



Carbon isotope fractionation patterns distinguish the transformation mechanisms for tris(1-chloro-2-propyl) phosphate (TCPP): Hydrolysis, photolysis, and natural pyrite-activated persulfate degradation

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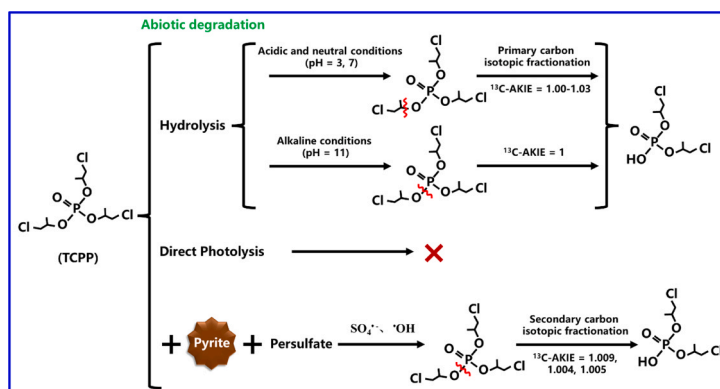
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HIGHLIGHTS

- The hydrolysis pathways of TCPP differ under different pH values.
- $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ are the dominant ROSs for TCPP degradation with NP/PDS.
- Fe(II)/Fe(III) cycling coupled with sulfur valence transformation produces ROSs.
- Cleavage of P–O bond is initial rate-limiting step for TCPP degradation with NP/PDS.
- Carbon isotope fractionation can trace different TCPP transformation pathways.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, carbon isotope analysis was employed to investigate hydrolysis and natural pyrite-activated persulfate (NP/PDS) degradation of TCPP. EPR and radical quenching experiments revealed that $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ were the dominant reactive oxygen species. The XPS, XRD, and FTIR results indicated Fe(II) served as the primary active site, generating $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$. For acidic and neutral hydrolysis, the apparent kinetic isotope effects (^{13}C -AKIE = 1.031 ± 0.004 and 1.030 ± 0.004 , respectively) were consistent with the intrinsic KIE associated with C–O bond cleavage (1.00–1.03), suggesting that C–O bond cleavage was the initial rate-limiting step. In contrast, negligible carbon isotope fractionation during alkaline hydrolysis indicated that P–O bond cleavage was the initial rate-limiting step. For degradation in the NP/PDS, the observed ^{13}C -AKIEs were 1.009 ± 0.001 , 1.004 ± 0.000 , and 1.005 ± 0.001 , respectively. These values were inconsistent with intrinsic KIEs expected for

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C-H (1.01–1.03) and C-Cl (1.02–1.03) bond cleavage but corresponded to the lower end of the intrinsic KIEs range for C-O bond cleavage, indicating that P-O bond cleavage was the initial rate-limiting step. Overall, this study demonstrates isotope analysis is a powerful tool for identifying the geochemical mechanisms of OPFRs in contaminated fields.

1. Introduction

Organophosphate flame retardants (OPFRs) are synthetic chemical polymers widely used in numerous commercial products, including building materials, furniture, floor polishes, varnishes, plastics, and anti-fire foaming agents [1]. Most OPFRs are employed as additive flame retardants and are physically blended into polymer substrates, making them susceptible to environmental release through volatilization, abrasion, and dissolution [2]. Consequently, OPFRs have been frequently detected in surface water and groundwater [3,4], marine environments [5,6], and even drinking water sources [7,8]. Tris (1-chloro-2-propyl) phosphate (TCPP) is one of the most widely used chlorinated OPFRs. The presence of chlorine atoms imparts relatively high-water solubility and chemical stability, contributing to its persistence in the environment and raising increasing concerns regarding its ecological risks. TCPP can induce toxicity in the kidneys, liver, and brain, impair reproductive function, and interfere with neural development in both humans and animals [9,10]. Consequently, understanding the environmental transformation pathways and fate of TCPP has become an important research priority.

Abiotic degradation of OPFRs primarily proceeds through reactive oxygen species (ROSS)-mediated pathways, involving oxidants such as hydroxyl radicals ($\bullet\text{OH}$), sulfate radicals ($\text{SO}_4^{\bullet-}$), and singlet oxygen ($^1\text{O}_2$) [11–13]. These radicals can attack specific chemical bonds within OPFR molecules, initiating decarboxylation, dehydrogenation, or dechlorination and ultimately resulting in their breakdown. Liu et al. investigated the degradation of tris(2-chloroethyl) phosphate (TCEP) by thermally activated persulfate and identified $\text{SO}_4^{\bullet-}$ as the dominant ROSS, accounting for approximately 93% of the degradation process. Their results suggested that $\text{SO}_4^{\bullet-}$ initiates dechlorination through attack on the C-Cl bond of the 2-chloroethyl side chain [14]. However, other studies have proposed that $\text{SO}_4^{\bullet-}$ preferentially cleaves the P-O bond and removes the 2-chloroethyl group ($-\text{OC}_2\text{H}_4\text{Cl}$) [14]. These findings indicate that both C-Cl and P-O bonds may be cracked by $\text{SO}_4^{\bullet-}$ for TCEP transformation. In contrast, studies on TCPP degradation under UV/ H_2O_2 conditions identified $\bullet\text{OH}$ as the predominant ROSS. In these systems, $\bullet\text{OH}$ primarily attacks the C-O bond of the oxygen-chlorinated isopropyl group, producing bis(1-chloro-2-propyl) phosphate as a major transformation product [15]. Similarly, during UV/ TiO_2 -mediated degradation of TCPP, $\bullet\text{OH}$ was reported to attack both the C-Cl bond and the methyl group ($-\text{CH}_3$) of the oxygen-chlorinated isopropyl moiety ($-\text{OC}_3\text{H}_6\text{Cl}$) attached to the central phosphorus atom [16]. Furthermore, in the degradation of triphenyl phosphate (TPhP) using biochar-supported nanoscale zero-valent iron (nZVI) to activate persulfate, both radical pathways ($\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$) and non-radical pathways ($^1\text{O}_2$) play significant roles [17]. Collectively, these findings highlight the critical role of ROSSs in the degradation of OPFRs. However, the identity of initial rate-limiting steps remains under debate. Moreover, the formation mechanisms of the dominant reactive species have not been fully elucidated. Therefore, advanced analytical approaches are required to better resolve the transformation pathways of OPFRs. Compound-specific isotope analysis (CSIA) has emerged as a powerful tool [18], offering mechanistic insights into their environmental transformation processes and providing a robust scientific basis for assessing their environmental source, fate, and remediation in contaminated environments [19].

Due to kinetic isotope effects, molecules containing lighter isotopes generally react more rapidly than those containing heavy isotopes, resulting in the enrichment of heavy isotopes in the residual substrate.

Such isotopic fractionation can be quantified using gas chromatography - combustion - isotope ratio mass spectrometry (GC-C-IRMS). The Rayleigh equation is applied to calculate the isotopic enrichment factor (ϵ) and apparent kinetic isotope effect (AKIE) values. By comparing experimentally derived AKIE values with intrinsic kinetic isotope effect (KIE) values associated with specific chemical reactions, it is possible to identify the initial bond-breaking step [20]. During the degradation of TCEP in a persulfate system, a significant carbon isotopic fractionation ($\epsilon_{\text{C}} = -1.6 \pm 0.2\text{‰}$) and a carbon apparent kinetic isotope effect (^{13}C -AKIE = 1.01) value were observed. Comparison of the measured isotope effects with theoretical KIE values for C-H oxidation (1.01–1.03) and C-Cl bond cleavage (1.06) [20], suggested that C-H bond cleavage was the initial rate-limiting step in TCEP degradation [13]. Liu et al. investigated persulfate-mediated degradation of TCEP and reported ^{13}C -AKIE and ^2H -AKIE values of 1.01 and 1.37–3.05, respectively, further supporting C-H bond cleavage as the primary rate-limiting step [21]. Wang et al. employed carbon isotopic fractionation to investigate the degradation of decabromodiphenyl ether (BDE-209) by thermally activated sodium persulfate. The observed ^{13}C -AKIE (1.015–1.028) values indicated that C-Br bond cleavage was the initial rate-limiting step [22]. Collectively, these findings highlight the unique capability of stable isotope analysis to elucidate transformation pathways of organic pollutants.

In this study, carbon isotopic fractionation was employed to reveal the transformation mechanism of TCPP. The objective included (1) investigating the degradation kinetics of TCPP under various transformation processes, including hydrolysis, indirect photolysis, and natural pyrite (FeS_2)-activated persulfate oxidation; (2) identifying the dominant reactive radicals involved in TCPP degradation; (3) characterizing major transformation products; and (4) determining carbon isotopic fractionation patterns associated with different transformation pathways. By integrating degradation kinetics, transformation product analysis, and isotope fractionation data, this study seeks to establish mechanistic links between isotopic signatures and degradation pathways.

2. Materials and methods

2.1. Chemicals

Tris(1-chloro-2-propyl) phosphate (TCPP, CAS No. 13674-84-5, purity $\geq 99\%$), HPLC-grade n-hexane, dichloromethane, methanol, and tert-butanol (TBA) were purchased from Shanghai Anpel Biochemical Technology Co., Ltd (Shanghai, China). 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, CAS No. 3317-61-1, purity $\geq 97\%$) and 2,2,6,6-tetramethylpiperidine (TEMP, CAS No. 768-66-1, purity $\geq 97\%$) were obtained from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, CAS No. 7775-27-1, purity $\geq 99\%$) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). All other reagents were of analytical grade and supplied by Guangzhou Chemical Reagent Factory (Guangzhou, China). Ultrapure water ($18.2 \text{ M}\Omega/\text{cm}$) was produced using a Milli-Q water purification system (Millipore, Billerica, MA, USA).

2.2. Experimental procedures

Natural pyrite (FeS_2) (NP) was obtained from Zhaoyuan, Yantai, Shandong, China. The pyrite samples were ground using a ceramic mortar and pestle in an anaerobic chamber and subsequently sieved to

obtain the desired particle-size fraction. To remove surface oxidation products, the pyrite was ultrasonically washed with 0.1 M nitric acid for 30 min, followed by repeated ultrasonic cleaning with methanol for 30 min. The treated pyrite was then freeze-dried, dry-sieved, and stored in the anaerobic chamber until use. Particles with diameters ranging from 80 to 200 μm were selected for all experiments. Due to the different degradation processes of TCP P caused by hydrolysis, UV-assisted natural pyrite degradation, and natural pyrite-activated persulfate degradation, the degradation rates vary significantly, different initial concentrations are adopted.

Hydrolysis experiments were conducted in amber glass bottles at room temperature ($25 \pm 1^\circ\text{C}$). The initial pH values were adjusted to 3, 7, and 11 using 0.1 M sulfuric acid and 0.1 sodium hydroxide solutions. The initial concentration of TCP P was 2.0 mg/L, and the reaction mixtures were continuously stirred at 500 rpm using magnetic stirrers. Samples were collected on 0, 10, 25, 45, 65, and 85 days. The collected samples were filtered through a 0.22 μm aqueous-phase membrane filter and diluted four times with ultrapure water prior to concentration analysis.

UV-assisted degradation experiments using natural pyrite were conducted under 254 nm and pH 7. The initial TCP P concentration was 20 mg/L, and the reaction mixtures were stirred at 500 rpm. The samples were collected at 0, 15, 30, 60, 90, 120, and 150 min, filtered through a 0.22 μm aqueous-phase membrane filter, and diluted 40 times with ultrapure water prior to concentration analysis.

Natural pyrite-activated persulfate degradation experiments were conducted at pH 3, 7, and 11, and the initial pH values were adjusted with 0.1 M sulfuric acid and 0.1 sodium hydroxide solutions. The reaction systems contained 5.0 g/L natural pyrite and 3.0 mM sodium persulfate (PDS), whereas the control groups contained either 5.0 g/L natural pyrite or 3.0 mM PDS. All reactions were carried out in 100 mL quartz glass reactors under dark conditions with magnetic stirring at 500 rpm. The initial concentration of TCP P was 20 mg/L. Samples were collected at predetermined time intervals and immediately quenched with pure methanol to terminate further reactions. Subsequently, the samples were filtered through a 0.22 μm organic-phase membrane filter and diluted 40 times with ultrapure water prior to concentration analysis.

For transformation product identification and carbon isotope analysis, TCP P was extracted from the aqueous phase using a mixture of dichloromethane and n-hexane (V/V = 1:1). Detailed extraction procedures and recovery rates are provided in the [Supporting information \(SI\)](#) (Section 1 and Fig. S1). All experiments were performed in triplicate.

2.3. Analytical methods

2.3.1. Characterization of natural pyrite

The surface morphology of the pyrite before and after the reaction with persulfate was characterized using scanning electron microscopy (SEM; Regulus 8100, Hitachi, Japan). Changes in elemental composition and oxidation states were analyzed using X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo Scientific, USA). Crystalline phase transformations associated with oxidation or reduction processes were examined using X-ray diffraction (XRD; Aeris, PANalytical, Netherlands). Surface functional groups and chemical structural changes were characterized by Fourier-transform infrared spectroscopy (FTIR; Nicolet iN10, Thermo Fisher Scientific, Germany). Detailed analytical procedures are provided in [SI \(Section 2\)](#).

2.3.2. Quantification of TCP P

The concentration of TCP P was determined using high-performance liquid chromatography coupled with electrospray triple quadrupole mass spectrometry (HPLC-MS/MS; Agilent 1260-6470, Agilent Technologies, USA). Detailed instrumental conditions and analytical procedures are described in [SI \(Section 3\)](#).

2.3.3. Identification of transformation products

Transformation products and degradation intermediates were identified using high-resolution mass spectrometry (HRMS) based on a Q-Exactive orbitrap high-resolution mass spectrometry (Q-Exactive; Thermo Fisher Scientific, Bremen, Germany). Detailed instrumental parameters and analytical procedures are described in [SI \(Section 4\)](#).

2.3.4. Carbon isotope analysis

Carbon stable isotope ratios were determined using isotope ratio mass spectrometry (IRMS; ISOPRIME 100, Elementar, Germany). The analytical procedures, calibration methods, and isotope quality-control protocols are provided in [SI \(Section 5\)](#).

Carbon stable isotope ratios are reported as $\delta^{13}\text{C}$ relative to Vienna Pee Dee Belemnite [19,20]. Isotope signature is expressed in per mil (‰) as Eq. (1) (Eq. (1)).

$$\delta^{13}\text{C} (\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000\text{‰}$$

$$= \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \times 1000\text{‰} \quad (1)$$

Where $\delta^{13}\text{C}$ is the isotopic composition of carbon for TCP P. ^{13}C is the heavy isotopes of the carbon. ^{12}C is the light isotopes. R is the ratio of the heavy isotope to light isotope, $(^{13}\text{C}/^{12}\text{C})_{\text{sample}}$ and $(^{13}\text{C}/^{12}\text{C})_{\text{standard}}$ are the isotopic composition of the TCP P and standard, respectively. Samples with negative $\delta^{13}\text{C}$ values are depleted in ^{13}C compared to the international reference standard.

Isotope enrichment factor for carbon, named as ϵ , is determined by plotting $\ln f_t$ versus $\ln((1000 + \delta^{13}\text{C}_t)/(1000 + \delta^{13}\text{C}_0))$ and determining the slope of the linear regression according to the Rayleigh equation (Eq. (2)) [19,20].

$$\ln\left(\frac{1000 + \delta^{13}\text{C}_t}{1000 + \delta^{13}\text{C}_0}\right) = \frac{\epsilon}{1000} \ln f_t \quad (2)$$

Where $\delta^{13}\text{C}_0$ and $\delta^{13}\text{C}_t$ are isotopic composition of carbon in TCP P at the beginning 0 and reaction time t , and f_t is the fraction of TCP P remaining at time t (Eq. (3)).

$$f_t = C_t/C_0 \quad (3)$$

Apparent kinetic isotope effect (AKIE) is achieved according to Eq. (4) [19,20].

$$\text{AKIE} = \frac{1}{1 + z \times \frac{n}{x} \times \epsilon / 1000} \quad (4)$$

Where n is the total number of atoms of the carbon, x is the number of atoms located at the reactive positions and z is the number of atoms in intramolecular competition. The ^{13}C -AKIE values are calculated for the remaining TCP P in the reaction systems and therefore $n = 9$, $x = 6$ and $z = 3$. Uncertainties of ϵ and AKIE values are reported as a 95% confidence interval.

2.3.5. ROSs identification

To identify the dominant ROSs involved in the natural pyrite-activated persulfate system, quenching experiments were conducted [23]. Tert-butanol (TBA, 1.0 M) was employed as a scavenger for $\bullet\text{OH}$ radicals, methanol (MeOH, 0.5 M) was used to quench both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ radicals, and furfuryl alcohol (FFA, 0.4 M) was applied as a scavenger for singlet oxygen ($^1\text{O}_2$) [24,25]. The volume ratio of scavenger solution to reaction solution was maintained at 1:100 to minimize disturbance. In addition, electron paramagnetic resonance (EPR) spectrometer (Bruker EMX Plus-10/12, Bruker, Bremen, Germany) was employed to directly detect ROSs. The spin-trapping agents 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine

(TEMP) were used to detect radical species and singlet oxygen, respectively [26,27].

3. Results and discussion

3.1. Degradation of TCP

The hydrolysis of TCP under different pH conditions is presented in Fig. 1(a). At pH 3, the hydrolysis efficiency reached 34.0% after 85 days, with a rate constant of 0.005 day^{-1} and a half-life of 139 days. Similar results were observed at pH 7. The hydrolysis efficiency was 36.0% after 85 days, with a rate constant of 0.005 day^{-1} and a half-life of 139 days. In contrast, at pH 11, the degradation efficiency increased to 48.0% after 85 days, corresponding to a rate constant 0.008 day^{-1} and a half-life of 87 days. The results indicate that the hydrolysis of TCP is pH-dependent and proceeds more rapidly under alkaline conditions. Similar pH-dependent hydrolysis behavior has previously been reported for organophosphate triesters in aqueous environments [28].

TCP degradation in natural pyrite under UV irradiation ($\lambda = 254 \text{ nm}$) is shown in Fig. 1(b). No significant degradation was detected in the natural pyrite system after 150 min. Under combined natural pyrite and UV irradiation conditions (254 nm), approximately 10% of TCP was degraded within 150 min, corresponding to a rate constant of 0.001 min^{-1} and a half-life of 693 min.

The degradation of TCP in the natural pyrite-activated persulfate system is presented in Fig. 1(c). Negligible degradation was observed in either the natural pyrite alone or the persulfate alone systems. In

contrast, approximately 99.0% of TCP was removed within 150 min in the natural pyrite-activated persulfate system. This substantial enhancement demonstrates the strong activation capability of natural pyrite toward persulfate.

3.2. pH evolution in the natural pyrite-activated persulfate system

Solution pH value plays a critical role in the performance of the natural pyrite-activated persulfate system, as it governs both persulfate activation and the generation of ROSs responsible for contaminant degradation [29]. Therefore, the effects of initial solution pH on TCP degradation and the temporal evolution of pH value during the reaction were systematically investigated. As shown in Fig. S2 (a), substantial degradation of TCP was achieved across the examined pH value range (3–11). However, acidic conditions favored TCP degradation. This aligns with prior findings [30]. The evolution of solution pH during the reaction is shown in Fig. S2 (b). The solution pH decreased significantly within the first 30 min of the reaction and subsequently stabilized at relatively low values. Specifically, the initial pH values of 3, 5, 7, 9, and 11 decreased to 1.9, 2.0, 2.1, 2.1, and 3.2, respectively.

Variations of dissolved Fe^{2+} and total dissolved iron concentrations throughout the reaction are illustrated in Fig. S3. Both Fe^{2+} and total dissolved iron increased rapidly during the first 30 min under all pH conditions, while the levels of Fe^{2+} gradually stabilized as the reaction proceeded. These results suggest the establishment of a dynamic equilibrium between iron release and iron consumption. The sustained dissolution of pyrite continuously released Fe^{2+} and increased dissolved

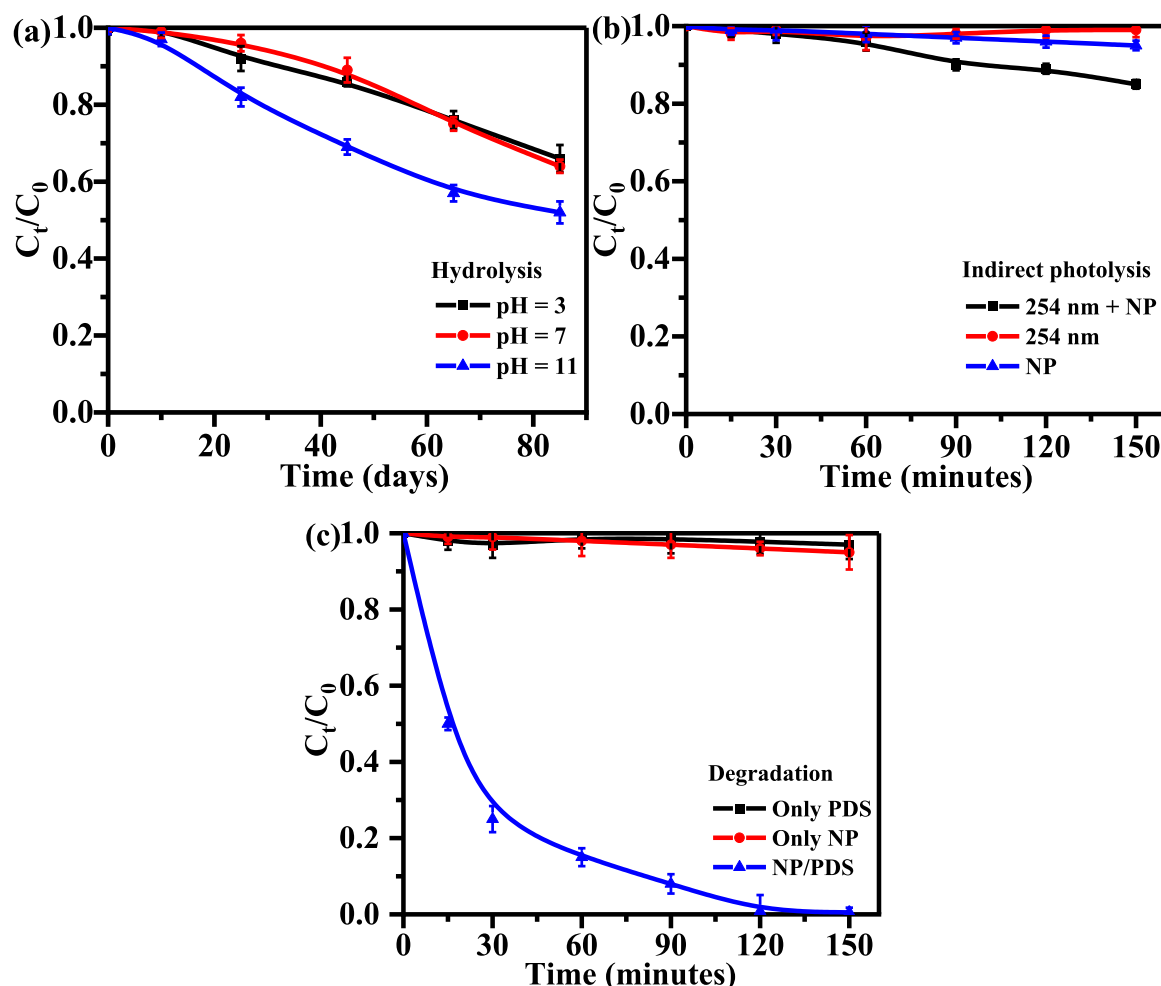


Fig. 1. The degradation of TCP in aqueous environments: (a) Hydrolysis; (b) Indirect photolysis; (c) Natural pyrite-activated persulfate degradation.

iron concentrations. During pyrite oxidation by dissolved oxygen, Fe^{2+} and H^+ are generated [31]. In addition, the reaction between pyrite and persulfate produces Fe^{3+} while releasing additional H^+ . The released Fe^{2+} can further activate persulfate, generating Fe^{3+} and sulfate radicals ($\text{SO}_4^{\bullet-}$) [32]. Collectively, these processes sustained Fe^{2+} availability and promoted progressive acidification of the system, as evidenced by the decline of pH values. The continuous release of Fe^{2+} during pyrite oxidation provided a stable source of activator for persulfate activation, generating abundant ROSs and facilitating TCPD degradation.

3.3. ROSs

To elucidate the degradation mechanism of TCPD in the natural pyrite-activated persulfate system, the ROSs involved were investigated through radical-quenching experiments and EPR spectroscopy. Competitive kinetic quenching experiments were conducted to quantify the contribution of ROSs to TCPD degradation. Methanol (MeOH) is known to effectively quench both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ radicals, whereas tert-butanol (TBA) preferentially scavenges $\bullet\text{OH}$ because its reaction rate constant with $\text{SO}_4^{\bullet-}$ ($4.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) is substantially lower than that with $\bullet\text{OH}$ ($6.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) [33]. Furfuryl alcohol (FFA) was employed as a selective scavenger for $^1\text{O}_2$, with reaction rate constants in the range of 10^6 – $10^7 \text{ M}^{-1}\text{s}^{-1}$ [34].

As shown in Fig. 2(a), the FFA quenching experiments indicated $^1\text{O}_2$ played only a minor role in TCPD degradation. In aqueous systems, $^1\text{O}_2$ can be generated through electron-transfer processes involving dissolved oxygen and pyrite-derived reactive intermediates [35]. Owing to its unique electronic configuration, $^1\text{O}_2$ exhibits high reactivity resulting from the spin-state transition from triplet oxygen. However, the degradation efficiency of TCPD remained above 90% after 300 min in the presence of FFA, with no significant difference compared to the unquenched controls ($P > 0.05$). This indicates that $^1\text{O}_2$ made a negligible contribution to TCPD degradation. In contrast, radical quenching experiments demonstrated that the addition of TBA significantly reduced the TCPD degradation efficiency to 22% within 300 min ($P < 0.01$), whereas MeOH almost completely suppressed TCPD degradation, resulting in a degradation efficiency of less than 5%. These results confirm that $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ are the primary ROSs responsible for TCPD degradation. Further calculation of radical contribution rates revealed that $\bullet\text{OH}$ accounted for 78.0% of the overall degradation, substantially exceeding the 22.0% contribution of $\text{SO}_4^{\bullet-}$. This finding indicates that $\bullet\text{OH}$ is the dominant oxidizing species in TCPD degradation.

The presence of $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, and $^1\text{O}_2$ was further verified by EPR spectroscopy (Fig. 2(b)). Consistent with the quenching experiments,

characteristic DMPO-OH (1:2:2:1 quartet, $g = 2.0056$) and DMPO- $\text{SO}_4^{\bullet-}$ signals were observed using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin-trapping agent. Owing to the short lifetime of $\text{SO}_4^{\bullet-}$, the signal intensity of DMPO- $\text{SO}_4^{\bullet-}$ was only about 15% that of DMPO-OH. Meanwhile, TEMP reacted with $^1\text{O}_2$ to generate a characteristic 1:1:1 triplet signal ($g = 2.0058$), confirming the coexistence of radicals and non-radical oxidizing species in the reaction system. However, $^1\text{O}_2$ was not a major contributor to TCPD degradation, as evidenced by the negligible inhibition observed in the FFA quenching experiments (degradation efficiency $> 90\%$, $P > 0.05$). Moreover, the diamagnetic nature of pyrite may limit spin-dependent pathways for $^1\text{O}_2$ generation, thereby restricting its production in the system [36,37]. Although $^1\text{O}_2$ can be produced in the natural pyrite-activated persulfate system through energy- or electron-transfer pathways [38], its oxidation potential ($E^\circ = 0.81 \text{ V}$ vs. normal hydrogen electrode (NHE)) is significantly lower than those of $\bullet\text{OH}$ ($E^\circ = 2.73 \text{ V}$ vs. NHE) and $\text{SO}_4^{\bullet-}$ ($E^\circ = 2.60 \text{ V}$ vs. NHE). This further demonstrates that $^1\text{O}_2$ is not a major ROS responsible for TCPD degradation. Collectively, these findings reveal that in the natural pyrite-activated persulfate system, TCPD degradation is predominantly governed by radical-mediated oxidation involving $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, with $\bullet\text{OH}$ serving as the dominant reactive species.

3.4. Characterization of natural pyrite

To characterize the physicochemical properties of natural pyrite before and after reaction, the X-ray fluorescence spectrometry (XRF), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) were employed to determine elemental composition, surface morphology, and surface chemical states, respectively. In addition, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were used to investigate changes in crystal and molecular structures.

XRF is based on wavelength-dispersive X-ray fluorescence, whereby elements emit abundant X-ray photons with specific energies that enable their identification and quantification [39]. The elemental composition obtained from XRF analysis is summarized in Tab. S1. The major elements were present in the following order: S (52.30%) $>$ Fe (31.00%) $>$ Si (6.68%) $>$ Mg (4.48%) $>$ Al (3.15%) $>$ Ca (1.30%) $>$ Cu (0.53%) $>$ K (0.48%) $>$ Na (0.25%) $>$ Ti (0.04%) = Mn (0.04%) $>$ P (0.02%) = Zn (0.02%). Based on the elemental composition, FeS_2 was identified as the dominant mineral phase, accounting for approximately 85 wt% of the sample.

SEM images of natural pyrite before and after reaction are presented in Fig. S4. Prior to reaction, the natural pyrite appeared as micrometer-scale aggregates composed of densely packed small particles. After the

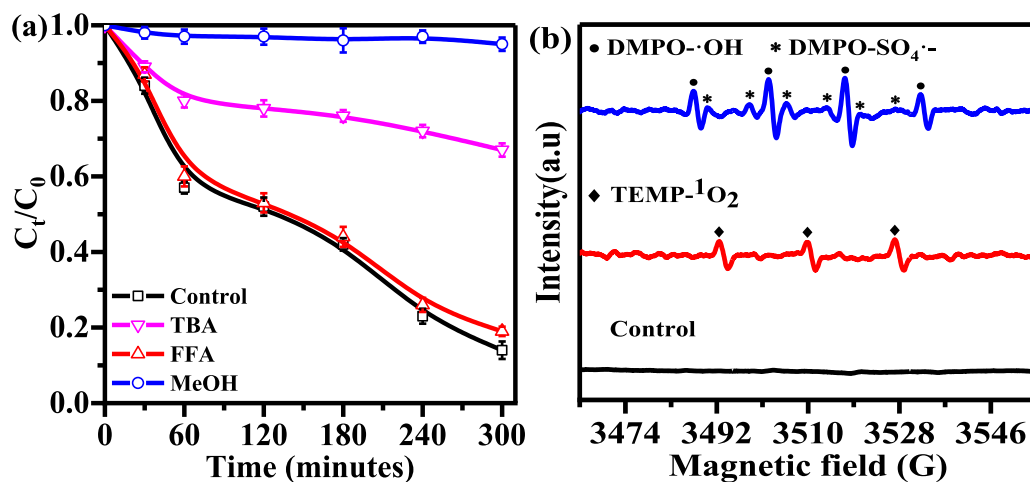


Fig. 2. (a) TCPD degradation with adding different quenchers in the natural pyrite-activated persulfate system; (b) EPR spectra generated with DMPO or TEMP in the natural pyrite-activated persulfate system.

reaction, the particles exhibited a more rounded morphology with smoother surfaces. These morphological changes are attributed to the dissolution-recrystallization process of Fe(II)/Fe(III) [40].

The crystalline structure of pyrite was examined using XRD (Fig. 3 (a)). The diffraction peaks at 33.1° , 37.1° , 40.8° , 56.3° , 59.0° , 61.7° , and 64.3° correspond well to the characteristic reflections of crystalline FeS₂. No additional peaks were observed after reaction, indicating that the crystal structure of pyrite remained largely unchanged during persulfate activation.

FTIR spectra of natural pyrite before and after reaction are shown in Fig. 3(b). The absorption band near 1000 cm^{-1} is assigned to Fe-O vibrations associated with FeO₆ coordination octahedra. The broad band centered around 3430 cm^{-1} corresponds to O-H stretching vibrations, while the band near 1630 cm^{-1} is attributed to the characteristic Fe-SO₄ peak [27]. The presence of these bands indicates surface hydroxylation and sulfation. Although only minor changes were observed in the intensities of the Fe-O and O-H bands, the peak intensity of Fe-SO₄ increased noticeably. In addition, peak shifts in the $400\text{--}1000\text{ cm}^{-1}$ range suggest subtle variations in S-S and Fe-S bonding states at the surface [41]. Collectively, these results demonstrate that natural pyrite preserves its FeS₂ framework during persulfate activation. Surface Fe(II) dissolution and sulfation are key interfacial processes driving persulfate activation. This structural robustness underpins the sustained catalytic performance of pyrite in the natural pyrite-activated persulfate system.

The XPS spectra confirmed the presence of Fe, S, C, and O at the surface of pyrite in the natural pyrite-activated persulfate system (Fig. 4 (a)). The carbon signal was primarily attributed to adventitious carbon contamination commonly observed during XPS analysis. To elucidate the role of iron species during persulfate activation, high-resolution Fe 2p XPS spectra of NP were analyzed (Fig. 4(b) and (c)). The peaks centered at binding energies of 705.5, 709.7, and 711.8 eV were assigned to Fe(II)-S, Fe(III)-O, and Fe(III)-S species [35,40], respectively. The presence of Fe(III) species is attributed to pyrite oxidation by dissolved oxygen during the reaction. After the reaction, the Fe(II) content decreased from 34.68% to 30.00%, while the proportion of Fe(III) increased from 65.32% to 70.00%, indicating that Fe(III) on the natural pyrite surface can be rapidly regenerated. Meanwhile, part of Fe(III) is subsequently reduced back to Fe(II), which further reacts with persulfate to generate Fe(III), thus enhancing the redox cycling between Fe(III) and Fe(II). These results indicate that persulfate can be activated by both dissolved Fe(II) and surface Fe(II) of pyrite. During this process, Fe(II) is oxidized to Fe(III) to generate ROSS, such as $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$.

The evolution of sulfur species was further investigated using high-

resolution S 2p XPS spectra (Fig. 4(d) and (e)). These peaks at 160.6, 161.1, 162.2, 162.7, and 167.5 eV were assigned to monosulfide (S^{2-}), disulfide (S_2^{2-}), polysulfide (S_n^{2-}), elemental sulfur (S^0), and surface-bound sulfate (SO_4^{2-}) [42,43], respectively. After the reaction, the levels of S^{2-} and S_2^{2-} decreased from 13.86% and 64.33–10.64% and 48.09%, respectively, while the proportions of $\text{S}^0/\text{S}_n^{2-}$ and SO_4^{2-} increased from 8.39% and 13.84–13.92% and 27.35%, respectively. These results demonstrate continuous oxidation of sulfur species during persulfate activation. S_2^{2-} and S^{2-} in pyrite serve as electron donors and reduce Fe(III) to Fe(II). In addition, these reduced sulfur species can be oxidized during persulfate activation to form high-valence sulfur species, such as $\text{S}_0/\text{S}_n^{2-}$ and SO_4^{2-} [44,45]. The activated persulfate is ultimately converted to SO_4^{2-} through a series of redox reactions, and some SO_4^{2-} may adsorb onto the pyrite surface. The pronounced increase in the SO_4^{2-} peak intensity indicates that sulfur species are ultimately oxidized to sulfate, which is consistent with the FTIR results.

The high-resolution O 1s spectra further revealed changes in surface oxygen-containing species during the reaction. Prior to reaction, two major peaks were observed at 530.5 (73.17%) and 531.5 eV (26.83%) (Fig. 4(f)), corresponding to lattice oxygen (O^{2-}) and surface-adsorbed oxygen-containing species, respectively [46]. After the reaction, a peak appears at approximately 530.5 eV (12.99%) (Fig. 4(g)), which is attributed to surface hydroxyl groups (Fe-OH). These Fe-OH species are associated with the generation of $\text{O}_2^{\cdot-}$ radicals and may further participate in the formation of surface hydroxyls [47]. Additionally, the peak intensity at 531.5 eV increased after the reaction, indicating the accumulation of SO_4^{2-} on the pyrite surface. This aligns with the trends observed in the S 2p spectra.

As illustrated in Fig. S5, surface Fe(II) activates persulfate via single-electron transfer, generating $\text{SO}_4^{\cdot-}$ ($E^\circ = 2.60\text{ V vs. NHE}$). These radicals subsequently react with $\text{H}_2\text{O}/\text{OH}^-$ to produce $\cdot\text{OH}$ ($E^\circ = 2.73\text{ V vs. NHE}$), establishing a radical chain degradation pathway. Meanwhile, Fe(III) in pyrite is reduced back to Fe(II) via Fenton-like reactions mediated by surface-coordinated water molecules or organic ligands [43]. This maintains a stable Fe(II) concentration and ensures continuous and efficient activation of persulfate.

3.5. Carbon isotope fractionation

As shown in Fig. 1(a) and Fig. 5(a), hydrolysis of TCPF under acidic and neutral conditions (pH = 3 and 7) resulted in degradation efficiencies of 34.0% and 36.0%, respectively, accompanied by significant carbon isotopic fractionation. The $\delta^{13}\text{C}$ values shifted from -32.83‰ to -31.38‰ (pH 3) and from -32.35‰ to -30.69‰ (pH 7), with

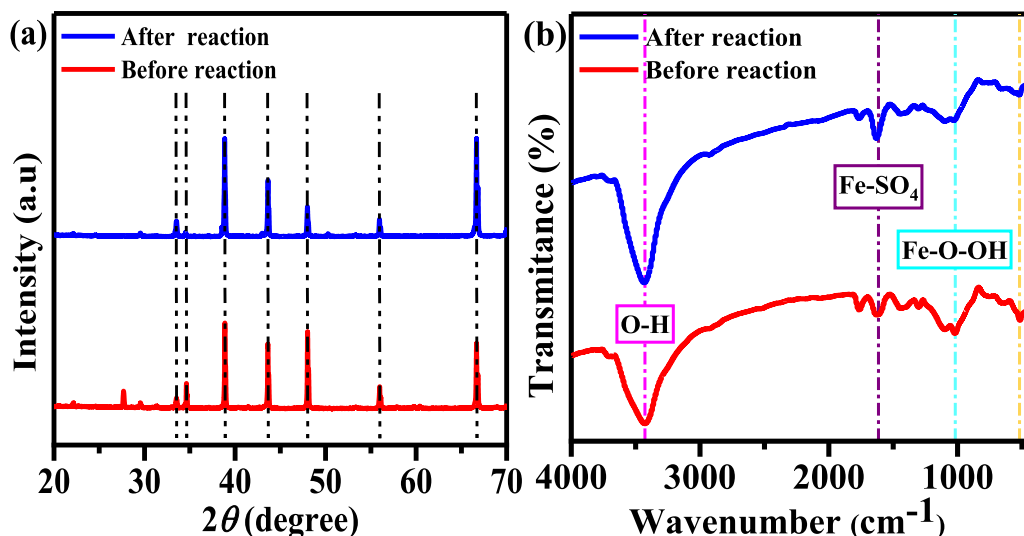


Fig. 3. (a) The XRD patterns of natural pyrite; (b) The FTIR spectra of natural pyrite.

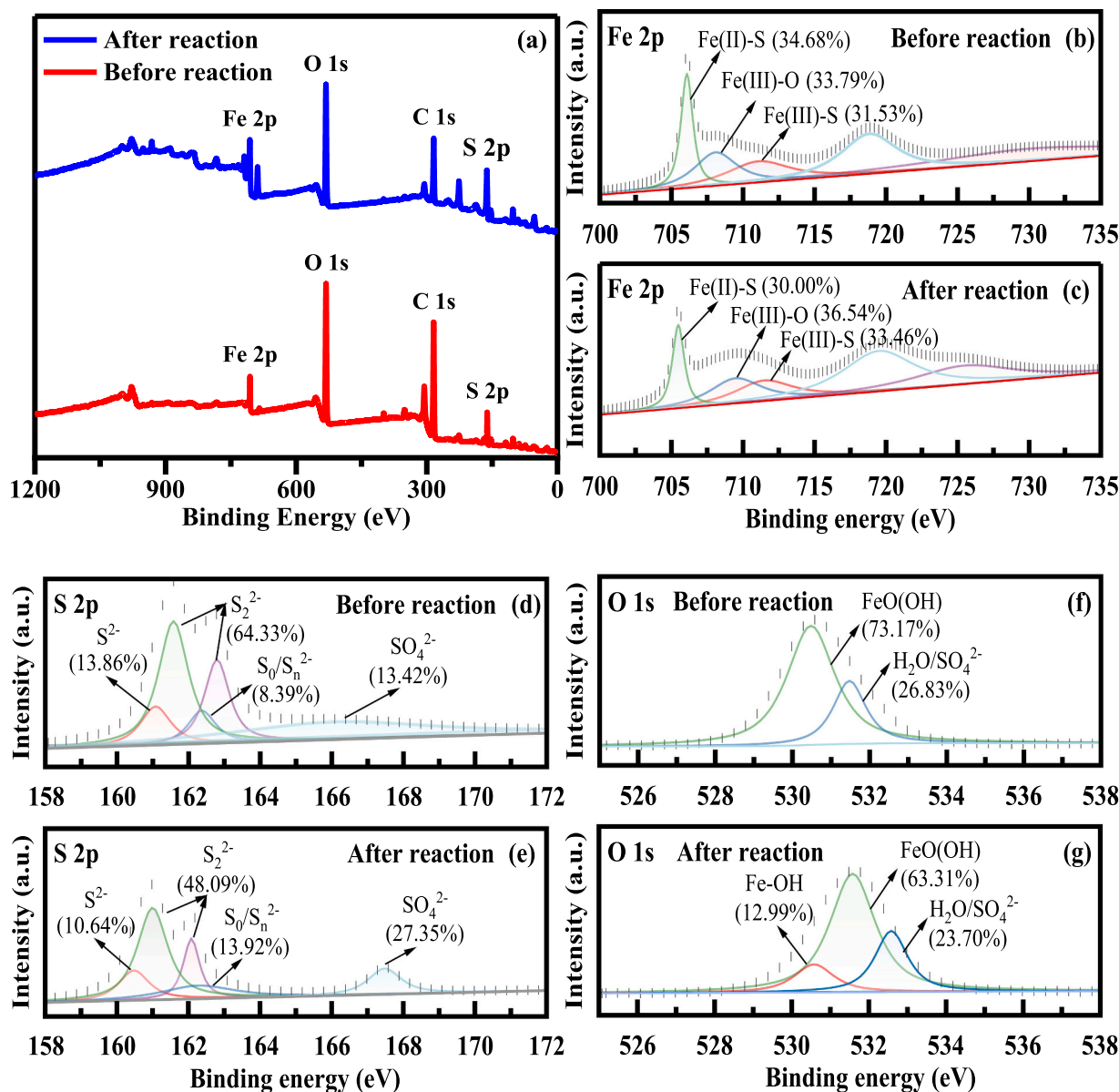


Fig. 4. (a) The XPS spectrum of the natural pyrite before and after the reaction, (b) and (c) Fe 2p, (d) and (e) S 2p, (f) and (g) O 1s.

variations exceeding the analytical uncertainty ($\pm 0.5\%$). Based on linear regression using the Rayleigh equation (Eq. (2)), the corresponding carbon isotope enrichment factors (ϵ_C) were $-3.34 \pm 0.46\%$ and $-3.09 \pm 0.83\%$, respectively (Table 1). The Rayleigh model was further applied to establish the relationship between the change of carbon isotopic composition and degree of degradation [19]. The carbon AKIE (^{13}C -AKIE) values calculated by the Rayleigh Eq. (4) were 1.031 ± 0.004 and 1.030 ± 0.004 (Fig. 5(b) and Table 1). In contrast, under alkaline conditions (pH = 11), although the hydrolysis efficiency of TCP was 48.0% (Fig. 1(a)), only negligible carbon isotopic fractionation was observed, with $\delta^{13}\text{C}$ values changing from -32.23% to -31.92% (within analytical uncertainty; Fig. 5(a)). The contrasting isotope behaviors under different pH conditions suggest that distinct reaction pathways dominate the initial rate-limiting step of TCP hydrolysis. Under acidic and neutral conditions, the significant carbon isotopic fractionation indicates that TCP hydrolysis involves the cleavage of carbon-containing bonds and is associated with a primary carbon isotopic fractionation. Furthermore, the carbon isotope effect (^{13}C -AKIE = 1.031 ± 0.004 , ^{13}C -AKIE = 1.030 ± 0.004) values are consistent with the intrinsic KIE values (1.00–1.03) reported for C–O

bond cleavage in the literature [20]. These results suggest that C–O bond cleavage is the dominant reaction pathway during TCP hydrolysis under acidic and neutral conditions. In contrast, under alkaline conditions, insignificant carbon isotopic fractionation (^{13}C -AKIE = 1) indicates that hydrolysis does not involve cleavage of carbon-containing bonds and is instead characterized by a secondary carbon isotopic fractionation. Therefore, the initial and dominant hydrolysis step under alkaline conditions is most likely the cleavage of the P–O bond.

For the natural pyrite-activated persulfate system, degradation efficiencies were 84.0%, 81.0%, and 87.0% at pH 3, 7, and 11, respectively (Fig. S2 (a)). These transformations were accompanied by minor carbon isotopic fractionation, with $\delta^{13}\text{C}$ values shifting from -31.65% to -30.05% (pH 3), -31.39% to -30.53% (pH 7), and -31.59% to -30.03% (pH 11) (Fig. 5(c)). The corresponding ϵ_C values were $-0.96 \pm 0.09\%$, $-0.46 \pm 0.04\%$, and $-0.54 \pm 0.11\%$, respectively (Fig. 5(d) and Table 1). The ^{13}C -AKIE values obtained from the Rayleigh equation Eq. (4) were 1.009 ± 0.001 , 1.004 ± 0.000 , and 1.005 ± 0.001 (Table 1).

Considering the molecular structure of TCP, which contains C–H, C–O, and C–Cl bonds, the observed ^{13}C -AKIE values of TCP are

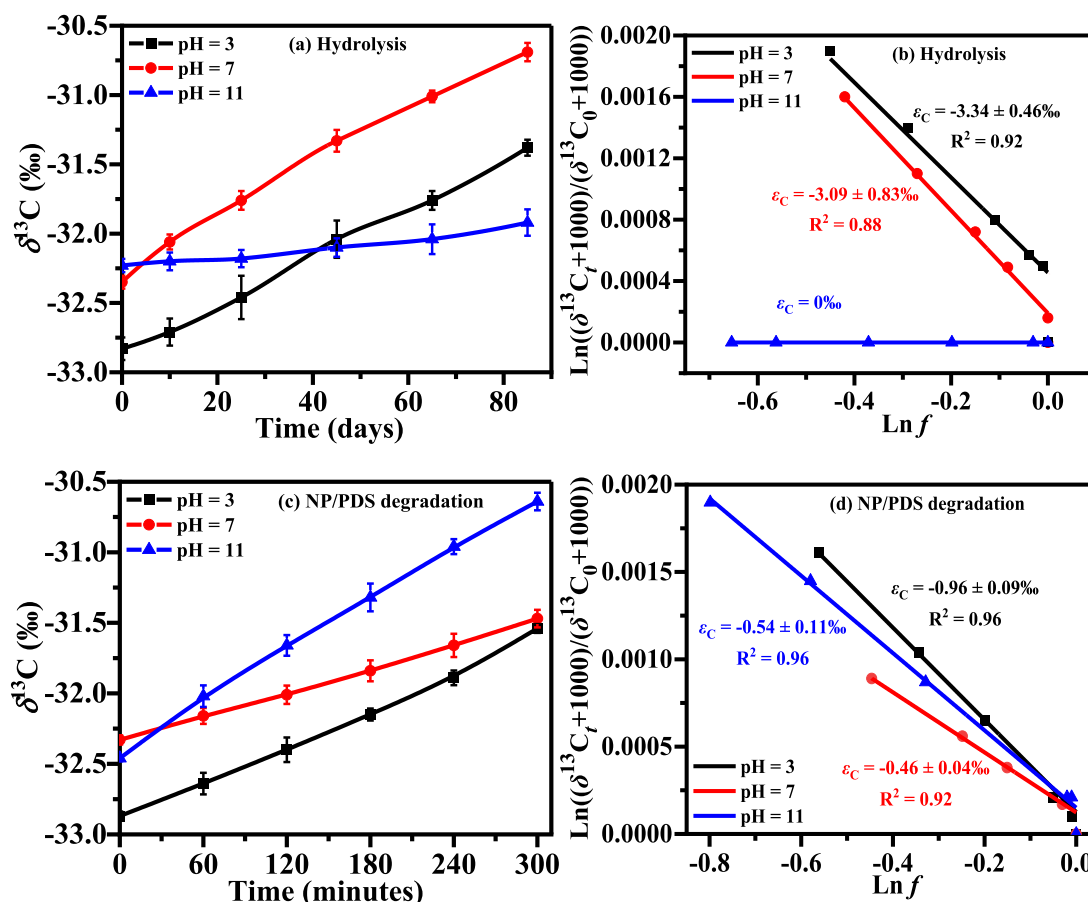


Fig. 5. Carbon isotopic fractionation of TCPP degradation and Rayleigh equation fitting for carbon isotopic fractionation under different pH conditions: (a) and (b) Hydrolysis; (c) and (d) Natural pyrite-activated persulfate degradation.

Table 1

Carbon isotope enrichment factors (ϵ_C) and apparent kinetic isotope effect (AKIE) values of TCPP degradation in different experiments.

Experiments	Conditions	n, x, and z	ϵ_C (‰)	R^2	^{13}C -AKIEs
Hydrolysis	pH = 3	$n = 9$, $x = 3$, and $z = 3$	-3.34 ± 0.46	0.92	1.031 ± 0.004
	pH = 7		-3.09 ± 0.83	0.88	1.030 ± 0.004
	pH = 11		0		1
Natural pyrite-activated persulfate	pH = 3	$n = 9$, $x = 3$, and $z = 3$	-0.96 ± 0.09	0.96	1.009 ± 0.001
	pH = 7		-0.46 ± 0.04	0.92	1.004 ± 0.000
	pH = 11		-0.54 ± 0.11	0.96	1.005 ± 0.001

n: the total number of carbon atoms in the molecule; x: the number of carbon atoms located at the reactive sites; z: the number of competing atoms within the molecule; ND: not detectable.

inconsistent with the intrinsic KIE values associated with C-H (1.01–1.03) and C-Cl (1.02–1.03) bond cleavage. Instead, they fall within the lower limit of the minimum intrinsic KIE values for C–O bond cleavage (1.00–1.03) [20]. These results indicate that the cleavage of C–H and C–Cl bonds is unlikely to be the dominant degradation pathway. In addition, the ^{13}C -AKIE values for TCPP degradation in the natural pyrite-activated persulfate system are close to the lower limit of the intrinsic KIE values range reported for C–O bond cleavage (1.00–1.03), indicating that C–O bond cleavage is not the rate-limiting step in the initial stage of the reaction. Previous studies have shown that

substantially smaller AKIE values are often observed for carbon atoms located adjacent to the reacting bonds [19,20]. Therefore, during TCPP degradation by natural pyrite-activated persulfate, the dominant reaction should be the cleavage of the P–O bond rather than the C–O bond. In this mechanism, the carbon atoms adjacent to the cleaved P–O bond experience only secondary carbon isotopic fractionation, resulting in the relatively small ^{13}C -AKIE values. Consequently, P–O bond cleavage is considered the initial rate-limiting step during TCPP degradation by natural pyrite-activated persulfate.

3.6. Transformation products and reaction mechanisms

Transformation products of TCPP formed during hydrolysis and natural pyrite-activated persulfate degradation were identified using a high-resolution quadrupole electrostatic field orbital trap mass spectrometer (Thermo Scientific™, Bremen, Germany). Product identification was based on a comprehensive analysis of molecular masses, isotopic distribution patterns, and MS fragmentation spectra. Owing to their low concentrations and/or transient nature, some intermediate species and transition states could not be detected in the experimental systems. Only one product bis(2-chloropropyl) hydrogen phosphate (P1: $\text{C}_6\text{H}_{13}\text{Cl}_2\text{O}_4\text{P}$, m/z 251.00) was identified across all hydrolysis conditions (Tab. S2 and Fig. S6). P1 with an $[\text{M} + \text{H}]^+$ value of 251.00 was detected in positive ionization mode. In contrast, a total of fourteen transformation products (P1–P14) were detected during TCPP degradation in the natural pyrite-activated persulfate system, with $[\text{M} + \text{H}]^+$ values of 251.00, 233.03, 174.99, 98.98, 266.99, 190.99, 343.00, 340.99, 309.04, 307.02, 323.03, 247.01, 225.13, and 183.08, respectively (Tab. S2 and Fig. S6). These products were identified as hydroxylated, ketone-containing, and carbonylated derivatives of TCPP.

Notably, P1 was the only common transformation product observed in both hydrolysis and natural pyrite-activated persulfate degradation. The detailed mass spectra, chemical structures, and retention times of these identified transformation products are provided in Tab. S2 and Fig. S6. In addition, the changes of fourteen transformation products (P1-P14) during TCPP degradation are provided in Fig. S7. As shown in Fig. S7, the primary product P1 is significantly greater than the other primary products (P7, P9, and P13).

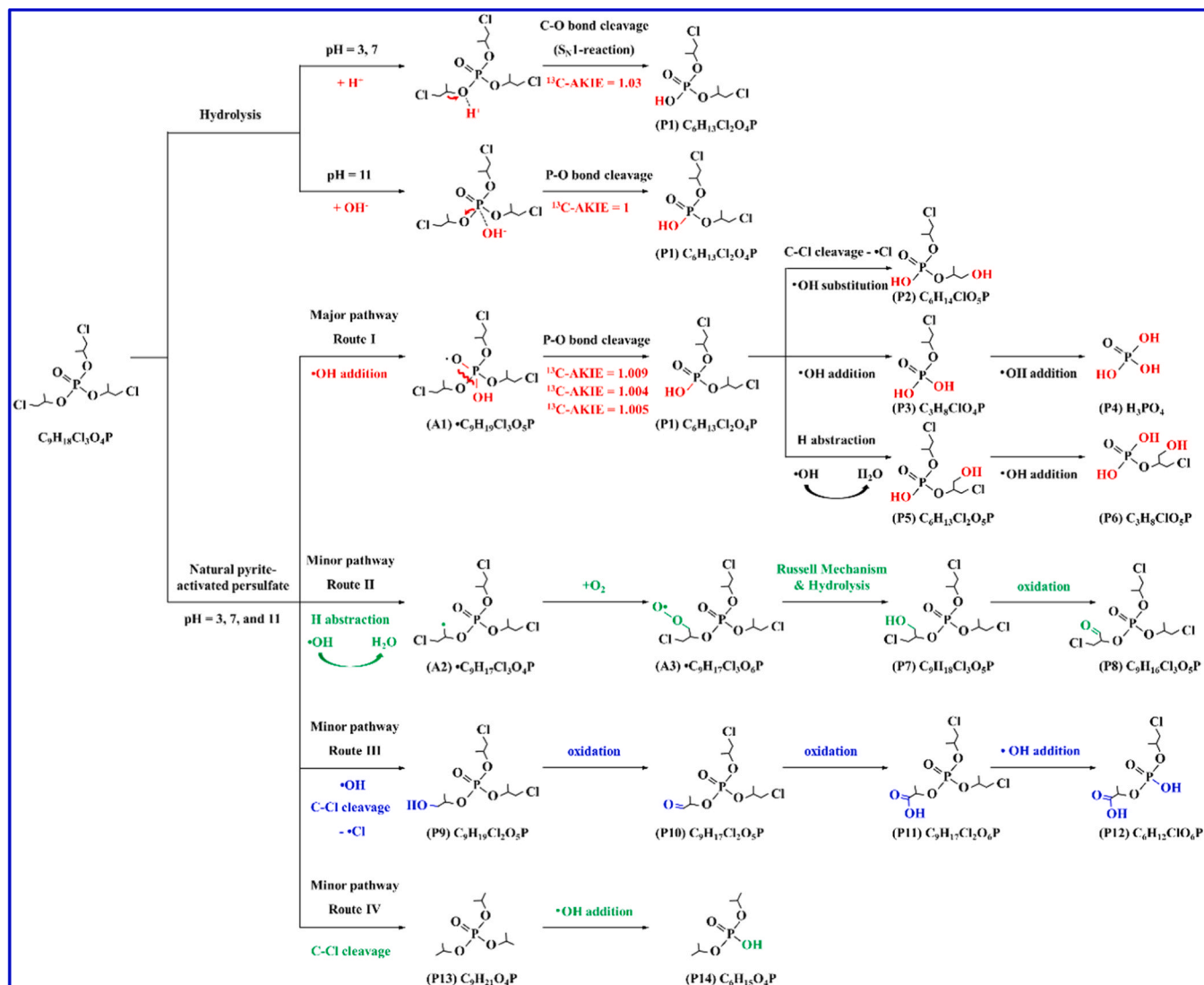
Based on the identified products and the carbon isotopic fractionation characteristic of hydrolysis and natural pyrite-activated persulfate degradation, plausible transformation mechanisms were proposed (Scheme 1).

For hydrolysis, P1 ($C_6H_{13}Cl_2O_4P$, m/z 251.00) was the sole detectable product across all examined pH conditions (pH 3, 7, and 11). However, distinct carbon isotope effects (^{13}C -AKIE = 1.031 ± 0.004 at pH 3; 1.030 ± 0.004 at pH 7; and 1 at pH 11) indicate that hydrolysis proceeds via different rate-limiting steps under varying pH conditions. Under acidic and neutral conditions (pH 3 and 7), the highly electronegative oxygen atoms in TCPP are readily protonated by hydrogen ions in solution. Subsequently, the C–O bonds undergo heterolytic cleavage, generating P1 and resulting in a primary carbon isotopic fractionation (Scheme 1). In contrast, under alkaline condition (pH 11), hydroxide ions nucleophilically attack the central phosphorus atom, followed by

heterolytic cleavage of the P–O bond. This process also yields P1 but is accompanied by secondary carbon isotopic fractionation (Scheme 1).

For natural pyrite-activated persulfate degradation, the reactive species $\cdot OH$ and $SO_4^{\cdot -}$ generated in the system participated in the transformation of TCPP. Based on the identified products, carbon isotopic fractionation patterns, and AKIE values, four transformation pathways were proposed.

Route I is the dominant transformation pathway (Scheme 1). In this pathway, $\cdot OH$ initially attacks the central phosphorus atoms, generating the transition-state radical A1 ($\cdot C_9H_{19}Cl_3O_5P$). The observed carbon isotopic fractionation characteristics and the measured AKIE values (^{13}C -AKIE = 1.009 ± 0.001 , 1.004 ± 0.000 , and 1.005 ± 0.001) indicate that the transformation is governed a secondary isotopic fractionation effect, suggesting that P–O bond cleavage constitutes the initial rate-limiting step. According, homolytic cleavage of a P–O bond results in the loss of one oxygen-chlorinated isopropoxy radical ($\cdot OC_3H_6Cl$), yielding bis(2-chloropropyl) hydrogen phosphate (P1, $C_6H_{13}Cl_2O_4P$, m/z 251.00). Subsequently, cleavage of the terminal C–Cl bond in P1, accompanied $\cdot OH$ substitution, produces (1-chloro-2-propyl) (1-hydroxy-2-propyl) hydrogen phosphate (P2, $C_6H_{14}ClO_5P$, m/z 233.03). Continuous $\cdot OH$ mediated substitution and hydrolysis of P1 further generate 1-chloropropan-2-yl dihydrogen phosphate (P3, $C_3H_8ClO_4P$, m/z 174.99) and phosphoric acid (P4, H_3PO_4 , m/z 98.98). In



Scheme 1. Proposed transformation pathways for TCPP under hydrolysis and natural pyrite-activated persulfate degradation.

addition, hydrogen abstraction from the terminal methyl group by $\bullet\text{OH}$ yields 1-chloro-3-hydroxypropan-2-yl (1-chloropropan-2-yl) hydrogen phosphate (P5, $\text{C}_6\text{H}_{13}\text{Cl}_2\text{O}_5\text{P}$, m/z 266.99), which is subsequently transformed into (1-chloro-3-hydroxyprop-2-yl) dihydrogen phosphate (P6, $\text{C}_3\text{H}_8\text{ClO}_5\text{P}$, m/z 190.99) through further $\bullet\text{OH}$ -induced substitution reactions.

Since the initial P–O bond cleavage induces only secondary carbon isotopic fractionation, and the experimentally determined ^{13}C -AKIE values closely match the intrinsic ^{13}C -AKIE values associated with P–O bond cleavage, Route I is considered to be the primary transformation pathway of TCPP. Ou et al. reported that during the degradation of TCEP under UV-activated persulfate conditions, $\text{SO}_4^{\bullet-}$ first attacks the central phosphorus atom, followed by P–O bond cleavage and elimination of an oxygen-ethyl-chloride arm [48]. Lian et al. demonstrated that the relatively elongated P–O bonds connecting the pyridyl moiety in chlorpyrifos is particularly susceptible to cleavage. Furthermore, the P–S and P–O bonds in dimethoate are relatively longer. They are more susceptible to attack and subsequent substitution reactions [10]. Previous studies have also demonstrated that similar organophosphorus compounds undergo hydroxyl addition at the central phosphorus atoms, followed by substitution reactions involving the loss of a chlorinated isopropyl group [10, 49, 50]. Collectively, these findings suggest that P–O bonds cleavage is the predominant transformation pathway in the natural pyrite-activated persulfate system.

Route II involves $\bullet\text{OH}$ -mediated hydrogen abstraction at the terminal methyl carbon of TCPP (Scheme 1). The initial step is homolytic cleavage of the C–H bond, generating a carbon-centered radical intermediate (A2, $\bullet\text{C}_9\text{H}_{17}\text{Cl}_3\text{O}_4\text{P}$). This intermediate rapidly reacts with dissolved oxygen to form a peroxy radical species (A3, $\bullet\text{O}_2\text{C}_9\text{H}_{17}\text{Cl}_3\text{O}_4\text{P}$). The peroxy radical typically undergoes bimolecular termination via a Russell-type mechanism [51], yielding corresponding hydroxylated 1-chloro-3-hydroxypropan-2-yl bis(1-chloropropan-2-yl) phosphate (P7, $\text{C}_9\text{H}_{18}\text{Cl}_3\text{O}_5\text{P}$, m/z 343.00). Subsequent oxidation of the hydroxyl group produces 1-chloro-3-oxopropan-2-yl bis(1-chloropropan-2-yl) phosphate (P8, $\text{C}_9\text{H}_{16}\text{Cl}_3\text{O}_5\text{P}$, m/z 340.99). From an isotope perspective, initial C–H bond cleavage would be expected to induce primary carbon isotopic fractionation. However, the experimentally observed ^{13}C -AKIE values are inconsistent with the intrinsic ^{13}C -AKIE values associated with C–H bond cleavage. Therefore, Route II is considered a minor transformation pathway of TCPP.

Route III involves homolytic cleavage of the C–Cl bond via the release of a chlorine radical, followed by $\bullet\text{OH}$ -mediated substitution, forming bis(1-chloropropan-2-yl)(1-hydroxypropan-2-yl) phosphate (P9, $\text{C}_9\text{H}_{19}\text{Cl}_2\text{O}_5\text{P}$, m/z 309.04) (Scheme 1). Subsequently, the hydroxyl group is further oxidized to yield the corresponding aldehyde product, bis(1-chloropropan-2-yl)(1-oxopropan) phosphate (P10, $\text{C}_9\text{H}_{17}\text{Cl}_2\text{O}_5\text{P}$, m/z 307.02) and the carboxylated product 2-((bis(1-chloropropan-2-yl)oxy)phosphoryl)oxy)propanoic acid (P11, $\text{C}_9\text{H}_{17}\text{Cl}_2\text{O}_6\text{P}$, m/z 323.03). Meanwhile, the oxygen-chlorinated isopropyl group ($\bullet\text{OC}_3\text{H}_6\text{Cl}$) may undergo further $\bullet\text{OH}$ substitution to generate 2-(((1-chloropropan-2-yl)oxy)(hydroxy)phosphoryl)oxy)propanoic acid (P12, $\text{C}_6\text{H}_{12}\text{ClO}_6\text{P}$, m/z 247.01).

Route IV is characterized by cleavage of C–Cl bonds on the alkyl chain, accompanied by hydrogen substitution, generating triisopropyl phosphate (P13, $\text{C}_9\text{H}_{21}\text{O}_4\text{P}$, m/z 225.13). Subsequent substitution of the oxygen-chlorinated isopropyl group ($\bullet\text{OC}_3\text{H}_6\text{Cl}$) by $\bullet\text{OH}$ leads to the formation of diisopropyl phosphate (P14, $\text{C}_6\text{H}_{15}\text{O}_4\text{P}$, m/z 183.08) (Scheme 1). Both Route III and Route IV involve initial C–Cl bond cleavage, which would be expected to induce primary carbon isotopic fractionation. However, the experimentally derived ^{13}C -AKIE values are inconsistent with the intrinsic ^{13}C -AKIE values associated with C–Cl bond cleavage. Therefore, Route III and Route IV are classified as minor transformation pathways of TCPP.

4. Conclusions

This study investigated the carbon isotopic fractionation behavior and transformation mechanisms of the organophosphorus flame retardant TCPP under hydrolysis and natural pyrite-activated persulfate systems. Hydrolysis of TCPP proceeded slowly, achieving a maximum removal efficiency of 48.0% after 85 days. In contrast, rapid degradation was observed in the natural pyrite-activated persulfate system, reaching 99.0% within 150 min. In this system, continuous acidification of the reaction system was accompanied by sustained release of Fe^{2+} and total dissolved iron. Radical identification experiments demonstrated that $\bullet\text{OH}$ (78%) and $\text{SO}_4^{\bullet-}$ (22%) were the dominant ROSs responsible for TCPP degradation. Structural and surface analyses further confirmed that Fe(II) sites on pyrite, coupled with Fe(II)/Fe(III) redox cycling and sulfur valence transformations, served as the key drivers for persulfate activation and radical generation. Product analysis revealed one hydrolysis product (bis(2-chloropropyl) hydrogen phosphate) and fourteen transformation products in the natural pyrite-activated persulfate system. Hydrolysis under acidic and neutral conditions was initiated by C–O bond cleavage, whereas under alkaline conditions, P–O bond cleavage dominated the initial rate-limiting step. In contrast, for the natural pyrite-activated persulfate system, the cleavage of P–O bonds was the initial rate-limiting step, making Route I the dominant transformation pathways. Routes involving C–H and C–Cl bond cleavage (Routes II–IV) contributed only marginally and were identified as minor pathways.

In summary, carbon stable isotopic fractionation provides a powerful tool for tracing the environmental transformation pathways of TCPP and elucidating its geochemical behavior under different reaction conditions. Future studies could integrate multi-element stable isotope approaches (e.g., H, C, and Cl isotopes) to further improve the resolution of transformation mechanisms for organophosphorus flame retardants in complex environmental systems.

CRedit authorship contribution statement

Jukun Xiong: Writing – review & editing, Visualization, Validation, Supervision, Software, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Suyun Chen:** Writing – original draft, Software, Methodology, Investigation, Conceptualization. **Zixuan Wei-Xiong:** Software. **Yingxin Yu:** Visualization, Resources. **Chang Yuan:** Writing – original draft, Data curation. **Meicheng Wen:** Methodology, Funding acquisition. **Wanjuan Wang:** Methodology, Funding acquisition. **Qinhao Lin:** Methodology, Funding acquisition.

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. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2026.143521](https://doi.org/10.1016/j.jhazmat.2026.143521).

Data availability

Data will be made available on request.

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