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Transport of 3,5,6-trichloro-2-pyrdionl (a main pesticide degradation product) in purple soil: Experimental and modeling

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ABSTRACT

Purple soil, a loamy entisol dominating the hilly central Sichuan basin in the upper reaches of Yangtze River, is low in organic matter content and abundant in macropores that form the rapid transport network for water and solutes including pesticides. However, effects of soil's macroporosity on transport of pesticides has not been quantitatively explored and simulated at the column scale. In this study, we explore the transport of 3,5,6-trichloro-2-pyrdionl (TCP), a main pesticide degradation product, in purple soil through experiments and simulations on typical farmland categories, including rice-rape and vegetable farmland. Soil water retention characteristics (SWRCs) and physical properties are measured to learn the hydraulic parameters and porous structures of the soil. Batch experiments are conducted to obtain the adsorption coefficient of TCP on soil, and breakthrough curves of Br^- (a conservative tracer) in undisturbed soil columns are applied to evaluate the hydrodynamics of TCP transport. The two-region model is used to simulate the transport processes, and the parameters are obtained by inversion simulation. It is found that TCP transport in purple soil exhibited complex patterns and is strongly affected by both chemical and physical non-equilibrium. A higher pollution risk on water body of rice-rape field is due to the stronger preferential flow and better pore connectivity despite the larger macroporosity observed in vegetable field. These results can provide useful data and modeling approach for evaluating the risk of pesticide leaching toward groundwater.

1. Introduction

3,5,6-trichloro-2-pyridinol (TCP) is the main degradation production of pesticide chlopyrifos, chlopyrifos-methyl and herbicide triclopyr (Chapman and Harris, 1980; Getzin, 1981; Rack, 1998; Racke, 1993; Yang et al., 2005; CDC, 2009). The typical degradation of both chlorpyrifos and tricopyr in the soil and water environments are shown in Fig. 1. Unlike its parental pesticide or herbicide, TCP exhibits anti-degradation ability, high water solubility and high migration capability, which would lead to the soil and water pollution easily (Manclus and Monotoya, 1995; Armbrust, 2001). As a consequence, TCP has been found in human body at a lower testosterone levels (Meeker et al., 2006; Morgan et al., 2005). Hence, learning the mechanisms of TCP transport is crucial to the regional environmental protection and human security.

Generally, the mechanisms of TCP in the soil environment include adsorption, desorption, convection and diffusion. Based on the batch experiment, the values of K_d are obtained: ranging from 0.45 to 2.86 L/kg in the soil of Australia (Baskaran et al., 2003) and China (Sun, 2011; Lei et al., 2015). As for the purple soil in southwestern China, the isothermal adsorption of TCP can be best fitted by Langmuir model with the R^2 of over 0.99 (Lei and Zhou, 2017), implying the monolayer adsorption on the surface site. Through the column experiment, the leaching of TCP on the packed soil columns are also studied by a breakthrough curve (BTC), and it has been revealed that about 65.5%–90% of the TCP have entered into the water body through water flow in the homogeneous soil environment (Sun, 2011; Lei et al., 2015). Apart from that, many studies are more emphasis on TCP residues (Randhawa et al., 2007; Khoshab, 2016), determination in some medias (Hines and Deddens, 2001; Brzak et al., 1998; Mauriz et al., 2007; Ormand, 1999; Li et al.,

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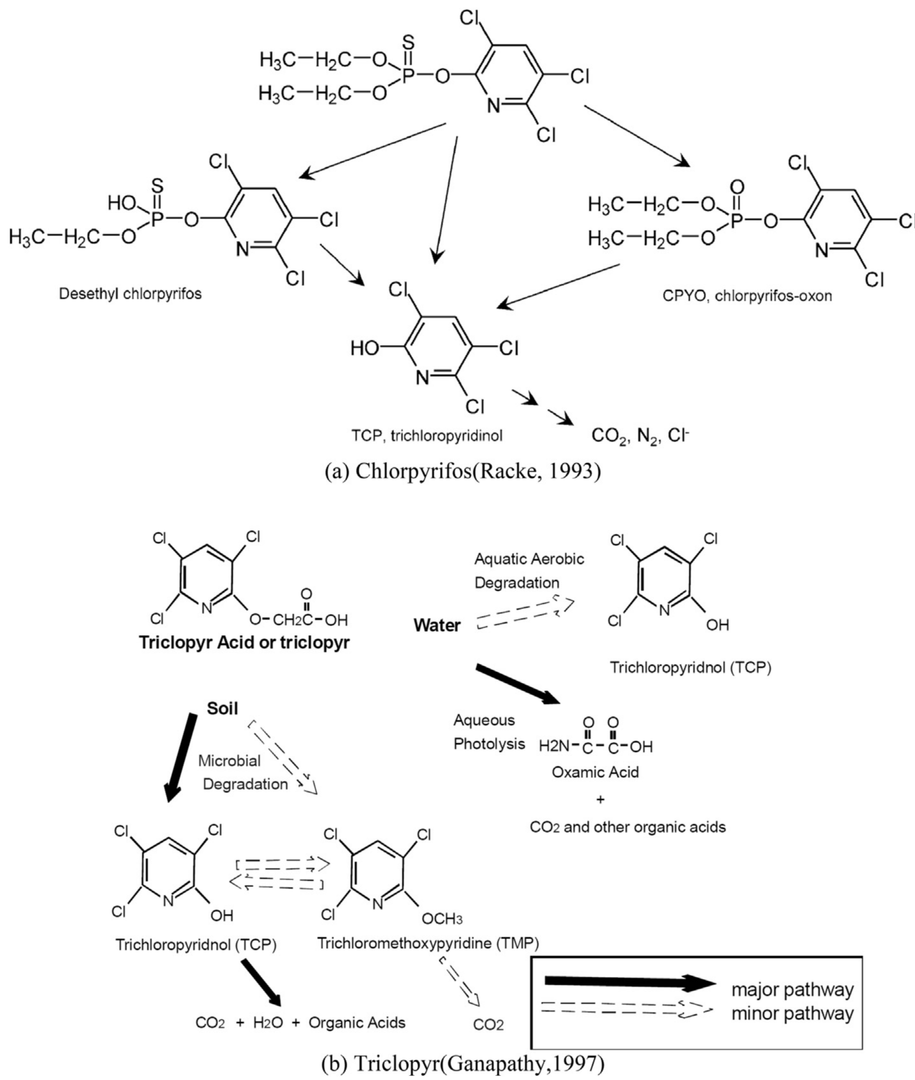

Fig. 1. Destination of chlorpyrifos and triclopyr in the environment.

2014) and biodegradation (Jabeen et al., 2015; Chen et al., 2012; Maya et al., 2012; Li et al., 2013). In the real field, especially in the purple soil region, the existence of macropore make the solutes transport through soil not only by matrix flow but also by preferential flow (Thomas and Phillips, 1979; Beven and Germann, 1982). However, it has not been well investigated to the TCP transport through preferential flow paths (PFP).

On the other hand, describing and predicting solute transport behavior in porous media are essential to manage soil and subsurface aquifer environment. The variety and complexity of physical, chemical and biological interactions between the solute and soil often make it very difficult to be solved this problem (Wang, 2002a,b). The fine-texture soil further increases the difficulty to predict solute transport behavior because of its heterogeneity, especially the existence of long and large continuous opening channel in field, which may be very important to the movement of water under certain condition (Beven and Germann, 1982). Pesticides could pass soil matrix and move quickly to subsurface soil layers due to PFP, particularly during rainstorm events soon after pesticide application (Flury, 1996; Kladivko et al., 2001; Maximilian et al., 2006). The equilibrium convection dispersion equation model (CDE) is the most widely used to simulate pesticide transport (Dousset et al., 2007), but it fails to simulate non-equilibrium process (Tang et al., 2009). The physical non-equilibrium process can be solved by establishing two-region (mobile-immobile) model (van Genuchten and Wagenet, 1989), for example, the simulated transport of atrazine and isoproturon agree well with the observation (Kamra et al., 2001). The non-equilibrium chemical process is induced by nonlinear non-equilibrium equation: the two-site model containing instantaneous and kinetic sites (Selim et al., 1977; van Genuchten and Wagenet, 1989). This model has been used by many authors to describe contaminants (isoproturon and metribuzin, TNT, TDX, simazine and PAH) in soil (Pot et al., 2005; Dontsova et al., 2006; Suárez et al., 2007; Ngo et al., 2014). Besides, the soil hydraulic and pore structure properties also have important effect on the transport of solutes, because of the larger contribution of macropores and saturated hydraulic conductivity (K_S) to drainage (Wang et al., 2015).

Purple soil is the main cultivated soil in upper reaches of the Yangte River, in southwest of China. It features the typical characteristics of low organic matter, high porosity, high saturated hydraulic conductivity and serious water loss and soil erosion (He, 2003). These characteristics not only lead to pesticide transport has a higher risk on water environment pollution in purple soil with slope cultivated land, but also result in a complex patterns of pesticide transport that contains non-equilibrium of physical and