ADSORPTION OF PHENOXYACID HERBICIDES BY SOIL FROM NORTH OF MOROCCO AMENDED WITH URBAN SEWAGE SLUDGE

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ABSTRACT

Three different soils from the Gharb area, a large agricultural zone at the north of Rabat (Morocco), amended or not with urban sewage sludges or biosolids, have been selected to study their interaction with herbicides. Dewatered urban sewage sludge, from a municipal wastewater facility in Granada (Spain), was used. Various phenoxyacid herbicides (2,4-D, mecoprop and dichlorprop), together with salycilic acid, have been selected. Adsorption kinetics and isotherms of the compounds in the three soils, amended or not with 2, 4 and 10% urban sewage sludge, have been carried out with the batch equilibration procedure. Analysis of the herbicides was performed by HPLC with DAD. The data were fitted to the Freundlich equation in all cases. For the three herbicides only a slight adsorption was found on non-amended soils. The addition of biosolids to the soils had a visible effect on herbicide adsorption at the highest dosage (10%) which is five times higher than permitted. At the recommended dosage (2%) a non-significant increase in adsorption was measured for the herbicides. Adsorption coefficients K_f were ranked as follows, 2,4-D > DCPP ≥ MCPP.

Keywords: *Adsorption isotherms, phenoxyacid herbicides, sewage sludge*

INTRODUCTION

The use of pesticides in Moroccan agriculture has been steadily increasing in the recent decade to cover different crops. Changes occurring in the climate have deeped Morocco in a chronic semi-arid area, which could affect pesticides in terms of persistence, mobility and degradation, mainly after severe storms or abundant irrigation.

Urban sewage sludges are being produced in large quantities as a result of European legislation. Their use, as that of other exogenous organic amendments, has been therefore suggested as a feasible remediation approach, since they supply and recycle nutrients and organic carbon (Berti and Jacobs 1996) and modify soil physicochemical properties (Díaz et al., 1993). The addition of these biosolids to soils with low organic matter content has been done with success to promote soil sorption and retard migration of some non-ionisable compounds, such as some triazine and organophosphorus pesticides (Barriuso et al., 1995; Sánchez-Camazano et al., 1997; Sánchez et al., 2003a, 2003b). However, sorption of ionisable compounds cannot be straightforward related to the indigenous or added soil organic matter.

MATERIALS AND METHODS

Soil. Soil was sampled from the upper layer (0-25 cm) in different sites of the Gharb region, at the north of Rabat (Morocco), with shortage in rain during the late decade. Various soils, commonly found in the area have been selected, whose main properties are shown in Table 1.

Table 1. *Physicochemical characteristics of the soil*

Soil	pH	Sa/St/Clay[#] (%)	O.M. (%)	C (%)	N (%)	Ca/Mg/K (cmol kg^{-1})	CEC (cmol kg^{-1})	Field cap. (1/3 bar) (%)	$CaCO_3$ total (%)
A	8.31	8.2/55.7/37.4	1.90	1.10	0.10	30.9/9.7/0.37	42.75	29.0	5.0
B	8.16	8.6/34.3/58.7	1.57	0.91	0.12	11.3/3.4/0.30	15.75	16.8	20.0
C	8.00	2.4/52.0/47.5	1.26	0.73	-	21.5/5.5/0.41	28.0	25.0	17.3

#Sa/St/Clay = Sand/Silt/Clay.

Organic amendments. The soil has also been amended with anaerobic biosolids, from a municipal wastewater facility in Granada (South of Spain) (Table 2).

Table 2. *Characteristics of the urban sewage sludge*

pH	O.M. (%)	Humic acids (%)	Fulvic acids (%)	Cd	Cr	Pb	Zn (mg kg^{-1})	Ni	Cu
7.2	40	1.6	0.47	2.5	60	349	772	103	284

Herbicides. Three phenoxyacid herbicides, 2,4-D, mecoprop (MCPP) and dichlorprop (DCPP), together with salicylic acid, a carboxylic acid, were studied. 2,4-D (pKa = 2.6) was from Dr. Ehrenstorfer (Augsburg, Germany). MCPP and DCPP (pKa = 3.8 and 3.0), as the racemic mixture, had been kindly supplied by BASF (Limburgerhof, Germany). Salicylic acid (pKa = 2.8) was from Aldrich (Madrid, Spain). Their purity was in all cases > 99.3%.

Adsorption isotherms. Sorption isotherms were carried out using a batch equilibration method and fitted to the Freundlich equation. Five g of soil samples with 20 mL of aqueous herbicide solutions (1, 2.5, 5, 7.5 and 10 mg L^{-1}) were mechanically shaken, in duplicate, end-over-end in a thermostatic chamber at 15 ± 1ºC for 24 h. A control of the herbicides solution without soil was also run. Then they were centrifuged at 3000 rpm at 18 ºC for 15 min (Eppendorf 5810R). A small volume of the supernatant was poured into an Eppendorf vial, further centrifuged at 15000 rpm for 20 min at 15 ºC (Sigma 2K15, Germany), filtered through a Millex filter type HV (Millipore), pore size 0.45 μm, and analysed as described below. Sorption isotherms were also carried out with soil samples amended with municipal sewage sludge at 2, 4 and 10% (w/w).

Extraction and analytical procedure. Herbicide samples were analysed by HPLC-DAD (Series 1100, Agilent, USA) on a Zorbax C8 column (5 μm, 150 x 2.1 cm) connected to an Eclipse XOB-C8 (2.1 x 12.5 mm) precolumn (Agilent, USA). Ten μl of the sample was injected at a flow rate of 0.2 mL min^{-1}, using as the mobile phase 45/55 (v/v) methanol/1% trifluoroacetic acid (Merck) at pH 3 ± 0.1. Detector wavelengths were 229 for the phenoxyacids and 237 nm for salicylic acid. Under these experimental conditions retention times of salicylic acid, 2,4-D, DCPP and MCPP were 3.7, 5.9, 8.8 and 9.6 min, respectively.

RESULTS AND DISCUSSION

No significant degradation was observed for any of the phenoxyacid herbicides and salicylic acid, for a period of up to 48 h, both at 4 and 15 ºC, which correspond to the refrigeration and incubation temperatures. Kinetics of the adsorption was rapid and 24 h were sufficient to retain the compounds.

Natural soils. The sorption of the herbicides was weak in all cases (Table 3), except for salicylic acid. The herbicides were slightly or not retained on the different soil samples, independently of the soil content in organic matter or clay, which are usually responsible for the retention of hydrophobic contaminants. No values for the Freundlich parameters were calculated for the majority of herbicides in natural soils due to insufficient adsorption which induced high deviation of the measurements.

***Table 3**. Freundlich coefficients (Kf (L kg^{-1}), 1/n and R2) for the adsorption isotherms of 2,4-D, DCPP, MCPP and salicylic acid in non-amended soils from Morocco, and amended with 2, 4 and 10% sewage sludge.*

	Salicylic acid			2,4-D			DCPP			MCPP		
	K_f	**1/n**	**R^2**	**K_f**	**1/n**	**R^2**	**K_f**	**1/n**	**R^2**	**K_f**	**1/n**	**R^2**
A	3.81	0.85	0.99	-			-			-		
A+2%	4.64	0.67	1.00	0.37	0.38	0.93	-			-		
A+4%	4.38	0.65	1.00	0.27	0.75	0.93	0.15	0.57	0.88	-		
A+10%	4.53	0.63	1.00	1.01	0.71	0.99	0.50	0.72	0.99	0.33	0.72	0.96
B	-			0.17	0.32	0.50	-			-		
B+2%	-			0.31	0.41	0.90	0.10	0.31	0.75	-		
B+4%	7.80	0.22	0.90	0.37	0.42	0.90	0.13	0.43	0.52	0.11	0.32	0.43
B+10%	3.37	1.05	1.00	0.73	0.75	0.99	0.55	0.61	0.95	0.43	0.50	0.58
C	-			-			-			-		
C+2%	2.98	0.29	0.87	0.29	0.27	0.85	-			-		
C+4%	2.49	0.33	0.90	0.40	0.60	0.99	0.31	0.11	0.39	-		
C+10%	3.30	1.04	1.00	0.61	0.83	0.98	0.96	0.37	1.00	0.61	0.38	0.92

It has been already reported, that these molecules are not retained on the soil surface because of repulsions between the negatively charged herbicides and the similarly charged OM and clay of the soil. At the pH of the soils, slightly basic due to their calcareous nature (Table 1), herbicides are ionised, thus not being appropriate for adsorption. Reddy and Gambrell (1987) found that the adsorption of 2,4-D was dependent on soil OM content and pH. Dubus et al. (2001) working with weak organic acids, 2,4-D, clofencet and salicylic acid, which have all pKa in the range of 2.6-2.8, found a relatively weak adsorption for 2,4-D, being salicylic acid and clofencet more strongly retained. This was attributed to the chemical structure of the latter two molecules, with the –COOH and –OH groups laying close to each other, which should permit the formation of bidentated complexes with metals. On the contrary 2,4-D, which does not share this particular structure, like MCPP and DCPP, was only slightly retained as it occurs in the Moroccan soils used in this study

Effect of the amendments. The K_f values for soil samples amended with sewage sludge (Table 3) reveal a weak to moderate adsorption of the herbicides, higher with increasing amount of sewage added. The Freundlich exponent, 1/n, less than 1, corresponds to the L-type in the Giles classification (Giles et al., 1974). In this type of isotherm the slope readily falls with an increase in the concentration, because vacant sites become more difficult to find with the progressive covering of the surface. The isotherms for the phenoxyacid herbicides showed that adsorption increased in all cases in the order MCPP ≤ DCPP < 2,4-D (Table 3). The same ranking was reported for MCPP and DCPP in calcareous soils (Matallo et al., 1998). This behaviour could be attributed to the chemical structure of the compounds, because of the branched aliphatic chain present in MCPP and DCPP but not in 2,4-D. Previous results with ionisable compounds, like 2,4-D and metsulfuron-methyl, have indicated an increase of herbicide adsorption when using the exogenous organic matter as the only substrate (Barriuso et al., 1997). MCPP and DCPP promoted their adsorption when peat was added at 4 and 10% (Matallo et al., 1998). No relationship between adsorption and pKa has been found in contrast to other anionic pesticides, such as sulfonylureas (Oliveira et al., 2001).

Caution should be taken with the amounts of applied sewage sludge, limited to 2-4% or 22.5-45 t ha^{-1} (Bellin and O'Connor, 1990), depending on the national legislations, because of the concern about the long-term buildup of heavy metals in the soil (Renner, 2000), which may have adverse effects on total soil microbial biomass and on bacteria fixing nitrogen.

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