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Difference in PAH release processes from tar-oil contaminated soil materials with similar contamination history

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Abstract

Tar-oil contaminated sites, for example, former manufactured gas- and tar-processing sites, pose a continuing threat to soil and groundwater in Europe. In this study, the release processes of polycyclic aromatic hydrocarbons (PAHs) of five soil materials from four locations in Germany are discussed. All materials were investigated by means of column outflow experiments. Variable flow conditions were applied to reveal possible rate-limited release processes. Flow conditions and high-resolution break through curves of the master variables dissolved organic carbon, turbidity, pH and electrical conductivity, are examined in consideration of their possible influence on PAH release. Although the history of the sites is similar with respect to age and type of contamination, different processes and time scales control the release and discharge of PAHs. For example, the release from a silt from Rositz and from a sandy reference material was governed by equilibrium and according to Raoult's Law, while a gravel from Munich and a clayey marlstone from the 'Testfeld Süd' released PAHs bound to particles and at non-equilibrium. Physico-chemical gradients as well as the nature of the residual tar phase are key parameters for the characteristics of release and transport. The results show that risk assessment at sites contaminated with tar-oil requires an experimental evaluation in order to estimate the PAH fluxes. Besides, it is crucial to consider the effect of mobile particles.

Keywords: Coal tar; Column experiment; Raoult's Law; Rate-limited release; Non-equilibrium; Flow interruption; Carrier; Co-transport; Risk assessment

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1. Introduction

Natural resources, such as soil and groundwater are frequently threatened by spills and leakage from former manufactured gas plants and tar-processing sites. Different factors affect the release of contaminants at such sites. At first, it must be acknowledged that a variety of coal-tar products was processed. The liquid fraction of the production process ranges from tar-oils consisting of organic compounds with low molecular weight and low boiling point to bituminous materials (tar pitch), which comprise mainly the residual fraction of the distillation process with high molecular weight compounds. Consequently, spills of non-aqueous-phase liquids (NAPL) are often chemically diverse. Once a NAPL entered the subsurface, it starts to migrate due to gravity and capillary forces. Its movement is mainly governed by physical properties such as its density and

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viscosity and soil texture and wettability (Bradford et al., 2003). Capillary forces are also responsible for a residual NAPL portion retained in the soil matrix. Various approaches are available for the numerical modelling of such two-phase transport including a residual NAPL (Wipfler and van der Zee, 2001; Van Geel and Roy, 2002). Pumphrey and Chrysikopoulos (2004) published a model for NAPL-drop formation and transport in the aqueous phase. Yet, in case of tar-oils and bitumen, a parametrization of models must be considered difficult due to the original chemical diversity of the contaminant phase and its diversity due to ageing and fractionation processes.

When all non-aqueous liquid is present as residual fraction, transport of contaminants still occurs within the pore water. Here, the spatial distribution of the residual NAPL has a crucial influence on the release behaviour of contaminants into the pore water. For example, due to a small surface to volume ratio, the dissolution from a NAPL pool is rather diffusion limited, while discontinuous NAPL blobs (e.g. in a smear zone) have a much larger contact area and equilibrium is obtained within the contact time with the percolation solution. This was observed in a large-scale tank experiment by Eberhardt and Grathwohl (2002). They found that equilibrium partitioning could be modelled according to Raoult's Law. Other researchers found that NAPL present in multipore ganglia might lead to restricted contact with water such that equilibrium conditions are not obtained (Conrad et al., 1992; Powers et al., 1992). Exposition of a dry soil to NAPL contamination might result in an irreversible NAPL wetting. Then, NAPL is present in surface coatings or even in intra-particle micropores (Heyse et al., 2002). The latter might again result in mass transfer limitations, while the high interfacial area of surface coatings might allow a rapid release (Karapanagioti et al., 2000). Apart from spatial distribution, aging processes alter the composition in particular at the interface to water and air and influence the release process. Depletion of volatile and highly soluble compounds and chemical transformations result in highly viscous interfacial films and thus in decreased mass transfer rates (Totsche et al., 2003).

In the unsaturated soil zone, the dissolution of PAHs in the soil water might play an insignificant role due to their low aqueous solubility and their high affinity to organic matter. Yet, they might be transported attached to colloids, which act as carriers. Apart from inorganic suspended solids, such as clay minerals, especially colloids of organic origin play an important role as carriers (Kretzschmar et al., 1999). Under these circumstances, the factors controlling the mobility of particles are essential for release and transport of PAHs. Colloids and particles can be mobilized during rain events by a decrease of the soil solution's ionic strength and by increased hydrodynamic forces caused by large flow velocities (Kaplan et al., 1993; Ryan and Gschwend, 1994). In preferential flow paths, these carriers are transported through the unsaturated zone and occur in the groundwater (Villholth, 1997; Sirivithayapakorn and Keller, 2003). Depending on the origin and fate of the carriers, the concentration of PAHs in the pore water might either be enhanced or reduced due to the presence of sorbents (Totsche et al., 1997; MacKay and Gschwend, 2001).

Column experiments offer the opportunity to study the release from porous materials under near-natural flow conditions. Yet, it is necessary to conduct these experiments with appropriate boundary conditions to allow the distinction of equilibrium and non-equilibrium (rate-limited) release. This is impossible in column experiments with a single pulse input due to insufficient information carried by the break through curve (BTC) (Totsche, 2001). Brusseau et al. (1997) showed that equilibrium and non-equilibrium conditions can be discerned by flow interruptions. Wehrer and Totsche (2003) derived an experimental design including flow interruptions and different flow velocities for short-term column experiments, which allows distinguishing between equilibrium and non-equilibrium release. This setup was tested with organically contaminated materials under saturated conditions (Wehrer and Totsche, 2005, 2008b; Totsche et al., 2006) and also with inorganic contaminants (Wehrer and Totsche, 2008a).

In this study, the results of column outflow experiments with substrates contaminated with tar-oils are compared with respect to PAH export. All samples originate from former manufactured gas- and tar-processing sites. Variable flow conditions were applied in order to identify rate-limited release processes. We demonstrate how different release processes and release rates can be identified by column outflow data and discuss the outflow behaviour with respect to pH, electrical conductivity (EC), dissolved organic carbon (DOC) and turbidity. Finally, we aim for the identification of the dominating release processes of PAHs, where these parameters might be of importance.

2. Materials and methods

2.1. Soil materials

Five contaminated soil materials originating from former manufactured gas- and tar-processing sites in Germany are compared in this study: A fine-textured soil material collected at the Rositz site (abbreviated subsequently as 'RS', Rositz silt), Thuringia, Germany (Totsche et al., 2003). A sandy material, provided by the BAM, Berlin, which served as reference material (RM) in the 'Sickerwasserprognose' (= seepage water prognosis) – project of the German Federal Ministry of Research and Development (Berger et al., 2004).