Journal of Hazardous Materials 179 (2010) 676–683

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Tenax TA extraction to assess the bioavailability of DDTs in cotton field soils

Xinglun Yang, Fang Wang, Chenggang Gu, Xin Jiang*

State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China

ARTICLE INFO

Article history:
Received 14 August 2009
Received in revised form 10 March 2010
Accepted 13 March 2010
Available online 19 March 2010

Keywords:
Bioavailability
Tenax extraction
DDT
Rapid-desorbing fraction

ABSTRACT

The rapid-desorbing fraction plays an important role in the bioavailability of organic pollutants in soil. In the present study, DDT's desorption from the cotton field soils was investigated by Tenax extraction. The results of the Tenax consecutive extraction (400 h) indicated that the rate constants were in the order of 10^{-1}, 10^{-2}, and 10^{-4} h^{-1} for the rapid, slow and very-slow desorption, respectively. The rapid-desorbing fraction was about 0.3 times the total soil DDTs, and about 2 times the Tenax 6 h-extracted fraction (single-point extraction). The rapid-desorbing fraction correlated well with the 6 h-extracted fraction ($p < 0.05$), implying the feasibility of measuring the rapid-desorbing fraction with Tenax 6 h-extration. The strong correlation with the carrot accumulation suggested that Tenax 6 h-extrated fraction could serve as a good predictor of DDT's bioavailability to carrot roots. Risk assessment demonstrated that when based on the rapid-desorbing concentration and 6 h-extracted concentration, about 60.7% and 17.9% of the soil samples were moderately polluted, however, up to 78.5% were moderately polluted when based on the total soil DDTs concentration. The risk assessment might be more representative when based on Tenax extraction because of the strong correlation with the carrot accumulation. Our results provided implications for site risk assessment and cleanup strategies.

1. Introduction

Up to now, the risk assessment of the sites contaminated by persistent organic pollutants (POPs) are mostly conducted based on the total soil concentration [1], which often results in overestimation of the risk because organisms respond only to the bioavailable fraction [2–4]. To reduce the uncertainty in risk assessment, the integration of bioavailability into the risk assessment frameworks has been recognized gradually in recent years [1,2,5].

The bioavailability of contaminants is dependent on the physical, chemical, and biological interaction associated with soil. The mechanistic concept of bioavailability involves binding, release, transport, uptake through a membrane, and incorporation into a living system [1,6]. Among those processes, of particular importance is desorption because in most cases, desorption is a rate-limited factor for bioavailability [6–8]. Conceptually, desorption of contaminants from soil particles proceeds in three phases: an initial, rapid-desorbing phase followed by the slow and then very-slow-desorbing phase [9]. Good correlations between bioavailability and the rapid-desorbing fraction were found in previous studies, in which organisms such as earthworms, Oligochaetes and microbe were investigated [2,10–13]. Therefore, the rapid-desorbing fraction was regarded as a good predictor for the bioavailability of POPs in soil [5,6,8,10,12,14–19].

With the attempt to determine the rapid-desorbing fraction which highly correlated to the bioavailability of POPs in soil, a wide variety of techniques have been proposed in recent years [20–25]. These techniques can be grouped into two complementary categories: biological assays and chemical techniques [1]. The former are the classic methods for the bioavailability assessment, but they are typically slow, expensive, and less precise [2]; the latter are thus considered as the applicable surrogates. Chemical techniques can replace biological assays if a strong correlation has been established between the defined fraction and the organism response.

Among the chemical techniques, Tenax TA (a polymer based on 2,6-diphenyl-p-phenylene oxide) extraction is one of the most promising techniques to measure the rapid-desorbing fraction [20,25,26]. Because of advantages such as large capacity, floating on the water and being separated easily, Tenax TA can be used as the sink for organic contaminants desorbing from geosorbents [20]. The consecutive desorption with Tenax (e.g., more than 200 h desorption) facilitates the study of the desorption kinetics of POPs, and the rapid-desorbing, slow and very-slow-desorbing fractions can be predicted with models such as the triphasic model [25,26]. However, it takes a long time for the consecutive desorption to predict the rapid-desorbing fraction, thus efforts have been made to overcome this shortcoming, and the single-point extraction (the Tenax beads were added only once and removed after extraction for several hours, e.g., 6 h) has been developed [5,10,18,27–29]. Cor-

* Corresponding author. Tel.: +86 25 86881195; fax: +86 25 86881195.
E-mail address: jiangxin@issas.ac.cn (X. Jiang).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.03.055

nelissen et al. [5] found Tenax 6 h-extracted fraction was about 0.5 times the rapid-desorbing fraction, later, more evidences also validated that both rapid-desorbing fraction and single-point extracted fraction were good predictors for the bioavailability of organic pollutants in sediment or soil [8,10,12,14–16,18,19]. In recent years, Tenax extraction was widely applied to assess the bioavailability of POPs in soil even though it had not been standardized by such international organizations as International Standardization Organization (ISO) [2,11,18,27,30,31]. For example, Oen et al. [32] used Tenax extraction to investigate the effect of quality and quantity of organic matter on the PAHs desorption from sediments; Li et al. [33] used Tenax extraction to guide the in situ bioremediation strategies for contaminated soil.

China has been a major producer and consumer of DDT since the 1950s until its production ban in 1983, accounting for nearly 20% of the global production [34]. After 1983, DDT production still continues primarily due to the demand of malaria control and production of dicofol. However, dicofol in Chinese market often contains high impurities of DDTs, therefore becomes an important source of DDT in China [34]. Qiu et al. [35] and Yang et al. [36] found that DDTs pollution in soil of cotton cultivation areas was serious because of the extensive application of dicofol with high impurities of DDTs for decades, and the most abundant compounds were p,p′-DDE, p,p′-DDT in cotton field soils [36]. However, little information about the actual risk was available because few studies have been done about this issue. As mentioned above, when based on the total soil concentration, the actual risk was often overestimated and could not be representative, therefore, it is necessary to study the rapid-desorbing fraction with Tenax extraction which is assumed to be a good predictor of bioavailability of POPs. The purpose of the present study is to investigate: (1) whether or not there is a strong relationship between the rapid-desorbing fraction of DDTs and bioaccumulation in cotton field soils; (2) whether or not the Tenax extraction can optimize risk assessment.

2. Materials and methods

2.1. Chemicals

Standard samples of p,p′-DDT, p,p′-DDE (purity >99.5%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Hexane (HPLC-grade) was bought from Tedia Company, USA. Petroleum ether, acetone and dichloromethane (analytical grade, Nanjing Chemical Reagent Co.) were distilled prior to use. Anhydrous sodium sulfate (Na_2SO_4) and diatomaceous earth was heated at 200 °C for 4 h. Silica gel (100 mesh) was activated at 130 °C for 2 h, added deionized water (3% of the silica gel weight) to deactivate the silica gel, homogenized and equilibrated for 6 h before use. Tenax TA (60–80 mesh) was purchased from Beijing KangLin Science & Technology Co. Ltd., China. Before use, the Tenax TA beads were rinsed with acetone and hexane and dried overnight at 75 °C.

2.2. Soil samples

Soil samples were collected from Tongzhou and Qidong, northern Jiangsu Province, China, where the cotton cultivation had a long history and a large cultivation area [36]. There were 28 soil samples collected. At each sample location, five cores were scooped with a pre-cleaned stainless steel scoop from a 100 m × 100 m plot and then mixed to provide a composite sample. Topsoil samples (from 0 to 10 cm depth) and subsoil samples (10–20 cm) were separately mixed for each sample location. The samples were stored in polyethylene bags when in the field. Once the samples were taken back into the lab, they were transferred to paper bags for air-dry and storage, then passed through 2-mm sieve and stored in glass bottles under about 4 °C until analysis or carrot cultivation. The basic physicochemical characteristics of soil samples were: pH 7.9, 2.2% organic matter, 38.2% clay, 52.6% silt and 9.2% sand.

2.3. Total soil concentration determination

With the approach of accelerated solvent extractions (ASE), the total soil DDTs extraction was performed with an ASE-200 (Dionex, USA) at a temperature of 100 °C, pressure of 1500 psi and static time of 5 min. Petroleum ether/acetone (4:1, v/v) was used as extraction solvent. To eliminate water, about 1 g of Na_2SO_4 was added into each vial of the soil extracts. Then the extract was concentrated first to 2 mL by a rotary evaporator, cleaned up with cartridges containing silica gel/Na_2SO_4, and finally eluted with 15 mL petroleum ether:dichloromethane (9:1). The elution was concentrated to 2 mL for GC analysis. To assure data quality, spike recovery samples containing known quantitation of the DDT standard was used to evaluate extraction efficiency.

2.4. Desorption determination by consecutive and single-point Tenax extraction

Tenax TA was used according to the method of Cornelissen et al. [26], briefly, 1 g of soil and 100 mL deionized water were brought into a 150 mL glass separatory funnel equipped with a Teflon stopper. Mercury chloride (1 mg) was added to prevent microbial degradation. Tenax TA beads (0.2 g) were then added to the funnels and shaken end-over-end on a shaker for certain time. Samples with total soil DDTs concentration higher than 50 ng g^{-1} were selected for single-point extraction (6 h extraction), and samples with total soil DDTs concentration higher than 500 ng g^{-1} were selected for desorption kinetics study (400 h consecutive extraction). For the consecutive extraction, at periodic intervals (10 min, 20 min, 30 min, 1 h, 2 h, 4 h, 8 h, 12 h, 24 h, 48 h, 96 h, 200 h and 400 h), Tenax beads were refreshed, rinsed for 3 times with 20 mL deionized water, then extracted by shaking with 2 × 10 mL of hexane:actone (*V*:*V* = 1:1) for 5 min. For the single-point extraction, the Tenax beads were added only once, separated after 6 h extraction, rinsed, and extracted by 2 × 10 mL of hexane:actone (*V*:*V* = 1:1) for 5 min. The combined extracts were then cleaned with silica gel and concentrated to 2 mL for GC analysis. Each soil sample was extracted by Tenax in triplicate.

To ascertain Tenax beads can offer enough absorption capacity for DDTs which can be released from soil, known amounts of DDTs (ranged from 50 to 2000 ng g^{-1}) were spiked into soil and kept in dark for 24 h. It was valid to assume that in 24 h, all the added DDTs did not age yet, and was able to be released because our preliminary studies showed that more than 85% of the added DDTs aged for 24 h could be extracted by Tenax beads in 10 h. Then, 1 g of amended soil was mixed with 0.2 g of beads in 100 mL deionized water in each separatory funnel and shaken as described previously. The beads were finally separated from the water and extracted with extract solvent. The recoveries of DDTs in all the artificially contaminated soils ranged from 90% to 95%. The results proved that 0.2 g of Tenax TA beads had sufficient sorption capacity to extract DDTs from 1 g of soil.

The data of the consecutive desorption were fitted with triphasic kinetic model to attain the kinetics parameters [5,8]:

$$\frac{S_t}{S_0} = F_r(e^{-k_r t}) + F_{sl}(e^{-k_{sl} t}) + F_{vl}(e^{-k_{vl} t}) \quad (1)$$

where S_0 and S_t was the amounts of DDT in soil at the start (0) and time t (h) of the desorption experiments (consecutive Tenax extraction); S_t/S_0 was the residue fraction of DDT in soil at time t (h); F_r, F_{sl}, F_{vl} was the rapid, slow, and very-slow-desorbing fraction,

Table 1
Total soil DDTs concentration in 28 soil samples.

Topsoils	p,p′-DDE (ng g^{-1})	p,p′-DDT (ng g^{-1})	Sum[a] (ng g^{-1})	Subsoils	p,p′-DDE (ng g^{-1})	p,p′-DDT (ng g^{-1})	Sum[a] (ng g^{-1})
3top	13.3	7.6	20.9	3sub	12.0	5.8	17.8
4top	412.9	92.7	505.6	4sub	437.0	90.6	527.6
5top	7.8	3.1	10.9	5sub	5.1	2.0	7.1
6top	102.1	91.9	194.0	6sub	124.7	149.4	274.1
7top	22.2	10.1	32.3	7sub	8.4	3.7	12.0
8top	4.8	3.2	8.0	8sub	5.3	3.5	8.8
9top	2.2	1.3	3.5	9sub	1.8	0.8	2.6
10top	2.8	3.3	6.0	10sub	4.1	2.2	6.3
11top	28.2	26.2	54.4	11sub	25.2	25.8	51.0
12top	92.1	31.9	124.0	12sub	106.6	31.9	138.5
13top	274.3	72.6	346.9	13sub	274.3	59.3	333.6
14top	80.0	19.1	99.0	14sub	84.4	18.7	103.1
15top	44.0	24.3	68.3	15sub	56.2	36.8	93.1
16top	101.6	23.3	124.9	16sub	143.6	29.2	172.8
17top	37.1	16.0	53.1	17sub	37.1	18.4	55.6
18top	545.9	126.0	671.9	18sub	479.4	138.1	617.5
19top	397.6	75.8	473.5	19sub	409.2	85.4	494.5
20top	79.4	27.0	106.3	20sub	58.8	55.7	114.5
21top	90.9	32.2	123.1	21sub	107.7	119.9	227.5
22top	183.9	26.7	210.6	22sub	297.1	31.0	328.1
23top	54.2	73.1	127.4	23sub	54.2	42.3	96.6
24top	49.4	27.8	77.2	24sub	54.4	26.1	80.5
25top	145.5	38.8	184.3	25sub	160.2	50.2	210.5
27top	497.5	70.9	568.4	27sub	500.9	75.1	576.0
28top	135.9	42.6	178.5	28sub	152.2	43.8	195.9
29top	91.4	45.6	137.0	29sub	89.0	49.0	137.9
30top	205.1	46.8	252.0	30sub	211.2	56.9	268.1
31top	181.3	58.0	239.4	31sub	254.8	66.3	321.1
Mean	138.7	39.9	178.6	Mean	148.4	47.1	195.5
SD[b]	152.5	31.9	179.5	SD[b]	153.2	40.4	181.8
Ranges	2.2–545.9	1.3–126	3.5–671.9	Ranges	1.8–500.9	0.8–149.4	2.6–617.5

[a] The summation concentrations of p,p′-DDE and p,p′-DDT.
[b] The standard deviations of the samples.

respectively; k_r, k_{sl}, k_{vl} (h^{-1}) were the first-order rate constants for rapid, slow, and very-slow desorption, respectively.

2.5. Carrot accumulation of DDTs in pot experiments

Air-dried, sieved soil samples (2 kg, the concentration gradient was considered when soil samples were selected) were put into pots in a greenhouse, wetted with deionized water. After equilibration for several days, carrot seeds (*Daucus carota*) were sown 1 cm below the soil surface in a grid pattern, covered with soil, and lightly watered. During the experimental period, temperatures in the greenhouse ranged from 23 to 28 °C. The carrots were fertilized with routine methods. After 3-month cultivation, both the carrot and the soil in each pot were sampled in triplicate at the same time. For the soil samples, DDTs was determined with Tenax 6 h-extraction. For the carrot roots, smashed sample was weighted and mixed with diatomaceous earth as a drying and dispersing agent for ASE extraction. The extract was cleaned and concentrated to 2 mL for GC analysis as mentioned above. The recoveries of DDTs in carrot were done by adding DDT standard in the control carrot roots.

2.6. GC analysis

Quantification of DDTs was achieved by Agilent 6890 gas chromatography equipped with a ^{63}Ni electro-capture detector (ECD) and an HP-5 fused capillary column (30-m length, 0.32-mm internal diameter, and 0.25-μm film thickness). The samples were quantified by external standards (seven levels of DDTs concentration were used: 0, 5, 10, 20, 50, 100, 200 ng g^{-1}, $r^2 > 0.99$). Average recoveries of DDTs for both soils and carrots were higher than 90%. Laboratory blank values for the compounds were generally low and posed no problem to the analytical quantitation. The overall reproducibility was evaluated using the replicate analyses ($n = 3$). The coefficient of variation (C.V.) was less than 0.2 in most of the cases. Thus, the reproducibility of the measurements was considered to be acceptable.

3. Results and discussion

3.1. Total soil DDTs concentration in cotton field soil samples

For topsoil samples (0–10 cm), p,p′-DDE, and p,p′-DDT were detected in all the samples (Previous studies showed that other DDTs, such as o,p′-DDT, o,p′-DDE, o,p′-DDD and p,p′-DDD were also detected in some samples, but accounted for less than 10% of the total soil DDTs in most cases and were neglected here), The mean concentrations, standard deviations (SD) and concentration ranges of each DDT compound in soil were summarized in Table 1. It showed that the total soil DDTs (the summation of p,p′-DDE, and p,p′-DDT) in cotton topsoil ranged from 3.5 to 671.9 ng g^{-1} with a mean concentration of 178.6 ng g^{-1}. The most abundant compound was p,p′-DDE (2.2–545.9 ng g^{-1}). The concentration of the DDTs was higher by a factor of about 4 when compared with the DDTs concentrations in Alabama soils reported by Harner et al. [37]. With regard to the subsoil samples (10–20 cm), the total soil concentration of DDTs ranged from 2.6 to 617.5 ng g^{-1} with a mean concentration of 181.8 ng g^{-1}, resembled the residue level in topsoil. Moreover, the DDT compositions in subsoil had similar pattern with that in the topsoil, e.g. the predominant compounds in subsoil were also p,p′-DDE (1.8–500.9 ng g^{-1}). The paired-samples *t*-test showed that the residue levels of either p,p′-DDT or p,p′-DDE were not significantly different ($p > 0.05$) between topsoil and subsoil, which probably reflected the long pesticide application history on the field.

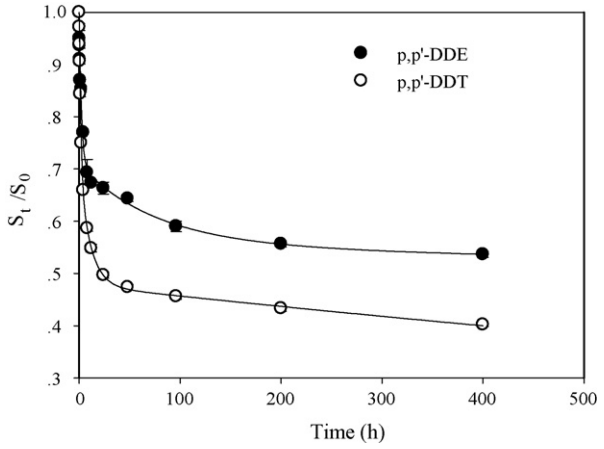

Fig. 1. Desorption kinetic of DDTs in soil sample (18top) with consecutive Tenax extraction, S_t/S_0 was the DDT residue fraction in soil at desorption time t (h).

3.2. Tenax consecutive extraction of DDTs from the cotton field soils

As mentioned above, the DDTs desorption kinetics from soils could be investigated by Tenax consecutive extraction. According to Table 1, 8 of 28 samples with total soil DDTs concentration about 500 ng g^{-1} were selected in order to demonstrate the desorption processes clearly. In Fig. 1, S_t/S_0 versus time was given for the desorption of p,p′-DDT and p,p′-DDE from one of the soil samples,18top (figures for other soil samples were not presented here), and the solid lines were obtained by curve fitting with Eq. (1). The kinetics parameters fitted by the model (Eq. (1)) were presented in Table 2.

Fig. 1 displayed that in the first 12 h, about 70% of the total soil p,p′-DDE and 60% of the total soil p,p′-DDT had not desorbed from the soil sample; after 200 h of desorption, about 60% of the total soil p,p′-DDE and 50% of the total soil p,p′-DDT remained in the soil, and after 400 h of desorption, up to about 55% of p,p′-DDE and 40% of p,p′-DDT were still on the soil solid phase. Fractions strongly resistant to desorption at long times were evident in all the soil samples. The usual explanation for these observations was: a part of the DDTs in the outer regions of the particles was "labile" and easy to be released from the solid phase; but another part of the DDTs had diffused into the organic matter matrix and micropore, and was sequestrated tightly with time [9].

Table 2
Rate constants and fractions for the rapid, slow, and very-slow desorption of DDTs in selected soil samples (with total soil DDTs concentration about 500 ng g^{-1}) predicted by the consecutive Tenax extraction.

Samples	F_r	k_r (h^{-1})	F_{sl}	k_{sl} (h^{-1})	F_{vs}	k_{vs} (h^{-1})
p,p′-DDT						
4top	0.283	0.155	0.363	0.074	0.354	0.0005
4sub	0.302	0.267	0.386	0.085	0.312	0.0005
18top	0.293	0.626	0.229	0.094	0.478	0.0004
18sub	0.288	0.538	0.235	0.057	0.477	0.0003
19top	0.378	0.122	0.259	0.062	0.363	0.0007
19sub	0.393	0.326	0.329	0.088	0.278	0.0006
27top	0.313	0.539	0.126	0.030	0.561	0.0002
27sub	0.451	0.454	0.229	0.056	0.320	0.0009
p,p′-DDE						
4top	0.256	0.855	0.390	0.053	0.354	0.0006
4sub	0.282	0.698	0.406	0.064	0.312	0.0008
18top	0.291	0.451	0.154	0.013	0.554	0.0001
18sub	0.303	0.706	0.169	0.028	0.538	0.0002
19top	0.274	0.216	0.311	0.078	0.415	0.0007
19sub	0.349	0.128	0.334	0.042	0.317	0.0008
27top	0.358	0.237	0.323	0.078	0.319	0.0005
27sub	0.401	0.563	0.274	0.066	0.325	0.0009

F_r, F_{sl}, F_{vl} were the rapid, slow, and very-slow-desorbing fraction, respectively. k_r, k_{sl}, k_{vl} (h^{-1}) were the first-order rate constants for rapid, slow, and very-slow desorption, respectively.

Table 2 showed that the rate constants for the rapid, slow, and very-slow desorption were about 10^{-1}, 10^{-2}, and 10^{-4} h^{-1}, respectively, which were similar in magnitude to other reported documents [12,14,25,26]. The rapid, slow, and very-slow-desorbing fractions for total soil p,p′-DDE ranged from 0.256 to 0.401, 0.154 to 0.406, and 0.312 to 0.554, respectively. The results implied that about half the total soil DDTs could hardly desorb from soil solid phase. From the predicted fractions for soil sample (18top), it could be roughly calculated that the first 10 h of desorption were dominated by rapid desorption, and from 10 to 100 and >100 h, was dominated by the slow and very-slow desorption, respectively. Moreover, the desorption kinetics between the topsoil and subsoil had no significant difference for either p,p′-DDT or p,p′-DDE (paired-samples t-test, $p > 0.05$), and among all the soil samples the desorption kinetics were quite comparable to each other (see Table 2), which was possibly due to the similarity of dicofol application history as well as the soil characteristics.

Cornelissen et al. [26] reported that the rapid-desorbing fractions decreased with the increasing hydrophobicity of the compounds from artificial contaminated soil [26]. But this was not always the case [14]. In our studies, the rapid-desorbing fractions of p,p′-DDT were not significantly lower than p,p′-DDE (paired-samples t-test, $p > 0.05$), which likely resulted from many other factors more than their hydrophobicity. Furthermore, Leppanen et al. [8] and Sormunen et al. [38] found the rapid-desorbing fractions decreased with increasing total soil concentration, but in our studies it was difficult to tell whether or not the same trend existed because the concentrations of the selected samples were quite similar.

3.3. Tenax 6 h-extraction of DDTs from cotton field soil samples

As above, it would take several hundred hours to predict the rapid-desorbing fraction, thus, it was necessary to simplify the technique of consecutive extraction with Tenax. A few studies held that there were significant correlations between the rapid-desorbing fraction and the Tenax 6 h-extracted fraction [5,10,14,27,31]. If this was the case, only several hours were needed to attain the rapid-desorbing fraction.

The Tenax 6 h-extracted concentrations in 22 samples with total soil DDTs concentration higher than 50 ng g^{-1} were summarized in Table 3 (according to the National Environmental Quality Standards for Soils of China (GB15618-95), it was considered that risk existed when the total soil DDTs concentration in soil was higher than 50 ng g^{-1}). It showed that the Tenax 6 h-extractable summation of p,p′-DDE and p,p′-DDT in topsoil ranged from 15.9 to 118.3 ng g^{-1}, with a mean concentration of 45.1 ng g^{-1}; the predominant compound was p,p′-DDE (7.5–98.0 ng g^{-1}), which resembled that in subsoil. Paired-samples t-test showed that the Tenax 6 h-extracted concentrations between the topsoil and subsoil has no significant difference for either p,p′-DDT or p,p′-DDE ($p > 0.05$).

Statistical analysis demonstrated a significant correlation between the Tenax 6 h-extracted concentration and the total soil DDTs concentration ($p < 0.05$). From plot C of Fig. 2, it could be seen that positive linear regression fitted the data very well, with r^2 0.91. From the Tenax 6 h-extracted fractions calculated based on Tables 1 and 3, it showed that, in topsoils, the Tenax 6 h-extracted fraction for p,p′-DDT, p,p′-DDE and sum DDTs ranged from 0.12 to 0.36 (mean 0.21), 0.11 to 0.39 (mean 0.29), and 0.12 to 0.32 (mean 0.22), respectively, which quite resembled that in subsoil.

Statistical analysis also proved there were significant correlations between the Tenax 6 h-extracted fraction and the rapid-desorbing fraction predicted by Tenax consecutive extraction ($p < 0.01$), and from the plot A and B of Fig. 2, it could be seen

Table 3
Tenax 6 h-extracted concentration of DDTs in 22 samples with total soil concentration higher than 50 ng g^{-1}.

Topsoils	p,p′-DDE (ng g^{-1})	p,p′-DDT (ng g^{-1})	Sum[a] (ng g^{-1})	Subsoils	p,p′-DDE (ng g^{-1})	p,p′-DDT (ng g^{-1})	Sum (ng g^{-1})
4top	63.2	29.8	93.0	4sub	62.1	31.1	92.5
6top	20.4	14.9	35.2	6sub	24.1	30.5	54.6
11top	10.2	6.1	16.3	11sub	7.8	6.9	14.7
12top	15.0	10.2	25.2	12sub	25.2	11.9	37.0
13top	47.3	24.5	71.8	13sub	55.5	19.8	75.3
14top	20.6	7.1	27.7	14sub	26.2	7.7	33.9
15top	12.5	7.8	20.3	15sub	14.3	11.7	26.0
16top	28.2	9.0	37.2	16sub	22.7	8.8	31.5
17top	10.2	6.0	16.2	17sub	11.0	7.2	18.2
18top	87.3	31.0	118.3	18sub	81.0	33.6	117.9
19top	59.6	23.1	82.7	19sub	74.5	22.7	97.2
20top	21.9	9.8	31.7	20sub	34.5	23.9	58.3
21top	21.1	10.8	31.9	21sub	24.2	19.7	43.9
22top	23.6	9.3	32.9	22sub	32.9	11.6	44.5
23top	7.5	8.4	15.9	23sub	7.5	9.9	17.3
24top	14.6	9.8	24.4	24sub	1.2	9.3	10.5
25top	33.5	10.1	43.6	25sub	23.1	18.2	41.3
27top	98.0	16.5	114.5	27sub	101.2	24.1	125.3
28top	22.2	14.5	36.7	28sub	25.6	12.5	38.1
29top	15.2	11.7	26.8	29sub	17.0	13.7	30.7
30top	30.8	15.9	46.7	30sub	32.7	18.3	51.0
31top	22.5	21.3	43.8	31sub	29.3	21.4	50.7
Mean	31.2	14.0	45.1	Mean	33.3	17.0	50.5
SD[b]	24.8	7.5	30.8	SD[b]	25.8	8.2	32.3
Ranges	7.5–98.0	6.0–31.0	15.9–118.3	Ranges	1.2–101.2	6.9–33.6	10.5–125.3

[a] The summation Tenax 6 h-extracted concentrations of p,p′-DDE and p,p′-DDT.
[b] The standard deviations of the samples.

that positive linear regression could be used to fit the data (r^2 was 0.82 and 0.74 for p,p′-DDE and p,p′-DDT, respectively). The slopes of the regression lines was 0.54 and 0.47 for p,p′-DDE and p,p′-DDT, respectively, namely, the ratios of the Tenax 6 h-extracted fraction to the rapid-desorbing fraction were approximate 0.5 for both p,p′-DDE and p,p′-DDT. These results were in agreement with other studies, e.g., Cornelissen et al. [5] found the 6 h-extracted fraction was about 0.5 times the rapid-desorbing fraction [5]. This result was interesting because it implied that the Tenax 6 h-extracted fraction could be used as an efficient technique to predict the rapid-desorbing fraction which was assumed to be highly related to bioavailability of POPs in soil.

3.4. Carrot accumulation in DDTs

In pot experiments, only a very small proportion of DDT were taken by carrot root, e.g., the concentration in carrot was 23.9 ng g^{-1} for p,p′-DDE in 18top, accounting for only 5% of the total soil concentration (545.9 ng g^{-1}). These results were consistent with previous studies, e.g., Wang et al. [39] and Trapp et al. [40] both

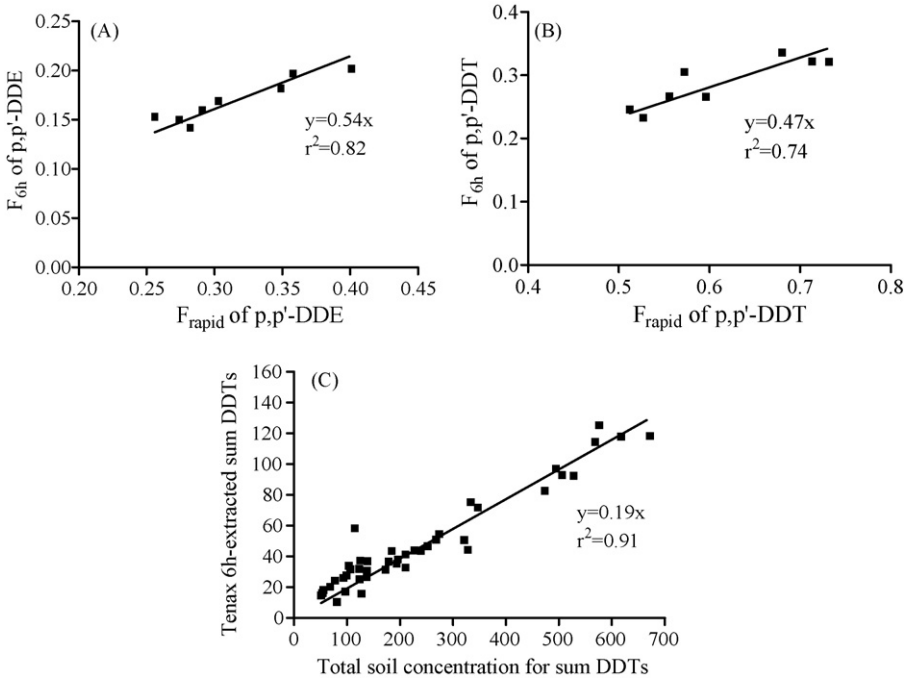

Fig. 2. The relationship between Tenax 6 h-extracted fraction and the rapid-desorbing fraction predicted from Tenax consecutive extraction (A and B); between the Tenax 6 h-extracted sum DDTs (p,p′-DDE plus p,p′-DDT) and the total soil concentration for sum DDTs (C).

Table 4
The bioaccumulation factor (BAF) of carrot root to DDTs in pot experiments.

Samples	BAF based on total soil concentration (C_{carrot}/C_{Total})		BAF based on Tenax 6 h-extracted concentration (C_{carrot}/C_{Tenax})	
	p,p′-DDE	p,p′-DDT	p,p′-DDE	p,p′-DDT
13top	0.06	0.08	0.37	0.26
16top	0.05	0.13	0.32	0.42
18top	0.05	0.03	0.28	0.23
18sub	0.05	0.04	0.28	0.30
27top	0.04	0.10	0.28	0.29
Mean	0.05	0.08	0.31	0.30

found only a small part of organic pollutants was accumulated by carrot root, and was mostly in peel rather than in core. Moreover, the accumulated DDTs by root from topsoil (18top) and subsoil (18sub) had no significant difference ($p > 0.05$), indicating that the bioavailability of DDTs were quite comparable between in the topsoil and in subsoil, which was agreement with the desorption characteristics of DDTs in soil.

Fig. 3 showed the relationship between the carrot accumulation and the total soil DDTs concentration (plot A and C) as well as the Tenax 6 h-extracted concentration (plot B and D). It demonstrated that the correlation was strong between carrot accumulation and the Tenax 6 h-extracted concentration, as a result, the values for linear regression were high, e.g., the adjusted r^2 was 0.91, 0.61 for p,p′-DDE and p,p′-DDT, respectively (see plot B and D). The correlation between carrot accumulation and the total soil p,p′-DDE concentration was also strong ($r^2 = 0.85$), nevertheless, the carrot accumulation was not correlated with the total soil p,p′-DDT concentration ($r^2 = -2.81$). The results indicated that the prediction of carrot accumulation could be optimized by the Tenax 6 h-extracted concentration instead of the total soil concentration.

In terms of carrot accumulation, of importance was the bioaccumulation factor (BAF, the ratios of DDTs concentration in carrot to the total soil concentration or Tenax 6 h-extracted fraction in the soil, namely, C_{carrot}/C_{Total} and C_{carrot}/C_{Tenax}, respectively). Table 4 showed that the BAF based on the total soil concentration was much smaller than those based on the Tenax 6 h-extracted concentration, for example, the BAF for p,p′-DDE was 0.31 when based on the Tenax 6 h-extracted concentration, which was about 6 times the one based on the total soil concentration. Theoretically, the variation of BAF should be small across the different concentration levels if a good predictor is chosen [8,41]. Table 4 showed that the variation of BAF based on the Tenax 6 h-extracted concentration was smaller than that based on the total soil concentration across different content levels, especially for p,p′-DDT, verifying that Tenax 6 h-extraction was better than the total soil concentration to describe the bioavailability of DDTs in soil. This observation was consistent with other studies, for example, Sormunen et al. [19] found if based on the rapid-desorbing concentration, BAF of oligochaeta to PCB77 was constant, however, if based on the total concentration in sediment, BAF varied significantly with concentrations.

There was an argument that the Tenax extraction would overestimate the bioavailable fraction of organic pollutants in soil or sediment, for example, Leppanen et al. [8] observed the Tenax extraction overestimated the bioavailable fractions of organic pollutants to three sediment species [8]; van der Heijden and Jonker

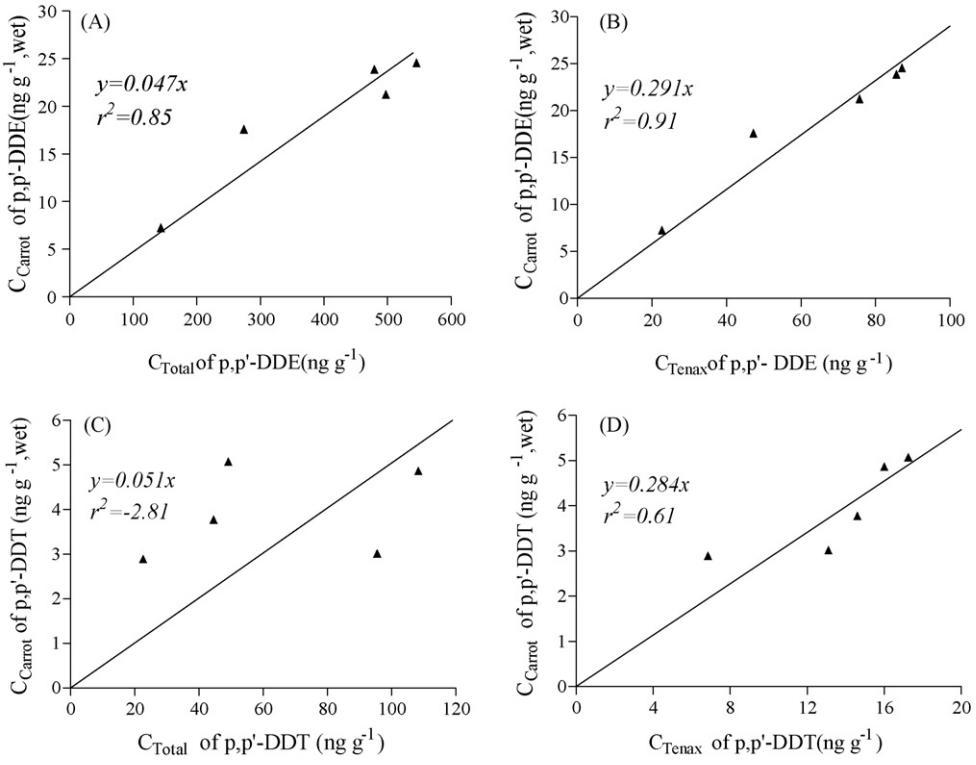

Fig. 3. The relationship between carrot accumulation and both the total soil concentration (A and C) and the Tenax 6 h-extracted concentration (B and D) in pot experiments.

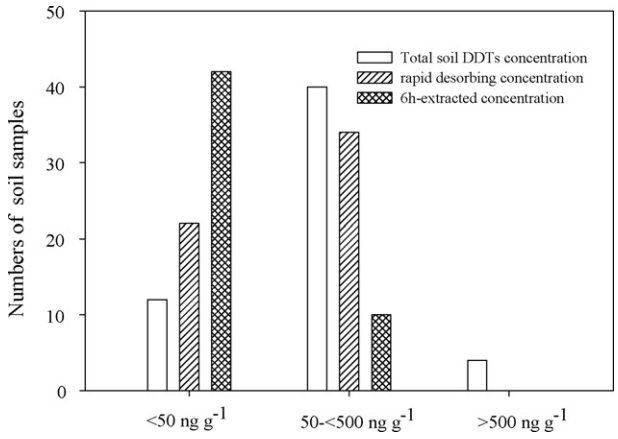

Fig. 4. Distribution of the cotton field soil samples based on both the total soil concentration and Tenax extracted concentration.

[42] reported that the Tenax 6 h-extraction over-predicted the biotic concentrations of PAHs in aquatic worms by a factor of more than 10. In the present study, the Tenax 6 h-extracted concentrations were about 3 times larger than the concentrations of DDTs in carrot roots. It may be due to the fact that the fraction extracted by Tenax included not only the bioavailable fraction to the carrot root, but also the potentially bioavailable fraction (bioaccessible) to the carrot root [6]. Even though, Tenax 6 h-extraction, which had stronger correlation with the carrot accumulation than the total soil concentration, could serve as a better predictor to the bioavailability of DDTs to carrot root. Furthermore, considering the significant linear correlation between the rapid-desorbing fraction and the Tenax 6 h-extraction (see Fig. 2), it also was reasonable to regard the rapid-desorbing fraction as a reliable predictor of DDTs bioavailability to carrot root.

3.5. Risk assessment based on both the total soil concentration and the Tenax-extracted DDTs concentration

The total soil concentration, rapid desorbing concentration and Tenax 6 h-extracted concentration was used to make a risk assessment, respectively. Since the consecutive desorption kinetics of DDTs were studied for 8 soil samples, thus the rapid-desorbing concentration was directly predicted for only part of the soil samples. In order to facilitate the risk assessment, 2 times the Tenax 6 h-extracted concentration served as the rapid-desorbing concentration according to Fig. 2 (the ratios of $F_{6\,h}$ to F_{rapid} was approximate 0.5 for both p,p′-DDE and p,p′-DDT, therefore, this assumption was acceptable). The results of risk assessments were showed in Fig. 4.

According to the National Environmental Quality Standards for Soils of China (GB15618-95), the soil was less polluted when the total soil concentration of DDTs was lower than 50 ng g^{-1} (first grade); moderately polluted when the concentration was between 50 and 500 ng g^{-1} (second grade); seriously polluted when the concentration was higher than 500 ng g^{-1} (third grade). In the present study, from Fig. 4, it demonstrated that when based on the total soil concentration, the DDTs contents in 12 samples were lower than the first grade (<50 ng g^{-1}), and contents in 40 samples were between the first and the second grade (<500 ng g^{-1}), and those in 4 samples were between the second and third grade (>500 ng g^{-1}). Namely, about 71.4% of the cotton soil samples were moderately polluted, and about 7.1% were seriously polluted. However, when based on the rapid-desorbing concentration and the 6 h-extracted concentration, the risk was much lower: the DDTs contents in 22 (39.3%) and 42 (75%) samples were lower than the first grade, respectively; in 34 (60.7%) and 10 (17.9%) samples were between the first and the second grade; and in no sample DDTs was higher than the third grade. The comparison indicated that the risk might be overestimated based on the total soil concentration, and the risks based on the rapid-desorbing concentration and 6 h-extracted concentration might be more representative because of the stronger correlations with bioavailability proved by the carrot accumulation.

It should be emphasized that the comparison of Tenax extracted concentrations to the soil quality criteria was not a legitimate one. Moreover, the comparison was not accurate because Tenax extraction was an operational and qualitative, not mechanistic, method to determine the fractions correlated with the bioavailability of organic pollutants [1]. Nevertheless, our intentions were to demonstrate how different results would be attained when the concentration correlated with bioavailability was used in a risk assessment; therefore, this comparison was acceptable to some extent. More great efforts were needed in order to integrate Tenax extracted concentration into the risk assessment.

4. Conclusions

The rapid-desorbing fraction was about 0.3 times the total soil DDTs, and 2 times the Tenax 6 h-extracted fraction. The significant correlations between the rapid-desorbing fraction and the Tenax 6 h-extracted fraction indicated the feasibility of measuring the rapid-desorbing fraction with Tenax 6 h-extraction. The strong correlations between carrot accumulation and the Tenax 6 h-extraction ascertained that the Tenax extraction could serve as a good predictor for the bioavailability of DDTs in soil, and the risk assessment based on the Tenax extraction might be optimized. The present study demonstrated that Tenax extraction, typically used in aquatic systems, was applicable to soils as well. Our results provided implication for site risk assessment and remediation contaminated by persistent organic pollutants.

Acknowledgements

This research was financially supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (Nos. KZCX2-YW-404, KZCX2-YW-Q02), the National Natural Science Foundation of China (No. 40801117), Jiangsu Municipal Natural Science Foundation (No. BK2008497), and the Innovative project of Chinese Academy of Sciences (No. ISSASIP0714).

References

[1] J. Harmsen, Measuring bioavailability: from a scientific approach to standard methods, J. Environ. Qual. 36 (2007) 1420–1428.
[2] D.E. Morrison, B.K. Robertson, M. Alexander, Bioavailability to earthworms of aged DDT, DDE, DDD, and dieldrin in soil, Environ. Sci. Technol. 34 (2000) 709–713.
[3] M. Alexander, Aging, bioavailability, and overestimation of risk from environmental pollutants, Environ. Sci. Technol. 34 (2000) 4259–4265.
[4] B.K. Robertson, M. Alexander, Sequestration of DDT and dieldrin in soil: disappearance of acute toxicity but not the compounds, Environ. Toxicol. Chem. 17 (1998) 1034–1038.
[5] G. Cornelissen, H. Rigterink, D.E.M. ten Hulscher, et al., A simple Tenax (R) extraction method to determine the availability of sediment-sorbed organic compounds, Environ. Toxicol. Chem. 20 (2001) 706–711.
[6] K.T. Semple, K.J. Doick, K.C. Jones, et al., Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated, Environ. Sci. Technol. 38 (2004) 228a–231a.
[7] R. Kraaij, W. Seinen, J. Tolls, Direct evidence of sequestration in sediments affecting the bioavailability of hydrophobic organic chemicals to benthic deposit-feeders, Environ. Sci. Technol. 36 (2002) 3525–3529.
[8] M.T. Leppanen, P.F. Landrum, J.V.K. Kukkonen, et al., Investigating the role of desorption on the bioavailability of sediment-associated 3,4,3′,4′-tetrachlorobiphenyl in benthic invertebrates, Environ. Toxicol. Chem. 22 (2003) 2861–2871.
[9] J.J. Pignatello, B.S. Xing, Mechanisms of slow sorption of organic chemicals to natural particles, Environ. Sci. Technol. 30 (1996) 1–11.
[10] T.E.M. Ten Hulscher, J. Postma, P.J. Den Besten, et al., Tenax extraction mimics benthic and terrestrial bioavailability of organic compounds, Environ. Toxicol. Chem. 22 (2003) 2258–2265.

[11] W.J. Braida, J.C. White, J.J. Pignatello, Indices for bioavailability and biotransformation potential of contaminants in soils, Environ. Toxicol. Chem. 23 (2004) 1585–1591.
[12] J.V.K. Kukkonen, P.F. Landrum, S. Mitra, et al., The role of desorption for describing the bioavailability of select polycyclic aromatic hydrocarbon and polychlorinated biphenyl congeners for seven laboratory-spiked sediments, Environ. Toxicol. Chem. 23 (2004) 1842–1851.
[13] J.C. White, M. Hunter, K.P. Nam, et al., Correlation between biological and physical availabilities of phenanthrene in soils and soil humin in aging experiments, Environ. Toxicol. Chem. 18 (1999) 1720–1727.
[14] J. You, P.E. Landrum, T.A. Trimble, et al., Availability of polychlorinated biphenyls in field-contaminated sediment, Environ. Toxicol. Chem. 26 (2007) 1940–1948.
[15] T.A. Trimble, J. You, M.J. Lydy, Bioavailability of PCBs from field-collected sediments: application of Tenax extraction and matrix-SPME techniques, Chemosphere 71 (2008) 337–344.
[16] E. Puglisi, A.J. Murk, H.J. van den Bergt, et al., Extraction and bioanalysis of the ecotoxicologically relevant fraction of contaminants in sediments, Environ. Toxicol. Chem. 26 (2007) 2122–2128.
[17] J. You, S. Pehkonen, D.P. Weston, et al., Chemical availability and sediment toxicity of pyrethroid insecticides to *Hyalella azteca*: application to field sediment with unexpectedly low toxicity, Environ. Toxicol. Chem. 27 (2008) 2124–2130.
[18] J. De Weert, A. De La Cal, H. Van den Berg, et al., Bioavailability and biodegradation of nonylphenol in sediment determined with chemical and bioanalysis, Environ. Toxicol. Chem. 27 (2008) 778–785.
[19] A.J. Sormunen, M.T. Leppanen, J.V.K. Kukkonen, Influence of sediment ingestion and exposure concentration on the bioavailable fraction of sediment-associated tetrachlorobiphenyl in oligochaetes, Environ. Toxicol. Chem. 27 (2008) 854–863.
[20] J.J. Pignatello, Slowly reversible sorption of aliphatic halocarbons in soils. 1. Formation of residual fractions, Environ. Toxicol. Chem. 9 (1990) 1107–1115.
[21] B. Strandberg, N. Wagman, P.A. Bergqvist, et al., Semipermeable membrane devices as passive samplers to determine organochlorine pollutants in compost, Environ. Sci. Technol. 31 (1997) 2960–2965.
[22] S.B. Hawthorne, C.B. Grabanski, Correlating selective supercritical fluid extraction with bioremediation behavior of PAHs in a field treatment plot, Environ. Sci. Technol. 34 (2000) 4103–4110.
[23] N.H. Chung, M. Alexander, Differences in sequestration and bioavailability of organic compounds aged in dissimilar soils, Environ. Sci. Technol. 32 (1998) 855–860.
[24] D.Y. Zhao, J.J. Pignatello, Model-aided characterization of Tenax (R)-TA for aromatic compound uptake from water, Environ. Toxicol. Chem. 23 (2004) 1592–1599.
[25] M.S. Greenberg, G.A. Burton, P.F. Landrum, et al., Desorption kinetics of fluoranthene and trifluralin from Lake Huron and Lake Erie, USA, sediments, Environ. Toxicol. Chem. 24 (2005) 31–39.
[26] G. Cornelissen, P.C.M. vanNoort, H.A.J. Govers, Desorption kinetics of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: Sediment extraction with Tenax(R) and effects of contact time and solute hydrophobicity, Environ. Toxicol. Chem. 16 (1997) 1351–1357.
[27] P.C.M. van Noort, G. Cornelissen, T.E.M. ten Hulscher, et al., Influence of sorbate planarity on the magnitude of rapidly desorbing fractions of organic compounds in sediment, Environ. Toxicol. Chem. 21 (2002) 2326–2330.
[28] P.F. Landrum, S.D. Robinson, D.C. Gossiaux, et al., Predicting bioavailability of sediment-associated organic contaminants for *Diporeia* spp. and Oligochaetes, Environ. Sci. Technol. 41 (2007) 6442–6447.
[29] Y.Z. Chai, J.W. Davis, S.A. Saghir, et al., Effects of aging and sediment composition on hexachlorobenzene desorption resistance compared to oral bioavailability in rats, Chemosphere 72 (2008) 432–441.
[30] Y.P. Xu, J. Gan, Z.J. Wang, et al., Effect of aging on desorption kinetics of sediment-associated pyrethroids, Environ. Toxicol. Chem. 27 (2008) 1293–1301.
[31] C.T.A. Moermond, I. Roessink, M.T.O. Jonker, et al., Impact of polychlorinated biphenyl and polycyclic aromatic hydrocarbon sequestration in sediment on bioaccumulation in aquatic food webs, Environ. Toxicol. Chem. 26 (2007) 607–615.
[32] A.M.R. Oen, G.D. Breedveld, S. Kalaitzidis, et al., How quality and quantity of organic matter affect polycyclic aromatic hydrocarbon desorption from Norwegian harbor sediments, Environ. Toxicol. Chem. 25 (2006) 1258–1267.
[33] J. Li, J.J. Pignatello, B.F. Smets, et al., Bench-scale evaluation of in situ bioremediation strategies for soil at a former manufactured gas plant site, Environ. Toxicol. Chem. 24 (2005) 741–749.
[34] X.H. Qiu, T. Zhu, L. Jing, et al., Organochlorine pesticides in the air around the Taihu Lake, China, Environ. Sci. Technol. 38 (2004) 1368–1374.
[35] X.H. Qiu, T. Zhu, B. Yao, et al., Contribution of dicofol to the current DDT pollution in China, Environ. Sci. Technol. 39 (2005) 4385–4390.
[36] X.L. Yang, S.S. Wang, Y.R. Bian, et al., Dicofol application resulted in high DDTs residue in cotton fields from northern Jiangsu province, China, J. Hazard. Mater. 150 (2008) 92–98.
[37] T. Harner, T.F. Bidleman, L.M.M. Jantunen, et al., Soil–air exchange model of persistent pesticides in the United States cotton belt, Environ. Toxicol. Chem. 20 (2001) 1612–1621.
[38] A.J. Sormunen, J. Koistinen, M.T. Leppanen, et al., Desorption of sediment-associated polychlorinated dibenzo-p-dioxins, dibenzofurans, diphenyl ethers and hydroxydiphenyl ethers from contaminated sediment, Chemosphere 72 (2008) 1–7.
[39] M.J. Wang, K.C. Jones, Uptake of chlorobenzenes by carrots from spiked and sewage sludge-amended soil, Environ. Sci. Technol. 28 (1994) 1260–1267.
[40] S. Trapp, A. Cammarano, E. Capri, et al., Diffusion of PAH in potato and carrot slices and application for a potato model, Environ. Sci. Technol. 41 (2007) 3103–3108.
[41] H.A. Morrison, F.A.P.C. Gobas, R. Lazar, et al., Development and verification of a bioaccumulation model for organic contaminants in benthic invertebrates, Environ. Sci. Technol. 30 (1996) 3377–3384.
[42] S.A. van der Heijden, M.T.O. Jonker, PAH bioavailability in field sediments: comparing different methods for predicting in situ bioaccumulation, Environ. Sci. Technol. 43 (2009) 3757–3763.