

PC1) Transformation and Partition Coefficient of 1,3-dichloropropene Fumigant

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1. Introduction

The movement of a fumigant in the soil is mainly a result of diffusion in the vapor phase. During this diffusion process there is a tendency to establish a concentration equilibrium in the vapor, water and soil. Characterization of the air-water (K_H) of 1,3-D is essential for understanding the migratory behavior of 1,3-D in the air, water and soil compartments of the environment. The K_H is one of the most important physical properties in determining the volatilization of 1,3-D between the air and water phases. The objectives of this study were to investigate the transformation of fumigant 1,3-D, and evaluate whether the air-water (K_H) of 1,3-D is affected by isomer.

2. Experimental

An air-water partition experiment was conducted to determine the distribution of 1,3-D between air and water at 20°C. Aqueous solutions, containing approximately 200, 400, 600, 800, 1,200 and 1,400 mg L⁻¹ of 1,3-D, were prepared in deionized water. Ten milliliters of each stock solution was transferred into a 21.6-mL headspace vial (triplicate samples), sealed with Teflon-faced butyl rubber septa and then vortexed for 2 min. The vials were kept in the dark and incubated at 20°C, and allowed to equilibrate for 16 h. A preliminary study showed that a 16 h period was adequate for achieving equilibrium. To determine the concentration of 1,3-D in the air phase (C_a), a 1 mL sample of the headspace was withdrawn with a gas-tight syringe and transferred into a GC vial containing 1 mL of hexane at 20°C, respectively. The GC vials were then vortexed for 2 min. To determine the concentration of 1,3-D in the water phase (C_w), 0.5 mL of aqueous phase was withdrawn with a gas-tight syringe and transferred into a 10-mL headspace vial containing 5 mL of hexane at 20°C. The headspace vials were vortexed for 2 min, and a portion of the hexane phase was then transferred into a GC vial and analyzed by GC using conditions as given above.

3. Results and Discussion

Transformation in the Aqueous Phase

Transformation of 1,3-D is an important factor in determining the fraction available for characterizing the volatilization of 1,3-D. The transformation of 1,3-D is described by first-order kinetics, using $C = C_0 \exp(-kt)$. Where C is the 1,3-D concentration (mg kg^{-1}) at time t (h), C_0 is the initial 1,3-D concentration (mg kg^{-1}), and k is the first-order rate constant (h^{-1}). Figure 1 show that the first-order rate constant of *cis*-1,3-D and *trans*-1,3-D was 0.077 d^{-1} and 0.083 d^{-1} , respectively. From the first-order rate constant, the half-life of *cis*-1,3-D and *trans*-1,3-D was 9.0 d and 8.3 d at 25°C , respectively. Chemical degradation of 1,3-D in water is mainly attributed to its hydrolysis in H_2O . In water, *cis*- and *trans*-1,3-D are initially hydrolyzed to corresponding *cis*- and *trans*-3-chloroally alcohol, which in turn are oxidized to the corresponding *cis*- and *trans*-3-chloroacrylic acid[13]. The activation energy (E_a) values were $100.1 \text{ kJ mol}^{-1}$ for *cis*-1,3-D and $103.0 \text{ kJ mol}^{-1}$ for *trans*-1,3-D[13]. There was little difference in the activation energy (E_a) values between the isomers of 1,3-D, which suggests identical rates of hydrolysis for the isomers of 1,3-D.

Gas-Liquid Phase Partition

The air-water partition coefficient (K_H Henry's law constant) is extremely important in determining how easily 1,3-D moves in soil and enters the atmosphere through volatilization[14]. The direct measurement of equilibrium concentrations of 1,3-D in the air (C_a) and liquid (C_w) phases was used to measure K_H . The dimensionless K_H is than obtained using $K_H = C_a / C_w$. To determine whether 1,3-D follows Henry's law, the linearity of K_H was determined over the aqueous concentration range of 100 mg L^{-1} to 500 mg L^{-1} . Figure 2 appeared to be linear with correlation coefficient of $r^2 > 0.99$. From the slope of these lines, the K_H values of *cis*-1,3-D and *trans*-1,3-D were 0.058 and 0.037 at 20°C , respectively. Our K_H values at 20°C agree well with those of Lebbink et al. [15] who reported K_H values of 0.055 and 0.037 for *cis*-1,3-D and *trans*-1,3-D at 20°C , respectively.

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