Use of Column Leaching Test to Study the Leachibility of Polycyclic Aromatic Hydrocarbons from Contaminated Soil

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استفاده از آزمایش نشت ستونی به منظور مطالعه میزان نشت هیدروکربن‌های آروماتیک چند حلقه‌ای (PAHs) از خاک آلوده

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Abstract

Column leaching tests become increasingly important for assessing the risk of release of pollutants from soil into water. In this study a column leaching test was designed to provide insight into the fate of selected PAHs in soils and their leaching behavior. Two columns (columns 1 and 2) were prepared based on a standard procedure in which 5 and 20 percent of contaminated soil were used, respectively. The percolates were collected at specified L/S ratios. Results showed relatively high initial concentrations of flourene, fluoranthene and benzo(a)anthracene for column 2. Released amounts of PAH compounds were decreasing with increasing molecular size, or rather the hydrophobicity of the compound. The effect of dissolved organic carbon on PAHs leaching was also investigated in this research. Approximately 2.45% and 0.67% of the total initial amounts of studied PAHs in the soil was leached in columns 1 and 2, respectively. Results showed that high PAHs concentration in the solid phase does not necessarily imply serious groundwater contamination risk during a leaching event (e.g. rain fall) and significant amount of contaminants may stay in the soil layer for a long time and do not leach down into groundwater.

Keywords: PAHs, Soil, Pollution, Adsorption.

چکیده

اهمیت آزمایشات نشت ستونی به منظور ارزیابی خطر انتشار آلاینده‌ها از خاک به درون آب رو به افزایش است. در این مطالعه آزمایش نشت ستونی به منظور درک عمیق‌تر از سرنوشت ترکیبات PAHs در خاک و رفتار نشت آن‌ها طرح‌ریزی شد. ستون‌های ۱ و ۲ که به ترتیب حاوی ۵ و ۲۰ درصد خاک آلوده بودند مطابق روش استاندارد تهیه شدند. شیرابۀ خروجی از ستون‌های خاک آلوده در نسبت‌های مشخصی از L/S جمع آوری شد. نتایج نشان داد غلظت‌های اولیۀ فلورن، فلورانتن و بنزو (آ) آنتراسن در شیرابۀ ستون دو نسبتاً بالا می‌باشد. مقدار ترکیبات PAH رها شده در آب با افزایش اندازه مولکولی و یا آب‌گریزی آن‌ها کاهش یافت. در این مطالعه هم‌چنین اثر کربن آلی محلول بر نشت PAHs بررسی شد. در ستون‌های ۱ و ۲ به ترتیب حدود ۲/۴۵ و ۰/۶۷ درصد کل PAH‌ها در خاک به درون آب نشت کرد. نتایج نشان داد غلظت بالای ترکیبات PAH در فاز جامد الزاماً به مفهوم خطر جدی برای آب زیرزمینی در حین یک رویداد نشت (مانند بارندگی) نبوده و ممکن است مقادیر قابل توجهی از آلاینده‌ها به مدت زیاد در خاک باقی مانده و به داخل آب زیرزمینی نشت نکنند.

کلمات کلیدی: PAHs، خاک، آلودگی، جذب.

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Introduction

Soil contamination by Polycyclic Aromatic Hydrocarbons (PAHs) represents a significant and often long-term source of groundwater contamination (Zanst, 2008). Polycyclic aromatic hydrocarbons comprise a large category of persistent organic compounds which can accumulate in soils and thereby threat groundwater resources. Many PAHs are considered as priority pollutants by the US EPA due to their toxic, mutagenic, and carcinogenic effects (Enell *et al.,* 2008). Oil spills, leakages, and pyrolytic sources, such as incomplete combustion, significantly contribute to the input of these chemicals into the environment (Celis *et al.,* 2006). The most important concern at most contaminated sites is the risk of groundwater contamination by leaching of pollutants contained in soils.

Measurement of the total remaining amount of PAHs in contaminated soil is a poor indicator of its potential environmental impact (Enell *et al.,* 2004) and can no longer be considered as a basis for establishment of site remediation strategies and decision making. Groundwater risk assessment should be based on actual release rates of contaminants and leaching characteristics because a significant fraction of total contaminant content is essentially non-leachable by water (Zanst, 2008). The point of compliance is the transition zone between unsaturated and saturated zone (Susset and Grathwohl, 2008). Usually the contaminant can be divided into two groups based on its potential release into water: 1) potentially leachable, which means a maximum amount of contaminant could be released into water under predefined worse conditions and 2) actual leachable, which is amount leached under the conditions imposed by material itself (Grathwohl and Van der Sloot, 2007). In Germany, legal regulations focus on the contaminant concentrations to be expected in the groundwater and not on the total contaminant concentration in soils or sediments (Susset and Grathwohl, 2008).

In recent years, several different methods to evaluate and determine desorption and leaching of hydrophobic organic compounds such as PAHs have been developed and compared (Enell *et al.,* 2004; Zanst, 2008). The stirred aqueous batch reactor is a common approach used for studying desorption of both organic and inorganic pollutants (Chiou *et al.,* 1998; Kan *et al.,* 1998). However, there are some disadvantages associated with batch tests such as the grinding effect which can increase the desorption rate of contaminants. Obtaining sufficient elution concentration, especially for analysis of hydrophobic organic compounds like PAHs is another drawback associated with this approach (Enell *et al.,* 2004).

During the last decade a paradigm shift occurred in leaching tests from batch towards column tests (Grathwohl and Van der Sloot, 2007). The German soil protection ordinance (BBodschV) requires column experiments for the leaching of organic contaminants. Findings of the German joint research project entitled "Sickerwasserprognose" over recent years are reflected in a current standardization project of the German Institute for Standardization (DIN). Leaching tests therefore are performed with the aim to determine the expected contaminant concentration in water which is in contact with solid materials. Column tests represent an established method for research purposes to determine desorption and dissolution rates of contaminants in contaminated materials. Beside concentration of PAHs, some parameters like DOC[1], pH, EC[2], and turbidity were also measured during this work to understand more about the factors effect PAHs concentration.

Materials and Methods

A column leaching test was carried out for a polluted soil sample, prepared from oil-polluted sites around the Oil Refinery of Tehran. The soil was dried in ambient air and passed through a 2-mm sieve before their use in the experiments. The soil type was determined as silty clay and contained 1.81 percent organic carbon. The initial soil amounts of the seven PAHs selected for investigation are given in Table 1.

Permeability of soils in columns 1 and 2 were 0.44 and 0.46, respectively. Column tests were performed in glass column with capacities of approximately 600 cm^3 (see Figure 1). The columns were filled with samples by placing them into the columns in five sub-layers, which were compacted slightly with the aid of a rammer (200 g) according to DIN CEN/TS 14405 (2004). Experimental set-up of column tests is presented in Table 2.

Table 1- Initial concentrations of the selected PAHs in contaminated soil.

PAH compound	Chemical Formula	Molecular Weight	Number of rings	C_s (µg/kg dry soil)
Naphthalene	$C_{10}H_8$	128	2	284.7
Fluorene	$C_{13}H_{10}$	166	3	774.8
Phenanthrene	$C_{14}H_{10}$	178	3	9847.5
Fluoranthene	$C_{16}H_{10}$	202	4	9311.5
Benzo(a)anthracene	$C_{18}H_{12}$	228	4	1958.3
Benzo(a)pyrene	$C_{20}H_{12}$	252	5	552.9
Indeno(1,2,3-c,d)pyrene	$C_{22}H_{12}$	276	6	326.6
Sum of 16EPA PAHs	-	-	-	39398.4

Table 2 - Experimental set-up of column test.

L/S ratio	Increasing up to L/s = 20 l/kg
Column diameter	6 cm
Filling height	20 cm
Flow rate	0.8 ml/min (5% polluted soil) and 0.3 ml/min (20% polluted soil), up-flow percolation
Leachant	Demineralized water
Ambient temperature	20 °C ± 1 °C
Contact time	5 h (5% polluted soil) , 15 h (20% polluted soil)
Test execution	DIN CEN/TS 14405:2004
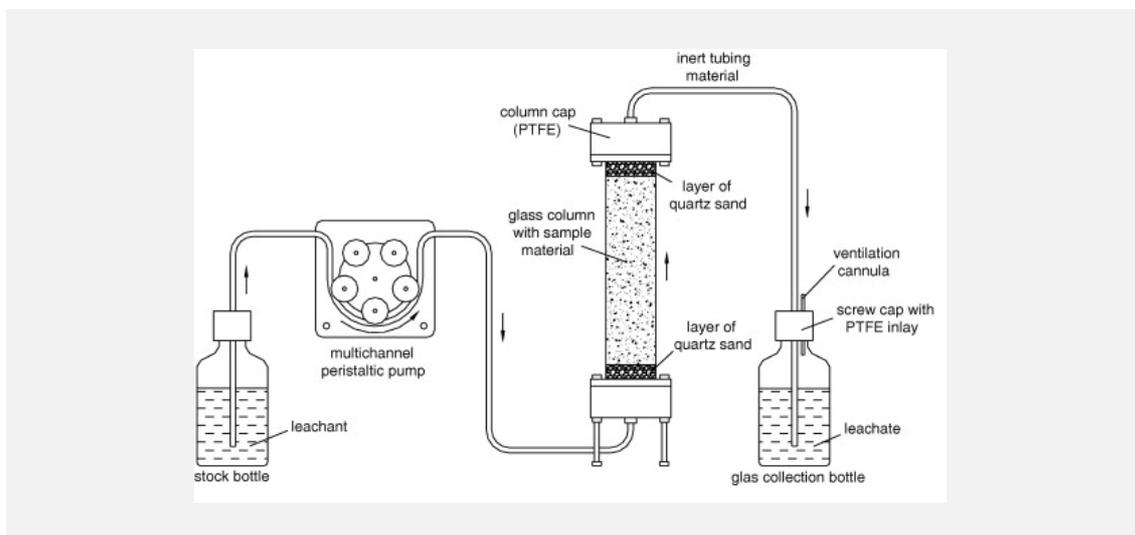
Figure 1- Schematic diagram of column leaching test set-up (Kalbe *et al.*, 2008).

Glass wool was placed on the bottom of the columns to prevent losses of soil and contamination of leachates with soil particles. Approximately 1 cm of a quartz sand layer was placed in the bottom of the columns to distribute the water flow through the soil material equally; the soil samples were placed above the quartz layer up to a height of approximately 20 cm. Soil samples were mixed with quartz sand (5% and 20% polluted soil sample) to facilitate the percolation through these fine-grained materials in the column. The main differences of the two columns were the amount of polluted soil as well as different contact time which affect the flow rate. Thereby it can be possible to study the influence of different applied contact times on leaching behavior. Some water (~ 20 g) was added during the mixing of the material with quartz sand to allow better cohesion of fine particles to the coarse grains. A second quartz sand filter layer was placed above the contaminated soil. Exact data on the mixing and the amount of materials in the columns are presented in Table 3. The column leaching procedure used in this study followed German Industrial Standards (DIN, 1998). Demineralized water was pumped by multi-channel peristaltic pump from the storage tank to the columns at a constant flow rate (Table 2). The columns were percolated from the bottom to the top in order to minimize the trapping of air bubbles. At the beginning of the tests, the columns were rapidly saturated with the leachant using a higher pump velocity. The columns and the storage tank are connected by PE-(PVC) tubing, whereas columns and glass-collection-bottle are connected by stainless steel tubing. This test was carried out for different liquid/solid ratios from 2 to 20 L/kg. The times needed for reaching a certain liquid solid ratio were not same for all the columns because of differences in the amount of soils inside the columns. The percolates were collected at specified L/S ratios, taking into account the amount of leachate required for the analytical procedure. The dark bottles kept in 4 °C temperature to avoid biodegradation in the leachate. The leachates were not filtrated as were clean due to self-filtration of the packed bed.

Percolates were analyzed for polycyclic aromatic hydrocarbon content. Turbidity, DOC, EC and pH of the leachates were also measured. Approximately 10 ml leachate was used to measure these parameters. Leachates were filtrated by MILEXHA 0.45μm diameter filter then used to measure DOC content by HighTOC analyzer (Elementar). The pH was measured using a digital pH 540 GLP instrument, equipped with a SenTix 81 glass electrode. Standard buffer solutions were used to calibrate the instrument. EC were measured by conductivity meter. Turbidity is caused by suspended particles that are generally invisible to the naked eye. It was measured by HACH 2100N Turbidimeter which sends the light through the solution and records the reflected light, so the more particle are in the solution the more turbidity is measured. When running turbidity measurement, sure had to be made that the turbidity measurement tubes are not scratched and the solution inside tubes should be bubbles-free, because scratch and bubbles have not same reflecting rate as the solution.

In order to measure PAHs, 10 ml of cyclohexan (solvent) and 10μl of internal standard injected into the bottles, the caps closed tightly, and the bottles left on the shaker for 1 hour. PAHs within cyclohexan then were extracted.

Before analysis 10 μl of internal standard were added to 1.5 ml extract (exact mass determined on a balance) and then the PAHs were measured by the GC.

Results

Effluent concentrations of polycyclic aromatic hydrocarbons from columns 1 and 2 are shown in Figures 2 and 4, respectively. The concentration and release of the PAHs investigated in this study are plotted against the liquid to solid ratio. The cumulative released amounts of PAHs (obtained by multiplying the concentrations by the L/S ratio and subsequently summing up) in the column tests 1 and 2 from the contaminated media are shown in Figures 3 and 5, respectively, which contain diagrams for the sum of 16 US EPA PAHs as well as single selected PAH compounds with two to six rings.

Table 3- Column parameters.

Column	1	2
Amount of sample (g)	41.6	162.4
Humidity (%)	2.12	2.12
Amount of dry sample (g)	40.72	158.96
Amount of quartz sand (g)	789.7	649.9
Amount of wet mixture (g)	849.7	833.4
Particle density of the sample (g/cm^3)	2.7	2.7
Particle density of quartz sand (g/cm^3)	2.64	2.64
Particle density of mixture (g/cm^3)	2.64	2.65
Filling volume (cm^3)	565.5	565.5
Bulk density (g/cm^3)	1.47	1.43
Porosity	0.44	0.46

Table 4- Leached amount of contaminants at L/S ratio of 20 l/kg.

| PAH compound	Column 1		Column 2	
	Leached amount (µg/kg)	Leached percentage of initial amounts in soil (%)	Leached amount (µg/kg)	Leached percentage of initial amounts in soil (%)
Naphthalene	2.86	1.00	0.18	0.06
Fluorene	58.25	7.51	9.54	1.23
Phenanthrene	0.9	0.01	0.45	0.004
Fluoranthene	81.17	0.87	0.69	0.007
Benzo(a)anthracene	4.26	0.22	0.98	0.05
Benzo(a)pyrene	0	0	0	0
Indeno(1,2,3-c,d)pyrene	0	0	0	0
Sum of 7 EPA PAHs	147.44	0.57	11.84	0.08
Sum of 16 EPA PAHs	968.37	2.45	266.07	0.67
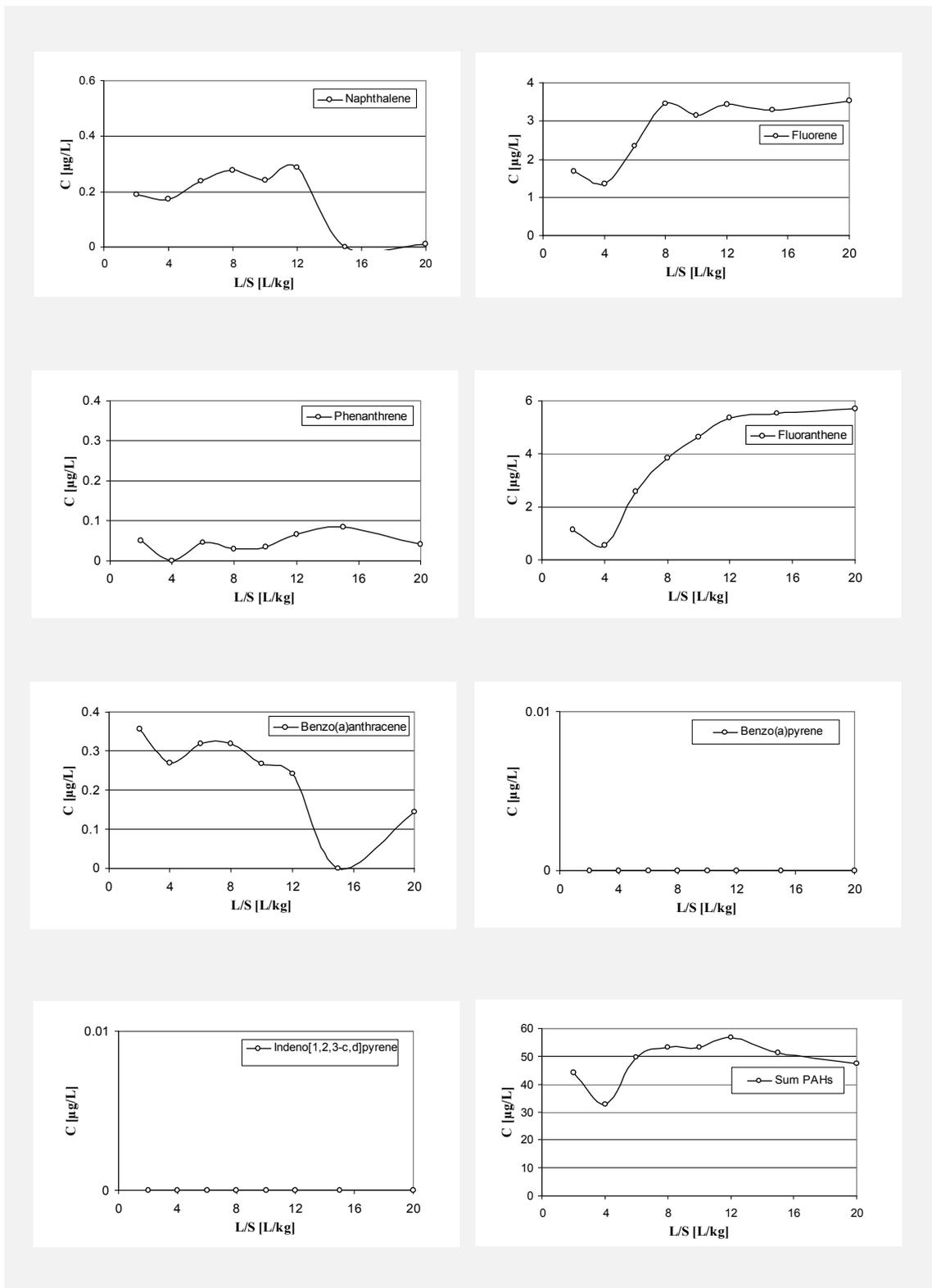
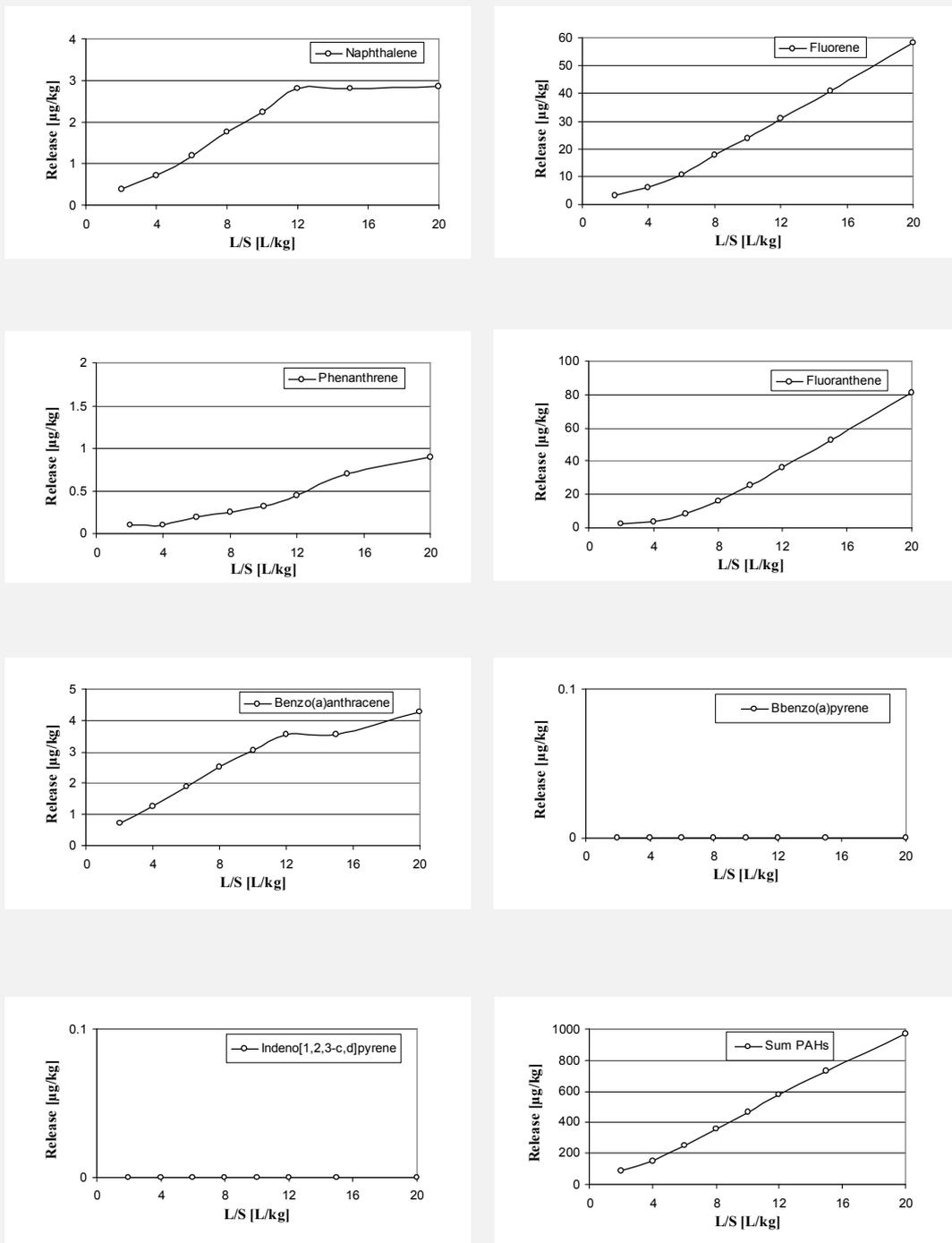**Figure 2 -** Concentrations of individual PAHs in column leachate for column 1.

Figure 3 - Cumulative release of studied PAHs in column leachate for column 1.
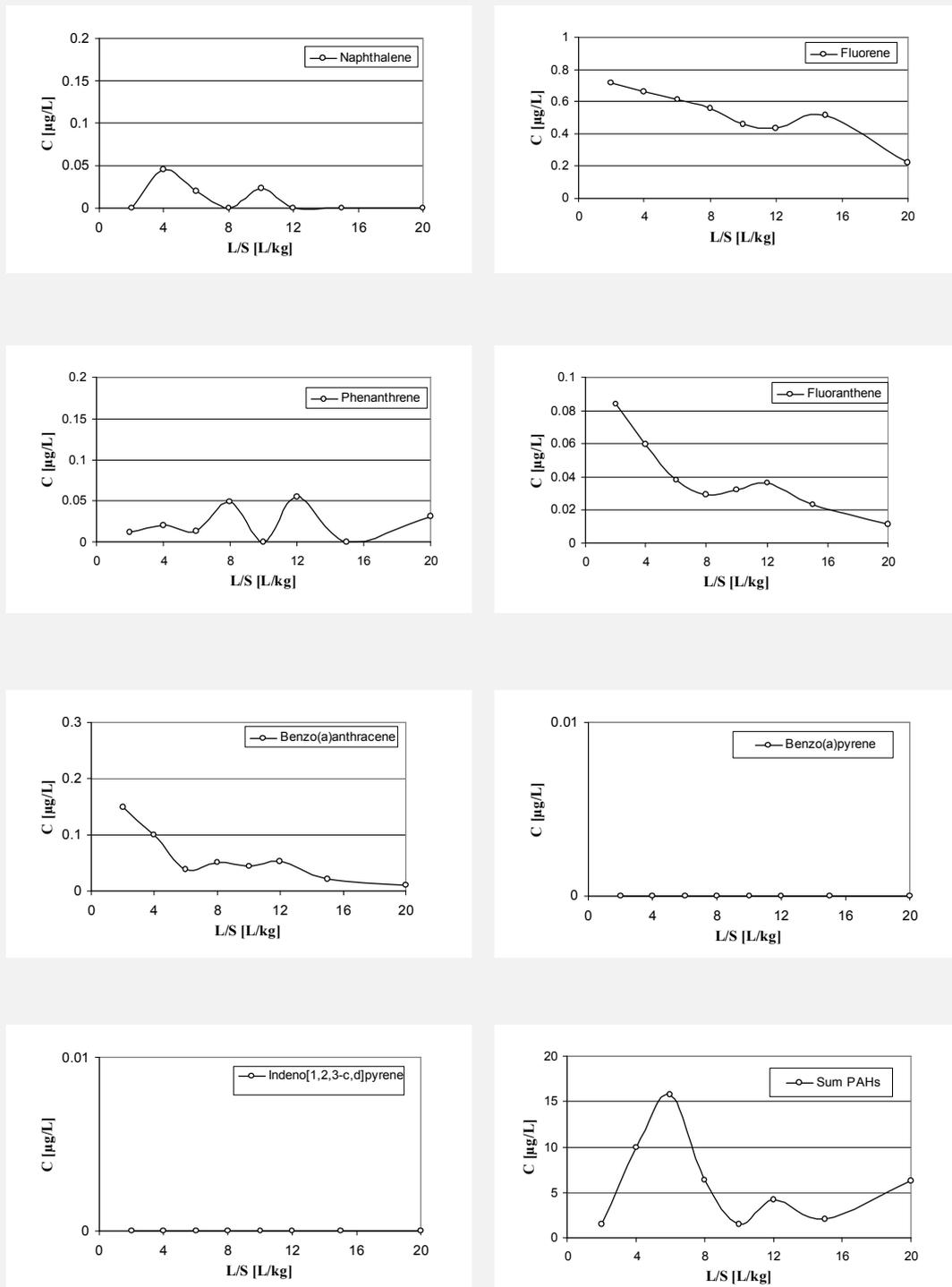
Figure 4 - Concentrations of individual PAHs in column leachate for column 2.
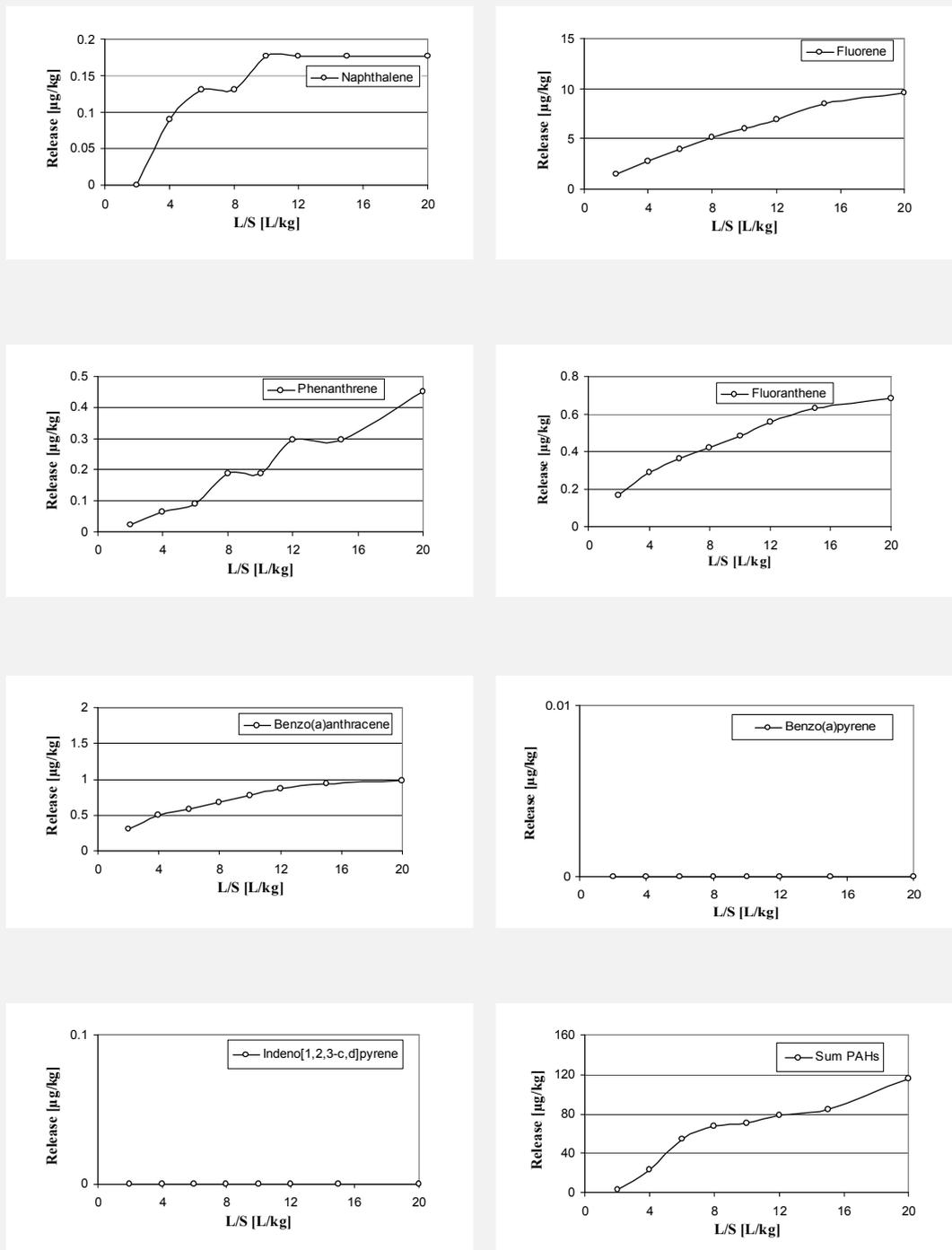
Figure 5 - Cumulative release of studied PAHs in column leachate for column 2.

Leached concentrations of DOC as a function of L/S are also shown in Figure 6. The results of EC, pH, and turbidity measurements for the column 2 are presented in Figure 7. Table 4 presents leached accumulated amount/kg soil at L/S ratio of 20 l/kg.

Discussion

PAHs are chemical compounds that consist of fused aromatic rings. They are of great concern as a pollutant and many of them have been identified as carcinogenic and mutagenic pollutants by various environmental agencies. For instance, US EPA has identified 16 PAHs as primary pollutants. Seven individual PAHs with two to six aromatic rings as well as some of these 7 PAHs were studied in this research. In order to allow comparison of leaching test results with each other, it is better to express the time based on the dynamic liquid to solid ratio (L/S), which is the amount of water percolated through the column after a certain time to the dry weight of the solids in the column.

Relatively higher initial concentrations were observed for investigated PAHs with 2, 3 and 4 rings compared to final concentrations. Initially the curves drop almost steeply to a low level for flourene, fluoranthene and benzo(a)anthracene for column 2. After L/S ratio of 6, the mentioned curve for benzo(a)anthracene remain constant for the remaining time. The release of PAHs in column 1 as a function of the L/S ratio is approximately linear for flourene, phenanthrene and fluoranthene at higher L/S ratios because almost constant quantities are mobilized after initial concentrations in the effluent. Initial concentrations of most studied PAH compounds (at L/S 2) in column 1 were almost comparable with the corresponding values of column 2; however their leaching behavior over the course of the experiment were somewhat different. Based on the obtained results, it seems that contact time of 5 and 15 hours are not sufficient to reach equilibrium conditions in this study. Increasing the contact time may lead to obtain more realistic liquid phase concentrations at lower L/S ratios which are closer to the saturation concentration (water solubility of the compounds from the mixtures, as expected from Rault's law). The initial circulation of leachate may also help to establish equilibrium condition as Enell *et al*. (2004) suggested. The contact time required to reach equilibrium conditions depends
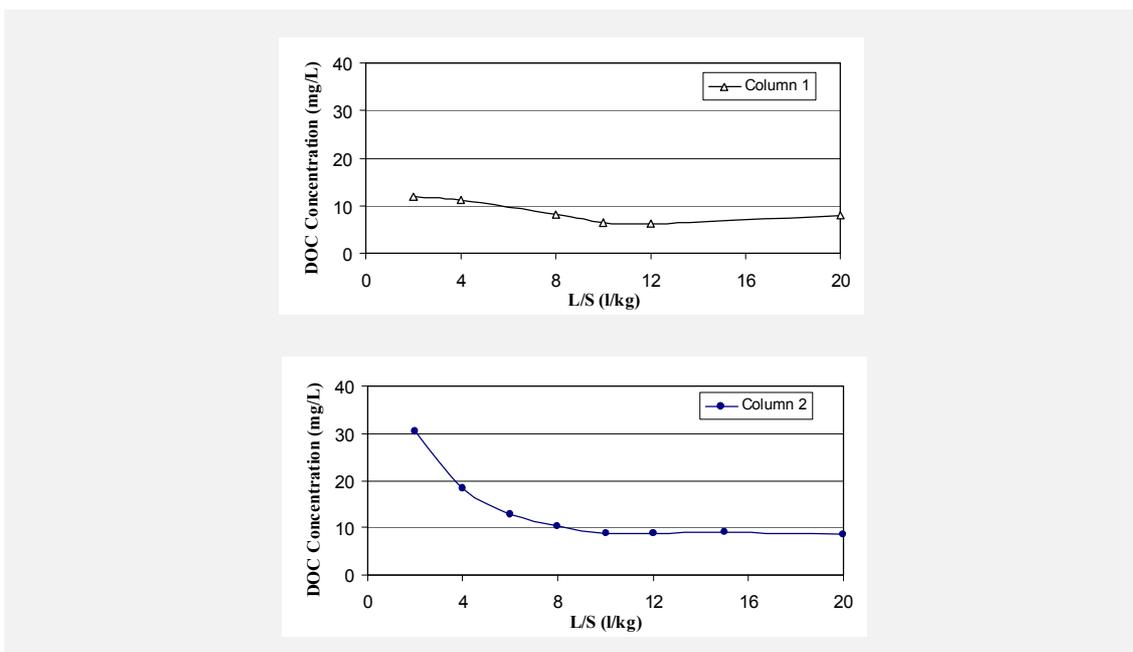

Figure 6 - Dissolved organic carbon (DOC) concentration in column effluent.
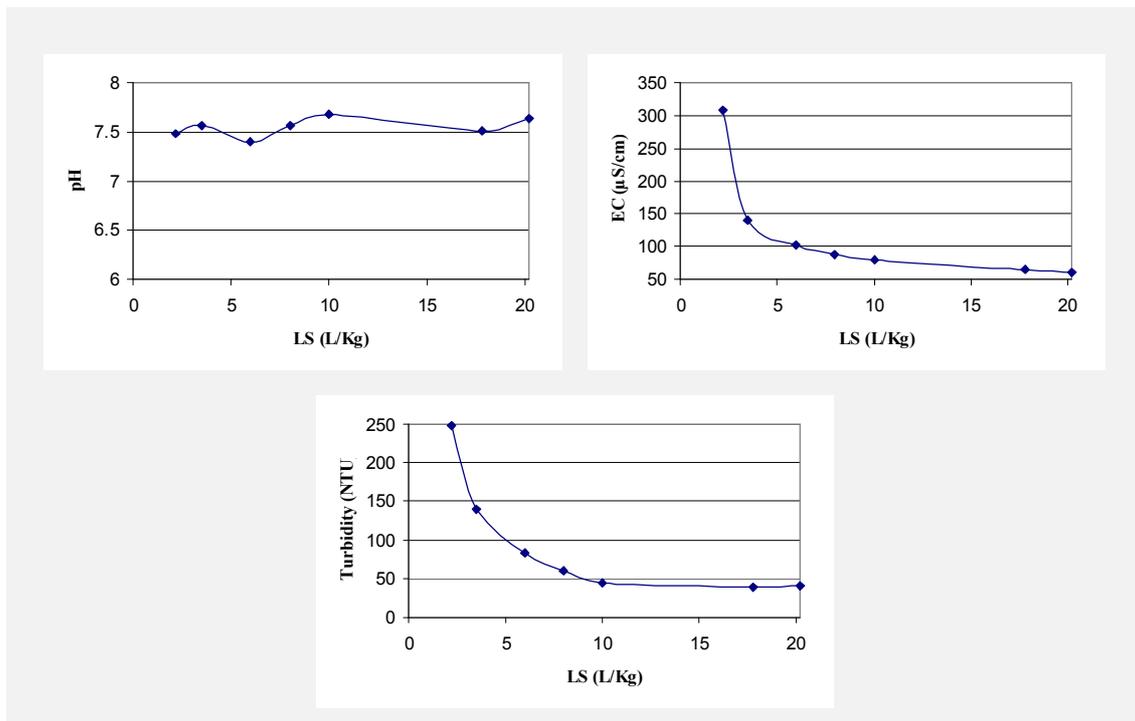
Figure 7- Turbidity, pH, and electrical conductivity of effluent for column 2.

on the combination of a soil type and species to be investigated (CEN, 2004). Once equilibrium condition established initial concentrations should become converged, irrespective of contaminated soil proportion.

Comparing the concentrations of fluorene, fluoranthene, and benzo(a)anthracene in columns 1 and 2 at different L/S ratios reveals that leaching behavior of the mentioned PAHs is more compatible with the expected concentrations based on the leaching theory and modeling results (data not shown), probably due to the higher applied contact time in column 2. The contact time of water with the material is a crucial factor affects equilibrium condition and column test results. Naphthalene release was unexpectedly low in both column 1 and column 2 probably due to non-equilibrium conditions established in the columns or evaporation of leachable amounts during column packing.

It should be noted that time is an important factor in leaching studies which often reflect in the results as

L/S ratio, because L/S ratio is directly correlated with time. In other words as time goes on, L/S ratio is also increased. Different proportion of contaminated soil used in the columns (5% and 20%) didn't yield results in the same order of magnitude at specific L/S ratios for naphthalene, fluorene, phenanthrene, fluoranthene, and benzo (a) anthracene. Leaching of benzo(a)pyrene and indeno (1,2,3-c,d) pyrene were independent from contaminated soil content of the columns. In other words, the results show that leaching behavior of the 5 and 6-ring PAH compounds investigated in this research depends on properties of the pollutant itself (e.g. k_{ow}), and not on column conditions (like contaminated soil content, flow rate, and etc.). Additionally, the comparison of the cumulative release of the pollutants between column 1 and 2 (Figures 3 and 5) doesn't yield a good agreement, except for benzo(a)pyrene and indeno(1,2,3-c,d) pyrene (with no release).

Fluorene, fluoranthene, and benzo (a) anthracene concentrations in the effluent of column 2 decrease

with L/S which may correspond to pollutant depletion in solid phase. However, in some cases (e.g. naphthalene and phenanthrene) leaching behavior doesn't follow this pattern. In addition, benzo(a)pyrene and indeno(1,2,3-c,d)pyrene concentrations in effluents remained zero over the course of the experiment (up to LS 20). This is originated from the fact that contaminants desorption and release from solid phase is governed by various factors like distribution coefficient (K_d) values for specific chemicals.

The heterogeneity of the contaminated soil and of the surface composition of pollutants adsorbed to the particles may be a probable reason for unexpected increase of some PAHs at higher L/S ratios (e.g. fluorine and fluoranthene concentrations in column test 1). For PAHs with low solubility (more hydrophobic compounds with higher k_d values like 5 and 6–ring PAHs) the dissolution last very long and the concentrations can be constant for several weeks (Susset and Grathwohl, 2008), as observed in this study. For compounds which sorb strongly to the solids the equilibrium conditions can prevail over extended periods of time. PAHs with higher solubility (e.g. naphthalene) can be leached out faster than more hydrophobic compounds. Decreasing concentrations indicate non-equilibrium condition. The shift between equilibrium and non-equilibrium conditions depends on the flow velocity, grain sizes and diffusion distances, sorption capacity and etc. The concentration in the effluent may decrease because of depletion of the compounds or because non-equilibrium conditions established in the column. The change to non-equilibrium conditions is indicated by a drop in concentrations followed by an extended tailing of the concentrations.

One important factor which has an influence on concentration of PAHs in the column effluent is colloid-facilitated transport of PAHs that takes place within the unsaturated soil zone (Kalbe *et al.,* 2008). Generally, the mobility of hydrophobic organic compounds like PAHs is influenced by the amount of particles and the amount of DOC that are mobilized (Kim *et al.,* 2002; Persson *et al.,* 2008). The leaching behavior of organic compounds in soils is mainly controlled by dissolution and/or sorption/desorption processes in connection with the presence of DOC. It should be noted that the total organic carbon content of the soil was 1.81 percent, but the parameter which was measured in water phase (leachate) was DOC, because it can affect leaching behaviour of PAHs. However other organic compounds in leachate were not determined. Figure 6 illustrated that DOC content in column tests decreases with increasing L/S ratio. Results show that DOC in the leachate was somewhat increased when the flow rate was decreased from 0.8 ml/min (for column 1) to 0.3 ml/min (for column 2), probably due to an increase in the contact time and getting closer to real equilibrium condition. However, results show that difference between flow rates of column 1 and 2 didn't affect the mobilization of colloids and DOC leaching pattern to a great extent which is in agreement with the obtained results by Persson *et al.* (2008) where 50% increase in flow rate didn't influence DOC leaching behavior. They suggested that changing the flow rate by 50% has little effect on the results of column leaching test.

By comparing Figures 2 and 4 with Figure 6, it can be seen that leached PAHs in most cases is not affected by DOC; however the DOC effect is observable in case of fluorene, fluoranthene, and benzo(a)anthracene leaching behaviors from column 2 where their concentrations are declining considerably and DOC content is decreasing as well. Dissolved organic matters can exert two different effects on the sorption of organic solutes by sorbent surfaces: 1) reduction in sorption due to solubilization effects and competition on sorbent sites and 2) enhancement of sorption when the solute-DOM complex has a greater affinity to the sorbent than the organic solute itself (Celis *et al.,* 1998).

Figure 7 shows that turbidity and EC decrease with increasing L/S ratio. In case of column 1 the whole leachates were required for PAHs analyses and

parameter measurements were conducted only at L/S 20, due to small volume of sample collected during leaching event. Turbidity, EC, and pH values obtained for the column 1 at L/S ratio of 20 were 288 NTU, 35 μS/cm, and 7.74, respectively. Therefore, in case of these parameters the discussion can solely be made for the column 2. The pH of the leachate in column 2 changed slightly during the column leaching test. The final pH value in column test 2 (7.63) was slightly higher than the initial value (7.48). But the pH variations were not so high that can affect the PAH leaching results. The pH leaching can influence DOC content in leachate (Persson *et al.*, 2008) and hence may affect leaching behavior of PAHs. Generally, the change in pH as a function of L/S was marginal (less than 1 pH unit) for column 2. The turbidity measurements in column 2 show that, initially, there are considerable amounts of suspended solids in the column effluent. The amounts of colloids in the leachate were increased when the flow rate was increased. Higher amount of turbidity observed in effluent of column 1 (288 NTU) at L/S ratio of 20 (final L/S) compared to turbidity in leachate of column 2 (40.3 NTU) at the same L/S ratio suggests that flow rate alteration may affect desorption kinetics for colloid particles; thereby influence colloid-facilitated transport of hydrophobic organic compounds like PAHs. Decreasing amounts of turbidity and EC with respect to L/S ratio in column 2 may be attributed to filtration effect of the soil in column as well as rapid depletion of dissolved salts in solid phase.

In a study by Kalbe *et al.* (2008) a column leaching test was performed up to L/S ratio of five. They found that PAH leaching is still not completed as L/S ratio of five. Since the flow rate in a column test is often fixed, the L/S ratio is directly proportional to the retention time. Therefore, higher L/S ratios correspond to longer durations and simulate conditions to observed long-term leaching patterns, thus L/S ratio was extended up to 20 in the current research in order to observe the leaching behavior of PAH compounds at higher L/S ratios. Comparing the results of the current study with those of Kalbe *et al.* (2008) confirm that release of PAHs from contaminated media continues after L/S ratio of five. However release rates decreases at higher L/S ratios in some cases (Figures 3 and 5). This is probably due to the fact that after the initial mobilization of the more soluble PAHs the contaminated release is governed by diffusion (Grathwohl, 1998).

The leaching pattern observed in this research suggests that the PAH compounds are not released as rapidly as many of the inorganic compounds, specially in the initial periods of leaching due to their different hydrogeochemical nature, thus remediation actions should be designed based on leaching characteristics of each compound and they should not be treated as inorganic pollutants. Sum of PAH concentrations in water are several orders of magnitude less than that of the in solid phase, mainly because of the low solubility of PAH compounds. During the whole time of the experiment (up to L/S ratio of 20) only 2.45% and 0.67% of the total initial amounts of studied PAHs in the soil were leached in column tests 1 and 2, respectively. This emphasizes the fact that contaminant concentration in water does not depend only on how much contaminated soil is in contact with water but mainly depends on water solubility of PAHs present in soil and their solid phase distribution contribute to their leaching behavior.

Table 4 indicates that released fractions of initial amounts are mostly decreasing with increasing molecular size, or rather the hydrophobicity of the compound. Leaching behavior of PAH compounds may also be variable for PAHs with the same number of rings. For instance, leached amounts of fluorene were significantly higher than those of phenanthrene in columns 1 and 2, while they both have three aromatic rings in their structure. One reason is that water solubility of fluorine is more than that of phenanthrene, thus affect their distribution coefficient and leaching behavior from soil column.

It should be noted that the total amount of leached PAHs is not a strong indicator of leaching behaviour

of PAH compounds and it would be better to study the environmental risks of PAH compounds based on their individual leaching behavior, because the distribution pattern of PAH compounds in solid phase may significantly influence on leached amounts of PAH compounds. In the other word, even if the same amounts of PAHs are present in two equal soil samples, different concentrations of total PAHs may be expected in leached water.

The cumulative release of PAH compounds from soil during leaching tests was considerably lower compared to solid phase concentrations of PAHs (Table 4). It can be even lower in the environment since silt and sand particles are often coated with clay particles in field, cemented together by organic matter, mineral oxides and carbonates. Thus if contaminants are associated with these coatings they are sheltered from equilibrium processes with the bulk solution (Enell *et al.*, 2004). In addition, increased release of phenantherne from an aged contaminated soil due to the disruption of soil aggregates was also reported (Hatzinger and Alexander, 1995). The sampling procedure and homogenization (sieving and gently mixing) may possibly destroy or change the aggregate structure of the soil to some extent, thus exposes new soil surfaces with readily desorbable PAH fractions (Enell *et al.,* 2004). Soil disruption may influence both column test results and the reproducibility of the column leaching test results as suggested by Susset and Grathwohl (2008). Availability of PAHs is altered by soil disturbance causing an increase in released contaminant amounts in laboratories compared to field condition.

A column leaching test performed in order to determine the expected concentrations of PAH compounds in water which is in contact with solid materials showed to be an applicable instrument to forecast leachate concentration for groundwater risk assessment. Our results indicated that leaching behavior of sum of PAHs is not the same as individual PAH compounds. Relatively high initial concentrations were observed for investigated PAHs

with 3, and 4 rings for column 2. Different proportions of contaminated soils used in columns affected leaching behavior of PAHs probably due to the lack of equilibrium establishment in columns. The contact time of water with soil is a crucial factor affects equilibrium condition and column test results. Different contact times applied in columns 1 and 2 affect the initial amounts of leached PAHs as well as leaching behavior. With a sufficiently long contact time of water with the material investigated, equilibrium between the contaminant content in the solid matter and its concentration in water can be achieved. Results indicated that distribution pattern of PAH compounds in solid phase considerably affect leached concentrations of PAHs. PAHs with low solubility sorb strongly to the solids lead to a very long-term release of contaminants. The equilibrium conditions can prevail over extended periods of time for these compounds. The results showed that released fractions of initial amounts are decreasing with increasing molecular size, or rather the hydrophobicity of the compound. The mobilization of colloids and DOC leaching pattern did not affect leached concentrations of PAH compounds to a great extent. Turbidity and EC decreased with increasing L/S ratio, while the pH didn't change considerably.

One advantage of column tests over batch or extraction tests is the possibility to observe the time-dependent release of contaminants which is required for the prediction of leaching behavior under field conditions. Results of the current study showed that only 2.45% and 0.67% of the total initial amounts of studied PAHs in the soil were leached in column tests 1 and 2, respectively (up to L/S ratio of 20). PAH compounds are expected to release more slowly in the environment compared to laboratory leaching tests due to soil disruption mainly caused by soil sampling and homogenization.

Aqueous concentration of PAH compounds, as long-term source of groundwater pollution, should be considered rather than total residual amounts in solid phase when remediation strategies are planned. If

conclusion from this study holds, high PAH concentrations in the solid phase does not imply serious groundwater contamination risk during a leaching event (e.g. raining) and a significant amount of contaminants may stay in the soil layer for a long time and do not leach down into groundwater, thus many contaminated sites do not need immediate remediation actions since they pose only low environmental, but long-term, risk. However, it should also be considered that PAH compounds may be transported by mobilized particles.

Endnotes
1- Dissolved organic carbon
2- Electrical Conductivity

Acknowledgments

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