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Sorption of Aldicarb Sulfoxide by Samples of Some Calcareous Soils From Turkey

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Abstract: Sorption of aldicarb and aldicarb sulfoxide was investigated spectrophotometrically on 16 soil samples. Ten of them were from the Çukurova region. The results showed that organic matter is the single soil property to give correlation with sorption of aldicarb. Clay minerals are also important in sorption but their effect is masked by fine carbonates and organic matter. $CaCO_3$ sorbs aldicarb weakly. Aldicarb sulfoxide was also sorbed by soil constituents very weakly.

Aldicarp ve Aldicarp Sülfoksitin Türkiye'nin Bazı Kireçli Topraklarında Tutulması

Özet: Aldicarb ve Aldicarb sülfoksit'in, 10'u Çukurova bölgesinden olmak üzere 16 toprak örneğinde tutulması, spektrofotometrik yöntem ile araştırılmıştır. Organik madde, aldicarb tutulması ile korelasyon veren tek toprak özelliği olmuştur. Kil minerallerinin de tutulmada önemli olduğu bulunmuş ancak etkisinin ince karbonat ve organik madde tarafından maskelendiği sonucuna varılmıştır. $CaCO_3$ aldicarb'ı zayıf bir şekilde tutmuştur. Aldicarb sülfoksit ise toprak bileşenleri tarafından çok zayıf bir şekilde tutulmuştur.

Introduction

Aldicarp (Temik), 2-methly-2-(methylthio) propionalaldehyde O-(methylcarbamoly) oxime, is an important carbamate insecticide. It constitutes more than 80% of insecticides used to protect cotton plants against whitefly (*Bemisia tabaci* spp.) in the Çukurova region in Türkiye. Although persistince (1), metabolism (2), degradation (3, 4), and movement (5) of this insecticide were examined widely, information on sorption by soil constituents is limited except for the works of Bromilow (6), Supak et al. (7), Felsot and Dahm (8), and Bromilow et al. (9).

The higher persistence of aldicarb sulfoxide (1), the main toxic metabolite of aldicarb along with aldicarb sulfone, gives a special place to this chemical in soil studies. Sorption is important because it largely controls the fate of pesticides in soil (10). This study is designed to find out the effect of some soil factors on the sorption of aldicarb and aldicarb sulfoxide. This is the first study which particularly uses calcareous soils in Türkiye as the sorbing material.

Materials and Methods

Materials

Surface soil samples of some widespread soil series from cotton growing areas in the Çukurova region were selected and calcareous soil samples from various geographical areas in Türkiye were also included. Pure samples of kaolinite, smectite, and chemically precipitated $CaCO_3$ were used as controls for better understanding of mechanisms involved in sorption of aldicarb in soils.

Soil Analyses: The soil samples were analyzed for sand, silt and clay by the hydrometer method (11). Organic matter was estimated by the Walkley-Black method (12) and total carbonate was determined was determined gas volumetrically (13). Active $CaCO_3$, as an estimate of the relative amount of fine $CaCO_3$, was evaluated by the method of Yaalon (14), and specific surface area by method of Bower and Gschwend (15), pH was measured potentiometrically in 1:1 soil-water ratio. Clay minerals were examined by X-ray diffraction using the procedures outlined by Jackson (16). The physicochemical characteristics of soil samples measured given in Table 1.

Sorption Studies: The sorption of aldicarb and aldicarb sulfoxide (pure chemilcals kindly supplied by Union Carbide Inc.) by soil samples was studied at a concentration of 4 µg/ml, a concentration normally encountered in soils after filed application (6). One gram of air-dry soil of <2 mm particle size was shaken on an end-over-end shaker for 4 hr at room temperature to attain equilibrium (7) with a 10 ml solution of aldicarb and aldicarb sulfoxide. The suspension was centrifuged and 2 drops of 1 M $CaCl_2$ solution were added to promote flocculation as requerid. In the clear supernatant the reduction the reduction in the concentration of pesticides added was determined. The color development method was essentially that of Johnson and Stansbury (17) with the exception that 1-naphthylamine hydrochloride was used as coupling agent instead of 1-naphthylamine. The amount of pesticide sorbed was obtained by subtracting the amount found in the solution from the amount added. The sorption was expressed by distribution coefficient (K_d), which is the ratio of the concentration of pesticide in the sorbed (µg/g of oven-dry soil) phase to the concentration of pesticide in the solution (µg/ml of solution) phase. A parallel sorption study was carried out with soil samples which were freed from organic matter and $CaCO_3$ using the methods described in Jackson (16).

Results and Discussion

Soprtion of Aldicarb: The sorption values of aldicarb and aldicarb sulfoxide are presented in Table 2.

The sorption values are generally low, but still much higher than those found by Supak et al. (7). Bromilow et al. (9) report a K_d value of 0.55 for a sandy loam soil with an organic matter content of 5.92 %. K_d/S values vary greatly indicating that sorption is not a function of the

Table 1. Some physicochemical characteristics of the soil samples.

Soil No.	Soil Samples	Locality	U.S. Soil Taxonomy	Dept (cm)	Particle Size Fraction Sand (%)	Silt (%)	Clay (%)	Organic matter (%)	$CaCO_3$ equiv. (%)	Active $CaCO_3$ (%)	pH (1:1)	Specific Surface Area (m^2/g)	Prominent Clay Minerals*
1	Arıklı Ap	Çukurova	Entic Chromoxerert	0-17	2.2	41.5	56.3	1.25	27.8	11.9	7.5	159	Sm>Ve, Ka
2	Arpacı Ap	Çukurova	Typic Xerofluvent	0-25	6.0	40.6	53.4	0.99	46.4	9.2	7.6	161	Sm>Ka, Ch
3	Bahçe Ap	Silifke	Aquic Xerofluvent	0-22	58.0	32.5	9.5	0.90	31.8	6.3	7.9	36	Sm
4	Balcalı Ap	Çukurova	Typic Rhodoxeralf	0-35	27.5	19.6	52.7	1.97	1.1	0.6	6.8	235	Sm
5	Çamlık Ap	Bursa	Typic Chromoxereret	0-27	9.1	28.7	62.2	2.71	11.3	5.6	7.6	111	Il>Ve
6	Çanakcı Ap	Çukurova	Typic Xerofluvent	0-22	3.5	57.3	39.2	0.82	21.4	6.4	7.7	118	Sm>Il, Ka
7	Çeltikçi Ap	Silifke	Aquic Xerofluvent	0-25	5.6	59.3	34.6	0.82	27.3	20.9	7.7	175	Sm>Il
8	Harran Ap	Şanlıurfa	Vertic Calciorthid	0-14	14.0	38.3	47.6	0.90	28.3	7.2	7.6	127	Sm
9	Helvacı A11	Çukurova	Vertic Halaquept	0-35	1.5	30.7	67.8	0.89	57.7	8.4	8.0	221	Sm>Ka, Ch
10	İncirlik Ap	Çukurova	Entic Chromoxerert	0-20	9.7	23.9	66.4	0.92	20.7	9.6	7.1	166	Sm>Ve, Il
11	Brown A11	Konya	Orthid	0-12	24.8	49.0	26.2	1.14	55.5	24.2	7.8	174	Se>Pa
12	Misis Ap	Çukurova	Vertic Xerochrept	0-30	7.6	22.2	70.2	0.94	6.6	4.3	7.5	354	sm>Il
13	Ortaçiftlik A11	Bursa	Entic Pelloxerert	0-27	9.2	20.9	69.9	2.41	1.5	0.3	7.2	74	Sm>Il
14	Rendzina A1	İzmir	Xeroll	0-10	42.3	26.4	31.2	15.90	31.5	9.3	7.3	263	Sm>Il
15	Rendzina A1	Van	Boroll	0-15	20.5	49.7	29.8	14.31	26.3	9.8	7.1	193	Sm>Il
16	Yenice Ap	Çukurova	Vertic Xerofluvent	0-20	1.6	42.3	56.1	0.90	23.6	12.5	7.7	68	Sm>Ve, Il

* Sm = Smectite group clay minerals; Ve=Vermiculite; Ka=Kaolinite; Se=Sepiolite; Pa=Palygorskite; Il=İllite; Ch=Clorite.

Table 2. Sorption values obtained with addition of 4 µg/ml aldicarb and aldicarb sulfoxide in soils with (A) and without (B) removed organic matter and on some pure clays and calcite.

Soil No	Aldicarb Sorption (A) (µg/g)	Aldicarb Sorption (A) (%)	Kd (ml/g)	Kd/S* (ml/m^2)	Aldicarb Sorption (B) (µg/g)	Aldicarb Sorption (B) (%)	Aldicarb Sulfoxide Sorption (A) (µg/g)	Aldicarb Sulfoxide Sorption (A) (%)
1.	7.1	17.7	2.26	0.0142	28.4	71.0	0.00	0.0
2.	3.4	8.9	0.99	0.0061	31.6	79.0	1.36	3.4
3.	10.3	25.8	3.47	0.0964	1.2	3.1	0.44	1.1
4.	13.3	33.2	5.16	0.0220	34.9	87.4	3.04	7.6
5.	9.2	23.0	3.22	0.0290	33.9	84.9	3.20	8.0
6.	3.8	9.4	1.08	0.0092	3.6	9.1	2.84	7.1
7.	12.1	30.3	4.44	0.0254	32.6	81.4	3.52	8.8
8.	6.7	16.8	2.14	0.0169	8.5	21.3	0.01	0.2
9.	18.3	45.8	8.75	0.0396	30.3	75.8	7.68	19.2
10.	9.3	23.2	3.19	0.0192	31.6	79.0	0.00	0.0
11.	3.4	8.5	0.94	0.0054	33.0	82.6	3.76	9.4
12.	13.6	34.1	5.72	0.0162	31.3	78.3	2.72	6.8
13.	11.3	28.2	4.20	0.0568	28.2	70.4	70.4	17.6
14.	18.5	46.2	8.89	0.0338	10.8	27.1	3.04	7.6
15.	18.9	47.4	9.47	0.0491	33.5	83.8	1.20	3.0
16.	9.0	22.5	3.01	0.0443	36.4	91.4	1.60	4.0
Pure Samples								
Kaolinite	3.6	9.0						
Smectite	25.2	63.7						
Calcite	3.6	9.0						

*: S is the specific surface area.

total surface area. Among the eight physicochemical caharcteristics, only organic matter gave a significant correlation with sorption values at the 1 % level (r=0.630) (Table 3). Previously, soil organic matter gave a correlation with Freundlich constant k (8). Exclusion of samples poor in organic matter and rich in clay content (nos. 7, 9 and 12) resulted in a closer correlation at the 0.1 % level (r=0.830). Similar results were obtained when per cent sorption was used as sorption parameter.

The results would indicate that soil constituents other than organic matter are involved in sorption. Sorption values obtained with samples freed from carbonates and organic matter supported the contention. Increased sorption with Arpacı (no. 2), Çeltikçi (no. 7), Brown (no. 11) and Yenice (no. 16) soil samples following treatments reveal cementation of strongly sorbing surfaces by fine carbonate and organic matter, similar to the phosphate sorption in calcareous soils (18). The treatments also show a weak sorption of aldicarb by $CaCO_3$ (Table 2). Decreases in sorption in clay-poor Bahçe (no. 3), Çanakcı (no. 6), and Rendzina (no. 14) soil samples reflect the effect of organic matter removed. Per cent sorption by treated samples was correlated with clay content at 5 % level (r=0.515). High sorption of pure smectite (63.7 %)

and low sorption of $CaCO_3$ (6 %) support tho findings obtained with soil samples. Pure kaolinite sorbed only 6 % of aldicarb. It appears that clay minerals, particularly smectites, would not show their full potency to sorb aldicarb in natural condition due to the cementing action of the other soil constituents.

Sorption of Aldicarb Sulfoxide: Aldicarb sulfoxide was sorbed by soil constituents much more weakly than aldicarb (Table 2). Weaker sorption of aldicarb sulfoxide than aldicarb was previously reported (6, 9). Pure samples of smectite, kaolinite and $CaCO_3$ sorbed 4.1 %, 3.6 %, and 9.5 % of aldicarb sulfoxide, respectively. Higher solubility of aldicarb sulfoxide apparently results in lower affinity of this chemical for the surfaces of soil colloids. Weak sorption signifies a greater potential mobility of a chemical through the soil column, a process which is mainly controlled by soil texture.

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Table 3. The correlation coefficients of aldicarb sorption derived from soil parameters (%).

Parameter	Correlation Coefficient
% Sand	+0.240
% Silt	-0.349
% Clay	+0.035
% Organic Matter	+0.630**
% $CaCO_3$	-0.127
% Active $CaCO_3$	-0.244
pH	-0.301
Specific Surface Area	+0.468

**: Significant at the 1% probability level.

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