et al., 2007). A significant contribution of wet deposition to the levels of the two compounds in the delta waters could also be excluded. Also in the present work it was checked the concentration of CMP and CMNP in rainwater, and the photonitration pathway of

CMP into CMNP was studied to get further insight into the environmental process. Other phototransformation intermediates of CMP were also identified under laboratory conditions, which could direct the choice of further compounds to be monitored in the delta.

Experimental

Reagents and materials. 4-Chloro-2-methylphenol (CMP, purity grade >95%) was purchased from Fluka, 2-methylphenol (MP, 97%), 4-nitro-2-methylphenol (MNP, 98%), HClO₄ (70%), and NaNO₃ (>99%) from Aldrich, H₃PO₄ (85%), HNO₃ (65%), 2-propanol (LiChrosolv gradient grade) and acetonitrile (LiChrosolv gradient grade) from VWR Int., NaNO₂ (97%) from Carlo Erba. Hematite (α -Fe₂O₃) was synthesised following the procedure of Leland and Bard (1987).

Study area and sampling. The schematic representation of the sampling area is illustrated in Fig. A (Supplementary Material). The Rhône river delta and its lagoon system are located in the southern part of France. The lagoon system (422 km²) can be divided into two sub-systems: the Vaccarès lagoon and the lower lagoons (Etang du Lion (EL) and Etang de l'Impérial (EI)), which are directly connected to the sea. The Rhône delta is devoted to intensive flooded rice cultivation. In the northern section of the delta (310 km²), irrigation water is pumped from the Rhône river and drainage water is returned to the river through a main ditch in Albaron (sampling point D1). The eastern section (87 km²) of the delta naturally drains into the Vaccarès lagoon by a low-slope ditch (sampling point D2). The concentrations of 4-chloro-2-methylphenol (CMP) and of the nitroderivative 4-chloro-2-methyl-6-nitrophenol (CMNP) were also measured in the lagoon system (sampling points L1 and L2) and in the river waters at the entrance of the delta (sampling point S1), during the spring-summer season 2005. Samples were collected with a stainless steel sampling bottle. At each site, a composite water sample was collected from approximately 4 to 5 vertical profiles (water column depth ranged from 10 cm to 1 m). Composite samples were joined together and filtered through 0.45 µm filters (cellulose acetate, Millipore), and subsequently split into pre-cleaned 500 mL glass bottles, prepared in duplicate and stored at 4°C until analysis. Duplicate samples were used for backup purposes in case of breakage of the primary sample, and for laboratory replicates. Two precipitation sampling stations were operated in the Rhône river delta. One station (R1) was located in the northern part of the delta while the second (R2) in the eastern part. Both stations were surrounded by paddy fields and close to a meteorological station. The rain collectors consisted of a 0.78 m² glass funnel coated with a Teflon foil, connected to a 2.5 L glass bottle. The funnel was manually uncovered and rinsed with deionised water and methanol just before each major rain event started. The bottles had been previously heated to 450°C for 8 h. Three major rain events were sampled from April to September 2005 (April 19th, May 20th and June 21st). Rain samples were refrigerated and filtered through 0.45 µm cellulose acetate filters immediately after collection, to avoid biodegradation processes (Schüssler and Nitschke, 2001).

Analytical procedures.

Sample pH was adjusted to a value of 5, and 500 mL samples were preconcentrated with solid phase extraction (SPE) on Oasis HLB 500 mg cartridges (Waters). The analytes were eluted with 2 × 5 mL methanol. The extract was evaporated to dryness and then redissolved in 200 µL of a water/methanol mixture (50:50 v/v). The analysis of the extract was performed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS), using an atmospheric pressure chemical ionisation (APCI) interface in negative ionisation mode as recommended for chloro- and nitrophenols (Puig et al., 1997). The most abundant product ion in MS² mode was chosen for LC-MS/MS analysis. The MS² spectrum of CMNP using the [M-H]⁻ ion at m/z 186 as precursor ion revealed a fragment ion at m/z 156 ([M-H-NO]⁻) as base peak. The MS² spectrum of CMP showed a minor fragment at m/z 35 that corresponds to the chloride ion. This transition was not very selective and its low efficiency resulted in poor sensitivity. Consequently, the ion at m/z 141 was selected as precursor and product ion in order to obtain cleaner chromatograms than in single ion monitoring (SIM) mode. The HPLC system consisted of a LiChrospher RP-18 column 250 mm × 4.6 mm i.d., 5 µm particle size. The mobile phase used in chromatographic separation consisted of a binary mixture of solvents A (methanol) and B (water) at a flow rate of 0.8 mL min⁻¹. The gradient was operated from 40 to 100 % A for 30 min and then back to the initial conditions in 5 min. The mass spectrometer was operated in multiple reaction monitoring (MRM) mode with unit mass resolution. The selected transition ions were 141>141, 186>156 and 222>164 for CMP, CMNP and 2,4-D d₃, respectively. 2,4-D d₃ was added as isotope labelled internal standard. A typical MRM chromatogram obtained after preconcentration of 500 mL of surface water is shown in Fig. B (Supplementary Material). Identification of the target analytes in unknown samples was based on the LC retention time and the unique combination of a precursor-product ion. Due to the lack of CMNP analytical standard, 2,4-dichloro-6-nitrophenol and 4-nitro-2-methylphenol were used for bracketing recovery value and limits of quantification (LOQs). The percent recovery was 78±8 % and 88–96±6 % for CMP and CMNP, respectively. Limits of quantification (LOQs) were 15 and 1–3 ng L⁻¹, respectively. Quantification was carried out by means of an isotope labelled internal standard (2,4-D d₃) procedure, because this is the only effective way to overcome the matrix ion suppression effects in LC-MS/MS (Freitas et al., 2004). Calibration curves were constructed by plotting the ratio peak area/internal standard peak area against concentration levels. This ratio remained constant whether the matrix was present or not.

Irradiation Experiments. A first set of experiments was aimed at identifying the transformation intermediates of CMP, with a particular focus on CMNP. Irradiation was carried out with a 0.5 L cylindrical immersion-type photoreactor (Heraeus TQ 150 Model, radiation path length 2 cm), equipped with a water-cooled, medium-pressure mercury lamp with maximum emission wavelengths at 313, 366, 406, 436, 546, and 578 nm (see Figure C in Supplementary Material). The reactor is made of Pyrex glass in order to cut off the wavelengths shorter than 290 nm. The whole

assembly was mounted on a magnetic stirrer and wrapped with aluminium foil. Initial pH was adjusted by dropwise addition of either 0.1 M NaOH or 0.1 M H₂SO₄. Aliquots of 1 mL were analysed at selected intervals after a filtration step through 0.45 µm filter membranes (cellulose acetate, Millipore). By-product identification was carried out by HPLC-MS² using an electrospray interface in negative ionisation mode. The HPLC system consisted of a Metachem C-18 column 150 × 2 mm i.d., 3 µm particle size (Varian), and an Esquire 6000 ion trap mass spectrometer (Bruker, Bremen, Germany). The mobile phase used in chromatographic separation consisted of a binary mixture of solvents A (methanol) and B (0.07 % formic acid solution) at a flow rate of 0.2 mL min⁻¹. The gradient was operated from 5 to 100 % A for 30 min and than back to the initial conditions in 5 min. The retention time of CMP and its intermediates under the adopted conditions and the precursor ions and fragments used for identification are reported in Table I (Supplementary Material).

Another set of experiments had the goal of elucidating the transformation pathway of CMP into MNP. Irradiation was carried out under a Philips TL 01 UV-Vis lamp, with emission maximum at 313 nm and 2.7 W m⁻² UV irradiance (the lamp spectrum is reported in Figure D, Supplementary Material). The solutions were placed into cylindrical Pyrex glass cells (4.0 cm diameter, 2.3 cm height), and magnetically stirred during irradiation. Total solution volume in the cells was 5 mL, and the total photon flux was 1.8×10⁻⁶ einstein L⁻¹ s⁻¹. After irradiation the samples were analysed with a VWR Hitachi HPLC coupled with a Diode Array Detector (DAD), equipped with L-2200 autosampler, L-2130 pump for low-pressure gradients, L-2300 column oven, L-2455 DAD detector, and a column Merck HiBar 250-4 (250 mm length by 4 mm diameter), packed with LiChrospher 100 CH-18/2 (particle diameter 10 µm). Elution was carried out with a 50:50 mixture of acetonitrile and aqueous H₃PO₄ (pH 3), at a flow rate of 1.0 mL min⁻¹. Injection volume was 60 µL, column dead time 1.7 min, and the DAD signal was acquired between 250 and 350 nm. The retention times and the quantification wavelengths were as follows (min; nm): 4-chloro-2-methylphenol (6.60; 282), 2-methyl-4-nitrophenol (4.75; 325), 2-methylphenol (4.55; 273).

Water used was of Milli-Q quality, the pH of the solutions was measured with a combined glass electrode connected to a Metrohm 713 pH meter.

Results and Discussion

Field data. Table 1 summarises the results (in µg L⁻¹) from rainwater and surface water samples analysed for CMP and CMNP from April to September 2005. The amount of precipitation is also presented. In the Rhône river delta, CMP mainly originated from the degradation of (4-chloro-2-methylphenoxy)-acetic acid (MCPA), a post emergent herbicide heavily used for rice farming (6000 kg; Comoretto et al., 2007). The detected MCPA levels, determined as described in Comoretto et al. (2007), are also reported in Table 1. MCPA was applied between mid-May and mid-June. Additionally, CMP can make up more than 7 % of the commercial herbicide (Reitzel et al., 2004).

This impurity was probably another source of CMP. CMP was primarily detected right after the main application period and, for instance, it peaked at a level of $1.12 \mu\text{g L}^{-1}$ on June 21st at the outlet of a major ditch (D1), which drained the paddy fields into the river. Generally, there was a certain trend in dilution into the lagoons with a maximum concentration value of CMP recorded at $0.18 \mu\text{g L}^{-1}$ on June 21st. These relatively high concentration values fell rapidly below the LODs of the analytical method in late September in the lagoon. The time trend of CMP and CMNP in sampling site D1 is reported in Fig. 1 (molar concentration values). Simultaneously to the decrease of CMP there was a steady increase of the concentration of CMNP. Peak concentrations of CMNP were observed with a delay of two weeks after the peak concentrations of CMP. The CMNP/CMP ratio changed markedly from 0.25 on June 21st to 1.9 on July 5th, suggesting a likely transformation of CMP into CMNP.

In an attempt to assess the possible contribution of precipitation to the surface water levels of CMP and CMNP, measurements of these compounds were also carried out in rain samples collected during the 3 major rain events occurred through the sampling period. The analytical data of the rainwater sampling stations R1 and R2, reported in Table 1, indicate that the rain events might prompt a very limited load of CMP and CMNP into surface waters.

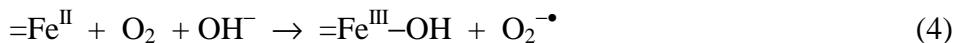
Moreover, CMP and CMNP were not found at the entrance of the Rhône delta and it was concluded that these compounds were not transported by the Rhône water dissolved phase. An additional pathway for the occurrence of CMNP could be the volatilization of the more volatile CMP, followed by gas-phase nitration into CMNP (Harrison et al., 2005), and final dry deposition of the nitroderivative back into the water phase. In this case however, given the very fast atmospheric diffusion rates, it would be difficult to account for the very variable space distribution of CMNP across the delta water. Finally, the results reported in Fig. .1 show that CMNP is environmentally more persistent than CMP.

Field data would suggest a transformation process of CMP into CMNP in the flooded fields or in the ditches/lagoons. Given the season when the CMNP build-up was observed, reasonable tentative hypotheses might be photonitration in surface water (Dzengel et al., 1999; Vione et al., 2002) or a corresponding microbiological process (Telscher et al., 2005), although very little is known on the latter issue at the moment. In a previous work, evidence has been found for photochemistry to be involved in the nitration of 2,4-dichlorophenol to 2,4-dichloro-6-nitrophenol (Chiron et al., 2007a). The following sections are an attempt to verify if the photochemical pathway is able to account for the field data also in the case of CMP and CMNP.

Irradiation experiments and by-product identification. Laboratory irradiation of CMP was carried out in the presence of photochemically active compounds (nitrate, hematite + nitrite), and the identification of the degradation intermediates was performed by LC-MS/MS. The goals of the irradiation experiments were: (*i*) identification of the conditions that can lead to the formation of CMNP from CMP, and most notably the assessment of the role of $\bullet\text{NO}_2$. Indeed, nitrogen dioxide is expected to play a major role in photonitration in aqueous solution (Mack and Bolton, 1999;

Dzengel et al., 1999; Vione et al., 2002); (*ii*) identification of other important phototransformation intermediates of CMP, which could be included in future monitoring campaigns of pesticides and their by-products in the Rhône delta.

The results of the irradiation experiments are reported in Scheme 1. The irradiation of CMP and nitrate around neutral pH mainly resulted into the substitution of the Cl atom with a nitroso or a nitro group. The nitroso and nitro derivatives were identified thanks to neutral losses of NO (30 amu) which can be used to characterize the nitro functional group (Williams and Perrault, 2000). The formation of CMNP from CMP was observed in the presence of hematite and nitrite under irradiation. These conditions are significant from both a mechanistic and an environmental point of view. As far as the reaction pathways are concerned, the system containing hematite and nitrite under irradiation is one of the most straightforward ways to produce the nitrating agent nitrogen dioxide (Chiron et al., 2007a). The irradiation of hematite in the visible promotes electrons from the valence to the conduction band, leaving holes in the valence band (Faust et al., 1989). The radical $\cdot\text{NO}_2$ would be produced upon reaction between nitrite and the valence-band holes of hematite. The processes that are most likely involved are the following (Key et al., 2008):



The formation of CMNP from CMP in the presence of $\cdot\text{NO}_2$ is interesting given the field data that suggest that the transformation is environmentally significant. Moreover, previous work has shown that the paddy fields in the Rhône delta are a favourable environment for photonitration processes, which are enhanced by both the chemical composition of water and its reduced depth (10 cm on average). The oxidation of nitrite by the $\cdot\text{OH}$ radical is a major source of $\cdot\text{NO}_2$ in the paddy fields under study, while the role of Fe(III) (hydr)oxides toward nitrite oxidation is more uncertain (Chiron et al., 2007a). The main issue is constituted by the speciation of Fe(III) in surface waters, which includes a large fraction of Fe complexes with organic matter in addition to the (hydr)oxide colloids (Borer et al., 2005). However, if the reactivity of hematite toward nitrite oxidation were comparable to the average one of the Fe(III) species, the role of Fe in the process could be similar or even higher than that of $\cdot\text{OH}$ (Chiron et al., 2007a). Moreover, the irradiation of CMP + nitrite alone yielded a significant amount of CMNP, together with the intermediates deriving from dechlorination/nitrosation and dechlorination/nitration (**I** and **II** in Scheme 1).

It is interesting to note that with hematite + nitrite under irradiation, 2-methyl-4-nitrophenol (4-nitro-*ortho*-cresol or MNP hereafter) was also formed from CMP. MNP was identified by comparing its retention time and its MS² spectrum with those of an authentic standard. This finding suggests that the dechlorination/nitration pathway involves $\cdot\text{NO}_2$ at some level.

From Scheme 1 it is apparent that MNP is formed under all the studied conditions. It can therefore be hypothesised that MNP could be a major intermediate of the transformation of CMP in the environment. MNP was not included in the field monitoring campaign, but the present results prompt for its consideration in future campaigns about the assessment of the risk from pesticides and their by-products in the water of the Rhône delta. Indeed, despite the lack of data on the health effects of MNP a similar compound, the herbicide dinitro-o-cresol (DNOC) is hepatotoxic in rats (Dere et al., 2007), and induces cell apoptosis in plants (Aranha et al., 2007).

Further irradiation experiments were dedicated to the elucidation of the transformation pathway of CMP into MNP (see the Supplementary Material). It could be concluded that the reaction takes place in two steps. The first step is the dechlorination of CMP into *ortho*-cresol, possibly initiated by HO₂[•], the second step is cresol nitration into MNP by •NO₂ (see Scheme 1).

Conclusions

As expected, MCPA was readily transformed into CMP after application in the paddy field water. More interestingly, CMP disappeared about as quickly as MCPA. The time trend of CMP and CMNP suggests that the latter would be an important transformation intermediate of CMP. The data also show that CMNP is environmentally more persistent than the parent molecule. This finding is very relevant to the environmental risk associated with the occurrence of these compounds. Available data suggest that the nitration of chlorophenols reduces their acute toxicity (Koegerkoepke et al., 1992; Chen et al., 2004), but the nitroderivatives could have more marked long-term effects associated with their genotoxicity (Heng et al., 1996; Chiron et al., 2007b).

The irradiation experiments suggested that the photonitration of CMP into CMNP involves nitrogen dioxide. Note that •NO₂ is also likely involved in the photonitration of 2,4-dichlorophenol to 2,4-dichloro-6-nitrophenol in the paddy fields of the delta (Chiron et al., 2007a).

Another important intermediate of CMP transformation is MNP, produced via a dechlorination/nitration pathway. The intermediate formation of *ortho*-cresol plays a significant role in the generation of MNP, which would most likely derive from the nitration of cresol by •NO₂.

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References

- Aranha, M. M., Matosa, A. R., Mendes, A. T., Pinto, V. V., Rodrigues, C. M. P., Arrabaca, J. D., 2007. Dinitro-o-cresol induces apoptosis-like cell death but not alternative oxidase expression in soybean cells. *J. Plant Physiol.* 164, 675-684.
- Borer, P. M., Sulzberger, B., Reichard, P., Kraemer, S. M., 2005. Effect of siderophores on the light-induced dissolution of colloidal iron(III) (hydr)oxides. *Mar. Chem.* 93, 179-193.
- Bouillon, R. C., Miller, W. L., 2005. Photodegradation of dimethyl sulfide (DMS) in natural waters: Laboratory assessment of the nitrate-photolysis-induced DMS oxidation. *Environ. Sci. Technol.* 39, 9471-9477.
- Bucheli, T., Müller, S., Heberle, S., Schwarzenbach, R., 1998. Occurrence and behavior of pesticides in rainwater, roof runoff and artificial stormwater infiltration. *Environ. Sci. Technol.* 32, 3457-3464.
- Caceres, T., Megharaj, M., Naidu, R., 2007. Toxicity of fenamiphos and its metabolites to the cladoceran *Daphnia carinata*: The influence of microbial degradation in natural waters. *Chemosphere* 66, 1264-1269.
- Canonica, S., Kohn, T., Mac, M., Real, F. J., Wirz, J., Von Gunten, U., 2005. Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds. *Environ. Sci. Technol.* 39, 9182-9188.
- Canonica, S., Hellrung, B., Müller, P., Wirz, J., 2006. Aqueous oxidation of phenylurea herbicides by triplet aromatic ketones. *Environ. Sci. Technol.* 40, 6636-6641.
- Canonica, S., 2007. Oxidation of aquatic organic contaminants induced by excited triplet states. *Chimia* 61, 641-644.
- Chen, J., Jiang, J., Zhang, F., Yu, H., Zhang, J., 2004. Cytotoxic effects of environmentally relevant chlorophenols on L929 cells and their mechanisms. *Cell Biol. Toxicol.* 20, 183-196.
- Chiron, S., Minero, C., Vione, D., 2006. Photodegradation processes of the anti-epileptic drug carbamazepine, relevant to estuarine waters. *Environ. Sci. Technol.* 40, 5977-5983.
- Chiron, S., Minero, C., Vione, D., 2007a. Occurrence of 2,4-dichlorophenol and of 2,4-dichloro-6-nitrophenol in the Rhône river delta (Southern France). *Environ. Sci. Technol.* 41, 3127-3133.
- Chiron, S., Barbat, S., De Méo, M., Botta, A., 2007b. In vitro synthesis of 1,N6-etheno-2'-deoxyadenosine and 1,N2-etheno-2'-deoxyguanosine by 2,4-dinitrophenol and 1,3-dinitropyrene in the presence of a bacterial nitroreductase. *Environ. Toxicol.* 22, 222-227.
- Comoretto, L., Arfib, B., Chiron, S., 2007. Pesticides in the Rhône river delta (France): Basic data for a field-based exposure assessment. *Sci. Total Environ.* 380, 124-132.
- Dere, E., Ferda, O., Tosonoglu, H., 2007. Hepatotoxicity of dinitro-o-cresol in rats (*Rattus norvegicus*). *Acta Vet.-Beogr.* 57, 497-507.
- Dzengel, J., Theurich, J., Bahnemann, D. W., 1999. Formation of nitroaromatic compounds in advanced oxidation processes: Photolysis versus photocatalysis. *Environ. Sci. Technol.* 33, 294-300.

- Faust, B. C., Hoffmann, M. R., Bahnemann, D. W., 1989. Photocatalytic oxidation of sulfur dioxide in aqueous suspensions of α -Fe₂O₃. *J. Phys. Chem.* 93, 6371-6381.
- Freitas, L., Götz, C., Ruff, M., Singer, H., Müller, S., 2004. Quantification of the new triketone herbicides, sulcotrione and mesotrione, and other important herbicides and metabolites, at ng/L level in surface waters using liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A* 1028, 277-286.
- Goncalves, C., Dimou, A., Sakkas, V., Alpendurada, M. F., Albanis, T. A., 2006. Photolytic degradation of quinalphos in natural waters and on soil matrices under simulated solar irradiation. *Chemosphere* 64, 1375-1382.
- Harrison, M. A. J., Barra, S., Borghesi, D., Vione, D., Arsene, C., Olariu, R. I., 2005. Nitrated phenols in the atmosphere: A review. *Atmos. Environ.* 39, 231-238.
- Heng, Z. C., Ong, T., Nath, J., 1996. In vitro studies of the genotoxicity of 2,4-dichloro-6-nitrophenol ammonium (DNCPA) and its major metabolite. *Mutat. Res.* 368, 149-155.
- Key, J. M., Paulk, N., Johansen, A. M., 2008. Photochemistry if iron in simulated crustal aerosols with dimethyl sulfide oxidation products. *Environ. Sci. Technol.* 42, 133-139.
- Kroegerkoepke, M. B., Koepke, S. R., Hernandez, L., Michejda, C. J., 1992. Activation of a beta-hydroxyalkylnitrosamine to alkylating agents – Evidence for the involvement of a sulfotransferase. *Cancer Res.* 52, 3300-3305.
- Lam, M. W., Tantuco, K., Mabury, S. A., 2003. PhotoFate: A new approach in accounting for the contribution of indirect photolysis of pesticides and pharmaceuticals in surface waters. *Environ. Sci. Technol.* 37, 899-907.
- Lam, M. W., Mabury, S. A., 2005. Photodegradation of the pharmaceuticals atorvastatin, carbamazepine, levofloxacin, and sulfamethoxazole in natural waters. *Aquat. Sci.* 67, 177-188.
- Leland, J. K., Bard, A. J., 1987. Photochemistry of colloidal semiconducting iron oxide polymorphs. *J. Phys. Chem.* 91, 5076-5083.
- Mack, J., Bolton, J. R., 1999. Photochemistry of nitrite and nitrate in aqueous solution: A review. *J. Photochem. Photobiol. A: Chem.* 128, 1-13.
- Manahan, S. E., 2005. Environmental Chemistry, 8th Edition. CRC Press, Boca Raton, FL.
- Minero, C., Chiron, S., Falletti, G., Maurino, V., Pelizzetti, E., Ajassa, R., Carlotti, M. E., Vione, D., 2007. Photochemical processes involving nitrite in surface water samples. *Aquat. Sci.* 69, 71-85.
- Mitsou, K., Koulianou, A., Lambropoulou, D., Pappas, P., Albanis, T., Lekka, M., 2006. Growth rate effects, responses of antioxidant enzymes and metabolic fate of the herbicide Propanil in the aquatic plant Lemna minor. *Chemosphere* 62, 275-284.
- Nélieu, S., Kerhoas, L., Sarakha, M., Einhorn, J., 2004. Nitrite and nitrate induced photodegradation of monolinuron in aqueous solution. *Environ. Chem. Lett.* 2, 83-87.

- Nélieu, S., Shankar, M. V., Kerhoas, L., Einhorn, J., 2007. Phototransformation of monuron induced by nitrate and nitrite ions in water: Contribution of photonitration. *J. Photochem. Photobiol. A: Chem.* 193, 1-9.
- Puig, D., Silgoner, I., Grasserbauer, M., Barcelo, D., 1997. Part-per-trillion level determination of priority methyl-, nitro- and chlorophenols in river water samples by automated on-line liquid/solid extraction followed by liquid chromatography/mass spectrometry using atmospheric pressure chemical ionization and ion spray interfaces. *Anal. Chem.* 69, 2756-2761.
- Reitzel, L., Tuxen, N., Ledin, A., Bjerg, P. 2004. Can degradation products be used as documentation for attenuation of phenoxy acids in groundwater? *Eviron. Sci. Technol.* 38, 457-467.
- Schüssler, W., Nitschke, L., 2001. Nitrophenols in precipitation. *Chemosphere* 42, 277-283.
- Shankar, M. V., Nélieu, S., Kerhoas, L., Einhorn, J., 2007. Photo-induced degradation of diuron in aqueous solution by nitrites and nitrates: Kinetics and pathways. *Chemosphere* 66, 767-774.
- Telsher, M. J. H., Schuller, U., Schmidt, B., Schäffer, A., 2005. Occurrence of a nitro metabolite of a defined nonylphenol isomer in soil/sewage sludge mixtures. *Environ. Sci. Technol.* 39, 7896-7900.
- Vialaton, D., Richard, C., 2002. Phototransformation of aromatic pollutants in solar light: Photolysis versus photosensitized reactions under natural water conditions. *Aquat. Sci.* 64, 207-215.
- Vione, D., Maurino, V., Minero, C., Pelizzetti, E., 2002. Phenol photonitration. *Ann. Chim. (Rome)* 92, 919-929.
- Vione, D., Falletti, G., Maurino, V., Minero, C., Pelizzetti, E., Malandrino, M., Ajassa, R., Olariu, R. I., Arsene, C., 2006. Sources and sinks of hydroxyl radicals upon irradiation of natural water samples. *Environ. Sci. Technol.* 40, 3775-3781.
- Vione, D., Minero, C., Housari, F., Chiron, S., 2007. Photoinduced transformation processes of 2,4-dichlorophenol and 2,6-dichlorophenol on nitrate irradiation. *Chemosphere* 69, 1548-1554.
- Virág, D., Naar, Z., Kiss, A. Microbial toxicity of pesticide derivatives produced with UV photodegradation. *Bull. Environ. Contam. Toxicol.* 79, 356-359.
- Williams, T., Perrault, H., 2000. Selective detection of nitrated polycyclic aromatic hydrocarbons by electrospray ionization mass spectrometry and constant neutral loss scanning. *Rapid Commun. Mass Spectrom.* 14, 1474-1481.

Table 1. Analytical data of MCPA, CMP and CMNP in the different sampling sites and dates. D1, D2: ditches, L1, L2: lagoons, R1, R2: rainwater sampling stations; S1: sampling station at the inlet of the delta. For the location of each sampling site see Figure A (Supplementary Material).

Compound	Sampling date	D1	D2	L1	L2	R1	R2	S1	Precipitation amount (mm)
MCPA ($\mu\text{g.L}^{-1}$)	19Apr05	n.d	n.d	n.d	n.d	n.d	n.d	n.d	69.1
	20May05	0.08	n.d	n.d	n.d	n.d	n.d	n.d	97.2
	21Jun05	4.24	1.54	0.24	0.14	n.d	n.d	n.d	13.9
	5Jul05	0.54	0.21	0.08	0.12	n.d	n.d	n.d	0
	18Jul05	n.d	0.03	n.d	n.d	n.d	n.d	n.d	0
	24Aug05	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0
	22Sep05	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0
CMP ($\mu\text{g.L}^{-1}$)	19Apr05	n.d	n.d	0.02	0.025	0.09	0.12	n.d	69.1
	20May05	0.04	0.03	n.d	n.d.	0.05	0.04	n.d	97.2
	21Jun05	1.12	0.92	0.12	0.18	0.02	0.02	n.d	13.9
	5Jul05	0.24	0.15	0.05	0.06	n.d	n.d	n.d	0
	18Jul05	0.03	0.04	n.d	n.d	n.d	n.d	n.d	0
	24Aug05	0.02	n.d	n.d	n.d	n.d	n.d	n.d	0
	22Sep05	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0
CMNP ($\mu\text{g.L}^{-1}$)	19Apr05	n.d	n.d	n.d	n.d	0.045	0.035	n.d	69.1
	20May05	n.d	0.03	n.d	n.d	0.14	n.d	n.d	97.2
	21Jun05	0.28	0.16	0.055	0.14	0.03	0.04	n.d	13.9
	5Jul05	0.45	0.36	0.28	0.34	n.d	n.d	n.d	0
	18Jul05	0.24	0.15	0.13	0.17	n.d	n.d	n.d	0
	24Aug05	0.085	0.043	0.05	0.08	n.d	n.d	n.d	0
	22Sep05	0.040	n.d	n.d	n.d	n.d	n.d	n.d	0

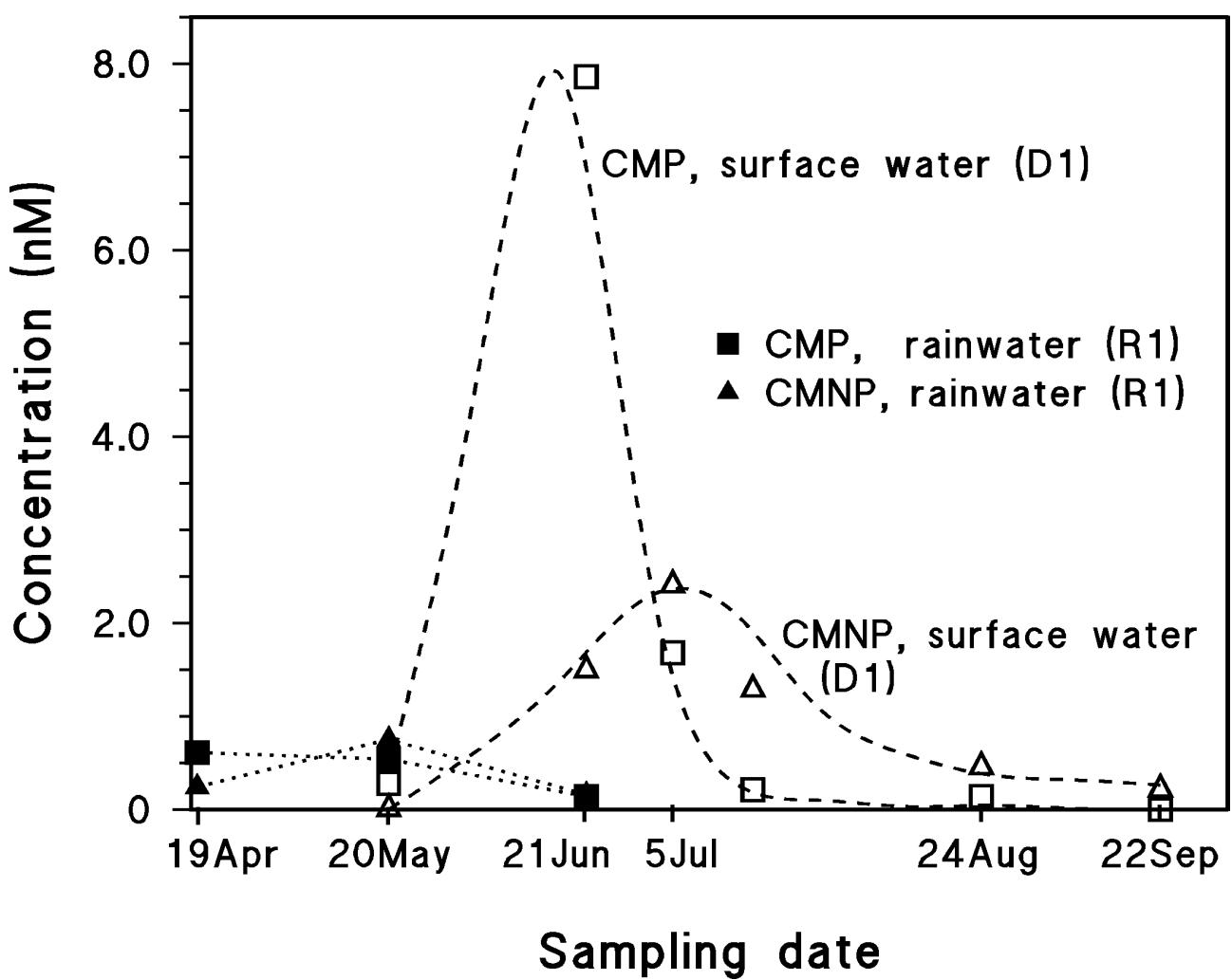
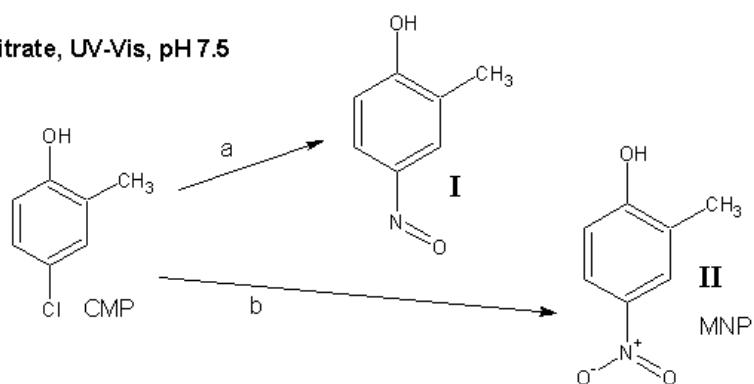
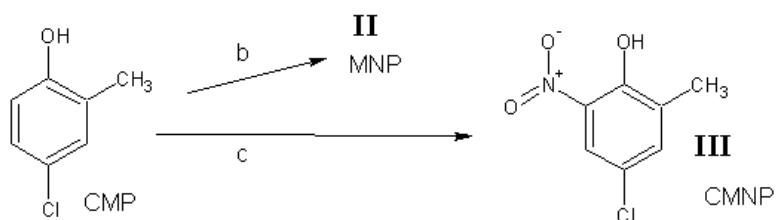


Figure 1. Time trends of CMP and CMNP in sampling sites D1 and R1 (see Figure A in the Supplementary Material for the sites location). The X-axis reports the sampling dates. In the case of surface water a similar time trend was also observed in the other sampling sites of the Rhône Delta (D2, L1, L2, see Table 1).

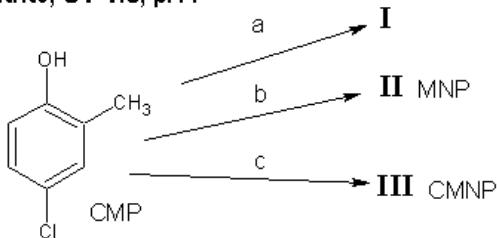
Nitrate, UV-Vis, pH 7.5



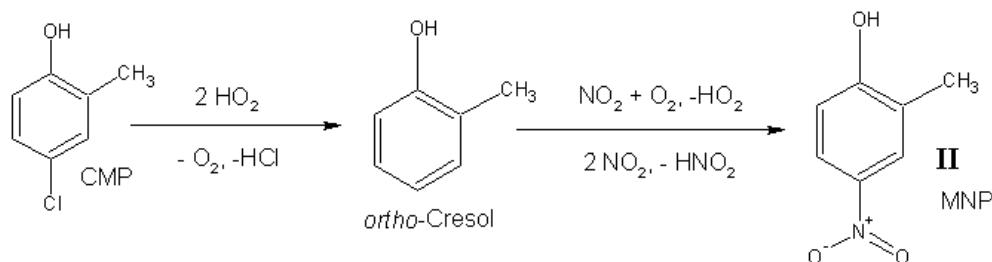
Hematite + nitrite, UV-Vis, pH 7



Nitrite, UV-Vis, pH 7



Transformation of CMP into MNP (pathway b)



Scheme 1. Pathways of CMP transformation under the different adopted conditions. Irradiation was carried out in the immersion-type photoreactor. For the lamp spectrum see Figure C in the Supplementary Material. The pathways are identified by letters: a = dechlorination/nitrosation; b = dechlorination/ nitration; c = nitration. For the elucidation of pathway b see the Supplementary Material.