Description of doctoral project and research results achieved to date

Subsurface contamination is a major concern in industrialized as well as in developing and emerging countries. The list of potential contaminants includes a wide variety of organic compounds used in industry, such as solvents and degreasers. Contaminants introduced into the unsaturated zone migrate as a liquid phase; however, they can also vaporize and migrate in a gaseous state. Contaminant vapor (gas) plumes emanating from liquid sources migrate easily in the unsaturated zone. Heavy vapors preferentially migrate downward due to their greater density and thus pose a potential threat to underlying aquifers.

This investigation seeks to explore fate and transport of carbon disulfide (CS$_2$) vapor and techniques for its remediation from the unsaturated zone. CS$_2$ was chosen as the model substance since it fulfills the physico-chemical requirements for density-driven vapor migration. It is highly volatile and in its gaseous state (air/nitrogen at saturated CS$_2$ concentration) characterized by a very high density (1.6) relative to air. CS$_2$, amongst others used for the manufacture of viscous rayon, is an industrial, non-polar solvent that has been found in 139 (11.2 %) contaminated sites on the U.S. EPA National Priority List (NPL). Hereby, the understanding of fundamental and relevant processes of vapor migration in dry and retention in partially water saturated porous media is of major importance.

The danger and the extent of vapor plumes emanating from liquid contaminants depend on various parameters: Permeability, porosity, and soil moisture content of the porous media influence advective and diffusive flow. The total contaminant mass directly affects the size of the vapor plume. The difference in density or molecular mass of the contaminant vapor relative to that of the soil air directly induces gravity driven migration. While vapor pressure in conjunction with the air-contaminant interfacial area affects the vaporization speed and thus controls the velocity of plume development as well as its spatial extent, migrating vapor plumes may be retarded by sorption, dissolution, and biodegradation in the subsurface. Eventually, atmospheric pressure and temperature influence these conditions.

These conditions or properties are responsible for triggering and determining migration in the subsurface. Given the complexity of vapor transport in the unsaturated zone, this investigation was divided into two major parts:

1. Characterization of relevant and fundamental processes.
2. Development of a remediation technique applicable in the unsaturated zone.

The first part, relevant and fundamental processes is subdivided into density-driven vapor migration and vapor retardation. Large-scale column experiments and numerical simulations were conducted to investigate the density-driven migration of carbon disulfide (CS$_2$) vapor. The experiments were conducted in large, vertical columns (i.d. = 0.109 m) of 4 m length packed with a dry porous medium. Different types of glass beads were used to investigate the sensitivity of migration to permeability. The porous medium was kept dry to avoid partitioning effects into pore water. Gas
samples were taken along the column throughout the experiment to quantify time and space dependent vapor migration. The experiments characterized the migration behavior of a heavy CS₂ vapor plume injected in the middle of the column. The vapor plume steadily migrated downward dependent on the total mass of injected CS₂ and permeability. The set-up of the experiment was reproduced in a 1-D, two-phase, two-component, isothermal, numerical model. Simulation results were compared with data from the vapor migration experiments. The results of the numerical model satisfactorily reproduced the migration behavior observed in the experiments but suggested slightly higher velocities than those observed. Thus the research presented improves the understanding of density driven, advective migration of a heavy contaminant vapor in a dry porous media at a large scale. It provides valuable experimental data not only for future research but particularly for the transfer to field situations.

Retention or retardation of vapors have been investigated in the past; however, further experimental investigation are sought which take into account transport characteristics such as migration velocity of these vapors in the unsaturated zone. Therefore, the experiments conducted in this second step employ vapor migration velocities which have been previously observed in density-driven migration experiments to connect these two processes. Furthermore, the component and water saturation dependent behavior of gas phase retention emphasizes the necessity for quantifying retardation effects of the contaminant carbon disulfide (CS₂) in unsaturated porous media. Thereby, fundamental knowledge about its potential to delay or prevent a contamination of an underlying aquifer is gained. Accordingly, the objective of this study was to quantitatively characterize retardation/retention of CS₂ on a large scale with clearly defined and controlled boundary conditions. The experiments were conducted in vertical stainless steel columns (ID = 0.109 m) of 2 m length packed with fine glass beads. They were carried out at dry conditions as well as at residual water saturation. In order to reproducibly obtain residual water saturations (initial conditions) as observed in the subsurface at a given distance above the groundwater table, the columns were saturated with water and subsequently drained under controlled conditions at predetermined capillary pressures prior to each run.

A finite slug containing both CS₂ vapor as well as a non-retarding, conservative tracer (argon) was injected via an injection section at the bottom of the column. Effluent concentrations of CS₂ and argon were measured online at the top outlet of the column. Tensiometers installed along the column at distinct positions measured capillary head to monitor the drainage process. Thereby, equally distributed water saturations could be verified and in-situ moisture content of the porous media were obtained. Gas flow rates were at controlled by mass flow controllers. They were chosen based on results from density-driven migration experiments. This experiment set-up enabled for quantification of retardation of CS₂ as a function of water saturation and seepage velocity, thus improving the understanding about how migrating CS₂ vapor is affected by retardation in partially saturated porous media.

The second part involved flume experiments exploring spill behavior and soil vapor extraction applied for remediation. The investigations were based on experiments with an emphasis on process differentiation under exactly defined boundary conditions. The remediation scheme involved the development of a suitable technique for in-situ remediation of a CS₂ spill and to test its feasibility and efficiency.

The investigation presented here focuses on the demonstration of a liquid spill in the unsaturated zone and confirmation of the applicability of soil vapor extraction as an effective remediation technique for a CS₂ spill in the unsaturated zone. The removal of a contaminant vapor in dry porous media was successfully shown in the vapor retardation column experiments presented earlier. This was taken to a more realistic scenario where the contaminant resided as a liquid phase (i.e. residual distribution or pool) in the unsaturated zone, from where it had to be remediated. Now, experiments were conducted in a 2-D flume to combine the investigation of a liquid spill of CS₂ into moist porous
medium and subsequent remediation by means of vapor extraction with specific emphasis on its efficiency and applicability for this particular contaminant. The main objective was to provide experimental data required for dimensioning of remediation parameters such as extraction flow rate and duration as a function of spill mass, hydrogeology and vaporization dynamics of CS₂ which highly affect efficiency in the field.

The goal of the experiment was to first observe different liquid CS₂ spills in a homogeneous porous medium at residual water saturation in a 2-D domain. In the second step, the heterogeneously distributed liquid contaminant residing in the pore space either residually or as pools or as a vapor source was to be removed by means of vapor extraction under controlled conditions. The spill and the subsequent migration of liquid CS₂ in the subsurface as well as the effects of SVE were observed visually and documented. Additionally, the performance of SVE for residual phase and/or pools was to be determined.

The experiments were conducted in a flume with dimensions of 1.00 x 0.70 x 0.12 m (L x H x W). The flume was filled with porous medium which was water saturated and subsequently drained prior to each experiment to obtain static water saturation (similar initial conditions for each run). Tensiometers installed at the rear side of the flume monitored the drainage process and ensured similar initial conditions regarding water saturation. Fine glass beads and Geba sand were used as a porous media. Their different grain size distribution was expected to influence migration behavior of liquid CS₂. Two different injection methods were applied to inject the spill with a predefined mass flux. Either a single-port injection via one port located at the upper center of the flume or a multi-port injection using 4 ports. The first method favored pooling of liquid CS₂ on lower permeable layers whereas the second method achieved a widespread contamination and reduced pooling. Two vertical wells, filtered over the entire flume height, were installed at the sides. Thereby, a horizontal flow regime could be induced and controlled during the entire remediation progress. CS₂ concentrations were measured online and additionally by means of gas samples at the outlet of the flume to ensure mass balance. In order to produce proof of concept, the influence of different porous media, spill and extraction rates on efficiency of the remediation process were studied.