Versuchseinrichtung zur Grundwasser- und Altlastensanierung

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Enhanced Natural Attenuation (ENA) for the in-situ biodegradation of heterocyclic hydrocarbons in groundwater project phase 2: field application

Goal

Heterocyclic aromatic hydrocarbons (HAH, NSO-HET) are ingredients of tar oil and toxic substances. Some of them are even carcinogenic. They are prevalent in groundwater in cases of tar oil contaminations. In general these substances are not chemically analysed. NSO-HET are comparatively 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 with external electron acceptor solutions for ENA affects the length of contaminant plume. The greater the dispersion, the shorter will be the plume.

While developing an injection technique, the mixing and transport processes are to be numerically simulated. The quantification of the self-purification potential for the heterocyclic hydrocarbons is based on the plume leaving the former gasworks. During a previous 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 relied on these investigations.

Detailed goals of the project are:

ZAG, University of Tübingen:

- development of a simple and fast analytical method to determine heterocyclic hydrocarbons,
- determination of the self-purification potential for heterocyclic hydrocarbons downstream of the former gasworks.

TZW-Karlsruhe:

- quantification of the natural biological degradation of heterocyclic hydrocarbons, including the adaptation of analytical microbiological methods to determine the number of colony forming units of NSO-degrading bacteria,
- simulation of the degradation of heterocyclic hydrocarbons using adequate 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.

Procedure

The procedure of the project partner VEGAS was:

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

Results

Field application at the “Testfeld Süd“:

Due to the location of the “Testfeld Süd” within a mineral water protection zone the permission from the environmental authorities (AfU), Stuttgart, Germany, was required. Due to the innovative approach it was necessary to submit a scientifically based petition. The most important aspects of the submission were the definition of the occurrence of toxic degradation products of PAH and NSO-HET, the definition of hydraulic benchmark data of the GCW-operation and the description of the chemical effects on the groundwater and the soil matrix. The instant decomposition of the hydrogen peroxide in the groundwater had to be confirmed. For the technical design the results of the “Large Fume” were used. Especially the decomposition of hydrogen peroxide in the “spherical” groundwater circulation flow of the GCW could be verified.

By means of the one year lasting pilot application on the “Testfeld Süd” which was located in the center of the plume of the former gasworks the effectiveness of the technology (addition of hydrogen peroxide by GCW) was verified. Before *VEGAS* started the GCW operation in summer 2006, the University of Tübingen installed a monitoring wells field up- and downstream the GCW consisting of seven groundwater wells (6”) and 30 direct-push monitoring wells (1”).

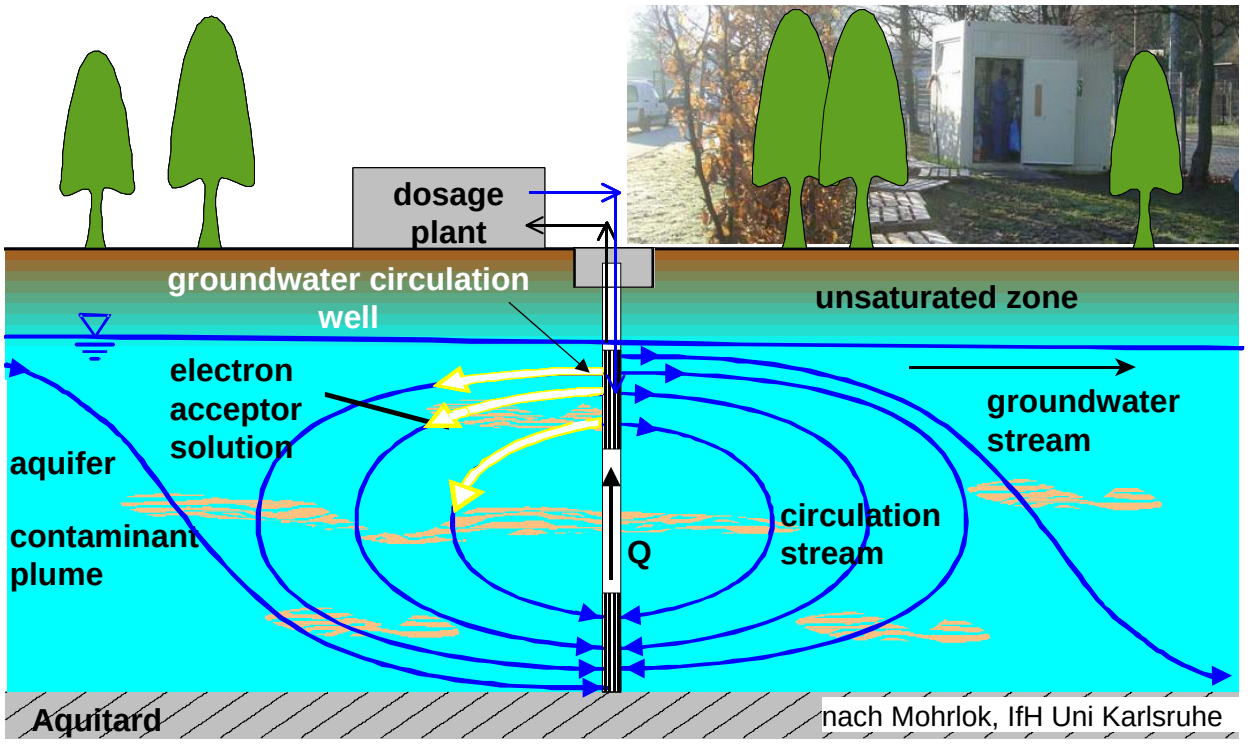

Figure 1: schematic diagram of the GCW „Testfeld Süd“

The plant for storage and dosage of hydrogen peroxide or aerial oxygen was installed in a frost protected 10-ft. container. After the extraction of the groundwater by means of the GCW a sand filter was used to separate precipitated iron. The electron acceptor solution was mixed in the groundwater and a second sand filter was used to avoid iron oxide release by the infiltrated oxi-

dised groundwater. The online monitoring of the treatment installation was realized by remote data transmission using a modem. All flow rates and pressures as well as the main parameters like temperature, conductivity, pH and redox potential of groundwater discharge and release were logged.

Beginning with the initial addition of oxygen to stimulate the microbial activity there were three tracer tests conducted. The conservative fluorescent tracer uranine was added through monitoring wells, which were located in a distance of 25 m upstream the GCW and located on a line transversal to the groundwater flow. The capture zone of the GCW was determined to range between 20 m width for a flux of 8 m³/h and 12m width for a flux of 1.5 m³/h. The numerical model was calibrated following the results of the tracer tests. The anisotropy of the aquifer matrix (1 → 6) and the effective porosity (0.25 → 0.15) were changed in the area of B86 (pumping well) and the close by located well B87. The adequate location of the monitoring wells downstream the GCW was verified by the detecting of the tracer breakthrough curves at these wells. Online operated fluorometers as well as automatic sampling and analysis by the ZAG (University Tübingen) helped to delineate the groundwater flow. The hydraulic parameters of the aquifer were determined based on the breakthrough curves using the momentum method. The movement of uranine during the second tracer test is shown in Figure 2. The spatial distribution of tracer is sketched using the relative amount of tracer mass of the standardized cumulative mass curve for the single monitoring wells. Once the standardized mass curve reaches the value of 1 (100%) this value is used for the following time steps to visualize the area tracer had been transported by the groundwater.

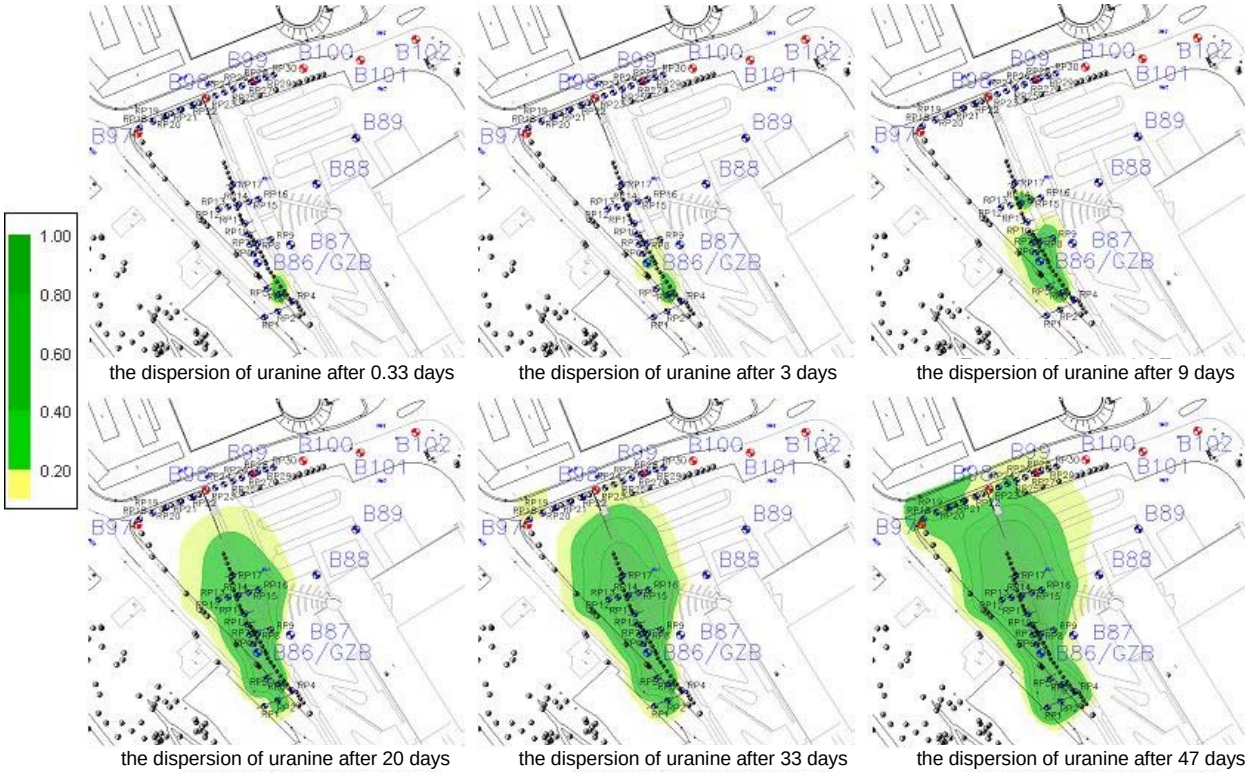

Figure 2: Spatial tracer distribution and dispersion addition in RP3

The increase of the transversal dispersion by the GCW was indicated by the width of the tracer breakthrough at the control plane CP2-3 located 30 m downstream the GCW. Tracer passed a cross-section of the aquifers over 25 m width (B97 – B98 – RP24). The groundwater velocity downstream of the GCW (B86) was found to be 1.6 m/d and the longitudinal dispersion was 2.1 m. The results of the tracer tests were implemented in the numerical flow model of the test site (Figure 3).

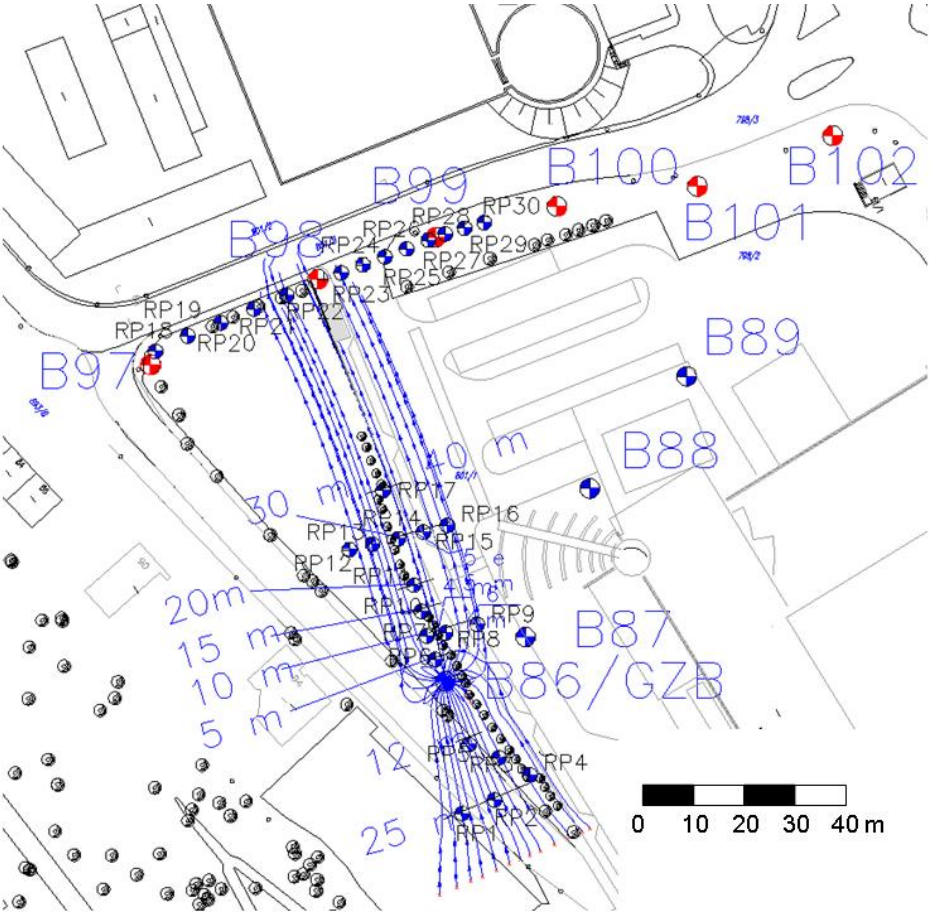

Figure 3: Numerical simulation of the GCW after the tracing tests

The chemical analyses by the project partner TZW Karlsruhe have shown that microorganisms, which were adapted to aerobic conditions by the addition of aerial oxygen will be able to crack hydrogen peroxide fast in order to use it as electron acceptor.

The initial aeration of the aquifer (August 2006) was realized by the mixing process of aerial oxygen into the circulated groundwater flow of the GCW. The concentration reached approximately 4.5 mg/L of oxygen. After one week of operation oxygen contents of 4.4 mg/L were detected in the region of the “spherical” circulated groundwater (RP 6) and 1.5 mg/L in the close vicinity of the GCW. At the same time the degradation of NSO-HET in the close vicinity of the GCW (RP6 – RP10) was observed.

During the addition of aerial oxygen the groundwater table increased continuously in the vicinity of the GCW. This effect was caused by precipitated iron hydroxide in the filter region of the GCW. After two weeks of operation the oxygen addition was stopped due to the formation of iron ochre. After a successful acid flushing the GCW could be operated with a flux of 4 m³/h

without any increase of the groundwater level. In the following NA-period, meaning no addition of oxidants, a natural iron reduction in the further region of the GCW should occur caused by the anaerobic groundwater. Even two months later no decline of the water level in the filter region was detected. But a clear decrease of the biological degradation of NSO-HET and PAH to a concentration level comparable to the period before starting the aeration was detected.

After the installation of a bag filter (100-50-10µm) for the separation of the iron hydroxide the mixing of hydrogen peroxide as electron acceptor started in December 2006. According to the laboratory tests the target concentration was 50 mg/L. Because of changing pressure conditions due to the iron deposition and filter cake formation the feed rates of the GCW oscillated significantly. The filter had to be cleaned every second day. This affected the constant dosage of hydrogen peroxide (Figure 4). In the beginning of February 2007 the hydraulic system was changed which led to a stable operation of the GCW and the mixing unit. Approximately 50% of the extracted groundwater was infiltrated into a satellite well (RP6, 2”). RP6 was located 5 m downstream of the GCW in the range of the groundwater circulation flow.

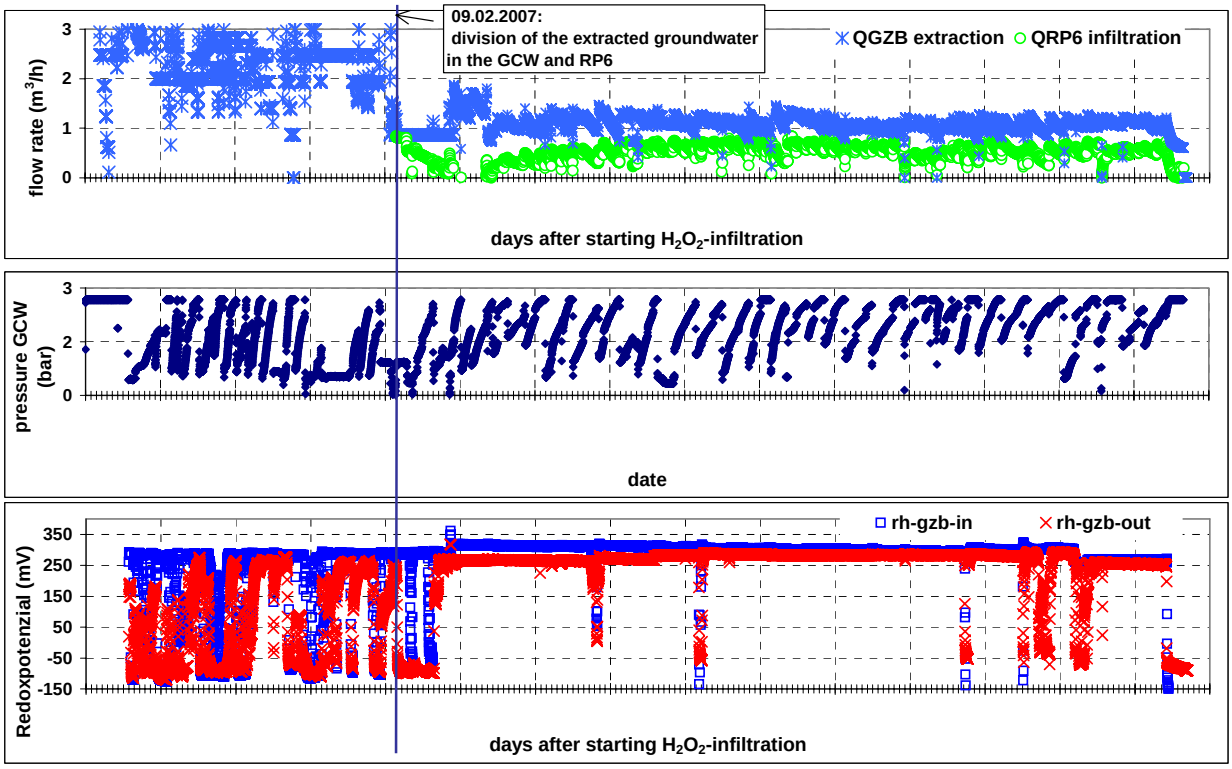

Figure 4: top: discharge of GCW (QGZB) and infiltration well (QRP6); middle filter pressure of the infiltration point; bottom: redox potential of GCW (blue) inflow and GCW (red) extraction flow

The validated numerical flow model indicated a capture zone of 12 m width and a range of infiltration of 14 m for the new system. From the hydraulic point of view the additional infiltration in RP6 downstream of the GCW caused a wider range of infiltration zone compared to the capture zone.

After six month of operation the oxygen content of the groundwater in the close vicinity and downstream at a distance of 25 m of the GCW were increased. The oxygen concentration

ranged between 1.5 and 16 mg/L. No aerobic conditions were found (O_2-content < 1.5 mg/L) at the control plane RP12-16 (30 m downstream of the GCW), see fig. 5.

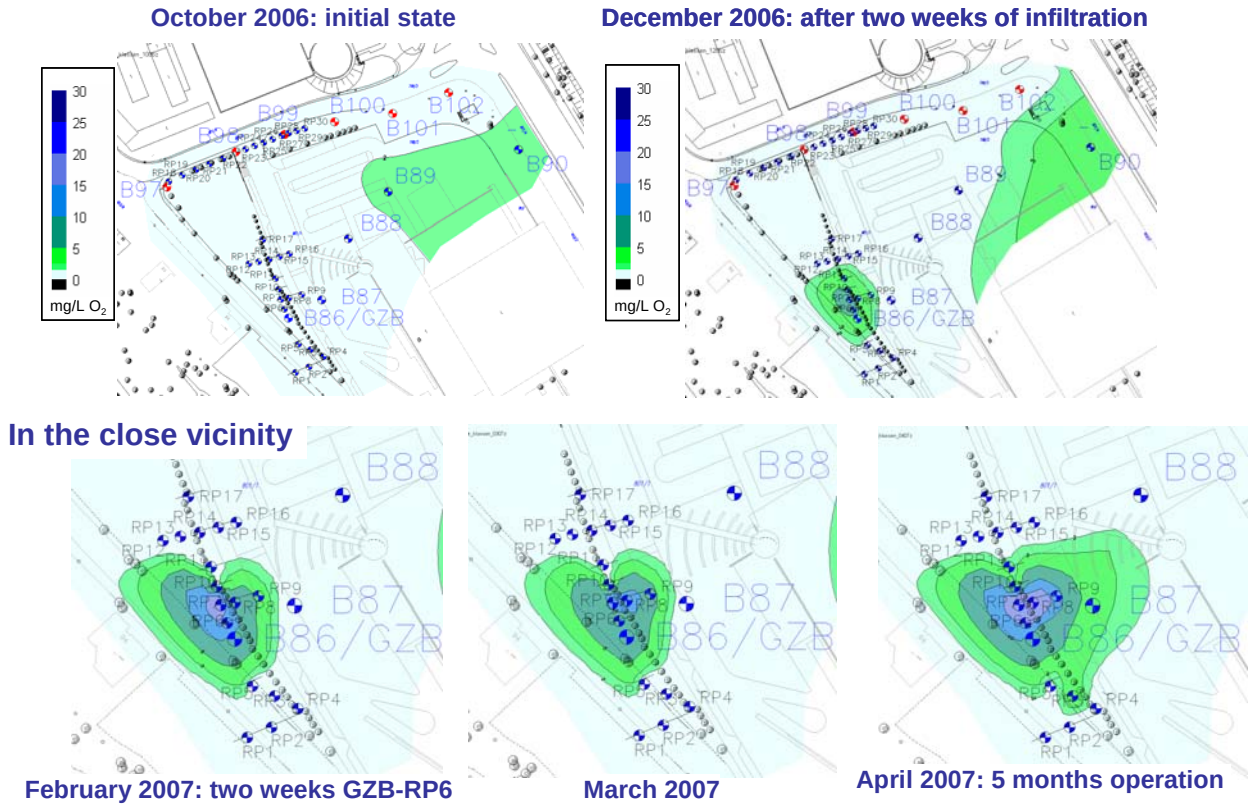

Figure 5: Development of the oxygen content in the vicinity of the GCW

During the pilot application the concentration of the PAH and NSO-HET were reduced by 55 – 80%. The contaminants were mainly degraded within the distance of 30 m downstream of the GCW (80%). Further downstream (B98, border of the property) a reduction of 55% related to the concentration in the GCW was determined. Considering the retardation processes of contaminants and oxygen in the plume a further increase of the reduction was expected for a longer time of operation. The temporal and spatial decline of the NSO-HET concentration (Figure 6) was comparable and at the same level of concentration as for PAH (Figure 7).

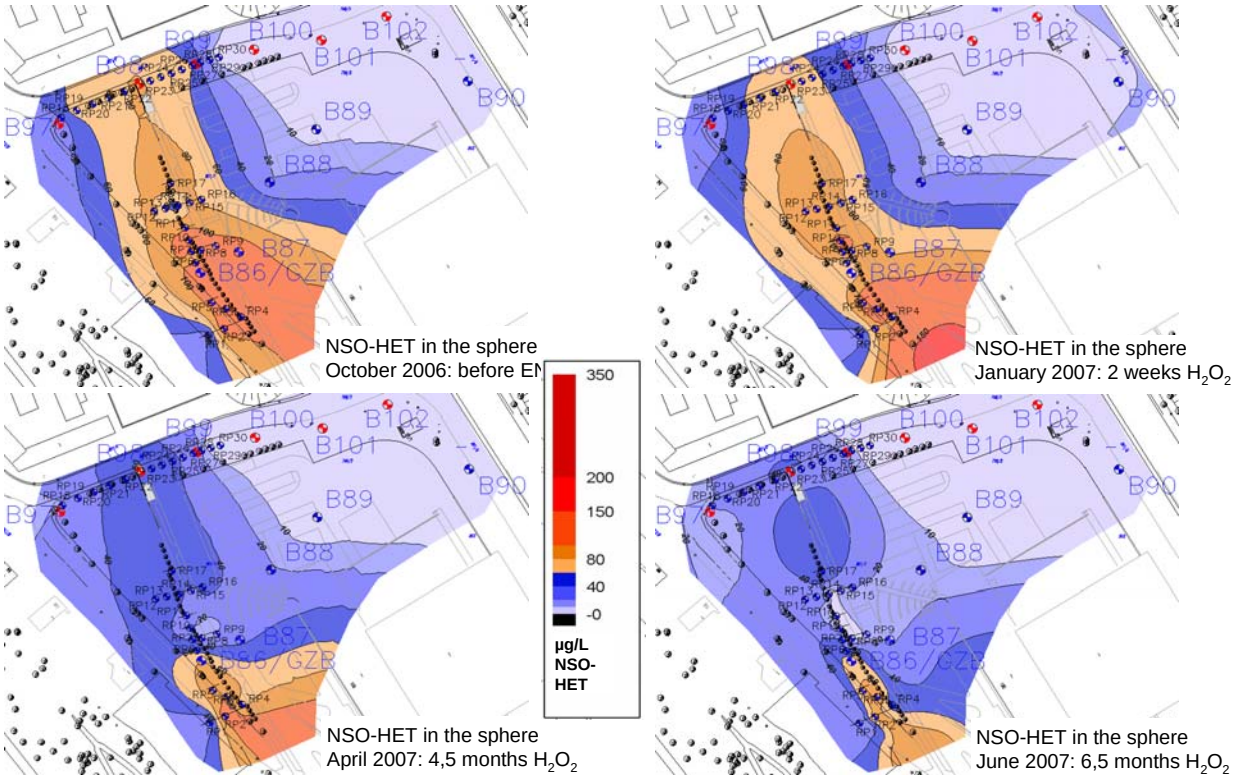

Figure 6: NSO-HET concentration during the addition of hydrogen peroxide

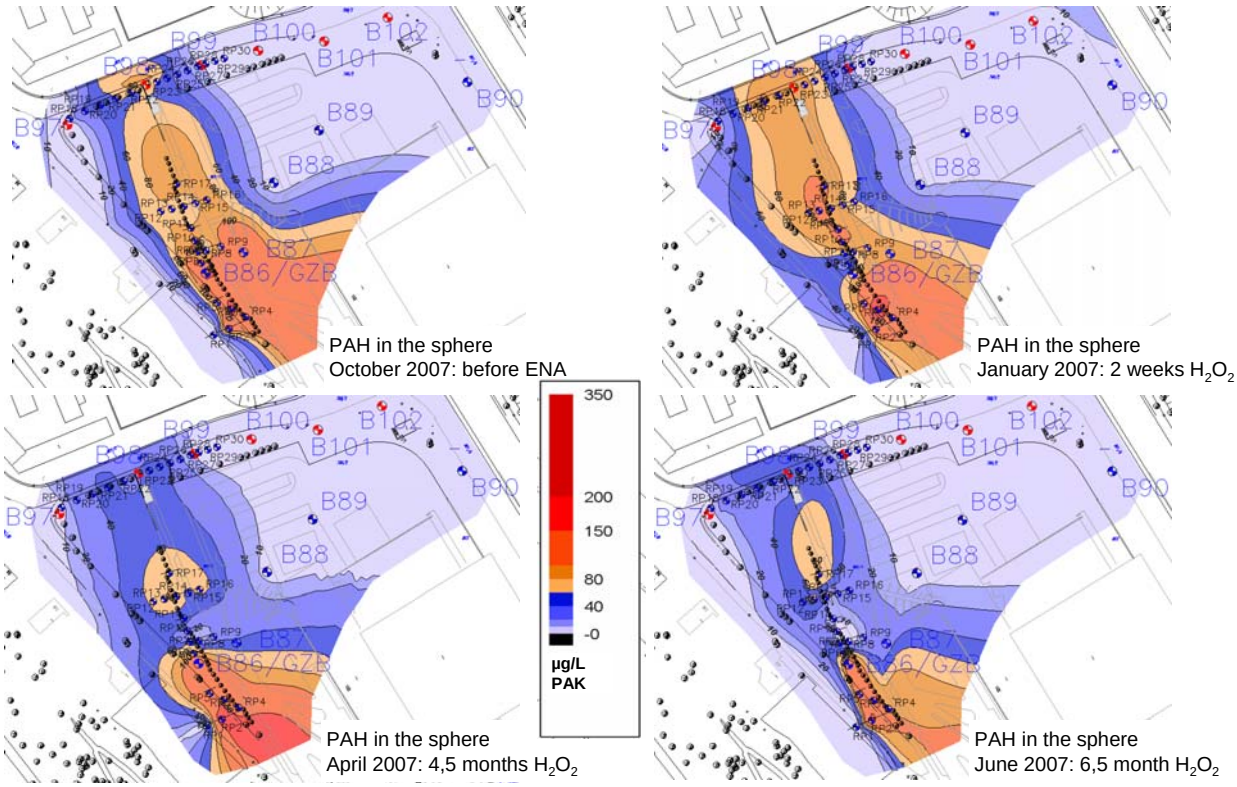

Figure 7: PAH concentration during the addition of hydrogen peroxide

The growths and development of the microorganisms population in the groundwater was screened regularly (MPN method) by the project partner TZW. In addition to the determination of the total viable aerobic count, the aerobic contaminant degrading bacteria just like the iron and nitrate reducing bacteria were determined.

After starting the addition of H_2O_2 there was a significant decrease of microbial numbers in the inlet and outlet flow of the GCW compared to the situation before H_2O_2 addition (Figure 8). This was caused by the toxic effect of hydrogen peroxide. Simultaneously the total viable count downstream of the GCW (RP7) increased significantly by a factor of 100 from 5.6*10^3 to 6.6*10^5. The well RP7 is located 10 m downstream the GCW and the highest oxygen concentration were measured in this groundwater. The number of aerobic contaminant degrading bacteria increased in this well in a comparable high degree. In zones with Fe (III) precipitation (RP11-RP17) the number of iron reducing bacteria increased by almost two orders of magnitude indicating an enhanced activity of this physiological group. This indicates the degradation of organic carbon and utilization of contaminants under iron reducing conditions. Actually, this is a quite interesting aspect for the operation of the GCW in an alternate mode, with or without the addition of oxygen and using the precipitated iron hydroxide and anaerobic degradation processes.

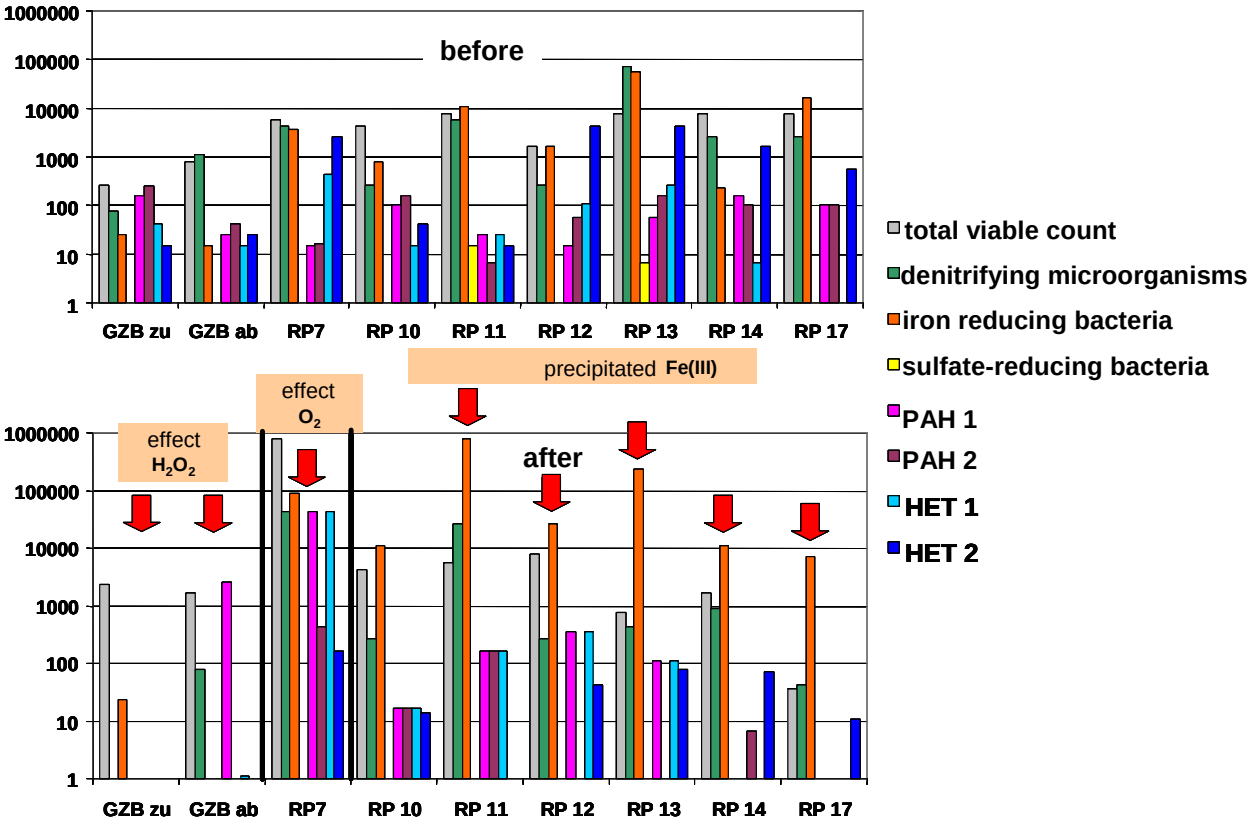

Figure 8: Comparison of the microbial numbers in the sphere of the GCW before and to the end of ENA.

Based on the costs of the first implementation including time-intensive maintenance work for the plant (bag filters exchange) and weekly determination of the process parameters in the groundwater influenced by the operation of the GCW the cost of an application on the field site were

estimated. The pilot application covered about 40% of the plume. During the designed field application 80% of the plume should be captured. For an extended operation two GCW are required. In addition to the existing GCW in B86 a second GCW was planned in B87. Also four new infiltration wells will be necessary. Due to the high amount of iron in the groundwater at the "Testfeld Süd" an automatically working iron filtration was planned. To monitor the effects of the ENA about 45 chemical analyses will be required, yearly.

With investment costs of 160.000 Euro and annual operation costs of 72.000 Euro the annually total costs will be about 88.000 Euro for an amortisation time of 10 years.

Summary and conclusion

During the research project a hydraulic remediation technology - the groundwater circulation well (GCW) - was upgraded and successfully used for a homogeneous and effective mixing of hydrogen peroxide in the contaminated groundwater. On a technical scale and during the field application an aerobic biological degradation of the persistent PAH (Acenaphthen) and NSO-HET was initiated. Degradation rate between 55 - 80% of the initial contaminant mass flux were achieved. In case of the completely hydraulic controlled model aquifer "Large Fume" an aerobic degradation rate of over 85% was determined. These high degradation rates were initiated by the addition of hydrogen peroxide causing high oxygen contents. In the close vicinity of the GCW oxygen contents in the groundwater between 10 – 20 mg/L resulted from the mixing process and a nearly instant decomposition of hydrogen peroxide into water and oxygen. The positive effects for the groundwater quality by the addition of hydrogen peroxide were verified in the pilot application.

The GCW is based on common well drilling techniques. The installation method of the system is stat-of-the-art and could be used for good permeable aquifers. Problems in the operation may result from high iron contents in the groundwater in combination with oxidants mixing (oxygen, hydrogen peroxide). As a simple and reliable technical solution the usage of "satellite wells" in the zone of the circulation flow has proved to be cost effective and to stabilize the operation and the control of the hydraulic system. The use of a monitoring well for the installation of a GCW was innovative. By this method existing wells can be used for the system. Monitoring wells are mostly existent on contaminated sites and located in the plume. Furthermore it was demonstrated that in contrast to earlier applications of GCW no large diameters of a GCW are necessary to control a groundwater circulation flow. So the investment costs are minor and the flexibility of the system is improved.

The developed numerical method for the simulation of the GCW offers the opportunity of the hydraulic design and dimensioning of an infiltration system with commercially available simulation software. Thus offers the opportunity for hydraulic engineers and consultants to consider nearly every geological and hydraulic situation at an early stage of the remediation design for contaminant plumes.

Based on the pilot application the estimated costs of ENA using hydrogen peroxide in order to treat about 80% of the contaminant mass flux of the plume at the pilot site are lower than the costs for standard hydraulic remediation techniques (pump & treat). ENA is comparable to the costs of passive systems (reactive barrier).

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