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# Parameters describing nonequilibrium transport of polycyclic aromatic hydrocarbons through contaminated soil columns: Estimability analysis, correlation, and optimization

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ABSTRACT

The soil and groundwater at former industrial sites polluted by polycyclic aromatic hydrocarbons (PAHs) produce a very challenging environmental issue. The description of PAH transport by means of mathematical models is therefore needed for risk assessment and remediation strategies at these sites. Due to the complexity of release kinetics and transport behavior of the PAHs in the aged contaminated soils, their transport is usually evaluated at the laboratory scale. Transport parameters are then estimated from the experimental data via the inverse method. To better assess the uncertainty of optimized parameters, an estimability method was applied to firstly investigate the information content of experimental data and the possible correlations among parameters in the two-site sorption model. These works were based on the concentrations of three PAHs, Acenaphthene (ACE), Fluoranthene (FLA) and Pyrene (PYR), in the leaching solutions of the experiments under saturated and unsaturated flow conditions.

The estimability results showed that the experiment under unsaturated flow conditions contained more information content for estimating four transport parameters than under the saturated one. In addition, whatever the experimental conditions for all three PAHs the fraction of sites with instantaneous sorption, $f$, was highly correlated with the adsorption distribution coefficient, $K_d$. The very strong correlation between the two parameters $f$ and $K_d$ suggests that they should not be simultaneously calibrated. Transport parameters were optimized using HYDRUS-1D software with different scenarios based on the estimability analysis results. The optimization results were not always reliable, especially in the case of the experiment under saturated flow conditions because of its low information content. In addition, the estimation of transport parameters became very uncertain if two parameters $f$ and $K_d$ were optimized simultaneously. The findings of the current work can suggest some reasons behind the optimization problems and indicate the type of experimental information additionally needed for parameter identification. To overcome the parameterization issues of PAH non-equilibrium transport, the experimental design, timescale, and model refinement need further improvement. The conclusions presented in this paper are not limited necessarily to PAHs, but may also be relevant to other organic contaminants with similar leaching behavior.



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## 1. Introduction

PAHs are a group of more than 100 molecules composed of at least 2 fused aromatic rings (Wang et al., 2013). PAHs are persistent organic pollutants with a low solubility in water and a low volatility. They are neutral, hydrophobic and non-polar molecules. These compounds are ubiquitous in the environment since they are present in air, water and soil. PAHs are produced during the burning of fossil fuels, can come from incomplete combustion of organic matter and are particularly abundant in closed gas plant sites where producer gas or coking gas were being manufactured (Li et al., 2010; Sun et al., 2012). Soil and sediments are considered to be the major sinks for PAHs (Zheng et al., 2012) and they were reported in soils in many countries, such as UK, Italy, Slovenia, Denmark and China (e.g., Chung et al., 2007; Essumang et al., 2011; Liu et al., 2010; Morillo et al., 2007; Peng et al., 2011). PAHs are strongly adsorbed to soil particles (Hansen et al., 2004). Nevertheless, PAHs can be associated to colloids or dissolved organic matter, which can enhance their downward transfer in soils and thus their possible release to groundwater (Magee et al., 1991; Thompson and Scharf, 1994; Villholth, 1999; Wehrer and Totsche, 2005). Therefore, they are of major interest because they are carcinogenic and mutagenic (White and Claxton, 2004). 16 PAHs have been classified by the American Environmental Protection Agency as priority pollutants given their high toxicity. Human beings are mainly exposed orally to PAHs from food or water or through the lungs by inhalation of the gases emitted. When absorbed by human beings, PAHs will be hydrolyzed and dehydrated and an anhydride will be produced. This anhydride is toxic because it will irreversibly fix amino-acids and will disturb RNA and DNA duplications, which will lead to mutation or cancer.

PAHs caused the pollution of soil and groundwater at many former industrial sites and became a significant environmental issue (Totsche et al., 2007). Understanding of the PAHs' release kinetic and transport behavior in contaminated soil is therefore required for risk assessment and remediation strategies at the contaminated PAH sites (Totsche et al., 2006, 2007). Generally, the interaction between organic contaminants and the solid phase is highly nonlinear (e.g., Wehrer and Totsche, 2005) and the release of contaminant is often limited by mass transfer kinetic (e.g., Brusseau and Rao, 1989; Culver et al., 2000; Seuntjens et al., 2001), which is indicated by diffusion and/or sorption kinetic. Depending on the physical or chemical factors, non-equilibrium transport is then represented by physical or chemical non-equilibrium models (Simunek and van Genuchten, 2008), respectively. Due to the complexity of release kinetic and transport behavior of PAHs, especially in the aged contaminated soils, the evaluation of PAHs' transport is generally performed by means of laboratory columns (e.g., Totsche et al., 2006; Wehrer and Totsche, 2003, 2005).

Mathematical models are crucial tools to understand and quantify transport processes. The application of a modeling tool describing non-equilibrium transport of a contaminant requires estimates of various parameters at the appropriate scale, especially for the transport parameters that play an important role in the fate of the contaminant such as distribution coefficient, mass transfer rate coefficient, etc. In the literature, various studies have reported that the velocity of flow strongly influences the transport behaviors of contaminants (e.g., Hanna et al., 2012; Marshall et al., 2000). Additionally, many studies have shown the existence of a significant difference between transport parameters measured through batch experiments and those obtained in the columns or field experiments by the inverse method (e.g., Dontsova et al., 2006; Moradi et al., 2005; Pot et al., 2005; Seuntjens et al., 2001).

The inverse estimation method is a promising way to estimate transport parameters required at the studied scale. This approach is increasingly used in the literature and showed much progress but the problem concerning the uncertainty and non-uniqueness of estimated parameters still exist (e.g., Kohne et al., 2004; Kohne et al., 2006; Simunek et al., 2001). There are various factors contributing to the non-uniqueness of the optimized parameters. These factors are mainly attributed to: (i) the precision of numerical code, i.e., precision of the numerical solution, presence of multiple local optimal solutions of the objective function (e.g., Kelleners et al., 2005); (ii) the limited optimal design of the experiment giving the low information content of the data used in the objective function (Kohne et al., 2006; Ngo et al., 2013; Simunek et al., 2001); and (iii) the strong correlations among parameters being estimated (Friedel, 2005; Kohne et al., 2006). According to Friedel (2005); the correlations between different parameters can be even considered as the most difficult factor that causes the uncertainty of model. Therefore, to avoid the influence of correlations among parameters on the optimization results and to better define optimization scenarios based on the proposed experimental conditions, it is necessary to evaluate the information content and the possible correlations between different parameters before estimating them. For doing so, we applied an estimability method developed by Yao et al. (2003) to look for insight into the above factors based on the available data collected from the experiments under saturated and unsaturated flow conditions. In the literature, this estimability technique has been successfully applied in various studies coming from different domains. For example, in the vadose zone hydrology, Ngo et al. (2013) have recently applied this method to investigate the estimability and correlations of the soil hydraulic parameters based on the experimental data being measured by the tensiometer and TDR sensors in a field lysimeter. Furthermore, the method of Yao et al. (2003) was applied in various studies in the chemical engineering to evaluate the estimability of the chemical models containing many parameters (e.g., Jayasankar et al., 2009; Kou et al., 2005; Marshall et al., 2000; Pan et al., 2011; among others).

The overall objectives of this paper were (i) to evaluate information content and the possible correlations among parameters based on the PAHs leaching from the aged contaminated soil columns under saturated and unsaturated flow conditions by using the estimability method; and (ii) to optimize the estimable parameters based on the available data and see how significantly the correlations among parameters influence the uncertainty of optimized parameters.

## 2. Material and methods

### 2.1. Experimental description

#### 2.1.1. Soil sample

The aged contaminated soil used for this study was sampled at a former coking plant site, located in the north east of France, in the Lorraine region (49°14′ N, 5°59′ E). The factory on this polluted site was stopped and torn down in