



## Pesticide degradation in water using atmospheric air cold plasma



Chaitanya Sarangapani<sup>a</sup>, N.N. Misra<sup>a,1</sup>, Vladimir Milosavljevic<sup>a</sup>, Paula Bourke<sup>a</sup>,  
Finbarr O'Regan<sup>b</sup>, P.J. Cullen<sup>a,c,\*</sup>

<sup>a</sup> BioPlasma Group, Dublin Institute of Technology, Dublin 1, Ireland

<sup>b</sup> National Pesticide Laboratory, The State Laboratory, Department of Agriculture, Food and the Marine, Kildare, Ireland

<sup>c</sup> School of Chemical Engineering, University of New South Wales, Sydney, Australia

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### ABSTRACT

A high voltage dielectric barrier discharge plasma reactor using atmospheric air as the inducer gas was studied for the degradation of pesticides (dichlorvos, malathion, endosulfan) in water. The degradation kinetics of the pesticides were studied using GC–MS as a function of plasma control parameters. Electrical characterisation of the plasma revealed that the plasma discharge consisted of filamentary streamers. Excited nitrogen, reactive oxygen species and OH radicals generated in the dielectric barrier discharge (DBD) plasma reactor were identified using optical emission spectroscopy. Ozone, used as an indicator for metastable oxygen species, was quantified within the reactor at concentrations of 1600, 2200, 2800 ppm after 8 min of plasma treatment for applied voltages of 60, 70, and 80 kV respectively. The degradation efficacy of pesticides after 80 kV and 8 min of plasma treatment were found to be  $78.98 \pm 0.81\%$  for dichlorvos,  $69.62 \pm 0.14\%$  for malathion and  $57.71 \pm 0.58\%$  for endosulfan. Degradation was found to follow first order kinetics. GC–MS analyses showed that the degraded compounds and intermediates formed were less toxic than the parent pesticide. A proposed mechanism of degradation of these pesticides is suggested.

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### 1. Introduction

Pesticides are widely used in modern agriculture to control crop infestation [1]. The benefits of pesticide usage include reduced crop losses and increased production per unit area of land. However, use of pesticides are often associated with risks to human and animal health along with detrimental effects to the environment [2]. Pesticides enter surface and ground water primarily as runoff from crops. Pesticide pollution has been recognized as an important global issue with scientists and environmental agencies tackling the problem with the development of more biocompatible pesticides which aim to minimise the side effects on the non-target species. However, even low levels of pesticides in drinking water may result in toxicity, with increased risk due to bio-accumulation and potential long term chronic effects [3,4]. In many cases, the environmental fate of pesticides is poorly understood, which is further complicated with the introduction of new ingredients

in pesticide formulations [5]. The potential hazards and damage caused by pesticides have been outlined by Walker et al. [6]. In order to minimise the potential health risks, various treatment processes have been investigated to remove pesticides from water, including photo catalysis [7–9], electrochemical degradation [10,11], Fenton oxidation [10], hydrogen peroxide oxidation [12], and ultrasound [13]. Physico-chemical techniques which have demonstrated treatment efficacy include adsorption [14], membrane technology [15], ozone, UV photolysis, ozone/ultraviolet (UV) photolysis [16,17], and ultrasonication [18]. Misra [19] reviewed the potential opportunities and challenges associated with various advanced oxidation processes for pesticide dissipation.

Recently, researchers have explored the potential of plasma discharges for pesticide degradation for food and water. Plasma is a partially or wholly ionised state of a gas consisting of positively and negatively charged ions, free electrons, free radicals and intermediate reactive atoms, molecules and UV photons with a net neutral charge [20]. Based on their thermodynamic energy levels, plasmas are broadly classified into thermal (hot) and non-thermal (cold) plasma. Until recently, industrial applications of plasma were mostly confined to material processing and electronics, including etching and deposition, bonding of plastics, and textile dyeing [21–23]. Due to technological developments it is now feasible to

\* Corresponding author at: BioPlasma Group, Dublin Institute of Technology, Dublin 1, Ireland.

E-mail address: [pjcullen@dit.ie](mailto:pjcullen@dit.ie) (P.J. Cullen).

<sup>1</sup> Present address: GTECH, Research & Development, General Mills IPL, Mumbai, India.

induce plasmas at near ambient temperatures and under atmospheric conditions. This approach has demonstrated significant antimicrobial effects for biological applications [24–26]. Process efficacy of cold plasma for microbial inactivation, packaging modification, pesticide dissipation and wastewater treatment has been recently reviewed [19,27–30]. As a novel treatment technology, plasma oxidation offers several advantages in the production of oxidising species such as radicals (e.g., H, O, OH<sup>•</sup>, etc.), molecules (e.g., H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, etc.) and UV light [27]. The unique ‘one pot’ generation of multiple reactive species for the degradation of contaminants makes the approach attractive as an advanced oxidation process (AOP). Several studies have demonstrated the successful degradation of pesticides in waste waters by plasma, including: endosulfan [31] and organophosphorus pesticides [1] using oxygen containing inducer gases. Some other studies of relevance include, cold plasma degradation of pesticides on fresh produce [32], maize films [1], and solid surface [33]. Recent work by our group with plasma discharges from dielectric barrier discharges (DBDs), operating at significantly higher voltage levels (of the order of 100 kV) than previously reported in the literature, point to significantly improved efficacy in terms of pesticide degradation and antimicrobial efficacy [34] when combined with retention of the plasma afterglow (generated reactive species). A particular advantage of the use of higher voltage is that atmospheric air can be used for generating plasma, instead of the commonly used noble or mixed gases, which combined with the low energy input (<150 W) makes the approach attractive for large volume treatments and scale-up.

Dichlorvos, malathion and endosulfan are frequently used in agricultural production. As these pesticides exhibit excellent efficacy against a number of difficult-to-control pests which can cause substantial loss of crops. However, these pesticides enter surface and ground water primarily as runoff from crops and may cause a threat to ecosystems. Dichlorvos is generally preferred because of its cost-effectiveness and wide range of bioactivity. Dichlorvos is a mutagen and a suspected carcinogen for human beings [35]. It has been reported that human exposure to dichlorvos leads to the disorder of glucose metabolism and causes hyperglycaemia [36]. The use of malathion is also of concern as apart from its own neurotoxic effects the associated products contain other cholinesterase inhibitors [37]. Endosulfan poses an environmental concern because of its high toxicity to fish (e.g., 96 h LC<sub>50</sub> 1.2 µg/L) [38]. A recent report from the European Union (EU) on water quality and pesticide pollution stated that the Environmental Quality Standards (EQS) for endosulfan was exceeded in 35% of monitored rivers [39]. Excessive discharges of these pesticide may significantly affect the ecosystem. The EU drinking water standards regulate a maximum contaminant level (MCL) of 0.1 µg/L for both dichlorvos and malathion, 0.2 µg/L for endosulfan and the sum of all pesticides at 0.5 µg/L, including any degradation by-products [40]. Consequently, these three test pesticides were selected to study the degradation behavior and degradation kinetics by DBD plasma. This study employs a high voltage large gap dielectric barrier discharge (DBD) in conjunction with a sealed reactor to examine the degradation of common pesticides. The work aims to quantify the efficacy of high voltage atmospheric air cold plasma for the degradation of test pesticides; dichlorvos, malathion, and endosulfan in water.

## 2. Materials and methods

### 2.1. Materials

Hexane, methanol (≥99.9% capillary GC-grade), high purity (>99.5%) dichlorvos, malathion and endosulfan standards were obtained from Sigma–Aldrich, Ireland. A cocktail of the three pesti-

cide standards was prepared in methanol at 0.5 mg/mL. Samples for treatment were diluted in 1 L distilled water to achieve a treatment concentration of 2 mg/L.

### 2.2. Plasma treatment

A schematic of the experimental set-up employed is presented in Fig. 1. The experimental apparatus consists of two aluminum plate electrodes of circular geometry (outer diameter = 158 mm), one of which was placed under a 2 mm thick dielectric for grounding and the other, over a 10 mm thick Perspex for the high voltage input. Within the inter-dielectric space a rigid polypropylene container of dimensions 310 mm × 230 mm × 22 mm was placed. Each removable container contained a petri-plate with 20 mL of the pesticide cocktail placed between the electrode spaces. The container acted as a closed chamber as well as an additional dielectric. In order to prevent escape of the reactive species generated during and after treatment, the containers were sealed inside a high barrier Cryovac BB3050 film. No attempt was made to optimise the infusion of the generated species into the sample. Atmospheric air was used as the working gas. The electrodes were connected to a high voltage step-up transformer (Phenix Technologies, Inc., USA) whose primary winding receives input at 230 V, 50 Hz and delivers a high voltage output in the range 0–120 kV<sub>RMS</sub>.

Treatment times of 0 (control), 2, 4, 6 and 8 min, at 60, 70 and 80 kV<sub>RMS</sub> were tested. Following treatment, the containers were stored at 16 °C for 24 h storage to ensure that the reactive species generated reacted with the samples. Treatment of all samples was carried out in duplicate at ambient temperature (25 ± 2 °C).

### 2.3. Electrical measurements

The voltage applied across the electrodes was monitored using a high voltage probe (North Star PVM-6) coupled to a voltage divider to allow recording of the full voltage waveforms with an oscilloscope (Agilent InfiniVision 2000 X-Series, Agilent Technologies Inc., USA). A current transformer probe (Bergoz CT-E1.0S) was used to record the current waveforms.

### 2.4. Ozone measurement

Ozone concentrations within the reactor were measured immediately after plasma treatment (for the maximum treatment times only), using Gastec ozone detection tubes (Product No. 18M, Gastec, Japan). These tubes contain a chemical reagent, which changes color after reaction with the specified gas. 10 mL of the gas was drawn from the container into the tube using a hypodermic needle gas and sampling pump (Gastec, Japan). To avoid leakage of the gas, a silicone septum with an adhesive was used at the point of gas sampling.

### 2.5. Optical emission spectroscopy

Optical emission spectroscopy of the plasma discharge was carried out using a Stellarnet EPP 2000C-25 spectrometer at a resolution of 1.5 nm. The light from the plasma was coupled via an optical fibre. The spectrometer operated in a wavelength window of 190–850 nm. The integration time was 5000 ms and 5 samples were averaged for the collection of spectra. The emission spectra were qualitatively analysed to assign chemical species to the peaks. The spectra were noise canceled, averaged and analysed using National Institute of Standards and Technology [41] atomic spectra database and published works [42,43] for the identification of active chemical species.

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