Adsorption study of $^{14}$C-paraquat in two Malaysian agricultural soils

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Abstract The adsorption equilibrium time and effects of pH and concentration of $^{14}$C-labeled paraquat (1,1′-dimethyl-4,4′-bipyridinium dichloride) in two types of Malaysian soil were investigated. The soils used in the study were clay loam and clay soils from rice fields. Equilibrium studies of paraquat in a soil and pesticide solution were conducted. Adsorption equilibrium time was achieved within 2 h for both soil types. The amount of $^{14}$C-labeled paraquat adsorbed onto glass surfaces increased with increasing shaking time and remained constant after 10 h. It was found that paraquat adsorbed by the two soils was very similar: 51.73 (clay loam) and 51.59 $\mu$g g$^{-1}$ (clay) at 1 $\mu$g/ml. The adsorption of paraquat onto both types of soil was higher at high pH, and adsorption decreased with decreasing pH. At pH 11, the amounts of $^{14}$C-labeled paraquat adsorbed onto the clay loam and clay soil samples were 4.08 and 4.05 $\mu$g g$^{-1}$, respectively, whereas at pH 2, the amounts adsorbed were 3.72 and 3.57 $\mu$g g$^{-1}$, respectively. Results also suggested that paraquat sorption by soil is concentration dependent.

Keywords Adsorption · pH · Concentration · Equilibrium time · Paraquat

Introduction

Adsorption is probably the most important mode of interaction between soil and pesticides, controlling the concentration of pesticide in the soil liquid phase. Adsorption may vary from completely reversible to totally irreversible. The extent of adsorption depends on the properties of both the soil and the pesticide compound, such as size, shape, configuration, molecular structure, chemical functions, solubility, polarity, polarizability, and charge distribution of interacting molecules and the acid–base nature of the pesticide molecule (Pignatello and Xing 1996).
Compounds and their metabolites adsorbed by ionic bonding, or cation exchange, can either exist in the cationic form in solution or be protonated to become cationic. Ionic bonding involves ionized, or easily ionizable, carboxylic and phenolic hydroxyl groups of humic substances. Bipyridylium pesticides such as paraquat binds to soil humic substances by ion exchange via their cationic group. They form highly stable and unreactive bonds with the carboxyl groups of the humic substances. However, according to Senesi (1993), possible binding sites on the humic complexes are not utilized due to steric hindrance effects. The effect of pH on binding has been reported for less basic pesticides such as the triazine herbicides (Weber et al. 1969), amitrole (Senesi et al. 1986), and dimefox (Grice et al. 1973), which become cationic depending on their alkalinity and the pH of the system, and also govern the degree of ionization of acidic groups of the humic substances (Gevao et al. 2000).

Paraquat (1,1′-dimethyl-4,4′-bipyridylium dichloride) has been used extensively as a non-selective aquatic and terrestrial herbicide. Much work has been published on the inactivation of paraquat by adsorption onto mineral soils, organic matter, and clays (Weber et al. 1965; Knight and Tomlinson 1967; Weber and Weed 1968).

Paraquat is rapidly and strongly bound to soil, with values of the sorption coefficient ($K_d$) often over 1,000 l kg$^{-1}$ (Cheah et al. 1997). In this bound state, the compounds are very difficult to extract and characterize and at the same time they tend to lose their biological activity. As it is difficult to extract and identify the bound residues, the best way to demonstrate the presence of soil-bound pesticide residues is through the use of the radio-labeled form of the pesticide.

Data on adsorption of paraquat in tropical soils such as those found in Malaysia is limited. Therefore, the experiment reported here was designed to determine the adsorption properties of the compound under laboratory conditions, which may be extrapolated to field conditions. The objective of this study was to investigate the adsorption of $^{14}$C-paraquat and to determine the fate of paraquat in two types of Malaysian soil namely clay loam and clay soil.

Materials and methods

Chemicals

Radio-labeled [ethyl-1-$^{14}$C] paraquat obtained from the Institute of Isotopes and Co. Ltd. Budapest and non-labeled paraquat from Dr. Ehrenstorfer’s Company in Germany were used in the study. The radioactive concentration of the radio-labeled paraquat was 100 μCi with a specific activity of 32.3 mCi mmol$^{-1}$. The radio purity of the supplied labeled compound was pre-checked by radio-TLC and found to be more than 95% pure. The $^{14}$C-paraquat was dissolved in distilled water in the laboratory and then labeled as RSS$_1$. Calcium chloride (CaCl$_2$) was purchased from Merck.

Apparatus

The TriCarb Liquid Scintillation Counter (LSC) Model TR 2550 AB used was purchased from Packard (Packard Instrument Co., Meriden, CT, USA). The reciprocating shaker bath was purchased from TungTec Instruments Co. Ltd, Taiwan. The bench top centrifuge, IEC, was purchased from Shimadzu, Japan. The liquid scintillation cocktail PICOFLUOR$^\text{TM}$ 15, was purchased from Packard. Decon 90$^\text{®}$ solution purchased from Decon Laboratories Ltd., UK, was used to wash all glassware.

Preparation of radioactive standard [ethyl-1-$^{14}$C] paraquat solution

One hundred μCi radio-labeled [ethyl-1-$^{14}$C] paraquat in 0.5 ml distilled water, of specific activity of 4,646.58 KBq/mg (32.3 mCi mmol$^{-1}$), was diluted with 9.5 ml distilled water and then labeled as RSS$_1$. Then a working standard solution of 1,850 KBq/mg (RSS$_2$) was prepared by pipetting 5 ml of the RSS$_1$ into a 1-l volumetric flask and