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# Degradation behaviour of methamidophos and chlorpyrifos in apple juice treated with pulsed electric fields

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ABSTRACT

Apple juice (13 °Brix) spiked with methamidophos and chlorpyrifos (2–3 mg/l of each compound) was treated by pulsed electric fields (PEF), and pesticide residues were quantified by gas chromatography with flame photometric detection (GC-FPD). Results showed that electric field strength (8–20 kV/cm) and pulse number (6–26 pulses) have significant effects on the degradation of methamidophos and chlorpyrifos. PEF treatment is effective for the degradation of methamidophos and chlorpyrifos residues in apple juice, and chlorpyrifos is much more labile to PEF than methamidophos. An increase in either pulse number or electric field strength could speed the degradation of methamidophos and chlorpyrifos, and the kinetics equations and related parameters quantitatively characterized the degradation behavior of the pesticides. The exponential model better fits the experimental data for all treatments than the linear model.



## 1. Introduction

Organophosphorus pesticides (OPPs) are one of the most important and widely used classes of agricultural pesticides, accounting for about 70% of the insecticides in current use in China. This widespread use poses a potential risk to human health because OPPs inhibit acetylcholinesterase and lead to the modification of cholinergic signaling (Pope, Karanth, & Liu, 2005). In addition, OPPs have been known to be cytotoxic (Giordano et al., 2007; Wagner, McMillan, & Plewa, 2005), genotoxic (Cakir & Sarikaya, 2005; Rahman, Mahboob, Danadevi, Saleha, & Grover, 2002), reproductively toxic (Kang et al., 2004) and immunotoxic (Crittenden, Carr, & Pruett, 1998; Yeh, Sung, Chang, Cheng, & Kuo, 2005). Therefore, there is a growing interest in dissipation of OPP residues in agricultural products and foods all over the world.

Concentrated apple juice (CAJ) has become an economically important food product in China, where export of CAJ accounts for nearly 50% of the world export volume. However, the application of OPPs has resulted in pesticide residues in fruit and deterioration of CAJ quality. Several methods have been demonstrated to be effective in the removal of pesticide residues, such as post-harvest storage (Athanasopoulos & Pappas, 2000; Pappas, Kyriakidis, & Athanasopoulos, 2003), ozone washes, and resin adsorption during processing (Karaca & Velioglu, 2007; Ong, Cash, Zabik, Siddiq, & Jones, 1996). Unfortunately, these methods can reduce nutritional and flavor qualities of the juice (Dan & Seth, 1990; Nijssen, 1991) and in the case of ozonation, may also produce by-products with higher toxicity than the original organophosphorus pesticides themselves (Hwang, Cash, & Zabik, 2002; Ikehata & El-Din, 2005). Thus, it seems to be necessary to develop innovative processing methods to decrease pesticide residues without undesirable effects. Pulsed electric field (PEF) is a novel non-thermal technology, causing few losses of flavor, color, taste or nutrients (Ayhan, Yeom, Zhang, & Min, 2001; Cortes, Esteve, & Frigola, 2008) compared to conventional thermal processing. PEF technology can inactivate microorganisms (Mosqueda-Melgar, Raybaudi-Massilia, & Martin-Belloso, 2007; Zhong et al., 2005;) and enzymes (Aguilo-Aguayo, Odriozola-Serrano, Quintao-Teixeira, & Martin-Belloso, 2008; Marsells-Fontanet & Martin-Belloso, 2007). This raises an interesting question of whether or not pesticide residues in apple juice can be dissipated by PEF treatment. This application of PEF, to the best of our knowledge, has not been reported. Methamidophos (*O,S*-dimethyl phosphoramidothioate) and chlorpyrifos [*O,O*-diethyl-*O*-(3,5,6-trichloro-2-pyridinyl) phosphorothionate] were used as representative examples in present study, because they are active ingredients in most organophosphorus formulations. The aim of

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this paper is to investigate whether both methamidophos and chlorpyrifos in apple juice can be degraded by PEF.

## 2. Materials and methods

### 2.1. Materials

Methamidophos (>95% pure) and chlorpyrifos (98.5% pure) were purchased from the China Agricultural Environment Protection and Inspection Center (Tianjin, China). All solvents were analytical grade and obtained from Beijing Beihua Fine Chemicals Co. (Beijing, China). Acetone and acetonitrile were redistilled before use. Concentrated apple juice (CAJ) at 78 °Brix was manufactured by a local factory and diluted to 13 °Brix (similar to raw apple juice, pH 3.86) for PEF treatment. The initial concentration of methamidophos was 0.004 ± 0.001 mg/l, but no residue of chlorpyrifos was detected. Standard stock solutions (100.0 mg/l) of methamidophos and chlorpyrifos were prepared in acetone. The above stock solutions were added to the reconstituted apple juice with final pesticide concentrations of 2–3 mg/l followed by PEF treatment.

### 2.2. PEF Treatment of apple juice

PEF treatment was performed using a laboratory scale apparatus (jointly designed by Tsinghua University and China Agricultural University, Beijing, China), which included a high voltage pulse generator, a treatment chamber (volume ($V$) = 2 ml), and a peristaltic pump. A schematic diagram of the apparatus is shown in Fig. 1. Two round parallel-plate electrodes with a 3.57 mm radius were made of stainless steel, and the gap between electrodes was 5 mm. The PEF treatment parameters used were as follows: exponentially-decaying wave, 1 Hz pulse frequency, 0.5 μF capacitor, and 10 ms pulse width. A thermocouple was attached to the exit of the chamber to monitor the post-treatment temperature. A 20 ml aliquot of apple juice was pumped through the treatment chamber under a given combination of PEF conditions. Different electric field strengths (8, 12, 16 and 20 kV/cm) and pulse numbers (6, 9, 12, 19 and 26) were used as treatments. The pulse number depends on the pulse frequency ($f$) and the flow rate ($v$, ml/s) of apple juice. The pulse number was calculated as $V \times f/v$, and total treatment time was calculated as the product of the pulse width and the pulse number. The temperature of treated apple juice was kept below 40 °C due to the short treatment time (60–260 μs). Each treatment was conducted in triplicate. The treated apple juice was stored at 4 °C and the pesticides were tested within one day after treatment.

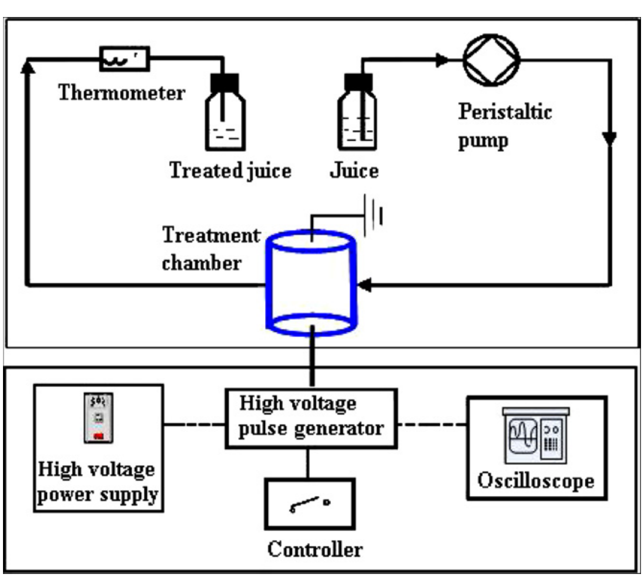


**Fig. 1.** Schematic diagram of the experimental PEF apparatus.

### 2.3. GC analysis of methamidophos and chlorpyrifos in apple juice

The extraction of pesticides was carried out according to a standard method established by the Ministry of Agriculture of China (2004) with some modifications. An aliquot of apple juice (20.0 ml) was mixed with 50.0 ml of acetonitrile in a conical flask (100 ml). The mixture was shaken vigorously for 15 min and filtered through Whatman No. 1 filter paper into a conical flask (100 ml) containing 10.0 g NaCl. The sample was centrifuged at 2000 g for 5 min. A 10.0 ml portion of the upper acetonitrile layer was carefully transferred to a glass test tube and evaporated to dryness under a stream of nitrogen in a water bath at 40 °C. The residue on the wall of glass tube was redissolved in 2.0 ml of acetone and transferred to vials for GC analysis.

Methamidophos and chlorpyrifos were detected with GC-14A (Shimadzu Corporation, Kyoto, Japan) equipped with a HP-5 fused silica capillary column (30 m × 0.53 mm, 1.5 μm, Hewlett Packard, Avondale, USA) and flame photometric detector (FPD). The injector and detector temperatures were 250 °C and 260 °C, respectively. The temperature program was as follows: 120 °C (1 min), 10 °C/min to 240 °C (7 min). Nitrogen carrier gas was used at the flow rate of 59.0 ml/min. Sample solution (2.0 μl) was injected in splitless mode, and the quantification of pesticide was performed using an external standard.

### 2.4. Degradation kinetics

#### 2.4.1. First order kinetics (linear model)

A general reaction rate expression for the degradation kinetics of pesticides can be written as follows (Timme, Frehse, & Laska, 1986; Ambrus & Lantos, 2002):

$$C_t = C_0 e^{-kt} \tag{1}$$

where $C_0$ and $C_t$ are the concentration of pesticide before and after treatment, $t$ is the treatment time and $k$ is the rate constant. Defining $S = C_t/C_0$ ($S$ is the persistent pesticide fraction) and combining into Eq. (1) gives the function of $\ln S$ *versus* $t$ as

$$\ln S = -kt \tag{2}$$

In order to directly reflect the effect of pulse number on the degradation of pesticides, we used $t = 10n$ in Eq. (2) and obtained the following:

$$\ln S = -10kn \tag{3}$$

which was used for degradation kinetics of pesticides in this study. In addition, the half-life ($n_{1/2}$) of pesticide upon PEF treatment could be calculated as

$$n_{1/2} = \frac{\ln 2}{10k} \tag{4}$$

where $n_{1/2}$ is the pulse number at which the concentration of pesticide is one-half the original concentration.

#### 2.4.2. Exponential model

Originally, an extension of the exponential model was proposed by Hülsheger, Potel, and Niemann (1981) to describe the microbial survival fraction ($S$) with PEF treatment time ($t$) by Eq. (1)

$$\ln S = -b_t \ln(t/t_c) \tag{5}$$

where $S$ is the survival rate of microbes (the ratio of living cell count before and after PEF treatment), $b_t$ is the coefficient, $t$ is treatment time, and $t_c$ is the critical treatment time corresponding to the