An experimental study of the gas-phase reaction between Cl atoms and *trans*-2-pentenal: Kinetics, products and SOA formation

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ABSTRACT

The gas-phase reaction of *trans*-2-pentenal (T2P) with Cl atoms was studied at atmospheric pressure and room temperature. A rate coefficient of $(2.56 \pm 0.83) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained using the relative rate method and isoprene, cyclohexane and ethanol as reference compounds. The kinetic study was carried out using a 300-L Teflon bag simulation chamber (IMT Lille Douai-France) and a 16-L Pyrex cell (UCLM-Ciudad Real-Spain), both coupled to the Fourier transform infrared (FTIR) technique. Gas-phase products and secondary organic aerosol (SOA) formation were studied at UCLM using a 16-L Pyrex cell and a 264-L quartz simulation chamber coupled to the FTIR and gas-chromatography-mass spectrometry (GC-MS) techniques. HCl, CO, and propanal were identified as products formed from the studied reaction and quantified by FTIR, the molar yield of the latter being $(5.2 \pm 0.2)\%$. Formic acid was identified as a secondary product and was quantified by FTIR with a yield of $(6.2 \pm 0.4)\%$. In addition, 2-chlorobutanol and 2-pentenoic acid were identified, but not quantified, by GC-MS as products. The SOA formation was investigated using a fast mobility particle sizer spectrometer. The observed SOA yields reached maximum values of around 7% at high particle mass concentrations. This work provides the first study of the formation of gaseous and particulate products for the reaction of Cl with T2P. A reaction mechanism is suggested to explain the formation of the observed gaseous products. The results are discussed in terms of structure-reactivity relationship, and the atmospheric implications derived from this study are commented as well.

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1. Introduction

It is well known that non-methane biogenic volatile organic compounds (BVOCs) account for approximately 90% of VOCs present in the atmosphere. BVOCs play an important role in the chemistry of the troposphere since their oxidation provides major reaction pathways for the formation of Secondary Organic Aerosols (SOAs) (Hoffmann et al., 1997; Griffin et al., 1999). In addition, the reactivity of BVOCs has an impact on the HO_x (OH + HO₂), NO_x (NO + NO₂) and the tropospheric ozone budgets. Therefore, it is important to understand the oxidation of BVOCs in the atmosphere to assess their role in the troposphere's chemistry. This is crucial for atmospheric models to predict the

formation of atmospheric photo-oxidants, SOA and the HO_x cycle (Kanakidou et al., 2005; Rudich et al., 2007).

Unsaturated aldehydes are BVOCs that may be emitted into the atmosphere from the enzymatic oxidation of linolenic and linoleic acids present in vegetation in response to stress (Winer et al., 1992; Hatanaka, 1993; Heiden et al., 2003; Seco et al., 2007).

They may also be formed in situ as a result of the oxidation of dienes in the atmosphere (Orlando and Tyndall, 2002). Besides their emission from biogenic sources, unsaturated aldehydes are also emitted into the atmosphere from anthropogenic sources such as the combustion of wood, polymers, tobacco and gasoline (Magneron et al., 2002) and from chemical industries (Crutzen and Graedel, 1986).

Atmospheric mixing ratios of unsaturated aldehydes are in the order of ppb. For instance, the mixing ratio of acrolein, the smallest unsaturated aldehyde, in several cities was reported to be up to 12 ppb (Seaman et al., 2006,). Larger unsaturated aldehydes, such as *trans*-2-pentenal (T2P), have also been detected in the atmosphere with mixing ratios of a few ppb in soybean seeds after anaerobic incubation (Gardner et al., 1996). T2P is also emitted by vegetation such as orange (Moshonas et al., 1973), tomato (Tandon et al., 2000) and black tea (Yamanishi et al., 1972). Besides, T2P is emitted directly from

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food products such as olive oil (Angerosa et al., 2000; Masella et al., 2019), milk powder (Cheng et al., 2019), wine (Saison et al., 2009; Martins et al., 2013), dry sausages, cheese and bread (Bianchi et al., 2007) or during food preparation as clam frying (Cheng et al., 2019). T2P has also been detected in human breath (Ruzsanyi et al., 2002) and cigarette smoke (Hatai et al., 2019). Further, this species is used to protect crop plants from pests and weeds (Rodríguez-Kabana et al., 2008).

Like other unsaturated aldehydes, once emitted into the atmosphere, T2P is expected to be removed mainly by reaction with OH and NO₃ radicals and by photolysis during the daytime (Houk, 1976; Calvert et al., 2011). However, reactions with chlorine (Cl) atoms may play an important role in the removal of these species in the atmosphere and maybe competitive with those due to the OH radicals. Heterogeneous ClNO₂ formation in polluted environments has been shown as a major route for the production of reactive gas-phase chlorine due to photolysis (Wang et al., 2019; Faxon et al., 2015). In coastal areas and in polluted northern hemisphere areas, the concentration of Cl atoms reaches 1×10^5 atoms cm⁻³ (Pszenny et al., 1993; Spicer et al., 1998; Ezell et al., 2002; Tackett et al., 2007) and 5×10^4 atoms cm⁻³ (Hos-saini et al., 2016), respectively, making the reactions of Cl with VOCs a potentially significant elimination route in the atmosphere for these species. Therefore, the study of these processes is necessary to assess the fate of these species in the atmosphere and to better evaluate the atmospheric implications of their oxidation processes.

To our knowledge, the rate coefficient for the T2P + Cl reaction (R1), k_{T2P} , was measured by Rodríguez et al. (2005) by a relative method at room temperature and an atmospheric pressure of air and N₂ in a Teflon bag using the GC-FID (Gas Chromatography-Flame Ionization Detector) method.

The value provided by Rodríguez et al., $(1.31 \pm 0.19) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, is the only experimental data for k_{T2P} . However, an estimation of k_{T2P} , calculated using the Structure-Activity Relationships (SARs) method, 3.47×10^{-10} cm³ molecule⁻¹ s⁻¹, is not in agreement with the experimental value (Teruel et al., 2009). This value is close to the gas kinetic limit for such a bimolecular elementary reaction. To elucidate this discrepancy, the present paper describes the determination of the rate coefficient k_{T2P} and aims at evaluating the impact of the Cl + T2P reaction in the removal of T2P in the atmosphere. In addition to the kinetic investigation, the identification and quantification of the gas-phase products and the SOA formation induced by reaction R1 are provided for the first time in the present work.

2. Materials and methods

2.1. Kinetic study

The kinetic study was carried out at 296 ± 2 K and 730 ± 20 Torr of air by a relative method using two set-ups described below.

2.1.1. D-ASC chamber (IMT Lille Douai, France)

A detailed presentation of this experimental set-up can be found elsewhere (Turpin et al., 2006), and only a brief description is given here. The Douai Atmospheric Simulation Chamber (hereafter D-ASC) is a 300-L Teflon bag enclosed inside a wooden box and equipped with a 2-L multiple-reflection optical cell with 10 m of optical path coupled to an FTIR spectrometer (Nicolet 550). The IR spectra of the gaseous samples (T2P and the reference compound and/or reaction products) were recorded with a resolution of 0.5 cm⁻¹ in the spectral range 4000–650 cm⁻¹ by accumulating 32 interferograms. In our experiments, Cl atoms were generated from the photolysis of molecular chlorine using 1 or 2 actinic lamps (Philips TMX 200 LS, emitting in the range 300–460 nm, $\lambda_{max} = 365$ nm), which were fixed on the internal walls of the box. All reactions were studied in purified zero air (relative humid-

ity < 2 ppm, CO and CO₂ < 80 ppb). T2P and the reference compounds were injected into the Teflon bag using syringes. The sampling was made automatically each 5 min for analysis by FTIR. At the end of each experiment, the Teflon bag and the optical cell were cleaned several times by filling with zero air followed by pumping.

2.1.2. 16-L cell (University of Castilla-La Mancha UCLM - Ciudad Real, Spain)

This experimental set-up was described in detail elsewhere (Balles-teros et al., 2009; Sleiman et al., 2014), and only a brief outline is provided here. It consists of a 16-L Pyrex White-type cell that has 96 m of optical path. The cell is equipped with a Nexus 870 Thermo Nicolet FTIR spectrometer. IR spectra were recorded with a resolution of 2 cm⁻¹ in the IR spectral range of 4000 to 650 cm⁻¹. The cell is surrounded by 4 actinic lamps (Philips TL-K 40 W, $\lambda_{max} = 365$ nm). All experiments were carried out in synthetic air (purity 99.999%, Air Liquide). The introduction of reactants in the gas-phase was done by expansion from a glass manifold system. At the end of each experiment, the cell was cleaned by filling with air and pumping down to 10⁻² mbar several times.

2.1.3. Rate coefficient determination

The relative rate coefficient of the gas-phase reaction of T2P with Cl was measured in the presence of a reference compound (isoprene, cyclohexane or ethanol) using either the D-ASC chamber or the 16-L cell. The experimental conditions used in this study are summarized in Table 1. The reactions of interest are the simultaneous reactions of T2P and the reference compound with chlorine atoms, with rate coefficients as k_{T2P} and k_{Ref} , respectively:

Before starting the kinetic study, tests were carried out to check the stability of T2P and the reference compounds by quantifying dark reactions (loss onto the walls and potential reaction with Cl₂) and photolysis processes. The loss rate coefficients due to dark reactions and to photolysis are defined as $k_{WL,X}$ and $k_{PL,X}$, where X could be either T2P or reference compound. The values are summarized in Table 1. The rate coefficients, k_L , accounting for all these secondary loss processes are included in Eq. (1). They typically represent from 6 to 15% of the logarithm components according to the reference compound employed in the experiments. The time evolution of the concentration of T2P and the reference compound is, then, described by the following expression:

$$\ln \left(\frac{[T2P]_0}{[T2P]_t} \right) - k_{L, T2P} t = \frac{k_{T2P}}{k_{Ref}} \left[\ln \left(\frac{[Ref]_0}{[Ref]_t} \right) - k_{L, Ref} t \right] \quad (\text{Eq. 1})$$

where $[T2P]_0$, $[Ref]_0$ and $[T2P]_t$, $[Ref]_t$ are the concentrations of T2P and the reference compound at times $t = 0$ and t , respectively, and $k_{L, T2P}$ and $k_{L, Ref}$ are the loss rate coefficients due to secondary processes for T2P and the reference compound, respectively. The linear least-square analysis at zero intercept of the $\ln([T2P]_0/[T2P]_t) - k_{L, T2P} t$ against $\ln([Ref]_0/[Ref]_t) - k_{L, Ref} t$ plot yields k_{T2P}/k_{Ref} . The rate coefficient of T2P toward chlorine atoms k_{T2P} was then calculated using the known rate coefficient k_{Ref} .

During the experiments performed in the D-ASC chamber, isoprene was used as the reference compound considering a Cl-rate coefficient k_{Isoprene} of $(4.80 \pm 1.25) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. This value is the average of those provided by (Ragains and Finlayson-Pitts, 1997; Fantechi et al., 1998; Orlando et al., 2003). In the 16-L cell, two

Table 1
Experimental conditions used during our kinetic study.

Reactor	Lamps	Compound	Initial concentration ($\times 10^{13}$ molecule cm^{-3})	$k_{\text{WL,X}} \pm \sigma_1^a$ ($\times 10^{-5}$ s^{-1})	$k_{\text{PL,X}} \pm \sigma_2^a$ ($\times 10^{-5}$ s^{-1})
D-ASC	1–2	T2P	5.0–15.1	1.73 ± 0.06	1.85 ± 0.10
				–	–
		Isoprene	5.914.8	6.55 ± 0.39	6.43 ± 0.41
				0.50 ± 0.12	0.54 ± 0.16
16-L cell	4	Cl ₂	25.0–37.3	2.42 ± 0.07	2.68 ± 0.12
		T2P	46.2–93.0	0.48 ± 0.15	2.95 ± 0.13
				–	–
		Cyclohexane	57.6–66.0	1.02 ± 0.08	3.57 ± 0.07
				0.11 ± 0.09	–
		Ethanol	74.4–110.0	1.07 ± 0.21	1.72 ± 0.07
				1.72 ± 0.07	–
		Cl ₂	66.0–132.0	2.08 ± 0.40	–

^a Uncertainty is $\pm 1\sigma$.

reference compounds were employed: ethanol ($k_{\text{Ethanol}} = (1.0 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2006) and cyclohexane ($k_{\text{Cyclohexane}} = (2.90 \pm 1.12) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This latter rate coefficient is the average of six values given by (Atkinson and Aschmann, 1985; Wallington et al., 1988; Rowley et al., 1992; Aschmann and Atkinson, 1995; Li and Pirasteh, 2006; Anderson et al., 2007). The error in k_{Ref} represents twice the standard deviation calculated from the averages of individual k_{Ref} .

The reagents (T2P and the reference compound) consumption in the D-ASC chamber was monitored as a function of time, using the following IR spectral features: $1175\text{--}1115 \text{ cm}^{-1}$ and $942\text{--}855 \text{ cm}^{-1}$ for T2P and isoprene, respectively. In the 16-L cell, the IR spectral features used were as follows: $1750\text{--}1700 \text{ cm}^{-1}$ for T2P, $2890\text{--}2830 \text{ cm}^{-1}$ for cyclohexane and $930\text{--}840 \text{ cm}^{-1}$ for ethanol. Once in the reactor, the gas mixture was allowed to stabilize for 40 min in the D-ASC chamber and 10 min in the 16-L cell. Indeed, the stabilization time of reagents is dependent on the volume of the reactor. The initial concentrations of T2P, reference compounds and Cl₂ were obtained based on the injected amounts (D-ASC) or the pressure measurements (16-L cell) and are summarized in Table 1.

The overall error Δk_{T2P} in the individual rate coefficient comes from statistical errors $\Delta k_{T2P}(\text{stat})$ and systematic errors $\Delta k_{T2P}(\text{syst})$ as follows:

$$\Delta k_{T2P} = \sqrt{\Delta k_{T2P}(\text{stat})^2 + \Delta k_{T2P}(\text{syst})^2} \quad (\text{Eq. 2})$$

Statistical errors $\Delta k_{T2P}(\text{stat})$ are calculated according to the following equation:

$$\frac{\Delta k_{T2P}(\text{stat})}{k_{T2P}} = \frac{\Delta(\text{Slope})}{\text{Slope}} + \frac{\Delta k_{\text{Ref}}}{k_{\text{Ref}}} \quad (\text{Eq. 3})$$

$\Delta(\text{Slope})$ comes from the determination of the slope in Eq. (1) and results from the least-squares analysis of Fig. 1. Δk_{Ref} is the uncertainty on the rate coefficient of the used reference compounds. In this work, this value represents two standard deviations obtained from the averaging of several values of k_{Ref} found in the literature, as explained above. Systematic errors $\Delta k_{T2P}(\text{syst})$ are estimated to 10%. They come mainly from the uncertainty in measuring the concentrations of the reagents (measurements of the areas of the spectroscopic peaks, possible inter-

Fig. 1. Plot of $\ln([T2P]_0/[T2P]_t) - k_{L,T2P}t$ vs. $\ln([Ref]_0/[Ref]_t) - k_{L,Ref}t$ according to Eq. 1. Data obtained using the D-ASC (isoprene) and the 16-L cell (cyclohexane and ethanol).

ference, and temperature instability). To minimize this error, 32 IR spectra were recorded for each experiment.

2.2. Mechanistic study

In independent experiments without adding a reference compound, the products formed during the gas-phase reaction of T2P with chlorine atoms were identified and quantified using two different detection methods: FTIR spectroscopy, coupled to the 16-L cell described above, and GC-MS technique, coupled to the 264-L Pyrex chamber (Ciudad Real-Atmospheric Simulation Chamber, CR-ASC), described below.

In the 16-L Pyrex cell, the concentrations of T2P and the formed products were followed in situ by monitoring the evolution of their IR absorption bands. The IR spectral features used for this analysis were as follows: 1180–1120 cm^{-1} for T2P, 875–817 cm^{-1} for propanal, 1840–1780 cm^{-1} for formic acid, 2230–2060 cm^{-1} for CO and 3100–2600 cm^{-1} for HCl. Examples of measured spectra are shown in Fig. S1. The identification of the products was done using standard reference libraries of IR spectra.

The CR-ASC set-up was presented in detail elsewhere (Ballesteros et al., 2009), and only a brief description is provided here. It consists of a 264-L Pyrex cylindrical reactor with four quartz windows on the sides. The chamber is surrounded by a set of 8 actinic lamps (Philips BL TL 40W/10 1SL/25, emitting in the range 340–400 nm, $\lambda_{\text{max}} = 365 \text{ nm}$) used to generate Cl atoms from the photolysis of Cl_2 . A GC-MS apparatus (Thermo Electron, Trace GC Ultra and DSQ II) was employed to analyze the gas mixture from the chamber. The Solid-Phase Micro-Extraction (SPME) technique was used for sampling the mixture using a 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane fiber as an adsorber. The coated fiber was exposed to the gas mixture during an optimized time of 15 min. The fiber samples were then thermally desorbed in the heated (at 523 K) GC injection port, and the products were analyzed by GC-MS by using temperature ramps that ranged between 313 and 573 K. The identification of the reaction products was carried out by using the electronic impact ionization mass spectrum of each retention time. The consumption of T2P and the formation of the products were examined by monitoring the areas of corresponding chromatographic peaks observed at a certain retention time. The initial concentrations of T2P and Cl_2 used for the mechanistic study are summarized in Table 2. Examples of a chromatogram and obtained mass spectra of the detected products are shown in Fig. S2.

2.3. Secondary organic aerosol (SOA) study

2.3.1. Experimental apparatus

The set-up used has already been presented elsewhere (Antiñolo et al., 2019). Hence, only a brief description will be given here with a special emphasis on the specificities of the present work. The study of the SOA formation in reaction R1 was carried out at $296 \pm 2 \text{ K}$ and $730 \pm 20 \text{ Torr}$ of synthetic air using both the CR-ASC and the 16-L cell

Table 2
Experimental conditions used during the mechanistic study.

Reactor	Lamps	Compound	Initial concentration range ($\times 10^{14}$ molecule cm^{-3})
16-L cell (4 runs)	3	T2P	2.78–5.91
		Cl_2	8.34–9.97
CR-ASC (2 runs)	8	T2P	9.05–9.64
		Cl_2	8.34–8.76

described above. Ranges of initial concentrations of T2P and Cl_2 were $(1.56\text{--}9.23) \times 10^{14}$ molecule cm^{-3} and $(1.55\text{--}15.8) \times 10^{14}$ molecule cm^{-3} , respectively. The loss of T2P, necessary to quantify the SOA yield, was measured using the FTIR spectrometer described in section 2.1.2. Cl atoms were generated in the CR-ASC as described in section 2.2.

A Fast Mobility Particle Sizer (FMPS) spectrometer (TSI 3091) was used to measure the number of particles formed with diameters ranging between 5.6 and 560 nm. Although it allows a time resolution of 1 s, averaged values for 1 min were considered in the present investigation. Mass concentrations were determined using an SOA density of 1.4 g cm^{-3} , which corresponds to the recommended value of Hallquist et al., 2009.

The gas mixture from the CR-ASC chamber entered in the FMPS through a $1 \mu\text{m}$ cut cyclone at a 10 L min^{-1} flow rate, and a 10 L min^{-1} filtered exhaust flow rate from the FMPS was then directed to the 16-L cell for FTIR measurements and then again to the CR-ASC, closing the circuit and allowing mixing of the gases in the system. Data were recorded with both FTIR and FMPS typically during 80 min as follows: 10 min before starting the reaction (dark measurements), 50 min under irradiation, followed by 20 min in dark conditions.

2.3.2. Determination of the SOA production

The SOA yield Y_{SOA} is defined by the following equation:

$$Y_{\text{SOA}} = \frac{M_{\text{SOA}}}{\Delta[T2P]} \quad (\text{Eq. 4})$$

From the time evolutions of the SOA mass production M_{SOA} and the reactant consumption $\Delta[T2P]$, it is possible to plot M_{SOA} as a function of $\Delta[T2P]$ and determine Y_{SOA} from the slope. Both M_{SOA} and $\Delta[T2P]$ were corrected to account for their loss in the dark when no Cl reaction is taking place, as explained in a previous study (Antiñolo et al., 2019). The loss of M_{SOA} was characterized during the last 20 min of each experiment under the dark conditions from the FMPS measurements, and its rate coefficient was in the $(5.22\text{--}6.97) \times 10^{-4} \text{ s}^{-1}$ range. $\Delta[T2P]$ was corrected considering the FTIR measurements of T2P in the first 10 min of the experiment under dark conditions from which it was possible to detect a loss rate coefficient within the $(1.16\text{--}20.8) \times 10^{-4} \text{ s}^{-1}$ range. Tests were also done to confirm that no SOA was formed during the Cl_2 dark reaction or exposure of T2P under the light.

In each experiment, M_{SOA} reaches a maximum value $M_{\text{SOA,max}}$, which is directly correlated to the SOA yield Y_{SOA} . Indeed, SOA formation can be described by the one-product model proposed by Pankow, 1994 for which the following equation was recommended by Odum et al., 1996:

$$Y_{\text{SOA}} = M_{\text{SOA,max}} \left(\frac{\alpha K_p}{1 + M_{\text{SOA,max}} K_p} \right) \quad (\text{Eq. 5})$$

where α is the mass-based gas-phase stoichiometric coefficient of a model product, and K_p represents its gas-particle partitioning equilibrium constant. The present study allows us to obtain these coefficients as explained in the discussion section 3.3.

2.4. Chemicals

The reagents employed were obtained from the following sources: T2P ($\geq 95\%$, Sigma-Aldrich), isoprene (99%, Sigma-Aldrich), cyclohexane (99.9%, Sigma-Aldrich), ethanol ($\geq 99.5\%$, Sigma-Aldrich), Cl_2 (10% in N_2 , Air Products) at IMT Lille Douai and Cl_2 (99.8%, Sigma-Aldrich) at UCLM.

3. Results and discussion

3.1. Kinetic study

The plots of $\ln([T2P]_0/[T2P]_t) - k_{L,T2Pt}$ vs. $\ln([Ref]_0/[Ref]_t) - k_{L,Ref}$ are presented in Fig. 1. Relative rate coefficients were obtained for each reference compound. Individual and average k_{T2P} are summarized in Table 3. The good linearity with a correlation coefficient greater than 98% and an intercept close to zero for all the reference compounds indicates that no other secondary reactions occur. The error reported on the average rate coefficient shown in Table 3 is two standard deviations. The overall error Δk_{T2P} in the individual rate coefficient values ranges from 24 to 42%.

Two determinations for the rate coefficient of the studied reaction exist in the literature: an experimental value, $(1.31 \pm 0.19) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Rodríguez et al., 2005), and a rate coefficient estimated using the SAR method, $3.47 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Teruel et al., 2009). The present value of $(2.56 \pm 0.83) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ lays between these two values.

k_{T2P} obtained in the present work is found to be higher than that provided by Rodríguez et al., also obtained using a relative method, by about a factor of 2. In Rodríguez et al.'s work, the losses of T2P and the reference compounds (ethane, propene and 1-butene) were monitored by GC-FID detection. The source of discrepancy with Rodríguez et al.'s work is not clear. First, the Cl-rate coefficients for the reference compounds used by Rodríguez et al. cannot be the reason for this discrepancy. These rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were $(5.85 \pm 0.55) \times 10^{-11}$ (Hitsuda et al., 2001), $(2.31 \pm 0.29) \times 10^{-10}$ (Stutz et al., 1998) and $(3.00 \pm 0.40) \times 10^{-10}$ (Orlando et al., 2003) for ethane, propene and 1-butene, respectively. Indeed, a re-evaluation of the value obtained by Rodríguez et al., for k_{T2P} using the rate coefficients recommended by IUPAC, 2006 for ethane and propene (5.9×10^{-11} and $2.70 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively), gives $k_{T2P} = 1.39 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which remains within the error bars given by these authors. The only difference that we can find between the two works, apart of the used technique, is that in Rodríguez et al.'s work the losses were not corrected although that wouldn't explain the discrepancy. It is important to note that in the present work, the rate coefficient of the reaction of T2P with Cl was measured in two different set-ups under different conditions. Very close rate coefficients values were obtained making our reported value reliable. The rate coefficient of the reaction of T2P with Cl atoms estimated by Teruel et al., 2009 using the SAR method is 25% higher than that determined in the present work. The source of this discrepancy is probably the uncertainties of the SAR method that aims to esti-

mate rate coefficients based on the reactivity of other compounds considering only their structure.

As generally observed for VOCs, Cl atoms are more reactive than OH radicals toward these species because they are stronger electrophiles than OH radicals. As expected, then, the rate coefficient for reaction R1 is almost 1 order of magnitude greater than the rate coefficient for the OH + T2P reaction, $3.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (average from Davis et al., 2007 and Albaladejo et al., 2002).

In Table 4, the rate coefficients of the reactions of a series of C₃-C₇ unsaturated aldehydes with Cl atoms are displayed. Our result confirms that the structure of unsaturated aldehydes has a very small impact on their reactivity towards Cl atoms, as was previously observed (Ullerstam et al., 2001; Colmenar et al., 2015) opposite to their reactivity towards OH and NO₃ radicals (Tables S1 and S2). The reactivity towards Cl seems to be fairly independent of the substitution on the olefinic carbons for unsaturated aldehydes, as stated by Blanco et al. (2010).

To evaluate the effect of the -CHO group on the reactivity, a comparison between the reactions of Cl with a series of unsaturated aldehydes to those with the corresponding alkenes would be useful. Unfortunately, no data are available in the literature for the reaction of Cl with *trans*-2-pentene, the corresponding alkene of T2P. However, data for other unsaturated aldehydes and their corresponding alkenes are available. The rate coefficients of the reactions of Cl with crotonaldehyde and 3-methyl-2-butenal (see Table 4) are 34% and 36% lower than those with *trans*-2-butene ($3.58 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ provided by Kaiser et al., 2007) and 2-methyl-propene ($3.38 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ provided by Blanco et al., 2010), respectively. This may be due to the negative inductive effect of the carbonyl-containing group, which may deactivate the double bond toward the Cl atom addition. However, this decrease in reactivity due to the electron-withdrawing effect may be compensated by the fact that the -CHO group is a reactive site. This was discussed in the study carried out by Thévenet et al., 2000, where the rate coefficient of the reaction of Cl with acrolein ($2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) was compared to that for propene ($2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and was shown to be slightly higher within uncertainties showing that the -CHO group is a reactive site, although H abstraction from the -CHO group remains a minor channel

Table 3

Rate coefficients for the reaction of T2P with Cl atoms at $296 \pm 2 \text{ K}$ and $730 \pm 20 \text{ Torr}$.

Reactor	Reference compound	k_{T2P}/k_{Ref}	$k_{T2P} \pm \Delta k_{T2P}^a$ ($\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
D-ASC	Isoprene (6 runs)	0.50 ± 0.04	2.40 ± 0.82
16-L	Cyclohexane (2 runs)	0.79 ± 0.01	2.29 ± 0.92
Pyrex cell	Ethanol (3 runs)	2.99 ± 0.08	2.99 ± 0.69
Average			2.56 ± 0.83^b

$k_{\text{Isoprene}} = (4.8 \pm 1.25) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see section 2.1.3).

$k_{\text{Ethanol}} = (1.0 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see section 2.1.3).

$k_{\text{Cyclohexane}} = (2.90 \pm 1.12) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see section 2.1.3).

^a Uncertainty calculated according to equations (4) and (5).

^b Two standard deviations.

Table 4

Summary of the rate coefficients for the reactions of a series of C₃-C₇ unsaturated aldehydes with Cl atoms.

Unsaturated aldehyde	k_{Cl} ($\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Reference
Acrolein ($\text{CH}_2=\text{CH}-\text{CHO}$)	2.2 ± 0.3	Thévenet et al. (2000)
	2.2 ± 0.3	Canosa-Mas et al. (2001)
	1.8 ± 0.3	Ullerstam et al. (2001)
	2.5 ± 0.7	Wang et al. (2002)
Crotonaldehyde ($\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$)	2.6 ± 0.3	Thévenet et al. (2000)
	2.2 ± 0.4	Ullerstam et al. (2001)
	3.2 ± 0.9	Wang et al. (2002)
3-methyl-2-butenal ($(\text{CH}_3)_2\text{C}=\text{CH}-\text{C}(\text{O})\text{H}$)	2.48 ± 0.71	Blanco et al. (2010)
Trans-2-pentenal ($\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CHO}$)	1.31 ± 0.19	Rodríguez et al. (2005)
	3.47	Teruel et al., 2009)
	2.53 ± 0.83	(SAR Estimation)
This work		
Trans-2-hexenal ($\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CHO}$)	1.92 ± 0.22	Rodríguez et al. (2005)
Trans-2-heptenal ($\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CHO}$)	2.4 ± 0.29	Rodríguez et al. (2005)

compared to the Cl-addition to the double bond, which is likely to be the major one as stated by these authors.

3.2. Mechanistic study

3.2.1. Molar yields of reaction products

This work represents the first mechanistic study on the T2P + Cl reaction. It has been carried out at 296 ± 2 K and 730 ± 20 Torr of total pressure. By FTIR, HCl, CO, propanal and formic acid were identified and quantified as products formed from the studied reaction (Fig. S1). Fig. 2 shows a typical concentration vs. time profile for the consumption of T2P and the formation of products. The plots of the $[Product]_t$ vs. $\Delta[T2P]$ for propanal and formic acid are shown in Fig. 3. $[Product]_t$ is the product concentration at a time t , $\Delta[T2P]$ is the consumed concentration of T2P at a time t . For propanal, a correction of its concentration was done according to the method described by Ceacero-Vega et al. (2012) and considering the IUPAC recommendation for the rate coefficient of the Cl-reaction with propanal: $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).

The molar yields obtained from the slopes of the plot depicted in Fig. 3 are: $(5.2 \pm 0.2)\%$ and $(6.2 \pm 0.4)\%$, for propanal and formic acid, respectively. The overall errors in the formation yields are due to systematic errors σ_{sys} mentioned above and statistical errors resulting from a least-squares analysis of the $[Product]_t$ vs. $\Delta[T2P]$ plots. CO is expected to be formed as a primary product and also as a final product from the studied reaction and may be generated in the oxidation of other species in the mechanism. For that reason, a molar yield for this compound is not reported in this work. HCl yield is not reported either because it may be a primary product, or it can be generated in the H-abstraction of other reaction products. Propanal is expected to be formed as a primary product from the reaction of T2P with Cl. Formic acid may be produced through the very rapid oxidation of other species generated in the oxidation of T2P or as a consequence of heterogeneous reactions on the chamber walls though no evidence of this phenomenon was observed in our experiments. The residual IR spectrum presented in Fig. S1 shows peaks that could correspond to ketene in the $2200\text{--}2100 \text{ cm}^{-1}$ region, according to Wallington et al. (1996), and 2-chlorobutanal considering the peak typical for a carbonyl group (1750 cm^{-1}), the bands due to C-H bending and stretching ($1500\text{--}1000 \text{ cm}^{-1}$ and $3000\text{--}2800 \text{ cm}^{-1}$, respectively) and the band that can correspond to the C-Cl stretching ($1000\text{--}650 \text{ cm}^{-1}$). However, none of these two compounds could be confirmed by FTIR or quantified given the lack of standards of these products.

Three of the peaks observed in the chromatogram obtained by GC-MS could be assigned to reaction products (Fig. S2). The peak detected at 4.03 min, for which the mass spectrum (MS) shows ions at $m/z = 106$ (molecular ion, M, tiny signal), 78 and 80 (fragment M-CO or M-C₂H₄ for the two Cl isotopes), 77 (M-C(O)H), and 41 (C₃H₅), could be assigned to 2-chlorobutanal, and that would confirm the observations made by FTIR. A chlorinated product that could not be identified was observed at 5.09 min retention time: its MS shows the isotopic pattern for Cl in the 77 and 105 peaks, although it was not possible to clearly identify the molecular ion. The last peak in the chromatogram, at 5.82 min, was attributed to 2-pentenoic acid, given that in the MS there are peaks at $m/z = 100$ (M), 82 (M-H₂O) and 55 (M-C(O)OH). This identification was confirmed by comparing the reference MS library installed in the GC-MS software used in this study. The quantification of these products was not possible due to the lack of standards. However, based on the area of the observed peaks in the chromatogram and assuming the same response for all of them, it seems that the yield of 2-chlorobutanal and the unidentified chlorinated product is higher than that for 2-pentenoic acid (Fig. S2). The carbon balance was calculated considering only propanal and CO. The obtained value was shown to not exceed 15% at the end of the reaction showing that additional formed oxidation products could not be detected or quantified.

3.2.2. Proposed reaction mechanism

As other unsaturated aldehydes (Canosa-Mas et al., 2001; Orlando and Tyndall, 2002; Magneron et al., 2002), the degradation of T2P initiated by Cl atoms is expected to proceed via two basic mechanisms: abstraction of the hydrogen atom from the -CHO group and/or addition to the C=C double bond. In Scheme 1, the reaction pathways that may justify the observed products are shown. The addition of a Cl atom may occur on two sites of the C=C double bond: adjacent to the -C(O)H group (α) or on the double-bonded carbon furthest from the aldehydic group (β). As seen in Scheme 1, the α -addition forms the $\text{CH}_3\text{CH}_2\text{CHCHClC(O)H}$ radical, which will react with O₂ followed by a reaction with RO₂ to lead to the corresponding chloroalkoxy radical $\text{CH}_3\text{CH}_2\text{C(O)HCHClC(O)H}$. The decomposition of this chloroalkoxy radical may proceed via two channels. The first one leads to the formation of propanal ($\text{CH}_3\text{CH}_2\text{C(O)H}$), 2-oxoacetylchloride (ClC(O)C(O)H), formyl chloride HC(O)Cl and CO. Propanal may further react with Cl atoms to form HCl and $\text{CH}_3\text{CH}_2\text{C(O)}$ radicals (Le Crâne et al., 2004). The second channel leads to the formation of

Fig. 2. Concentration-time profiles for T2P and the major products observed by FTIR using the 16-L cell. Initial concentrations: $5.91 \times 10^{14} \text{ molecule cm}^{-3}$ for T2P and $9.09 \times 10^{14} \text{ molecule cm}^{-3}$ for Cl₂.

Fig. 3. Product yields for HC(O)OH and propanal.

chloromalonalddehyde (C(O)HCHClC(O)H) and acetaldehyde $\text{CH}_3\text{C(O)H}$. Among these products, only propanal and CO were observed and quantified in this work.

The β -addition mechanism proceeds through the $\text{CH}_3\text{CH}_2\text{CHClCHC(O)H}$ radical, which will react with O_2 followed by a reaction with RO_2 to lead to the $\text{CH}_3\text{CH}_2\text{CHClC(O)HC(O)H}$ radical. This radical may decompose to lead to the formation of 2-chlorobutanal ($\text{CH}_3\text{CH}_2\text{CHClC(O)H}$) identified by GC-MS, but not quantified and further to the formation of CO identified and quantified by FTIR. The decomposition of the $\text{CH}_3\text{CH}_2\text{CHClC(O)HC(O)H}$ radical may also lead to the formation of glyoxal (C(O)HC(O)H) and 1-chloropropanal ($\text{CH}_3\text{CH}_2\text{C(O)Cl}$) after the conversion of the reaction of the chloroperoxy radical $\text{CH}_3\text{CH}_2\text{C(O}_2\text{)HCl}$ with RO_2 . Glyoxal (C(O)HC(O)H) and 1-chloropropanal were not observed in this work, suggesting that this channel either does not occur in the timescale of the experiments or is a minor route in the mechanism. Note also that glyoxal may be readily photolyzed under UV irradiation. The $\text{CH}_3\text{CH}_2\text{CHClC(O)HC(O)H}$ radical may react with O_2 to form chloropropylglyoxal ($\text{CH}_3\text{CH}_2\text{CHClC(O)C(O)H}$). This product may be the unidentified one observed by GC-MS but could not be confirmed.

The H-abstraction from the $-\text{C(O)H}$ group may form the $\text{CH}_3\text{CH}_2\text{CHCHC(O)}$ radical and HCl. In the presence of O_2 , the $\text{CH}_3\text{CH}_2\text{CHCHC(O)}$ radical may be converted to the peroxy radical $\text{CH}_3\text{CH}_2\text{CHCHC(O)O}_2$, which generates 2-pentenoic acid ($\text{CH}_3\text{CH}_2\text{CHCHC(O)OH}$) and ozone in the presence of HO_2 . 2-pentenoic acid was detected in SPME/GC-MS analysis. On the other hand, the $\text{CH}_3\text{CH}_2\text{CHCHC(O)O}_2$ radical may also react with RO_2 and generate the $\text{CH}_3\text{CH}_2\text{CHCHC(O)O}$ radical. This radical can decompose to carbon dioxide (CO_2) and ethylvinyl radical ($\text{CH}_3\text{CH}_2\text{CHCH}$), which is converted to the $\text{CH}_3\text{CH}_2\text{CHCH(O}_2\text{)}$ radical in the presence of O_2 . The reaction of this latter with RO_2 may lead to the formation of butanal ($\text{CH}_3\text{CH}_2\text{CH}_2\text{C(O)H}$) not observed in this work. The reaction of $\text{CH}_3\text{CH}_2\text{CHCH(O}_2\text{)}$ with RO_2 may also lead to propanal and CO formation, both quantified by FTIR in this work.

In the light of the discussion above, the relative contribution of addition and abstraction channels in the suggested mechanism could not be determined. In fact, the product formed only through the β -addition channel and observed in this work (2-chlorobutanal) could not be quantified. Among the products expected to occur from the α -addition channel, only propanal and CO were detected in this work. These products may also be formed through the other channels, as mentioned before.

Scheme 1. Proposed mechanism for the reaction of T2P with Cl atom: α -addition (a), β -addition (b) and H-abstraction (c).

3.3. SOA study

Fig. S3 shows the relationship between the initial concentrations of T2P and Cl_2 with $M_{\text{SOA},\text{max}}$. A clear dependency of $M_{\text{SOA},\text{max}}$ on the amount of Cl_2 introduced in the system was observed, whereas no obvious correlation can be identified with the initial concentration of T2P.

Typical aerosol size distributions at several reaction times for given initial concentrations of T2P and Cl_2 are presented in Fig. S4. In Fig. 4, the SOA mass concentration M_{SOA} is plotted as a function of the consumed T2P. The SOA yield Y_{SOA} is obtained from linear least-squares analysis. The values of Y_{SOA} are summarized together with the experimental conditions in Table 5. Despite the data scattering (Fig. 5), the calculated Y_{SOA} fits reasonably well to a one-product model (Odum et al., 1996), given by Equation (5). A least-square regression on the data gives the following parameters: $\alpha = (9.95 \pm 2.52) \%$ and $K_p = (6.00 \pm 2.68) \times 10^{-4} \text{ m}^3 \mu\text{g}^{-1}$. Uncertainties are statistical and represent two standard deviations (2σ).

Many products result from the oxidation of a VOC, so this fitting allows for easy comparison of yield curves, but, as reported by Cai and Griffin (2006), the fitted parameters provide no specific information about the real oxidation products and ascribing meaning to them should be avoided.

The SOA formation yields for the reaction of other unsaturated compounds with Cl have been previously determined. For *trans*-2-methyl-2-butenal, Y_{SOA} were recently determined to be between 0.26 and 1.65 % (Antiñolo et al., 2020). These SOA yields are a little lower than the values determined in the present work for the reaction of Cl with T2P.

Fig. 4. SOA mass concentration M_{SOA} produced from the T2P + Cl reaction as a function of the consumed T2P with an initial concentration of 4.03×10^{14} molecule cm^{-3} for T2P and 6.72×10^{14} molecule cm^{-3} for Cl_2 . The SOA yield Y_{SOA} is obtained from a linear least-squares analysis.

Table 5

Experimental conditions and results obtained for the SOA study.

$[\text{T2P}]_0 (\times 10^4 \mu\text{g m}^{-3})$	$[\text{Cl}_2]_0 (\times 10^4 \mu\text{g m}^{-3})$	$\Delta[\text{T2P}] (\times 10^4 \mu\text{g m}^{-3})$	$M_{\text{SOA,max}} (\times 10^2 \mu\text{g m}^{-3})$	$Y_{\text{SOA}}^a (\%)$
8.03	1.86	1.80	1.20	0.82 ± 0.02
9.39	2.43	1.75	1.75	1.15 ± 0.02
13.14	4.28	3.08	3.42	1.34 ± 0.02
3.30	3.16	1.56	3.39	2.07 ± 0.09
12.62	8.45	4.75	9.11	2.15 ± 0.02
2.23	2.43	0.88	2.56	2.47 ± 0.08
5.75	8.07	3.36	8.18	2.59 ± 0.05
3.05	8.07	1.67	8.20	2.79 ± 0.08
2.99	8.33	1.62	9.72	3.79 ± 0.10
5.75	7.89	2.19	8.97	3.79 ± 0.10
9.32	13.74	2.79	13.48	4.26 ± 0.11
6.69	12.41	4.31	15.89	4.62 ± 0.27
2.23	7.00	1.35	9.88	4.77 ± 0.28
7.89	18.97	4.89	21.56	5.17 ± 0.39
6.59	16.10	4.43	16.62	5.24 ± 0.54
9.32	17.34	2.46	19.00	6.16 ± 0.10

^a Y_{SOA} is determined from the slope of $M_{\text{SOA,max}}$ vs. Y_{SOA} . Errors are 2σ .

4. Atmospheric implications and conclusion

The atmospheric lifetime τ_{Cl} of T2P due to its reaction with Cl is estimated from k_{T2P} obtained in this work according to the following equation: $\tau_{\text{Cl}} = 1/(k_{\text{T2P}} \times [\text{Cl}])$. $[\text{Cl}]$ represents the global tropospheric concentration of Cl of 1×10^3 atoms cm^{-3} averaged over 24 h (Wingenter et al., 1999). With this value, a τ_{Cl} of 44 days is calculated. The reaction of T2P with Cl may become significant in coastal areas and in polluted northern hemisphere areas where the concentration of Cl atoms can reach 1×10^5 molecules cm^{-3} (Singh et al., 1996) and 5×10^4 atoms cm^{-3} (Hossaini et al., 2016), respectively, yielding to a lifetime shorter than 1 day which makes the reaction of T2P with Cl a potentially significant elimination route in the atmosphere. The calculated lifetime of T2P due to its reaction with OH is 7 h using a 24-h average concentration of 1×10^6 molecules cm^{-3} for OH (Atkinson et al., 1997) and the average of the rate coefficient values reported in the literature by (Davis et al., 2007) and (Albaladejo et al., 2002) ($3.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). A short lifetime (5 h) of T2P is calculated for its reaction with NO_3 radicals showing that this process is an important removal pathway for T2P during nighttime (Kalalian et al., 2019). These authors provided a lifetime of 9 days towards reaction with ozone. The tropospheric lifetime considering the four chemical removal pathways, is shorter than 3 h. Further, the UV cross-sections of T2P have been recently determined by Kalalian et al. (2019). A lower limit of 44 min was provided by these authors for the T2P lifetime due to photolysis in the UV solar actinic region. This value was calculated using a quantum yield of unity and a photolysis rate corresponding to June 30 at midday for Paris (zenith angle = 26°). It should be noted however that the overall quantum yield in the actinic region for T2P are not known and that for smaller unsaturated aldehydes such as *trans*-crotonaldehyde it has been found to be quite small since Magneron et al. (2002) obtained an upper value of 0.03 for this species.

The degradation products (and molar yields) of T2P in the presence of air were HCl, CO, and propanal ($5.2 \pm 0.2\%$). Besides, chlorinated products, such as 2-chlorobutanal, were identified as reaction products of the T2P + Cl reaction but could not be quantified. Highly oxidized compounds, such as 2-pentenoic acid and formic acid ($6.2 \pm 0.4\%$), were also detected in this work. Formic acid can be produced as a consequence of heterogeneous reactions on the chamber walls.

Given the formation of HCl, the T2P + Cl reaction may contribute to the acidity of marine atmospheres. On the other hand, in polluted areas (high- NO_x conditions), the formation of CO may contribute to

Fig. 5. Plot of SOA yield Y_{SOA} as a function of $M_{SOA,max}$ for the reaction between T2P and Cl.

photochemical pollution via its OH-reaction, which produces CO_2 and H atoms that quickly combine with O_2 to form HO_2 radicals regenerating OH and producing O_3 in the troposphere. It is important to note that in polluted areas, the reaction of T2P with Cl may be a source of other toxic molecules such as PAN type species. In addition, the chemical mechanism displayed in Scheme 1 for NO_x -free conditions will evolve by including $RO_2 + NO$ and $RO_2 + NO_2$ reactions.

As observed in this work, the high particle mass concentration was due to the large amount of T2P present in the system (22.5 ppm). In a real atmosphere, the mixing ratio of T2P is at ppb levels. Considering the small SOA yield formed in the T2P + Cl reaction ($Y_{SOA} < 7\%$), it is not expected that T2P could contribute to the formation of ultrafine particles in clean atmospheres. The dependence of Y_{SOA} with the maximum SOA mass is well-described by a one-product absorptive model that yielded the Odum's parameters α and K_p , the latter being two orders of magnitude lower than those reported for α -pinene, β -pinene and D-limonene (Cai and Griffin, 2006). Even though the uncertainties in Y_{SOA} are high due to the lack of knowledge in the SOA density, the determined SOA yields are in the order of magnitude of those reported for the Cl + toluene reaction (Cai et al., 2008) and other similar biogenic compounds as isoprene (Wang and Ruiz, 2017).

Additionally, insights in the reaction mechanism for the degradation of T2P initiated by Cl atoms were reported here. From the obtained results, the first step of the reaction mechanism seems to proceed mainly by H-abstraction of the aldehydic group and by β -addition of Cl atoms to the double bond. The carbon balance calculated in this study did not exceed 15% at the end of the reaction showing that additional oxidation products could not be detected or quantified. Further studies, with complementary detection techniques, are clearly needed to better understand the mechanism and accurately evaluate the carbon balance and the relative contribution of addition and abstraction channels in this mechanism.

Credit authors statement

A.Girra: experiments, M. Antiñolo: experiments and supervision, A. Canosa: reviewing, A. Tomas: reviewing, E. Jiménez: methodology, G. El Dib: supervision, writing and reviewing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2021.130193>.

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