



## Procyanidolic oligomers enhance photodegradation of chlorothalonil in water *via* reductive dechlorination

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### ABSTRACT

Chlorothalonil is an important broad-spectrum fungicide with an annual application rate of above ten thousands of tons of its active ingredient on agricultural crops world-wide. The effect of procyanidolic oligomers on photo degradation of chlorothalonil was investigated under sunlight and artificial lights. Procyanidolic oligomers enhanced photodegradation of chlorothalonil in paddy, reservoir, pond and distilled waters for 1.8, 4.6, 2.7 and 22.8 fold, respectively, relative to the procyanidolic oligomers free control. The mechanism was evidenced as a radical reduction reaction by electron paramagnetic resonance spectroscopy. Upon exposure to high-pressure mercury light, chlorothalonil produced 2,4,5-trichloro-1,3-dicyanobenzene, 2,5-dichloro-1,3-dicyanobenzene and 5-chloro-1,3-dicyanobenzene that were isolated, identified and characterized. Chlorothalonil underwent primarily step-wide photo reductive dechlorination in the presence of procyanidolic oligomers, which avoided the production of the highly toxic 4-hydroxy chlorothalonil. Procyanidolic oligomers possessed strong reductive property to photo reductive dechlorination. The results contributed to understanding of chlorothalonil phototransformation and high potential of using natural product procyanidolic oligomers as an additive to minimize aquatic toxicity and pollution of chlorothalonil.

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## 1. Introduction

Chlorothalonil (2,4,5,6-tetrachloro-1,3-dicyanobenzene, CTL) is a broad-spectrum, nonsystemic fungicide commonly applied on a large number of agricultural crops, especially vegetables and fruits. The annual application rate of its active ingredient was approximately ten thousands of tons on agricultural crops world-wide. Owing to its wide use and persistence in the environment, CTL is commonly detected in vegetables and fruits [1,2], soil and surface water [3,4], ground water and greenhouse air [5,6]. In addition, CTL has been used as an alternative to tributyltin in antifouling paints to prevent the growth of fouling organisms [7]. Since CTL and its metabolites are highly toxic to fish, aquatic invertebrates [8] and amphibians [9], as well as it could cause serious marine pollution impacting a number of marine species other than the fouling organisms [10], CTL pollution is of concern.

The main metabolites of CTL in aquatic environments include 4-hydroxy chlorothalonil (4-OH-CTL) [11] and other degradation products, which are derived from dechlorination [12,13] and oxidation/hydration [14,15]. To remediate CTL toxicity to aquatic species, many chemical treatments [15–20] were investigated to accelerate the degradation of CTL utilizing oxidation process. The feature of such treatments was generation of hydroxyl radicals giving rise to induce photodegradation which leads to the production of 4-OH-CTL. Unfortunately, 4-OH-CTL is approximately 30 times more toxic than its parent compound CTL. The acute oral LD<sub>50</sub> values of 4-OH-CTL and CTL on rat are 332 and 10,000 mg/kg, respectively [21]. In addition, 4-OH-CTL is more persistent than CTL in the environment [20]. Therefore, methods to enhance CTL degradation and generate less toxic products in the environment are needed to manage CTL aquatic pollution. In our previous study, the natural product epigallocatechin gallate (EGCG) was used to promote the degradation of CTL [22], but the mechanism and the pathway of photodegradation were not studied.

In our continuous efforts to search for a natural product possessing stronger reducing power in comparison to EGCG, procyanidolic oligomers (OPC) were investigated for roles on pho-

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tolysis efficiency, photodegradation pathways and mechanisms of chlorothalonil in aqueous solutions. OPC are the second most abundant plant polyphenolic compounds after lignin which could be found in most plants, especially epidermis, seeds, and seed coats of purple or red pigmented plants [23]. Additionally, OPC can be produced via *in vitro* cell culture of *Vaccinium pahalae* [24]. OPC have attracted increasing attention due to their potential health benefits such as antioxidant activity and the ability to scavenge reactive oxygen and nitrogen species. It has been hypothesized that the free radical scavenging properties of OPC may reduce the risk of cardiovascular diseases and cancer [25,26]. As OPC is the economical source and nontoxicity to human, it is significant to study OPC's reduction potential to photodegrade chlorothalonil as it represents its general value of such enhanced degradation in the environment.

## 2. Experimental

### 2.1. Chemicals and reagents

All chemicals and reagents were purchased from Chem Service and used as received. Chlorothalonil (99.1%), 4-OH-CTL (99%), OPC (95%), 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, 97%) and *N,N*-dimethyl-*p*-nitrosoaniline (PNDA, 98%) were purchased from J&K Chemical Ltd. (Shanghai, China). Acetonitrile (Assay  $\geq$ 99.9%, HPLC/Spectro) and methanol (Assay  $\geq$ 99.9%, HPLC/Spectro) were purchased from Tedia Co. (Fairfield, USA).

### 2.2. Photodegradation experiments

The photocatalytic degradation experiments were conducted under sunlight and a rotary photochemical reactor equipped with a 150 W high-pressure mercury lamp (HPML, emission line spectrum at 365 nm). An electric fan and cycled condensate water were used to control the temperature and to prevent the thermal catalytic effects. The speed of quartz tube surrounding light source in the photochemical reactor was 4 r/min. The distance between the quartz tube and the light source was 15 cm. The light intensity was 10,000–11,000 Lx for a high-pressure mercury lamp, and 84,000–93,000 Lx for direct sunlight (N31°52', E117°17'). The temperature of the reaction system was maintained at  $25 \pm 1$  °C except for the sunlight treatment which temperatures varied between 25 °C and 30 °C. A rotary water bath was used to maintain the temperature and the quartz tube was tilted at a 30° angle with the ground to face the sun directly. CTL standard stock solution was 1.0 g/L (3.76 mmol/L) in acetonitrile. The concentration of OPC was prepared at 5.0 g/L. To determine the effect of OPC on photodegradation of CTL in aqueous solution, CTL standard stock solution and OPC solution were transferred into 100 mL flasks at a mole to mole ratio (CTL:OPC) of 1:0, 1:1.8, 1:4.5, 1:9.0, 1:22.5, and 1:45 (CTL was 1.88  $\mu$ mol/L). To the flasks, double-distilled water was added and subjected to brief ultrasonication. An aliquot of 10 mL reaction solution of CTL and OPC was transferred to a quartz cuvette that was covered with a stopper and placed under different light sources.

Paddy, reservoir and pond waters (Table 1) were used to determine the effect of OPC on photodegradation of CTL in natural water. To a quartz cuvette, an aliquot of 10 mL reaction solution of CTL and OPC (CTL:OPC of 1:9.0, CTL is 1.88  $\mu$ mol/L) was transferred, then covered with a stopper and placed under sunlight. The quartz

tube was tilted at a 30° angle with the ground to face the sun directly. The light intensity was 84,000–93,000 Lx for direct sunlight (N31°52', E117°17'), and the temperature of the water solution varied between 25 °C and 30 °C.

### 2.3. Photodegradation of CTL and analysis of 4-OH-CTL in distilled water

An appropriate amount of CTL standard stock solution was transferred to a 100 mL volumetric flask and OPC was added at a mole to mole ratio of 1:9 (CTL is 1.88  $\mu$ mol/L). The mixture solution was diluted with double-distilled water and subjected to brief ultrasonication. Controls contained no OPC. An aliquot of 20 mL of the mixture was transferred to a quartz tube with a stopper and exposed to HPML. Afterwards, samples were taken at different times to measure the concentrations of CTL and chloride ion. The flasks completely covered with aluminum foil were used as a dark control, while the other conditions remained the same as the treatments. The samples were taken at different time intervals and each treatment was repeated twice. After incubation, the photoreaction mixtures were filtered through a 0.45  $\mu$ m membrane filter. The concentrations of CTL and 4-OH-CTL in the filtrate were determined and analyzed immediately by HPLC or stored at 4 °C.

Quantitative analysis of CTL and 4-OH-CTL were performed on an Agilent 1200 HPLC system equipped with an Agilent HC-C18 column (4.6 mm  $\times$  250 mm, 5  $\mu$ m) at a detection wave length of 236 nm and 248 nm, respectively (Agilent Technologies, USA). CTL and 4-OH-CTL were respectively eluted with 80% aqueous acetonitrile and a mixture of acetonitrile/0.5% phosphoric acid solution (60:40 v/v) at a flow rate of 1.0 mL/min. The column temperature was 30 °C. The injection volume was 10  $\mu$ L or 20  $\mu$ L. The limit of detection for CTL and 4-OH-CTL was 0.01 mg/L.

### 2.4. Detection of hydroxyl free radicals ( $\bullet$ OH) and chloride ion

Hydroxyl free radicals ( $\bullet$ OH) and chloride ion were determined by UV spectro photometer and ion chromatograph according to previously published methodologies [22].

### 2.5. Analysis of the other photolytic products of CTL

The mixture of photolytic products of CTL was partitioned with 20 mL of methylene chloride using a separatory funnel three times. After organic solvent extracts were combined, methylene chloride was evaporated with a rotary evaporator at 40 °C in a water bath. The residues were dissolved in 10 mL of acetone. The samples were then analyzed on an Agilent GC-MS (7890A-5975) system equipped with a HP-5 (30m  $\times$  0.25mm  $\times$  0.25  $\mu$ m) column. The oven temperature was started at 55 °C, ramped at 5 °C/min to 200 °C followed by another ramp of 1 °C/min to 210 °C, held for 2 min and finally to 270 °C at 20 °C/min (held for 3 min). Helium was used as carrier gas at a constant flow of 1 mL/min. The temperatures of the injector, ion source and the interface were set at 240, 240 and 290 °C, respectively. The MS was operated in electron impact mode with an ionization potential of 70 eV and the spectra were obtained at a scan range from *m/z* 50 to 450 (selective scan mode). The scan time was 50 min. The injection volume was 3.0  $\mu$ L.

**Table 1**  
The property of paddy, reservoir, and pond waters.

Natural Water	Turbidity FTU	Conductivity ms/cm	pH	Hardness mg/L	DO mg/L	COD mg/L	BOD <sub>5</sub> mg/L	TOC mg/L	Cl <sup>-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	NO <sub>2</sub> <sup>-</sup> mg/L
Paddy	1.8	0.29	7.42	264	4	342	2.4	15.08	46.4	75.9	0.59
Reservoir	1.4	0.15	7.09	124	15.2	8	6.4	9.62	14.6	27.9	0.53
Pond	2.3	0.32	7.38	140	4.8	72	2.4	27.82	52.1	72.5	0.57

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