

Reduction of dieldrin uptake from contaminated soil by cucumber (*Cucumis sativus* L.) using activated charcoal amendment

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extended abstract

Introduction

Although, organochlorine pesticides (OCP) are banned nowadays in most countries, they can still be present in soils and taken up by crop plants. 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 (1). One option to reduce OCP uptake by crop plants from polluted soils is to immobilize the pesticides by adding binding agents. The goal of this study was to evaluate the potential of soil amendments with powdered activated charcoal (AC) and its concentrations to reduce the uptake of dieldrin residues, an important representative of OCP, by cucumber plants (*Cucumis sativus* L.) from a contaminated horticultural soil.

Given that total OCP concentrations are poor indicators of OCP uptake by plants it would be very desirable to know an extraction method that can be used to indicate the phytoavailability of bound OCP residues. OCP extraction by means of Tenax® beads is a method that showed promising potential in this regard in previous studies. Tenax® is a porous polymer and used as an infinite sink for the desorption of organic pollutants from soils (2) and sediments (3). We therefore explored the suitability of Tenax® beads as extractant to assess the phytoavailability of dieldrin soil to cucumbers from the same soil. Concomitantly, Tenax® extractions could also serve as a long-term quality control measure of pollutant sequestration by AC amendment. Further objectives of this study were to characterize desorption kinetics of native dieldrin from control and AC amended soil by consecutive Tenax® extractions, and to assess the influence of cucumber cultivation on dieldrin availability to cucumber plants as quantified by Tenax® extractions.

Material and Methods

We performed two pot experiments (2006 and 2007) in which cucumber plants (*Cucumis sativus* L.) were grown in horticultural soil. The cultivation of the cucumbers and the AC treatment of the soil were described previously by Hilber et al. (4). Briefly, the soil selected from a Swiss survey (5) was mainly contaminated with weathered dieldrin ($70 \mu\text{g kg}^{-1}$). Five-litre pots were used in all experiments and each AC treatment (0, 200, 400, and $800 \text{ mg}_{\text{AC}} \text{ kg}^{-1}$ soil) was carried out in six replicates. After the AC-amended soil was filled into the pots, it remained in the green house for eight days. Thereafter, the soils were irrigated with 0.3 L water per pot and the 16-days old cucumber plants grown from seeds were planted, one plant per pot. Cucumbers were harvested once they were ripe, in 2006 after 13 and in 2007 after 11 weeks. The analysis of dieldrin in cucumber fruits was described previously by Hilber et al. (4) and by Anastassiades et al. (6).

Consecutive Tenax® extractions were conducted with moist, untreated (0 mg_{AC} kg⁻¹), and treated soil (800 mg_{AC} kg⁻¹) from the 2007 experiment after the cucumbers had been harvested. Deionised water (150 mL) and 3 g Tenax® were immediately added to each of the soil samples (40-50 g) in Schott bottles after sampling. The bottles were closed and horizontally shaken at 175 rpm. The Tenax® beads were exchanged by another 3 g after 1, 7, 31, 199, 535, and 1039 hours by skimming. OCP were extracted from the Tenax® beads by adding 30 mL n-hexane for a few seconds. The analysis of Tenax® extracts (consecutive and single) was described by (7).

The following first order rate model was used to identify three different desorption kinetics/fractions (F_{rap} , F_{slow} and $F_{v.slow} = 1 - F_{rap} - F_{slow}$), according to Cornelissen et al. (8):

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

$C_{cum.des}(t)$ 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 accelerated solvent extraction (ASE), and k_{rap} , k_{slow} , $k_{v.slow}$ [h⁻¹] are the desorption rate coefficients for the respective compartments.

Single (6 h) Tenax® extractions were carried out with pot soils from 2006 prior to cucumber planting, and after 13 weeks in planted and unplanted AC amended soil. For the extraction we followed the procedure proposed by Ten Hulscher et al. (3). One gram of soil sample was filled into a separation funnel together with 1.5 g Tenax® beads and 70 mL deionised water. After six hours of shaking horizontally at 175 rpm, the Tenax® beads were separated from the soil suspension and treated similarly to the consecutive extractions.

Results and discussion

Dieldrin concentrations in cucumber fruits ranged from 2 ng g⁻¹ fw in AC treated soils to about 12 ng g⁻¹ fw in a control soil, and concentrations were equal or lower in AC amended soils than in their controls (Figure 1). In 2006, the AC treatments significantly reduced dieldrin concentrations by almost a factor of three (see lower case letters above columns). In contrast, they had no effect at all on dieldrin concentrations in 2007. AC comparisons by the Bonferroni test of the pooled data (see capital letters above columns) revealed significant reductions of dieldrin between 400 and 800 mg_{AC} kg⁻¹ amendments compared to the control soil. The data illustrate that AC amendment is – under certain conditions – capable of changing a situation where tolerance values are surpassed (2006 cucumbers from control soil) into one which are satisfactory.

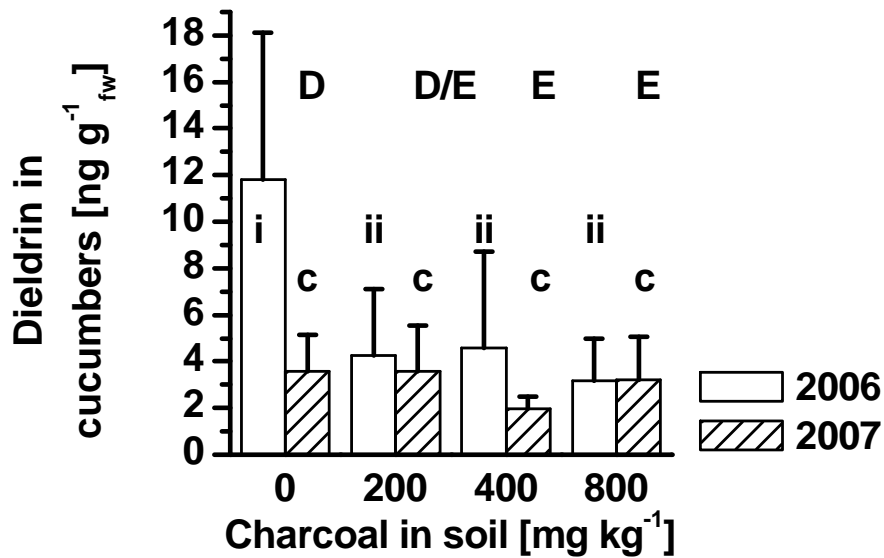


Figure 1: Dieldrin concentrations in $\text{ng g}^{-1}_{\text{fw}}$ in cucumbers in dependence of activated charcoal (AC) amendments and year. The growth period was 13 and 11 weeks in 2006 and 2007, respectively. Error bars are standard deviations of 6 replicates. In Bonferroni tests, columns of the same year with different letters differ significantly and capital letters indicate the pooled years.

Dieldrin Tenax® extractions from the control soil and the soil amended with $800 \text{ mg}_{\text{AC}} \text{ kg}^{-1}$ were modelled using eq. 1. The cumulative extraction is depicted in Figure 2 for the control and the AC amended soil, respectively.

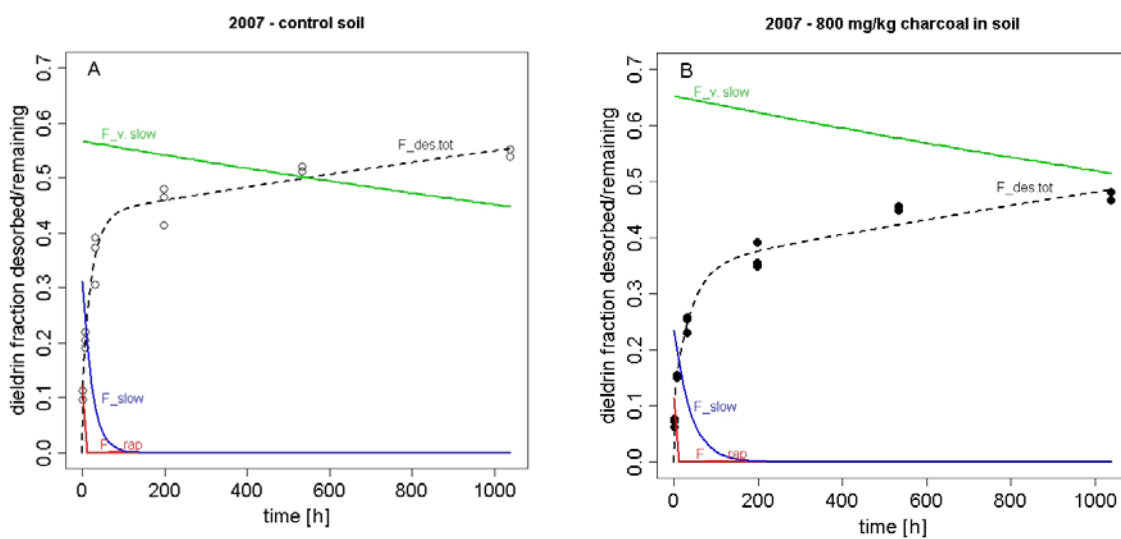


Figure 2A&B: Cumulative desorption of dieldrin from and fractions remaining in the control soil (A) and the soil treated with $800 \text{ mg}_{\text{AC}} \text{ kg}^{-1}$ (B) over time in 2007. The dashed lines through the data points represent the fitted model curves of the totally Tenax® extracted

dieldrin, coloured lines represent the dieldrin extracted from the rapidly (red), slowly (blue), and very slowly (green) desorbing fractions.

According to the model, the F_{rap} fraction desorbed within a short time of about an hour (Figure 2). The F_{slow} fraction was depleted after about 100 – 200 hours. These results from the control soil indicate that both the fast and the slow dieldrin fraction 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 1000h. Less dieldrin desorbed from the AC amended than from the control soil. If AC amendment is an effective measure, F_{rap} or F_{slow} should decrease while $F_{v,slow}$ should increase. In fact, Figures 2A&B show an increased $F_{v,slow}$ in the AC amended soil compared to the control soil. $F_{v,slow}$ was about 8.6% higher in the AC amended soil compared to the unamended soil. 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 $F_{v,slow}$.

The concentrations of single Tenax® extractable dieldrin from planted and unplanted pots were significantly smaller at the beginning than at the end of the growth period in the 2006 experiment (Figure 3). Overall, the AC amendments reduced Tenax® extractable dieldrin concentrations. This effect increased with the duration of the experiment. Bonferroni tests showed that Tenax® extractable dieldrin was significantly reduced in the $800 \text{ mg}_{AC} \text{ kg}^{-1}$ soil compared to the control soil at the end of the experiment, but not at the beginning. The presence of plants made no difference on the increase of Tenax® extractable dieldrin over the duration of the experiment, and did not affect the effectivity of AC amendment.

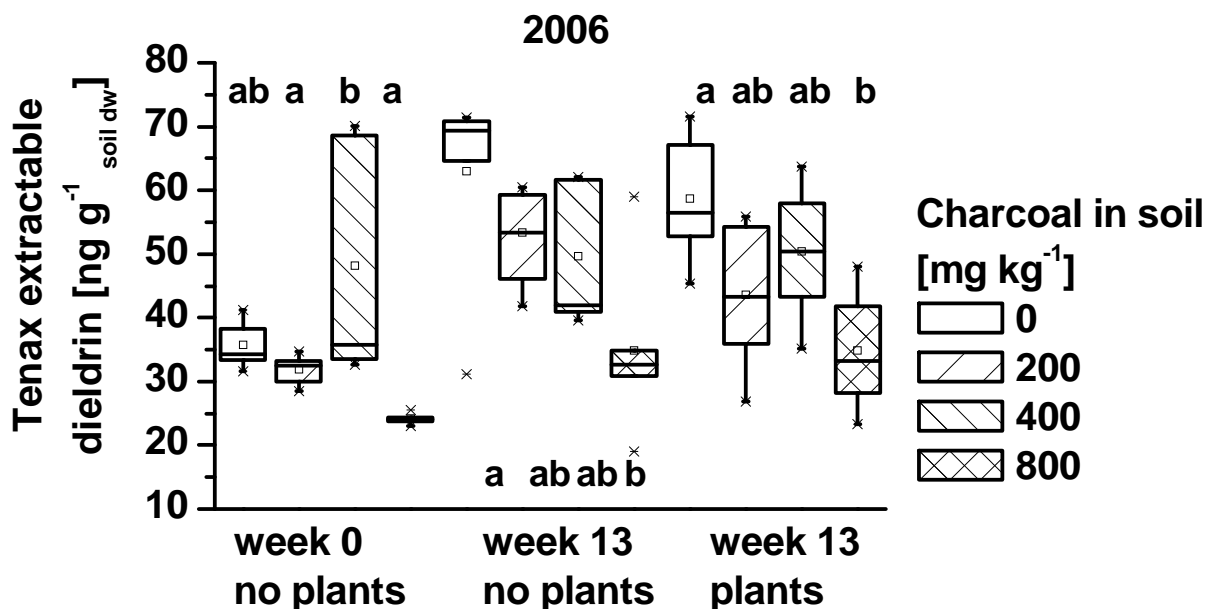


Figure 3: Tenax® extractable (6h) dieldrin concentrations at the beginning and the end of the experiment in 2006 in ng g^{-1}_{dw} in soil and dependence of activated charcoal (AC) amendments. Box plots represent six replicates, and those with different letters differ significantly according to the Bonferroni test.

Conclusions

AC amendment of 800 mg_{AC} kg⁻¹ could reduce the dieldrin fw concentrations by 0-66% compared to the untreated soil. At the highest AC amendment there was no significant change in 6h Tenax® extractable dieldrin with time, indicating that any mobilized dieldrin was effectively bound by the AC, 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. We conclude, that Tenax® extractions are probably not an ideal measure to reflect long-term uptake by plants. But Tenax® extractions mirrored the AC effect. 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.

References

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