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 To determine the concentration of 1,3-D in the air phase ($C_a$), a 1 mL sample of the headspace was withdrawn with a gas-tight syringe and transferred into a GC vial containing 1 mL of hexane at 20°C, respectively.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 To determine the concentration of 1,3-D in the water phase ($C_w$), 0.5 mL of aqueous phase was withdrawn with a gas-tight syringe and transferred into a 10-mL headspace vial containing 5 mL of hexane at 20°C. The headspace vials were vortexed for 2 min, and a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 shows 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\(_2\)O. In water, cis- and trans-1,3-D are initially hydrolyzed to corresponding cis- and trans-3-chloroallyl alcohol, which in turn are oxidized to the corresponding cis- and trans-3-chloroacrylic acid[13]. The activation energy (\( Ea \)) values were 100.1 kJ mol\(^{-1}\) for cis-1,3-D and 103.0 kJ mol\(^{-1}\) for trans-1,3-D[13]. There was little difference in the activation energy (\( Ea \)) 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 (\( Ca \)) and liquid (\( Cw \)) phases was used to measure \( K_H \). The dimensionless \( K_H \) is then obtained using \( K_H = Ca / Cw \). 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.

Reference


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