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## Short Communication

## Can rainwater induce Fenton-driven degradation of herbicides in natural waters?

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## HIGHLIGHTS

- The ingredients ( $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ ) for Fenton reaction are naturally present in many open waters.
- Fenton-driven degradation is likely to affect herbicide behavior and fate in natural waters.
- Microcosm experiments using three common herbicides were conducted to test the hypothesis.
- Rapid degradation occurred under  $\text{Fe}^{2+}$ – $\text{H}_2\text{O}_2$  combinations likely to be encountered in the field.
- The findings shed some light on an overlooked natural process of environmental significance.

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## ABSTRACT

Microcosm experiments were conducted to examine Fenton reaction-driven degradation of three common herbicides exposed to a variety of  $\text{Fe}^{2+}$ – $\text{H}_2\text{O}_2$  combinations that are likely to be encountered in natural water environments. The results show that these combinations had significant ( $P < 0.05$ ) effects on removing the water-borne herbicides. This discovery sheds some light on the possible role of rainwater-borne  $\text{H}_2\text{O}_2$  in inducing Fenton reaction in many natural waters such as lakes, streams, estuaries and tidal zones, fishponds and paddy fields that may contain ferrous ion at micromolar levels. The research findings obtained from this preliminary work provide a rationale for undertaking further study to confirm the presence of an overlooked naturally-occurring process that may lead to rapid dissipation of many herbicides and other organic pollutants in open water environments. Our immediate follow-up work is to continue the laboratory-scale investigations under more complex experimental conditions, including the uses of various natural water samples for the experiments. This will provide a basis for future field-based study.

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## 1. Introduction

Contamination of natural waters by herbicides from agricultural run-off and other sources has been a major environmental concern (Nyström et al., 1999; Cedergreen et al., 2004; Aida et al., 2006; Iriti et al., 2009; Vervliet-Scheebaum et al., 2010), especially in ecologically sensitive areas (Haynes et al., 2000). Understanding the behavior and fate of these pollutants in the affected aquatic systems is important for developing appropriate agricultural practices to effectively limit the discharge rates of herbicides to the acceptable levels.

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Upon entering natural waters such as streams, lakes, estuaries, reservoirs, ponds and wetlands, the concentration of herbicides tend to decrease as a result of dilution, degradation (Nesbitt and Watson, 1980; Tanaka et al., 1996; Giacomazzi and Cochet, 2004; Housari et al., 2011), and immobilization by adsorption onto colloids (Ying and Williams, 2000). In-water decomposition of herbicides in natural waters could take place through hydrolysis, photolysis and microbial metabolism (Tanaka et al., 1996; Stangroom et al., 1998; Boschin et al., 2007; Cessna, 2008). However, for many herbicides, the degradation rates by these processes are low under the conditions encountered in natural water environments (Canle et al., 2001; Okamura, 2002; Navarro et al., 2004; Djebbar et al., 2008).

Fenton-type reactions have been employed as a major chemical mechanism for the development of advanced oxidation process (AOP) to break down water-borne pesticides (Barbusiński and Filipiek 2001; Kassinos et al., 2008; Oturan et al., 2009, 2011). When

ferrous ion ( $\text{Fe}^{2+}$ ) is in contact with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), hydroxyl radical ( $\cdot\text{OH}$ ) is generated as shown in the following chemical equation:



Hydroxyl radical is a non-selective, extremely powerful oxidant that is capable of destroying a wide range of organic molecules within a short period of time (Westerhoff et al., 1999; Lee and Gunten, 2010). However, such purpose-developed technologies are only suitable for controlling point-source pollution of organic pollutants. It has limited application, in a practical sense, to open water environments.

Nevertheless, the ingredients for triggering Fenton reaction may be naturally present during rainfall events when agricultural herbicides are flushed from the soils into water environments.  $\text{H}_2\text{O}_2$  is a common constituent of rainwater (Willey et al., 1996; Gonçalves et al., 2010).  $\text{Fe}^{2+}$  is also present in many surface water environments such as lakes (Diez et al., 2007), estuaries and tidal zones (Mackey and Mackay, 1996; Sanders et al., 2012), streams affected by acid drainage from coastal acid sulfate soils and sulfidic mine sites (Lin et al., 1998, 2007; Espana et al., 2007), oceans (Kuma et al., 1992), fishponds (Mansour and Sidky, 2002), and any surface water types affected by  $\text{Fe}^{2+}$ -rich groundwater or landfill leachate (Lorah et al., 2009). In particular, paddy fields that are used for growing rice and other semi-aquatic crops usually have an elevated level of  $\text{Fe}^{2+}$  (Becker and Asch, 2005). The standing water on these farmlands could contain high concentrations of herbicides due to direct herbicide input for on-farm weed control. Therefore, Fenton reaction-driven degradation of herbicides is likely to occur in natural water environments where the conditions are met. To the best of our knowledge, so far there has been no attempt to explore such a possibility.

We have initiated investigations into the possible degradation of organic pollutants by Fenton-type reactions in natural water environments. Laboratory microcosm experiments have been conducted to test our hypothesis. In this short communication, the preliminary results for three widely used agricultural herbicides in simplified aqueous systems are presented to demonstrate the link between their degradation and the exposure to a variety of the  $\text{Fe}^{2+}$ - $\text{H}_2\text{O}_2$  combinations that are likely to be encountered in natural water systems. It is realized that field conditions are much more complex. Further microcosm experiments with increasing complexity and field-based study are needed to test whether the Fenton reaction-driven degradation of herbicides takes place in more realistic scenarios.

## 2. Materials and methods

### 2.1. Materials

All chemical reagents used in the experiments were of analytical reagent grade. Ultrapure water (18.2 M $\Omega$  cm) was used throughout the entire course of all the experiments.

Three commonly used herbicides (diuron, butachlor and glyphosate) were selected for the experiments. The analytical standards of these selected herbicides were purchased from the Shanghai Anpel Scientific Instrument Co., Ltd. The purity of the diuron, butachlor and glyphosate standards was 98%, 98 % and 97%, respectively.

### 2.2. Experimental design

A total of nine  $\text{Fe}^{2+}$ - $\text{H}_2\text{O}_2$  combinations were set for the herbicide degradation experiment with the concentration of both  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  ranging from 5 to 50  $\mu\text{M}$ . In addition, three concentration

levels were also set for “ $\text{Fe}^{2+}$  only” and “ $\text{H}_2\text{O}_2$  only” systems. The aqueous system without the added  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  served as the control. Each experiment was performed in triplicate in a room with the temperature being controlled at  $25 \pm 1$  °C.

Centrifuge tubes (capacity: 10 mL) were used as batch reactors. For each reactor, 4 mL of a relevant herbicide stock solution with appropriate concentration were added into the tube, followed by simultaneous addition of 3 mL of an appropriate  $\text{Fe}^{2+}$  stock solution and 3 mL of an appropriate  $\text{H}_2\text{O}_2$  stock solution. The ingredients of the controls and all the treatments are given in Table 1.

After addition of all the ingredients, the tube was capped, hand-shaken for 30 s, and stood for 1 h before taking samples for determinations of residual herbicides.

### 2.3. Analytical methods

#### 2.3.1. Extraction and determination of diuron

The following procedure was used for extracting residual diuron in the solution after 1-h reaction: place 1 mL of the sample in a 250 mL separatory funnel and then add 30 mL of methanol, 30 mL of NaCl (25%) and 30 mL of dichloromethane; shake for 2 min and release the water; repeat the above procedure twice; the organic-dominated solvent was further dehydrated by adding anhydrous sodium sulfate and then condensed on a rotary evaporator (with temperature set at 40 °C) to 2 mL. The extract was purified by passing through an Anpelclean Alumina-N SPE column and frozen at  $-25$  °C prior to analysis.

An Agilent 1100 HPLC equipped with an ultraviolet absorption detector was used to determine diuron in the extracts. A LiChrospher C18 reversed-phase column (250 mm  $\times$  4.6 mm) was used for separation and the mobile phase was a mixture of methanol and water at a volume ratio of 65 to 35. The flow rate was set at 1.0 mL  $\text{min}^{-1}$ . The column temperature was maintained at 25 °C, and the detector was set at a wavelength of 245 nm.

#### 2.3.2. Extraction and determination of butachlor

The following procedure was used for extracting residual butachlor in the solution after 1-h reaction: place 1 mL of the sample in a 250 mL separatory funnel and then add 30 mL of 99:1 hexane/acetone mixed solution; shake for 2 min and release the water; repeat the above procedure for twice, the organic-dominated solvent was further dehydrated by repeatedly adding 30 mL of anhydrous sodium sulfate solution (5%) and releasing aqueous phase for three times. The dehydrated sample was then condensed on a rotary evaporator (with temperature set at 40 °C) to 2 mL. The extract was further purified on a florisil cartridge and then frozen at  $-25$  °C prior to analysis.

An Agilent 1100 HPLC equipped with an ultraviolet absorption detector was used to determine butachlor in the extracts. A LiChrospher C18 reversed-phase column (250 mm  $\times$  4.6 mm) was used for separation and the mobile phase was a mixture of methanol and water at a volume ratio of 80 to 20. The flow rate was set at 1.0 mL  $\text{min}^{-1}$ . The column temperature was maintained at 25 °C, and the detector was set at a wavelength of 236 nm.

#### 2.3.3. Determination of glyphosate

The solution after 1-h reaction was passed through a 0.22  $\mu\text{m}$  membrane filter and stored at 4 °C in a refrigerator prior to analysis.

Glyphosate in the solution was determined using a DIONEX ICS-900 ion chromatography system, fitted with an electron capture detector, a 250  $\mu\text{L}$  sample injection loop, an IonPac AG11-HC (4 mm  $\times$  50 mm) guard column and an IonPac AS11-HC (4 mm  $\times$  250 mm) analytical column. KOH was used as the mobile phase and the eluent flow rate was set at 1.00 mL  $\text{min}^{-1}$  with an injection volume of 250  $\mu\text{L}$ .

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