A QSAR Study on the Persistence of Fungicides in the Environment

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ABSTRACT

The main purpose of this article is to investigate the persistence of fungicides in the environment. QSAR models using four types of reactivity descriptors were constructed to predict the degradation rate constants and examine chemical interactions, to further assess and classify the environmental risks of fungicides. Two major findings emerged. First, the model results show that the degradation in surface water of fungicides is mainly affected by the polarization. The maximum nucleophilic condensed local softness is the most important descriptor. Second, both polarization and chemical potential affect degradation in the soil. The maximum electrophilic condensed local softness is the most important descriptor. The findings not only identified 20 kinds of high ecological risk fungicides, but also showed that phthalimides, sulfamides, and antibiotics are less harmful to the environment because of low persistence and low bioconcentration factors. This approach provides a basis for interpreting chemical interactions between fungicides and environment.

KEYWORDS

Bioconcentration, Fungicide, Mobility, Persistence, Quantitative Structure-Activity Relationship, Soil

INTRODUCTION

Green Chemistry has become a new standard that is reliable and safer for both consumers and environment (Maertens et al., 2014). Developers need to follow up design rules that incorporate safety and environmental issues into chemicals development (Hansen, Maynard, Baun, Tickner, & Bowman, 2013). As to environment health aspects, the destiny of chemical substances has become more important. In agricultural production, humans often use pesticides to ensure stable production. At first, it does not harm health directly. However, it enters into organism tissue by bioconcentration. Organochlorine pesticides such as hexachlorocyclohexane (HCH) and dichlorodiphenyl-trichloroethane (DDT) are ubiquitous anthropogenic environmental contaminants. As a matter of fact, they are persistent toxins that accumulate in food and pose high risk to ecosystems and human health (Bhanti & Taneja, 2007; Lozowicka, 2015; Nakata et al., 1998; Willett, Ulrich, & Hites, 1998). Besides these, Das & Das (2004) noticed a positive correlation between total organochlorine residues and the percent of fat content in muscle of fish from the south patches of the Bay of Bengal (Das & Das, 2004). There is a correlation between the bioconcentration factor (BCF) by the fish and the water solubility and octanol-water partition coefficient of pesticides. In

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fish tissues, the abundance of pesticides in the liver is higher than other components due to the weight of lipids. Pesticide residues in foods in the food chain pose potential health risks to humans (Chen, Shi, Shan, & Hu, 2007; Guo, Meng, Tang, & Zeng, 2008; Kanazawa, 1981; Szlinder-Richert, Barska, Mazerski, & Usydus, 2008). Moreover, the pesticides have a potential to leach to lower soil horizons if degradation in the soil is slow. Monkiedje and Spiteller (2002) investigated the sorptive behavior of phenylamide fungicides. In their study, adsorbed fungicides were not firmly retained by soil particles, and their adsorption was reversible (Monkiedje & Spiteller, 2002). Singh (2002) studied the correlation between triazole fungicides and soil properties. The study suggested that soil organic carbon content, is the main controlling factor for triazole adsorption (Singh, 2002). Last but not the least, the persistence of pesticide also should be talked over. Previous studies on pesticides reported that soil colloids could affect degradation and persistence (Camazano & Martin, 1983; S. U. Khan, 1978; Lutze et al., 2015; Perdue & Wolfe, 1982; Wei, Furrer, Kaufmann, & Schulin, 2001). Villedieu, et al. (1995) investigated the kinetics of alkaline hydrolysis of the dicarboximide fungicides in micellar solutions compared with the kinetics in aqueous media. In their study, the rate of affected dicarboxamidine ring opening was attributed to micelle-substrate association (Villedieu, de Savignac, & Calmon, 1995). However, multiple applications of pesticides to soil accelerate its degradation in soil. Yu, et al. (2009) point out there is no inhibitory effect on soil microbial community because it altered the balance of soil microorganisms by the enrichment of specific strains (Yu, Chu, Pang, Xiang, & Fang, 2009). Results of these studies reveal that pesticides have highly diverse fates in the environment. Therefore, investigating the property along with understanding the mechanisms of these reactions is an important prerequisite for assessing risks.

The quantum-chemical methodology has become increasingly helpful in understanding many aspects of the chemical-biological interactions in toxic, pharmacological and environmental science processes. Through molecular descriptors used in statistical analyses, mechanisms of the chemical interactions in various biological systems are elucidated. Chang, et al. (2014) have used four types of quantum-chemical reactivity descriptors, including electronic chemical potential, condensed local softness, atomic partial charge and the inverse of apolar surface, building quantitative structure-property relationships (QSPRs) and illustrate the four basic interactions (electron flow, polarization, electrostatic interaction and hydrophilic interaction) between volatile organic compounds (VOCs) and organoclays (Chia M Chang et al., 2014).

For the reasons described above, the current study investigates the impact of the electronic characteristic on the persistence of fungicides by developing new QSAR models. From three aspects of mobility, bioconcentration, and persistence, the modeling was done to evaluate further the risk and hazards of fungicide on the environment.

MATERIALS AND METHODS

Rate Constants Data

The k and $k_{oil}$ values of 30 different compounds were calculated from the half-life obtained from the literature (Croucher, Jewess, & Roberts, 2007; Mackay, Shiu, Ma, & Lee, 2006; Tanji & Sullivan, 1995).

Computational Methods

The calculations were performed using the Gaussian 09 software package (Frisch et al., 2009). Initial molecular geometries of fungicides were optimized at the Austin Model 1 (AM1) semi-empirical level without symmetry constraints.

The accessible surface area was calculated using the VEGA ZZ software (PSA, probe radius=1.4 angstrom, density=10) (Pedretti, Villa, & Vistoli, 2003). The results of computed surface area involve polar surface area (PSA) and apolar surface area (APSA).
QSPR-Modeling for the Second Virial Cross-Coefficients of Binary Organic Mixtures

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