In-situ Characterization of NAPLAquifer Contamination by Partitioning and Interfacial Tracers

J. Danzer, R. Klein, B. Setarge, P. Grathwohl

INTRODUCTION

Partitioning and interfacial tracers have been recently used to determine the saturation and interface of non aqueous phase liquids (NAPL) in groundwater (JIN ET AL., 1995; ANNABLE ET AL., 1997; SARIPALLI ET AL., 1997; SETARGE, 1998; WANG ET AL., 1998) . This poster presents the results of laboratory batch and column experiments which were conducted with contaminated and uncontaminated aquifer material from a former manufactured gas plant site in southwest Germany (Kehl). At that field test site a pilot-test of surfactant enhanced aquifer remediation will be conducted in 1998.

Partitioning and interfacial interwell tracer tests (PITT) will be used to determine the coal tar saturation and tar/water interface before and after the surfactant flushing. The advantage of this method is, that saturation and interface information is obtained in a nonintrusive manner over a larger volume than can be obtained from discrete soil borings

Partitioning tracers partition between the NAPL and the mobile water while interfacial tracers adsorb at the interface between NAPL and water (see Fig. 1).

Due to these interactions the tranport velocity of the tracers (partitioning and interfacial) reactive decreased (retardation) compared to the non-reactive, conservative tracer as they move with groundwater through a NAPL contaminated aquifer or soil column The NAPL saturation and interface can be calculated from the retardation knowing the partition coefficients of the partitioning tracer and the area per molecule of the interfacial tracer, respectively.

RESULTS

The BTCs of the partitioning tracers through an undisturbed field core not contaminated by tar oil is shown in figure 4. The partitioning tracers were not retarded in the absence of tar oil and behave like the conservative tracer.

The BTCs of the partitioning tracers through an The press of the participant dolumn with known tar oil saturation of 4 % is shown in figure 5. The retardation factors (R_a) were obtained by moment analysis of the BTCs. The tar oil saturation (S.) was calculated from the measured retardation factor by use of the following equation

where the NAPL/water partition coefficient (K_{nu}) was

The partitioning tracer BTCs through the undisturbed,

The plantuoling factor BTCs infoging the undustribed, contaminated field core from the manufactured gas plant site is shown in figure 5. The determined tar oil saturation was about 30 % of the pore volume. The column was then flushed with a mixture of 70

determined in independent batch tests (table 1)

Eq. (1)

1.0 IPA 0.9 4M2P v 0.8 NaC1 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0 Pore Volumes

Figure 4: Pulstype BTCs the partitioning tracers through an undisturbed soil column in the absence of tar oil. (column length L = 100 cm, cross sectional area the off (contain length 2 - 100 cm, persons $n_s = 0.35$, flow velocity v, = 0.256 m h⁻¹, dispersivity a = 0.065 m, Peclet number Pe = 15). No retardation compared to the conservative tracer NaCl can be



and 30 % anionic surfactant solution (BASF/VEGAS) to remediate the column by enhanced solubilization, i.e. an increase of the apparent solubility of tar oil compounds such as polycyclic aromatic hydrocarbons (PAH) by surfactant micelles. A second partitioning tracer test was carried out after the surfactant flushing (figure 6). The determined tar oil saturation was below 20 %. The results of the artifically contaminated quartzsand column and the "natural" contaminated

Table 2: Retardation factors (Ra) and calculated tar oil saturation (S_{ω}) according to equation (1) for the breakthrough experiments QS and the field core FS1 before and after surfactant flushing



Figure 5: BTCs (continous feed) of the partitioning tracers through an artifically contaminated quartz sand column QS with known tar oil saturation. $(L = 16 \text{ cm}, \text{ A} = 0.0028 \text{ m}^2, \text{ n}_e = 0.33, \text{ v}_s = 0.256 \text{ m} \text{ h}^{-1}, \text{ a}$

0.0022 m. Pe = 136)

Figure 1 : Partitioning and interfacial interwell tracer test (PITT) to determine the tar oil saturation and interfacial rea between tar oil and groundwater at a former manufactured gas work plant at the field test site at Kehl (southwest Germany). Injection wells II - I2, extraction wells E1 - E3, multilevel sampling wells MLW1 - MLW 4.

MATERIALS

Four partitioning tracers were selected which had been used for determination of tar oil saturation, already (HAYDEN AND LINNEMEYER, 1997). The partition coefficients of the tracers between NAPL (tar oil) and water (K_{nu}) were determined in batch experiments. The partition coefficients range in between 1 and 22 and are summarized in table 1 beside other physico-chemical properties. The partition coefficients were constant with espect to tar oil saturation and initial tracer concentration. An surface active agent (anionic surfactant) was used as interfacial tracer. Below the critical micelle concentration (CMC) the surfactant monomers adsorb in a monolayer at the interface between tar oil and water. The linear alcohol ether sulfate with two ethoxylation units is considered to be biodegradable. It is restistant to precipitation with ions present in groundwater (Ca, Mg etc.) and does not adsorb onto the aquifer materia

valley aquifer. It is a sandy gravel and consist of carbonates, metamorphic rock fragments and quartz The organic carbon content of the sand fraction is 0.02 % and the effective cation exchange capacity ECEC is about 10 meg kg-1.

Table 1: Physico-chemical properties of the tracers used



Figure 6: BTCs of the partitioning tracers through an undisturbed field core (FS1) contaminated with tar oil before surfactant flushing. Determined tar oil saturation about 30 %. (L = 100 cm, A = 0.0072 m^2 , n_z = 0.15, v_z = $0.098 \text{ m} \text{ h}^4$, a = 0.43 m, Pe = 2.3)

The interfacial area A_{in} between tar oil and water was determined by the adsorbed mass of interfacial tracer (figure 8) and was found to be about 1450 m². The interface/volume ratio of the tar oil has a value larger than 50 000 cm⁻¹. This indicates that the tar oil is present as small blobs and coatings of the grains within he porous mediu



Figure 8: BTC of the interfacial tracer through undisturbed field core (FS1) contaminated with tar before surfactant flushing.



Figure 7: BTCs of the partitioning tracers through an undisturbed field core (FS1) contaminated with tar oil after surfactant flushing. Determined tar oil saturation about 17 %

CONCLUSIONS

The tar oil saturation of an undisturbed soil core from a The tai of saturation of an immistance soft color form a former manufactured gas plant site could be reasonably well determined by the selected partitioning tracers. The NAPL/water interface was determined by an interfacial tracer. The high interface/volume ratio indicates that the tar oil is present as coatings of the grains within the aquifer. A decrease of the tar oil saturation due to surfactant flushing could be measured by the partitioning tracers as well

REFERENCES

Annable, M. D., Jawitz, J. W., Rao, P. S. C., Dai, D. P., Kim, H. K., Wood, A. L. (1997): Field evaluation of interfacial and partitioning tracers for characterization of effective NPL-water contact areas, even the for Contact and the second secon ter J. (1998): Transport of surfactants and coupled tran stured coulder material Discontation University of Table

vden, N. J., Linnemayer, H. C. (1997): Investigation of partitioning tracers for emining coal tar saturation in soil, American Chemical Society, Division of ironmental Chemistry Preprints of Extended Abstracts; Vol. 37 (1): 247-248

Jin, M., Delshad, M., Dwarakanath, V., McKinney, D. C., Pope, G. A., Sepa Tilburg, C. E., Jachson, R. E. (1995): Partitioning tracer test for detection, ex remediation performance assessment of subsurface nonaqueous phase liq

Annable, M. D., Rao, P. S. C., (1997): Estimation of no-water interfacial areas in porous media following mobiliza on. Sci. Technol. 31, 3384-3388 ning and interfacial tracers for characte rge, B. (15

Wang, P., Dwarakanath, V., Rouse, B. A., Pope, G. A., Sepehrmoori, K. (1998): Partition FUNDING alc Arth Baden-Württemberg, Germanyster from

Contaminated and uncontaminated, undisturbed soil

COLUMN EXPERIMENTS

The column setup is shown in figure 2. Sodium chloride was used as conservative tracer and measured conduct was used as contextvarie tracer and interstret on-line by a conductivity detector. The partitioning tracers were analyzed using a GC-FID The interfacial tracer was measured by a TOC-analyzer. The column effluent concentration is plotted with respect to the inflow concentration C, versus the



Figure 2: Sketchmap of the experimental setup of the column experiments

dimensionless time of exchanged pore volumes as a breakthrough curve (BTC). The hydrodynamic parameters such as pore volume and dispersivity were

identified by fitting an analytical solution of the advection dispercion equation (OGATA & BANKS, 1961) onto the BTC of the conservative tracer (figure

Pore V

conservative tracer NaCl and the fitted solution of the advection dispersion equation to determine

hydrodynamic parameters (OGATA & BANKS, 1961).

curve (BTC) of the

Figure 3: Breakthrough

HS076

2,3DM2B 0

2,4DM3F

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