1.   INTRODUCTION

This works comprises three different aspects. The first one is the use of column experiments for the investigation of the sorption process of chlorinated organic compounds in porous medium; the second aspect is the implementation of the analytical technique, which consists in the adaptation of the relatively new method based on the Solid-Phase Microextraction (SPME) technique coupled with gas chromatography; and the last aspect is the development of a computer program used to analyse the experimental data of the column experiments.

1.1   Transport and Sorption of Contaminants in Aquifers

In the last two decades the transport and fate of contaminants in aquifers, specifically chlorinated organic compounds, has become an important topic because the possible impact of the migration pattern of contaminant plums released from hazardous waste sites, landfills, or accidental spills on groundwater systems that could posses a potential danger on drinking water supplies. Investigating and understanding the physical, chemical, and biological processes that influence the solute transport in saturated media, and the associated mechanisms is important for predicting the fate and transport, and for selecting cleanup technologies. Furthermore, after detecting a risk zone, it is important to evaluate the feasibility to apply a remediation technique or to monitor if Natural Attenuation processes may take place, because it is recognized that a complete subsurface restoration is in most cases prohibitively, due to the high costs associated, and probably unnecessary (McMillan and Werth, 1999). In a remediation approach the Natural Attenuation processes include dispersion, dilution, sorption,

volatilisation, biodegradation, and chemical or biological reactions. Under favourable conditions these processes act to reduce the mobility, toxicity and concentration of contaminants in the subsurface, *i.e.* soil and groundwater, without human intervention (Wiedemeier et al., 1998).

1.2 Sorption Impact on the Mobility of Contaminants

Sorption plays an important role in the decision of a remediation action because it impacts the migration of the substances due to a retardation in the mobility of the contaminants in the aquifer (Bedient et al., 2000). Additionally the complexities and heterogeneities at the site contribute to the difficulty on elucidating the mechanisms in the transport process. It has been observed on the field, that two time scales are present in the adsorption and desorption of contaminants in soils, one fast on the order of minutes to hours, and a slow one in the order of weeks to months (Grathwohl and Reinhard, 1993, Werth and Reinhard, 1999). Specially, the slow sorption may hinder the ability to predict the long-term transport and fate because it contributes to the extended concentration tailing observed at many field sites.

In natural aquifers, more than two contaminants are often encountered at the site, and the question arises if a competitive effect could take place and how this could affect the remediation of a site. This problem was often ignored because it is not easily observed and the mechanisms for a competition are not clear. But this topic is gaining attention again, because the presence of a competitive effect reveals that certain contaminants have more affinity to adsorb in specific sites in the aquifer. This competition may induce a faster transport of some of the contaminants as expected.

Therefore predicting the slow transfer rates and the competitive effect are important to predict clean-up times or the risk that the contaminants plume poses to potential receptors, like groundwater or drinking water bodies in populated areas.

1.3   Objective

In natural systems more than two components are always present which could lead to a competitive sorption, which is often neglected due to other processes could mask its effects. This thesis is motivated in order to understand the role of the competitive sorption between compounds of similar structure and composition that may take place in porous media with low organic carbon content. If a competition between species exists, that would mean that specific sorption sites would be responsible for that effect.

This work hast three objectives. The first objective is to hone a protocol that would result in fast, reliable and reproducible headspace-SPME analysis of water samples containing chlorinated ethenes. This protocol is applied as the sampling method in soil column experiments to acquire highly accurate breakthrough curve data. The factors that could most strongly affect the quality of the assay results, *e.g.* storing time, extraction temperature, and the ratio V_T/V_w, are evaluated.

The second objective and the central part of this work is to demonstrate the competitive sorption in an homogeneous model soil, represented by silica gel, and to model the breakthrough curve data with the advection-dispersion equation with valid physical models for diffusion in porous media and competitive sorption. The use of 1,2-*cis*-dichloroethene (*cis*-DCE) and trichloroethene (TCE) as model contaminants is justified because they are widespread studied and they are found in many aquifer sites, like in Lauf a.d. Pegnitz (Germany). A special column equipment is proposed to reach this objective, taking care of the volatility and sorption of the substances. The transport is simulated at low temperature (10 °C) and at low concentrations as in the site of Lauf.

The third objective is to develop a code to analyse the experimental breakthrough curve data under competitive conditions. The Moving Concentration Slope method, developed by per Moldrup (Moldrup et al., 1992), is proposed to solve the transport and reaction equations. The mathematical modelling is implemented in a self written numerical procedure in Fortran, named **NEMMCS** (Non-equilibrium Multispecies Moving Concentration Slope).

1.4 Outline of This Thesis

A general literature review is covered in Chapter 2. This section comprises the properties of the chlorinated ethenes, the surface chemistry of the silica gel. A description of the mass transport in saturated porous media is covered, and the competitive adsorption isotherms are explained in this section.

The mathematical modelling of the transport model in saturated media for analysing breakthrough curve data is found in Chapter 3, taking as basis the advection–dispersion equation. This section covers the physical- and chemical non-equilibrium models. The competitive sorption is considered, the multicomponent isotherms, extended Freundlich or extended Langmuir are implemented. The mathematical procedure used to solve the coupled equations is described in this chapter. The Moving Concentration Slope scheme for the modelling of the breakthrough curve is implemented and described.

Chapter 4 deals with the materials and experimental procedures used in this thesis followed by the description of the column experiments, and the development of the analytical method based on Solid-Phase Microextraction and gas chromatography.

The protocol for the analysis of aqueous samples containing chlorinated ethenes is explained in Chapter 5. Preliminary results from column experiments are used as a basis to develop a specific SPME method for column experiments. The factors that could influence the results are discussed, and the recommendations for the sampling procedure are given.

In Chapter 6, the results and conclusions of the column experiments conducted to investigate the competitive sorption of *cis*-DCE and TCE in an homogeneous porous model soil, silica gel, are discussed. The experimental isotherm data is analysed with the Freundlich and Langmuir isotherms. The effective diffusivity parameter was optimised with an inverse modelling technique. The overshoot phenomenon, the increase of the concentration of one of the solutes above its input concentration, observed in these experiments is discussed.