

Chlorination of organophosphorus pesticides in natural waters

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Abstract

Unknown second-order rate constants for the reactions of three organophosphorus pesticides (chlorpyrifos, chlorfenvinfos and diazinon) with chlorine were determined in the present study, and the influence of pH and temperature was established. It was found that an increase in the pH provides a negative effect on the pesticides degradation rates. Apparent second-order rate constants at 20 °C and pH 7 were determined to be 110.9, 0.004 and 191.6 M⁻¹ s⁻¹ for chlorpyrifos, chlorfenvinfos and diazinon, respectively. A higher reactivity of chlorine with the phosphorothioate group (chlorpyrifos and diazinon) than with the phosphate moiety (chlorfenvinfos) could explain these results. Intrinsic rate constant for the elementary reactions of chlorine species with chlorpyrifos and diazinon were also calculated, leading to the conclusion that the reaction between hypochlorous acid and the pesticide is predominant at neutral pH.

The elimination of these pesticides in surface waters was also investigated. A chlorine dose of 2.5 mg L⁻¹ was enough to oxidize chlorpyrifos and diazinon almost completely, with a formation of trihalomethanes below the EU standard for drinking water. However, the removal of chlorfenvinfos was not appreciable. Therefore, chlorination is a feasible option for the removal of organophosphorus pesticides with phosphorothioate group during oxidation and disinfection processes, but not for the elimination of pesticides with phosphate moiety.

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1. Introduction

Pesticides are a group of artificially synthesized substances used in farms to control pests and to enhance agricultural production. However, the use of pesticides also represents a water quality risk in agricultural areas since these compounds can contaminate surface waters and groundwaters. The fate of pesticides under drinking water treatment conditions is a concern due to the potential adverse health effects of consuming contaminated potable water [1]. Most pesticides present in surface water are not removed or transformed during physical-chemical treatment processes (coagulation/flocculation, sedimentation, and filtration) [2]. Therefore, more efficient processes, such as chemical oxidation or activated carbon adsorption, are needed to remove pesticides during drinking water production.

The European Water Framework Directive (WFD), Directive 2000/60/EC, establishes a new framework for Community action in the field of water policy. This WFD includes a list

of 33 priority substances which represent a significant risk to the European aquatic environment (Decision No. 2455/2001/EC of the European Parliament and of the Council of 20 November 2001). Several water-soluble pesticides are included in the above mentioned list, some of them corresponding to the organophosphorus pesticide group, such as chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] and chlorfenvinfos [*O,O*-diethyl-*O*-1-(2',4'-dichlorophenyl)-2-chlorovinyl-phosphate]. Diazinon [*O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate], although is not included in the list of priority substances, has been included in the present research because of the widely use in agricultural practices and moderate toxicity. Concern about this group of pesticides arises from the large amount applied and their persistence in the environment, since these compounds are toxic and can also affect the central nervous systems of humans [3].

In order to achieve an adequate control of pesticides in drinking water, it is necessary to know details of their behavior, not only in water resources, but also in the water purification processes. The chemical oxidants commonly applied in drinking water treatment are ozone and chlorine. Previous studies focused on the ozonation of organophosphorus pesticides reported that

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these compounds are generally reactive towards ozone, being phosphate derivatives more resistant to ozonation than thiophosphate derivatives [4–8]. However, very few studies are focused on the chlorination of organophosphorus pesticides. The chlorination of chlorpyrifos has been investigated by Wu and Laird [9] and Duirk and Collette [10], who reported that chlorpyrifos oxon is the main degradation byproduct. Similarly, diazinon is oxidized by chlorine to diazinon oxon [11]. Apparent second-order rate constants for the chlorination of chlorpyrifos and diazinon have been determined at neutral or basic pH [10,11]. The oxidation of chlorfenvinfos with chlorine has not been investigated yet. The oxidant selected in the present work was chlorine because it is used worldwide in large quantities for preoxidation treatments and final disinfection [12]. Chlorine reacts mainly with activated aromatic systems, neutral amines and double bonds, leading to the formation of halogenated organic compounds, some of which exhibit a potentially carcinogenic activity (trihalomethanes (THMs) and haloacetic acids (HAAs)) [13].

The objectives of the present study were the determination of second-order rate constants for the reaction of chlorine with chlorpyrifos, chlorfenvinfos and diazinon and the establishment of the influence of some operating variables, such as pH and temperature, on chlorination rate constants. In addition, a reaction mechanism was proposed allowing the calculation of intrinsic rate constants for the elementary reactions of each pesticide with chlorine species (hypochlorous acid and hypochlorite). Finally, the oxidation of the selected pesticides by chlorine in a natural water was investigated in order to verify the validity of the previously determined rate constants, assess the formation of THMs, and evaluate the efficiency of chlorine treatment for pesticide removal.

2. Experimental

Chlorpyrifos was obtained from Supelco (Bellefonte, PA) at 99.5% purity and chlorfenvinfos and diazinon were purchased from Riedel de Haën (Seelze, Germany) at 97.2 and 99.0% purity, respectively. Other chemicals were of analytical grade or higher. Solutions of pesticides, analytical reagents, chlorine, and phosphate buffers were prepared with ultra-pure water produced from a Milli-Q (Millipore) water purification system. Stock solutions of chlorine were prepared by diluting a commercial solution of sodium hypochlorite (4% active chlorine, Panreac) and standardized spectrophotometrically in presence of excess of iodide to form triiodine (ϵ at 351 nm = 25700 M⁻¹ cm⁻¹) [14].

2.1. Analytical methods

Concentrations of pesticides were determined by HPLC, using a Waters Chromatograph equipped with a 2487 Dual Absorbance Detector and a Waters Nova-Pak[®] C18 Column (15 cm × 0.39 cm). The pesticides detection was performed at 230, 245 and 248 nm for chlorpyrifos, chlorfenvinfos and diazinon, respectively. The mobile phase was composed of a mixture methanol-aqueous solution of phosphoric acid 1 × 10⁻² M (78:22 in volume for chlorpyrifos and 68:32 for chlorfenvin-

fos and diazinon), the elution flow rate was 1 mL min⁻¹ and the injection volume was 50 μL. In the experiments performed with the mixture of pesticides dissolved in natural waters, a gradient elution of methanol (A) and aqueous solution of phosphoric acid 1 × 10⁻² M (B) was used by varying the volume percentage of A from 60 to 80% over 15 min.

The chlorine concentration in natural water experiments was analyzed by the ABTS method [15]. Spectrophotometric measurements were performed with a Unicam Helios β spectrophotometer. pH measurements were carried out with a Crison electrode and a Crison GLP-22 pH-meter, which was calibrated with standard buffer solutions (Crison). THM concentrations were measured by gas chromatography (GC), using head space (HS) injection and electron capture detection (ECD), according to a method adapted from Golfinopoulos et al. [16].

2.2. Rate constants of chlorine with chlorpyrifos, chlorfenvinfos and diazinon

Chlorination experiments of each pesticide were conducted under pseudo-first-order conditions, where chlorine was at least 15 folds in excess. The temperature was varied in the range 11–30 °C (for chlorpyrifos) and the pH between 5 and 9 with 10 mM phosphate buffer. In a typical experiment, a 100 mL volume of buffered pesticide solution (4 μM for chlorpyrifos and chlorfenvinfos and 10 μM for diazinon) was prepared in a batch reactor (serum vial of 110 mL), which was capped with PTFE-faced silica septum and located in a thermostatic bath. The experiments were started after addition of an aliquot of the chlorine stock solution into the reactor while stirring (for 5 s). The initial chlorine concentration ranged from 1.2 × 10⁻³ to 5.5 × 10⁻⁵ M. At fixed time intervals, 2 mL of sample was rapidly transferred with a syringe into a HPLC vial containing 10 μL of thiosulfate (0.1 M) to stop the reaction. The residual pesticide concentrations were analyzed directly by HPLC.

2.3. Experiments with natural water

To investigate the oxidation of pesticides by chlorine in natural waters, some experiments were performed with surface water from Lake Villar del Rey (VR), located in the South-West of Spain (pH 7.3, DOC = 6.7 mg L⁻¹, [bicarbonate] = 0.6 mM, [ammonia] = 2.3 μM). This water was filtered through a 0.45 μm cellulose nitrate filter within 24 h after collection and stored at 4 °C until use. In addition, some experiments were performed with VR water after a previous treatment (Pretreated water, PT) which consisted of coagulation with aluminium sulfate, followed by flocculation by means of a commercial anionic polyelectrolyte and sedimentation during 8 h (pH 7.3, DOC = 4.5 mg L⁻¹, [bicarbonate] = 0.3 mM, [ammonia] = 2.1 μM). The initial dose of chlorine was 3 mg L⁻¹, typical of preoxidation or intermediate oxidation steps during drinking water treatment. These experiments were performed at pH 7 (by buffering the water sample with phosphate, 10 mM) and 20 °C in a batch reactor of 500 mL. The initial concentrations of pesticides spiked into the water samples were 1 μM.

Two samples were withdrawn periodically from the reactor: the first one for residual chlorine analysis; and the second for pesticides and THMs analysis after quenching the excess of chlorine with thiosulfate.

In addition, some experiments were performed in static dose mode by varying the initial chlorine concentration (0–3 mg L⁻¹). These experiments were started by adding different amounts (in the order of μ L) of the chlorine stock solution to aliquots of 17 mL of buffered pesticides solutions (1 μ M). The residual pesticide and THMs concentrations were analyzed after 24 h, time enough for complete chlorine consumption.

3. Results and discussion

3.1. Kinetics of the reaction of chlorine with chlorpyrifos, chlorfenvinfos and diazinon

The rate constant for the reaction of chlorine with the selected organophosphorus pesticides was investigated under pseudo-first-order conditions ([chlorine] \gg [pesticide]) in a batch system, and varying the pH in the range 5–9 (experimental conditions given in Table 1). Previous investigations on chlorination of several groups of organic micropollutants such as phenolic derivatives and pharmaceuticals over a wide pH range have demonstrated that the reaction between chlorine and organic compounds could be described by second-order kinetics, first-order in active oxidant (HOCl + OCl⁻) and first-order in organic compound [17,18]. Based on these studies, it can be assumed that the reaction of chlorine with the selected pesticides (P) follows second-order kinetics:

$$-\frac{d[P]}{dt} = k_{app}[P][Cl_2]_t = k_{obs}[P] \quad (1)$$

where k_{app} is the apparent second-order rate constant (pH-dependent as will be discussed later), $[Cl_2]_t$ is the total

Table 1
Chlorination experiments performed at pH 7.2 and 20 °C with chlorpyrifos (CPF), chlorfenvinfos (CVF) and diazinon (DZN)

Experiment	[chlorine] (M)	T (°C)	pH	$k_{obs} \times 10^3$ (s ⁻¹)	R ²
CPF1	5.5×10^{-5}	20	7	6.18	0.995
CPF2	8.2×10^{-5}	20	7	9.07	0.993
CPF3	1.1×10^{-4}	20	7	12.28	0.997
CPF4	5.5×10^{-5}	20	5	16.45	0.995
CPF5	5.5×10^{-5}	20	6	8.67	0.974
CPF6	5.5×10^{-5}	20	8	1.33	0.993
CPF7	5.5×10^{-5}	20	9	0.21	0.993
CPF8	5.5×10^{-5}	11	7	4.42	0.984
CPF9	5.5×10^{-5}	30	7	9.74	0.976
CVF1	1.2×10^{-3}	20	6	0.006	0.996
CVF2	1.2×10^{-3}	20	7	0.005	0.991
CVF3	1.2×10^{-3}	20	8	0.004	0.989
CVF4	1.2×10^{-3}	20	9	0.003	0.993
DZN1	1.5×10^{-4}	20	5	181.43	0.981
DZN2	1.5×10^{-4}	20	6	66.39	0.991
DZN3	1.5×10^{-4}	20	7	28.74	0.996
DZN4	1.5×10^{-4}	20	8	9.36	0.997
DZN5	1.5×10^{-4}	20	9	1.69	0.997

[CPF]₀ = 4 μ M; [CVF]₀ = [DZN]₀ = 10 μ M.

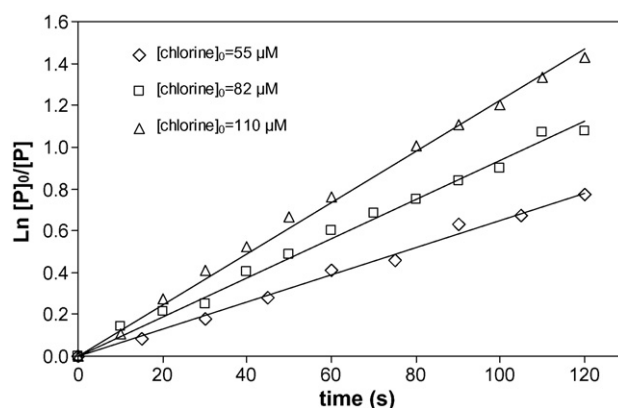


Fig. 1. Pseudo-first-order kinetic plot for the chlorination of chlorpyrifos at 20 °C and pH 7.0. The solid line is a linear least-squares regression of the data.

concentration of chlorine species (HOCl + ClO⁻) and k_{obs} is the pseudo-first-order rate constant. The total chlorine concentration remained almost constant during the reaction time, thus being $k_{obs} = k_{app} [Cl_2]_{t0}$. The integration of Eq. (1) leads to:

$$\ln \frac{[P]_0}{[P]} = k_{obs} t \quad (2)$$

Therefore, the representation of the first term of Eq. (2) versus time must lead to a straight line for each experiment. Fig. 1 presents the results from experiments performed with chlorpyrifos at a range of chlorine concentrations and at pH 7.0 (Experiments CPF1-CPF3 in Table 1). As can be observed, points lie satisfactorily around straight lines, whose slopes are the pseudo-first order rate constants. After linear regression analysis ($r^2 > 0.99$), the calculated values of k_{obs} are summarized in Table 1. The reaction order with respect to chlorine was determined from a plot of k_{obs} values versus the initial concentration of chlorine (data not shown). A linear plot could be drawn ($r^2 > 0.99$), which confirms that the rate of chlorpyrifos disappearance is also first-order with respect to chlorine concentration. From the slope of this plot, the apparent second-order rate constant at pH 7.0 was determined to be $110.9 \text{ M}^{-1} \text{ s}^{-1}$. The rate of chlorpyrifos disappearance, therefore, is first-order in the concentrations of chlorine and pesticide. Similarly, the rate of chlorfenvinfos and diazinon chlorination can be considered of second-order, and consequently, k_{app} has been determined dividing k_{obs} by the initial chlorine concentration for the remaining experiments.

The temperature effect on the apparent second-order rate constant for the chlorination of chlorpyrifos was investigated in the range 11–30 °C in experiments performed with similar concentration of chlorpyrifos (4 μ M) and chlorine (55 μ M) at pH 7.0 (Table 1). The obtained values for the apparent second-order rate constant were 80.4, 110.9 and $177.1 \text{ M}^{-1} \text{ s}^{-1}$ at 11, 20 and 30 °C, respectively. The activation energy was calculated to be 29.6 kJ mol^{-1} . This activation energy is similar to 30.0 kJ mol^{-1} proposed by Zhang and Pehkonen [11] for the chlorination of diazinon. The activation energy for the chlorination of chlorfenvinfos and diazinon were not investigated in the present study, although the values above discussed for chlor-

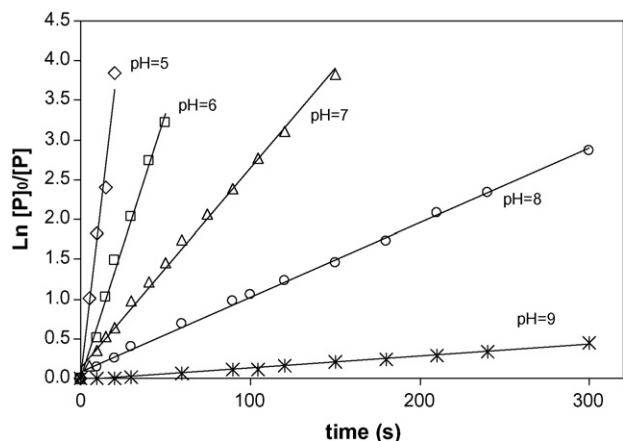


Fig. 2. Influence of the pH on the pseudo-first-order rate constant for the chlorination of diazinon at 20 °C. Initial concentrations of diazinon and chlorine were 1×10^{-5} and 1.5×10^{-4} M, respectively. The solid line is a linear least-squares regression of the data.

pyrifos and diazinon leads to the conclusion that the activation energy for the chlorination of organophosphorus pesticides is around 30 kJ mol^{-1} .

The influence of the pH was investigated in the pH range of 5–9 in experiments performed with similar initial concentration of both chlorine and pesticide (Table 1). Fig. 2 shows the first-order plot for the group of experiments performed with diazinon, taken as an example (Expts. DZN1 to DZN5 in Table 1). Again, the experimental results obtained for the chlorination of diazinon fit well a pseudo-first-order kinetic model. From the experimental values of k_{obs} (Table 1), k_{app} was determined for each pesticide at each pH, being the obtained values presented in Table 2. While chlorpyrifos and diazinon react with chlorine at a moderate rate, the chlorination rate of chlorfenvinfos is almost negligible. Therefore, the reactivity order is diazinon > chlorpyrifos >> chlorfenvinfos. Moreover, it can be observed in Table 2 that the oxidation of the selected pesticides is favored at low pHs.

This pH-dependence was described by considering the speciation of chlorine (reaction 3, pK_{a3} 7.5 [19]), the acid-catalyzed reaction of HOCl with the pesticide (reaction 4), and the reactions of the pesticide with HOCl (reaction 5) and OCl^- (reaction 6).

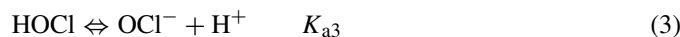


Table 2
Apparent second-order rate constants ($\text{M}^{-1} \text{s}^{-1}$) for the chlorination of the selected pesticides at different pHs

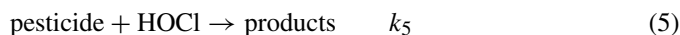
pH	Chlorpyrifos	Chlorfenvinfos	Diazinon
5	299.1	nd	1209.5
6	157.6	0.005	442.6
7	110.9	0.004	191.6
8	24.2	0.003	62.4
9	3.8	0.002	11.3

nd: not determined.

Table 3

Intrinsic rate constants for the elementary reactions of chlorine species with chlorpyrifos and diazinon

Rate constant	Chlorpyrifos	Diazinon
k_4 ($\text{M}^{-2} \text{s}^{-1}$)	1.56×10^7	1.04×10^8
k_5 ($\text{M}^{-1} \text{s}^{-1}$)	144.1	264.9
k_6 ($\text{M}^{-1} \text{s}^{-1}$)	<1	3.2



From this reaction set, the elimination of a particular pesticide can be written as follows:

$$-\frac{d[\text{P}]}{dt} = (k_4[\text{HOCl}][\text{H}^+] + k_5[\text{HOCl}] + k_6[\text{OCl}^-])[\text{P}] \quad (7)$$

Taking into account the speciation of chlorine (reaction 3), Eq. (7) is transformed into Eq. (8):

$$-\frac{d[\text{P}]}{dt} = \left[(k_4[\text{H}^+] + k_5) \left(\frac{[\text{H}^+]}{[\text{H}^+] + K_{a3}} \right) + k_6 \left(\frac{K_{a3}}{[\text{H}^+] + K_{a3}} \right) \right] [\text{P}][\text{Cl}_2]_t \quad (8)$$

where $[\text{Cl}_2]_t = [\text{HOCl}] + [\text{OCl}^-]$. Finally, by comparing Eq. (1) and Eq. (8), the apparent second-order rate constant at each pH, k_{app} , is given by Eq. (9):

$$k_{\text{app}} = \frac{k_4[\text{H}^+]^2 + k_5[\text{H}^+] + k_6 K_{a3}}{(K_{a3} + [\text{H}^+])} \quad (9)$$

Eq. (9) allowed the evaluation of the intrinsic rate constants for the elementary reactions, which were determined by a non-linear least-squares regression of the experimental pH profile of k_{app} . The obtained values for k_4 , k_5 and k_6 for the chlorination of chlorpyrifos and diazinon are detailed in Table 3. These calculations were not performed for chlorfenvinfos due to fact that its low reactivity with chlorine might introduce considerable relative errors on the values of these intrinsic rate constants. At the same time, Fig. 3 depicts the experimental and

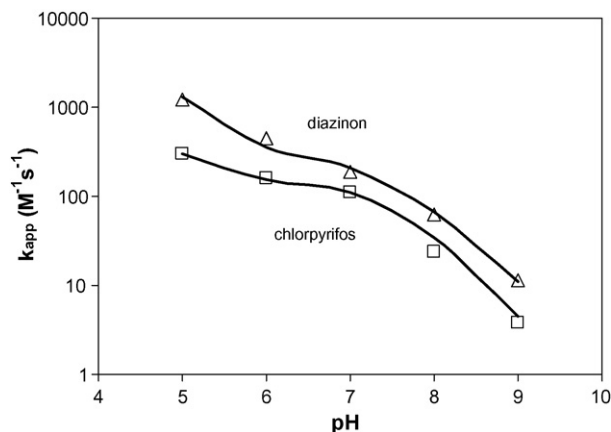


Fig. 3. pH-dependence of the apparent rate constants for the reaction of chlorine with chlorpyrifos and diazinon. The lines are calculated according to Eq. (9).

theoretical (calculated from Eq. (9) and the values of intrinsic rate constants) pH profiles of the apparent second-order rate constants for the reaction of chlorpyrifos and diazinon with chlorine. The reasonable good agreement between the experimental values (symbols) and the calculated (lines) confirms the proposed reaction set. The continuous decrease of k_{app} in the pH range from 5 to 9 indicates that the main reaction pathway at circumneutral pH range is the reaction between the pesticide and HOCl (reaction 5). In effect, the acid catalyzed reaction becomes important at $pH < 5$ and the rate constant for reaction 6 is two orders of magnitude smaller than the corresponding rate constant for reaction 5 (Table 3). Therefore, the acid catalyzed reaction of the pesticide with HOCl (reaction 4) as well as the reaction of the pesticide with OCl^- (reaction 6) can be considered as negligible during chlorination of natural waters (pH region 6–8). As a consequence of the negative effect, the pH of the natural water must be adjusted to below 7.5–8 during the chlorination process to ensure adequate pesticides removal.

This negative pH-dependence of the chlorination rate of the selected pesticides confirms the results reported by Duirk and Collette [10] for chlorpyrifos and by Zhang and Pehkonen [11] for diazinon. These authors determined intrinsic rate constants for the reactions between chlorine species and the pesticides. Thus, Duirk and Collette [10] investigated the chlorination of chlorpyrifos over the pH range of 6.3–11 and proposed a value of $477.8 M^{-1} s^{-1}$ for the rate constant of the reaction between HOCl and chlorpyrifos, higher than $144.1 M^{-1} s^{-1}$ determined in the present study. This difference could be due to the fact that the acid-catalyzed reaction (reaction 4) was not included by Duirk and Collette [10] in their reaction set, and therefore, the value proposed for reaction 5 is overestimated. The acid-catalyzed reaction has been included in the chlorination reaction set of different organic pollutants such as phenolic compounds [17], pharmaceuticals [18] and cyanotoxins [20] to explain the increase in the reaction rate observed at pH below 6. Similarly, Zhang and Pehkonen [11] studied the chlorination of diazinon in the pH range of 9.5–11, and determined for its reaction with HOCl (reaction 4) a rate constant of $130 M^{-1} s^{-1}$, which is lower than $264.9 M^{-1} s^{-1}$ determined in the present study. Zhang and Pehkonen [11] did not include the acid-catalyzed reaction and calculated the rate constants for the elementary reactions from values of k_{app} determined at high pHs (9.5–11). These calculations (with extrapolation from high pHs to neutral pH) might introduce a considerable relative error in the rate constant of reaction 5, which is predominant at circumneutral pH. Moreover, according to the rate constants published in these previous studies, chlorine would react faster with chlorpyrifos than with diazinon at neutral pH, in opposition to the reactivity order deduced in the present study. In order to clarify this controversy, competitive chlorination experiments have been performed with these pesticides in natural waters, being the obtained results discussed later.

On the other hand, chlorine reacts with the phosphorothioate subgroup of organophosphorus pesticides, oxidizing the thiophosphate moiety (P=S) to the corresponding oxon (P=O) [9–11]. The oxidation products formed, chlorpyrifos oxon and diazoxon, are relatively stable in the presence of chlorine at pH

7. Therefore, it is assumed that the oxons are resistant to further oxidation by aqueous chlorine. Oxidation products from chlorine attack on a different location of the pesticide molecule have not been identified. These results explain the moderate reactivity of chlorpyrifos and diazinon (both with the P=S moiety) to form chlorpyrifos oxon and diazoxon, and the almost negligible reactivity of chlorfenvinfos (with the P=O moiety). Then, it can be concluded that organophosphorus pesticides with phosphorothioate moiety can be oxidized by chlorine to the corresponding oxon derivative, while organophosphorus pesticides with phosphate moiety are very stable in the presence of chlorine. However, the oxon form is more susceptible to neutral and alkaline hydrolysis compared to the parent pesticide [21].

3.2. Oxidation of organophosphorus pesticide during chlorination of natural waters

The elimination of the selected pesticides in Lake Villar del Rey and Pretreated waters was investigated in order to assess the validity of the rate constants previously determined and to evaluate the efficiency of the chlorination process with respect to pesticides removal and disinfection byproducts formation. Time-resolved experiments were run with an initial chlorine dose of $3 mg L^{-1}$, typically found in full-scale drinking water treatments where chlorine is used in the preoxidation or intermediate oxidation steps. The initial pesticide dose spiked into the water was $1 \mu M$ and the pH and temperature were kept constants at 7 and $20^\circ C$, respectively.

Fig. 4 shows the results obtained in the experiment performed with Lake Villar del Rey water. It can be observed a fast initial chlorine decay due to fast reactions of chlorine with organic and inorganic matter present in the water (instantaneous chlorine demand). Then, chlorine consumption becomes slower until complete depletion which was reached after 4 h. Diazinon elimination was very fast, being completely removed after 10 min with the mentioned chlorine concentration of $3 mg L^{-1}$. Oxidant exposure (CT-value) needed to eliminate diazinon was calculated to be $35.3 mg min L^{-1}$. Chlorpyrifos oxidation was also fast, being almost completely oxidized after 1 h. The CT-value required for complete chlorpyrifos removal

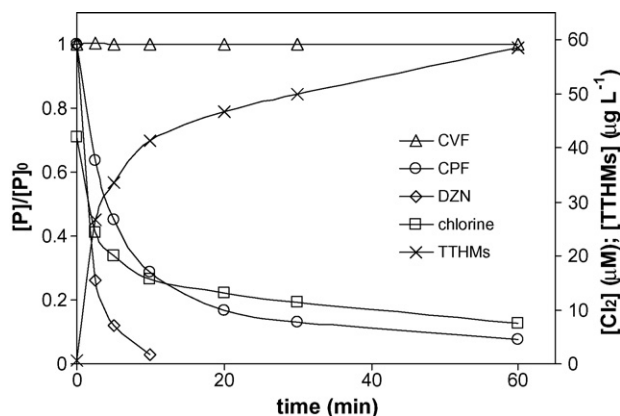


Fig. 4. Chlorine residual, pesticide removal and TTHMs formation in the experiment performed with Lake Villar del Rey water at pH 7 and $20^\circ C$.

was $55.5 \text{ mg min L}^{-1}$. However, chlorfenvinfos oxidation was not appreciable, being its concentration fairly constant during the chlorination experiment. As a consequence of these results, the reactivity order for the chlorination of the investigated pesticides is diazinon > chlorpyrifos > chlorfenvinfos. This reactivity order is in accordance with the values of the apparent rate constants determined for the chlorination of these three pesticides at pH 7 in ultra-pure water.

A negative consequence of the chlorination process is the formation of disinfection byproducts, especially THMs. The formation of THMs during the chlorination process has also been measured, being the total concentration (TTHMs) formed in the experiment carried out with Lake Villar del Rey water depicted in Fig. 4. The TTHMs concentration increased continuously up to $85 \mu\text{g L}^{-1}$ when chlorine was completely consumed. This TTHMs is close to the EU standard value of $100 \mu\text{g L}^{-1}$ in drinking water [22]. However, the TTHMs concentration was about $60 \mu\text{g L}^{-1}$ after one hour, when diazinon and chlorpyrifos were almost completely oxidized (Fig. 4). Chloroform was the dominant THM (around 60–70 % of TTHMs), followed by bromodichloromethane. The formation of chlorodibromomethane and especially of bromoform was not significant.

Similar trends were obtained in the time-resolved experiment carried out with Pretreated water and 3 mg L^{-1} of chlorine. Since the organic content of this water was lower (DOC of 4.5 mg L^{-1} versus 6.7 mg L^{-1} in Lake Villar del Rey water), chlorine consumption was slower, leading to a higher chlorine exposure. As a consequence, the oxidation rate of diazinon and chlorpyrifos was higher, being completely oxidized within 30 min. The oxidation of chlorfenvinfos was again not appreciable. At the same time, the formation of TTHMs was lower, only $38 \mu\text{g L}^{-1}$ after 30 min, and with a final concentration after complete chlorine consumption of $61 \mu\text{g L}^{-1}$.

The results obtained in the static dose experiments performed with Lake Villar del Rey and Pretreated waters are depicted in Fig. 5. It can be observed a positive influence of the initial chlorine concentration on pesticide removal and on the formation of THMs. The complete elimination of diazinon and chlorpyrifos was reached with chlorine doses of 3 and 2.5 mg L^{-1} in Lake Villar del Rey and Pretreated waters, respectively. However, the elimination of chlorfenvinfos was not appreciable due to its low reactivity with chlorine. The reactivity order for the chlorination of these pesticides (diazinon > chlorpyrifos >> chlorfenvinfos) agrees with the values of the second-order rate constants at pH 7 shown in Table 2. With the chlorine dose required for diazinon and chlorpyrifos removal, the final TTHMs formation was below 90 and $40 \mu\text{g L}^{-1}$ in Lake Villar del Rey and Pretreated waters, respectively, and therefore, below the maximum value of $100 \mu\text{g L}^{-1}$ permitted by EU regulations. As a result, TTHMs formation is not a limiting factor for the oxidation of chlorpyrifos and diazinon in natural waters by chlorine. However, if chlorfenvinfos had to be oxidized by chlorine, the chlorine doses and stability in the surface water required would be very high, which would lead to a TTHMs formation considerable above the EU drinking water standard. Again, pesticide removal was greater in the Pretreated water while the TTHMs formation was lower because of the lower organic matter content.

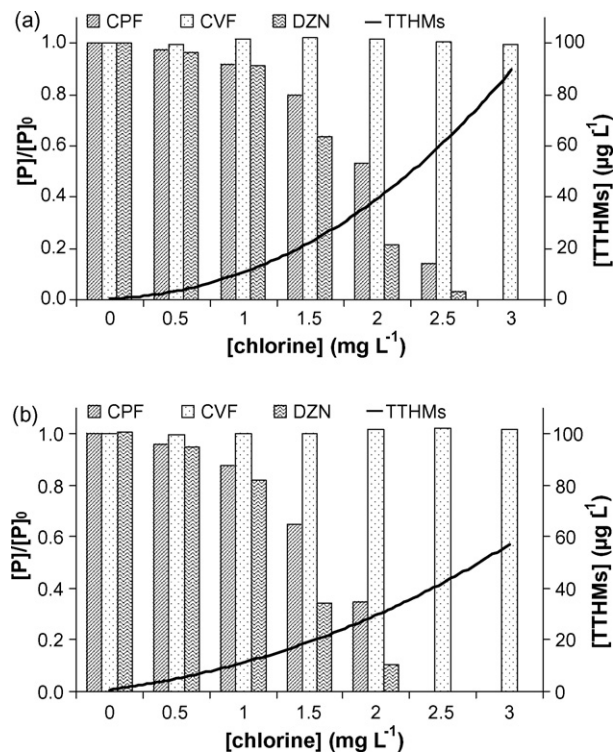


Fig. 5. Influence of the initial chlorine dose on the pesticide oxidation and TTHMs formation in experiments performed in static dose mode with Lake Villar del Rey (a) and Pretreated (b) waters at pH 7 and 20°C .

As a consequence, chlorine application in a preoxidation or intermediate oxidation steps within drinking water treatment train is a feasible option for the removal of diazinon and chlorpyrifos. However, chlorine is not a suitable oxidant for chlorfenvinfos elimination. Therefore, chlorine can only be applied for the removal of organophosphorus pesticides with phosphorothioate moiety. Instead, ozone or advanced oxidation processes must be applied in the treatment of natural waters contaminated with organophosphorus pesticides with phosphate functionality such as chlorfenvinfos [8].

As it was explained before, the rate constants for the reactions of chlorine with the selected pesticides were determined in Milli-Q water. It is interesting to evaluate whether these rate constants can be applied to predict the oxidation of pesticides in natural waters. In order to perform this evaluation, a kinetic model has been formulated allowing us to predict the pesticide elimination in natural water from the chlorine decay and the previously calculated rate constants. Thus, with the experimental chlorine concentrations, the chlorine exposure (CT value), defined as the integral of chlorine concentration over the reaction time, was determined. Then, with the CT value and the rate constants, the concentration of pesticide can be calculated from Eq. (10), where k_{app} is the apparent second-order rate constant for the reaction of chlorine with the pesticide under consideration:

$$[P] = [P]_0 \exp(-k_{\text{app}}CT) = [P]_0 \exp\left(-k_{\text{app}} \int_0^t [\text{Cl}_2] dt\right) \quad (10)$$

For this purpose, k_{app} at the desired pH have been calculated from Eq. (9) and the values of the intrinsic rate constants

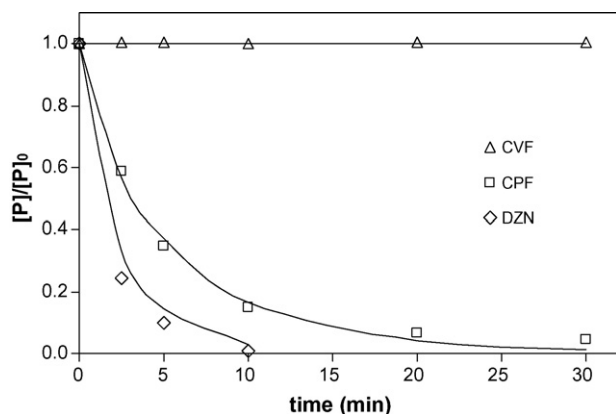


Fig. 6. Experimental results (symbols) and predicted values (lines) for the pesticide oxidation during the chlorination of Pretreated water ($[\text{chlorine}]_0 = 3 \text{ mg/L}$; $T = 20^\circ\text{C}$; $\text{pH} 7$).

reported in Table 3. This kinetic approach has been successfully applied to predict the oxidation of micropollutants with other oxidants such as ozone [23], permanganate [24] or chlorine dioxide [25]. Following this procedure, Fig. 6 illustrates the oxidation of the selected pesticides in Pretreated water (symbols represent experimental data; lines represent theoretical predictions). A fairly good coincidence between experimental and theoretical values can be observed, which demonstrates that the rate constants determined in pure water at high concentration of reactants can be used to predict the elimination of the selected pesticides during chlorination of natural waters if chlorine exposure is known.

3.3. Significance of organophosphorus pesticide chlorination in drinking water treatment processes

The efficiency of pesticide elimination during a chlorination process depends on the chlorine stability in the drinking water being treated, and on the reactivity of chlorine towards the pesticide. The chlorine stability varies with the natural water quality parameters such as NOM, ammonia and bromide concentrations, as well as with the treatment conditions (pH and temperature). Therefore, in order to predict pesticides removal, in addition to the knowledge of pesticides chlorination rate constants, chlorine decay kinetics has to be characterized for each particular water, for both an oxidation pretreatment and a final disinfection stage. In any case, the chlorination treatment is efficient if the pesticide concentration is reduced to levels below the drinking water standards, while meeting drinking water regulations with respect to THMs formation.

Based on the previously evaluated apparent second-order rate constants at several pHs, the half-life times showed in Fig. 7 were determined for chlorpyrifos at a constant residual chlorine concentration of 1 mg L^{-1} (typical of a primary disinfection stage) and 0.5 or 0.2 mg L^{-1} (typical of a final disinfection step). The elimination of chlorpyrifos takes place in the order of min at pH 6–7 and hours at pH above 8. As a consequence, pH is a key variable in the chlorination process and should be kept at around neutral or slightly acidic. Therefore, when calcium or sodium hypochlorite are used in high dose then the pH will

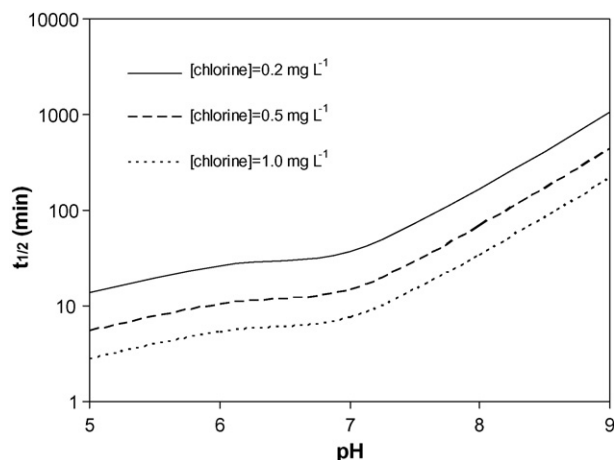


Fig. 7. Chlorpyrifos half-life values for chlorination at different pHs and 20°C . Initial chlorine concentrations (0.2 , 0.5 and 1.0 mg L^{-1}) were assumed to be constants.

need to be adjusted to below 8 to guarantee the efficiency of the process. Based on the higher values of the rate constants for the chlorination of diazinon, lower half-life times would be required for diazinon oxidation. However, the half-life times for chlorfenvinfos are above 100 days, not available in waterworks and distribution systems.

Half-life values included in Fig. 7 were calculated assuming a constant oxidant concentration during the overall treatment process, which is not a realistic situation. Instead, a parameter that includes the oxidant decay within the reactor is the oxidant exposure (CT). The CT value required for achieving a certain elimination of a pesticide in a batch process can be calculated from the following equation:

$$\text{CT} = \frac{-\ln([\text{P}]/[\text{P}]_0)}{k_{\text{app}}} \quad (11)$$

where $[\text{P}]_0$ and $[\text{P}]$ are the initial and final concentrations of pesticide, and k_{app} is the apparent second-order rate constant for the chlorination of the pesticide at a given temperature and pH.

Eq. (11) is also valid for an ideal plug-flow reactor (PFR), where the hydraulic residence time (HRT) is considered instead of reaction time. However, in drinking water treatment practices, full-scale reactors have non ideal flow behavior and can be considered as hybrid of PFR and completely stirred tank reactor (CSTR). The PFR and CSTR represent the most and least efficient reactor configurations, respectively [26]. In the extreme case of ideal CSTR, the CT required to oxidize a certain pesticide can be calculated from Eq. (12):

$$\text{CT} = \frac{([\text{P}]_0/[\text{P}] - 1)}{k_{\text{app}}} \quad (12)$$

Table 4 compiles the CT values required for the removal of 99% of chlorpyrifos and diazinon at several pHs (6–8) and temperatures (in the range 10 – 30°C) in a batch or plug-flow reactor. It can be observed the negative effect of the increasing pH and the positive influence of the increasing temperature on the required CT values. These CT values are comparable to those required for achieving 99.9% (3 log) inactivation of *Giardia* cyst and

Table 4

Chlorine exposure (CT, mg min L⁻¹) required to remove 99% of chlorpyrifos and diazinon and to eliminate 99.9% of *Giardia cyst* and 99.99% of viruses in a PFR or a CSTR

T (°C)	pH	PFR				CSTR	
		CPF	DZN	<i>Gia. Cysts</i>	Virus	CPF	DZN
10	7	67.8		130	6	1457.1	
20	7	49.1	28.4	65	3	1056.3	611.4
30	7	30.8		40	2	661.5	
20	6	34.6	12.3	45	3	743.3	264.7
20	8	225.2	87.3	95	3	4840.9	1877.4

one order of magnitude higher than those required for achieving 99.99% (4 log) inactivation of viruses at pH 6 through 8 (CT values for *Giardia cyst* and viruses published by the USEPA [27]). However, the pH influence is more pronounced in chlorpyrifos and diazinon elimination than in bacteria or viruses disinfection.

Table 4 also collects the CT values required for the oxidation of 99% of chlorpyrifos and diazinon at several pHs and temperatures in a CSTR. The CT values are around 20 times higher than the corresponding to PFR. These calculations are an example of the best and worst cases of operating conditions for the removal of chlorpyrifos and diazinon and might serve for establishing safety chlorine dose in oxidation or disinfection processes.

4. Conclusions

The reactions of chlorpyrifos, chlorfenvinfos and diazinon with chlorine in ultra-pure water fit overall second-order kinetics over a wide pH range, first-order with respect to both pesticide and chlorine. It was found that an increase of pH has a negative effect on the apparent second-order rate constants, and therefore, on the pesticide degradation rate. From these apparent second-order rate constants, intrinsic rate constants for the elementary reactions of chlorpyrifos and diazinon with aqueous chlorine species (hypochlorous acid and hypochlorite) were evaluated. The results indicate that the main reaction at circum-neutral pH range is the reaction between the pesticide and HOCl. The reactivity order of the investigated pesticides with chlorine is diazinon > chlorpyrifos >> chlorfenvinfos. Chlorine reacts with the phosphorothioate subgroup of diazinon and chlorpyrifos to form the corresponding oxon (P=O) derivatives, which are resistant to further chlorine attack. Therefore, chlorfenvinfos, which posses the P=O moiety, is very stable in the presence of chlorine.

Experiments performed with natural waters spiked with the studied pesticides demonstrated that chlorine doses of 2.5 mg L⁻¹ were enough to oxidize diazinon and chlorpyrifos almost completely. However, chlorfenvinfos removal was negligible. With this chlorine dose, the formation of THMs was below the EU standard for drinking water. From these results, it can be concluded that chlorination is a suitable option for oxidation of diazinon and chlorpyrifos during drinking water treatment, whereas the oxidation of chlorfenvinfos is too slow and requires a high chlorine concentration that would lead to TTHMs formation above the EU standard for drinking water.

The chlorine exposure (CT values) required to reduce 99% of chlorpyrifos in batch or PFR are comparable to those required for achieving 99.9% (3 log) inactivation of *Giardia cyst* and one order of magnitude higher than those required for achieving 99.99% (4 log) inactivation of viruses at pH 6 through 8. These results lead to the conclusion that chlorpyrifos and diazinon can be readily oxidized during drinking water disinfection with chlorine.

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