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Characterization of the fate and distribution of ethiprole in water-fish-sediment microcosm using a fugacity model

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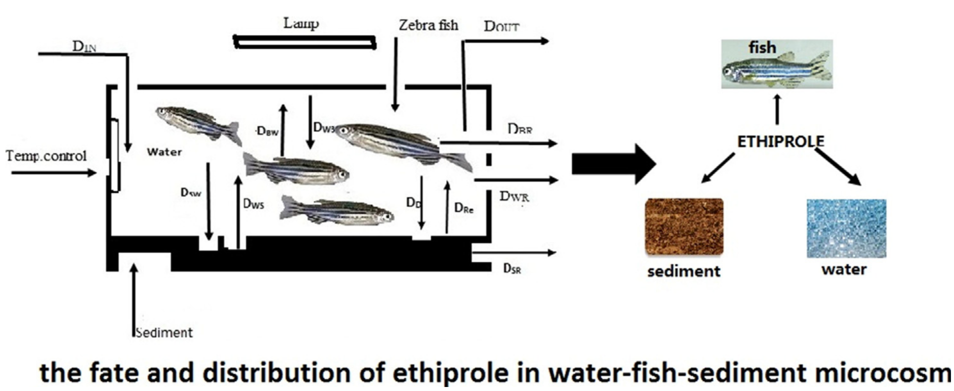
HIGHLIGHTS

- A dynamic pesticide fate model of ethiprole in microcosm was developed.
- The model was first used to predict the fate and transport of pesticide in aquatic microcosm.
- The H and K_{ow} have an important impact on both the distribution and variance of the contaminant concentration for ethiprole.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel, relatively simple and effective three-compartment level IV fugacity model was developed to quantitatively describe the fate, transformation and transport of ethiprole in an aquatic system. Chemical equilibrium was assumed to apply within each bulk compartment. Expressions are included for degradation reactions, advective flow, emission, and interphase transport by non-diffusive and diffusive processes. The simulated results closely matched the results obtained from the experiments. The model indicated that at 25 °C (day:night = 12 h:12 h), after approximately 672 h, Results of the model calculations showed that the ethiprole was degraded by both photolysis and microorganisms in the water accounts for 86.8% (account for 90.4%, 95.4% in Beijing (BJ) and Hunan (HN) microcosm respectively) of the total removal, the ethiprole was removed by advective outflow accounts for 0.15% (accounts for 0.05%, 0.1% in HN and BJ microcosm respectively) of the total removal, the ethiprole were removed by biodegradation in sediment and fish, accounts for 8.54% and 5.55% (accounts for 2.52% and 2.03%, 5.6% and 3.7% in HN and BJ microcosm respectively) of the total removal respectively in HLJ microcosm. It indicates that biodegradation and photolysis in the water phase were the most important removal process, and most of the ethiprole was distributed in the water phase. A sensitivity analysis of the input parameters indicates that the Henry's law constant (H) and octanol-water partition coefficient (K_{ow}) parameters are the both most sensitive to the ethiprole concentration in the medium, which suggests that the H and K_{ow} have important impact on both the distribution and variance of the contaminant concentration. The mass balance under steady-state conditions showed that over 90% of ethiprole stay in water for all microcosm. This finding demonstrates that water plays a key role in the fate of ethiprole, acting as the major sink for contaminants in the stimulation system.

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1. Introduction

Pesticides are broadly used to maintain high levels of agricultural production; but, they can also lead to contamination of surface and ground water (Li et al., 2015). Studies have demonstrated that <0.1% of applied pesticide reaches its intended target and that the majority is dispersed into the environment (i.e., the water, the air and the sediment) (Pimentel, 1995; Ucar and Hall, 2001; Pimentel et al., 2003). The presence of pesticides in the aquatic environment, as well as their ecotoxicological effects on flora and human health, have been well documented. Hence, it is necessary to study the distribution, transport and fate of pesticides in aquatic ecosystems and manage their impact on human health and environmental safety.

Ethiprole has been recently registered in many countries for rice and cotton cultivation for it special mode of action and shows no cross-resistance arising (Punyawattoe et al., 2013). Unfortunately, until now, no published data are currently available on its behaviour in aqueous systems. Only a few analysis methods for ethiprole enantiomers in rice and for the degradation and adsorption of ethiprole in soil have been reported (Liu et al., 2014; Zhao et al., 2012). Therefore, the present study was initiated to evaluate the transport, distribution and fate of ethiprole in an aquatic ecosystem.

Many mathematical models have been proposed to investigate the transport, distribution and fate of chemicals in the environment (Bingli et al., 2008; Cao et al., 2004; Colombo et al., 2013; Luo et al., 2008; Wang et al., 2012). Among these, the fugacity model has been shown to be proven useful to regulators for it has been successfully applied to estimate the fate of different chemicals in different regions (Ethier et al., 2008; Kim et al., 2013; Li et al., 2006). Such models have been developed based on the thermodynamics equilibrium, mass balance principles and the fugacity concept. A level III fugacity model is based on a steady-state assumption; but, it could not simulate the dynamic processes that lead to a steady state. Therefore, level IV fugacity model is most suitable for simulate the behaviour and fate of chemical processes in the environment. There are many successful examples of the application of fugacity models. For example, Breivik developed a fugacity-based model to study the fate of two hexachlorocyclohexane isomers in the Baltic Sea (Breivik and Wania, 2002; Li et al., 2006), QWASI (Quantitative Water Air Sediment Interaction) model has been used to investigate organic chemical distribute and transport in lakes, Huang et al. studied the fate and distribution of NP in an aquatic environment using a level IV fugacity model (Huang et al., 2007).

The impact of pesticide contamination in aquatic ecosystem is tremendous. Microcosms have been widely used as a research method for the environmental fate of pesticides and have a series of advantages such as authenticity, flexibility, a high performance-price ratio and security (Colombo et al., 2013; Laabs et al., 2007; Van den Brink et al., 2009). In an artificial microcosm, the incubation conditions can be controlled and the fate of the target compound can be clearly understood.

In this study, a level IV fugacity model was chosen to simulate the transfer and fate of ethiprole in an aqueous microcosm. The differential equations of a level IV fugacity model were solved using the Runge-Kutta method. The distribution of the ethiprole concentrations in sediment, water and fish, the transfers and distribute between these compartments were estimated. The result show that the predicted concentrations of ethiprole are in good agreement with the observed ones. It also investigates the impacts of the final fate and distribution of ethiprole in different environmental compartments after the water was contaminated and how ethiprole is eliminated from the polluted water. The H and K_{ow} have important impact on both the distribution and variance of the contaminant concentration. K_{ow} is usually measured by equilibrating layers of water and octanol containing the solute of interest at subsaturation conditions and analyzing both phases. If K_{ow} is high, the concentration in water is necessarily low, and even a small quantity of emulsified octanol in the aqueous phase can significantly increase the apparent concentration. The Henry's law constant (H) is conventionally expressed as a ratio of partial pressure in the vapor to the concentration in the liquid. The most commonly used measures of concentration are mole fraction (x) and amount-of-substance concentration (c, expressed in mol/m^3) which yield either. H is also slightly dependent on the temperature dependence of water density and hence molar volume. At last, this data along with other available information can be helpful for the risk assessment of ethiprole in an aquatic environment. This work also provides a new approach to study pesticide environmental impacts, and provide environmental parameters and model framework for studying the fate of other pesticides.

2. Materials and methods

2.1. Materials and chemicals

The three different agricultural sediments representing different climatic environments and physicochemical properties were obtained from the 0–15 cm surface layer in fields from three distinct sites in China. This three types of test sediment were taken from BJ, HN and HLJ province and it had not been exposed to ethiprole. The sediment was air-dried at room temperature, and small rocks and grasses were removed. It took 21 days to activate microorganism before incubation. The physicochemical properties of the sediment were tested by the standard methods used in China (Nanjing Institute of Soil Science of Chinese Academy of Sciences, 1978). The characteristics of the sediment are listed in Tables 1 and 2.

An ethiprole standard of was bought from the Institute for the Control of Agrichemicals, Ministry of Agriculture. Chromatography grade acetonitrile was purchased from Sigma-Aldrich. Ultra-pure water was prepared using a Milli-Q reagent water system. Florisil, primary secondary amine (PSA) and octadecylsilane (C_{18}) were bought from Agela Technologies Inc. Zebra fish were bought from the Gaofeng Aquarium and water was dechlorinated prior.

A standard stock of ethiprole (100 mg/L) was prepared in acetonitrile. Standard working solutions of 5, 10, 50,100, 500 and 1000 μg L^{-1} were prepared from the stock solution by dilution with acetonitrile. Matrix-matched standard solutions ware obtained at 5, 10, 50,100, 500 and 1000 μg L^{-1} by adding black sample extracts to each serially diluted standard solution.

2.2. Instrumentation

A Waters Acquity UPLC system and UPLC binary solvent manager and an Acquity column heater equipped with a Waters Acquity UPLC BEH C18 column (2.1 × 100 mm 1.7-μm particle size). Separation was carried out by gradient elution using solvent A (0.2% formic acid aqueous solution) and solvent B (chromatography grade acetonitrile) ratio at flow rate of 0.3 mL min^{-1} for 5 min and a 5 μL sample was injected. The gradient program was as follows: time 0 min, 30% A; 1.5 min, 30% A; 3 min, 70% A; 3.1 min 70% A; 4.0 min 30% A. The column was kept at 40 °C to reduce the viscosity.

The eluted compounds were monitored using a triple–quadrupole mass-spectrometer (TQD) equipped with an electrospray ionization (ESI) source. MS/MS detection was performed in a positive ionization mode; the monitoring conditions were optimized for ethiprole. The multiple reaction monitoring mode was used for ethiprole.

2.3. Microcosm establishment

A water-fish-sediment microcosm was established to investigate the distribution, transport and fate of ethiprole in an aquatic system and polluted water was added at a certain speed. The microcosm included a glass aquarium (40 cm wide × 50 cm high × 70 cm long) with 10 kg sediment homogenously placed on the bottom. Water was slowly delivered into the aquarium, and the water level was maintained at 38 cm (100 L) throughout the experiments. A heater and a thermometer