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Corresponding Author: Dr. Monica Cristina Gonzalez, PhD.

Corresponding Author's Institution: INIFTA; University of La Plata

First Author: Monica Cristina Gonzalez, PhD.

Order of Authors: Monica Cristina Gonzalez, PhD.

Abstract: The reaction of phosphor-containing pesticides such as methidathion (MT) and dimethoate (DM) with dichloride radical anions (Cl₂^{•-}) was investigated. The second order rate constants (1.3 ± 0.4) $\times 10^8$ and (1.1 ± 0.4) $\times 10^8$ M⁻¹ s⁻¹, were determined for the reaction of Cl₂^{•-} with MT and DM, respectively. A reaction mechanism involving an initial charge transfer from the sulfide groups of the insecticides to Cl₂^{•-} is proposed and supported by the identified transient intermediates and stable reaction products. The formation of chlorinated by-products was determined. The unexpected consequences of an efficient Cl₂^{•-} reactivity towards MT and DM on the degradation capacity by Advanced Oxidation Procedures applied to polluted waters containing the insecticides and Cl⁻ anions is discussed.

Suggested Reviewers: Alessandra Bianco Prevot PhD
Professor, Chemistry, University of Torino
alessandra.biancoprevot@unito.it

Galo Carrillo Le Roux PhD
Professor, Department of Chemical Engineering, University of Sao Paulo, Brazil
galoroux@usp.br

Norman A Garcia PhD
Professor, Chemistry Department, Faculty of Science, University of Rio Cuarto, Argentina
ngarcia@exa.unrc.edu.ar

Sixto Malato Rodriguez PhD
Professor, Plataforma Solar de Almeria, SPAIN
Sixto.malato@psa.es

Dear Editor,

Please find enclosed the manuscript entitled: “**Chloride anion effect on the advanced oxidation processes of methidathion and dimethoate: role of $\text{Cl}_2^{\cdot-}$ radical**” by Paula Caregnato, Janina A. Rosso, Juan M. Soler, Antonio Arques, Daniel O. Mártire, and Mónica C. Gonzalez. The manuscript describes the reaction kinetics and mechanisms of phosphorated insecticides and $\text{Cl}_2^{\cdot-}$ radicals and their implication in the AOP treatment of contaminated waters.

The total length of the manuscript is 7000 words (including figure captions, Tables and references).

The authors do not have conflict of interest and all of them have actively collaborated in the experiments and discussion of the results.

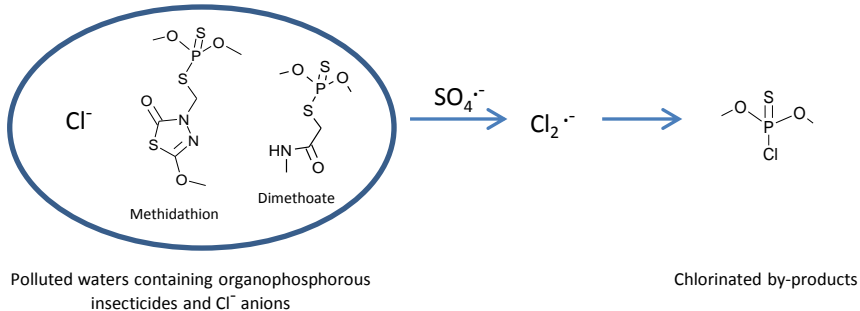
Hopping that the manuscript is suitable for its publication in Water Research,
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Highlights

- Cl atoms and $\text{Cl}_2^{\bullet-}$ radicals efficiently react with methidathion and dimethoate.
- Undesirable toxic chlorinated by-products are formed upon de degradation of methidathion and dimethoate in the presence of chloride anions.
- The presence of chloride anions severely affect AOPs pollutant degradation.

Graphical Abstract (for review)

The effect of chloride anions on AOPs pollutant degradation



1 **Chloride anion effect on the advanced oxidation processes of methidathion and**
2 **dimethoate: role of $\text{Cl}_2^{\bullet-}$ radical**

3
4 Paula Caregnato^a, Janina A. Rosso^a, Juan M. Soler^b, Antonio Arques^b, Daniel O.
5 Mártire^a, and Mónica C. Gonzalez. ^{a*}

6 ^a Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad
7 de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo 16, Sucursal
8 4, (1900) La Plata, Argentina. E-mail: gonzalez@inifta.unlp.edu.ar.

9 ^b Grupo de Procesos de Oxidación Avanzada, Departamento de Ingeniería Textil y
10 Papelera, Universidad Politécnica de Valencia, Campus de Alcoy, Plaza Ferrandiz y
11 Carbonell s/n, 03801 Alcoy, Spain

12 *Corresponding author. Tel.: (+54) 221-425-7430; fax: (+54) 221-425-4642.

13 E-mail address: gonzalez@inifta.unlp.edu.ar (M.C. Gonzalez)

14

15 **Abstract**

16 The reaction of phosphor-containing pesticides such as methidathion (MT) and
17 dimethoate (DM) with dichloride radical anions ($\text{Cl}_2^{\bullet-}$) was investigated. The second
18 order rate constants $(1.3 \pm 0.4) \times 10^8$ and $(1.1 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, were determined for the
19 reaction of $\text{Cl}_2^{\bullet-}$ with MT and DM, respectively. A reaction mechanism involving an
20 initial charge transfer from the sulfide groups of the insecticides to $\text{Cl}_2^{\bullet-}$ is proposed and
21 supported by the identified transient intermediates and stable reaction products. The
22 formation of chlorinated by-products was determined. The unexpected consequences of
23 an efficient $\text{Cl}_2^{\bullet-}$ reactivity towards MT and DM on the degradation capacity by
24 Advanced Oxidation Procedures applied to polluted waters containing the insecticides
25 and Cl^- anions is discussed.

26

27 **Keywords**

28 Organophosphorous pesticides; degradation; chloride anion; flash-photolysis,
29 chlorinated byproducts.

30

31

32

33 1. Introduction

34 Advanced Oxidation Processes (AOPs) are reported to be a promising alternative to
35 remediate effluents which cannot be treated by conventional biological treatments. Most
36 AOPs involve the *in situ* generation of highly reactive species such as hydroxyl and
37 sulfate radicals, which are able to oxidize a wide range of chemicals. Titanium dioxide
38 heterogeneous photocatalysis and the photo-Fenton process are among the most widely
39 employed AOPs capable of removing toxic pollutants, such as pesticides. However, the
40 presence of phosphates, carbonates, chlorides and surfactants in the water matrix has a
41 remarkable influence on the process as they may decrease their efficiency (Soler et al.,
42 2009) (Laat et al., 2006) (Machulek et al., 2007) (Mora et al., 2009) (Dell'Arciprete et
43 al., 2012) (Tsuneda et al., 2002).

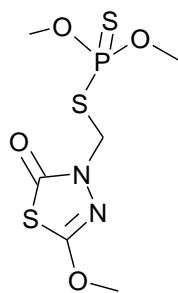
44 The presence of chloride anions in groundwater and surface water in rural and urban
45 areas is widespread. The input of NaCl from seawater intrusion along coastal areas,
46 animal and human waste in rural areas, leaking landfills and natural saline seeps in other
47 areas has created progressively worsening problems with water quality (Panno et al.,
48 2002). Therefore, the effect of Cl⁻ on AOPs pollutant degradation is an important factor
49 to account for, since Cl⁻ efficiently scavenges HO• and SO₄•⁻ radicals (Ross et al.,
50 1998) and is able to form Fe³⁺ complexes in photo-Fenton processes (Machulek et al.,
51 2007). Both effects lead to the formation of chlorine-containing radicals, namely Cl₂•⁻ /
52 Cl• (Machulek et al., 2007) (Liu et al., 2010) and a concomitant reduction in the active
53 oxidant yield. However, organic compounds can also react with Cl atoms and Cl₂•⁻
54 radicals; hence, the presence of these radicals in the reaction media might produce
55 changes in the photo-oxidative pathways and formation of undesirable toxic chlorinated

56 by-products (Liu et al., 2010). In fact, reported computer simulations (Laat et al., 2006)
57 on the rates of decomposition of H₂O₂ by ferric ion and on the rate of oxidation of an
58 organic solute in homogeneous aqueous solution indicated that in the presence of [Cl⁻]
59 > 10 mM more than 99% of the generated HO• are converted into Cl₂•⁻. Therefore, the
60 formation rate and reactivity of Cl₂•⁻ radicals must be taken into account in the
61 efficiency evaluation of a given AOP which operates in the presence of chloride anions.
62 The determination of kinetic parameters and pathways of reactions involving Cl₂•⁻ and
63 Cl radicals with the organics are of importance to these purposes.

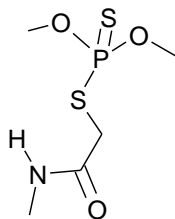
64 The removal of phosphor-containing pesticides, such as methidathion (MT) and
65 dimethoate (DM) (see Scheme 1) by photo-Fenton is well reported in the literature
66 (Ballesteros et al., 2009) (Oller et al., 2005). The solar photo-Fenton treatment at pilot
67 plant scale of a mixture of four commercial pesticides also containing MT and DM
68 showed similar chemical composition and comparable biocompatibility, though longer
69 irradiation periods were needed to reach the desired mineralization when Cl⁻ was
70 present (Soler et al., 2009). In the present manuscript we investigate the kinetics and
71 reaction mechanisms of Cl₂•⁻ radical anions with MT and DM and evaluate the
72 importance of these reactions during the AOP treatment of a polluted water containing
73 both, the insecticides and chloride anions.

74

75 *Scheme 1:* Chemical structure of the insecticides methidathion (MT) and dimethoate
76 (DM).



MT



DM

77

78 2. Material and methods

79 2.1. Reagents

80 The pesticides employed in this work, MT and DM were purchased from Sigma-Aldrich
81 (Pestanal). Sodium chloride and sodium peroxodisulfate were obtained from Merck.
82 Water employed in all experiments was Milli Q grade ($>18 \text{ M}\Omega \text{ cm}$ $<20 \text{ ppb}$ organic
83 carbon). The pH of the samples was measured with a Consort C832 pH-meter.

84 2.2. Conventional Flash Photolysis Experiments.

85 Flash-photolysis experiments were carried out using a conventional apparatus, Xenon
86 Co. model 720C with modified optics and electronics. Two collinear quartz Xenon
87 high-intensity pulsed flash tubes, Xenon Corp. P/N 890-1128 (FWHM $\leq 20 \mu\text{s}$), with a
88 continuous spectral distribution ranging from 200 to 600 nm and maximum around 450
89 nm were used. The analysis source was a high pressure mercury lamp (Osram HBO-100
90 W). The optical path length of the 1 cm internal diameter quartz sample cell was 10 cm.
91 The monochromator collecting the analysis beam (Bausch & Lomb, high intensity) was
92 directly coupled to a photomultiplier (RCA 1P28), which output was fed into a digital
93 oscilloscope (HP 54600B). Digital data were stored in a personal computer. The
94 emission of the flash lamps was filtered with an aqueous solution highly concentrated in
95 the corresponding organic compound in order to avoid photolysis of the substrate. The

96 temperature (20 ± 3 °C) was measured inside the reaction cell with a calibrated Digital
97 Celsius Pt-100 Ω thermometer. Freshly prepared solutions were used in order to avoid
98 possible thermal reactions of peroxodisulfate with the substrates. To avoid product
99 accumulation, each solution was irradiated only once.

100 *2.3. Bilinear regression analysis:* For each experimental condition, several absorbance
101 decay profiles at different detection wavelengths were taken. Absorbance is thus a
102 function of wavelength and time. Taking advantage of the linearity of the absorbance
103 with both, concentrations and absorption coefficients, a bilinear regression analysis was
104 applied to the experimental absorption matrix in order to retrieve information on the
105 minimum number of species and on their relative concentration profiles and absorption
106 spectra (San Román and Gonzalez, 1989).

107 *2.4. Computer simulations:* The kinetic model for computer simulation is based on
108 component balances and equilibrium equations formulated in terms of a differential
109 algebraic equations system which is solved by Gear's Stiff method and a least squares
110 estimation criterion as described elsewhere (Alegre et al., 2000).

111 *2.5. Determination of by products*

112 In order to identify the main reaction products formed after the reaction of Cl_2^- with the
113 insecticides, 250 mL of solutions containing sodium chloride, the pesticide and sodium
114 peroxodisulfate were irradiated using a cylindrical reactor described elsewhere
115 (Dell'Arciprete et. al, 2010). An axial immersion low pressure mercury lamp Heraeus
116 TNN 15/35 which emits nearly monochromatic radiation at 254 nm was used as
117 irradiation source. To minimize the photolysis of the pesticides, ratios of $[\text{S}_2\text{O}_8^{2-}]$
118 $\times \epsilon_{\text{S}_2\text{O}_8^{2-}} : [\text{Insecticide}] \times \epsilon_{\text{Ins}} > 100$ should be used, where ϵ stands for the molar

119 absorption coefficient. Therefore, the experimental conditions $[MT] = 3 \times 10^{-4}$ M and
120 $[S_2O_8^{2-}] = 0.25$ M were used in experiments with MT, and $[DM] = 1 \times 10^{-3}$ M and
121 $[S_2O_8^{2-}] = 0.1$ M for experiments with DM. Chloride concentration in these experiments
122 was 4 M.

123 After selected periods of irradiation, the reactor was emptied and the treated solution
124 was concentrated by means of solid phase extraction: 100 mL of the aqueous solution
125 were flown through a LiChrolut EN 200 mg (Merck) cartridge and the adsorbed organics
126 recovered with 3 mL of methanol. A GCMS-QP2010S (Shimadzu) gas chromatograph
127 equipped with a quadrupole mass analyzer was employed to identify major
128 intermediates formed along the process. The temperature program for GC analysis
129 involved an increase from 60°C to 250°C at a rate of 5°C/min rate. A Meta X5
130 Teknokroma column was used.

131 **3. Results**

132 *3.1. Rate constant determination for the reaction of $Cl_2^{\bullet-}$ with MT and DM.*

133 Dichloride radical anions, $Cl_2^{\bullet-}$, were formed by reaction of chloride ions with sulfate
134 radical anions, $SO_4^{\bullet-}$, generated upon the UV-photolysis of $S_2O_8^{2-}$ solutions of pH $5.5 \pm$
135 0.5 (George et al, 2002), reaction (1) in Table 1. In the presence of chloride at
136 concentrations $> 10^{-4}$ M (Alegre et al., 2000), $SO_4^{\bullet-}$ radicals are readily depleted
137 yielding chlorine atoms, as shown in reaction (2). Reaction of Cl with Cl^- ions
138 reversibly yields $Cl_2^{\bullet-}$ radical ions, reactions (3) and (4). Both, Cl and $Cl_2^{\bullet-}$ radicals

139 absorb below 380 nm with molar absorption coefficients at 340 nm, $\epsilon^{340} = 3800 \text{ M}^{-1}\text{cm}^{-1}$
 140 (Yu et al., 2004) and $9600 \pm 500 \text{ M}^{-1}\text{cm}^{-1}$ (Nagarajan et. al, 1985), respectively.

141 Table 1 about here

142 Time-resolved experiments with $0.6 \text{ M} > [\text{Cl}^-] > 0.3 \text{ M}$ and $[\text{S}_2\text{O}_8^{2-}] = 1.5 \times 10^{-2} \text{ M}$ show
 143 a transient species with an absorption maximum at 340 nm, whose spectrum is in
 144 agreement with that reported for the $\text{Cl}_2^{\bullet-}$ radical ions (Adams et al., 1995). The
 145 concentration of $\text{Cl}_2^{\bullet-}$ is expected to be much higher than that of Cl under our
 146 experimental conditions, as the equilibrium constant for the reversible reactions (3) and
 147 (4) is $K_{3,4} = 1.4 \times 10^5 \text{ M}^{-1}$ at 298 K (Buxton et al., 1998). Hence $\epsilon(\text{Cl}_2^{\bullet-}) \times [\text{Cl}_2^{\bullet-}] /$
 148 $\epsilon(\text{Cl}) \times [\text{Cl}] > 1.1 \times 10^5 \text{ M}^{-1}$ is obtained, thus indicating that the absorbance of chlorine
 149 atoms is negligible compared to that of $\text{Cl}_2^{\bullet-}$. Additions of either [DM] or [MT] <
 150 $6.25 \times 10^{-5} \text{ M}$ to these solutions also show fast formation of $\text{Cl}_2^{\bullet-}$. In the presence of
 151 increasing insecticide concentrations, the decay of the transient is accelerated (see
 152 Figure 1 for experiments in the presence and absence of MT). For both insecticides, the
 153 transient absorbance at 340 nm could be well fitted to a mixed first and second order
 154 decay rate law given by equation (1), also shown in Figure 1.

155
$$A^\lambda(t) = \frac{k_F}{\left(\frac{2 \times k_B}{\epsilon^\lambda \times l} + \frac{k_F}{A_o^\lambda} \right) \times e^{k_F \times t} - \frac{2 \times k_B}{\epsilon^\lambda \times l}} \quad \text{Equation (1)}$$

156 $A^\lambda(t)$ in equation (1) is the absorbance at time t and wavelength λ ; k_B and k_F stand for
157 the second and the pseudo first order decay rate constants, respectively; ε^λ is the molar
158 absorption coefficient at wavelength λ , A^λ_o is the absorbance immediately after the flash
159 of light, and l is the optical path length of the cell.

160 Figure 1 about here.

161 The parameter k_B did not depend on the insecticide concentration, as expected for the
162 recombination of $Cl_2^{\bullet-}$ radical ions (reaction (5)). On the other hand, for each amount of
163 chloride, k_F depends on the insecticide (DM or MT) and on its concentration as shown
164 in figure 1 *left inset*.

165 The effect of the insecticides on the decay rate of $Cl_2^{\bullet-}$ may be understood if reactions
166 (6) and (7) efficiently compete with the decay reactions of $Cl_2^{\bullet-}$ and Cl , reactions (5),
167 (8), (9), and (10) in Table 1. The efficient removal of HO^\bullet radicals by the insecticides
168 (reaction (12)) does not allow the attainment of equilibrium conditions for the complex
169 reversible reaction system of $Cl / Cl_2^{\bullet-}$ with water and hydroxide anions, which may be
170 considered as simple first-order reactions schematized by reactions (8) to (11) (Mártire
171 *et al.*, 2001). For solutions of pH in the range from 3 to 6 and $[Cl^-] > 0.3$ M, the
172 conditions: $K_{3,4} \times [Cl^-] > 1$, $k_{10} \times [HO^-] < k_9$ and $k_8 / (K_{3,4} \times [Cl^-]) \ll k_9$ apply (Alegre *et al.*,
173 2000) (Mártire *et al.*, 2001). With these considerations, the apparent first order decay
174 rate constant of $Cl_2^{\bullet-}$, k_F , is given by equation (2), for both MT and DM insecticides.
175 The acronym INS stands for MT or DM.

$$k_F = k_9 + \left[\frac{k_{7INS}}{K_{3,4} \times [Cl^-]} + k_{6INS} \right] \times [Ins] \quad \text{Equation (2)}$$

177 Plots of k_F vs. [MT] or [DM] (Figure 1 *left inset*) yield straight lines as expected from
 178 eq. (2). The intercepts of these plots yield for both insecticides $k_9 = (750 \pm 350)$, on the
 179 order expected for this rate constant (see Table 1). In turn, the slopes “ S_{INS} ” seem to be
 180 linearly correlated with $[Cl^-]^{-1}$, in agreement with eq. (2) assuming $S_{INS} =$
 181 $(k_{7INS}/(K_{3,4} \times [Cl^-] + k_{6INS}))$. The intercept of the linear plots of S_{INS} vs. $[Cl^-]^{-1}$ (as shown in
 182 Figure 1 *right inset* for MT) yield $k_{6MT} = (1.3 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{6DM} = (1.1 \pm$
 183 $0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. However, the statistical analysis of the data indicates that there is a
 184 35% probability that S_{INS} is not correlated with $[Cl^-]^{-1}$. If this is the case, the data points
 185 correspond to independent measures of k_{6INS} , which values are coincident, within the
 186 experimental error, with those obtained assuming a linear correlation of the variables.
 187 This situation may be understood considering that, even for the extreme case that
 188 reaction (7) were diffusion-controlled ($k_{7INS} \sim 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), the condition
 189 $k_{7INS}/(K_{3,4} \times [Cl^-] \ll k_{6INS}$ (see eq. (2)) holds for $[Cl^-] > 0.3 \text{ M}$. Therefore, determination
 190 of a reliable value for k_{7INS} is not possible from our experiments.

191 The reported rate constants for the reaction of hydroxyl radicals with MT and DM are
 192 $7.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Marin et al., 2011), reaction (12) in
 193 Table 1. These values, ca. 50 times higher than those measured for $Cl_2^{\bullet-}$, might explain
 194 the slower removal observed for both pesticides by solar photo-Fenton when performed
 195 in the presence of chloride ions under experimental conditions where the more efficient
 196 HO^{\bullet} oxidant has been partly replaced by the milder $Cl_2^{\bullet-}$ radical.

197 *3.2 Organic transients formed after MT and DM reactions with Cl₂^{•-} radicals:*

198 A bilinear analysis of the absorption traces obtained in the wavelength interval from 290
199 to 600 nm in experiments performed with [S₂O₈²⁻] = 1.5×10⁻² M, [Cl⁻] = 0.45 M and
200 either [MT] = 6.25×10⁻⁵ M or [DM] = 2.2×10⁻⁴ M showed the formation of two
201 transients for each insecticide with spectra and decay profiles shown in figures 2*a* and
202 2*b* for MT and DM, respectively. Short-lived transients with absorption maxima in the
203 range from 320 to 340 nm and lifetimes of 0.17 and < 0.10 ms were observed for MT
204 and DM, respectively. Considering that the transient spectra resembles that of Cl₂^{•-}
205 radicals (circles in Figures 2*a* and 2*b*) and the observed lifetimes are on the order of
206 those expected for Cl₂^{•-} radicals under each particular experimental condition, these
207 transients were assigned to Cl₂^{•-} radicals.

208 

209 The longer lived transients observed for MT and DM decay in the ms time-range and
210 show important absorption at 280 - 310 nm (triangles in Figures 2*a* and 2*b*).
211 Considering that these intermediates are only observed in flash photolysis experiments
212 involving both, Cl₂^{•-} radicals and the insecticides, they are expected to be due to organic
213 transients formed after reactions (6). As will be discussed latter in the text, they are
214 assigned to sulphenyl radical cations.

215 *3.3. Identification of stable reaction products.*

216 Pesticide solutions containing $S_2O_8^{2-}$ and Cl^- anions were continuously irradiated at 254
217 nm during 10 minutes and then analyzed by GC-MS. Table 2 shows the mass to charge
218 ratios, retention times, and assigned chemical structures of the major by-products
219 identified.

220 Table 2 about here

221 Reactive $SO_4^{\bullet-}$ and HO^{\bullet} radicals are also present in the reaction mixture; $SO_4^{\bullet-}$ radicals
222 as precursors of $Cl / Cl_2^{\bullet-}$ radicals, reactions (1) and (2), and HO^{\bullet} radicals as a
223 consequence of $Cl / Cl_2^{\bullet-}$ reactions with water, reactions (8) - (11). Since high
224 concentrations of the insecticides were used in the continuous irradiation experiments
225 performed to determine the products of reaction (6), the generation of detectable
226 concentrations of products due to the reaction between the insecticides and HO^{\bullet}
227 (reaction (12)), $SO_4^{\bullet-}$ (reaction (13)), and Cl radicals (reaction (7)), should not be ruled
228 out. To evaluate the magnitude of this contribution, a computer program was built to
229 simulate the generation of oxidized products formed from the different reactions. To
230 this purpose, reactions (1) to (13) along with the reactions of $SO_4^{\bullet-}$ with water and
231 peroxodisulfate ions (reactions (14) and (15), respectively), and $SO_4^{\bullet-}$ bimolecular
232 recombination (reaction (16)), were taken into account. The reaction rate constants used
233 are those depicted in Table 1. Initial parameters were the analytical concentrations of
234 reactants and the continuous irradiation conditions. To this purpose, $SO_4^{\bullet-}$ radicals were
235 assumed to be formed at a rate of $8.5 \times 10^{-6} M s^{-1}$ as expected for the irradiation with a 15
236 W low-pressure Hg lamp (incident photonic flux at 254 nm = $6.1 \times 10^{-6} E s^{-1}$) of a 0.25

237 M $S_2O_8^{2-}$ solution ($S_2O_8^{2-}$ photodissociation quantum yield 0.5 - 0.7 (Criquet et al.,
238 2009)) contained in a 2.5 cm optical pathway reactor.

239 The simulation shows that the generation of products from the reactions of the
240 insecticides with $SO_4^{\bullet-}$ and Cl radicals under the experimental conditions used are
241 negligible while those for the reaction of DM and MT with HO^{\bullet} are 5 and 13 %,
242 respectively, as shown in Table 3. Therefore, the identified products are mainly formed
243 after the reaction of the insecticides with $Cl_2^{\bullet-}$.

244 Table 3 about here

245 3.4. Reaction mechanisms

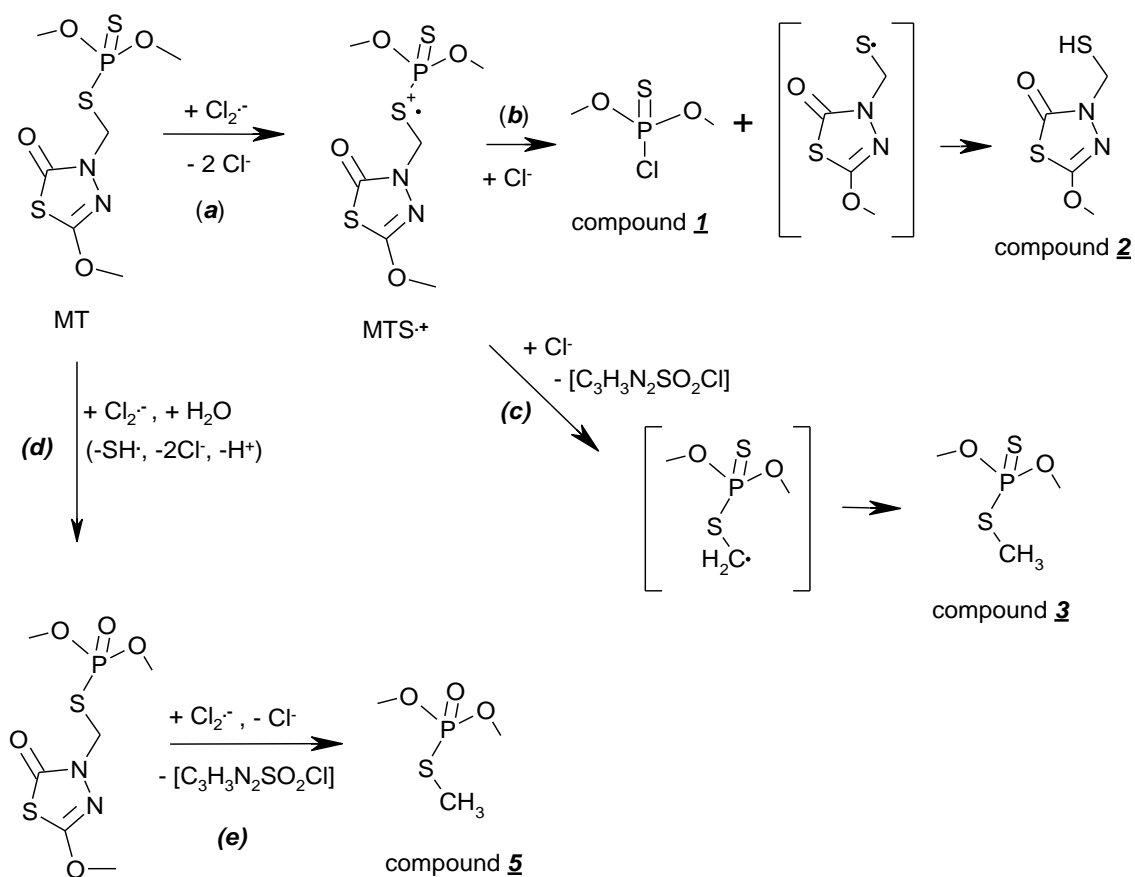
246 The $Cl_2^{\bullet-}$ radicals are prone to undergo charge transfer reactions with most substrates,
247 and in particular with organic sulfides (Mishra et al., 2005). In fact, it was early reported
248 by Asmus and Hiller (Asmus et al., 1977) (Asmus et al., 1980) (Hiller *et al.*, 1981) that
249 $Cl_2^{\bullet-}$ radicals are involved in an exchange equilibrium with sulfides yielding chloride
250 anions and neutral radicals comprising a three electron sulfur-chlorine bond
251 (represented as $S:\cdot Cl$) and absorbing around 390 nm. The latter radicals may further
252 dissociate to Cl^- anions and sulphenyl radical cations which exhibit absorption in the
253 300 nm – 400 nm range depending on the substituents (Jonah et al., 2001) (Asmus,
254 1987) (Asmus, 1977) (Varmenot et. al, 2001). Formation of sulphenyl radical cations is
255 supported by the nature of the observed reaction products, the MT and DM organic
256 transients absorption below 320 nm (see Figure 2), and the low reactivity of the
257 transients towards O_2 (Glass, 1999). In fact, MT has been reported to undergo a charge

258 transfer reaction with the organic photocatalysts triphenylpyrylium and
259 triphenylthiapyrylium (Arques et al., 2009).

260 Scheme 2 shows the proposed mechanism for MT. A charge transfer mechanism
261 between the insecticide and $\text{Cl}_2^{\bullet-}$ radicals leads to the formation of the sulphenyl radical
262 cation $\text{MTS}^{\bullet+}$, reaction pathway (a). Chloride ions may further induce the heterolysis of
263 S-P bonds of $\text{MTS}^{\bullet+}$ to yield compound 1 and an organic radical leading to compound 2
264 after H-atom abstraction, pathway (b). Otherwise, Cl^- -assisted $\text{C}_\alpha\text{-N}$ fragmentation of
265 $\text{MTS}^{\bullet+}$ yields compound 3, pathway (c).

266 Organophosphorous compounds with the thiono S=P structure, are known to hydrolyze
267 to their oxon forms, O=P, via a specific base hydrolysis (Rav-Acha, 2007). However,
268 for solution pHs of 5.5 and after 10 minutes irradiation, hydrolysis is expected to be of
269 little significance. On the other hand, they have been reported to efficiently yield the
270 oxon derivatives upon chlorination of their aqueous solutions (Tahara et al., 2006). In
271 particular, hypochlorite anions have been found to act as a nucleophile accelerating MT
272 hydrolysis (Duirk et al., 2008). No clear evidence on the oxon formation mechanism is
273 obtained from the present study. Formation of compound 4 probably involves the
274 interaction of $\text{Cl}_2^{\bullet-}$ with the S atom of the thiono structure followed by water addition
275 and displacement of S, pathway (d). A charge transfer mechanism between compound 4
276 and $\text{Cl}_2^{\bullet-}$ radicals involving a sulphide radical cation leads to the formation of
277 compound 5, as depicted in reaction path (e).

278 *Scheme 2: Proposed reaction mechanism for the reaction of MT with chloride radical*
 279 *anions. Transients and stable compounds in brackets are proposed, but not detected.*

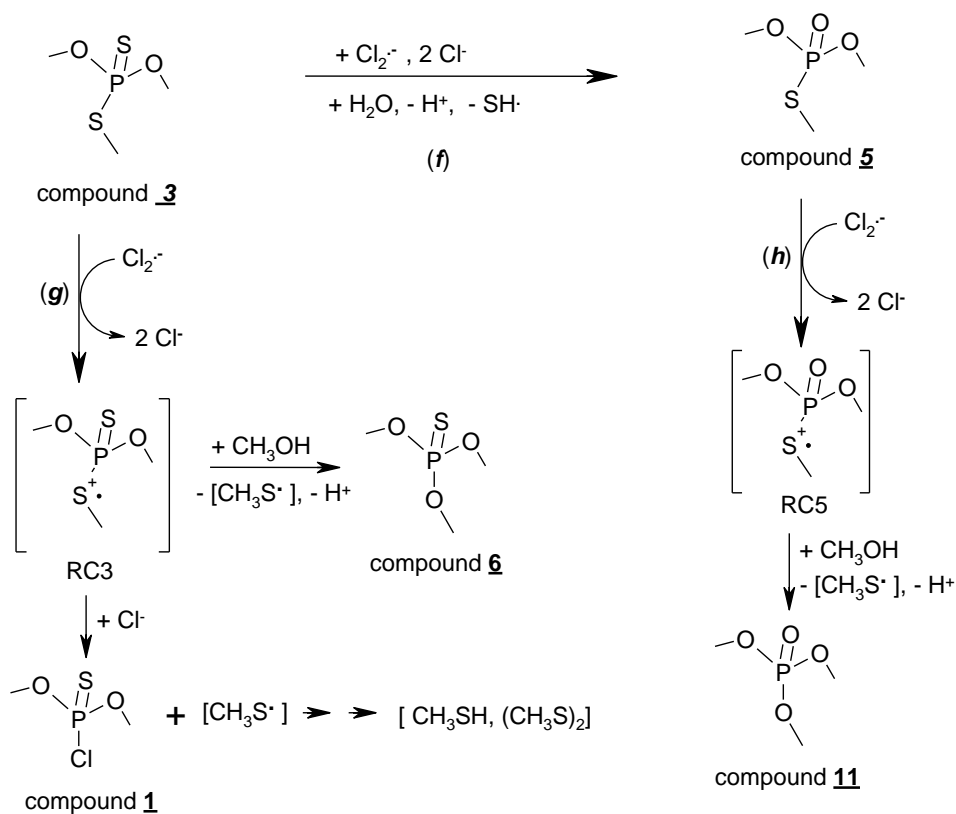


280 compound 4

281 In Scheme 3, pathway (f) shows formation of compound 5, the oxon derivative of
 282 compound 3. Further oxidation of compound 3 with $\text{Cl}_2^{\bullet-}$ radicals leads to the radical
 283 cation RC3, pathway (g), which upon chloride addition yields compound 1 and CH_3SH .
 284 Methanol and CH_3SH may be formed as a consequence of the degradation of the
 285 phosphoric acid methylesters and methylthioates by-products to phosphates. Methanol
 286 is able to react with RC3 to yield compound 6. Generation of SH_2 and CH_3SH in the
 287 reaction mixture, as also observed in the Fenton degradation of MT (Garcia, 2007),
 288 facilitates the H-abstraction reactions proposed in Schemes 2 to 4.

289 *Scheme 3*: Proposed reaction mechanism for the oxidation of compound 3. Transients
 290 and stable compounds in brackets are proposed, but not detected.

291



292

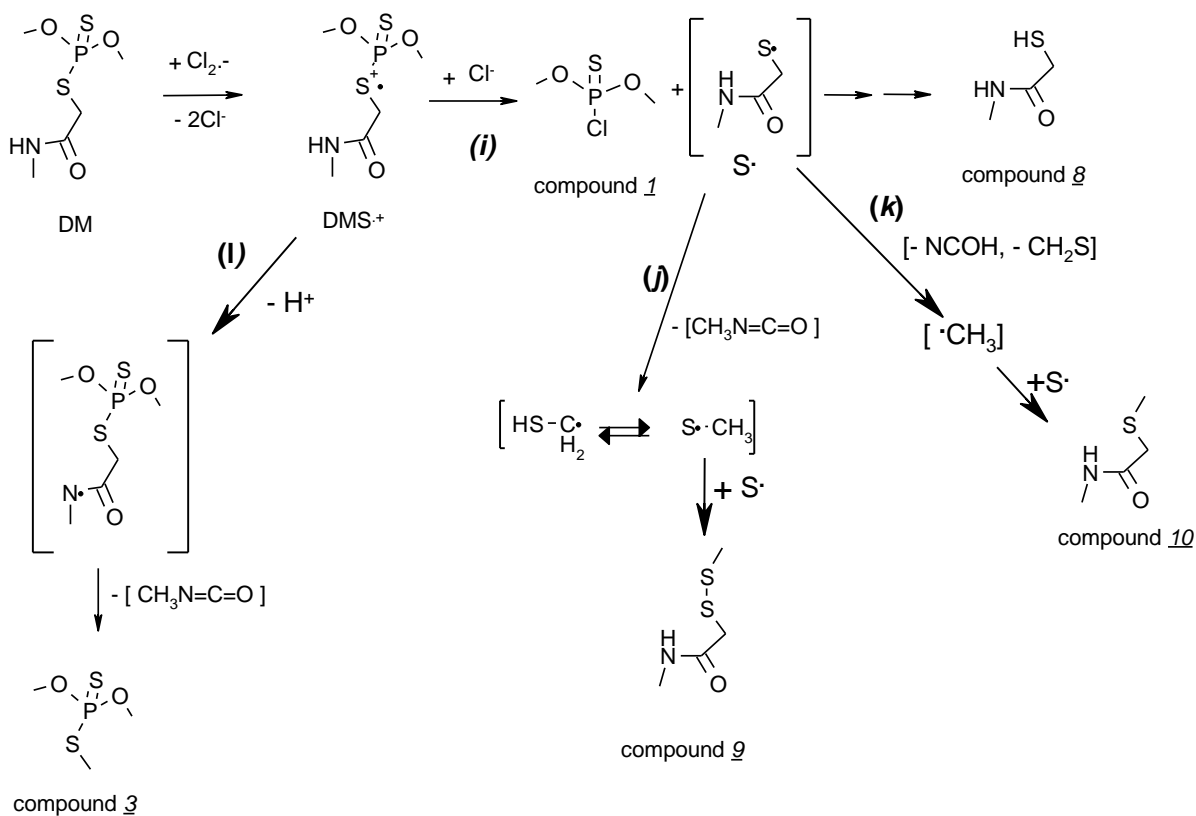
293 Major intermediates were also detected in the case of DM (see Table 2). It is interesting
 294 to note that some of the intermediates are coincident with those detected in MT
 295 degradation (compounds 1, 3, and 5), which correspond to the degradation by-products
 296 of the phosphothioester moiety of the pesticides. Compounds 11, 8, 5, and 3 have been
 297 previously reported in the TiO₂-mediated photocatalytic decomposition of DM
 298 (Evgenidou et.al, 2006) (Calza et al., 2008) and these compounds together with
 299 compounds 10 and 9, in the thermal degradation of DM (Andreozzi et. al, 1999).
 300 Similar reaction paths are likely to take place in the reaction of DM with Cl₂^{•-} radicals.

301 Scheme 4 shows the charge transfer mechanism between DM and $\text{Cl}_2^{\bullet-}$ leading to the
302 formation of the corresponding S-centered radical cation $\text{DMS}^{\bullet+}$. As already discussed
303 for MT, formation of compounds 1 and 8 may be explained by the heterolytic cleavage
304 of the S-P bond of $\text{DMS}^{\bullet+}$ involving a sulphenyl radical (S^\bullet), reaction path (i).
305 Rearrangement of radical S^\bullet and further heterolysis yielding a methyl sulphenyl radical
306 and recombination of the latter with S^\bullet leads to the formation of compound 9, reaction
307 path (j). Otherwise, rearrangement of radical S^\bullet and further heterolysis yielding a
308 methyl radical and recombination of the latter with S^\bullet leads to the formation of
309 compound 10, reaction path (k). On the other hand, $\text{C}_\alpha\text{-C}_\beta$ fragmentation (Schöneich et
310 al., 2001) of $\text{DMS}^{\bullet+}$ yields compound 3, reaction path (l).

311 As discussed above, compound 3 leads to the formation of 5 (see Scheme 3). Oxidation
312 of compound 5 with $\text{Cl}_2^{\bullet-}$ radicals leads to the radical cation RC5, pathway (h).
313 Addition of methanol to RC5 may lead to the formation of compound 11. Since the
314 oxon derivative of DM was not observed among the detected products, its formation
315 seems not to be favored under our experimental conditions.

316

317 *Scheme 4:* Proposed reaction mechanism for the reaction of DM with chloride radical
318 anions. Transients and stable compounds in brackets are proposed, but not detected.



321 O,O- dimethyl phosphorochloridothioate is the main chlorinated by-product formed by
 322 the reaction of both, MT and DM with $\text{Cl}_2^{\bullet-}$. Because of its toxicity, this compound is
 323 environmentally relevant. On the other hand, compounds 4 and 5 are expected to show
 324 an increased toxicity relative to their precursors since the thiophosphate (P=S) moiety is
 325 replaced by the more toxic oxon (P=O) group (Tahara et al., 2006) (Duirk et al., 2008).
 326 As generation of $\text{Cl}_2^{\bullet-}$ has been reported in the photo-Fenton process in the presence of
 327 chlorides (Machulek et al., 2007), formation of toxic compounds in photo-Fenton
 328 reaction under these conditions should not be ruled out. In fact, the small decrease in the
 329 biodegradability observed for DM and MT mixtures treated by solar Photo-Fenton
 330 (Soler et al., 2009) in the presence of Cl^- compared to experiments in its absence may
 331 be attributed to the different reaction products formed.

332

333 **4. Discussion**

334

335 The presence of chloride anions in polluted waters generally reduces the AOPs
336 depletion efficiency of organic pollutants because of the scavenging of active oxidizing
337 radicals by chloride anions (Fang et al, 2012). Chlorine and $\text{Cl}_2^{\bullet-}$ radicals formed in
338 these systems may also initiate the oxidation of pollutants thus minimizing the negative
339 effect of Cl^- on AOP efficiency. In fact, we found here that the insecticides
340 methidathion and dimethoate efficiently react by an electron transfer pathway with $\text{Cl}_2^{\bullet-}$
341 radicals. Therefore, these insecticides might be expected to be degraded by AOPs even
342 in the presence of chloride anions. However, toxic chlorine-containing products may
343 form under these conditions.

344 Because chlorine, $\text{Cl}_2^{\bullet-}$, and HO^\bullet radicals are interrelated by a complex scheme of
345 reactions (see Table 1), predictions on the effect of Cl^- on the depletion rates of the
346 insecticides are not straightforward. To understand the behavior of the reaction system,
347 the kinetic behavior of MD and MT depletion in contaminated waters containing $[\text{Cl}^-] =$
348 $0.0, 10^{-4}, 10^{-3}, 10^{-2},$ and $0.4, \text{ M}$ at different pHs was modeled assuming an artificial AOP
349 producing HO^\bullet radicals at a rate of $8.5 \times 10^{-6} \text{ M s}^{-1}$ and considering a minimum reaction
350 mechanism. Reactions (3) to (12), and HO^\bullet radical recombination, reaction (17), were
351 considered. The system was allowed to evolve until a steady concentration of $\text{Cl}, \text{Cl}_2^{\bullet-},$
352 and HO^\bullet radicals was attained and the concentration of products linearly increased with
353 the reaction time. To compare the amount of products obtained in the presence and

354 absence of chloride ions, an arbitrary value of 100% was assigned to the total molar
355 concentration of products simulated in its absence. Simulation of high insecticide
356 conversions were avoided, since the number of reactions of unknown rate constants
357 geometrically increases with the increasing number of reaction products.

358 The effect of pH due to reaction (10) is negligible up to 9. Figure 3 shows that the
359 presence of chloride anions in the range from 10^{-4} to 0.4 M inhibits the depletion
360 efficiency of 6.25×10^{-5} MT, though it does not follow a linear correlation with $[\text{Cl}^-]$.
361 Chloride anion concentrations $> 10^{-4}$ M are already capable of scavenging HO^\bullet radicals.
362 However, the higher $[\text{Cl}_2^{\bullet-}] : [\text{Cl}]$ ratios established for higher $[\text{Cl}^-]$ (reversible reactions
363 (3) and (4)) and the good efficiency of the insecticide reaction with $\text{Cl}_2^{\bullet-}$ radicals
364 (reaction (6)) lead to a partial recuperation of MT degradation capacity for $[\text{Cl}^-] > 10^{-3}$
365 M. In fact, for $[\text{Cl}^-] = 10^{-3}$ M, MT is depleted by HO^\bullet , Cl and $\text{Cl}_2^{\bullet-}$ radicals, while for
366 $[\text{Cl}^-] = 0.4$ M, depletion is mainly due to $\text{Cl}_2^{\bullet-}$ radicals. Moreover, Figure 3 *inset* shows
367 that the extent of inhibition also depends on the concentration of insecticide, as the
368 lower insecticide concentrations show the higher decrease in the degradation efficiency
369 even for $[\text{Cl}^-]$ as low as 10^{-4} M. A similar discussion applies to DM. An important
370 consequence of the depletion of MT and DM by $\text{Cl}_2^{\bullet-}$ radicals is the detrimental
371 formation of toxic by-products.

372 Figure 3 about here

373 The previous discussion further supports the participation of $\text{Cl}_2^{\bullet-}$ radicals unexpected
374 effects on AOPs efficiency. Yang et al. (Yang et al., 2005) studied the methylene blue

375 (MB) and orange II (OII) degradation by TiO_2 / UV light in the presence of $[\text{Cl}^-]$. These
376 authors reported little influence on the degradation efficiency of both dyes in the
377 presence of $[\text{Cl}^-] < 0.01$ mol/L. However, for $[\text{Cl}^-] > 0.10$ mol/L they reported opposite
378 effects: a significant degradation inhibition was observed for MB while OII showed an
379 enhanced degradation. Also, $\text{Cl}_2^{\bullet-}$ radicals may also be responsible for the increased
380 decolorization of Orange 7 by peroxodisulfate in the presence of 0.1 M chloride anions
381 (Wang et al., 2011).

382 **5. Conclusion**

383 The phosphor-containing pesticides methidathion (MT) and dimethoate (DM)
384 chemically react with $\text{Cl}_2^{\bullet-}$ radical anions with rate constants $(1.3 \pm 0.4) \times 10^8$ and $(1.1 \pm$
385 $0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The sulfide group of the insecticides is the preferred site
386 of attack initiating the degradation of the insecticides. Chlorinated by-products were
387 observed among the identified degradation products.

388 Computer simulation models predict that chloride anions present in polluted waters are
389 able to scavenge the active oxidizing radicals produced by the AOP technologies to
390 generate Cl atoms and $\text{Cl}_2^{\bullet-}$ radicals. Because of the efficient reactions of MT and DM
391 with $\text{Cl}_2^{\bullet-}$ radicals, these processes are expected to have an important contribution in the
392 AOP treatment of the insecticide's contaminated waters also containing high levels of
393 chloride anions. However, toxic chlorine-containing products are formed under these
394 conditions.

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403 **References**

- 404 Adams, D. J., Barlow, S., Buxton, G. V., Malone, T., Salmon, G. A., 1995. Evaluation of
405 the stability constant of Cl_2 in neutral aqueous solution. *Journal of the Chemical*
406 *Society, Faraday Transactions* 91 (18), 3303-3305.
- 407 Alegre, M. L., Geronés, M., Rosso, J. A., Bertolotti, S. G., Braun, A. M., Mártire, D. O.,
408 Gonzalez, M. C., 2000. Kinetic study of the reactions of chlorine atoms and $\text{Cl}_2^{\bullet-}$
409 radical anions in aqueous solutions. 1. Reaction with benzene. *Journal of Physical*
410 *Chemistry A* 104 (14), 3117- 3125.
- 411 Andreozzi, R., Ialongo, G., Marotta, R., Sanchirico, R., 1999. The thermal
412 decomposition of dimethoate. *Journal of Hazardous Materials* 64 (3) 283-294.
- 413 Asmus, K.D., Bahnemann, D., Bonifačić, M., Gillis, H. A., 1977. Free radical oxidation
414 of organic sulphur compounds in aqueous solution. *Faraday Discussions of the*
415 *Chemical Society* 63 (0), 213-225.
- 416 Asmus, K.D., Bonifačić, M., 1980. Stabilization of oxidized sulphur centres by halide
417 ions. Formation and properties of $\text{R}_2\text{S}\cdot\text{X}$ radicals in aqueous solutions. *Journal of the*
418 *Chemical Society, Perkin Transactions* 2, 758-762.

419 Arques, A., Amat, A.M., Santos-Juanes, L., Vercher, R.F., Marín, M.L., Miranda, M.A.,
420 2009. Abatement of methidathion and carbaryl from aqueous solutions using organic
421 photocatalysts. *Catalysis Today* 144 (1–2), 106–111.

422 Ballesteros Martín, M.M., Sánchez Pérez, J.A., Casas López, J.L., Oller, I., Malato
423 Rodríguez, S., 2009. Degradation of a four-pesticide mixture by combined photo-
424 Fenton and biological oxidation. *Water Research* 43 (3), 653-660.

425 Buxton, G. V., Bydder, M., Salmon, G. A., 1998. Reactivity of chlorine atoms in
426 aqueous solution. Part 1. The equilibrium $\text{Cl}^{\text{MNsbd}} + \text{Cl}^-\text{Cl}_2^-$. *Journal of the Chemical*
427 *Society, Faraday Transactions* 94 (5), 653-657.

428 Calza, P., Massolino, C., 2008. Light induced transformations of selected
429 organophosphorus pesticides on titanium dioxide: Pathways and by-products
430 evaluation using LC-MS technique. *Journal of Photochemistry and Photobiology A:*
431 *Chemistry* 199 (1), 42-49.

432 Criquet, J., Karpel Vel Leitner, N., 2009. Degradation of acetic acid with sulfate radical
433 generated by persulfate ions photolysis. *Chemosphere* 77 (2), 194–200.

434 Dell’Arciprete, M. L., Santos-Juanes, L., Arques, A., Vercher, R.F., Amat, A. M.,
435 Furlong, J.P., Mártire, D.O., Gonzalez, M.C., 2010. Reactivity of neonicotinoid
436 pesticides with singlet oxygen. *Catalysis Today* 151 (1-2), 137–142.

437 Duirk, S. E., Desetto, L. M., Davis, G.M., 2008. Fate of High Priority Pesticides During
438 Drinking Water Treatment. Document by the U.S. Environmental Protection Agency,
439 Office of Research and Development Washington D.C. 20460.

440 Evgenidou, E., Konstantinou, I., 2006. Study of the removal of dichlorvos and
441 dimethoate in a titanium dioxide mediated photocatalytic process through the
442 examination of intermediates and the reaction mechanism. *Journal of Hazardous*
443 *Materials* 137 (2), 1056-1064.

444 Fang, G.D.; Dionysiou, D.; Wang, Y.; Al-Abed, S.R.; Zhou, D.M., 2012. Sulfate
445 radical-based degradation of polychlorinated biphenyls: Effects of chloride ion and
446 reaction kinetics. *Journal of Hazardous Materials* 227– 228, 394– 401.

447 García-Ripolla, A., Amat, A.M., Arques, A., Vicente, R., López, M.F., Oller, I.,
448 Maldonado, M.I., Gernjak, W., 2007. Increased biodegradability of Ultracide in
449 aqueous solutions with solar TiO₂ photocatalysis. *Chemosphere* 68 (2), 293–300.

450 George, C., Chovelon, J. M., 2002. A laser flash photolysis study of the decay of SO₄^{•-}
451 and Cl₂^{•-} radical anions in the presence of Cl⁻ in aqueous solutions. *Chemosphere* 47
452 (4), 385-393.

453 Glass, R. S., 1999. Sulfur Radical Cations. *Topics in Current Chemistry*. Springer-
454 Verlag Berlin Heidelberg, Vol. 205, pp. 1.

455 Herrmann, H., Reese, A., Zelhrer, R., 1995. Time-resolved UV/VIS Diode Array
456 Radical Anions in Aqueous Solution Absorption Spectroscopy of SO_x-(x=3, 4, 5).
457 *Journal of Molecular Structure* 348 (4), 183-186.

458 Hiller, K.O., Asmus, K.-D., 1981. Oxidation of Methionine by X in Aqueous Solution
459 and Characterization of Some Three-electron Bonded Intermediates. A Pulse
460 Radiolysis Study. *International Journal of Radiation Biology* 40 (6), 583-595.

461 Jonah, C. D., Madhava Rao, B. S., 2001. *Radiation Chemistry: Present Status and*
462 *Future Trends*, 1st ed. Elsevier: Amsterdam, The Netherland, Chapter 4, pp. 755.

463 De Laat, J., Le, T. G., 2006. Effects of chloride ions on the iron(III)-catalyzed
464 decomposition of hydrogen peroxide and on the efficiency of the Fenton-like
465 oxidation process. *Applied Catalysis B: Environmental*. 66 (1-2), 137.

466 Liu, H., Zhao, H., Chen, S., Quan, X., Zhang, Y., 2010. Photochlorination of bisphenol
467 A by UV-Vis light irradiation in saline solution: effects of iron, nitrate and citric
468 acid. *Environmental Chemistry* 7 (6), 548-553.

469 Machulek Jr., A., Moraes, J. E. F., Vautier-Giongo, C., Silverio, C. A., Friedrich, L.
470 C., Nascimento, C. A.O., Gonzalez, M. C., Quina, F. H., 2007. Abatement of the
471 Inhibitory Effect of Chloride Anions on the Photo-Fenton Process. *Environmental*
472 *Science & Technology* 41 (24), 8459 - 8463.

473 Marin, M.L., Lhiaubet-Vallet, V., Santos-Juanes, L., Soler, J., Gomis, J., Arques, A.,
474 Amat, A.M., Miranda, M.A., 2011. A photophysical approach to investigate the
475 photooxidation mechanism of pesticides: Hydroxyl radical versus electron transfer.
476 *Applied Catalysis B: Environmental* 103 (1-2), 48–53.

477 Mártire, D. O., Rosso, J.A., Bertolotti, S.G., Carrillo Le Roux, G., Braun, A.M.,
478 Gonzalez, M.C., 2001. Kinetic study of the reaction of chlorine atoms and $\text{Cl}_2^{\cdot-}$
479 radicals anions in aqueous solutions. II. Reaction with chlorobenzene, toluene and
480 benzoic acid. *Journal of Physical Chemistry A* 105 (22), 5385 - 5392.

481 Mishra, B., Priyadarsini, K. I., Mohan, H., 2005. Pulse radiolysis studies on reaction of
482 $\cdot\text{OH}$ radical with N-acetyl methionine in aqueous solution. *Research on Chemical*
483 *Intermediates* 31 (7-8), 625-632.

484 Mora, V.C., Rosso, J.A., Mártire, D.O., Gonzalez, M.C., 2009. Phenol depletion by
485 thermally activated peroxydisulfate in the presence of additives: A clean method for
486 the degradation of pollutants. *Chemosphere* 75 (10), 1405–1409.

487 Nagarajan, V., Fessenden, R. W., 1985. Flash Photolysis of Transient Radicals. 1. $\text{X}_2^{\cdot-}$
488 with X = Cl, Br, I, and SCN. *Journal of Physical Chemistry* 89, 2330-2335.

489 Oller, J., Gernjak, W., Maldonado, M.I., Fernandez, P., Blanco, J., Sanchez, J.A.,
490 Malato, S., 2005. Photocatalytic treatment of dimethoate by solar photocatalysis at
491 pilot plant scale. *Environmental Chemistry Letters* 3 (5), 118-121.

492 Taylor, J. R., 1982. *An Introduction to error analysis*. University Science Books. Mill
493 Valley, California, pp. 270.

494 Panno, S.V., Hackley, K.C., Hwang, H.H., Greenberg, S., Krapac, I.G., Landsberger, S.,
495 O'Kelly, D.J., April 22, 2002. Source identification of sodium and chloride
496 contamination in natural waters: preliminary results. In *Proceedings of the 12th*
497 *Annual Conference of the Illinois Groundwater Consortium*.
498 www.siu.edu/orca/igc/index.html. Makanda, (IL).

499 Rav-Acha, C., Groisman, L., Mingelgrin, U., Kirson, Z., Sasson, Y. Gerstl, Z., 2007. A
500 Mechanistic Study of Methyl Parathion Hydrolysis by a Bifunctional Organoclay.
501 *Environmental Science & Technology* 41 (1), 106-111.

502 Ross, A. B., Mallard, W. G., Helman, W. P., Buxton, G. V., Huie, R. E., Neta, P., 1998.
503 NDRL-NIST Solution Kinetics Database, 1998. Notre Dame Radiation Laboratory,
504 Notre Dame, IN and National Institute of Standards and Technology, Gaithersburg,
505 MD, Available on the web at: <http://kinetics.nist.gov/solution/> (March 2012)

506 San Roman, E., Gonzalez, M.C., 1989. Analysis of spectrally resolved kinetic data and
507 time resolved spectra by bilinear regression. *Journal of Physical Chemistry* 93 (9),
508 3536-3540.

509 Schöneich, C., Miller, B., Hug, G.L., Bobrowski, K., Marciniak, B., 2001.
510 Intermolecular complexes between sulfide radical cations from β -hydroxy sulfides
511 and phosphate. *Research on Chemical Intermediates* 27 (1,2), 165–175.

512 Soler, J., Garcia-Ripoll, A., Hayek, N., Miro, P., Vicente, R., Arques, A., Amat, A.M.,
513 2009. Effect of inorganic ions on the solar detoxification of water polluted with
514 pesticides. *Water Research* 43 (18), 4441–4450.

515 Tsuneda, S., Ishihara, Y., Hamachi, M., Hirata, A., 2002. Inhibition effect of chlorine
516 ion on hydroxyl radical generation in UV-H₂O₂ process. *Water*
517 *Science and Technology* 46 (11-12), 33-38.

518 Varmenot, N. , Remita, S., Abedinzadeh, Z., Wisniowski, P., Strzelczak, G.,
519 Bobrowski. K., 2001. Oxidation Processes of N,S-Diacetyl-L-cysteine Ethyl Ester:
520 Influence of S-Acetylation. *Journal of Physical Chemistry A* 105, 6867-6875.

521 Wang, P., Yang, S., Shan, L., Niu, R., Shao, X., 2011. Involvements of chloride ion in
522 decolorization of Acid Orange 7 by activated peroxydisulfate or peroxymonosulfate
523 oxidation. *Journal of Environmental Sciences* 23 (11), 1799–1807.

524 Yang, S., Chen, Y., Lou, L., Wu, X., 2005. Involvement of chloride anion in
525 photocatalytic process. *Journal of Environmental Science (China)* 17 (5), 761-765 .

526 Yu, X., Bao, Z., Barker, J. B., 2004. Free Radical Reactions Involving Cl, Cl₂^{•-}, and
527 SO₄^{•-} in the 248 nm Photolysis of Aqueous Solutions Containing S₂O₈²⁻ and Cl⁻.
528 *Journal of Physical Chemistry A* 108 (2), 295-308.

529 Yu, X., 2004. Critical Evaluation of Rate Constants and Equilibrium Constants of
530 Hydrogen Peroxide Photolysis in Acidic Aqueous Solutions Containing Chloride
531 Ions. *Journal of Physical and Chemical Reference Data* 33 (3), 747-763.

532 Tahara, M.; Kubota, R.; Nakazawa, H.; Tokunaga, H.; Nishimura, T., 2006. Analysis of
533 active oxon forms of nine organophosphorus pesticides in water samples using gas
534 chromatography with mass spectrometric detection. *Journal of Health Science* 52 (3),
535 313–319.

536

537 **Figure Captions**

538 **Figure 1:** Absorbance traces at 340 nm obtained in experiments with solutions
539 containing $[S_2O_8^{2-}] = 1.5 \times 10^{-2}$ M and $[Cl^-] = 0.45$ M in the presence (curve *a*) and
540 absence (curve *b*) of 1.04×10^{-5} M of MT. The grey lines stand for the fitting to equation
541 1. *Left Inset:* Plots of k_F vs $[MT]$ for experiments with $[Cl^-] = 0.345$ (●) and 0.5 M (Δ).
542 *Right Inset:* Plot of the slopes “S” vs. $[Cl^-]^{-1}$. The fitting to a straight line yields $r^2 =$
543 0.32. Note that the percentage probability that five data points of two uncorrelated
544 variables give a correlation coefficient $|r| = 0.56$ is $\sim 35\%$ (Taylor, 1982). The
545 symbols size is on the order of the experimental error, unless otherwise specified by the
546 error bars.

547

548 **Figure 2:** Transient spectra retrieved by a bilinear computer analysis of the absorption
549 traces obtained from flash photolysis experiments performed with air saturated solutions
550 of pH 5.5 containing $[S_2O_8^{2-}] = 1.5 \times 10^{-2}$ M, $[Cl^-] = 0.45$ M, and (a) $[MT] = 6.25 \times 10^{-5}$
551 M, (b) $[DM] = 2.2 \times 10^{-4}$ M. The symbols (●) and (▲) stand for the short and longer-
552 lived components, respectively, and (○) is the reported spectrum of the $Cl_2^{\bullet-}$ radical.
553 *Inset:* Contribution of the short- (black curve) and long-lived (grey curve) transients to
554 the absorbance of the traces at 320 and 290 nm, respectively, for the experiments in the
555 main figure.

556

557 **Figure 3:** Expected consumption efficiency of MT during treatment by an artificial
558 AOP producing HO• radicals at a rate of $8.5 \times 10^{-6} \text{ M s}^{-1}$. Polluted waters of pH 3
559 containing $[\text{MT}] = 6.25 \times 10^{-5}$ and different $[\text{Cl}^-]$ were considered. The consumption due
560 to the different scavengers is depicted as: dark grey: HO•, light grey: $\text{Cl}_2^{\bullet-}$, black: Cl.
561 *Inset:* Expected effect on the consumption efficiency of MT during treatment by the
562 same artificial AOP of polluted waters of pH 3 containing $[\text{Cl}^-] = 1 \times 10^{-4} \text{ M}$ and
563 different $[\text{MT}]$. The % converted MT in this plot is normalized to that observed in the
564 absence of chloride anions for the same MT concentration.

565

566 **Table Captions**

567

568 **Table 1** - Manifold of reactions taking place upon UV-light activation of
569 peroxodisulfate in the reaction mixture containing $\text{S}_2\text{O}_8^{2-}$, Cl^- , and the insecticide. The
570 corresponding rate constants, k , at 25 °C are also shown. The acronym INS stands for
571 MT or DM.

572 (a) Second order rate constants are given unless otherwise indicated.

573 (b) v is the rate of $\text{SO}_4^{\bullet-}$ formation, I_{abs} is the absorbed photonic flux and $\phi(\text{SO}_4^{\bullet-})$ is
574 the peroxodisulfate photodissociation quantum yield.

575 (c) Yu, (2004); Alegre et al. (2000); Ross et al. (1998).

576 (d) k values from this work.

577 (e) Marin et al. (2011).

578 (f) Assumed diffusion –controlled for simulation purposes, in agreement with reported
579 rate constants for the reaction of Cl with organic sulfides (Ross et al., 1998).

580 (g) Herrmann et al. (1995).

581

582 **Table 2:** Oxidation by-products formed after the reaction of $\text{Cl}_2^{\bullet-}$ with the insecticides.

583 GC retention times, R_t , and MS mass to charge ratios m/z are given together with

584 assigned products.

585

586 **Table 3:** Percentage of products formed by the reactions of the insecticides with HO^\bullet ,

587 $\text{SO}_4^{\bullet-}$, Cl^\bullet , and $\text{Cl}_2^{\bullet-}$ radicals obtained from the computer simulations of steady state

588 irradiation experiments with $[\text{Cl}^-] = 4 \text{ M}$ and either $[\text{MT}] = 3 \times 10^{-4} \text{ M}$ and $[\text{S}_2\text{O}_8^{2-}] =$

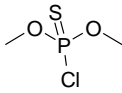
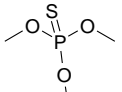
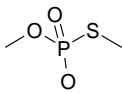
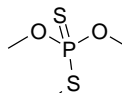
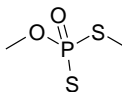
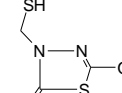
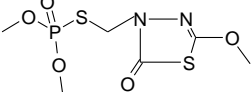
589 0.25 M or $[\text{DM}] = 1 \times 10^{-3} \text{ M}$ and $[\text{S}_2\text{O}_8^{2-}] = 0.1 \text{ M}$.

590

TABLE 1

				$k / \text{M}^{-1}\text{s}^{-1}$ (a)	
$\text{S}_2\text{O}_8^{2-}$	+	hv	\rightarrow 2 $\text{SO}_4^{\bullet-}$	$\nu = I_{\text{abs}} \times \phi(\text{SO}_4^{\bullet-})$ (b)	(1)
$\text{SO}_4^{\bullet-}$	+	Cl^-	\rightarrow Cl + SO_4^{2-}	4.7×10^8 at I = 0.1 M (c)	(2)
Cl	+	Cl^-	\rightarrow $\text{Cl}_2^{\bullet-}$	8.5×10^9 (c)	(3)
$\text{Cl}_2^{\bullet-}$	\rightarrow	Cl + Cl^-		$6.0 \times 10^4 \text{ s}^{-1}$ (c)	(4)
$\text{Cl}_2^{\bullet-}$	+	$\text{Cl}_2^{\bullet-}$	\rightarrow Cl_2 + 2 Cl^-	3.3×10^9 (c)	(5)
$\text{Cl}_2^{\bullet-}$	+	INS	\rightarrow Organic transient	$k_{6\text{MT}} = (1.3 \pm 0.4) \times 10^8$ (d)	(6)
				$k_{6\text{DM}} = (1.1 \pm 0.4) \times 10^8$ (d)	
Cl	+	INS	\rightarrow	(f)	(7)
Cl	+	H_2O	\rightarrow HO^\bullet + HCl	$2 \times 10^5 \text{ s}^{-1}$ (c)	(8)
$\text{Cl}_2^{\bullet-}$	+	H_2O	\rightarrow HO^\bullet + 2 Cl^- + H^+	$< 1.3 \times 10^3 \text{ s}^{-1}$ (c)	(9)
$\text{Cl}_2^{\bullet-}$	+	HO^-	\rightarrow HO^\bullet + 2 Cl^-	$4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (c)	(10)
HO^\bullet	+	Cl^-	\rightarrow Cl + HO^-	$4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (c)	(11)
HO^\bullet	+	INS	\rightarrow	$k_{12\text{MT}} = 7.1 \times 10^9$ (e)	(12)
$\text{SO}_4^{\bullet-}$	+	INS	\rightarrow	(f)	(13)
$\text{SO}_4^{\bullet-}$	+	H_2O	\rightarrow SO_4^{2-} + HO^\bullet + H^+	$(6.6 \pm 0.4) \times 10^2$ (g)	(14)
$\text{SO}_4^{\bullet-}$	+	$\text{S}_2\text{O}_8^{2-}$	\rightarrow $\text{S}_2\text{O}_8^{\bullet-}$ + SO_4^{2-}	$(6.3 \pm 1.5) \times 10^5$ (g)	(15)
2 $\text{SO}_4^{\bullet-}$	\rightarrow	$\text{S}_2\text{O}_8^{2-}$		5×10^8 (c, g)	(16)
2 HO^\bullet	\rightarrow	H_2O_2		5.2×10^9 (c, g)	(17)

TABLE 2

	R_t (min)	Fragmentation m/z	Product assignment
MT	6.05	160 (130, 97, 47)	 <p>O,O- dimethyl phosphorochloridothioate, compound <u>1</u>.</p>
	6.3	156 (126, 109, 93, 79, 63)	 <p>O,O,O-trimethylthiophosphoroate, compound <u>6</u>.</p>
	9.3	156 (141, 126, 110, 109, 95, 80, 79, 47)	 <p>Trimethylphosphorothioate, compound <u>5</u>.</p>
	11.25	172 (141, 126, 125, 109, 95, 94, 93, 79, 63, 47)	 <p>O,O,S-trimethyl thiophosphorothioate, compound <u>3</u>.</p>
	14.3	172 (126, 125, 79, 47)	 <p>O, S, S-trimethylphosphorodithioate, compound <u>7</u></p>
	17.1	178 (146, 145, 132, 85, 58)	 <p>Compound <u>2</u></p>
	30.9	286 (145, 142, 109, 85)	 <p>Compound <u>4</u></p>

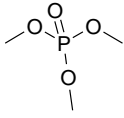
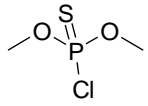
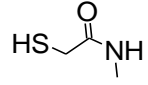
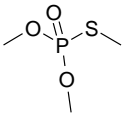
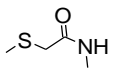
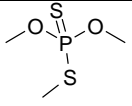
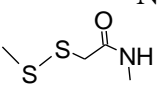
	32.9	302 (177, 157, 145, 126, 125, 109, 85, 79, 63, 58)	MT
DM	5.45	140 (110, 95, 79, 55)	 O,O,O-phosphoric acid trimethylester, compound <u>11</u>
	6.05	160 (130, 97, 79, 63, 47)	 Compound <u>1</u> .
	8.8	105 (73, 58)	 Compound <u>8</u>
	9.4	156 (141, 126, 110, 95, 79, 58)	 Compound <u>5</u>
	9.9	119 (73, 58)	 2-S- methyl-(N-methyl) acetamide, compound <u>10</u>
	11.3	172 (125, 93, 79)	 Compound <u>3</u>
	16.6	151 (105, 93, 79, 73, 58, 45)	 N-methyl, acetomethyldi- sulfide, compound <u>9</u>
	25.3	229 (125, 93, 87, 79, 63, 58, 47))	DM

Table 3[Click here to download Table: Table 3.docx](#)

Table 3

	[SO ₄ ^{•-}]	[Cl]	[Cl ₂ ^{•-}]	[HO [•]]
DM	0,03	0,19	94,56	5,22
MT	0.01	0,11	86,78	13,10

Figure 1

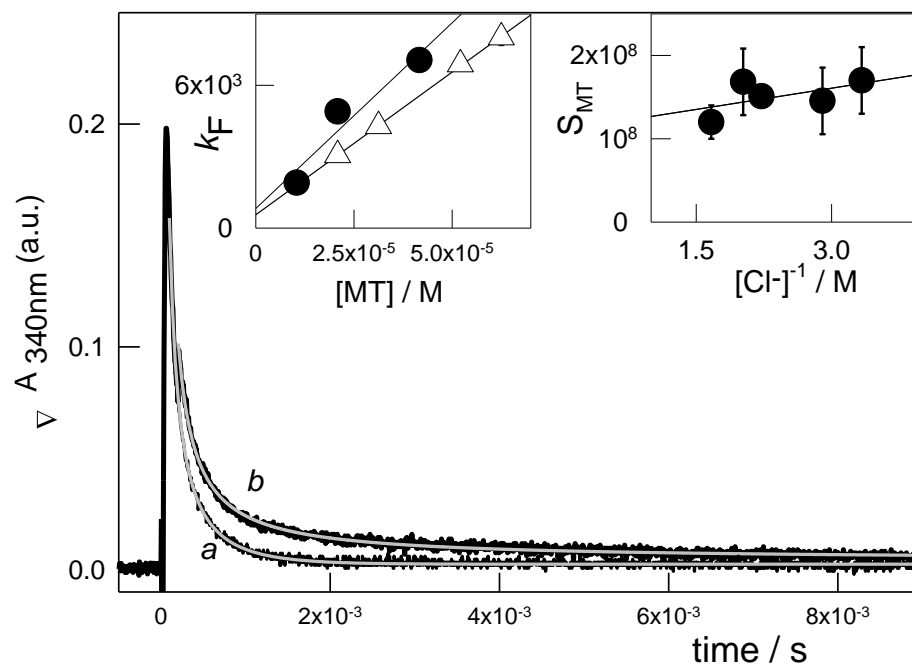


Figure 2

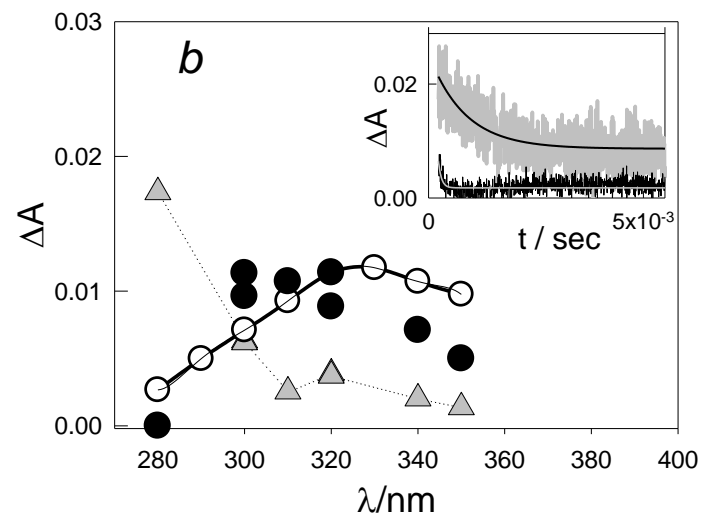
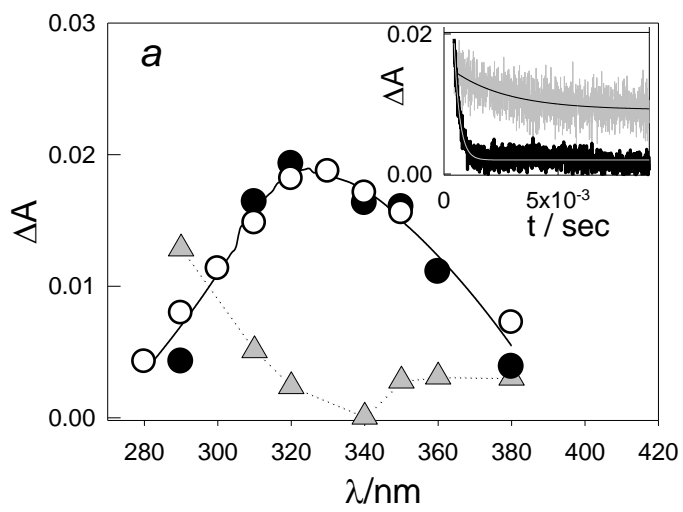


Figure 3

