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Pesticide and element release from a paddy soil in central Vietnam: Role of DOC and oxidation state during flooding

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ABSTRACT

Insecticide and element release from submerged soils in paddy rice farming systems causes potential hazard to local drinking water wells during the annual monsoon flood season. Intact soil columns collected from paddy fields in the Hue province in Vietnam was submerged with 100 mm artificial floodwater. Experiments were performed under aerobic and anaerobic conditions with and without addition of dissolved organic carbon (DOC). The intact soil columns were spiked with the insecticides fenobucarb, endosulfan and dichlorodiphenyltrichloroethane (DDT), and later flooded. After 24, 48 and 72 h, the floodwater samples were collected to analyze release of elements and insecticides. Insecticide release into floodwater depends on their initial concentration in the soil and was enhanced by the presence of DOC under aerobic conditions more than under anaerobic conditions. Release of Al, Cu, Ni and Pb increased in the presence of DOC in floodwater under aerobic conditions. Meanwhile As, Co, Fe, Mn, Sb and Zn release only increased under anaerobic conditions with highest release without DOC added. Several elements and all three insecticides studied show increased release to floodwater in response to DOC and reducible elements respond to the anaerobic conditions in the soil source.

1. Introduction

Agrochemicals are widely applied to protect crops from pests and increase yield. However, these agrochemicals are also a major source of aquatic pollution (El Bakouri et al., 2007, 2008; Yu et al., 2007). Many studies focusing on the fate, distribution and transport of pesticides in paddy fields indicated that the applied pesticides are causing surface and ground water pollution (Buschmann et al., 2008; Cerejeira et al., 2003; Sudo et al., 2005; Trinh et al., 2017; Varca, 2012; Watanabe et al., 2007).

Rice is often grown in wetlands, and paddy soils are flooded during nearly the entire cultivating period because flooding conditions are important for the development of the rice crop (Kögel-Knabner et al., 2010). In a wetland environment, the fate and release of various types of organic and inorganic contaminants is affected by anaerobic conditions (Borch et al., 2010), concentration of particulate organic carbon (POC) and dissolved organic carbon (DOC) (Luo et al., 2009). Maillard et al. (2011) also showed that DOC plays an important role in transporting hydrophobic pesticides in wetlands and enhances the water solubility of some organic pollutants and pesticides (Chiou et al., 1986; Kalbitz et al., 1995; Zsolnay, 1996). Dichlorodiphenyltrichloroethane (DDT) and endosulfan desorption are increased by increased DOC (Gonzalez et al., 2010). Additionally, DOC can affect the mobility of heavy metals in a soil system and increase the concentration of dissolved divalent and trivalent metal cations. DOC can build metal complexes with these cations and enhance their detaching from mineral surfaces (Berggren, 1992; Hue et al., 1986; Pohlman and McColl, 1988; Tyler, 1981). Under flood conditions, O_2 depletion occurs as a consequence of oxidation of organic matter resulting in decreasing redox potential (Eh) and reduction of Mn(III/IV), Fe(III) and SO_4^{2-} to Mn(II), Fe(II) and HS^- (Murase and Kimura, 1997). Therefore, a release of water soluble organic degradation products and certain elements absorbed to Mn- and Fe-oxides can be observed (Amery et al., 2007; Koopmans and Groenenberg, 2011; Phyu et al., 2006).

Vietnam is an agricultural country, and rice is the main cereal crop, which is cultivated in an area covering 3.8 million hectares, accounting for 11.5% of country's area. A large amount of pesticides have been used in Vietnamese agriculture. According to Quyen et al. (1995), over 40,000 tons of pesticides were used in Vietnam in 1995, and the use of pesticides reached 50,000 tons per year in 2004 (Yue et al., 2011).

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Studies of paddy fields in Vietnam also showed that there are relatively high concentrations of pesticides in water and soil (Anyusheva et al., 2012; Carvalho et al., 2008; Hoai et al., 2010, 2011; Minh et al., 2006, 2007a; Toan et al., 2007: Trinh et al., 2017). Pesticides such as DDT and endosulfan (α/β-isomers in a 70:30 ratio), which were banned from agricultural use, due to their persistence in the environment and tendency to bio-accumulate (UNEP-Chemicals, 2004) were still found in some agricultural soils (Hoai et al., 2011; Nishina et al., 2010; Trinh et al., 2017). Fenobucarb is one of the most widely applied insecticides in many paddy growing countries to prevent rice thrips, leafhopper and plant hopper infestations (Chapalamadugu and Rasul Chaudhry, 1992). However, it also causes a potential risk to aquatic environments (Cong et al., 2006; Lamers et al., 2011). To date, studies on the behavior of pesticides in paddy rice fields in Vietnam have only concentrated on conventional paddy rice fields in the Red River and Mekong Delta (Hung and Thiemann, 2002; Minh et al., 2007b; Nhan et al., 1998; Toan et al., 2009); meanwhile, paddy fields in the center of Vietnam are flooded during the rainy season every year (ADPC, 2003). The pesticide application period is October to January, which is during the rainy season and this leads to an increased risk of surface and ground water pollution.

Therefore, the aim of this study was to investigate release of insecticides and elements from the soil of paddy fields into water under flood conditions. The specific objectives were to study: *i*) the release of insecticides and elements from intact soil columns into artificial floodwater, and *ii*) the effect of DOC on the release of insecticides and elements under aerobic and anaerobic conditions.

2. Materials and methods

2.1. Sample collecting

Intact soil columns were obtained from a wet paddy field in the Huong Toan commune (16°30′52″N, 107°32′16″E) near Hue city (Central Vietnam). The soil columns were sampled within a 5 m^2 area using 10 cm diameter polyvinyl chloride tubes to a depth of 25 cm. The soil columns were sealed and stored in a cooling box until arrival to the laboratory, and were later transported to University of Copenhagen and stored at −4 °C until the experiments.

2.2. Chemicals

Standard solutions of fenobucarb, endosulfan and p,p′-DDT with concentrations of 500, 100 and 500 μg L^{-1}, respectively were used, and all organic solvents were gas chromatography (GC) grade obtained from Sigma-Aldrich. A DOC solution with a concentration of 765 mg C L^{-1} was prepared from a DOC solution isolated from the Norway spruce forest soil and with fulvic acid properties (Strobel et al., 2001). The solution was filtered using 0.45 μm nylon filter, and the DOC concentration was determined before use.

2.3. Analysis

2.3.1. Insecticides extraction

Insecticides in water samples were extracted according to Kadokami et al. (2009) with some modifications. Briefly, 2 g NaCl was added to a 100 mL water sample, and liquid-liquid extraction was performed twice with 15 and 10 mL dichloromethane for 10 min. The extracted solution was dehydrated with anhydrous sodium sulphate. 25 mL of hexane was added into the extract and the solution was concentrated to approximately 5 mL by use of a Glas-col.'s digital Pulse Mixer with nitrogen gas. Hexane was added to the concentrate until a volume of approximately 10 mL was reached, and the resulting solution was re-concentrated to exactly 1 mL and kept in a vial at −20 °C until the gas chromatography–mass spectrometry (GC/MS) analysis.

Insecticides analyses: Insecticides were determined by GC/MS (TRACE GC 2000) with an auto-sampler, and a capillary column ZB-5MSi (30 m × 0.25 mm × 0.25 μm) (Phenomenex). Helium was used as a carrier gas (40 cm s^{-1}) for injection with 1.0 μL in splitless mode. The temperature of the injector, ion source and transfer line were 250 °C, 200 °C and 300 °C, respectively. The GC temperature program was set to 40 °C (2 min) with a ramp up to 300 °C (8 °C min^{-1}) and held at 300 °C (4 min).

2.3.2. Quality assurance and control of the insecticides determination

Method blanks, repeatability tests, and recovery studies by 100 μg L^{-1} standard addition for each insecticide to samples were used. The recovery rates of fenobucarb, endosulfan and p,p′-DDT were 119, 98 and 97%, respectively. Limits of determination (LOD) for fenobucarb, endosulfan and p, p′-DDT were 4, 4, and 4 μg L^{-1}, respectively.

2.3.3. Elements analyses

Element concentrations in water samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) (Agilent Technologies 5100 ICP-OES) using external calibration and recalibration for every 10 samples. Sensitivity drift was below 5%. Quality controls were performed by including blank analysis and digested samples of Soil Certified Reference Material Montana II soil – SRM 2711a, National Institute of Standards and Technology (NIST). Good recoveries (mean, 80–120%) were obtained for Al, As, Cd, Co, Cr, Cu, Fe, Mn, Pb and Zn.

2.3.4. Other parameters analyses

pH was determined using a combined glass electrode (Metrohm, 6.0228.000). Fe(II) was determined as an indicator for anaerobic conditions as the Fe(II)-Ferrozin complex at 562 nm wavelength in a Lambda 25UV–Vis Spectrometer (Perkin Elmer). The concentration of DOC in water samples was determined by a Total Organic Carbon Analyzer (Shimadzu, TOC–Vcpn and autosampler ASI-V).

2.4. Insecticides and elements release studies

2.4.1. Floodwater

An artificial floodwater sample was produced using the OECD recommended composition for reconstituted surface water (OECD, 2004); the ion concentration of the applied water was approximately one fourth of the OECD recommendations to account for the dilution during flooding. The reconstituted floodwater were added 73.5 mg $CaCl_2 \cdot 2H_2O$, 15 mg $MgSO_4 \cdot 7H_2O$, 16.2 mg $NaHCO_3$ and 1.4 mg KCl per liter Milli Q water, and sonicated for 15 min.

2.4.2. Insecticides spiked soil columns

Before initiation of flood conditions, the intact soil columns were left at room temperature for one day. A Teflon sleeve with a sharpened edge was inserted inside the soil column approximately 1 cm down in the soil. Twenty milliliters of floodwater and a spike of 1 mL methanol containing a mixture of fenobucarb, endosulfan, and DDT at different concentrations were added to the soil column. The soil columns were then left one day under nitrogen flow for evaporation of water until the mass of the columns equaled the initial mass of the soil column before the addition of floodwater.

2.4.3. Flood experiments under aerobic conditions

Three experiments with different addition of insecticides were carried out; the first soil column was spiked with 0.03, 0.075 and 0.15 mg kg^{-1} of fenobucarb, endosulfan and DDT, respectively, whereas the second and third column were spiked with 0.075, 0.15 and 0.38 μg and 0.15, 0.3, 0.6 mg kg^{-1}.

The insecticide spiked soil column was flooded with 400 mL water corresponding to a flooding of 100 mm. The floodwater was stirred with a Teflon mixing rod at a distance of 5 cm from the soil surface at a