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Measurement of Aqueous Phase Transport of Residually Held Benzene in Greek Soils

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Organic contaminants are commonly found in the soil in the form of organic solvents and fuels. After infiltrating into soil, some is retained in the unsaturated zone. These substances may remain in the soil for decades contaminating groundwater (Pinder 1982). The presence of even minute amounts of organic contaminants in the water necessitates difficult and expensive purification treatment to render it suitable for human consumption.

The problem of organics contamination is complex because organic contaminants may be found in the unsaturated zone in at least 7 out of 13 possible physicochemical - phase loci (Lyman et al. 1992): vapors as a component of soil atmosphere; dissolved in the water film surrounding soil particles; sorbed to soil particles or rock surface (after migrating through the water); as liquid in the pore spaces between soil particles; sorbed onto colloidal particles in water; sorbed onto or into soil microbiota; and dissolved in the mobile pore water. In each locus, different processes influence the organic contaminant phase distribution, chemical transformations, and movement in the soil.

This soil column study was directed toward evaluating residual benzene leaching from six Greek soils under conditions of stable, vertical unsaturated flow. Benzene was chosen because it is a common constituent of liquid fuels. Liquid fuels are stored in aboveground and underground storage tanks. Accidental spills of these fuels into the soil may cause extensive contamination of groundwaters. Such spills are considered as high risk in the Balkans, an area witnessing frequent and strong earthquakes.

MATERIALS AND METHODS

A four-stage procedure was followed. First, a simulation of an accidental benzene spill into the soil was induced. Second, drainage of the benzene from the soil by gravity and moderate suction occurred. Third, initiation of stable, vertical, unsaturated flow of water in the soil was obtained. Fourth, daily measurement of the benzene concentration in the leachate for approximately 10 days was performed.

The soil water regime was precisely defined. Zalidis et al. (1997) showed that the initial soil water content influences organic contaminants retention and

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movement. The use of soil - packed columns enabled the control of the soil water regime, i. e., the initial soil moisture and the water flow velocity.

The laboratory setup was succesfully used by Zalidis et al. (1991). Glass cylindrical columns, 30 cm long and of 5.44 cm internal diameter, were used. Column materials were such to minimize benzene losses due to adsorption or volatilization. Thus, the teflon caps at both ends of the column had teflon rings to prevent direct lid contact with the columns. The top end cap had a hole through which de-aired, aqueous $CaSO_4$ solution (approximately 2%) was applied for leaching purposes. The bottom end cap also had a hole to allow collection of the effluent. A glass syringe was attached to this hole to collect the effluent under suction that was created by a vacuum pump with pressure regulator.

The column was filled with air - dried soil which was previously ground and sieved through a 2 mm mesh sieve. Six Greek soils were used. The apparent specific weight after filling and other characteristics of the six soils are shown in Table 1.

Table 1. Measured and derived characteristics of the six Greek soils that were used to pack the columns

Soil	ASW g cm^{-1}	Sand %	Silt %	Clay %	Textural class	Org. matter %	Clay: Org. C ratio	stimated benzene K_d L kg^{-1}
Bariko	0.89	14.7	66.7	18.7	SiL	9.0	4	4.3
Zacharato	1.26	33.6	26.4	40.0	CL	1.8	36	0.9
Mitrousi	1.19	2.5	32.9	64.6	C	2.0	59	0.9
Larisa	1.38	38.3	43.4	18.2	L	1.4	23	0.7
Terpylos	1.16	34.9	19.5	45.6	C	2.1	38	1.0
Griva	1.14	47.8	34.4	17.9	L	1.8	18	0.8

ASW: Apparent Specific Weight

Estimated Organic C: 1 g Org. C ~ 1.73 g Org. Matter

K_d: distribution coefficient estimated as per Green and Karickhoff (1990)

The column was slowly saturated with the 2% $CaSO_4$ solution applied from the effluent end using a Mariott device. Then, a porous steel membrane of 30 kPa nominal suction (approximately field capacity) was placed at the bottom of the column. Prior to its placement, the membrane was saturated with the same $CaSO_4$ solution used for saturation. The column was then drained by gravity and moderate suction (20 kPa) applied at the column's bottom end with a vacuum pump. Liquid outflow lasted for about 2 days, till the outflow was negligible.

The steel membrane was removed and the column was infiltrated with benzene applied through the effluent opening using a Mariott device. A steel membrane of 30 kPa nominal suction, saturated with benzene, was placed at the column's base.

Then, the column was drained by gravity and moderate suction (20 kPa) applied with a vacuum pump. Drainage continued until the outflow was negligible.

A steel membrane saturated in $CaSO_4$ solution was placed at the bottom of the column and unsaturated vertical flow was initiated as follows: $CaSO_4$ solution was dripped from the top inlet hole at a rate of 2.82 mL hr^{-1}. To maintain the unsaturated flow a suction of 20 kPa was applied through the bottom cap hole. Leachate samples were periodically collected in the glass syringe adapted to the effluent hole. As soon as 2 mL of leachate was collected, it was quickly injected into a 4 mL glass vial. The vial was tightly sealed with a stopper lined with silicone (outside) and teflon (inside) and stored at 0°C till analysis. Samples did not freeze at this temperature because of the various dissolved substances they contained. The samples were analyzed within two days.

For the Mitrousi soil, which had very low infiltration rate to $CaSO_4$ solution, the flow was lowered to 0.65 mL hr^{-1}.

Benzene concentration in the leachate samples was measured using high-pressure liquid chromatography, at the Laboratory of Analytical Chemistry of the School of Chemistry, Aristotle University of Thessaloniki, Greece. The apparatus was Shimadzu HPLC QA, detector SSI UV500, integrator Hewlett Packard 3396II with column Nucleosil 100-5 C_{18}, 150x4, 6 mm I.D. The mobile phase was methanol: water (90:10) and flow rate was 1 mL min^{-1}.

RESULTS AND DISCUSSION

The Bariko, Zacharato, Terpylos, and Griva soils did not appreciably differ in total benzene leaching (Figure 1) in spite of the differences in their characteristics (Table 1). The cause must be sought in the mechanisms regulating benzene retention in soil. Is it possible that adsorption to organic matter and clay is not significant in the first place?

According to Green and Karickhoff (1990) benzene is somewhat polar because its solubility in the water (1880 mg L^{-1} or 2.3 10^{-2} M) exceeds an (arbitrary) limit of 300 mg L^{-1} or 2.3 10^{-3} M. However, because it does not behave as a weak acid nor as a weak base, its adsorption may be estimated as for truly non-polar substances, with a Freundlich - type equation:

$$q = K_d C^n \qquad [1]$$

where q = mass of the substance adsorbed per kg of soil (mg kg^{-1}), K_d = distribution coefficient between liquid and solid phase, C = equilibrium concentration of benzene in the liquid phase and n = degree of equation, ≤ 1.

The distribution coefficient (K_d) is either measured or estimated with the equation:

$$K_d = K_{oc} f_{oc} \qquad [2]$$

where K_{oc} = the distribution coefficient between liquid phase and organic matter, and f_{oc} = the percent of organic carbon in the soil (1 g organic carbon - 1.73 g organic matter). The value of K_{oc} for benzene is 83 L kg^{-1} (Hasset et al. 1983). The K_d value for each soil may be calculated from Eq. [2] and the data of Table 1.

Bariko had the highest calculated K_d (4.3 L kg^{-1}). If the degree n in Eq. [l] is 1, the concentration C is, assuming a local equilibrium, approximately the concentration in the leachate, 200 - 600 mg L^{-1} (we would expect higher concentrations, close to benzene solubility in water. Yet, it seems that local equilibrium conditions did not exist). From Eq. [1], and given that the soil in the column weighs 0.640 kg, the absorbed benzene is 550 - 1650 mg, which is only a small fraction (4 - 11%) of the residual benzene mass at the onset of unsaturated flow. Note that the Freundlich - type relationship holds for low equilibrium concentrations in the liquid phase, below 1-3 mg L^{-1} (Green and Karickhoff 1990). Therefore, the fraction of adsorbed benzene for Bariko is even less. This explains why the differences in the organic matter content of the soils did not cause differences in the retention of benzene.

The study by Hayden et al. (In press) supports these findings because it shows that the presence of organic matter in soil makes no difference in residual gasoline saturation, if the soil is initially water wet, at a suction of 30 kPa. The presence of the residual water effectively fills the small pores and coats the surface of the soil making these places inaccessible to gasoline.

The six soils markedly differed in clay content. Green and Karickhoff (1990), however, note that for clay to contribute to the adsorption of non-polar organic molecules, the ratio of clay fraction to organic carbon fraction must exceed 60. In other words, it is only when the clay content markedly exceeds the organic C content that adsorption to clay dominates. In none of the soils tested the above ratio exceeded 60.

The Larisa and Mitrousi soils show the highest cumulative leaching (Figure 1). For the Larisa soil this is due to the somewhat higher concentrations of benzene in the leachate, though it is similar in texture to the Griva soil. The Larisa soil has higher apparent specific weight after packing (Table 1). Denser packing usually means a decrease in the number of larger pores. Larger pores are easier to squeeze by compaction while intraaggregate micropores remain unaffected. This results in a smaller relative frequency of the larger “ganglia” (trapped benzene droplets) that led to a better local equilibrium of the benzene with the aqueous phase. That benzene exists as very thin films and ganglia is supported by Hayden and Voice (1993) who took cryo-scanning electron and X-ray images of wet sand at various organic contaminants (iodo benzene) saturations. At approximately 1% residual organic contaminants saturation by volume, films of organic contaminants could not be detected on sand grains, while water films were detectible. So, at this residual saturation, organic contaminants exists either as very thin films, or isolated ganglia or lenses. Hunt et al. (1988) showed that the smaller the ganglia, the higher the benzene concentrations in the leachate, and vice versa. The increased contact area between benzene and water, which is effected by the smaller ganglia, promotes mass transfer of benzene to the water.

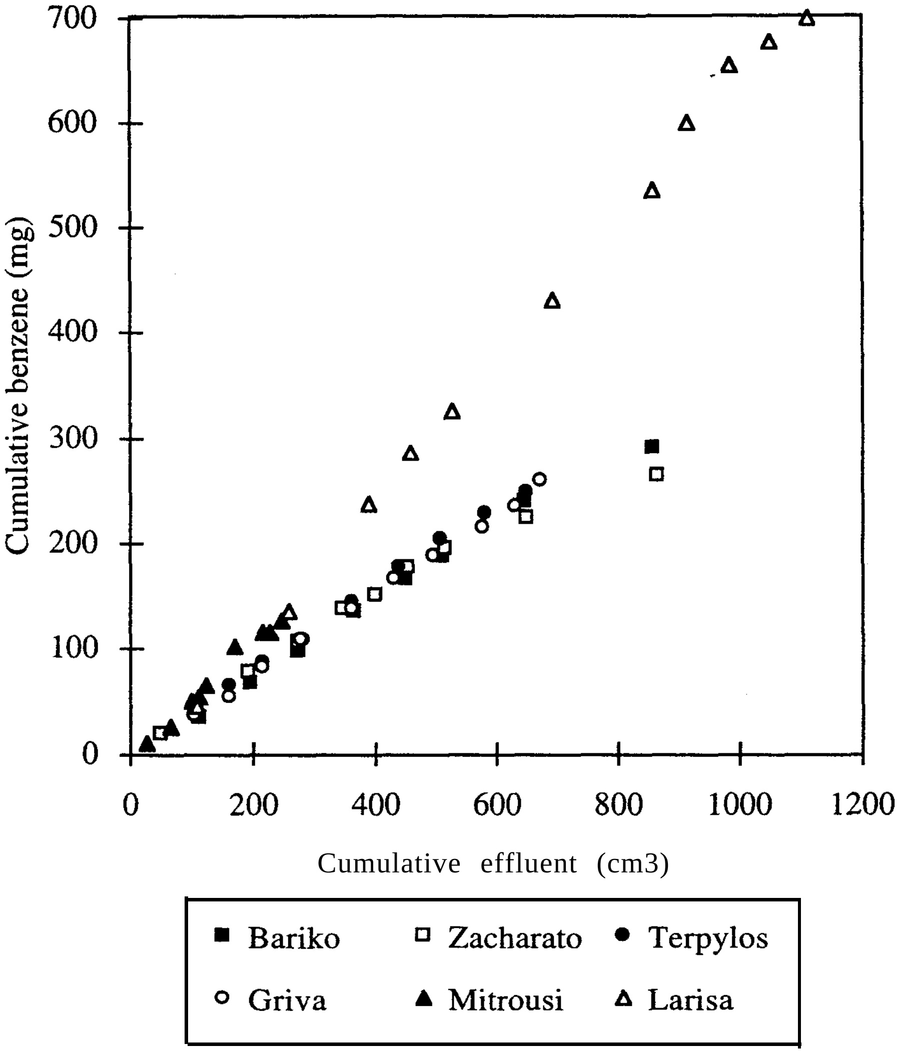

Figure 1. Cumulative benzene mass in leachate against cumulative effluent.

With regard to the Mitrousi soil, the flow of $CaSO_4$ solution was only 0.65 mL hr^{-1} as compared to 2.82 mL hr^{-1} in the other soils, due to the low infiltration rate of this soil. Hunt et al. (1988) demonstrated that the aqueous solubility of organic contaminants is inversely proportional to the water flow velocity in the soil. Apparenlty, the longer contact time between the two phases promotes the mass transfer of benzene in the water This explains the higher benzene concentrations in this soil and consequently the higher cumulative mass loss in the leachate.

That the leachate concentrations were generally less than benzene solubility (1800 mg L^{-1}) was probably because local equilibrium between the two phases was not reached. Certainly a long-term benzene leaching experiment is needed in the future.

These data offer a proximate estimate of the benzene mass which is expected to leach below the unsaturated zone following an accidental spill under stable, vertical, unsaturated flow conditions. Under real conditions the benzene leaching phenomenon would be more complex because the flow velocity of water is variable. Also, the solubility of benzene changes when the substance is found in mixture, e. g., in gasoline (Zalidis et al. 1991).

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