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Adsorption, leaching and phytotoxicity of some herbicides as single and mixtures to some crops

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Abstract The study investigated adsorption, leaching potential, and phytotoxicity of alachlor, bromacil, and diuron on melon, Molokhia, and wheat in Gaza strip. Plant height was used to estimate growth inhibition (phytotoxicity). Growth inhibition data were regressed versus concentrations of corresponding herbicide to estimate EC_{50} value. The lowest EC_{50} value indicates the highest phytotoxicity. Adsorption results indicated that alachlor, bromacil and diuron have different shapes. Leaching potentials indicated that alachlor totally disappeared from the top 5 cm and accumulated at a deeper depth whereas bromacil and diuron accumulated in the top 8 cm of soil layer with a decreasing intensity at deeper depth. Phytotoxicity tests showed that diuron has the lowest EC_{50} values on melon (1.64) and Molokhia (0.15) whereas bromacil has the lowest one on wheat (0.08), values are in (mg/kg soil). Results of binary mixtures showed that the mixture contained alachlor and diuron was the most toxic to melon, whereas mixture contained alachlor and bromacil was the most toxic to Molokhia and wheat. Tertiary mixture (alachlor + bromacil + diuron) was more toxic on Molokhia than melon and wheat, EC_{50} values were 3.02, 32.174, and 633.9 TU/kg soil on Molokhia, melon, and wheat respectively. An interesting outcome of the study is that Molokhia was the most sensitive plant and binary mixtures showed synergistic phytotoxicity.

1. Introduction

Alachlor, bromacil and diuron are herbicides widely used for weed control over the world. Alachlor is a chloroacetanilide herbicide, used to control annual grasses and certain broadleaf weeds in field corn, soybeans and peanuts. It inhibits protein synthesis in plant root (Walker and Keith, 1992). Bromacil belongs to Uracil herbicide used for brush control on non-cropland areas. It is especially useful against perennial grasses. Diuron, one of the most commonly used herbicides, belongs to Urea derivatives that are applied as pre-emergence and post-emergence to control broadleaf weeds in a wide variety of annual and perennial broadleaf and grass weeds (Gooddy et al., 2002). Diuron is relatively persistent in the environment (with a half-life of over 300 days). Herbicide may enter freshwater ecosystems by different ways and pose potential risks for several aquatic organisms. Application of herbicides resulted in contamination of groundwater (Riparbelli et al., 1996), food samples (El-Nahhal, 2004) and soil samples (Vryzas et al., 2012). This situation was associated

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with health disabilities (Abu Mourad, 2000) and chronic diseases (Safi, 2002). In addition applied herbicides in soil were adsorbed on clay minerals (Franco et al., 1997), organoclay complexes (Nir et al., 2000), soil organic matter (Sánchez-Camazano et al., 2000; Rojas et al., 2013, 2014), and dissolved organic matter from a biodigester (Dal Bosco et al., 2012).

Moreover, the presence of herbicides as mixtures may create synergistic effects that can alter the balance of the ecosystem (Wendt et al., 2004). Farmers from Gaza strip claimed damaging growth of wheat, melon, and Molokhia plants cultivated in soils previously treated with alachlor, bromacil and/or diuron. Moreover, detailed information about phytotoxicity of herbicide mixtures to crops are not available elsewhere whereas in Palestine no reports are found. Accordingly, the authors designed this study to: (1) characterize the adsorption, leaching potential and phytotoxicity of alachlor, bromacil and diuron as individuals, binary and tertiary mixtures to, melon, Molokhia and wheat to satisfy the needs of the farmers, (2) characterize the synergistic or antagonistic effects of these herbicides.

2. Materials and methods

Technical material, purity 99% of alachlor, bromacil and diuron were purchased from Sigma Chemical Co., Germany. Their solubility in water is 170.3, 807, and 36.4 mg/l for alachlor, bromacil and diuron respectively. The applied rate of alachlor or bromacil is 2 kg/ha to control annual grasses and many broad leaved weeds in many crops, whereas for diuron it is 0.6 kg/ha for selective control of germinating grass and broad-leaved weeded in many crops including asparagus, tree fruit, sugar cane, cotton, alfalfa, cereals, sorghum and perennial grass seed crops, data were collected from Tomlin (2000). Melon, Molokhia, wheat seeds, and plastic pots were purchased from a local certified shop for agricultural products in Gaza.

2.1. Soil collection

Soil samples were collected from the 0 to 30 cm depth of an agricultural area has the following GPS information (N, 31°33′ 55.14″; E, 34°28′ 16.75″). It believed to be free of herbicide application at least 5 years. Soil sample was air-dried, sieved through 2 mm mesh and storied in plastic bags at laboratory conditions. Soil pH, salinity, organic mater content and soil texture were analyzed according to the Standard Method.

2.2. Adsorption experiments

The stock solutions of alachlor, bromacil and diuron were prepared by dissolving 30 mg in 1 L distilled water. The adsorption was measured at room temp (25 ± 2 °C), following the procedure previously reported (El-Nahhal and Lagaly, 2005). In this procedure appropriate aliquots of the aqueous stock solution of each herbicide was diluted with water to 25 mL and added to 50 mg Gaza soil in 30-mL centrifuge tubes. The final concentration of soil was 1 g/L. The dispersions were kept under continuous agitation during 48 h. The supernatant was separated by centrifugation at 20,000*g* for 0.5 h. Alachlor was determined by HPLC as described by Chen et al. (2011), in this procedure HPLC conditions were a reversed phase C-18 column was utilized to separate alachlor from other species using an acetonitrile/water mixture (1:1) containing 0.1 M phosphate buffer solution at pH 7.0 as the mobile phase. Detection was carried out with a UV-detector operated at 210 nm and at a flow rate of 0.1 μL/min. whereas bromacil and diuron concentrations were determined as in El-Nahhal and Lagaly (2005). In this procedure the concentration of bromacil in the supernatants was determined by Waters 717 HPLC with UV detector (detection wavelength 280 nm). Column: Nova-Pak C18 (inner diameter 3.9 mm, length 150 mm), flow rate: 20 μL/min. The mobile phase was methanol/water 50/50 (v/v). For the case of diuron, the same HPLC machine was used with changes in the detection wavelength to be 254 nm, flow rate: 1 mL/min and the mobile phase was methanol/water 70/30 (v/v).

The experiments were conducted at pH 7.33 ± 0.15.

The adsorbed amount of each herbicide was calculated from the depletion of the initial and remaining concentrations (Nir et al., 2000).

2.3. Leaching experiments

Leaching of herbicides in soil was performed using micro-column techniques with slight modifications of those of El-Nahhal et al. (2014). In these techniques transparent plastic columns with 1 cm diameter and 15 cm long were filled with 2 mm mesh sieved sandy soils. Appropriate amount of the field rate of each herbicide which corresponds to 0.88 mg/kg soil for alachlor and bromacil, and 0.25 mg/kg soil for diuron was applied on surface areas of the plastic columns. Each column was irrigated with 25 ml water operated at 0.33 ml/1 min. The columns were held standing for 48 h for equilibrium then closed from the top, laid down and sliced along their length. One row of test plant (Molokhia) was sown along the columns and irrigated with 3 ml water after 1 day. Then irrigation continues every day. Plant height (cm) was taken as the indicator of herbicide leaching and phytotoxicity indicates the accumulation of herbicide concentration. The experiments were held in the growth chamber at 25 ± 2 °C and sprinkle irrigation was performed as needed. Plant height was determined 16 days after sowing and used as indicators to estimate the herbicide presence at different soil depths in the column. The percent of growth inhibition (%GI) (phytotoxicity) at a soil depth was calculated according to Eq. (1) (El-Nahhal et al., 2014):

$$\%\mathrm{GI} = 100 * (P_c - P_t)/P_c \qquad (1)$$

where P_c and P_t are the shoot height of the control and the treated samples at any soil depth.

2.4. Phytotoxicity of single tests

Phytotoxicity of alachlor, bromacil or diuron to wheat, melon, and Molokhia were determined as growth inhibition. The tested concentrations of alachlor and bromacil are 0, 0.06, 0.11, 0.22, 0.44, 0.88 and 1.76 mg/kg soil, whereas the tested concentrations of diuron were: 0.005, 0.01, 0.02; 0.075, 0.1 and 0.15 mg/kg. Following the procedure described by El-Nahhal et al. (2014), single toxicity tests were carried out using plastic pots under laboratory conditions. Plant heights were taken 2 weeks after germination and used to estimate

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