Suction of subsoil air as a remedial action for volatile chlorinated hydrocarbons
Laboratory experiments and computer simulations

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ABSTRACT: Suction of subsoil air can be used for the removal of volatile organics from the unsaturated zone. A numerical model is presented which describes the air flow, the phase transfer processes of the volatile compounds and the transport of the gaseous organics through a porous medium. The results of the program system are compared with the results of laboratory experiments.

INTRODUCTION

The contamination of soil and groundwater with chemical compounds e. g. volatile chlorinated hydrocarbons (CHC) demands effective methods of decontamination. During the process of air suction an air stream flows from the soil surface through the contaminated zone to a well. The liquid organic substances evaporate corresponding to their vapor pressures into this air stream. Until now this technique is based only on empirical knowledge [1,2]. Futher investigations are given in [3] - [7]. The purpose of this paper is to present a mathematical model system describing the essential physical and chemical processes determining the progress of decontamination by air suction.

THEORY

The following differential equations calculate the pressure distribution and the mass transport in a porous medium:

$$\frac{n_{ae}}{p}\frac{\delta p}{\delta t} = -\frac{k_0 \cdot k_{rg}}{p \cdot \mu_g} \cdot (\text{grad } p)^2 + \text{div}\left[\frac{k_0 \cdot k_{rg}}{\mu_g} \cdot \text{grad } p\right] \quad (1)$$

p : pressure, k_0 : intrinsic permeability, k_{rg} : rel. permeability of the gas, μ_g : dynamic viscosity of the gas, n_{ae} : effective, airfilled porosity, t : time

$$\frac{\delta C_g}{\delta t} = \text{div } D \cdot (\text{grad } C_g - \frac{v_{fg}}{n_{ae}} \cdot C_g) + \Gamma \cdot (C_{og} - C_g) - \frac{\delta S}{n_{ae} \cdot \delta t} \quad (2)$$

D : dispersion coefficient, S : concentration of the sorbed phase

The solution of equation (1) gives pressure heads as a function of space and time. As a result of a threedimensional pressure distribution surfaces of equal pressure can be interpolated. Air flows perpendicular to the isosurfaces. The Darcy law expresses the filter velocity of the air flow. Both equations are solved numerically with the method of finite differences.

Phase Transfer Liquid-Gas

Because water always forms the wetting and CHC the non wetting phase, the surface of the soil particles and the small pores in between are occupied by water. Only the larger interstices can be filled up by later infiltrating CHC up to the amount of CHC_{max}, which can be hold in a dry soil against the force of gravity. The remaining pore space contains soil air. Because of their high vapor pressure CHC evaporate quickly into the airfilled pores. The CHC are then transported within the generated air stream. Because of the thermodynamic equilibrium the decreasing CHC-concentration in the gas phase effects a compensation by diffusion to reach the saturated vapor pressure. This occurs as long as there is CHC in liquid phase present (Fig. 1). The increase of CHC-concentration in the gas phase is effected, firstly, by the delivering of CHC-molecules from the liquid phase into the electric double layer, which surrounds these liquid CHC-drops. Secondly, by the transport of particles by diffusion from this electric double layer into the airfilled pore space. The last process is slower than the first one and controls the velocity of phase transfer. The increase of CHC-concentration in the gas phase $C_{g,diff}$ caused by phase transfer liquid-gas can be expressed as:

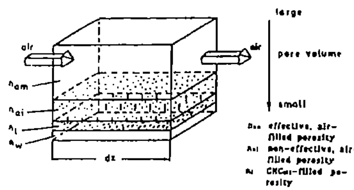

Fig.1 Phase transfer liquid-gas during suction of soil air

$$C_{g,diff} = (C_{g0} - C_{gi}) \cdot (1 - e^{-\Gamma \cdot t}) \qquad (3)$$

C_{g0} : vapor saturation density, C_{gi} : initial vapor concentration, Γ : reaction constant

The reaction constant Γ $[s^{-1}]$ is dependent on the pore geometry and apparent vapor diffusion coefficient. A mass balance model gives the temporary and local distribution of liquid CHC in soil. The number of particles, transfered to the gas phase were calculated with the ideal gas law. This number must be subtracted from the remaining number of particles in the liquid phase. Because of pathways becoming longer for the particles in the pores during the process the reaction constant Γ will get smaller. This effect is considered by a linear function between Γ and the remaining number of particles (Fig. 2). Comparing the measured with the calculated results of a simple mixed-cell model the order of magnitude of the reaction constant Γ could be defined as ca. 10^{-3} - 10^{-1} $[s^{-1}]$.

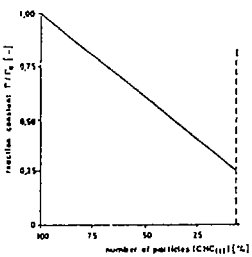

Fig.2 Reaction constant Γ in dependency of the number of particles in liquid phase

LABORATORY EXPERIMENTS

Laboratory experiments were carried out to investigate the transport parameters and to verify the computer simulation. The set-up consists of columns and cuvettes, which allow a one- or twodimensional consideration of mass transport. The set-ups are filled with soil of different water content nearly homogeneously. The distribution of pressure is measured. The pressure measuring devices are equally placed along the cuvettes. Variations of the position and the kind of air inlet (point and/or line source) are possible. The pressure measuring devices are then replaced by tensiometers and septa to take soil air samples out of the cuvettes. An analysis of the air samples by gas chromatography allows to design the distribution of vapor phase CHC-concentration.

A sand and a silt are used. Adsorption of CHC on the sand has not to take into account, because it has a loss of ignition of 0.1%. For the silt the adsorption can be described with a Freundlich isotherm. The utilized CHC are Trichloromethane, 1.1.1-Trichloroethane, Trichloroethene and Tetrachloroethene.

Sampling and Laboratory Analysis

A certain volume of soil air is sucked through a small glas column (Fig. 3) filled with a non-polar synthetic resin, XAD-4 (Rohm and Haas), either by a syringe or a vacuum pump. The CHC are adsorbed on the resin. The resin is filled in a Headspace-vial and the quantitative analysis is done by Gas Chromatographic Headspace analysis. The used Gas Chromatograph is a GC8500 of Perkin-Elmer with a HS 101 (Headspace Injector), an ECD and a capillar column.

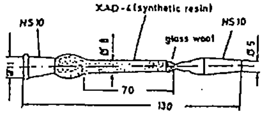

Fig.3 Air sampling with adsorption in test tube (mm)

EXPERIMENTAL PROCEDURE

Fig. 4 shows the arrangement of a cuvette-experiment. The air stream from the top to the both sides generates a pressure distribution where the flow velocities decrease from the top to the bottom. After contamination a period of 24 - 48 hours is necessary to allow the airfilled pore volume becoming saturated with $CHC_{(g)}$ by diffusion and to allow the liquid CHC to spread to residual saturation. Then the air stream is passed through the system and samples are taken over a period of several hours until the contamination is sucked off.

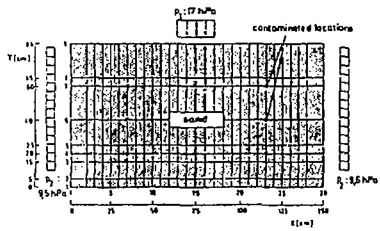

Fig.4 Arrangement of the experiment

Simulation and Discussion

The calculation of the steady state pressure distribution under the given boundary conditions (Fig. 6) is followed by the determination of the velocity of the air flow by Darcy's law with respect to the variation of relative permeability (Fig. 6). Knowing the velocity of the air flow and its direction it is possible to solve the transport equation (2). The calculation of the respective phase transfer liquid-gas is carried out within every time step Δt.

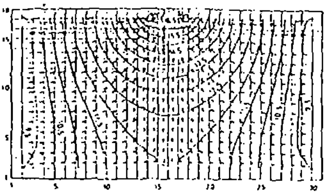

Fig.5 Pressure distribution and flow-field

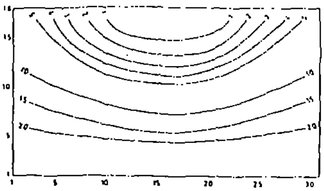

Fig.6 Lines of equal travel time, total flow rate of 5.52 l/min

CHC Transport

During the model calibration with respect to the non-steady state progress of vapor phase concentration in the soil the permeabilities, dispersivities, and the reaction constant are varied predominantly. Fig. 7 shows a comparison of the experimental and simulated results. Three intervalls have to be considered. Fig. 7a shows a time short after the beginning of decontamination where the vapor phase concentration changes rapidly. At this period ('starting phase') the gaseous CHC, spread by diffusion from the liquid drops before decontamination, are carried away by the air stream. The next period has hardly no alterations of the distribution of vapor phase CHC-concentration. Because of the phase transfer processes a thermodynamic equilibrium is built up in this 'evaporation phase' (Fig. 7b). The 'end phase' begins as soon as the storage of liquid CHC is exhausted at any location of the contaminated area.

EXPERIMENTAL RESULTS

SIMULATED RESULTS

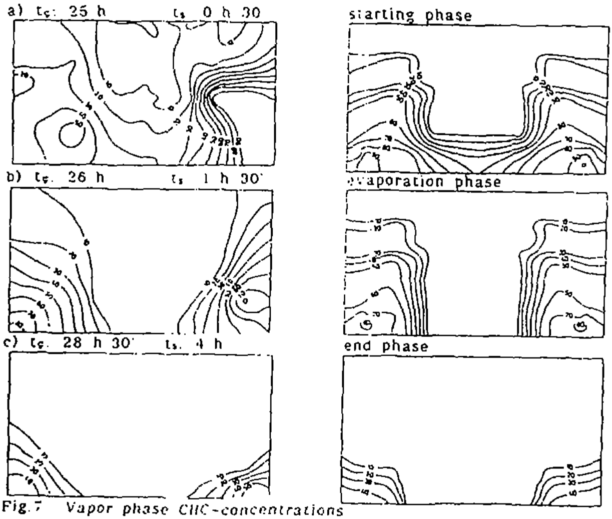

Fig.7 *Vapor phase CHC-concentrations*

Now CHC-concentrations decrease and approach a low level rapidly (Fig. 7c). The reduction of CHCs in the pores proceeds corresponding to the air flow velocities. At different locations in the contaminated area breakthrough curves have been measured and were compared with calculated breakthrough curves (Fig 8). The average vapor phase CHC-concentration during the evaporation phase and the duration of this period are mainly dependent on:

1) The order of magnitude of the reaction constant Γ.
2) The amount of liquid CHC.
3) The length of the pathway of the stream through the contaminated area up to the considered locations
4) The velocity of the air stream along the pathway through the contaminated area.

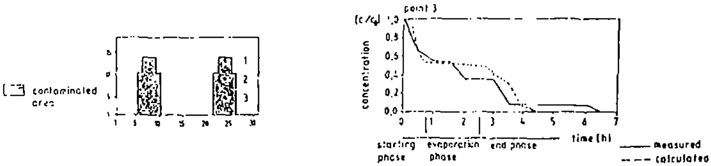

Fig.8 Breakthrough curve

SUMMARY AND CONCLUSIONS

The physical and chemical processes within the unsaturated zone during suction of subsoil air as a remedial action of CHC-contaminated soil have been analyzed. A numerical model system has been built up to describe the flow and transport processes with a special interest on the phase transfer liquid-gas. This system contents:

1) A flow-model to calculate pressure distributions and flow-fields
2) A mixed-cell model to compute the order of magnitude of the reaction constant Γ.
3) A transport model, which describes the non-steady state vapor phase transport of CHC in the soil.

The results of the program system have been verified by laboratory experiments with different soil types and boundary conditions. Different periods during decontamination have to be considered, the starting phase, the evaporation phase and the end phase. The velocity of the air stream has to be optimized to get the best success of decontamination. The reaction constant Γ gives the maximum number of particles evaporated into the pore volume within one time step.

The comparison between measured and calculated vapor phase concentration distributions for different soil types and boundary conditions shows that the transport processes within the air stream and the phase transfer processes liquid-gas of these compounds can be predicted with good accuracy. The next step is the transfer to field scale.

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