

Long-term sorption behaviour of (4-chloro-2-methylphenoxy) acetic acid and phenanthrene in a cultivated soil

EDGAR HILLER^{1*}, VERONIKA TATARKOVÁ¹ and MIKULÁŠ BARTAL²

¹Department of Geochemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, SK-842 15 Bratislava 4, Slovak Republic; hiller@fns.uniba.sk

²High School of Chemistry, Račianska 78, Vlčie hrdlo 50, SK-821 07 Bratislava, Slovak Republic; mikulas.bartal@gmail.com

*Corresponding author

EDGAR HILLER: Comenius University in Bratislava, Faculty of Natural Sciences, Department of Geochemistry, Mlynská dolina, 842 15 Bratislava, Slovak Republic
e-mail: hiller@fns.uniba.sk, phone: +421 2/602 96 218, fax: +421 2 602 96 217

Abstract

The laboratory batch studies were conducted to evaluate the effect of the soil contact time (aging) on the sorption-desorption characteristics of phenanthrene and weak acid herbicide MCPA in one soil. Sorption isotherms were measured after the soil contact times of 2, 30, and 180 days. Desorption kinetic profiles were determined after 2 and 180 days to observe changes in organic chemical release from the soil. The sorption isotherms of two organic chemicals fitted well to the linear and the Freundlich sorption models and were practically linear at each soil contact time. The results indicated no increase in sorption of phenanthrene and MCPA in soil with increased contact time. Although the desorption equilibrium was achieved within 1 day for all of the systems evaluated, the extent of desorption decreased significantly for both organic chemicals, when contact time increased from 2 to 180 days. This result indicated that aging might affect the distribution of organic chemicals within sorption sites of the soil matrix.

Key words: sorption kinetics, aging, Freundlich isotherm, linear isotherm, desorption

Introduction

Recently, some studies of organic chemical sorption by soils have shown that sorption is not a rapid process and may take several hundreds of days to achieve sorption equilibrium (Park et al., 2004; Sharer et al., 2003a; Ball and Roberts, 1991). The tendency of sorbed organic chemicals to become more strongly retained with increased time has a significant impact on bioavailability, desorption, extractability and degradation of the aged residues. Conrad et al. (2002) documented a decline in pyrene extractability by organic solvents from the sediment and in its bioavailability to the oligochaete worm (*Lumbriculus variegatus*) with time. Hatzinger and Alexander (1995) observed that phenanthrene added to soil was increasingly more resistant with time to biodegradation and extraction by organic solvents. Moreover, the extent of desorption in soils decreased significantly with increased contact time for some chlorobenzenes and atrazine (Park et al., 2004; Lesan and Bhandari, 2003; Sharer et al., 2003a). These laboratory studies confirm the observed resistance to degradation and desorption of organic chemicals in the historically field-contaminated soils, where they have been in soil for the long time periods (Kan et al., 2000; Erickson

et al., 1993). It is believed that these observations are mainly due to the sequestration of significant amounts of compound in the interior sites of the soil with increasing soil contact time or aging (Alexander, 1995). Ignoring the above mentioned facts can lead to an underestimation of the true extent of sorption, wrong predictions about mobility and bioavailability of organic contaminants, and perhaps an overestimation of the health risks to humans and animals (Alexander, 2000).

The objective of this study was to extend the recent knowledge of the effects of soil contact time on the sorption-desorption behaviour of two organic chemicals with different water solubility and hydrophobicity in soil using well-controlled laboratory experiments. Sorption isotherms and desorption kinetics for phenanthrene and herbicide MCPA were obtained after 2, 30, and 180 days of incubation.

Methodology

A soil A-horizon (loamy-sand, Albic Luvisol) was collected from an agricultural field situated close to the village of Hažín, Michalovce district, eastern Slovakia. According to the Unified Trigonometric Land Network,

the agricultural field has the following coordinates: S-JTSK(x) = -207866.90 and S-JTSK(y) = -1237067.32. The soil was air-dried, crushed, and sieved through a 2 mm mesh. Selected soil properties were determined in the laboratory of the Slovak University of Agriculture in Nitra. The soil contains 30.8, 52.5, and 16.7 % sand, silt, and clay, respectively, with an organic carbon content of 1.21 % and pH value of 6.32. The soil clay fraction consisted mainly of illite, kaolinite, quartz, and smectite.

Phenanthrene and MCPA [(4-chloro-2-methylphenoxy)acetic acid] used in the sorption-desorption experiments as model organic contaminants were purchased from Aldrich Chemical Co. and Dr Ehrenstorfer GmbH, respectively. The physicochemical properties of the sorbates are shown in Table 1. The stock solution of phenanthrene was prepared by dissolving it in HPLC-grade methanol. Solutions of phenanthrene for the sorption-desorption experiments were prepared in the background aqueous solution consisting of 0.01 M CaCl₂ and 100 mg l⁻¹ NaN₃ dissolved in Milli-Q water. The NaN₃ was added to prevent biodegradation during batch studies. Four initial phenanthrene concentrations ranging from 0.05 to 1.05 mg l⁻¹ were used. The amount of methanol carrier added from the stock solution was always less than 0.05 % by volume. The stock solution of MCPA was prepared directly by shaking an amount of MCPA in 0.01 M CaCl₂ plus 100 mg l⁻¹ NaN₃ aqueous solution. Five different MCPA solutions with concentrations ranging from 0.5 to 100 mg l⁻¹ were prepared by diluting the stock solution with 0.01 M CaCl₂ and 100 mg l⁻¹ NaN₃ aqueous solution.

Altogether 300 mg (phenanthrene experiments) or 2 g (MCPA experiments) of soil were weighed into 12-ml glass centrifuge tubes enclosed in aluminium foil, and a 9-ml or 5-ml aliquot of phenanthrene or MCPA solution was added. After closure, the tubes were shaken on a reciprocating shaker for either 2 days (for the incubation time of 2 d) or 4 d (for the 30- and 180-d incubation times). After shaking, the tubes of 2-d incubation time were analysed immediately and the tubes of 30- and 180-d aging were stored in the dark with episodic shaking. After the given soil contact time, the duplicate samples were centrifuged for 30 min at 5 000 rpm, and supernatants were sampled for a high-performance liquid chromatography (HPLC) analysis. The control samples without soil were also prepared in the same way and used to account for possible losses due to volatilization and sorption of phenanthrene and MCPA to the centrifuge tubes. Average system losses

were shown to be consistently less than 3 % of the initial solute concentrations, therefore no correction was required. Analysis by HPLC confirmed that phenanthrene and MCPA were not degraded over the course of the 180 d experiment since only peaks with the same retention times as the standards were found. The amount of phenanthrene and MCPA sorbed was calculated by the difference between the amount initially added and that remaining in the solution after sorption.

For the desorption experiments, sorption was established as described above at a single initial phenanthrene and MCPA concentrations of 0.5 and 10 mg l⁻¹, respectively. The tubes were incubated for the time period of 2 and 180 d and manipulated as described above. Then, a 1-ml aliquot of phenanthrene and MCPA solutions were taken for HPLC analysis. The remaining supernatants were carefully removed (totally, 8 ml for phenanthrene and 3 ml for MCPA). Phenanthrene- or MCPA-free 0.01 M CaCl₂ solution amended with 100 mg l⁻¹ NaN₃ in the same volume as removed was added to the tubes to bring the volume back to the original. The tubes were shaken for 1 h, 5 h, 10 h, 1 d, 2 d, 3 d, 4 d and 5 d. At the appropriate time interval, duplicate tubes were centrifuged and the supernatants were analysed for phenanthrene and MCPA concentrations using HPLC analysis.

The concentrations of organic chemicals in the water before and after equilibration were analysed using a reverse-phase HPLC system (Hewlett-Packard model 1100) equipped with a fluorescence detector (Hewlett-Packard 1046A) set at 250 nm and 232 nm for phenanthrene and MCPA analysis, respectively. A Supelcosil LC-PAH 57945 and Lichrosphere-100 RP columns were used for analysis of phenanthrene and MCPA, respectively. External solution standards were used to establish linear calibration curves for a fluorescence detector. For phenanthrene, the mobile phase used was a mixture of acetonitrile and water (90:10 by volume). The mobile phase used for MCPA was a mixture of acetonitrile and 0.03 M acetic acid solution containing 5 % acetonitrile in a ratio of 50:50 (v/v) at a flow rate of 1.0 ml min⁻¹ (isocratic elution). The average uncertainty for the measured concentrations was about ±5 %.

Results and discussion

The sorption data for all three soil contact times fitted well to the linear sorption model ($S = K_dC$) and the Freundlich model ($S = K_fC^{1/n}$) where S denotes the concentration of

Tab. 1
Physicochemical properties of phenanthrene and MCPA

	Phenanthrene ^a	MCPA ^b
Molecular weight/g mol ⁻¹	178.2	200.6
Melting point/°C	99.5	117.0
Density/g cm ⁻³	1.17	1.56
Octanol-water partitioning coefficient logK _{ow}	4.57	0.46 (at pH 7)
Aqueous solubility at 25 °C S _w /mg l ⁻¹	1.29	825
Dissociation constant pK _a	–	3.07 (weak acid)

^aAs cited in Xia and Ball (1999); ^bAccording to Tomlin (2001)

sorbate in the soil (mg kg^{-1}), C is the sorbate concentration in solution after sorption (mg l^{-1}), K_d is the linear distribution coefficient (l kg^{-1}), K_f is the Freundlich sorption coefficient ($\text{mg}^{1-1/n} \text{kg}^{-1} \text{l}^{1/n}$) and $1/n$ describes curvature of the sorption isotherm. In general, the sorption isotherms for all systems at all soil contact times were linear with the $1/n$ values close to 1 and not statistically different from 1 at the 0.05 probability level (Fig. 1a, b and Table 2). As can be seen in Fig. 1a and Table 2, the sorption of phenanthrene did not increase from 2 to 180 d as the observed K_d values remained constant for contact times between 2 to 180 d. These results agree well with the observations of Kan et al. (1994) that sorption of phenanthrene reached equilibrium

within 1 d. However, Gamst et al. (2004) and Huang and Weber (1998) observed continuous increases in sorption of naphthalene and phenanthrene in soils for contact times ranging from 1 d to 21 d and from 1 d to 368 d, respectively. Several hypotheses regarding the observed slow sorption kinetics of hydrophobic organic chemicals have been proposed, however hindered intraparticle diffusion through the narrow pore network of the soil particles (Ball and Roberts, 1991) and through the soil organic matter (Weber and Huang, 1996; Brusseau et al., 1991) seem to be the more reasonable theories. Therefore, the constant sorption of phenanthrene observed in this study does not appear to support these theories, but as it was emphasized by Huang

Tab. 2

Linear distribution coefficients (K_d), organic carbon distribution coefficients ($K_{oc} = K_d/f_{oc}$) and Freundlich sorption parameters (K_f and $1/n$) for phenanthrene and MCPA sorption in soil

	Contact time (day)	K_d (l kg^{-1})	K_{oc} This study		K_f ($\text{mg}^{1-1/n} \text{kg}^{-1} \text{l}^{1/n}$)	$1/n$
Phenanthrene	2	117.2 (5.2) ^a	9 686	12 589-	138.8 (22.1) ^a	1.098 (0.091) ^a
	30	120.3 (11.3)	9 942	23000 ^b	205.6 (37.7)	1.299 (0.103)
	180	108.2 (4.0)	8 942	14 791 ^c	115.1 (21.0)	1.037 (0.107)
MCPA	2	0.39 (0.02)	32	27-156 ^d	0.56 (0.27)	0.919 (0.110)
	30	0.42 (0.02)	35	55-124 ^e	0.57 (0.20)	0.932 (0.081)
	180	0.43 (0.07)	36		0.31 (0.64)	1.078 (0.479)

^a95 % confidence interval in parentheses; ^bFrom Chiou et al. (1998) and Karickhoff et al. (1979); ^cValue from $\log K_{oc} = 0.989 \log K_{ow} - 0.346$ (Karickhoff, 1981); ^dFrom Socías-Vicianá et al. (1999); ^eFrom Hiller et al. (2008)

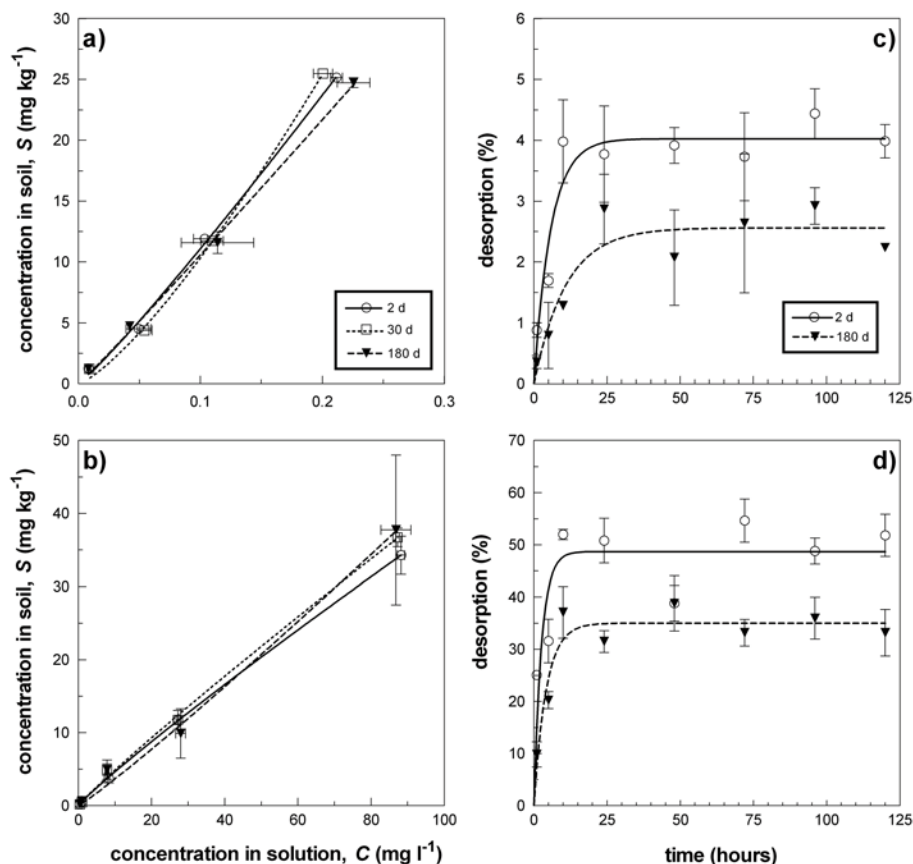


Fig. 1. Sorption isotherms for a) phenanthrene and b) MCPA at soil contact times of 2, 30, and 180 days, and percentage of desorption of c) phenanthrene and d) MCPA from soil versus time after soil contact times of 2 and 180 days. Error bars represent mean \pm standard deviation.

and Weber (1998), the differences in the reported sorption rates are likely in part due to differences in the initial concentration levels employed and the types of sorbent organic matter. The sorption of MCPA did not change with increasing soil contact time, as indicated by constancy of the K_d values (Table 2). This result contradicts with that obtained by Sharer et al. (2003b) who observed an increase in sorption of 2,4-D, the herbicide familiar to MCPA, with increased contact time. The authors hypothesized that the less polar organic chemicals would exhibit faster sorption kinetics than the polar organic chemicals and this was attributed to the increased reactivity of polar chemicals with polar functional groups of soil organic matter (Xing and Pignatello, 1996; Brusseau and Rao, 1989). The experimental organic carbon distribution coefficient value of phenanthrene ($K_{oc} = K_d/f_{oc}$) agreed well with other literature values (Chiou et al., 1998; Karickhoff et al., 1979) and that estimated from the phenanthrene K_{ow} value according to the regression equation of Karickhoff (1981) (Table 2). This result implies that phenanthrene partitioning into the soil organic matter was the predominant sorption mechanism. The K_{oc} value of MCPA is similar to those obtained in previous studies (Hiller et al., 2008; Socias-Viciana et al., 1999) and much lower compared with that of phenanthrene, reflecting its low sorption by the soil and high mobility. The differences in the sorption of phenanthrene and MCPA were obviously due to differences in their water solubilities and hydrophobicities, as commonly observed for other organic compounds (Briggs, 1981).

Desorption kinetic data are shown in Fig. 1c, d, where the desorbed amount was expressed as a percentage of the total sorbed amount. Desorption equilibrium was achieved within 1 d for all of the systems evaluated (Fig. 1c, d). However, as can be seen from Fig. 1c, d, the extent of desorption decreased significantly for both organic chemicals when contact time increased from 2 d to 180 d. After 2 d, approximately 4 % phenanthrene and 50 % MCPA were desorbed, while with prolonged contact time for 180 d only 2.5 % phenanthrene and 34 % MCPA could be desorbed in one desorption step. The decline in desorption extent of phenanthrene and MCPA with increased contact time reported in this study is consistent with observations from previous studies where nondesorbable fractions of different organic chemicals were found to significantly increase with increased aging (Sharer et al., 2003a, b). The effects of aging on the desorption of chemicals in soils are likely associated with continuous diffusion and retention of compound molecules into remote and inaccessible region within the soil matrix, although exact mechanisms of aging are still poorly understood. The results of this study as well as studies of soils from field sites with aged and freshly added organic chemicals (Erickson et al., 1993; Scribner et al., 1992; Pignatello and Huang, 1991; Steinberg et al., 1987) suggest that the extent of desorption decreases significantly with time of aging. Such reductions in desorption are found to be associated intimately with a decline in bioavailability and biodegradability of organic chemicals in soils. Steinberg et al. (1987) showed that very low release of the native 1,2-dibromoethane into aqueous

solution from the soil was associated with its negligible degradation, whereas the freshly added 1,2-dibromoethane was readily desorbed and degraded. These findings were explained in terms of a diffusion-based model where organic chemical migrates deeper into unavailable sites with the soil matrix as a consequence of long exposure times. Erickson et al. (1993) observed no desorption of the native polycyclic aromatic hydrocarbons from the field-contaminated soil and only their very limited degradation by PAH degrading organisms.

Conclusions

The results of this study show that soil contact time ranging from 2 to 180 d had no effect on the extent of phenanthrene and MCPA sorption. The sorption isotherms were approximately linear at all incubation times. Despite the fact that there was no observable increase in the retention of phenanthrene and MCPA with the soil contact time, the extent of their desorption from soil decreased significantly between 2 d and 180 d of incubation. The fraction of phenanthrene and MCPA that did not desorb after one step desorption increased from 96 % and 50 % to 97.5 % and 66 % when soil contact time increased from 2 to 180 d, respectively. Thus, the prolonged time that organic chemical residues remain in a soil may affect their re-distribution within sorption sites of the soil matrix as well as their leaching, bioavailability, and toxicity.

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Dlhodobé sorpčné správanie sa kyseliny (4-chlór-2-metylfenoxy) octovej a fenantrénu v obrábanej pôde

V posledných desaťročiach sa preukázalo, že sorpcia organických látok v pôdach nie je rýchly fyzikálno-chemický proces, ale naopak, pomalý, pričom ustálenie termodynamickú rovnováhu v sústave pôda – vodný roztok môže prebiehať stovky dní, ba dokonca až niekoľko rokov (Ball a Roberts, 1991). Čoraz silnejšia fixácia akumulovaných organických látok v pôde s pribúdajúcim časom kontaktu s pôdnymi zložkami má veľký dosah na ich bioprístupnosť do rastlín a živočíchov, desorpciu, výťažnosť organickými rozpúšťadlami, toxicitu, biologickú a chemickú transformáciu (Sharer et al., 2003a; Conrad et al., 2002; Hatzinger a Alexander, 1995). Predpokladá sa, že tieto fenomény sú spôsobené izoláciou molekúl organických látok vo vnútorných polohách pôdných komponentov, ktorej význam narastá s pribúdajúcim časom zdržania organickej látky v pôde (Alexander, 1995). Zanedbanie tejto skutočnosti môže viesť k podhodnoteniu reálnej sorpčnej kapacity pôdneho prostredia, k nesprávnemu odhadu pohyblivosti a bioprístupnosti kontaminujúcich organických

látok, a dokonca aj k nadhodnoteniu zdravotných rizík pre živé organizmy, vrátane človeka (Alexander, 2000).

Hlavným cieľom tejto štúdie bolo rozšíriť súčasné poznanie o vplyve času kontaktu s pôdou na sorpčné a desorpčné správanie sa dvoch organických látok s rozdielnou rozpustnosťou vo vode v obrábanej pôde pomocou laboratórnych experimentov. Sledovalo sa to pre fenantrén (polycyklický aromatický uhľovodík, ktorý je bežným produktom spaľovania fosílnych palív a biomasy) a MCPA (aktívna chemická látka používaná ako herbicíd) pri nasledovných časoch kontaktu s pôdou: 2, 30 a 180 dní. Základné fyzikálne a chemické vlastnosti sledovaných organických látok v tejto štúdii sú uvedené v tab. 1.

Stanovené závislosti koncentrácie organických látok sorbovaných v pôde (S) od ich koncentrácie zostávajúcej v roztoku (C) vyhovovali lineárnej adsorpčnej izoterme ($S = K_d C$), ako aj Freundlichovej adsorpčnej izoterme ($S = K_f C^{1/n}$), kde K_d je lineárny rozdeľovací koeficient ($l\ kg^{-1}$), K_f je Freundlichov koeficient ($mg^{1-1/n}\ kg^{-1}\ l^{1/n}$) a $1/n$

udáva zakrivenie adsorpčnej izotermy. Adsorpčné izotermy pre všetky sledované sústavy a časy kontaktu s pôdou boli približne lineárne, pretože hodnoty $1/n$ oscilovali okolo 1 (obr. 1a, b a tab. 2). Ako tiež možno vidieť z obr. 1a a tab. 2, sorpcia fenantrénu sa nijak nezvýšila pri dlhších časoch kontaktu v porovnaní s časom 2 dni, pretože hodnoty K_d pre jednotlivé časy kontaktu s pôdou sa nezmenili. Tieto výsledky sú v súlade s výsledkami štúdie Kana et al. (1994), ktorí zistili, že ustálenie sorpčnej rovnováhy fenantrénu v sedimente sa dosiahlo za 1 deň. Na druhej strane, Huang a Weber (1998) pozorovali kontinuálny nárast v sorpcii fenantrénu pôdami s pribúdajúcim časom kontaktu od 1 dňa do 368 dní. Na vysvetlenie pomalej sorpcie existuje viacero fyzikálnych predstáv, no najpravdepodobnejšie sa zdajú byť tie založené na difúzii rozpustených molekúl pórmí v agregátoch pôdy a cez pôdnu organickú hmotu (Ball a Roberts, 1991; Brusseau et al., 1991). Naše výsledky však nepotvrdzujú tieto predstavy, ale ako zdôrazňujú autori Huang a Weber (1998), zistené rozdiely v rýchlosti sorpcie fenantrénu v pôdach medzi publikovanými štúdiami sú čiastočne spôsobené rozdielmi v použitých počiatočných koncentráciách fenantrénu v roztoku a v zložení a štruktúre pôdnej organickej hmoty. Ani v prípade MCPA neboli pozorované žiadne významné zmeny v ustálení sorpčnej rovnováhy (obr. 1b a tab. 2). Tento výsledok je v protiklade s pozorovaním autorov Sharer et al. (2003b), ktorí zistili nárast sorpcie 2,4-D v pôde s rastúcim časom kontaktu, čo je organická látka veľmi podobná herbicídu MCPA.

Závislosť desorbovaného podielu od času je znázornená na obr. 1c, d. Sledované desorpčné sústavy dosiahli rovnovážny stav za 1 deň (obr. 1c, d). Čo je však na prvý pohľad viditeľné z obr. 1c, d, v porovnaní s časom kontaktu 2 dni sa desorbovaný podiel oboch testovaných organických látok významne znížil po čase kontaktu 180 dní. Výsledky tejto štúdie, ako aj ďalších (Sharer et al., 2003a, b; Steinberg et al., 1987) ukazujú, že desorbovaný podiel organických látok z pôd sa môže znížiť s pribúdajúcim časom zdržania týchto látok v pôdach. Hoci presný fyzikálny mechanizmus je dodnes neznámy, predpokladá sa, že zníženie desorpcie organických látok z pôdy s pribúdajúcim časom kontaktu je spôsobené difúznou migráciou rozpustených molekúl organických látok do ťažko dostupných polôh v rámci pôdnej matrice. So zníženou intenzitou desorpcie potom úzko súvisí pokles v ich bioprístupnosti pre mikroorganizmy, ktoré majú schopnosť rozkladať tieto látky (Erickson et al., 1993; Scribner et al., 1992; Pignatello a Huang, 1991).

V závere možno konštatovať, že čas kontaktu organických látok s pôdou nemal žiadny preukázateľný vplyv na sorpčnú kapacitu pôdy a intenzitu sorpcie fenantrénu a herbicídu MCPA. Napriek tomu sa však miera ich uvoľňovania z pôdnej matrice po 180 dňoch kontaktu pôdy s rozpustenými molekulami znížila približne o 1/3 v porovnaní s časom kontaktu 2 dni. Dá sa usudzovať, že čas zotrvania rezíduí organických látok v pôde môže ovplyvniť ich redistribúciu v sústave pôda – voda a súčasne ich transport, bioprístupnosť a toxicitu.