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Assessing the Phytoavailability of Dieldrin Residues in Charcoal-Amended Soil Using Tenax Extraction

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Consecutive and single Tenax extractions were applied to characterize the effectiveness of activated charcoal (AC) amendments to reduce the phytoavailability of dieldrin in a natively contaminated horticultural soil. Dieldrin desorption from untreated and 800 mg_{AC} kg^{-1} soil was well described by a model with three dieldrin fractions of different kinetics: a rapidly (F_{rap}), slowly (F_{slow}), and very slowly ($F_{v.slow}$) desorbing fraction. The AC amendment resulted in a transfer of dieldrin from the F_{slow} to the $F_{v.slow}$ fraction. The $F_{v.slow}$ increased by nearly 10% compared to the control soil. Dieldrin extractability by Tenax from AC amended soils was not influenced by the cultivation of cucumber plants indicating the stability of this remediation technique. Dieldrin extractability by Tenax at the beginning of plant growth correlated only weakly with the dieldrin content of the cucumbers at harvest. Therefore, the potential of Tenax extractions to predict the uptake of dieldrin by cucumbers appears to be limited.

INTRODUCTION

Organochlorine pesticides (OCP) were once applied worldwide, but are banned nowadays in most countries because of their ecotoxicity, bioaccumulation, and persistence. These properties make them a matter of concern today and in the future (1). OCP residues can still be present in soils and be taken up by crop plants even decades after applications have ceased. This is a particular problem in cucumbers and other plants of the family of *Cucurbitaceae* because they appear to facilitate the release of OCP residues from soil much more than other plant species (2).

One option to reduce OCP uptake by crop plants from polluted soils is to immobilize the pesticides by adding binding agents. In particular, activated carbon (AC) has been proposed to immobilize organic contaminants in soils (3, 4). More specifically, this approach was also applied to horticultural soils with OCP residues (5, 6). AC reduced dieldrin concentrations in cucumbers up to 57% and 66% in two recent studies (5, 6).

Given that total OCP concentrations are poor predictors of OCP uptake by plants and that OCP may be taken up by cucumbers, although OCP concentrations in soil solution are below the detection limit (7), it would be very desirable for risk identification purposes to know an extraction method that can be used to predict the phytoavailability of bound OCP residues. OCP extraction by means of Tenax beads is a method that has shown promising potential in this regard in previous studies. Tenax is a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide and is used as an infinite sink for the desorption of organic pollutants from sediments (8) and soils (9). The quantification of Tenax extractable fractions has been used by many researchers to assess the bioavailability of organic contaminants in these matrices. Extraction of organic contaminants for 6 h by Tenax usually captures the pollutant fraction that is most available for accumulation by organisms in soils and sediments (9−13). Tenax extractions can also be used to characterize the accessibility of hydrophobic contaminants to organisms (14). Accessibility determined by Tenax or another mild extraction method is an operationally defined parameter (15) that is independent from the properties and behavior of recipient organisms (7).

To our knowledge, Tenax has never been applied in the context of phytoavailability assessments of organic pollutants. The goal of this study was to explore the suitability of Tenax beads as extractants to assess the phytoavailability of dieldrin, an important representative of OCP, from a historically contaminated horticultural soil to cucumbers. If feasible, this would present a simple and fast method for risk identification and a valuable decision-making tool in agricultural soil management. Concomitantly, Tenax extractions could also serve as a long-term quality control measure of pollutant sequestration by AC amendment. In particular, the objectives of the study were (i) to characterize the desorption kinetics of native dieldrin from control and AC amended soil by consecutive Tenax extractions; (ii) to assess the influence of cucumber cultivation on dieldrin availability as quantified by Tenax extractions; and (iii) to evaluate the prediction potential of Tenax extractions for dieldrin uptake by cucumbers by correlating Tenax extractable dieldrin before cucumber cultivation with the dieldrin content of cucumber fruits at harvest.

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MATERIALS AND METHODS

Materials and Reagents. Powdered activated charcoal (AC) was obtained from Norit SX Ultra, Sigma Aldrich GmbH (Buchs, Switzerland) and fulfilled the US food chemical codex (*16*). Tenax beads 60–80 mesh, 177–250 μm were purchased from MS Wil GmbH (Wil SG, Switzerland). Hydromatrix was purchased from Separtis (Grenzach-Wyhlen, Germany) and NaN$_3$ ($\geq$99.0%) from Fluka (Buchs, Switzerland). All materials and chemicals used in the experiments and for the chemical analysis of the soil and the cucumber samples are listed in Hilber et al. (*5*).

Cultivation of Cucumbers in AC Amended, Dieldrin Contaminated Soil. We performed two pot experiments in a nonclimatized greenhouse in which cucumber plants (*Cucumis sativus* L.) were grown in horticultural soil, one in 2006 and the second in 2007. The cultivation of the cucumbers and the AC treatment of the soil were described previously by Hilber et al. (*5*). Briefly, the soil (2.2% organic carbon, 9.9% clay, 62.6% silt, and a pH of 6.3) was mainly contaminated with dieldrin (70 μg kg^{-1}) and to a much lesser degree ($<$10 μg kg^{-1} in each case) by the following compounds: pentachloroaniline, *p,p'*-DDE, *o,p'*-DDD, and *o,p'*-DDT (*17*)). Five-liter pots were used in all experiments, and each AC treatment was carried out in six replicates. AC was added to the soil at concentrations of 200, 400, and 800 mg$_{AC}$ kg^{-1}. The control soil was not amended with AC, but treated similarly. The AC was added to tap water and then mixed into the soil. The amount of water added with the AC was calculated to result in a water content of 50% of the soil's water holding capacity (WHC). After the soil was filled into the pots, it remained in the green house for eight days. Thereafter, the soil was irrigated with 0.3 L of water per pot, and the 16-day old cucumber plants grown from seeds were planted, one plant per pot. During the growth periods, the soil was fertilized once a week with a mineral nutrient fertilizer solution of 0.1%. The mineral fertilizer was added dissolved in the irrigation water according to the plant's growth stage. Cucumbers were harvested once they were ripe, in 2006 after 13 weeks and in 2007 after 11 weeks. In 2006, cucumbers were growing more slowly because of less favorable temperature and air humidity than in 2007.

Consecutive Tenax Extractions. Consecutive Tenax extractions were conducted as in Cornelissen et al. (*18, 19*) with moist soil collected from the 2007 experiment after the cucumbers had been harvested. About five soil cores were taken per pot from three pots with untreated soil (0 mg$_{AC}$ kg^{-1}) and three pots treated with 800 mg$_{AC}$ kg^{-1} soil. The five cores of each pot were bulked to a composite sample of 40 to 50 g each. Additionally, a separate soil sample was taken from each pot in order to determine the water content by oven-drying for 24 h at 100 °C.

Prior to each use, the Tenax beads were rinsed with acetone, hexane, and demineralized water (10 mL g^{-1} Tenax) for 30 min and dried overnight at 100 °C. Deionized water (150 mL) and 3 g of Tenax were added to each of the soil samples (40–50 g) in 250 mL glass bottles, type Schott Duran (Mainz, Germany) with PE screw cap, immediately after sampling. This amount of Tenax was considered sufficient to accommodate the total amount of dieldrin present in the samples. Similar (*20*) or even orders of magnitude higher amounts of organic compounds have been absorbed to Tenax in previous studies (*8, 21*). The Schott bottles were closed and horizontally shaken at 175 rpm. The Tenax beads were exchanged after 1, 7, 31, 199, 535, and 1039 h. Prior to this experiment, we tested whether dieldrin would be degraded over time. For this purpose 30 mg of NaN$_3$ (*8*) was added to some preliminary soil samples and extracted for 1, 7, 31, and 199 h. No significant difference in dieldrin concentration between NaN$_3$ containing and NaN$_3$ free samples was observed (data not shown). The addition of NaN$_3$ was therefore considered unnecessary.

At the defined times, the Tenax beads were removed by skimming and exchanged by another 3 g. If necessary, water was added to the mark indicated at the beginning of the experiment to compensate for losses. OCP were extracted from the Tenax beads by adding 30 mL of *n*-hexane for a few seconds. Losses of dieldrin were compensated for by spiking the samples with 0.04 mL of a 10 μg mL^{-1} ^{13}C$_{12}$-dieldrin solution in isooctane as extraction standard. The extracts were evaporated to 2 mL in a six position Syncore Analyst (Büchi Flawil, Switzerland) and further concentrated to 0.2 mL by a Supelco Visidry (Supelco Buchs, Switzerland) with N$_2$ gas. Tetrachloronaphthalene (TCN; 0.01 mL of a 1 μg mL^{-1}

solution in isooctane) was added as an injection standard to the concentrated sample and analyzed by gas chromatography–mass spectrometry (GC-MS; Agilent, HP 6890/5973, Agilent Technologies Basel, Switzerland). The GC-MS method is described in Hilber et al. (*5*). Dieldrin concentrations of 0, 1000, 2000, and 5000 ng mL^{-1} were used to establish a linear calibration curve with 2000 ng mL^{-1} ^{13}C$_{12}$-dieldrin as internal standard.

For mass balance assessment, one replicate of the control and AC amended soil sample was analyzed after 199 h and the soil slurry subjected to accelerated solvent extraction (ASE; Hilber et al. (*5*)). About 10 g of soil slurry was filled onto and covered with about 1 g of hydromatrix packed in a stainless-steel cell. Losses of dieldrin were controlled by the use of the respective ^{13}C$_{12}$-dieldrin analogue as extraction standard, which was spiked to soil samples as 0.02 mL of a 10 μg mL^{-1} solution in isooctane. Each ASE cell was extracted twice (extraction program as in Hilber et al. (*5*)). The two extracts were combined and dried over about 20 g of MgSO$_4$. The extracts were analyzed by GC-MS in the electron impact mode as described by Hilber et al. (*5*). ASE extractions, the consecutive Tenax extractions, and corrections of the soil losses during the experiment accounted for 95 to 102% of the total extractable dieldrin present in the system.

Single Tenax Extractions. Single Tenax extractions were carried out with the pot soils at cucumber harvest (2006 and 2007). For each AC treatment, six replicate extractions were performed (see Cultivation of Cucumbers in AC Amended, Dieldrin Contaminated Soil). Additional Tenax extractions were carried out with pot soils from 2006 prior to cucumber planting and after 13 weeks in unplanted AC amended soil.

One composite soil sample was collected from each pot by taking several cores that were then bulked, mixed, air-dried, and sieved to 250 μm grain size. For the extraction, we followed the procedure proposed by Ten Hulscher et al. (*9*). One gram of soil sample was filled into a separation funnel together with 1.5 g of Tenax beads and 70 mL of deionized water. After six hours of continuous shaking on a horizontal shaker (SM 25, Haska AG, Bern Switzerland) at 175 rpm, the Tenax beads were separated from the soil suspension. The separation was easy and rapid because the soil sank to the bottom, whereas the Tenax beads floated on top or adhered to the glass wall of the separation funnel. OCP extractions from the Tenax beads were conducted as described before. Losses of dieldrin were controlled by spiking the samples with 0.04 mL of a 1 μg mL^{-1} ^{13}C$_{12}$-dieldrin solution in isooctane as extraction standard. Dieldrin was analyzed by GC-MS as described by Hilber et al. (*5*). Dieldrin concentrations of 0, 50, 100, 200, and 300 ng mL^{-1} were used to develop a matrix-matched, linear calibration curve with 200 ng mL^{-1} ^{13}C$_{12}$-dieldrin as internal standard. Mean relative standard deviation for each extraction time and two AC treatments for duplicates was 11.5%.

Dieldrin Analysis in Cucumber Samples. The analysis of cucumber fruits was described previously by Hilber et al. (*5*). Immediately after harvest, the cucumber fruits were washed, cut coarsely (e.g., 3 × 3 cm), and put into a freezer (−80 °C). Subsequently, the samples were analyzed for dieldrin according to QuEChERS (*22*). From the cryogenically milled (mill type Kneubühler AG Luzern, Switzerland) and homogenized sample, a subsample of 5 g was extracted with 5 mL of acetonitrile (ACN). Losses of dieldrin were compensated for by the use of the respective ^{13}C$_{12}$-dieldrin analogue as extraction standard, which was spiked to cucumber samples as 0.025 mL of a 10 μg mL^{-1} solution in isooctane. The sample was shaken vigorously by hand for 1 min, and the QuEChERS salt mixture was added. The sample was shaken again and centrifuged by a Labofuge 200 (Heraeus AG, Zurich, Switzerland). A subsample of 1 mL of the supernatant was cleaned and dried. Additionally, a liquid/liquid extraction not foreseen in the QuEChERS method was performed from ACN to isooctane as a further cleanup step. Therefore, 2 mL of isooctane was added to 1 mL of ACN. The liquids were shaken for 1 min by vortex (HASKA AG, Bern, Switzerland), and the isooctane was collected in 10 mL reaction vials. This procedure was repeated twice. The isooctane was concentrated afterward to 0.2 mL, transferred to GC-MS vials, and the injection standard was added (TCN, 0.01 mL of a 1 μg mL^{-1} solution in solvent isooctane). The samples were measured by GC-GC-MS configuration according to Bucheli and Brändli (*23*). Dieldrin was detected in single ion monitoring (SIM) mode, using [237]$^{-•}$/[239]$^{-•}$ for dieldrin, and [242]$^{-•}$/[244]$^{-•}$ for ^{13}C$_{12}$-dieldrin as quantifying and qualifying ions, respectively. OCP concentrations of 0, 1, 5, 10, 50, and 100 ng mL^{-1} were used to develop a matrix

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matched, linear calibration curve with 25 ng mL^{-1} ^{13}C$_{12}$-dieldrin as internal standard. Absolute recoveries ranged from 60 to 122% and relative recoveries from 92 to 112%. Limit of detection for dieldrin in this method was 0.8 ng g^{-1} cucumber fresh weight. All blanks were below the detection limit. The coefficient of variation for method precision ranged from 11.2 to 31.2% (n = 2).

Data Analysis. The following first order rate model was used to identify three different desorption kinetics, i.e., a rapidly, a slowly, and a very slowly desorbing fraction (F_{rap}, F_{slow}, and $F_{v.slow}$ = 1 − F_{rap} − F_{slow}), respectively, according to Cornelissen et al. (*18*):

$$\frac{C_{cum.des}(t)}{C_{tot}(\infty)} = 1 - (F_{rap}e^{-k_{rap}t} + F_{slow}e^{-k_{slow}t} + F_{v.slow}e^{-k_{v.slow}t}) \quad (1)$$

$C_{cum.des}(t)$ is the cumulative desorbed dieldrin concentration [ng g^{-1}] at time t [h], $C_{tot}(\infty)$ [ng g^{-1}] is the total dieldrin concentration at infinite time corresponding to the totally extractable dieldrin concentration by ASE (70 ng g^{-1}), and k_{rap}, k_{slow}, and $k_{v.slow}$ [h^{-1}] are the desorption rate coefficients for the respective compartments.

Analysis of variance (ANOVA) and Bonferroni tests were used to elucidate any differences of the dieldrin Tenax extractions from 2006 with and without plants. Significance was indicated if the *p*-value was ≤0.05.

RESULTS AND DISCUSSION

Comparison of Desorption Kinetics from Control and AC Amended Soil, Determined by Consecutive Tenax Extractions. Dieldrin extractions from the unamended (control) soil and the soil amended with 800 mg$_{AC}$ kg^{-1} in the experiment of 2007 were modeled using a triphasic desorption model (eq 1). The cumulative extraction is depicted in **Figure 1** for the control and the AC amended soil. The calculated rapidly, slowly, and very slowly desorbing initial fractions as well as the corresponding rate constants are listed in **Table 1**. The rate constants of k_{rap}, k_{slow}, and $k_{v.slow}$ for dieldrin in both soils (**Table 1**) were similar to those reported in the literature for PAHs, PCBs, and chlorobenzenes (*7, 12, 18−20, 24, 25*).

According to the model, the F_{rap} fraction desorbed within a short time of about an hour (**Figure 1**). The F_{slow} fraction was depleted after about 100−200 h. These results from the control soil indicate that both the fast and the slow dieldrin fractions probably had enough time to redistribute with AC in the AC amended soil over the contact time of 11 weeks, although pot soils were not water-saturated. Note that some 40−50% of the total ASE extractable dieldrin amount (70 ng g^{-1}) was not available to Tenax desorption within the investigated time period of 1000 h.

At any given extraction time and for all replicates, less dieldrin desorbed from the AC amended than from the control soil (**Figure 1**). ANOVA revealed a significant influence of the AC amendment (*p*-value = 0.036). If AC amendment is an effective measure, F_{rap} or F_{slow} should decrease while $F_{v.slow}$ should increase. In fact, **Table 1** as well as **Figure 1A,B** show an increased $F_{v.slow}$ in the AC amended soil compared to that in the un-amended soil. $F_{v.slow}$ was about 8.6% higher in the AC amended soil compared to that in the unamended soil at the beginning of the Tenax experiment. In contrast, F_{slow} was lower in the AC amended soil than in the control soil. Hence, AC amendment provoked a shift from dieldrin formerly bound in F_{slow} to $F_{v.slow}$. These results agree well with those of Moermond et al. (*26*) who found that black carbon caused slow desorption of PCBs and PAHs and that it reduced biota-to-sediment accumulation factors (BSAF) describing the transfer of these compounds to benthic invertebrates. Other researchers (*27−29*) also have shown that AC acts as a superadsorbent with very slow release kinetics.

From **Figure 1A,B** and **Table 1**, it is difficult to assess whether overall phase distribution equilibrium of dieldrin in the AC
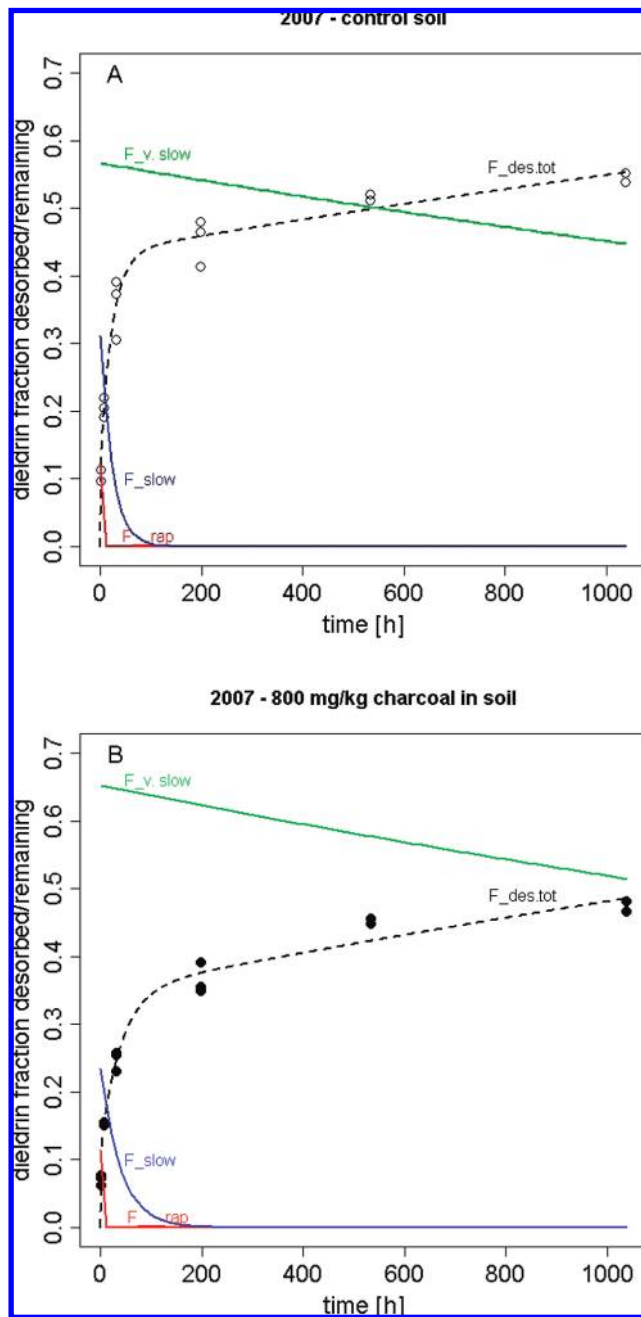

Figure 1. Cumulative desorption (empty and filled circles) of dieldrin from and fractions remaining in the control soil (**A**) and the soil treated with 800 mg$_{AC}$ kg^{-1} (**B**) over time in 2007. The dashed lines through the data points represent the fitted model curves of the totally Tenax extracted dieldrin. The colored lines represent the dieldrin remaining in the rapid (red), slow (blue), and very slow (green) fractions. Dieldrin desorbed fractions are obtained by dividing individual concentrations by the total ASE extractable concentration of 70 ng g^{-1}.

amended soil was reached. Still, some qualitative comparisons with literature data concerning AC amendment can be made, which are illustrative. Morelis and van Noort (*30*) determined the kinetics of phenanthrene (a compound with an octanol−water partition coefficient similar to that of dieldrin) desorption from different activated carbons. Similar to our totally desorbed dieldrin fraction (**Figure 1B**), they found continuously increasing desorption from high energy (HE) sites (average Gibbs free energies for adsorption at 298 K were fairly constant at −15 ± 4 and −5 ± 4 kJ mol^{-1} for the HE and low energy (LE) domains,

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Table 1. Rapidly, Slowly, and Very Slowly Desorbing Fractions at Initial Time and Corresponding Rate Constants of Dieldrin in the Soils as Determined by the Model (eq 1)

	control soil	AC amended soil (800 mg$_{AC}$ kg^{-1} soil)
Fractions [-][a,b]		
F_{rap}	0.12 ± 0.03	0.12 ± 0.02
F_{slow}	0.31 ± 0.04	0.23 ± 0.02
$F_{v.slow}$	0.57	0.65
Desorption Rates [h^{-1}][a,b]		
k_{rap}	1.29 ± 0.76	0.82 ± 0.29
k_{slow}	0.04 ± 0.01	0.03 ± 0.006
$k_{v.slow}$	0.0002 ± 0.00006	0.0002 ± 0.00004

[a] Estimated from the model (eq 1). [b] $\pm$ standard error.

respectively (*31*)) over a time of 3500 h. This suggests that organic compounds are not irreversibly adsorbed by AC but can be desorbed again very slowly. The influence of time and soil cultivation on Tenax extractability was therefore studied and is presented in more detail below.

The treatment of 800 mg$_{AC}$ kg^{-1} soil reduced the total Tenax desorbable dieldrin (F$_{des.tot}$) by roughly 0.1 after 1039 h (**Figure 1**). At the same time, it increased F$_{v.slow}$ by about 0.05. This corresponds to an absolute increase of about 3.5 to 7.0 ng g^{-1} dieldrin, i.e., 5 to 10% of the total dieldrin (70 ng g^{-1}). If we assume that it were basically these 5 to 10% which migrated from the native soil to AC and consider the amount of AC added, we estimate the amount of dieldrin bound to AC to range from 4.4 to 8.8 μg g^{-1} AC. These concentrations can be compared with dieldrin adsorbed to AC during the removal from drinking water. Ormad et al. (*32*) achieved 85% removal of initially 500 ng L^{-1} dieldrin by adding 10 mg L^{-1} of an AC that was comparable (1000 m^2 g^{-1}, 40 μm particle size) to the one used here (1200 m^2 g^{-1}, 25 μm particle size). This removal corresponds to a one-point log K_{AC} of 5.75 L kg^{-1}. The load of about 42 μg dieldrin per g AC in their study is a factor of 5 to 10 higher than that in our case. Hence, it seems that the AC adsorption capacity was not fully exploited in our experiment. Several reasons may account for this: (i) the overall phase distribution equilibrium of dieldrin in the AC amended soil was not yet reached; (ii) only about 60% of the total dieldrin was available for redistribution in the first place (40% was not Tenax extractable within the given time frame); and (iii) AC adsorption sites might have been attenuated by soil constituents (*33*).

Using the model (eq 1), we also calculated the 6 h desorbed fraction from the consecutive Tenax extractions in both soils. About two-thirds of it consisted of the complete fast desorbing fraction, whereas the other third was the slowly desorbing fraction. Thus, a 6 h extraction, which is commonly suggested as an indicator of the bioavailable fraction, comprises also of the slowly desorbing fraction in our case. Nevertheless, we decided to approximate the phytoavailable dieldrin in the cucumber experiments with the common extraction time of 6 h for reasons of simple and fast handling, and to be able to compare our single Tenax extractions with results from other researchers (*9, 12*).

Influence of Cucumber Growth on Dieldrin Availability Assessed by 6 h Tenax Extractions. Note that the data presented here are not directly comparable to those discussed above in **Figure 1** because of the different soil sampling time (2006 after 13 weeks and 2007 after 11 weeks) and soil processing (drying and sieving vs moist processing; for details see Materials and Methods). For instance, control soils with cucumbers yielded a 6 h Tenax extractable dieldrin of about 60 ng g^{-1} in 2006 (**Figure 2**, week 13, plants, unamended soil) but only some 7 ng g^{-1} in 2007
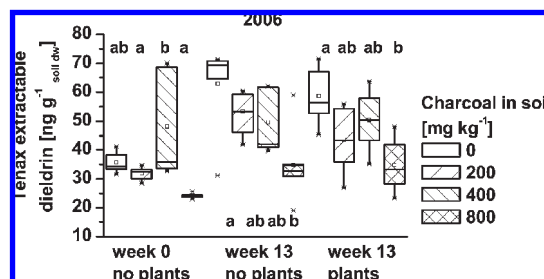

Figure 2. Tenax extractable (6 h) dieldrin concentrations at the beginning and end of the experiment in 2006 in ng g$_{dw}^{-1}$ in soil and dependence of activated charcoal (AC) amendments. Box plots represent six replicates, and those with different letters differ significantly according to the Bonferroni test. Boxes represent the interquartiles (from 25% to 75%) of the samples, the line in the box shows the median, the small square indicates the arithmetic mean, whiskers indicate the smallest and highest nonoutlier values, and the crosses below and above the boxes the 1% and 99% percentile, respectively.

(**Figure 1A**). Nevertheless, relative comparisons of the data obtained from samples treated identically (as done in this and in the above section, respectively) are reasonable and justified.

The concentrations of Tenax extractable dieldrin were in general significantly (*p*-value = 0.0001) smaller at the beginning than at the end of the growth period in the 2006 experiment (**Figure 2**). In the soil amended with 400 mg$_{AC}$ kg^{-1}, the Tenax extractable dieldrin concentrations varied strongly, although the median was similar to that in the other treatments. Overall, the AC amendments reduced Tenax extractable dieldrin concentrations. This effect increased with the duration of the experiment (data not shown). Bonferroni tests showed that Tenax extractable dieldrin was significantly reduced in the 800 mg$_{AC}$ kg^{-1} soil compared to that in the control soil at the end of the experiment, but not at the beginning (after AC-soil contact time of eight days). Bonferroni tests include multiple comparisons. Thereby the *p*-value is multiplied with the number of comparisons (6), making the test very restrictive. As a consequence, the difference of Tenax extractable dieldrin between control soil and AC soil at the beginning of this experiment was not significant, although the box plots do not overlap. According to the ANOVA, the addition of AC had a significant effect on Tenax extractable dieldrin also at the beginning (*p*-value = 0.001) and not only at the end (*p*-value = 0.006) of the 2006 experiment. The presence of plants made no difference on the increase of Tenax extractable dieldrin over the duration of the experiment (*p*-value = 0.295) and did not affect the effectiveness of AC amendment.

The difference between unplanted soil sampled at the beginning and the end of the experiment was that the soil had undergone many wetting and drying cycles during this time. White et al. (*34*) reported that soil wetting and drying increased the extractability of aged organic compounds. Makeyeva (*35*) found that wetting and drying increased the specific internal soil surface, and Smit et al. (*36*) found faster desorption rates of dieldrin in sediments with small particle size fractions than with large ones. All together, we hypothesize that grinding and repeated wetting and drying of our soil probably facilitated the Tenax extraction of dieldrin to such an extent that it was capable of desorbing amounts as high as those extracted by ASE (70 ng g^{-1} dw, **Figure 2**, week 13 no plants, unamended soil). With respect to the agricultural use of such soils, this finding poses questions as to the mobility and phytoavailability of aged OCP residues.

Only at the highest AC amendment was there little change in Tenax extractable dieldrin with time (*p*-value = 0.097), indicating that any mobilized dieldrin was effectively bound by the AC,

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which is important in practical applications of such amendments. This result is also in line with the observed increase in the very slow desorption fraction in the AC amended soil (see above).

Correlation of Tenax Extractable Dieldrin in Soil with Dieldrin Uptake by Cucumbers. To evaluate the prediction potential of Tenax extractions for dieldrin uptake by cucumbers, we compared the Tenax extractable dieldrin at the beginning of the experiment with the dieldrin withdrawal by cucumbers. The cucumber plants extracted about 1 to 2 orders of magnitude less dieldrin over 11 and 13 weeks than the Tenax beads within 6 h (**Figure 3A,B**). Three main causes are likely to be responsible for this large difference. First, Tenax beads were mixed in a soil/water suspension, where diffusion of dieldrin happened without physical limit. In contrast, the plant roots probably repeatedly faced unsaturated pore water conditions. Second, Tenax beads were in contact with a suspension of all soil particles, whereas the plant roots were only in touch with a minor fraction of the soil. Third, the processing of the soil samples used for the Tenax extractions by air-drying, sieving, and resuspension may have mobilized fractions of dieldrin that were not available before.

The relationship between the Tenax and the cucumber plant extractable dieldrin differed among the two years. In 2007, Tenax extraction varied quite strongly between AC treatments, while plant uptake was not affected much. In contrast, in 2006 dieldrin uptake by cucumbers depended less on the AC treatments, but the cucumber size caused variation in dieldrin withdrawal, while Tenax extractions remained unaffected by AC amendments. The results show that the dieldrin uptake by plants was not limited by the pool of available dieldrin represented by the Tenax

extractions (or, conversely, that the Tenax extractions greatly overestimated the phytoavailable dieldrin fraction). After deleting two outlier values in the 2006 data and one in the 2007 data, the correlation between Tenax extractable dieldrin and dieldrin uptake into cucumbers was significant for 2007 (p-value = 0.001, R^2 0.4) but not for 2006 (p-value = 0.43, R^2 0.04). Still there was only a weak relationship between the two variables for both years. The relationship was essentially the same for the cucumber fruits as for the whole plants because the uptake of OCP into plant organs other than fruits was minor (data not shown). Similar correlations were tested for dieldrin concentrations of cucumbers versus Tenax extractable dieldrin concentrations at harvest, but they were of no significance for both years. We think that the weak correlation was caused by the strongly contrasting temporal scales of the parameters. The 6 h Tenax extraction captures only a momentary situation of pollutant availability, whereas cucumbers are exposed to dieldrin over the whole time of growth, which includes and integrates parameters of importance for availability and uptake of pollutants, such as temperature, humidity, wet−dry cycles, and so forth. This was already indicated by the variability of 6 h Tenax extraction data as presented and discussed above (**Figure 2**, week 0 no plants vs week 13 no plants).

In the literature, there are further examples of weak or nonexistent correlations between Tenax extraction and bioavailability. Morrison et al. (*37*) found correlations between earthworm uptake and Tenax extraction for DDT and its metabolites but not for dieldrin. Smreczak et al. (*38*) found a strong positive linear relationship between the inhibition of nitrification and the concentration of Tenax extractable phenanthrene in soil. But in that study, the soil was freshly contaminated, and the contaminant concentrations were several orders of magnitude higher than those in our study.

We conclude, that Tenax extractions are probably not an ideal measure to reflect long-term uptake by plants. Nevertheless, they may still be suitable to reflect short-term exposure situations and uptake by soil organisms that interact more intensely with the matrix. Moreover, Tenax extractions mirrored the AC effect, and this method could therefore be used as a quality control measure for in situ remediation strategies such as AC amendment. These areas of research deserve further investigations.

Figure 3. Withdrawal (% of the total dieldrin in soil) of dieldrin by cucumbers at the end of the experiments in 2006 (**A**) and 2007 (**B**) vs 6 h Tenax desorbed dieldrin at the beginning expressed in percent of the total mass of dieldrin in the soil pots with different amounts of AC. The growth period was 13 and 11 weeks in 2006 and 2007, respectively.

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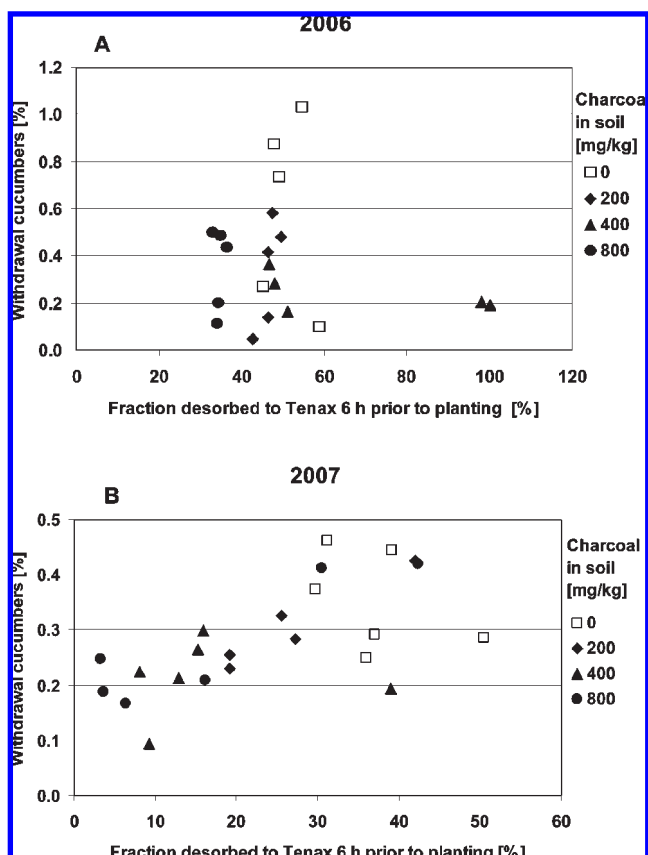
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