Chemosphere 74 (2009) 1450–1456

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Sorption of alpha and beta hydrophobic endosulfan in a Vertisol from southeast region of Turkey

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ARTICLE INFO

Article history:
Received 19 September 2008
Accepted 3 December 2008
Available online 20 January 2009

Keywords:
Pesticide
Endosulfan
Adsorption
Desorption
Contamination
Vertisol

ABSTRACT

Endosulfan has been applied to control numerous insects in a variety of food and non-food crops. Limited information is available on dynamics of this pesticide in the soil. The objective of this research was to determine the adsorption–desorption behavior of the alpha (α) and beta (β) endosulfan in a Vertisol from the southeast region of Turkey, where cotton is the main crop in the large irrigated lowlands. The α and β endosulfan were adsorbed considerably and Freundlich adsorption–desorption isotherms fitted the α and β endosulfan data ($R^2 > 0.98$). Freundlich adsorption coefficients (K_f) for the α endosulfan ranged between 21.63 and 16.33 while for the β endosulfan they were between 14.01 and 17.98 for the Ap and Bw2 horizons. The difference of K_f values of α and β endosulfan for two horizons were explained with the slight difference in the amount of organic matter and clay, but considerable difference in Fe contents of the two horizons. Alpha and β endosulfan K_{fd} values were 118.03 and 45.81 for the Ap and 48.08 and 68.71 for the Bw2 horizons. Higher adsorption and desorption behavior of the endosulfan isomers for the same horizon was attributed to poor physical bonding between the endosulfan molecule and the surfaces of fundamental soil particles. This fact is thought to increase the effective use of endosulfan in agriculture with a possibility of its movement to the surface and groundwater in the Vertisol studied.

1. Introduction

Identifying and understanding the mechanisms controlling the fate of pesticides which are a threat for non-target organisms and one of a possible sources of contamination of water resources are still remaining to be a great public concern (Soulas and Lagacherie, 2001). The study of pesticide fate is, therefore, vital for both maintaining environmental quality and optimizing sustainable agricultural practices (Cupples et al., 2000).

Endosulfan (6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,3,4-benzodioxathiepin-3-oxide) is a chlorinated pesticide ($C_9H_6Cl_6O_3S$) of the cyclodiene group (Fig. 1). It is composed of two stereoisomers of alpha (α) and beta (β) endosulfan in approximate ratio of 70:30 (Mersie et al., 2003). It is being used extensively throughout the world for the control of numerous insects in many of food and non-food crops (Lopez-Blanco et al., 2002; Kumar and Philip, 2006).

Because of its persistence and toxicity, endosulfan contamination poses a significant environmental concern (Kullman and Matsumura, 1996). Extensive use of this pesticide more than a decade for cotton plantation in the Harran plain, southeast of Turkey is great concern regarding the potential transport in the environment.

Sorption is one of the key processes affecting the fate of agrochemicals in the sediment-water–soil environments (Thorstensen et al., 2001). A complete understanding of the adsorption and desorption of endosulfan is needed for better understanding mechanisms and the prediction of pesticide movement in soils and aquifers (Clausen et al., 2001). Sorption of pesticides by inorganic clay particles and organic matter may take place by one or more of the following interactions: Van der Waals forces, H bonding, dipole–dipole interaction, ion exchange, covalent bonding, protonation, ligand exchange, cation bridging, water bridging, and/or hydrophobic partitioning. Sorption can also affect the persistence, biodegradability, leachability, and volatility of pesticides. Surrounding ecosystems can be impacted if conditions are conducive to pesticide drift, leaching, or surface runoff (Pierzynski et al., 1994).

As it is known in the literature, co-solvent content is recognized to be one important factor influencing adsorption. Ying and Kookana (2002) indicated that methanol had less effect on adsorption than did acetonitrile. Ravanel et al. (1999) found that the use

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doi:10.1016/j.chemosphere.2008.12.015

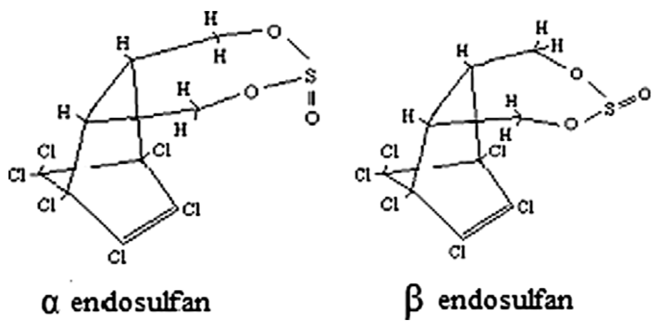

Fig. 1. The molecular structure of α and β endosulfan.

of methanol reduced the adsorption and caused a large increase in pesticide mobility. Since the methanol fraction increases the solubility of fipronil, a concomitant decrease in its adsorption is very likely. Several complementary hypotheses also have been proposed to explain the direct competition between the pesticide and solvent for adsorption sites, pesticide-co-solvent interactions via hydrophobic character and interactions of methanol with organic matter (OM), resulting in shrinking or swelling of the OM, which affects pesticide adsorption (Bobé et al., 1997).

The tendency of pesticides to leach from the soil is closely related to their solubility and their potential for adsorption. Strongly adsorbed molecules are not likely to move down the profile (Cox et al., 1998). Likewise, conditions that encourage adsorption will discourage leaching. Leaching is apt to be favored by water movement, taking place most readily in sandy soils that are low in clay and organic matter content but more permeable to water movement.

The use of uncontrolled and large amount of pesticides may deteriorate the soil and groundwater quality. The fate of the endosulfan as an insecticide has not been examined yet thoroughly in Turkey and specifically in the Harran Plain where the country's cotton production is concentrated. The hypothesis to be tested was that endosulfan isomers are likely adsorbed substantially by the Vertisol which is dominated by simectite silicate clay mineral causing an increase in the use of endosulfan applied in agriculture The objectives of the research were to: (i) investigate the adsorption and desorption behavior of α and β endosulfan in the selected Vertisol under cotton and; (ii) explain the adsorption–desorption mechanisms of this pesticide in the Ap and Bw2 horizons of this soil.

2. Materials and methods

2.1. Study area and soil samples

Soil samples were taken from a Vertisol profile in the Harran plain, Şanlıurfa, Turkey (Fig. 2). This plain is intensely (>90%) cultivated with cotton. The plain has 141,500 ha of irrigable land and is located between 36°43′–37°10′ North latitudes and 38°47′–39°10′ East longitudes. The plain has a semi-arid climate with almost no precipitation between June and September. The long-term mean annual precipitation is about 284.2 mm, the mean annual atmospheric temperature is about 18 °C, and the evaporation is 1884 mm (Yeşilnacar and Güllüoğlu, 2007).

The soils of the plain are mainly clayey, and pH values are slightly alkaline (pH 7.50–8.00). The minimum permeability values of the soils are between 0.22 and 3.51 m/day (DSI, 2003). Majority of soils in the plain are classified as Vertisol according to Soil Survey Staff (1999).

Soil samples were taken from the Ap (0–27 cm) and Bw2 (40–55 cm) horizons in a profile excavated on the Haran soil series map unit. Adsorption–desorption tests were applied on the samples from Ap and Bw2 horizons to establish the fate of endosulfan in the solum. The Ap is the horizon that receives the endosulfan and Bw2 horizon is an intermediate transition zone to subsoil horizons and groundwater.

Air-dried, sieved (<2 mm) samples were processed for the analysis of basic soil characteristics. Particle size distribution was determined using Bouyocus hydrometer method. Soil pH was measured in a 1:1 (w/v) soil to 0.01 M $CaCl_2$ solution mixture (Hendershot et al., 1993). The organic matter content was determined using modified Walkley-Black method. Cation exchange capacity (CEC) was measured using sodium-acetate method. The bulk density and lime (carbonate) content were determined using cylinder method and a calsimeter, respectively (Tüzüner et al., 1990). Total and dithionite–citrate extractable iron-oxide $(Fe_2O_3)_D$ were determined according to the method described by Sheldrick (1984).

2.2. Chemicals

Analytical grade endosulfan isomers were provided by Sigma–Aldrich with a chemical purity of 99%. All organic solvents used were HPLC grade; standard solutions of α and β endosulfan were prepared in an acetone matrix. Endosulfan stock solutions were

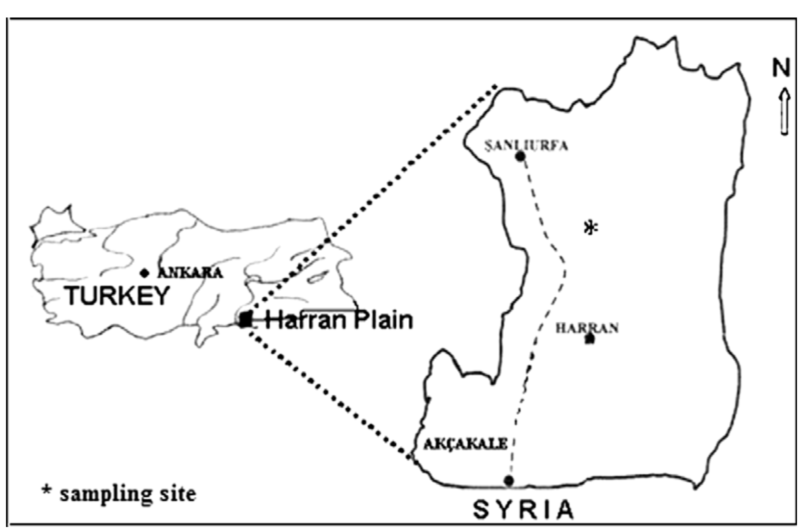

Fig. 2. Location map of the Harran plain.