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Adsorption and Degradation of Benfuracarb in Three Soils in Hunan, People's Republic of China

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Benfuracarb ($C_{20}H_{30}N_2O_5S$), an effective broad-spectrum carbamate pesticide, is used for treatment of soils, leaves and seeds and controls a wide range of insects (Osaki et al. 1992). Its molecular weight is 410 and its structural formula is showed in figure 1. Benfuracarb is a sulfenylated derivative of carbofuran (3,3-dihydro-2,2-diethyl-7-benzofuranyl-methylcarbamate). Studies have suggested that carbofuran have been identified as potential endocrine disruptor (Lyons 1999; Song and Wang 2001; Ma and Gu 2003). Therefore, benfuracarb and its degradation product, carbofuran, in environment have attracted extensively interests from environmental scientist and public. During recent decades, benfuracarb has been studied with focus on pest control (e.g. Huijbregts et al. 1995; Norio et al 1994; Tanaka et al. 1985; Clay et al. 1980a; 1980b), environmental toxicity (Valenzuela et al. 1999; Stehrer-Schmid et al. 1995) and environment monitoring (Valenzuela et al. 2001; Tanaka et al. 1985). The present study focuses on adsorption and degradation of benfuracarb in different soils in order to give a better basis for judging if the pesticide pollutes the environment, including ground water, and thus assess the environmental safety, and to give advice for proper use.

MATERIALS AND METHODS

Soil samples were collected in the field where benfuracarb and carbofuran had never been used. Top soils (a mixture of soil from the upper 20 cm) were sampled at five sampling sites for each of the three soil types. After removing coarse fragments and root debris, the air-dried samples were passed through a 2 mm sieve prior to analyses. Basic characteristics of experimental soil samples (Table 1) were determined by methods according to Chinese Soil Association (1983).

Standards (benfuracarb, purity>97%; carbofuran, purity>99.7%; 3-hydroxy-carbofuran, purity>99.8%) were provided by Otsuka Chemicals Co. Ltd., Japan. Florisil (60-100 mesh) from Supelco Inc. (Bellefonte, PA, USA) was used as sorbents in the cleanup columns. Florisil was activated at 550°C for 12 h and partially deactivated with 0.5% water prior to use. Chromorsorb W AW DMCS

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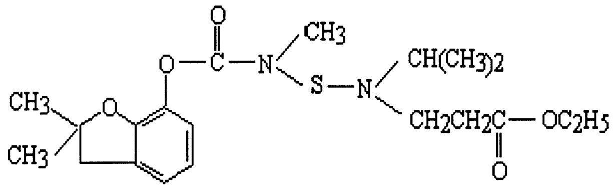

Figure 1 The structural formula of benfuracarb (ethyl N-2, 3-dihydro-2,2-dimeth -yl-benzofuran-7-yloxy-carbonyl (methyl) aminothio-N-isopropyl-β-alaninate)

Table 1 Basic characteristic of experimental soil samples.

Soils	Sampling sites	Water content (g/kg)	Organic matter (g /kg)	CEC (cmol/kg)	pH (H_2O)	Clay content (%) <0.01	Clay content (%) <0.001
Quaternary red earth	Changsha suburb	3.52	2.71	7.3	4.0	58.8	32.5
Fluvoaquic soil	Changsha county	3.48	1.45	9.1	5.5	28.5	7.6
Tidial sand earth	Xiangying county	1.75	4.00	17.3	5.5	35.4	14.4

used as support was passed through an 80-100-mesh sieve. 3%OV-1 (as a stationary phase in chromatographic column) was analytically pure. All solvents (e.g. acetone, petroleum ether, CH_2Cl_2) were redistilled prior to use or were of chromatographic quality.

The gas chromatography (GC) (SP-502, Lunan chemical instrument plant), was equipped with a nitrogen and phosphorus detector (NPD) and a chromatogram data handler (SSC-922, Shanghai analysis instrument plant). The GC column was 3 mm in inner diameter and 2 m in length. A Soxhlet extractor, Kuderna-Danish (K-D) concentrators (Shanghai glass instrument plant), a constant temperature incubator, an oscillator, a rotatory evaporator (Beijing medical apparatus and instruments plant) with a vacuum pump and a thermostat water bath, a sterilizer and a super centrifuge were used in the experiments.Helium (≥99.99%) was used as carrier gas, hydrogen as combustion gas, air as assistant combustion gas. The oven temperatures were set at 230°C (for benfuracarb), 180°C (for carbofuran), 210°C (for 3-hydroxycarbofuran), respectively. Both the inlet temperature (vaporization room) and detector temperature were set at 280°C. Identification was accomplished using relative retention time techniques while quantification was done by comparison of peak areas of samples to those of standards at known concentrations. Injection volume was 1μL.

Degradation of benfuracarb in soils was studied by culturing soil samples at constant temperature in laboratory and taking samples for analysis at selected times. For each of the three kinds of soils, 84 samples of 20 g were prepared. Water (about 10 ml) was added and samples cultured 3 days at 28°C. Soil samples were divided into two groups, 42 samples of each kind of soils, one group was given sterile treatment: temperature 121°C, pressure 10 kg, 5 h per day for 3 days. The chemical to be tested was added to the two groups of soil samples. The soil from each treatment was transferred to a 250 mL triangular flask and added 50 mL acetone. After shaking for one hour and filtering by a vacuum pump, the filtrate was concentrated to about 30 mL by a rotatory evaporator, added 150 mL distilled water and 6 g NaCl, and extracted 3 times with 50 mL CH_2Cl_2. The collected extract was dried by anhydrous sodium sulfate, concentrated to about 5 mL in a K-D concentrator, concentrated further at room-temperature almost to dryness, and added 2 mL of 9:1 petroleum ether/ethyl acetate (V/V). The concentrated solution was transferred to the glass column (The column was packed in the following order: a plug of glass wool in the bottom, 2 g anhydrous sodium sulfate, 5 g Florisil and 2 g anhydrous sodium sulfate. Before use, the column was pre-washed with 20 ml petroleum ether, 10 mL ethyl acetate). The column was eluted with 90 mL of 9:1 petroleum ether/ethyl acetate for determination of benfuracarb, or eluted with 70 mL 7:3 petroleum ether/ethyl acetate (V/V) for determination of carbofuran. The collected extract was concentrated almost to dryness and adjusted to 10 mL with acetone which serves as a keeper and injection solvent. Benfuracarb, carbofuran and 3-hydroxycarbofuran were determined by GC.

Benfuracarb standard solution (5 mL, 18.0 mg/L) and 5mL of 0.05 mol/L $CaCl_2$ solution were transferred to a 150 mL triangular flask with a stopper and 5.000 g of soil sample were added. After oscillating the flask for 2, 4, 6, 8, 10, 12, 14, 16, 18 or 24 h, the mixture was centrifuged at 3000 rpm for 10 min. Five mL of supernatant was transferred to a separation funnel containing 150 mL distilled water and 6 g NaCl, and extracted three times with 50, 30 and 20 mL of CH_2Cl_2, respectively. The extract was collected and removed water by anhydrous sodium sulfate, concentrated till about 2 mL in a K-D concentrator, transferred to the glass column (see previous section), wetted with 20 mL petroleum ether, elute as a wash and discard with 40 mL petroleum ether/ethyl acetate (95:5, v/v), then elute with 60 mL of petroleum ether/Ethyl acetate (9:1, v/v), and collected in the other K-D concentrator to about 1 mL. The volume was adjusted to 10 mL with acetone for determination on GC. The solid in the tube was transferred to a 150 mL triangular flask by washing with 40 mL 1.00 mol/L of HCl solution. The mixture was filtered after oscillating 30 min. The pH value of filtrate was adjusted to 13 with 10 mol/L NaOH solution. After extraction and cleanup (methods are the same as above) the filtrate was analyzed by GC.

The organic carbon adsorption constant, K_{oc}, of benfuracarb in the three soils was determined by a batch equilibrium method. First an amount (0; 2; 4; 6; 8; 10 mL) of benfuracarb standard solution (18.0 mg/L) was transferred to six triangular flasks (150 mL). To each flask 25 mL of 0.01 mol/L $CaCl_2$ solution (equivalent to the ion strength of the groundwater at Changsha) and water till 35 mL were added. Soil samples (5.000 g) were then transferred to the flasks. The mixture was transferred to a tube for centrifugation, the flask washed with 0.05 mol/L $CaCl_2$ solution, and centrifuged 10 min after mixing 12 h in thermostat water bath at 25±0.1℃. The upper layer solution was extracted and purified using the method described in the previous section. Denoting the concentration of benfuracarb in soil when adsorption equilibrium is reached C_S (mg/kg), we get as $C_S=(A-C\times V)/W$

where A is amount of benfuracarb added (mg); C is concentration of benfuracarb in water at equilibrium (mg/L); V is volume of solution in equilibrium (L); W is soil weight (kg).

One replicate sample per 7 samples was analyzed on GC. The precision was judged as acceptable when percent difference between duplicate sample analyses for benfuracarb, carbofuran and 3-hydroxycarbofuran is lower than 10%, 10% and 15%, respectively. The accuracy was determined by analyzing standard samples which concentrations have been known. Average recoveries ± relative standard deviations (RSD%) are shown in table 2. Detection limits for amounts on GC were 6×10^{-11} g for benfuracarb, 5×10^{-11} g for carbofuran, and 8×10^{-11} g for 3-hydroxycarbofuran, respectively.

Table 2 Average recoveries ± relative standard deviations (RSD%) of benfuracarb, carbofuran and 3-hydroxycarbofuran.

Soil sample	Conc. added ($mg\ L^{-1}$)	Recoveries(%)± relative standard deviations (RSD%)		
		Benfuracarb	Carbofuran	3-hydroxycarbofuran
Quaternary red earth	0.05	79.5±7.0	101±6.2	106±9.1
	0.50	88.7±5.2	96±5.4	89±5.5
	5.00	89.5±6.2	94±5.3	99±5.3
Fluvoaquic soil	0.05	106.0±7.2	97±4.0	83±6.8
	0.50	94.7±6.4	105±7.0	101±6.8
	5.00	97.6±3.2	102±6.6	96±6.0
Tidial sand earth	0.05	84.0±6.2	93±3.7	79±7.5
	0.50	88.5±6.1	105±6.0	95±5.1
	5.00	92.0±7.2	98±6.3	107±6.8

RESULTS AND DISCUSSION

The degradation rate of a pesticide in soils is determines its persistence and, ultimately its harm to the environment. Degradation may occur by biological-, chemical-, or photochemical reactions which may occur simultaneously or sequentially (Bollag and Liu 1990). The main degradation modes are oxidation, reduction, hydrolization and ring scission. One may distinguish between biodegradation and chemidegradation by comparing results for soils given sterile treatment with those for a non-sterile treated soil (Han, 1993). Results for the three soils studied are depicted in Figure 2. Degradation rate of a pesticide is usually expressed by the half-life ($T_{1/2}$). The degradation in soils is a first-order reaction (Dykaar and Kitanidis 1996; Wu and Nofziger 1999), $C=C_0e^{-kt}$, and $T_{1/2}=\ln2/k$, where C is the concentration of the pesticide in soil (mg/kg) at time t (day, d); C_o is initial concentration (mg/kg); k is the degradation rate constant (d^{-1}) and $T_{1/2}$ degradation half-life (d). Regression analysis were performed on the logarithmic form of the equation, $\ln C=-k\,t+\ln C_0$. K values and half-lives are listed table 3. The study shows that degradation was slower in samples given sterile treatment; thus both chemical and biological degradation of benfuracarb occur. However, the difference in K (and $T_{1/2}$) between treated and untreated samples was small showing that chemical degradation is the dominating process. Clay et al. (1980a) described

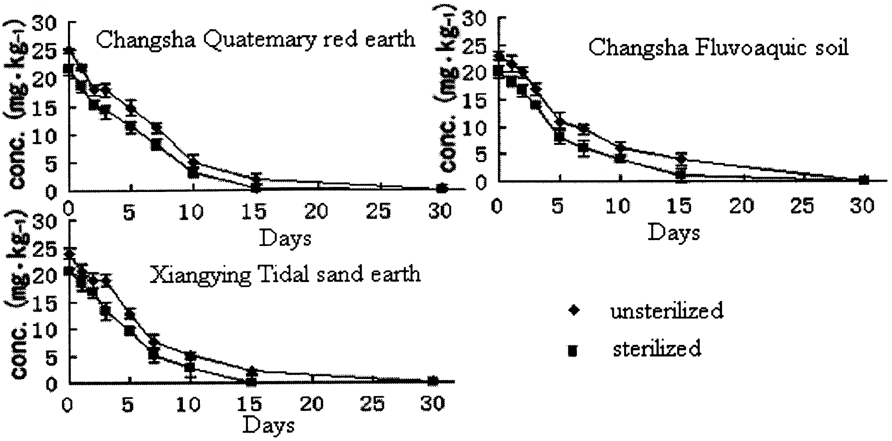

Figure 2 Degradation curve of benfurcarb in three soils

Table 3 Half-lives of benfuracarb in soil.

Soils	Regression equtions	R^2 values	k values	Δk %	$T_{1/2}$ (Days)
Quaternary red earth	*Y=1.4358-0.0826X	-0.9376	0.0826	6.6	8.4
	Y=1.385-0.0882X	-0.9404	0.0882		7.9
Fluvoaquic soil	*Y=1.356-0.0781X	-0.9808	0.0781	15.4	8.9
	Y=1.333-0.0909X	-0.9889	0.0909		7.6
Tidial sand earth	*Y=1.3836-0.0698X	-0.9987	0.0701	19.6	9.9
	Y=1.3806-0.0854X	-0.9863	0.0854		8.1

* denotes sterile treatment; Y=LnC; X denotes time t (days)

the metabolism of carbonyl-labeled ^{14}C samples of dibutylaminosulfenyl carbofuran (DBSC) and morpholinosulfenyl carbofuran (MSC), chemicals similar to benfuracarb. They found that within 30 the degradation was essentially chemical, and there was little relationship with microorganism in soils. Conversion to carbofuran by cleaving of the N-S bonds in DBSC and MSC was fast and carbofuran was subsequently oxidized, hydrolyzed and cleaved. This is in accordance with our results. Our studies showed that within 30 days, benfuracarb degradated very fast (Figure 2). The amount of carbofuran, which was detected as a metabolic product, varied irregularly with time (Table 4). Micro amounts of 3-hydroxycarbofuran were detected in some cases, but never before day 7 (Table 4). Clay et al. (1980b) summarized the mechanisms: first carbofuran was produced by the degradation of benfuracarb; secondly, the concentration and degradation rate of carbofuran were initially low; thirdly, there is no N-S bond (where chemidegradation easily occurs) in carbofuran, therefore the chemical stability of carbofuran is higher than of benfuracarb; and finally biodegradation plays a more important role in carbofuran degradation than in benfuracarb degradation.

Adsorption equilibrium was reached after about 10 hours (see above). In our studies we assumed that equilibrium was reached after 12 hours. Concentration in soil (C_S, mg/kg) was plotted against concentration in water (C, mg/L) (Figure 3). Such

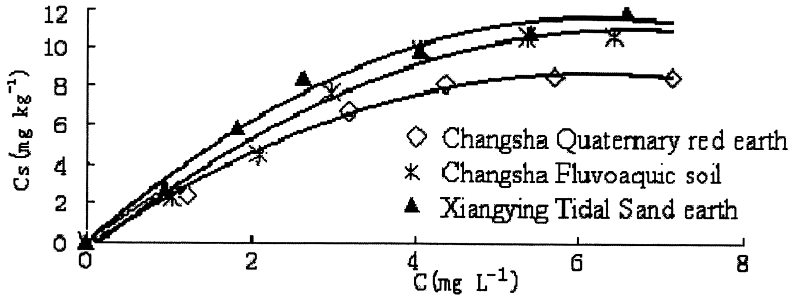

Figure 3 Benfuracarb adsorption isotherms in the three soil types (25℃)

Table 4 The degradation of benfuracarb in soil (mg/kg).

Soil	Treatments		days								
			0	1	2	3	5	7	10	15	30
QRE	Sterile	CF	ND	0.68	0.85	1.10	1.00	0.37	1.06	0.47	ND
		3-CF	ND	ND	ND	ND	ND	ND	ND	0.04	ND
	Unsterilized	CF	1.13	2.18	2.34	0.84	1.97	3.00	2.78	1.36	0.20
		3-CF	ND	ND	ND	ND	ND	ND	0.05	0.08	ND
FAS	Sterilized	CF	0.40	1.05	0.44	0.93	0.40	1.00	3.10	0.50	ND
		3-CF	ND	ND	ND	ND	ND	ND	0.05	0.04	ND
	Unsterilized	CF	2.70	4.03	0.85	1.73	1.28	4.23	5.59	0.19	0.27
		3-CF	ND	ND	ND	ND	ND	0.03	0.07	0.12	ND
TSE	Sterilized	CF	0.76	2.00	3.18	3.1	1.30	1.20	1.57	1.55	ND
		3-CF	ND	ND	ND	ND	ND	ND	0.05	ND	ND
	Unsterilized	CF	0.94	2.38	1.52	2.89	1.34	5.86	2.54	3.41	ND
		3-CF	ND	ND	ND	ND	ND	0.17	0.07	0.06	ND

QRE denotes Quaternary red earth; TSE denotes Tidial sand earth; FAS denotes Fluvoaquic soil; CF denotes Carbofuran; 3-CF denotes 3-hydroxycarbofuran; ND denotes blow detection limit

Table 5 Linear equations and adsorption parameters of benfuracarb in soils.

Soils	Organic carbon (g kg^{-1})	Linear equations	r	K_f	K_{oc}
Quaternary red earth	15.7	lg (C_S) =0.8785lgC+0.4609	0.9328	2.896	184
Fluvoaquic soil	8.3	lg (C_S) =0.9826lgC+0.3021	0.9694	2.010	242
Tidial sand earth	23.3	lg (C_S) =0.7666lgC+0.5951	0.9372	3.936	169

Table 6 Mobility of chemicals and their organic carbon/partition coefficient (K_{oc})

Classification grades	K_{oc}	Mobility	Classification grades	K_{oc}	Mobility
1	0-50	Very strong	4	500-2000	Weak
2	50-150	Strong	5	2000-5000	Very weak
3	150-500	Medium	6	>5000	No mobile

adsorption equilibrium curves of a pesticide in the water-soil system may be described by the Freundlich equation $C_S=K_f{\cdot}C_a$ (Fushiwaki and Urano 2001), where a is a constant and K_f the adsorption constant. To determine the constants we used the logarithmic form of the Freundlich equation, $\lg (C_S) = a \lg C+\lg (K_f)$. The linear equations and adsorption parameters of benfuracarb in soils are listed in table 5. The correlation coefficients r of lgC vs lg (C_S) were above 0.93. K_f increased in the order Fluvoaquic soil < Quaternary red earth < Tidal sand earth. In agreement with this, benfuracarb was found to migrate most easily in Fluvoaquic soil. However, the migration was more rapid in Tidal sand earth thanin Quaternary red earth in contrast to what might have been expected from the K_f values. According to the data in table 5, absorption isotherm curves of benfuracarb in the three soil types can be expressed as: Changsha Quaternary red earth: $C_S=2.896C^{0.879}$; Changsha Fluvoaquic soil: $C_S=2.01C^{0.983}$; Xiangying Tidal sand earth: $C_S=3.936\ C^{0.767}$. The adsorption constant K_f increases with an increase in the organic carbon content in soils showing that organic carbon content is an important factor affecting adsorption. Many studies have shown that a constant less dependent on soil type is obtained by defining $K_{oc} = K_f$/(fraction of organic carbon in soil) (Irace-Guigand and Aaron 2003; Han 1993). K_{oc} usually expresses the hydrophobicity of the pesticide and may be used to estimate migration and predict behavior of an organic pesticide in the environment. McCall (1980) classified mobility of pesticides according to the K_{oc} value as shown in Table 6. According to this classification benfuracarb shows medium mobility.

The results of adsorption studies which showed medium mobility of benfuracarb in the studied soils indicated that rational use of benfuracarb entails little danger of ground-water contamination. The fast degradation of benfuracarb in soils (half-life 7.5–10 days in our experiments) further reduces the danger of environmental damage. However, because there are differences between laboratory studies and field application (i. e. the field soils may be less homogeneous and the field environmental conditions more complicated), it cannot be excluded that contamination of groundwater may occur. Considering the abundant current use of the pesticides in the area furthermore, regular monitoring is needed to evolve a strategy to manage the environmental hazards due to the pesticide and its degradation products. More field data need to be obtained especially while benfuracarb is applied in fields with high groundwater level or light texture soil or in areas with higher precipitation.

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