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Column leaching tests on soils containing less investigated organic pollutants

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ABSTRACT

Column tests are a common tool to investigate the leaching behavior of contaminated soil and waste materials. In contrast to inorganic analytes, fewer studies with organic contaminants are available based on column tests. This paper is aimed at the question if soil materials contaminated with organic pollutants can be reliably investigated by column tests. Soils contaminated with TPH (total petrol hydrocarbons), PFC (perfluorinated surfactants) and the biocide tebuconazole were used for column percolation tests. Differences in the leaching behavior are mainly driven by partitioning behavior between organic carbon and water, which can be estimated from log K_{OW} values and size and shape of molecules. PFC show higher release (10–50% for individual compounds) than pesticides (3.7–5.3%) and TPH (<1%) at liquid to solid ratio of 4 l/kg. All eluate concentrations are low with maximum concentrations of 50 µg/l for PFC and 1–2 mg/l for pesticides and TPH. Despite this, the observed standard deviations are quite small suggesting good repeatability. In general the observed concentration trends are similar to that from lysimeter studies found in the literature and thus, it can be concluded that laboratory column experiments are a reliable tool for organic compounds with various physico-chemical properties.

1. Introduction

Soils can be contaminated by various sources: deposits from airborne pollution, application of pesticides, sewage sludge or fertilizers and by residues of abandoned industrial sites from the past. For assessment of the risk these chemicals pose to the environment and human health, not only the direct impact on the soil, but also transport to other environmental compartments has to be considered. Transport to the unsaturated zone and to groundwater via seepage water depends always on soil properties as organic carbon content and soil pH as well as compound specific properties such as sorption behavior and water solubility (Grathwohl and Susset, 2009). Depending on the presence of pH sensitive functional groups this behavior may even change with pH changes (Bronner and Goss, 2010). Furthermore the influence of a single parameter on the overall effect is often ambiguous: e.g. strong sorption of compounds to the soil matrix will lead to a slow transport through the soil and a high attenuation capacity. In contrast to this the transport may be facilitated if the contaminant is adsorbed to dissolved organic carbon (DOC). Thus, it is commonly accepted that total concentrations are not a suitable measure to evaluate the risk soil contaminants pose to groundwater resources e.g. (Grathwohl and van der Sloot, 2007; Susset and Leuchs, 2008).

Laboratory leaching tests as column percolation tests have been proven to be fundamental tools for the assessment of groundwater impact by contaminated soils or waste materials. They enable the investigation of time dependent leaching behavior of granular materials by collecting several eluate fractions at defined liquid to solid ratios (Kalbe et al., 2007).

Parameters influencing the test results are the grain size of the investigated material, the porosity of the material packed into the column, and the flow velocity of the eluent through the column, i.e. contact time between eluent and material. As soils are normally sieved to grain sizes below 2 mm before testing, grain size influence is mostly less relevant for this kind of material. The contact time and the flow velocity are not independent, but are connected in the following way (DIN, 19528, 2009-01):

$$v = \frac{V * n}{t * 60} \quad (1)$$

where v is the flow velocity in ml/min, V is the volume of the column filled with the sample in cm^3, n is the porosity of the sample (dimensionless) and t is the contact time in h. Due to this relationship either the flow velocity or the contact time shall be fixed. In the German standard the contact time is set constant facilitating the comparison between column tests of different set-up.

The aim of percolation tests in a regulatory perspective is to determine the release (also called source term) of contaminants. Together with modeling of the contaminant transport, the risk for groundwater can be estimated. Lysimeter studies may include both terms and reflect in general field situations closer (Grathwohl and Susset, 2009; Susset and Grathwohl, 2011). Due to the higher effort and costs lysimeter studies are limited for special investigations under field conditions and are not suitable for routine applications (Kalbe et al., 2008), while

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column tests are a reasonable compromise between cost and closeness to field conditions.

For this purpose, a new standardized column test procedure (DIN 19528) (DIN, 19528, 2009-01) was established as a tool for source term determination and subsequent prognosis of concentrations of contaminants in seepage water associated with the amendment of the German Ordinance on Soil Protection and Contaminated Sites. This leaching standard has been validated so far for a variety of inorganic substances but in the case of organic pollutants only for polycyclic aromatic hydrocarbons (PAH). Other frequently occurring pollutants such as total petroleum hydrocarbons (TPH), polychlorinated biphenyls (PCB) and phenols have been addressed recently in a further robustness validation study (Berger et al., 2012).

Further less investigated organic pollutants as PFC and two pesticides (tebuconazole and propiconazole) which are coming into consideration in the framework of new German and international regulations were investigated within this study in order to check if soil materials contaminated with such pollutants can be reliably evaluated by column tests. All model substances and compound groups chosen here are recognized contaminants and have been detected in soil and groundwater (Loos et al., 2010; Pinedo et al., 2013; Sanchez-Gonzalez et al., 2013; Zareitalabad et al., 2013). Among these TPH are in the focus of environmental scientists and regulators since many years as typical sources include all facilities dealing with crude oil and oil products. TPH is a group parameter including several hundreds of single chemicals comprising aromatic and aliphatic hydrocarbons as major components and unsaturated hydrocarbons (alkenes and alkanines) and alkylnaphthalines as minor components (Saari et al., 2008). The mobility of the TPH to groundwater depends in general on the chain length or molecular weight and is in general limited because of low water solubility (Mohamed et al., 2007).

Propiconazole and tebuconazole are both fungicides belonging to the group of triazoles. Both are used in agriculture especially for crops and vineyards and as wood preservatives. Both fungicides are stable towards hydrolysis and biodegradation, but only propiconazole fulfills the criteria for persistent compounds. Tebuconazole has embryotoxic and teratogenic effects in three species (rabbit, rat, mice) (European Commission, 2007, 2013). Although PFC have been used for half a decade in several fields e.g. in fire-fighting foams, in cosmetics and textiles as water repellent agent (Lindstrom et al., 2011), this group of compounds is only recently in the focus of environmental scientists. The application of contaminated sewage sludge as fertilizer is one of the major sources for PFC in soils (Sun et al., 2011). PFC are persistent (Saez et al., 2008) in soil due to missing natural mechanisms for degradation. PFC possess a half-life of several years in humans and are of concern for negative health effects (Lindstrom et al., 2011). The mobility of these compounds mainly depends on the chain length (Gellrich et al., 2012) and especially compounds with a chain length smaller than eight C-atoms show higher water solubilities (Gellrich et al., 2012).

In summary, all exemplary chosen compounds are of environmental concern as they are already detected in the environment, are not easily degradable and show adverse effects to organisms and are thus regulated or intended to be regulated in the near future. The aim of this work is to broaden the knowledge about the applicability of column leaching tests for the investigation of organic contaminants to facilitate the risk assessment of such compounds.

2. Materials and methods

2.1. Processing of the test materials

Table 1 gives an overview about the soils used in this study including their characteristics. The soil containing PFC was sampled in April 2011 on a German site, where sewage sludge was applied. After the arrival of samples the soil was air dried and subsequently sieved to particle sizes

Table 1
Origin and characteristics of soil samples investigated.

Compound class	PFC					Pesticides		TPH
Analytes	PFBA (perfluorobutanoic acid)	PFHxA (perfluorohexanoic acid)	PFHpA (perfluoroheptanoic acid)	PFOA (perfluorooctanoic acid)	PFOS (perfluorooctane sulfoate)	Tebuconazole	Propiconazole	Total petrol hydrocarbon
Origin of soil		Contaminated site, maize farmland, Hochsauer-land, Germany				Spiked soil		Blended soils
Soil type		Sandy loamy silt				Sandy silt		Medium sand
pH [−]		8				5.4		8.5
Corg [weight %]		7.02				4.26		0.65
Solid matter content [mg/kg]	0.03	0.03	0.03	0.54	1.70	67.6	63.4	522 (C10–C22) 1725 (C10–C40)
Analytical method		Ultrasonic extraction methanol; HPLC–MS/MS (DIN 38414-14)				Ultrasonic extraction methanol; UHPLC		Extraction hexane; GC-FID (DIN ISO 9377-2)