ABSTRACT

Laboratory measurements of the retention of 10 phenoxyacetic pesticides in soil amended with progressive concentrations of humic acid (HA) ranging from 1 to $10^4$ mg kg$^{-1}$, showed sorption patterns depending on the pesticide structure and form (acid or ester). Some results point to competitive effects between pesticide and HA in the presence of the soil mineral matrix, partly accounting for a negative effect of low HA addition rates (< 100 mg kg$^{-1}$) in the sorption of phenoxyacetics, mainly in acid forms.

INTRODUCTION

The effect of soil organic matter in enhancing pesticide sorption in soil has been widely studied [1–6]. In addition to relatively weak physico-chemical interactions such as H-bonding, charge-transfer, or hydrophobic interactions, there is also a series of irreversible processes in which the molecular encapsulation into the flexible threedimensional network of HAs or covalent bondings are probably involved [7–11]. The assessment of factors related to pesticide sorption in soils is of prime importance both to forecast the active concentration of pesticide applied on agricultural soil, and to identify potential environmental hazards connected to groundwater contamination [3, 12–14]. In particular HAs interact with compounds of low molecular weight to a relative extent much greater than the soil mineral fraction. For that reason, the addition to soil of low amounts of HA salts (i.e., soluble humates) is generally assumed to play a significant role on the immobilisation of pesticide residues. Nevertheless, the low application rates recommended for soluble humates in agriculture are expected to have a negligible effect on most of the soil properties [15]. In the case of some specific processes (i.e., the assumed physiological effect of HA on root development, the mobilisation of soil microelements, or the sorptive interactions with trace amounts of xenobiotics) it is more probable that low concentrations of HA could play a significant role. The present study deals with the factors related to pesticide sorption in semiarid soil treated with increasing concentrations of soluble K-
humate. The aims of the study are: i) to quantify the effect of the HA application rates on the retention of 10 phenoxyacetic acids, both in absolute terms and in relation to the intensity of soil organo-mineral interactions; ii) to check the concentration threshold from which the addition of the HA significantly enhances the sorption; iii) to compare the sorption patterns of these pesticides in the acid and ester forms; and iv) to provide experimental data for further research on functional relationships between molecular structure of pesticides and their mobility in soil systems.

MATERIAL AND METHODS

Pesticides studied

The following pesticides were used for sorption measurements: 2,4-D (2,4-dichlorophenoxyacetic acid) (PolyScience Corp.); 2,4-DB (2,4-dichlorophenoxybutyric acid) (PolyScience Corp.); MCPA (2-methyl-4-chlorophenoxyacetic acid) (Chem Service); Silvex (2,4,5-trichlorophenoxypropionic acid) (PolyScience Corp.); 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) (PolyScience Corp.); 2,4-D methyl ester (2,4-dichlorophenoxyacetic acid methyl ester) (Chem Service); 2,4-DB methyl ester (4-(2,4-dichlorophenoxybutyric acid methyl ester) (PolyScience Corp.); MCPA methyl ester (2-methyl-4-chlorophenoxyacetic acid methyl ester) (Labor Dr. Ehrenstorfer); Silvex methyl ester (2-(2,4,5-trichlorophenoxypropionic acid methyl ester) (PolyScience Corp.); 2,4,5-T methyl ester (2,4,5-trichlorophenoxyacetic acid methyl ester) (PolyScience Corp.). In the case of methyl esters (comparatively low solubility in water) a previous solution in the minimal volume of acetonitrile was prepared and the final volume was adjusted with water to 1 dm³.

The soil-humic acid system

The soil, taken from the 0–20 cm horizon of a Calcic Luvisol in the experimental farm 'La Higuera', (CSIC, Toledo, Spain), has a pH of 4.5, organic C content of 5 g kg⁻¹, cation exchange capacity of 125 mmolc kg⁻¹, sand content of 780 g kg⁻¹, and clay content of 140 g kg⁻¹. A 10 g dm⁻³ K-humate solution adjusted to pH 7.0 with HCl was used to prepare soil mixtures with 1, 10, 1 000, 5 000 and 10 000 mg HA (kg soil)⁻¹. The first concentration was representative for usual application rates of soluble humates, whereas the latter is more representative for an optimum situation in agricultural soil. The control sample corresponded to the soil treated with a KCl solution with the same pH and concentration as the HA solutions. The HA used was extracted from sapric peat (Lugo, Northern Spain) and had C%=60.04, O+S%=32.08, N%=2.48, % carboxyl carbons (NMR)=12.0, % aromatic carbons=31.3, % O-alkyl carbons 32.5, and % alkyl carbons =24.0 [11, 16].

Sorption measurements

Samples of 5 g of HA-treated soils (air-dried and ground to pass a 2 mm mesh) were treated in replication with 10 cm³ of a 25 mg dm⁻³ pesticide solution, shaken for 12 hours at 25°C and left in contact for another 12 h. The suspension was centrifuged at 22 000 g and pesticide concentration in the supernatant solution was estimated by using derivatographic spectroscopy [11]. The calibration lines were built up from the intensities of the valleys in the second derivative spectrum in the range at between 270 and 310 nm.
RESULTS

I. The sorption values of the 2 forms of the 5 phenoxyacetic molecules studied (Figure 1) suggest quite a direct relationship between the concentration of HA and the pesticide retention. The maximum sorption was found in 2,4-DB when treated with 10 000 mg kg\(^{-1}\) HA (22.6 mg (kg soil\(^{-1}\)) which represents an increase of 300% as regards control soil (Table 1) and the lowest with 2,4-D (4.6 mg (kg soil\(^{-1}\)) at the same HA dose.

II. Very small but significant decreases in the enhancement of pesticide sorption as regards control soil (Table 1) were observed with low HA doses (ca. 1 mg kg\(^{-1}\)). It is interpreted as a competitive effect between pesticide and HA to be fixed on the mineral matrix.

III. In all cases the retention was significantly higher when the pesticide was applied as methyl ester, as regards the corresponding acid form.

IV. The HA concentration threshold from which the organic matter inputs enhances the retention of the pesticides studied (Table 1, bold figures) in general was at between 1 and 5 000 mg kg\(^{-1}\) HA. It was in overall much lower for esters than for the corresponding acids. In the practice, HA concentrations higher than 5 000 mg kg\(^{-1}\) are required to produce an enhancement of pesticide sorption of the untreated soil (exception: MCPA, which requires 10 000 mg kg\(^{-1}\) HA).

Figure 1. Pesticide sorption in soil treated with progressive HA doses (@ acid form; ■ methyl ester form).
Table 1. Relative enhancement in pesticide retention in soil treated with increasing HA doses (percentage increase as regards control soil).

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REFERENCES