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Leachability of volatile fuel compounds from contaminated soils and the effect of plant exudates: A comparison of column and batch leaching tests

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HIGHLIGHTS

- Contaminant leachability was influenced by soil composition.
- Soil organic matter hindered leaching of the most hydrophobic contaminants.
- Soil inorganic components hindered leaching of the least hydrophobic contaminants.
- Batch shaking favoured contaminant desorption and annulled differential sorption.
- Plant exudates influence soil-contaminant interactions.

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ABSTRACT

Volatile fuel compounds such as fuel oxygenates (FO) (MTBE and ETBE) and BTEX (benzene, toluene, ethylbenzene and xylene) are some of the most soluble components of fuel. Characterizing the leaching potential of these compounds is essential for predicting their mobility through the soil profile and assessing the risk of groundwater contamination. Plant root exudates can play an important role in the modification of contaminant mobility in soil–plant systems, and such effects should also be considered in leaching studies. Artificially spiked samples of A and B horizons from an alumi-umbric Cambisol were leached in packed-columns and batch experiments using Milli-Q water and plant root exudates as leaching agents. The leaching potential and rate were strongly influenced by soil-contaminant interactions and by the presence of root exudates. Organic matter in A horizon preferably sorbed the most non-polar contaminants, lowering their leaching potential, and this effect was enhanced by the presence of root exudates. On the other hand, the inorganic components of the B horizon, showed a greater affinity for polar molecules, and the presence of root exudates enhanced the desorption of the contaminants. Column experiments resulted in a more realistic protocol than batch tests for predicting the leaching potential of volatile organic compounds in dissimilar soils.

1. Introduction

Benzene, toluene, ethylbenzene and xylene (BTEX) and the fuel oxygenates (FO) methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) are some of the most volatile and water-soluble components of fuel. These compounds can readily migrate to air or leach to groundwater [24]. Volatile compounds have caused significant contamination of groundwater in many countries, and much money has been invested in research and remediation systems since the 1970s [25]. Hence, understanding fluid transport through the vadose zone and studying the effects of attenuating contaminants (including volatilization, sorption, dispersion or biodegradation) are essential for predicting the fate of the contaminants and for risk assessment and development of appropriate remediation procedures [25].

Particularly, the interaction between soil and contaminants can greatly affect the mobility of MTBE, ETBE and BTEX. If a significant amount of sorption occurs in the unsaturated zone, contaminants will leach slowly and accumulation of contaminants in the groundwater will be minimized. Sorption is mainly affected by soil

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components and physical and chemical properties [20]; thus the composition and type of soil in which the fuel leak has occurred and the leachability of volatile fuel contaminants, should therefore, be taken into account for correct management of fuel leaks and for preventing or minimizing groundwater contamination.

Leaching tests aim to determine the fraction of contaminants that are loosely bound to soil components and thus mobilized into the water phase. The tests are therefore used to assess the risk of release of potential pollutants from solids into groundwater, seepage water or surface waters [14]. The most commonly used methods of determining contaminant leachability are batch and packed-column tests. In batch equilibrium tests, the soil is shaken in the leaching solution for a fixed length of time to allow equilibrium between the contaminants in solution and in the soil. Many protocols have been developed by different organizations. The following are some of the most widely used batch-type leaching experiments: the toxicity characteristic leaching procedure (TCLP), initially developed by the US Environmental Protection Agency (USEPA Method 1311, [28]) to evaluate the water contamination by solid residues; the batch method developed by the Organization for Economic Cooperation and Development (OECD) in its "Guidelines for the Testing of Chemicals"(OECD Guideline 106, [22]) and used to predict or estimate the availability, leaching, or run-off of chemicals in soil samples; and methods developed by the European Committee for Standardization (CEN EN 12457, [8]) and by the International Organization for Standardization (ISO/TS 21268). The most important differences between these protocols are the liquid to solid ratios, the composition of the leaching solution, and the solid particle size. These procedures enable calculation of soil–water distribution coefficients (K_d), which are widely used in contaminant dynamics modelling [4]. In packed-column leaching tests, contaminated soil is placed in columns through which a leaching solution is passed and the amount of contaminant dissolved in the liquid phase from the present in the soil is then determined. This type of test is usually used when the aim is to assess time-dependent source concentrations [26]. Column leaching tests are closer to natural conditions than other laboratory tests [17] as they simulate the flow of water through the solid material [14].

In a previous study [6], we investigated the effect of plant root exudates on the mobility of volatile fuel compounds sorbed to several samples of soil and soil components. For this purpose, we used a closed batch experiment approach carried out in headspace analysis vials (without a centrifugation step), for comparative assessment and indirect characterization of the modification of contaminant mobility in the absence and presence of root exudates. Root exudates can produce significant changes in physicochemical soil and contaminant properties, which may greatly influence sorption–desorption processes, and therefore, the mobility and bioavailability of soil contaminants [31,21]. Therefore, the role of root exudation on the soil–plant-contaminant system can strongly affect the final fate of the contaminants in the environment and should therefore be investigated towards a better understanding of these complex interactions.

The aim of the present work was to characterize and compare the leachability of FO and BTEX from spiked soils with different properties using a packed closed-column system specially designed for volatile contaminants. Furthermore, we compared these results with those obtained in a batch experiment in order to evaluate the suitability of both protocols for determining the leaching potential of mobile fuel organics. The samples were leached with Milli-Q water and with a root exudate solution collected from plants of the perennial grass *Holcus lanatus*, for evaluation of the effect of root exudation on the modification of volatile fuel compounds leachability.

2. Materials and methods

2.1. Reagents

The following reagents were used in the study: benzene (purity, 99.8%; grade, PAI-ACS (UV-IR-94HPLC-GPC)); toluene (purity, 99.8%; grade, PAI-ACS (UV-IR-HPLC-GPC)); ethylbenzene (purity, 99%; grade, PS); *o*-xylene (purity, 99%; grade, PA (Reag.USP. Ph. Eur)); *m*-xylene (purity, 99%; grade, PA (Reag. Ph. Eur)); *p*-xylene (purity, 99%; grade, PA (Reag.USP)); MTBE (purity, 99.7%; grade, PAI (PAR)); and ETBE (purity, 99%; grade, PA (Reag. USP)). Some physicochemical properties of these contaminants are presented in Table 1. Fluorobenzene (purity, 99%) was used as a surrogate standard. All reagents were purchased from Panreac Química, S.L.U. (Barcelona, Spain), except fluorobenzene, which was purchased from Sigma–Aldrich Co, LLC (Madrid, Spain). The spiking solution contained each of the reagents at a concentration of 100 mg L^{-1} in methanol (purity, 99.9%; grade, PAI (PAR)).

2.2. Collection of natural root exudates

Natural root exudates were collected from seedlings of the perennial grass *H. lanatus*, as previously described in [6]. Briefly, 3–4 week old seedlings, previously germinated on sterile 1:1 vermiculite:perlite mixture, were transferred into sterile 500-mL Erlenmeyer flasks containing continuously aerated 0.5-strength Hoagland's nutrient solution. Plants were allowed to grow for 4 weeks before the root exudates were sampled. Exudates were collected by transferring the plants to sterile 0.4 mM $CaCl_2$ solution. After 24 h, the plants were removed and the exudate solution was immediately filtered (0.2 μm), frozen and lyophilized to minimize microbial degradation. This protocol was repeated until the required volume of root exudate solution was obtained.

The lyophilized exudate solutions thus obtained were then redissolved in sterile Milli-Q water to obtain a dissolved organic carbon concentration (DOC) of approximately 20 mg C L^{-1}. The DOC

Table 1
Physicochemical properties of MTBE, ETBE and BTEX.

Contaminant	Boiling point (°C)	Water solubility (g L^{-1})	Vapour pressure (Pa)	log K_{ow}	log K_{oc}
MTBE[a]	55.0	51.6	31156	1.06	1.10
ETBE[b]	69.0	50.0	28000	1.48	1.57
Benzene[c]	80.1	1.8	12654	2.16	1.82
Toluene[c]	110.6	0.5	3786	2.69	2.17
Ethylbenzene[c]	136.2	0.1	1546	3.15	2.51
m-Xylene[c]	139.1	0.2	833	3.20	2.62
p-Xylene[c]	138.4	0.2	787	3.15	2.43
o-Xylene[c]	144.5	0.2	767	3.15	2.45

[a] [9].
[b] [10].
[c] [19].