Versuchseinrichtung zur Grundwasser- und Altlastensanierung

Universität Stuttgart
Institut für Wasserbau

Wissenschaftlicher Leiter *VEGAS*
Jürgen Braun, PhD ☎ 685-67018
Technischer Leiter *VEGAS*
Dr.-Ing. H.-P. Koschitzky ☎ 685-64716

Versuchseinrichtung zur Grundwasser- und Altlastensanierung · *VEGAS*
Institut für Wasserbau · Universität Stuttgart · Pfaffenwaldring 61 · D-70550 Stuttgart

Pfaffenwaldring 61
D - 70550 Stuttgart
Telefon +49 (0) 711 685 -64717
Telefax +49 (0) 711 685 - 67020
E-Mail: vegas@iws.uni-stuttgart.de

Enhanced Natural Attenuation (ENA) for the in-situ biodegradation of heterocyclic hydrocarbons in groundwater project phase 1: laboratory investigation and pilot plant

Goal

Heterocyclic aromatic hydrocarbons (HAH) are substances that are toxic, some of them are even carcinogenic; they are prevalent in groundwater in cases of tar oil contaminations. In general, these substances are not analysed. They are relatively persistent against biological degradation and because of their high mobility, long plumes may extend in the groundwater.

In contrast to the commonly investigated contaminants (BTEX and PAH, for example), field experience indicates that natural degradation and retardation processes are not sufficient for remediation or attenuation processes. A stimulation of the biological degradation processes is therefore required at many sites (Enhanced Natural Attenuation (ENA)).

The aim of the project is:

a) optimisation of the analytical methods,

b) quantification of the natural in-situ degradation potential,

c) investigation of the stimulation of biological degradation, and the

d) development of methods concerning the injection of nutrient solutions into the subsurface in order to achieve an optimal mixing of nutrients with the contaminant plume.

The efficiency of the mixing process is limited by transversal dispersion. The limited supply of external electron acceptor solutions for Natural Attenuation affects the length of contaminant plume. The greater the dispersion, the shorter the plume.

While developing an injection technique, the mixing and transport processes are to be numerically simulated. The quantification of the self-purification potential of the heterocyclic hydrocarbons is related to the plume leaving the former gas-work. During a former DFG project the site, the tar oil plume and the behaviour of the contaminants (BTEX and PAH) were already investigated in detail. The current project relies heavily on these investigations.

The detailed aims of the project are:

ZAG, University of Tübingen:

- development of a simple, fast analytical method to measure the heterocyclic hydrocarbons,
- determination of the self-purification potential of heterocyclic hydrocarbons downstream of the former gas-work site.

TZW-Karlsruhe:

- quantification of the natural biological degradation of heterocyclic hydrocarbons, including the adaptation of analytical microbiological methods to measure the number of colony forming units of heterocyclic-degrading bacteria,
- simulation of the degradation of heterocyclic hydrocarbons by suitable electron acceptor solutions and co-substrates.

VEGAS, University of Stuttgart:

- development of an injection technique to optimise the mixing of solutions in the groundwater.

ZAG, VEGAS, TZW:

- demonstration of the biological process of ENA in one of VEGAS containers (Large Flume at the VEGAS facility).
- in-situ application of the developed technique at the field site after a successful demonstration of ENA in the Large Flume.

Figure 1: the "Large Flume" at the VEGAS facility

Procedure

The procedure of the project partner VEGAS was:

1. literature review / internet research concerning commercially available injection techniques,
2. small-scale investigations of different injection techniques concerning a wide range of mixing effects,
3. investigation of transversal mixing of the injected solutions and the contaminant plume in the model aquifer of the Large Flume at the VEGAS facility,
4. pilot study at the site „Testfeld Süd".

Results

In order to get information about the injection techniques which have been established, internet research and literature review have been carried out.

Considering the field site and the previously selected liquid injection of nutrients, the following injection techniques were selected:

1. groundwater circulation well (GCW): roller-shaped groundwater circulation is induced by means of pumps and infiltration ports in vertical wells, located in hydraulically separated filter sections. The injected nutrient solutions (electron acceptors) are completely mixed within the circulating groundwater flow pattern.

2. multi-level wells (MLW): the liquid electron acceptor solutions are directly infiltrated into the groundwater flow at different levels of hydraulically separated filter sections in vertical or horizontal wells and thus accelerate the biological degradation downstream of the wells.

Both systems were tested at the 2-D scale in flume experiments (Figure 2).

Figure 2: 2-D flume experiment for the visualisation of flow and transport processes using different injection systems

Small-scale experiments:

Both injection systems were tested and compared by small-scale experiments and numerical simulations.

A numerical simulation of the operation of a GCW with the infiltration of a tracer solution into the lower filter section and extraction of the groundwater by the upper filter section (Figure 3, right) led to the result that the injected solution was mixed completely with the groundwater. The ratio between groundwater flow and discharge of the GCW was set to one (extraction rate = infiltration rate). The numerical simulation was in accordance with the experimental results (Figure 3, left). The tracer solution was homogeneously mixed into the groundwater flow downstream the GCW for the selected ratio of flow rates.

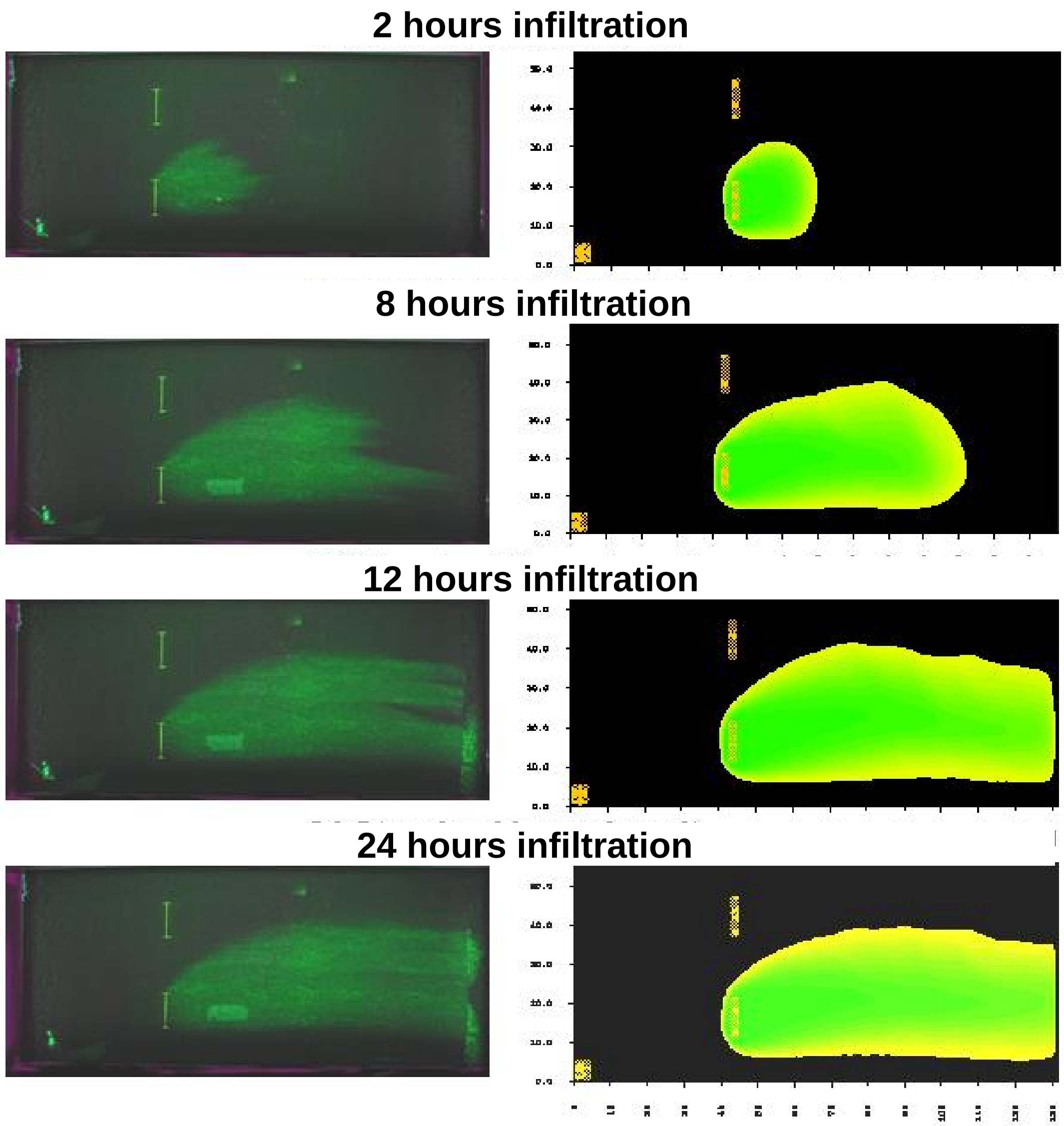

Figure 3: Comparison of experimental (left) and numerical results (right) concerning tracer mixing using GCW

The alternative system of multi-level wells (MLW) offers the opportunity to use a comparably low infiltration rate. The mixing of the nutrients however, is based on transversal dispersion and therefore requires a comparatively high number of infiltration wells. Thus the costs for well installation increase.

A comparison between experimental results and the numerical simulation for a groundwater flow - infiltration rate ratio of 2:1 shows a downstream, spreading tracer streamline (Figure 4). The layered nature of the aquifer model and the low dispersion coefficient of the soil limit transversal dispersion. A primarily horizontal distribution of the tracer solution was observed, because of the prevalent horizontal layer structure.

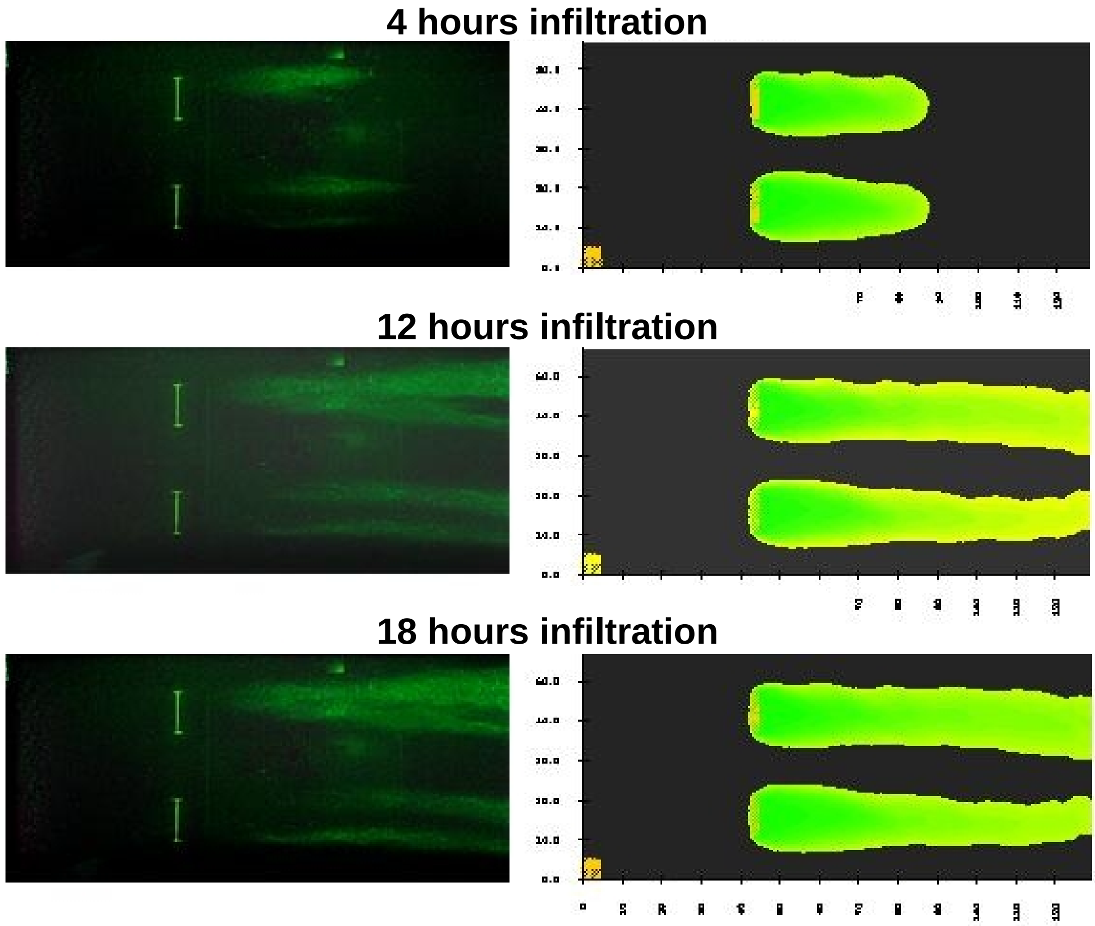

Figure 4: Comparison of experimental results (left) and numerical simulation (right) concerning tracer mixing using MLW

In contrast to this, the GCW increases the transversal mixing by generating crosswise oriented flow lines close within the range of the wells (Figure 5, left)

Another disadvantage concerning the infiltration and mixing process of the MLW system is the deflection of the groundwater flow lines in the range of the wells (Figure 5, right). This hinders a rapid mixing of the nutrients, the infiltration zone is circumvented by the groundwater streamlines. Using an insufficient hydraulic system (a well gallery with high infiltration rate, for example) may cause groundwater flow to circumvent the degradation zone.

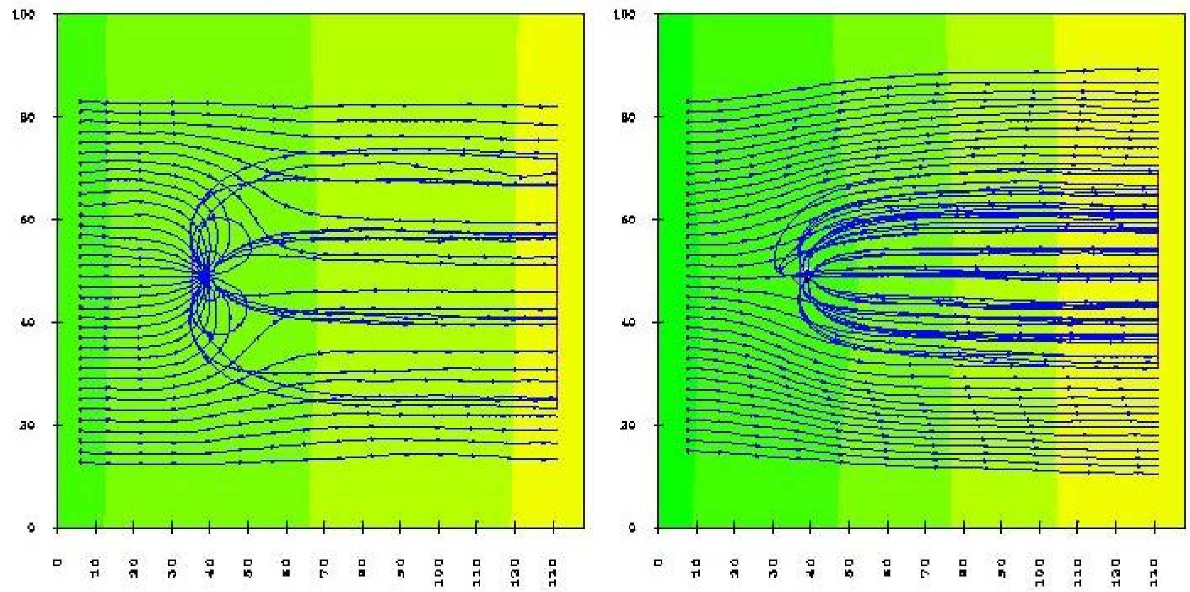

Figure 5: Comparison of flow patterns using GCW (left) and vertical wells (right) for similar infiltration rates

The numerical simulation and experimental results (Figures 3 and 4) are in good accordance. Therefore, the hydraulic design of the injection technique at the field site may be solved by numerical means, using the hydraulic parameters at the field site.

ENA experiment in the "Large Flume" at the VEGAS facility

The ENA experiment in the "Large Flume" at the VEGAS facility was running about more then two years to clarify the operating stability and hydraulic effectiveness of the GCW in a large-scale experiment. During this experiment the enhancement of biological degradation of heterocyclic hydrocarbons by adding hydrogen peroxide as oxygen carrier was verified.

To do so, the infiltration of nutrient solutions is to be measured during an ENA experiment in the Large Flume at the VEGAS facility. A prototype of the GCW was manufactured and placed in a 3-inch percussion ram filter in the Large Flume (Figure 6).

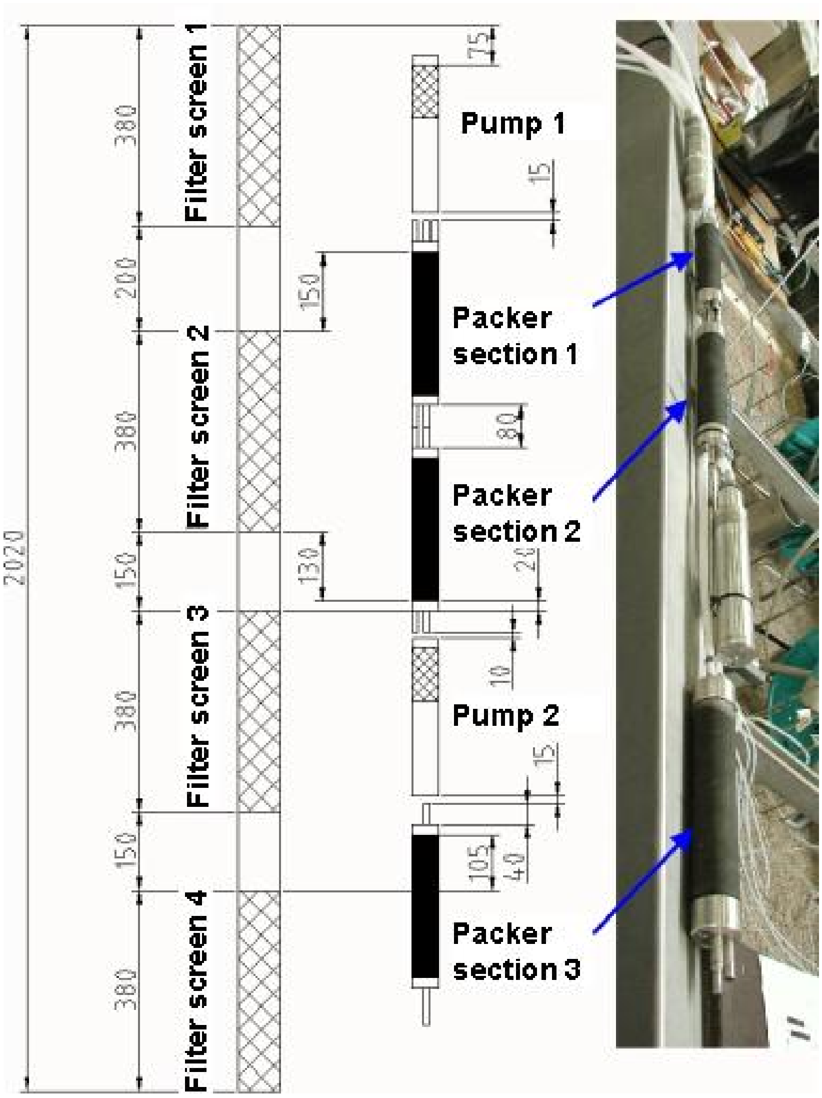

Figure 6: Prototype of the GCW for the application in the Large Flume

The first analysis of heterocyclic hydrocarbons by the project partner, ZAG, University of Tübingen, showed the absence of HAHs in the plume of the tar oil "blob" zone of the Large Flume. It is assumed that the continuous operation of the model aquifer in the Large Flume (2000 – 2004) caused a wash out of the polar heterocyclic hydrocarbons, because of their comparably high solubility in water.

To resolve this, in agreement with the project partners, the "blob" zone of residual tar oil, designated as the "source" had to be excavated to avoid any sorption effects with the addition of an artificial heterocyclic hydrocarbon mixture. The "blob" zone was displaced by an infiltration filter chamber (Figure 7) without disturbing the soil structure in the flume. The infiltration of a heterocyclic hydrocarbon mixture, that is similar to the mixture found at the field site "Testfeld Süd", is now intended.

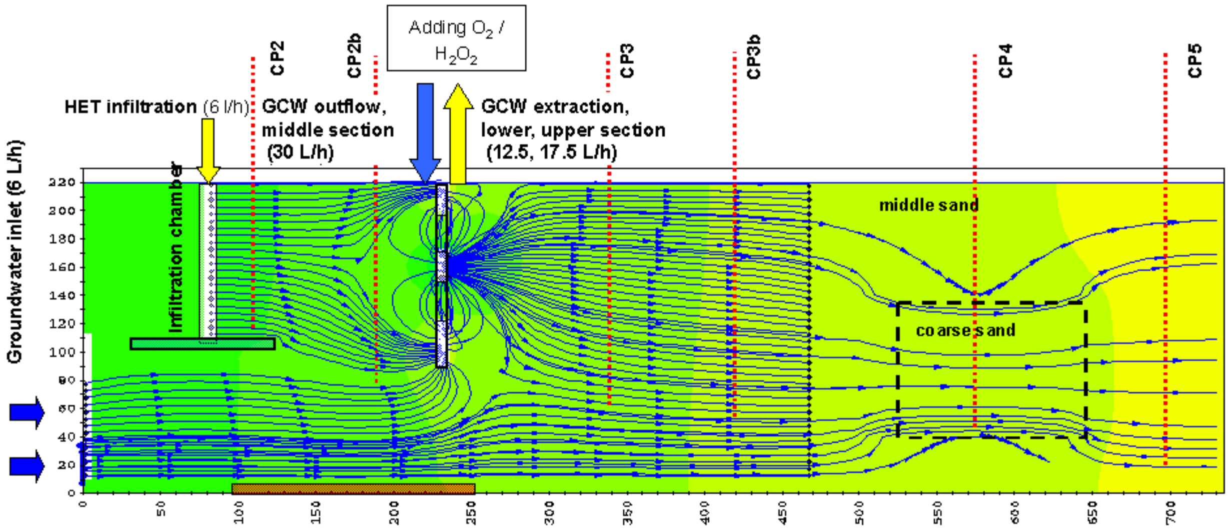

Figure 7: Set up of the Large Flume and the ENA experiment with visualized flow field

At the beginning of 2004 the GCW was installed in a 3" percussion ram filter in the Large Flume. The groundwater was extracted through the lower filter and the upper filter sections of the well. After adding with the selected electron acceptor solution (TZW), the nutrients were infiltrated through the medium filter section of the GCW. Because of this operating mode there are two intersecting roller-shaped groundwater circulation. The groundwater flow - infiltration rate ratio of 2.5:1 ensured that the total contaminant source could be remediated. The emerging roller-shaped groundwater circulation covered 80% of the total groundwater flow.

In the period between April and June 2004 tracer tests were carried out to see the hydraulic conditions in the Large Flume and the effectiveness of mixing the electron acceptors in the groundwater by the GCW. The collected data were used to calibrate the numerical simulation. During the first test the tracer was continuously infiltrated in the infiltration chamber. Measurements of the tracer concentration in all sampling planes (CP 2 – CP4) after 10 days showed an inhomogeneous distribution of the tracer upstream of the GCW. On the other hand, the distribution of the tracer downstream of the GCW seemed to be comparatively homogeneous.

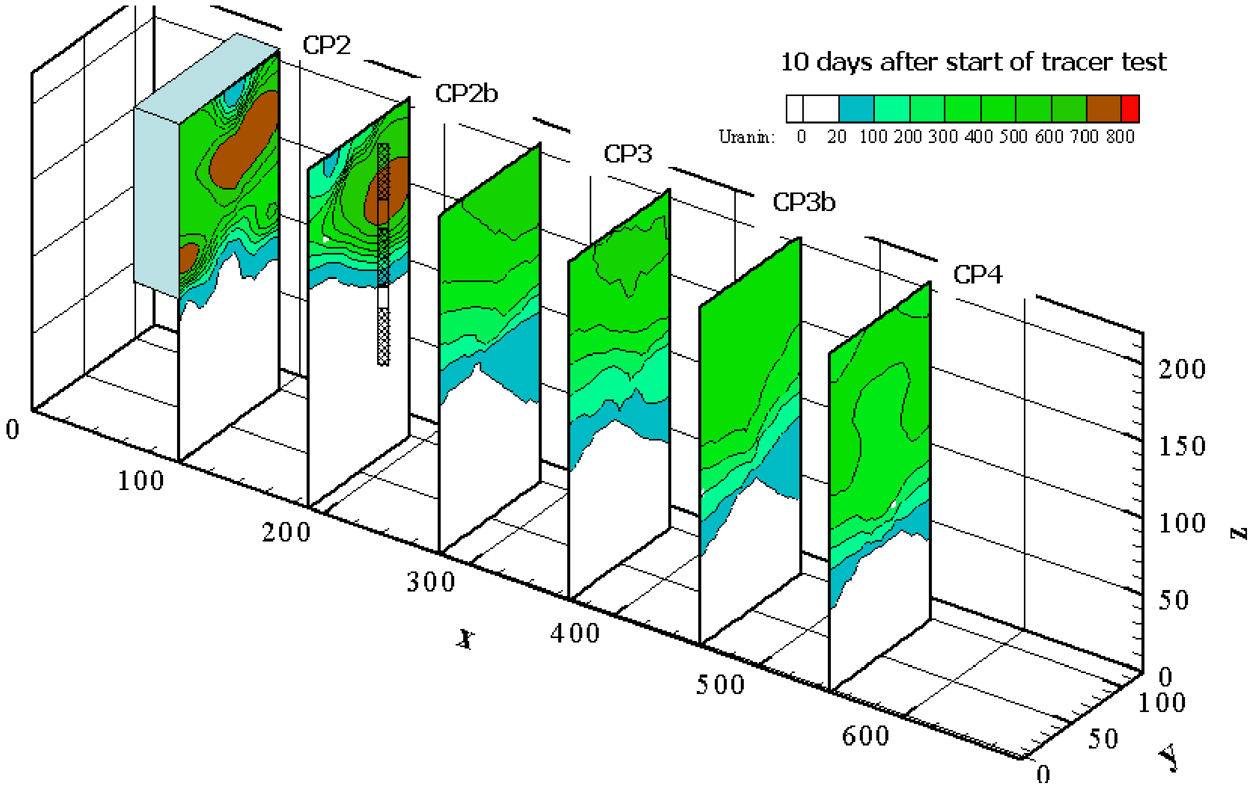

Figure 8: Distribution of the tracer in the Large Flume, 10 days after starting the first tracer test

A second tracer test was conducted in order to elaborate the calibration of the numerical simulation. The tracer was infiltrated through the GCW. The number of sampling ports was doubled and continuous measurements were carried out. For the numerical simulation the sand was arranged in layers with variation of the hydraulic transmissibility.

In direct comparison with the numerical results the experimental results certify the successful calibration of the numerical simulation (Figure 9), which is used for a secured interpretation of the GCW and for the rate balancing of heterocyclic compounds in the different measuring planes.

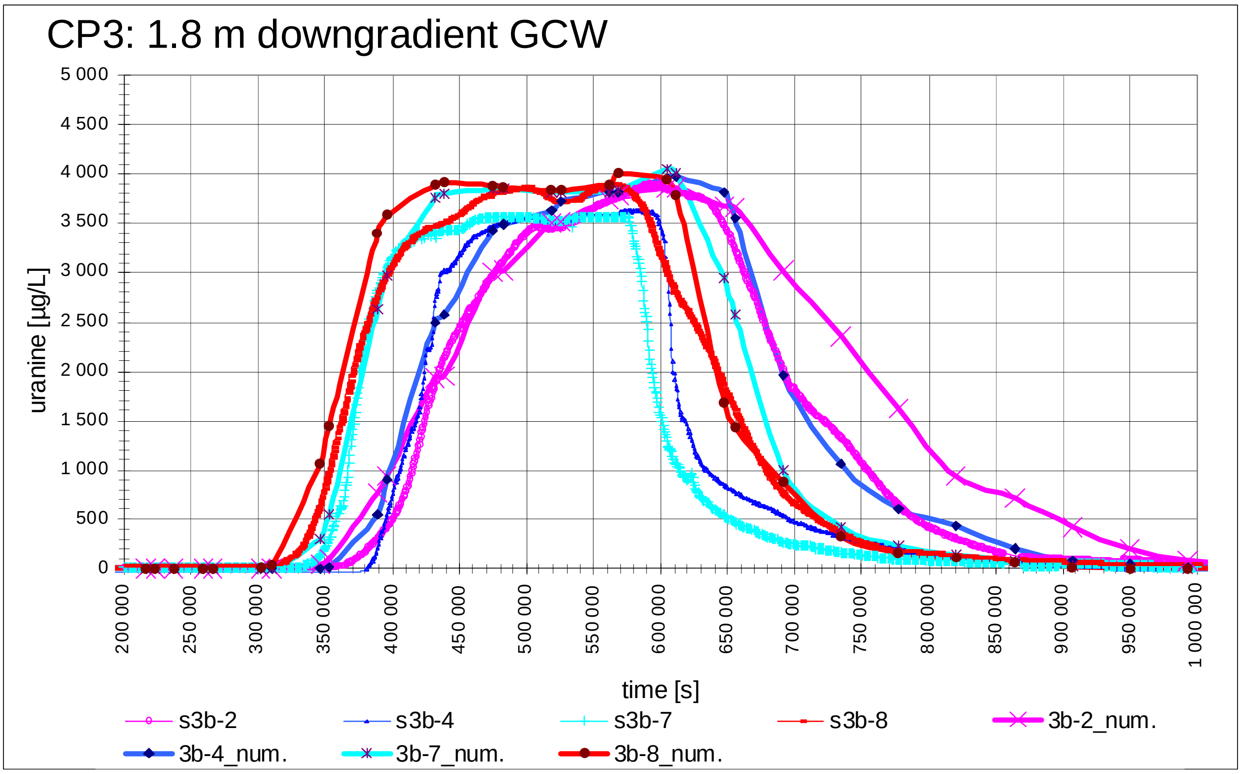

Figure 9: Comparison of the numerically calculated (s3b-2_num, s3b-4 num, s3b-7 num and s3b-8 num) and experimental tracer breakthrough curves (s3b-2, s3b-4, s3b-7, s3b-8).

During different test phases aerial oxygen or hydrogen peroxide with different concentration (H_2O_2, 50 mg/L, 25 mg/L) or no liquid electron acceptor solution in the intermittent operation, respectively, sulfate as electron acceptor were injected by the GCW into the ground flow for analysing the biological degradation and to simulate the conditions at the field site.

According to the chosen electron acceptor the oxygen content developed (Figure 10). The injection of hydrogen peroxide showed downstream the groundwater circulation an approximate stoichiometric conversion to oxygen and water (50 mg/L H_2O_2 → 20 mg/L O_2) (CP3, fig.7). With the addition of aerial oxygen the oxygen concentration was 5 mg/L., see fig. 10.

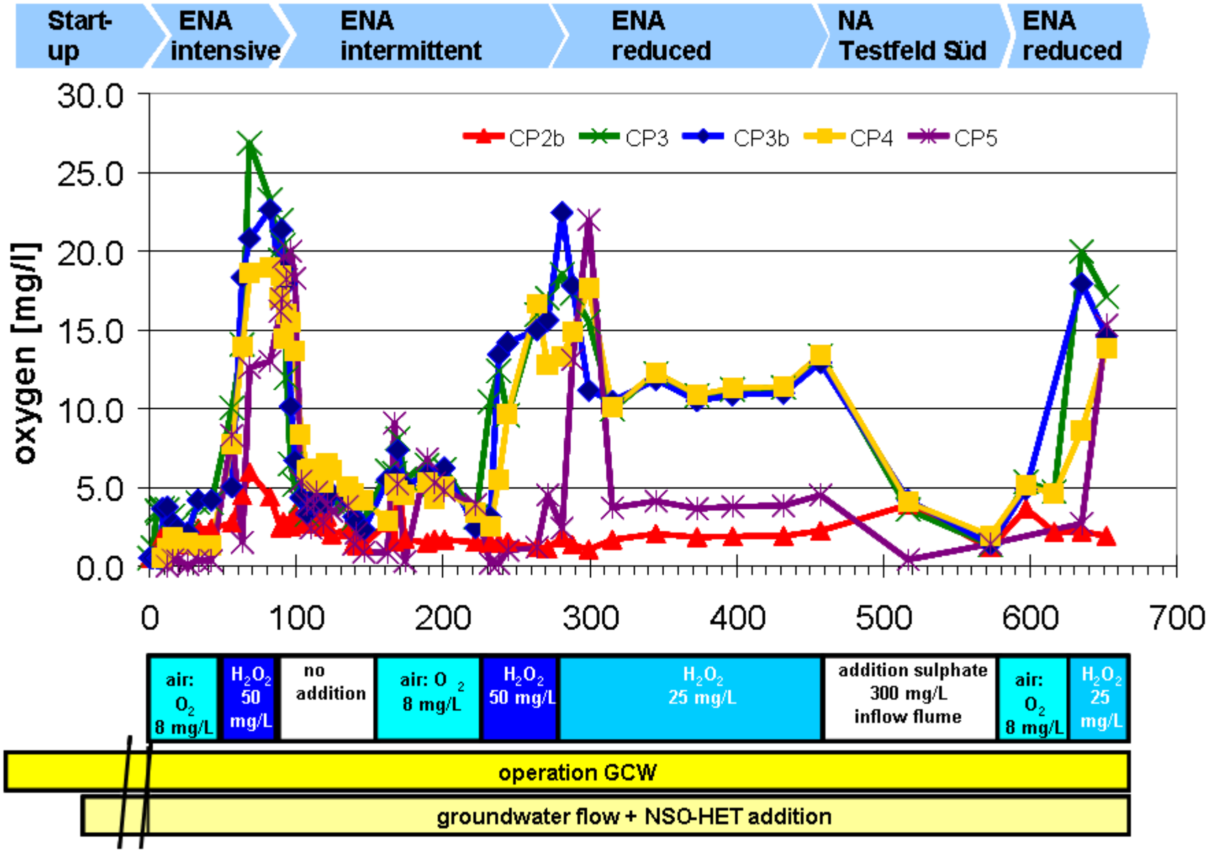

Figure 10: chronological sequence of the oxygen distribution

According to the oxygen content the biological degradation occured primary in the zone of the groundwater circulation caused by the GCW (Figure 11). An almost entire decomposition occured by the addition of aerial oxygen (Figure 11, left).

An almost total aerobic biological degradation was determined during the addition of hydrogen peroxide (Figure 11). During the intermittent operation the circulation of the groundwater in the GCW caused an oxygen content of about 3 mg/L. In the \`spherical´ groundwater circulation of the GCW a degradation about 50% took place. Downstream of the GCW (CP3), however, the degradation rate was about 90% (Figure 11, middle). The addition of sulfate as electron acceptor (NA phase) reduced the oxygen content below 2 mg/L. As consequence of the “anaerobic” conditions the degradation rate decreased clearly below 10% (Figure 11, right).

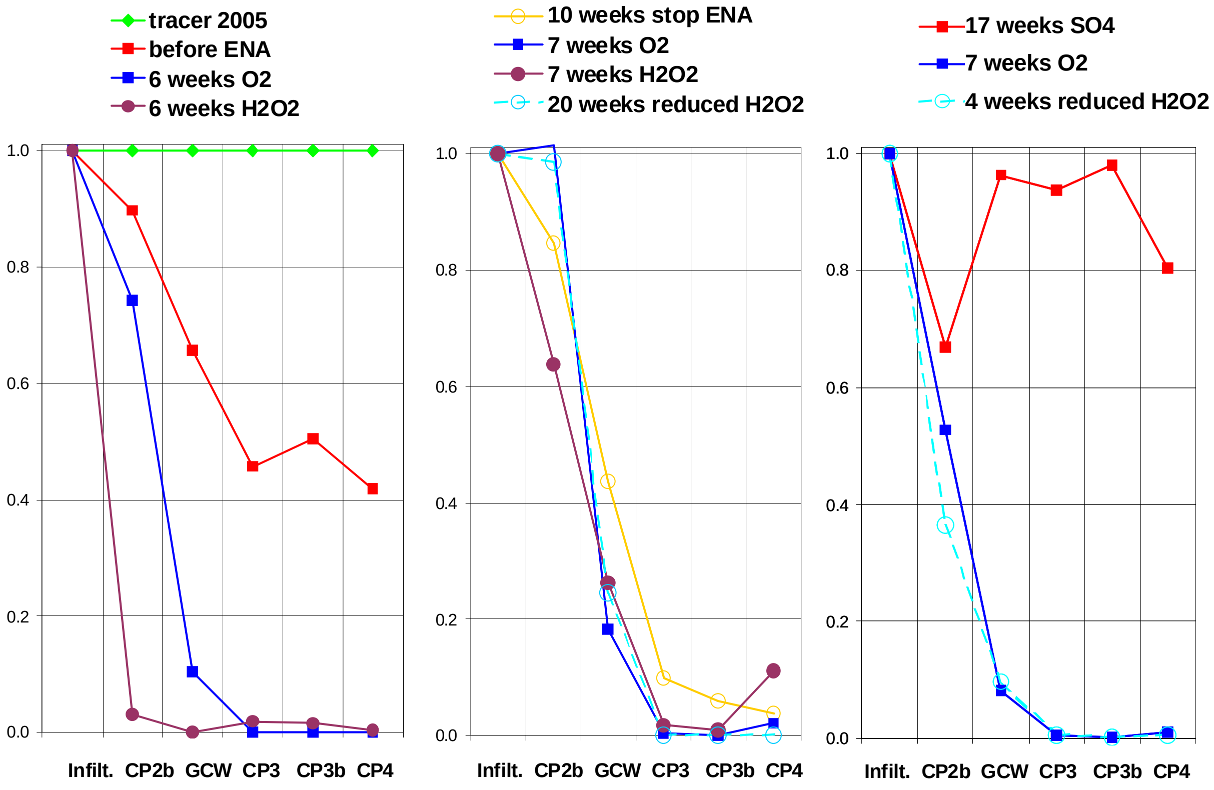

Figure 11: Standardized NSO-HET concentration

Facing the positive results, it is foreseen to apply the technology in a field trial. The mixing of hydrogen peroxide into a natural aquifer requires the permission of the local authorities. The permission was given after a very defined planning and argumentation concerning the positive effects on the groundwater quality by adding an oxygen-bearing chemical that will be autolysed into water and oxygen within the flow field of the GCW.

A numerical model using commercially available numerical codes was developed to describe the complex hydraulic system of a GCW in order to transfer the results from the Large Flume to the field site and to design the operation of the GCW to achieve a maximum radius of influence at a minimal pumping rate. Following the simulations, a discharge of 15 m^3/h will cause an up-gradient width of groundwater capture of approximately 10 m.

The test site is located in the Neckar valley. The field trial was designed and planned. It was planned to install several monitoring and observation wells for mass balancing and hydraulic tests (tracer and pumping tests), one GCW and a treatment unit to mix the electron acceptors. The duration of the field trial was planned for one year. It was planned to start with an initial aeration of the aquifer (two months), then release of hydrogen peroxide (50 mg/L) for eight months and finally a two-months periodical aeration.

Summary and conclusion

Heterocyclic hydrocarbons (NSO-HET) are ingredients of tar oil, commonly found downgradient of former gasworks sites. Most NSO-HET are highly mobile due to their high water solubility and low biodegradation rates under anaerobic conditions.

Based on the extension and contaminant distribution of the plume (~ 800 m long) downgradient of a former gasworks in Southern Germany, the most applicable technology for enhancing the natural degradation of PAH, BTEX and NSO-HET was selected and tested under controlled conditions in a large physical model (artificial aquifer in the Large Flume of *VEGAS*).

Numerical simulations and lab experiments indicated that natural dispersion will not lead to a wide-ranging homogeneous distribution and mixing of the required electron acceptors (oxygen) in the aquifer. The Groundwater Circulation Wells technology (GCW) can be applied to achieve a maximum mixing of the electron acceptor solution with the groundwater. A spherical groundwater circulation is induced by means of ex- and infiltration ports in vertical wells. Infiltration and exfiltration ports are located in hydraulically separated filter sections.

A GCW was installed in the Large Flume to mix either oxygen from the ambient air or hydrogen peroxide homogeneously in the groundwater contaminated with the relevant NSO-HET from the field site. During the investigations, an almost complete degradation was determined for both types of electron acceptors. Hydrogen peroxide (50 mg/L) is disproportioned within less than two days into water and oxygen causing an oxygen concentration of more than 20 mg/L. The aerobic degradation of the contaminants is significantly increased, even upgradient of the GCW within the inner circulation of the wells system.

Oxygen infiltration was found to be less efficient, limited by the lower concentrations of oxygen (< 5 mg/L) but it causes lower costs for the operation than hydrogen peroxide. To reduce costs for the long-term operation of this ENA measure, it is advised to create aerobic conditions using hydrogen peroxide release and then switch to aeration in order to maintain the biological degradation. The results of the Large Flume experiment indicated a periodical infiltration of air / hydrogen peroxide.

Acknowledgement

The cooperative project was funded by the Federal Ministry of Education and Research, Germany, Funding Priority ´KORA´*.

Special thanks go to the project partners, ZAG, University of Tübingen, GZG, University of Göttingen and TZW Karlsruhe for the constructive cooperation.

The development and application of an infiltration system for electron acceptors was funded under BMBF-FKZ: 02WN063.

* The Funding Priority ´KORA`, Retention and Degradation Processes to Reduce Contaminants in Groundwater and Soil.

Contact

Dr.-Ing. Hans-Peter Koschitzky (project leader)

Dipl.-Ing. (FH) Oliver Trötschler

Dipl.-Ing. (FH) Thomas Haslwimmer