

Desorption, Persistence, and Leaching of Dibenzofuran in European Soils

R. Celis,* M. Real, M. C. Hermosín, and J. Cornejo

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) and their heterocyclic analogs (hetero-PAHs) represent the predominant chemical classes in many contaminated soils. Despite the fact that hetero-PAHs are more soluble and hence potentially more mobile and bioavailable than similar nonsubstituted compounds, the existing information about the fate of these compounds in the soil environment is limited. In this article, laboratory experiments were designed to assess the desorption, persistence, and leaching behavior of the hetero-PAH dibenzofuran in four European soils with different physicochemical characteristics. Previous research has shown that organic matter was important in the extent of sorption of dibenzofuran by the soils studied, although sorption was not predictable exclusively from the organic carbon content. Dibenzofuran desorption isotherms showed little hysteresis, in particular from higher equilibrium points of the sorption isotherms, indicating weak interaction mechanisms between dibenzofuran and the soils. The half-life of dibenzofuran in the soils during incubation experiments ranged between 5 and 55 d, depending on soil type and experimental conditions. In general, the persistence of dibenzofuran decreased with the organic carbon content of the soils (0.56–2.09%) and with temperature (4°C/20°C) and increased with the initial concentration of the chemical in soil (10 mg kg⁻¹/100 mg kg⁻¹). Leaching tests, performed in hand-packed and undisturbed soil columns, indicated that dibenzofuran is likely to move slowly through the soil profile, although dissolved organic matter and soil structure can influence the amount of dibenzofuran leached. The effect of dissolved organic matter on leaching of dibenzofuran was found to be soil dependent and less important than the effect of soil structure.

SOIL and ground water contamination by polycyclic aromatic hydrocarbons (PAHs) and their heterocyclic analogs (hetero-PAHs) containing N, S, or O is a widespread problem in industrialized countries. These organic compounds represent the predominant chemical classes in soil of former coal gasification sites, tar oil distillation plants, and wood-preserving facilities (Meyer and Steinhart, 2001). Oil spills, leakages, and pyrolytic sources, such as incomplete combustion, significantly contribute to the input of these chemicals into the environment (Traulsen et al., 1999). Soils contaminated with creosote, a product of high-temperature treatment of hard coal, contain hundreds of different organic compounds where PAHs constitute about 85%, hetero-PAHs 5–15%, phenolic compounds 1–10%, and monoaromatic hydrocarbons < 1% (Broholm et al., 1999; Meyer et al., 1999).

Because of the presence of the heteroatom, hetero-PAHs have larger water solubilities than the corresponding PAHs (Meyer et al., 1999), which may result in

greater mobility and bioavailability compared with similar nonsubstituted compounds. For instance, when water comes in contact with creosote, polar compounds are enriched in the aqueous phase, and the fraction of hetero-PAHs increases to 35 to 40%, whereas the fraction of PAH compounds decreases to about 15% (Kiilerich and Arvin, 1996; Broholm et al., 1999). Therefore, regarding ground water contamination arising from contaminated soils, hetero-PAHs usually represent a larger problem than PAHs (Johansen et al., 1997; Broholm et al., 1999). In fact, high concentrations of hetero-PAHs, such as thiophene, benzothiophene, dibenzothiophene, benzofuran, dibenzofuran, pyridines, quinolines, indole, and carbazole, have been detected in ground water at creosote-contaminated sites (Johansen et al., 1997). In addition, the larger presence of these compounds in the aqueous phase compared with nonsubstituted compounds enhances their bioavailability and consequently the risk of ecological and human effects. In this regard, a number of hetero-PAHs have been reported to display toxic, mutagenic, and carcinogenic properties, even when present in low concentrations (Meyer et al., 1999).

Although they can be more mobile and bioavailable than their nonsubstituted analogous, little is known about the environmental fate of hetero-PAHs (Traulsen et al., 1999; Meyer and Steinhart, 2000). In fact, the heteroaromatic compounds containing nitrogen, sulfur, or oxygen in the aromatic ring are not normally included in the chemical analysis of contaminated sites. The polar metabolites from the degradation of creosote are not usually analyzed (Kiilerich and Arvin, 1996). Extensive knowledge about the environmental fate of the more hydrophilic fraction of compounds present in contaminated soils has been stressed as important in improving risk assessments and success evaluation of remediation technologies (Langbehn and Steinhart, 1994; Meyer et al., 1999; Vila et al., 2003).

The present study was designed to provide insight into the fate of an oxygen-substituted hetero-PAH (dibenzofuran) in four European soils differing in their physicochemical characteristics. The sorption behavior of dibenzofuran in a number of soils, including those selected for this study, was reported in a previous article (Celis et al., 2006). Here, batch, incubation, and column leaching tests were designed to assess the desorption, persistence, and leaching behavior of dibenzofuran in selected soils. Because dissolved organic matter can strongly influence the transport of hydrophobic organic compounds, such as PAHs and related compounds, by formation of dissolved organic matter (DOM)-solute complexes (Rav-Acha and Rebhun, 1992; Sabbah et al.,

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Abbreviations: BTC, breakthrough curve; DOM, dissolved organic matter; HPLC, high-performance liquid chromatography; PAHs, polycyclic aromatic hydrocarbons.

2004), the effect of dissolved organic matter on dibenzofuran leaching was also investigated.

MATERIALS AND METHODS

Chemical and Soils

Dibenzofuran ($C_{12}H_8O$) is a three-ring heteroaromatic compound of molecular weight 168 g mol^{-1} and water solubility about 5 mg L^{-1} at 25°C (Fig. 1). Dibenzofuran of purity $> 99\%$, purchased from Sigma (Madrid, Spain), was used in this study.

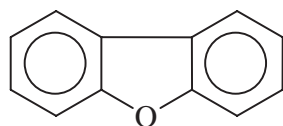
Four agricultural soils from different edaphoclimatic regions of Europe were selected for this study. The soils were sampled from the top 0- to 20-cm layer, air dried, and passed through a 2-mm aperture sieve before their use in the experiments. Relevant physicochemical characteristics of the soils are given in Table 1. The procedures followed for soil characterization are described in Celis et al. (2006).

Sorption–Desorption Experiments

Dibenzofuran sorption–desorption isotherms on soils were obtained by the batch equilibration procedure using glass centrifuge tubes closed with Teflon caps. Triplicate soil aliquots (0.5 g) were equilibrated with 10 mL of aqueous solutions of dibenzofuran by gently rotating in an end-over-end shaker (30 rpm) at $20 \pm 2^\circ\text{C}$ for 24 h. A preliminary kinetic experiment showed that an apparent equilibrium was reached within 24 h and that no significant degradation occurred during this period. Initial dibenzofuran solutions (5, 10, 15, and $20 \mu\text{M}$) were prepared in 10 mM CaCl_2 from a stock 10 mM dibenzofuran solution prepared in acetone. The amount of acetone in the initial dibenzofuran solutions was therefore $< 0.2\%$. After equilibration, the suspensions were centrifuged at $5000 \times g$ for 1 h, and 5 mL of the supernatant solution was removed using a glass pipette for subsequent analysis by high-performance liquid chromatography (HPLC) as described below. The amount of dibenzofuran sorbed was calculated by difference between the initial and final solution concentrations. Initial solutions without soil were shaken for 24 h and served as controls.

Desorption was measured immediately after sorption from the two equilibrium points of the sorption isotherms corresponding to the initial concentrations 10 and $20 \mu\text{M}$. The 5 mL of supernatant removed for the sorption analysis were replaced with 5 mL of 10 mM CaCl_2 solution. After shaking at $20 \pm 2^\circ\text{C}$ for 24 h, the suspensions were centrifuged, and the concentration of dibenzofuran was determined in the supernatant. This desorption procedure was repeated three times. All sorption and desorption experiments were conducted in triplicate.

Sorption–desorption isotherms were fitted to the Freundlich equation: $C_s = K_f C_{eq}^n$, where C_s ($\mu\text{mol kg}^{-1}$) is the amount of chemical sorbed at the equilibrium concentration C_{eq} ($\mu\text{mol L}^{-1}$), and n (unitless) and K_f ($\mu\text{mol}^{1-n} \text{ L}^n \text{ kg}^{-1}$) are the empirical Freundlich constants, which can be calculated from the



Dibenzofuran

Fig. 1. Molecular structure of dibenzofuran.

Table 1. Physicochemical characteristics of the soils used.

Soil property	P2	Askov	Borris	Kettering
Country of origin	Spain	Denmark	Denmark	UK
Soil texture [†]	SCL	SL	SL	SCL
Sand [‡] , %	68.4	68.4	69.8	47.2
Silt [‡] , %	10.4	18.8	20.5	24.7
Clay [‡] , %	20.3	10.4	6.9	24.5
Inorganic C, %	< 0.1	ND [§]	ND	< 0.1
Organic C, %	0.56	1.39	1.67	2.09
CEC [¶] , $\text{cmol}_c \text{ kg}^{-1}$	22.8	10.6	11.8	19.2
pH	7.3	6.3	6.4	6.7

[†] SCL, sandy clay loam; SL, sandy loam.

[‡] Differences between the sum sand + silt + clay and 100% correspond to the organic matter + carbonate content of the soils.

[§] ND, not detected.

[¶] CEC, cation exchange capacity.

linear plot of $\log C_s$ against $\log C_{eq}$. Hysteresis coefficients, H , were calculated according to $H = n_{des}/n$, where n and n_{des} are the Freundlich n constants obtained from the sorption and desorption isotherms, respectively (Barriuso et al., 1994; O'Connor et al., 1980).

When sorption was determined at a single initial concentration of $10 \mu\text{M}$, a distribution coefficient, K_d (L kg^{-1}), was calculated by dividing the amount of chemical sorbed, C_s ($\mu\text{mol kg}^{-1}$), by the equilibrium solution concentration, C_{eq} ($\mu\text{mol L}^{-1}$).

Incubation Experiment

The dissipation curves of dibenzofuran in the different soils were obtained by means of an incubation experiment in which the soils (500 g) were spiked with dibenzofuran at two different concentrations (10 and 100 mg kg^{-1} air-dried soil), following a spiking protocol based on that proposed by Brinch et al. (2002). Briefly, a subsample of 25% of the air-dried and sieved soil (125 g) was wetted with 60 mL distilled water and spiked with 15 mL of an acetone solution of dibenzofuran (2 or 20 mM) to give the final concentrations of 10 and 100 mg kg^{-1} soil. The spiked 125 g-soil aliquot was thoroughly homogenized, and the acetone was allowed to evaporate for 16 h. After evaporation of the solvent, the remaining 75% of the soil (375 g) was mixed with the spiked soil subsample by adding sequentially three portions of 125 g of unspiked soil. To compensate for the solvent lost during evaporation, the moisture content was re-adjusted to 15% (w/w) with distilled water. The spiked soils were incubated in glass jars at two different temperatures (4 and 20°C) for 72 d. The moisture content was maintained at a constant level throughout the experiment by adding distilled water as necessary. The soils were sampled periodically and frozen until analyzed. Dibenzofuran was extracted by shaking 10 g of duplicate soil samples with 15 mL of acetonitrile for 24 h, and the extracts were analyzed by HPLC. A preliminary experiment showed that this extraction procedure recovered $> 95\%$ of the dibenzofuran freshly applied to the soils.

Leaching Experiments

We studied leaching of dibenzofuran under hand-packed (homogeneous) and undisturbed soil conditions. The effect of dissolved organic matter on leaching of dibenzofuran was also investigated. The hand-packed soil columns consisted of 20-cm length \times 3-cm i.d. glass columns filled with air-dried and sieved soil (P2, Askov, Borris, and Kettering). Glass wool plus 10 g of sea sand was placed on the bottom of the columns to prevent losses of soil and contamination of leachates with soil particles. The columns were hand-packed with 180 g of soil, and 10 g of sea sand was placed on the soil surface. The undisturbed soil columns consisted of 20-cm length \times 20-cm i.d. PVC col-

umns filled with undisturbed P2 soil, taken from the field plot located in Sevilla (Spain). The hand-packed and undisturbed columns were saturated with water and allowed to drain for 24 h, and the amount of dibenzofuran corresponding to an application rate of 10 or 100 kg ha⁻¹ was applied to the top of the columns dissolved in acetone. After application of the chemical, the columns were leached with 20 mm d⁻¹ of distilled water or a dissolved organic matter extract for 20 d. The dissolved organic matter extract consisted of a diluted commercial humic amendment (Liquid Fertiomont, Fertilizantes Montañío, Spain) containing an amount of dissolved organic C of approximately 6 g L⁻¹ (Cox et al., 2000). Leachates from the hand-packed and undisturbed soil columns were collected daily and analyzed by HPLC. At the end of the leaching experiment, soil samples of approximately 50 g were taken from different depths of the columns (0–5, 5–10, 10–15, and 15–20 cm depth) and extracted once with 100 mL of acetonitrile by shaking mechanically at 20 ± 2°C for 24 h. The suspensions were centrifuged (30 min at 5000 × g), filtered, and analyzed by HPLC to determine the amount of dibenzofuran at different depths of the soil columns. All leaching experiments were conducted in triplicate.

Analysis of Dibenzofuran

Dibenzofuran was determined by HPLC using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector.

The following chromatographic conditions were used: Novapack C18 column (150 mm length × 3.9 mm i.d.) (Waters), acetonitrile/water (70:30) eluent mixture at a flow rate of 1 mL min⁻¹, 25-μL injection volume, and UV detector at 280 nm. External calibration curves with standard solutions of dibenzofuran between 1 and 500 μM were used in the calculations.

RESULTS AND DISCUSSION

Sorption–Desorption

The sorption behavior of dibenzofuran by a number of soils, including those selected for this work, has been reported in detail by Celis et al. (2006). The results indicated that organic matter plays a primary role in the sorption of dibenzofuran, although sorption was not predictable exclusively from the organic C content of the soils. Thus, soils with greater clay contents (Kettering and P2) were found to present smaller organic C-normalized sorption coefficients, K_{oc} , than those containing less amount of clay (Borris and Askov). Organic matter heterogeneity and domain blockage arising from organic matter-clay interactions and associated pH shifts seemed to be the most likely causes of the different K_{oc} values for the soils (Celis et al., 2006).

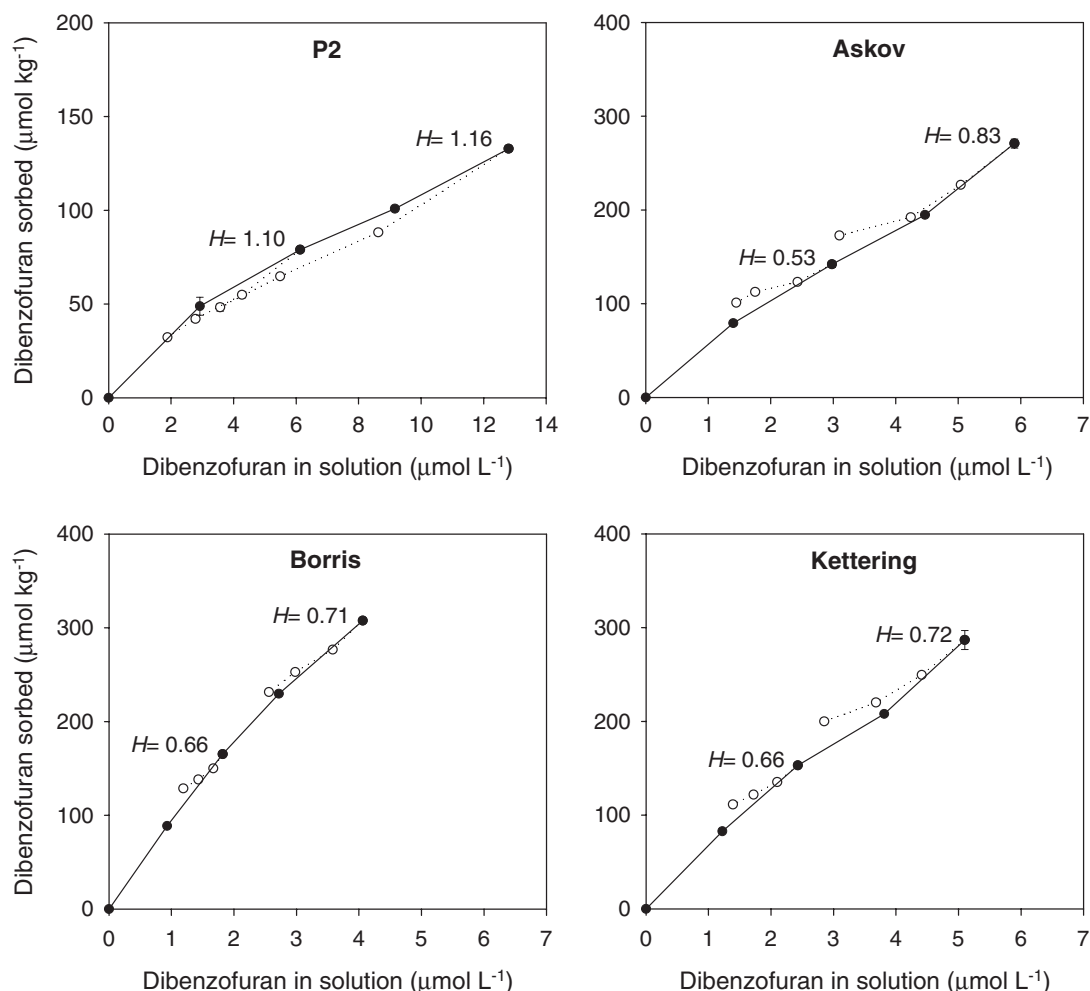


Fig. 2. Dibenzofuran sorption–desorption isotherms on soils and hysteresis coefficients, $H = n_{des}/n$, calculated at two points of the sorption isotherms.

Dibenzofuran desorption isotherms showed little hysteresis with $H (= n_{des}/n)$ values ≥ 0.53 (Fig. 2), indicating that weak interaction mechanisms predominate between dibenzofuran and the soils. For all four soils, the hysteresis coefficient (H) corresponding to the initial concentration $10 \mu M$ was found to be smaller than that measured at the initial concentration $20 \mu M$ (Fig. 2). This behavior has been observed for the sorption of other organic compounds in soil and has been attributed to sorption site heterogeneity, where the existing irreversible, high-energy sorption sites are occupied first (i.e., at lower concentration) (Celis and Koskinen., 1999; Albarrán et al., 2003). Nevertheless, for the Askov, Borris, and Kettering soils, hysteresis was evident at the last desorption steps only (Fig. 2). Taking into account that appreciable degradation of dibenzofuran occurred in these soils within 3 to 5 d, in particular at low concentration of dibenzofuran (see below), degradation could have contributed to the observed hysteresis during the last desorption steps (Koskinen et al., 1979).

Persistence

Dissipation curves for dibenzofuran in the four soils at two temperatures and two spiking concentrations are given in Fig. 3. The sigmoidal shape of the dissipation curves are typical of degradation of compounds used as

microbial growth substrate (Kearney et al., 1997), with lag periods ranging from 3 to 50 d depending on soil type, temperature, and spiking concentration. According to Fig. 3, the half-life of dibenzofuran in the soils tested ranges from about 5 to 55 d, depending on soil type and experimental conditions. In general, degradation of dibenzofuran occurred faster in the Kettering soil and slower in the P2 soil (except at $4^\circ C/100 \text{ mg kg}^{-1}$), presumably reflecting differences in the microbial activity of these soils as a result of their different organic matter contents (Table 1). The degradation curves for dibenzofuran in the Askov and Borris soils, with similar organic matter contents, were similar. The persistence of dibenzofuran in all four soils decreased with temperature ($4^\circ C/20^\circ C$) and increased with the initial concentration of the chemical in soil ($10 \text{ mg kg}^{-1}/100 \text{ mg kg}^{-1}$). Therefore, the soil organic matter content, initial concentration of dibenzofuran, and temperature were important factors determining the persistence of dibenzofuran in the soils studied.

Leaching

Less than 0.03% of the dibenzofuran applied to the hand-packed soil columns was recovered in the leachates. At the end of the leaching experiment (i.e., after application of 400 mm of water within a 28-d period) and

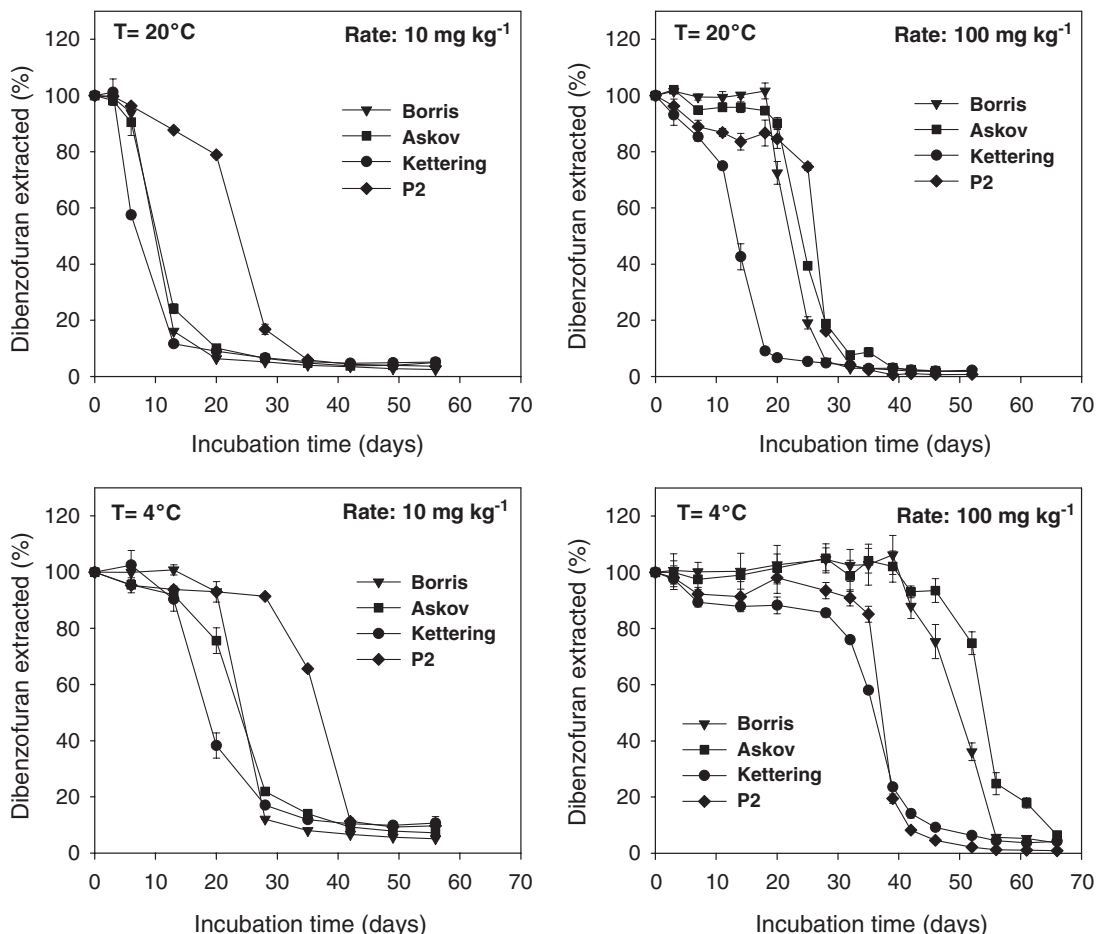


Fig. 3. Dissipation curves of dibenzofuran in soils at different temperatures and initial concentrations.

for the two application rates tested (10 and 100 kg ha⁻¹), dibenzofuran accumulated in the top 0 to 10 cm of the soils (Fig. 4). The P2 soil also presented an appreciable amount of dibenzofuran in the 10- to 15-cm soil layer. These results reflect a slow movement of dibenzofuran along the soil columns. The slightly greater breakthrough of dibenzofuran in the low organic matter content P2 soil can be related to the low sorption of dibenzofuran by this soil (Celis et al., 2006).

The total amounts of dibenzofuran extracted from the hand-packed soil columns at the end of the leaching experiment (Fig. 4) ranged from 12 to 65% of the amount applied for the experiment at 10 kg ha⁻¹ and from 27 to 87% when dibenzofuran was applied at 100 kg ha⁻¹. For all four soils, the percentage of dibenzofuran recovered from the soil columns at the end of the leaching experiment increased with the amount applied. Assuming the amounts not recovered are due to degradation of the organic compound during the leaching experiment, degradation of dibenzofuran was exacerbated at the lower application rate. This finding agrees with the results of the incubation experiment (Fig. 3) and with the effect of the application rate on the degradation of organic compounds in soil reported by other authors (Gan et al., 1995; Beigel et al., 1999). Also in accordance with the incubation results, degradation of dibenzofuran during column leaching was greatest for the Kettering soil. Nevertheless, taking into account the

duration of the leaching experiment (28 d), degradation of dibenzofuran under column leaching conditions seemed to be less pronounced than that observed after the same experimental period in the static incubation test at 20°C (Fig. 3). Similar differences in persistence under batch and column leaching conditions have been reported, suggesting that the persistence of contaminants during soil leaching processes can be greater than expected from measurements conducted in static batch systems (Evans, 1998; Celis et al., 2005).

Dissolved organic matter influenced the leaching of dibenzofuran through hand-packed columns of the Borris and P2 soils, but the effect was soil dependent. Thus, DOM enhanced the amount of dibenzofuran leached when added to the Borris soil, but it reduced the leaching of the compound when added to the P2 soil (Fig. 5). To explain this result, we should consider that DOM can exert two different effects on the sorption of organic solutes by sorbent surfaces (Rav-Acha and Rebhun, 1992; Celis et al., 1998): (i) reduction in sorption due to solubilization effects and competition on sorbent sites and (ii) enhancement of sorption when the solute-DOM complex has a greater affinity to the sorbent than the organic solute itself. In fact, we determined a K_d value for dibenzofuran (initial concentration 10 μ M) in the Borris and P2 soils in the presence and absence of the DOM extract and found that DOM reduced the K_d value of dibenzofuran in the Borris soil

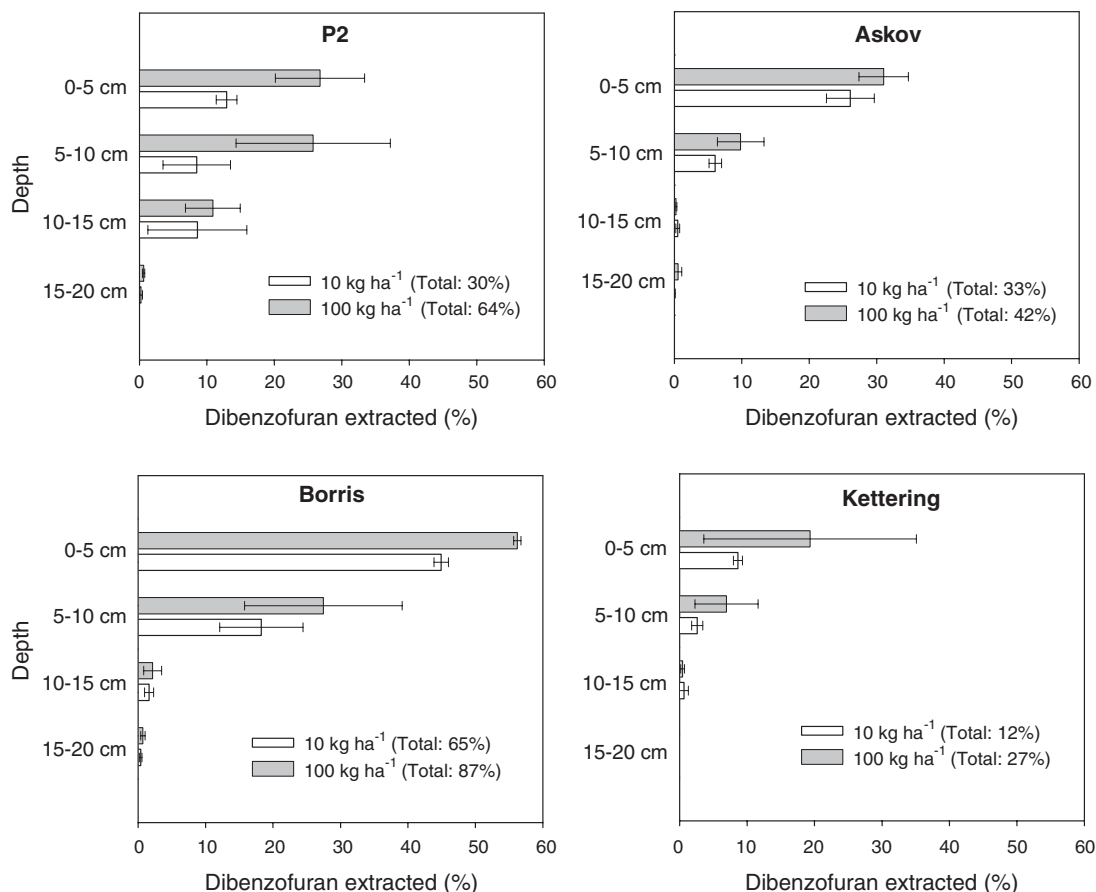


Fig. 4. Dibenzofuran extracted from different depths of hand-packed soil columns at the end of the leaching experiment.

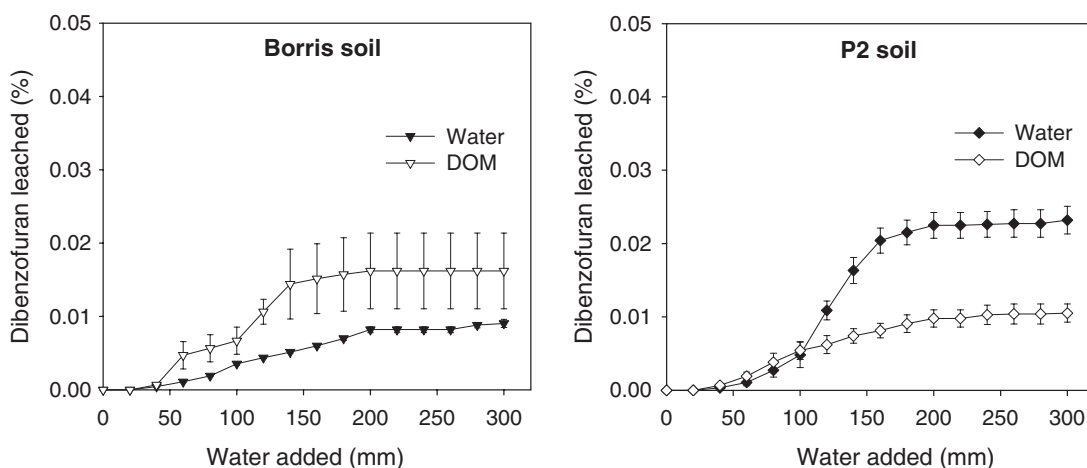


Fig. 5. Cumulative breakthrough curves (BTCs) of dibenzofuran in hand-packed columns of Borris and P2 soils eluted with water and with dissolved organic matter (DOM). Dibenzofuran was applied at 100 kg ha⁻¹ in all cases.

(from 63 to 45 L kg⁻¹) but led to an increase in the K_d value of dibenzofuran in the P2 soil (from 17 to 33 L kg⁻¹). Previously, an increase in the aqueous solubility of dibenzofuran from 4.4 mg L⁻¹ (in water) to 13.2 mg L⁻¹ (in the DOM extract) demonstrated the interaction between the organic compound and the DOM. These results strongly suggest that facilitated transport of dibenzofuran as DOM-pollutant complexes operated in Borris soil, whereas preferential sorption of those complexes by soil particles operated in P2 soil, reducing the leaching of the organic compound (Fig. 6). The most likely cause of the different behavior observed for the Borris and P2 soils is their different clay content (Table 1) because clay is known to be a major component in binding to DOM and in reducing the movement of DOM through the soil profile (Cornejo and Hermosín, 1996; Shen, 1999; Cox et al., 2000).

Figure 7 shows the breakthrough curves (BTCs) for dibenzofuran (100 kg ha⁻¹) in undisturbed columns of the P2 soil eluted with water and with DOM. For comparison purposes, the BTC of dibenzofuran in hand-

packed columns of the P2 soil has been included in Fig. 7. The total amount of dibenzofuran recovered in leachates from the undisturbed soil columns was small (0.54% of the amount applied to the top of the columns), revealing little leaching of the compound (Table 2). Nevertheless, this amount was about 25 times greater than that observed under hand-packed conditions (0.023%). This result strongly suggests that preferential flow through macropores can be a major mechanism for dibenzofuran leaching through soil. It also illustrates how soil manipulation can have a large effect on leaching measurements/results. The variability associated with the BTCs of dibenzofuran under undisturbed conditions (Fig. 7) can be related to the inherent heterogeneity of soil structure.

As found in hand-packed conditions, dibenzofuran accumulated in the top 0–10 cm of the undisturbed soil columns (not shown), supporting slow movement

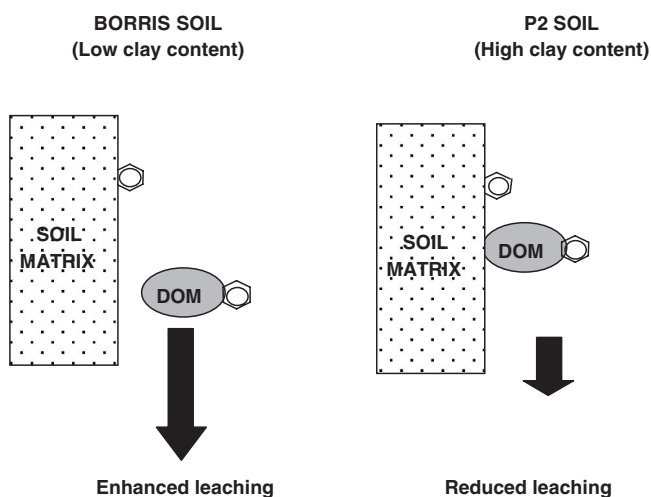


Fig. 6. Possible mechanisms operating during dibenzofuran leaching through the Borris and P2 soils in the presence of dissolved organic matter (DOM).

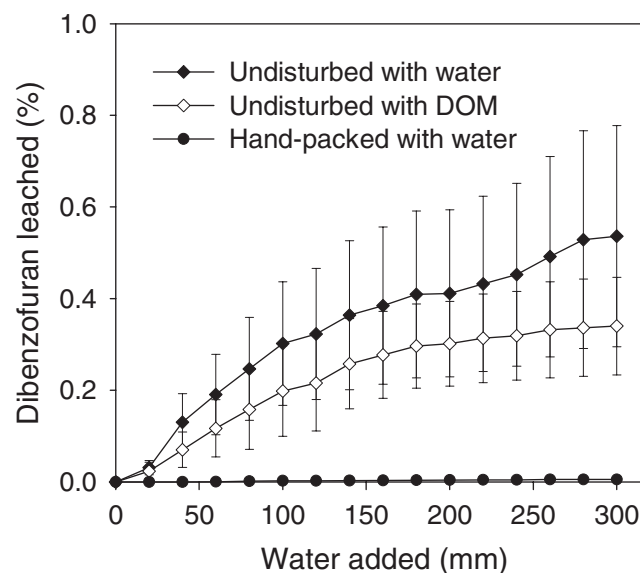


Fig. 7. Cumulative breakthrough curves (BTCs) of dibenzofuran in hand-packed (eluted with water) and undisturbed (eluted with water and with dissolved organic matter [DOM]) columns of P2 soil. The application rate was 100 kg ha⁻¹ in all cases.

Table 2. Dibenzofuran leached, extracted from the soil column, and not recovered during leaching experiments with the P2 soil.

	Hand-packed columns		Undisturbed columns	
	Eluted with water	Eluted with DOM	Eluted with water	Eluted with DOM
Leached, %	0.023 ± 0.002†	0.010 ± 0.001	0.54 ± 0.24	0.34 ± 0.11
Extracted from soil, %	64 ± 17	80 ± 2	27 ± 2	45 ± 1
Not recovered, %	35.98	19.99	72.46	54.66

† Value ± standard error.

through a matrix-flow mechanism. However, the total recovery of dibenzofuran from the undisturbed soil columns (27%) was less than the amount recovered from the hand-packed soil columns (64%) (Table 2). This could have been the result of enhanced degradation of the compound under undisturbed soil conditions.

The effect of DOM on leaching of dibenzofuran under undisturbing conditions was to reduce leaching in P2 soil (Fig. 7, Table 2), as found under hand-packing conditions (Fig. 5). Nevertheless, differences were not statistically significant due to the large variability associated with the dibenzofuran BTCs in undisturbed columns (Fig. 7). As seen in Fig. 7, the effect of soil structure and the inherent spatial variability associated with the undisturbed soil columns seemed to be the major factors influencing the leaching of dibenzofuran in soil, with DOM playing a secondary role.

CONCLUSIONS

Batch, incubation, and column leaching tests were designed to characterize the fate of dibenzofuran in four European soils with different physicochemical characteristics. The persistence of dibenzofuran in the soils during incubation experiments was influenced by the soil organic matter content, temperature, and initial concentration of dibenzofuran in soil, with dibenzofuran half-lives ranging from 5 to 55 d. The relatively high sorption of dibenzofuran by the soils studied resulted in slow matrix-flow of this compound through hand-packed and undisturbed soil columns. After application of 400 mm water, the amount of dibenzofuran leached from hand-packed and undisturbed columns were small (<0.03% and <0.6%, respectively), and dibenzofuran accumulated in the top 0 to 10 cm of the soil columns. The amount of dibenzofuran leached was affected by the presence of DOM and by soil structure (homogenized/undisturbed). The effect of DOM on dibenzofuran leaching was dependent on soil type and seemed to be considerably less important compared with the effect of soil structure. On the basis of the high organic carbon content of the DOM used in this study, the leaching of dibenzofuran under field conditions is expected to be dominated by the preferential flow associated with the inherent macroporosity of the unaltered soil structure rather than by matrix flow or DOM-facilitated transport.

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