ELSEVIER

Journal of Chromatography A, 977 (2002) 17–25

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Fast and precise determination of phenthoate and its enantiomeric ratio in soil by the matrix solid-phase dispersion method and liquid chromatography

Zhao-Yang Li, Zhi-Chao Zhang*, Qi-Lin Zhou, Ru-Yu Gao, Qin-Sun Wang

Institute of Elemento-Organic Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

Received 12 June 2002; received in revised form 21 August 2002; accepted 21 August 2002

Abstract

A fast and precise method was developed for the determination of phenthoate and its enantiomeric ratio (ER) in three soil samples. A recently developed sample pretreatment technology—matrix solid-phase dispersion (MSPD) was used to extract phenthoate simply and effectively. MSPD conditions, i.e. solid-phase Florisil amount, water content of Florisil–soil mixture, the constituent and volume of the eluting solvent, were optimized stepwise. The MSPD extract was directly used for quantitative determination of phenthoate by silica-based high-performance liquid chromatography (HPLC) with UV detection. The recoveries of phenthoate from three different types of soils fortified at three levels of 0.1, 1, 10 μg/g ranged from 75 to 94% with RSDs of 1.5–6.5%. On this basis, phenthoate was further isolated from the remainder of MSPD extract by silica-based HPLC and then ER determined on HPLC with cellulose tris-3, 5-dimethylphenylcarbamate as chiral stationary phase. The ERs determined in the soils spiked with racemic or enantiomer-enriched phenthoate agreed sufficiently well with those in the corresponding standard solutions. Finally, the proposed method was successfully applied to the study of enantioselective degradation of phenthoate in the three soils under laboratory conditions. High enantioselectivity was observed in the two alkaline soils with (+)-enantiomer degrading faster than the (−)-enantiomer, while there was little to no enantioselectivity in the acidic soil. The methodology can be used to study the enantioselective environmental behavior of chiral pollutants.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Matrix solid-phase dispersion; Enantiomeric ratio; Phenthoate; Pesticides

1. Introduction

In the case of chiral pollutants, environmental studies have historically neglected to determine the adverse effects associated with particular enantiomers, and which enantiomer may persist in various environmental media [1,2]. The racemic signature is thought to remain unchanged by physical–chemical removal mechanisms such as hydrolysis and photolysis reactions. However, the mechanisms of microbial degradation and biological metabolism may be enantioselective and thus result in different effects and fate in environmental media [3,4]. Analysis of chiral compounds in various biological compart-

*Corresponding author. Tel.: +86-22-2350-7973; fax: +86-22-2350-7980.

E-mail address: zczhang@nankai.edu.cn (Z.-C. Zhang).

0021-9673/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0021-9673(02)01342-0

ments may provide valuable insight into how chemicals are accumulated, degraded, and translocated within ecological chains [5,6].

Phenthoate [*O*,*O*-dimethyl *S*-(α-(carboethoxy)-benzyl)phosphorodithioate] is a widely-used agricultural insecticide for the control of insects and pests on citrus, corn and vegetables. Due to the presence of an asymmetric carbon in the chemical structure (Fig. 1), phenthoate is chiral and the two enantiomers exhibit different insecticidal activity [7]. Thus information on the persistence of individual enantiomers in a field situation is very important when assessing the possibility of developing a single enantiomer as a commercial insecticide.

It is evident that the ER determination method of chiral pollutants is the crucial procedure in enantioselective studies. In fact, it has already become the bottle neck of this subject. In the present study, a method of enantioselective determination of phenthoate in soils was effectively developed. The method, combining the matrix solid-phase dispersion technique (MSPD) with HPLC clean-up procedure, can be exploited for study of the enantioselective environmental behavior of chiral pollutants.

MSPD is a relatively developed extraction–clean-up technique characterised by simplicity and sensitivity [8,9]. In MSPD, extraction and clean-up are carried out in a single step, which can avoid the general drawbacks of other traditional methods, such as the use of a large amount of solvent and glassware, the laborious extraction procedure and the occurrence of troublesome emulsions. MSPD has been reported to extract pesticides, drugs, and vitamins from vegetables [10,11], milk [12], and biological tissues [13], etc. Several review papers have appeared recently [14,15], but to our knowledge, no

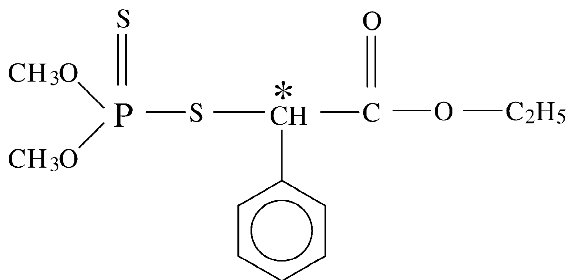

Fig. 1. Chemical structure of phenthoate.

studies are available in the literature on the extraction of samples from soil matrices using this method. In the present study, phenthoate was spiked in three different soils and was then extracted by MSPD technique. Optimization of different parameters, such as the amount of solid support, the polarity and volume of eluent was carried out. On the basis of MSPD, pure phenthoate sample was furthermore fractionated on an HPLC silica gel column. The sample was then resolved on a chiral HPLC column to determine the enantiomeric ratio (ER) values almost without any interference. The above method proved to be simple, rapid and accurate by the evaluation of fortified soil samples. Finally, the established method was used to study the enantioselective degradation of phenthoate in three different soils under laboratory conditions.

The aims of the present study were: (1) to develop an MSPD method for extracting phenthoate from different soil matrices, (2) to establish a rapid and precise method to determine phenthoate and its ER values in soil samples, and (3) to study the enantioselective degradation of phenthoate in different soils.

2. Experimental

2.1. Chemicals and materials

Racemic phenthoate (98%) was obtained from Bayer (Monheim, Germany). Enantiopure phenthoate enantiomers (99%) were prepared via enantiomeric resolution of the racemic phenthoate by chiral HPLC under the same chromatographic conditions described in Section 2.6. The first eluted enantiomer was assigned to be the dextrorotatory enantiomer ((+)-phenthoate), and the second the levorotatory enantiomer ((−)-phenthoate), respectively, based on chiroptical measurements of the single enantiomers using a polarimeter supplied by Shanghai POI Factory (Shanghai, China). Absolute configurations of the two enantiomers of phenthoate were not determined in this study.

Methanol, *n*-hexane, ethyl acetate 2-propanol were all analytical grade, redistilled and filtered through a 0.45-μm filter before use. Anhydrous sodium sulfate was analytical grade, heated at 400 °C before use.

Florisil (60–100 mesh) was bought from Fluka (USA), activated at 650 °C for 3 h before use. A stock solution (1000 μg/ml) of phenthoate was prepared in methanol and preserved at 4 °C. Standard working solutions of various concentrations were prepared daily by appropriate dilution of aliquots of the stock solution.

The two alkaline soils (soil 1 and soil 2) were collected from different sites in Tianjin, China and the acidic soil (soil 3) was collected from Hubei Province, China. The physical and chemical characteristics of the three soils are summarized in Table 1. Prior to treatment with phenthoate, the soils were carefully air-dried and then sieved through a 20-mesh sieve.

2.2. Chromatography

A liquid chromatograph equipped with a Varian model 2010 pump (Varian, Northeast Florham Park, NJ, USA), a Rheodyne model 7125 injector with a 20-μl loop, a Varian model 2050 UV detector (detection wavelength was set at 230 nm) and an HP 3394 integrator (Hewlett-Packard, Palo Alto, CA, USA) were used.

2.3. MSPD extraction of phenthoate from soils

For the preparation of fortified soil sample, a volume of between 50 and 100 μl of the standard working solutions was added to 4.00 g of dry soil. It was then mixed thoroughly. Soil samples spiked with phenthoate at three concentration levels of 10, 1 and 0.1 μg/g were prepared, respectively.

Then 4.00 g of fortified soil sample was placed into a mortar (50-ml capacity) and 3 ml (3 g) of water, 6 g of Florisil were added. The soil–Florisil–water mixture was gently blended for 10 min using a glass pestle to obtain a homogeneous mixture. This mixture was then introduced into a 30×1.5 cm I.D. glass chromatographic column containing a coarse porosity fritted glass disc, and 2 cm of anhydrous sodium sulfate. Finally, a 1.0-cm layer of anhydrous sodium sulfate was placed at the top of the column. The column was lightly tapped to remove air pockets. A 30-ml volume of *n*-hexane/ethyl acetate (7:1, v/v) was added to the column and the sample was allowed to elute dropwise by gravity. The initial 15 ml of eluted extract was collected into a graduated tube. The eluent was blown to dryness in a water bath of 50 °C under a mild nitrogen stream, and was re-dissolved in a 0.5-ml volume of HPLC mobile phase described in Section 2.4. The sample solution was subjected to quantitative HPLC analysis of phenthoate. Recovery experiments were carried out in quadruplicate at three fortification levels: 10, 1 and 0.1 μg/g. The extraction procedure described above is based on the data obtained from different optimization assays (see Section 3.1).

For incubation samples (water content 23%), 5.20 g of soil (corresponding to 4.00 g dry mass) was transferred into the mortar and water content was adjusted to 3 g by adding 1.8 ml of water, then 6 g of Florisil was added.

Table 1
The properties of the three soils used in the study

Soil	Organic matter (%)	pH	Soil type		
			Sand (%)	Silt (%)	Clay (%)
Soil 1	0.717	8.2	34	40	26
Soil 2	2.158	8.1	2	52	46
Soil 3	1.367	5.4	26	36	38

2.4. Quantitative determination of phenthoate by HPLC

The analytical column was a silica gel column (Dalian Elite Co. Ltd., China), 250×4.6 mm I.D., 5-μm particle size with a guard cartridge of the same phase (30×4.6 mm I.D.). The mobile phase, operated at 1 ml/min, consisted of an isocratic mixture of *n*-hexane/2-propanol (100:0.1, v/v). Phenthoate was quantified using the external standard method.

2.5. Isolation of phenthoate from MSPD extract

Before the determination of the ERs, the remainder of the sample solution after quantitative analysis was further cleaned by HPLC as follows. The sample solution was blown slightly to dryness under a stream of nitrogen, and was re-dissolved in a little more than 20-μl mobile phase described in Section 2.4. The sample solution was used to isolate the phenthoate by HPLC under the same chromatograph-

ic conditions used in quantitative analysis as described in Section 2.4. Collection of the fraction of column eluent was conducted after a 5-s delay since the appearance of UV response of the phenthoate and the collection lasted for 50 s until phenthoate was eluted completely. The corresponding fraction was also blown to dryness under a gentle flow of nitrogen. According to the amount of phenthoate, an appropriate volume of mobile phase described in Section 2.6 was added to dissolve it, and the solution was ready for the determination of ER of phenthoate using chiral HPLC.

2.6. Determination of ER value of phenthoate by chiral HPLC

The chiral HPLC was carried out with a Chiralcel OD column (Daicel Chemical Industries, Japan), which contains cellulose tris-3,5-dimethylphenylcarbamate as chiral stationary phase, 250×4.6 mm I.D., 10-μm particle size with a guard cartridge of the same phase (30×4.6 mm I.D.). The mobile phase, operated at 1 ml/min, consisted of an isocratic mixture of *n*-hexane/2-propanol (100:0.8, v/v).

The enantiomeric ratio (ER) was defined as ER= A_1/A_2, where A_1 and A_2 are the peak areas of the first eluted (+)- and second eluted (−)-enantiomers, respectively. Replicate injections (n=2–3) were made for the measurements.

2.7. Treatment and incubation of soils

The procedures for the treatment and incubation of the three soils were the same. Prior to treatment with phenthoate, the soil was adjusted to a moisture content of 23% and put aside in the dark at room temperature. After a 7-day activation period, 30 g of the soil (corresponding to 23 g of dry mass) was weighed into a 50-ml conical flask. Then, 80 μl of stock solution of racemic phenthoate was applied dropwise to give an application rate equivalent to 2.67 μg/g. After thorough mixing, the flask was sealed with cotton-wool plugs and stored at 20 °C in the dark. Periodically, 5.20 g of soil (equivalent to 4.00 g dry mass) was removed for analysis. Duplicate samples were taken immediately after fortification and mixing, and single samples periodically thereafter.

3. Results and discussion

3.1. MSPD extraction

One of the outstanding advantages of MSPD is that extraction and clean-up are carried out in a simple single step. The type and amount of solid phase, the content of water in solid phase-sample mixture, and the type and volume of eluting solvent are the key factors, which should be carefully selected to achieve the highest recovery for the analyte(s) of interest while eliminating most of the interfering matrix components [13–15].

The MSPD extraction is very simple, rapid and requires only small sample sizes and solvent volumes [14,15], and 4.00 g soil sub-samples were used in this paper. Florisil, which is the most frequently used adsorbent in our laboratory for column chromatographic purification in pesticide residue analysis, was used as solid phase. In this method, Florisil retains some of its adsorption activity and plays an important role in the exclusion of impurities. The aim of adding water is to deactivate partially Florisil so that phenthoate can be eluted easily. With the mechanical shearing force of blending, the sample matrix is unfolded and dispersed over a large area on Florisil. Polar matrix materials are associated with the Florisil surface, while the hydrophobic phenthoate remains weakly bound on the sorbent surface. According to the polarity of phenthoate, a proper eluting solvent is then used to extract phenthoate effectively with the least amount of interfering materials. In this study, the optimization of MSPD conditions, i.e. the amounts of Florisil and water content, the constituent and volume of the eluting solvent, was optimized stepwise.

First, a screening experiment was carried out to determine the proper amounts of Florisil and water. Different amounts of Florisil and water were added into 4.00 g soils with the fortification level of 1 μg/g, to check up the MSPD extraction effect. The results reported in Table 2 show that the highest recoveries were obtained under anyone of the three conditions (Florisil/water): 8 g/4 ml, 6 g/5 ml and

Table 2
Mean recoveries (%)±RSDs (%) (n=3) of phenthoate by MSPD extraction from 4.00 g of soil fortified at 1 μg/g using different amounts of Florisil and water

Soil	Florisil (g)+water (ml)						
	4+1	4+2	6+1	6+3	6+5	8+2	8+4
Soil 1	81.0±4.1	85.1±1.2	65.3±6.2	93.6±2.7	92.2±4.4	84.6±2.9	94.0±3.3
Soil 2	79.4±1.6	74.3±2.3	53.7±3.8	82.7±6.2	84.5±3.7	78.6±4.6	82.2±2.7
Soil 3	70.2±2.7	72.0±2.5	61.4±1.8	79.3±4.1	78.9±4.5	73.4±3.3	77.7±4.1

Phenthoate was collected in every 3-ml fraction during elution using n-hexane–ethyl acetate (7:1, v/v) as eluting solvent, and then the fractions containing phenthoate were combined for quantitative HPLC analysis (Section 2.4).

6 g/3 ml. Further considering the clean-up effect, which was reflected in the chromatograms of quantitative HPLC, and the cost of Florisil used per run, the most appropriate amounts of Florisil and water were finally determined to be 6 g and 3 ml, respectively, for 4.00 g of dry soil sample. In addition, 0.5 g of Florisil was once packed below the Florisil–soil blended mixture in the MSPD column, but no obvious improvement was observed in the elimination of interference. So the sequential clean-up was omitted in later study.

Owing to the low to moderate polarity of phenthoate, we selected n-hexane to be the eluent with ethyl acetate adjusting the polarity. The effects of eluent and its volume were studied by collecting phenthoate in every 3-ml fractions during elution using a sample fortified at 1 μg/g. Recoveries of phenthoate from spiked soil 2 using as eluting solvent a mixture of n-hexane and ethyl acetate with different ratio, respectively, are illustrated in Fig. 2. When the volume ratio of n-hexane to ethyl acetate is <7:1, as the polarity of the eluting solvent was increased, the recovery increased slowly with more interfering compounds. This was evidenced by the color of the extraction solutions observed after solvent concentration and by the impurity peaks in the HPLC chromatograms. When the volume ratio of n-hexane to ethyl acetate is >7:1, the extracts became clear, but recoveries were quite unsatisfactory. Therefore a mixture of n-hexane–ethyl acetate (7:1, v/v) was finally selected to be the eluting solvent. The cumulative recoveries on eluting are shown in Fig. 3. The required volume was only 15 ml, which is much less than in traditional methods.

In conclusion, the MSPD conditions for extraction of phenthoate from 4 g (dry mass) soil sample were proposed to be 6 g of Florisil, 3 ml of water, with collection of the initial 15-ml fraction using n-hexane–ethyl acetate (7:1, v/v) mixture as eluting solvent. Representative chromatograms of extraction of non-spiked and spiked soil samples under the MSPD conditions mentioned above are shown in Fig. 4. The nature of the interfering peaks has not been identified. The peaks in the chromatograms of three non-spiked soils appear at different retention times with different heights, indicating the different composition and quantity of organic matters in the three soils.

The MSPD extraction requires only small sample

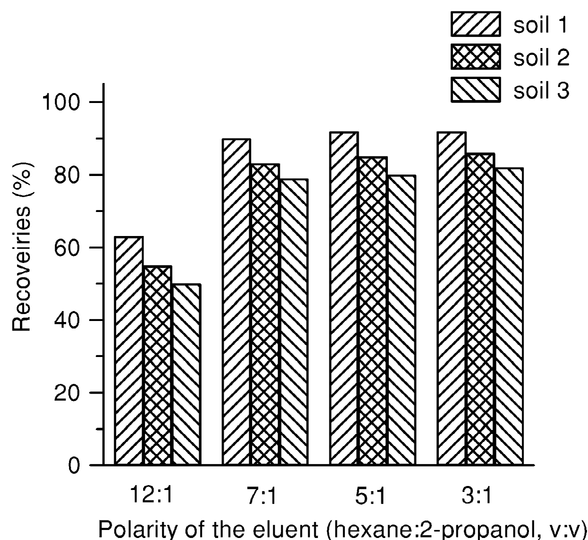

Fig. 2. Effect of different eluent polarity on recoveries of phenthoate from 4.00 g of soil 2 spiked at 1 μg/g. In the case that the volume ratio of n-hexane to ethyl-acetate is 12:1, the initial six fractions of 3 ml of eluent were combined for the recovery test; and in the other cases, the initial five fractions of 3 ml of eluent were combined.

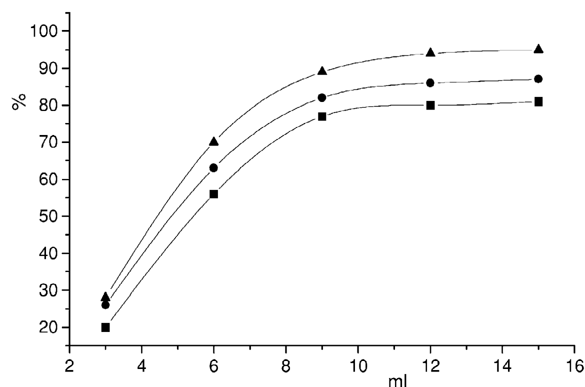

Fig. 3. The cumulative recoveries of phenthoate from 4.00 g of soil spiked at 1 μg/g as a function of eluent volume. Eluting solvent: *n*-hexane–ethyl acetate (7:1, v/v); ▲, soil 1; ●, soil 2; ■, soil 3.

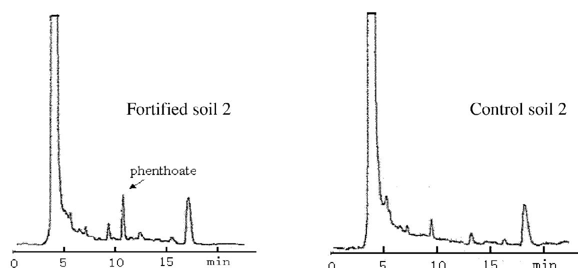

Fig. 4. Representative chromatograms of the MSPD extraction from 4.00 g of soil sample fortified with phenthoate at 1 μg/g and non-fortified soil sample. The result for soil 2 is shown, which was typical. For the experimental conditions, see Experimental section.

sizes, and sub-samples of homogenized sample are often used for MSPD analysis to improve the homogeneity [14,15]. A 4-g dry soil sub-sample was used for method development in this study. For other amounts of soil sample, it can be deduced that the required amounts of Florisil and water could be determined proportionally to the dry mass of the soil sample, on the basis of the proposed MSPD conditions for 4-g dry soil; however, the volume of the collected elution fraction must be determined via cumulative recovery test. It should be noted that for soil samples with a certain water content, the water contained in the sample itself should be considered. In the case of incubation samples (water content 23%) in this study, 5.20 g of soil sample corresponded to 4.00 g dry soil weight and 1.20 g (ml) water, thus the Florisil amount needed was 6 g and the water added was calculated to be 1.8 ml (3 ml−1.2 ml) to adjust the total water amount to be 3 g (ml).

3.2. Recovery study results

Table 3 summarizes the average recoveries from the three soils at three fortification levels of 0.1, 1.0 and 10 μg/g obtained under the proposed experimental conditions. Average recoveries were all above 75% with RSDs of 1.5–6.5% (n=4). On the basis of three times the noise level, the limit of detection (LOD) for phenthoate in soil was calculated to be 0.02 μg per g dry soil. So the established method of MSPD extraction followed by HPLC/UV can be used for rapid and precise analysis of phenthoate residue in soils.

3.3. Determination of ERs of phenthoate in soils

Despite the great success of enantiomeric separation of large amounts of pesticides [16–18], one should pay much attention to the accuracy of the determined ERs of chiral pollutants in environmental samples. Owing to the low levels of pollutants in

Table 3
Mean recoveries (%) and RSDs (%) (n=4) of phenthoate in 4.00 g of three different soils spiked at three levels obtained using the MSPD method followed by high-performance liquid chromatography under the proposed experimental conditions

Soil	10 μg/g		1 μg/g		0.1 μg/g	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Soil 1	92.5	4.8	93.6	2.7	90.7	1.5
Soil 2	83.1	1.9	82.7	4.2	75.9	4.3
Soil 3	82.8	3.2	79.3	4.1	80.8	6.5

For the proposed experimental conditions, see Sections 2.3 and 2.4.

environmental samples and the complexity of environmental samples, potential errors may be caused by various reasons [19,20], such as peak distortions by inadequate instrumentation, co-elution of impurities, inversion of configuration during chiral separation, etc. Every enantiomer separation adds one more peak to the number to be resolved in samples and the proper determination of ERs is a difficult task, which requires improved techniques. We once tried to inject the MSPD extracts of spiked soil directly into the chiral HPLC without further clean-up. But variation of the ERs of phenthoate determined by successive injections was intolerantly great, and the baseline was very unstable. The phenomenon got worse and worse as injection number increased. These were caused by: (1) coelution of impurities and phenthoate and, (2) the interference of the strongly retained compounds and the large amount of compounds corresponding to the first tailed large peak in quantitative HPLC chromatograms (Fig. 4). In view of the above mentioned facts, phenthoate was then isolated from the remainder of the MSPD extracts by silica-based HPLC (see Section 2.5). The environment involved in the isolation procedure was achiral, therefore, in principle the procedure did not change the ER of phenthoate.

The sample remaining after quantitative HPLC was treated and analyzed according to the above-proposed method (see Sections 2.5 and 2.6). The results are shown in Table 4. The determined ERs of phenthoate in soils spiked with racemic phenthoate at three levels of 10, 1, 0.1 μg/g were 1.02–0.99 with RSDs<1.4%, which is in very good agreement with the ER (1.01±1.2% (n=6)) of standard working solution (16 μg/ml) of phenthoate. It is obvious that the determined ERs of phenthoate both in spiked soils and in standard working solution agree sufficiently well with the theoretical value of 1 within the error limits of this method. To further assess the ER determination method, the soils were spiked with non-racemic phenthoate ((+)/(−)=0.52 and (+)/(−)=2.1) at the level of 0.1 μg of total phenthoate enantiomers per g. Their determined ERs are also in very good agreement with those of the corresponding standard solutions. The results are also shown in Table 4.

On the basis of the assessment study, it is concluded that the proposed method could precisely determine the ER values of phenthoate in the three soils.

3.4. Enantioselective degradation of phenthoate in three soils

The established method for determination of phenthoate and its ER in soil was applied to study the enantioselective degradation of phenthoate in three different types of soils. The natural water content of the three soils collected were between 20 and 25%, and consequently 23% water content was adopted in the incubation experiment to agree with the nature of the three soils. The concentrations and ERs of phenthoate in the three soils at 0, 1, and 3 days of incubation time are listed in Table 5. Phenthoate degraded readily in the two alkaline soils (soil 1 and

Table 4
Enantiomeric ratio values±RSDs (n=4) of phenthoate in three soils spiked with racemic/non-racemic phenthoate at different levels determined under the proposed experimental conditions

Standard soil	Spiked with racemic phenthoate (+)/(−)=1.01±1.1% [a]			Spiked with non-racemic phenthoate	
				(+)/(−)=0.52±0.6% [b]	(+)/(−)=2.10±1.2% [b]
	10 μg/g	1 μg/g	0.1 μg/g	0.1 μg/g	0.1 μg/g
Soil 1	1.02±1.7%	1.01±1.6%	1.00±1.6%	0.52±1.1%	2.10±2.0%
Soil 2	1.00±1.7%	0.99±1.2%	1.01±1.3%	0.52±1.4%	2.09±1.5%
Soil 3	1.00±1.7%	1.00±0.9%	1.01±0.7%	0.52±2.0%	2.10±1.9%

For the proposed experimental conditions, see Sections 2.3, 2.5 and 2.6.

[a] Enantiomeric ratio value±RSD (n=6) of racemic phenthoate standard solution (the sum of the concentrations of the two enantiomers, 16 μg/ml).

[b] Enantiomeric ratio value±RSD (n=6) of enantiomer-enriched phenthoate standard solution (the sum of the concentrations of the two enantiomers, 1.6 μg/ml).

Table 5
Concentrations (μg/g) and ER values of phenthoate in three soils at various incubation times

		Incubation time		
		0 day	1 day	3 days
Soil 1	Concentration	2.50 (100)[a]	0.88 (35.2)	0.35 (14.0)
	ER	1.01	0.82	0.70
Soil 2	Concentration	2.20 (100)	0.98 (44.5)	0.40 (18.2)
	ER	1.01	0.86	0.78
Soil 3	Concentration	2.16 (100)	1.88 (87.1)	1.36 (65.0)
	ER	1.01	1.00	0.99

For analysis method and the experimental conditions for incubation of phenthoate in soil, see Sections 2.3–2.7.
[a] Values in parentheses expressed as percent of total concentration at zero time.

soil 2) to levels <18% of the initial concentration after 3 days of incubation. The ER values changed from initially 1.0 to 0.68 for soil 1, and to 0.75 for soil 2. Fig. 5 depicts the corresponding enantioselective analysis in soil 1.

However, in the acidic soil 3, phenthoate degraded much more slowly than the two alkaline soils and the ER values were approximately 1.0 at all incubation times, suggesting there may be little to no enantioselective activity present in this type of soil. The difference in enantioselectivity of degradation is probably caused by the different groups of related microbial genotypes existing in the three soils. This difference is in accordance with previous reports [21–23] concerning different ER values of the same chiral compounds accumulating and metabolizing in different environmental matrices.

A detailed study of enantioselective degradation of phenthoate in these three soils will be reported later.

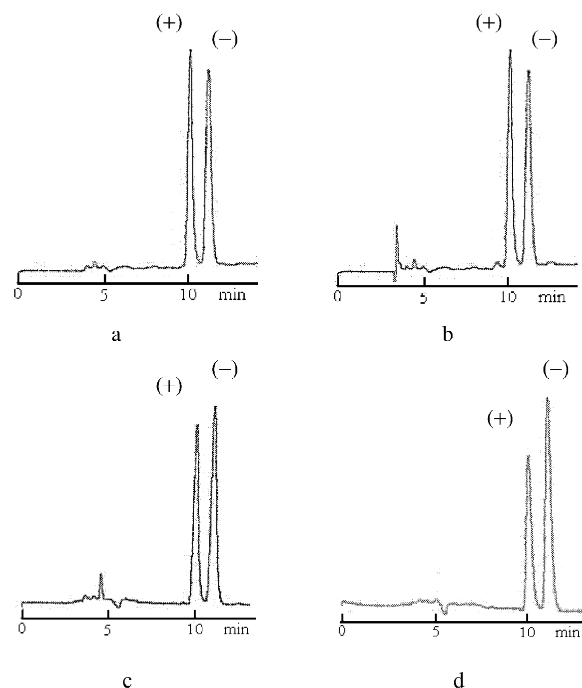

Fig. 5. Enantiomeric separation of phenthoate in standard racemic solution and extracted from soil 1. (a) Phenthoate standard; (b) after 0-day incubation; (c) after 1-day incubation; (d) after 3-day incubation. For the experimental conditions, see Experimental section.

4. Conclusions

The MSPD technique was successfully applied to the extraction of phenthoate from three soils. Compared with classical methods, the MSPD procedure is simple, less labor intensive and does not require preparation and maintenance of equipment. Troublesome emulsions can also be avoided effectively. Furthermore, the method of enantiomeric ratio determination of phenthoate in soils was successfully developed by HPLC silica gel column clean-up of MSPD extract followed by chiral HPLC analysis. This method was successfully applied to the study of enantioselective degradation of phenthoate in three soils. The evaluation of the above method showed that it was simple, rapid and precise. The methodology can be exploited for study of the enantioselective environmental behavior of chiral pollutants in environmental media.

Acknowledgements

Financial support provided by the National Natural Science Foundation of China (No. 29907002) and the Education Ministry of China is gratefully acknowledged.

References

[1] D.W. Armstrong, G.L. Reid, M.L. Hilton, C.D. Chang, Environ. Pollut. 79 (1993) 51.
[2] D.L. Lewis, A.W. Garrison, K.E. Wommack, A. Whittemore, P. Steudler, J. Melillo, Nature 401 (1999) 898.
[3] C. Zipper, M.J.F. Suter, S.B. Haderlein, M. Gruhl, H.E. Kohler, Environ. Sci. Technol. 32 (1998) 2070.
[4] H.R. Buser, M.D. Müller, Environ. Sci. Technol. 29 (1995) 664.
[5] J.J. Ridai, T.F. Bidleman, B.R. Kerman, M.E. Fox, W.M.J. Strachan, Environ. Sci. Technol. 31 (1997) 1940.
[6] K. Wiberg, R.J. Letcher, C.D. Sandau, R.J. Norstrom, M. Tysklind, T.F. Bidleman, Environ. Sci. Technol. 34 (2000) 2668.
[7] A. Miyazaki, J. Pestic. Sci. 22 (1997) 136.
[8] S.A. Barker, A.R. Long, C.R. Short, J. Chromatogr. 475 (1989) 353.
[9] L. Kadenczki, Z. Arpad, I. Gardi, A. Ambrus, L. Gyorfi, G. Reese, W. Ebing, J. AOAC Int. 75 (1992) 53.
[10] E. Viana, J.C. Moltó, G. Font, J. Chromatogr. A 754 (1996) 437.
[11] M. Fernández, Y. Picó, J. Mañes, J. Chromatogr. A 871 (2000) 43.
[12] A.R. Long, L.C. Hsieh, M.S. Malbrough, C.R. Short, S.A. Barker, J. Assoc. Off. Anal. Chem. 73 (1990) 379.
[13] M. Zhao, F. van der Wielen, P. de Voogt, J. Chromatogr. A 837 (1999) 129.
[14] S.A. Barker, J. Chromatogr. A 885 (2000) 115.
[15] S.A. Barker, J. Chromatogr. A 880 (2000) 63.
[16] M. Dondi, M. Flieger, J. Olsovska, C.M. Polcaro, M. Sinibaldi, J. Chromatogr. A 859 (1999) 133.
[17] N. Ôi, H. Kitahara, R. Kira, J. Chromatogr. 535 (1990) 213.
[18] R.Y. Gao, G.S. Yang, H.Z. Yang, Z.Y. Chen, Q.S. Wang, Chin. J. Chem. 7 (1999) 92.
[19] W. Vetter, V. Schurig, J. Chromatogr. A 774 (1997) 143.
[20] V. Schurig, J. Chromatogr. 441 (1988) 135.
[21] R.L. Falconer, T.F. Bidleman, S.Y. Szeto, J. Agric. Food Chem. 45 (1997) 1946.
[22] C.S. Wong, A.W. Garrison, W.T. Foreman, Environ. Sci. Technol. 35 (2001) 33.
[23] H.R. Buser, M.D. Müller, Anal. Chem. 64 (1992) 3168.