

Lecture Session (LeS): E.1 In-situ chemical oxidation-1

ENA OF HETEROCYCLIC HYDROCARBONS USING HYDROGEN PEROXIDE AND GROUNDWATER CIRCULATION WELLS – PILOT APPLICATION IN THE PLUME OF A FORMER GASWORKS

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Introduction

Heterocyclic hydrocarbons (NSO-HET) containing nitrogen (N), sulphur (S) or oxygen (O) atoms are constituents of tar oil, commonly found downstream of former gasworks sites (Zamfirescu & Grathwohl, 2001, Piepenbrink et al. 2005). Typical NSO-HET's are benzofuran, methyl-benzofurans, methyl-quinolines, acridine or carbazole. Different field studies indicate that most NSO-HET are highly mobile due to their high water solubility. The low anaerobic biodegradation rates cause long contaminant plumes. Some NSO-HET are highly toxic and carcinogenic (Sagner et al. 2007, Eisenträger et al. 2008). Aerobic biological degradation was found to be effective in batch and column experiments.

Based on the hydro-geology of the quaternary aquifer and the contaminant situation along the plume (800 m long, 70 m wide) downstream of a former gasworks site (Testfeld Süd, TFS) in Stuttgart, Germany, an applicable technology to enhance the natural degradation of PAH and NSO-HET was selected. The technology was tested under controlled conditions in a large physical model (Large Flume of VEGAS). Based upon the promising results (Trötschler et al. 2005) of the Large Flume experiment the ENA-technology was tested and demonstrated in a twelve-month lasting field trial.

This technology uses a groundwater circulation well system (GCW) to mix hydrogen peroxide (H_2O_2) into the anaerobic plume. A "spherical" groundwater circulation is induced by hydraulically separated ex- and infiltration filter-sections in a vertical well (Mohrlok et al. 2000). In this manner, the water is spiked with moderate H_2O_2 concentrations of 50 mg/L which leads to an oxygen concentration of approximately 20 mg/L in the circulated groundwater to stimulate the aerobic biological degradation of PAH and NSO-HET.

The field trial was finished in July 2007. During one year of operation of a GCW, hydrogen peroxide was infiltrated for about 7 months. The influence of the aeration of the groundwater on microbiological degradation of PAH and NSO-HET was determined by means of integral pumping tests (IPT). Additionally, groundwater was sampled from 1" direct push wells located on control planes with high resolution and 6" groundwater wells forming three control planes perpendicular to the groundwater flow. Control measurements indicated a reduction of NSO-HET and PAH concentration between 55 and 80%. Thus a reduction of the emissions leaving the site by almost a factor of 2 can be assumed.

Biodegradation of NSO-heterocyclic hydrocarbons

Biodegradation of NSO-HET is limited under anaerobic conditions. In the presence of ferric iron, anaerobic biodegradation of the nitrogen containing heterocyclic compounds was demonstrated in batch and column experiments. However, heterocyclic compounds such as methylated benzofurans, benzothiophene and the 3 ring NSO-HET proved to be relatively persistent under anaerobic conditions (see Tiehm & Sagner, Lecture Session (LeS): D. 5 Fate & transport-1).

Under aerobic conditions, all NSO-HET detected at the site proved to be biodegradable. Experiments with O_2 addition or H_2O_2 addition revealed that – after an adaption period – concentrations up to 100 mg/L H_2O_2 are tolerated by aerobic microorganisms. (Sagner et al. 2005). However, it was found that facultatively anaerobic microorganisms previously grown under anaerobic conditions will faster adapt to oxygen than to hydrogen peroxide (see Tiehm & Sagner, Lecture Session (LeS): D. 5 Fate & transport-1). Therefore all investigations on a technical scale (Large Flume of VEGAS) and in the field were initially started with oxygen (air) supply before shifting to hydrogen peroxide.

During two parallel column experiments (length of 50 cm, seepage velocity: 35 cm/d) with soil and groundwater from the pilot site (TFS) (under aerobic conditions with an anaerobic reference column) the addition of H₂O₂ concentrations up to 107 mg/L resulted in an almost complete biodegradation of the pollutants. Under anaerobic conditions the elimination of NSO-HET was not observed in the reference column.

Selection of infiltration technique and development of numerical simulation model

The effectiveness of ENA strongly depends on a homogeneous and far-ranging mixing of the electron acceptors with the groundwater. Due to site geology (medium permeable quaternary aquifer) and based on numerical pre-simulations a groundwater circulation well (GCW) was chosen as the most effective technology for mixing. The technical system was tested in the long-term experiment in the Large Flume of VEGAS. During these investigations a complete aerobic degradation of PAH and NSO-HET using hydrogen peroxide was observed (Piepenbrink et al. 2006). At the same time a numerical simulation model was developed and calibrated for the Large Flume to design the field application (discharge, dimension of packer in well, dimension of circulating flow field).

Pilot application on a former gasworks site

Based on the very promising results of the Large Flume experiment regarding the hydraulic effectiveness of the GCW and the complete aerobic degradation of PAH and NSO-HET the technology was applied on the pilot site starting in summer 2006.

To monitor the contaminant degradation processes 25 direct-push monitoring wells (1") and 11 groundwater wells (6") were installed. The wells were located along the groundwater flow direction (centre-line) in a distance of 5, 10, 15, 30, 40 and 80 m, respectively, down gradient the GCW (B86). At a distance of 10, 30 and 80 m three control planes of 3, 4 and 12, respectively, monitoring wells were arranged. Additionally five 1" monitoring wells and a control plane of 6" groundwater wells were installed in a distance of 125 m upstream the GCW.

The pilot application was divided into the following six steps:

1. Determination of contaminant mass flux and spatial contaminant distribution
2. Determination of the range of influence (capturing zone) by tracer test, intermittent operation of GCW (3 months) without mixing of electron acceptors
3. Adaptation of local microorganism to aerobic conditions (3 weeks) by adding oxygen (air) to the circulating groundwater flow
4. Initialisation and increase of aerobic microbial activities (6 weeks); high discharge of GCW and mixing of hydrogen peroxide
5. Increase and maintain of aerobic biodegradation (5 months); reduced discharge of GCW, mixing of hydrogen peroxide and operation of an additional infiltration well within the range of circulation flow field of GCW
6. Final determination of contaminant mass flux by Integral Pumping Tests (IPT) and spatial contaminant distribution

Initial field screening and installation of GCW

After accomplishing the IPT the operation of the GCW including process technology started in an existing 6" monitoring well (B86) in the western part of the plume. During the initial operation of the GCW without adding electron acceptors groundwater samples were taken at the control planes CP1, CP2 and CP3 and from 30 direct-push monitoring wells RP1 – RP30 (Figure 1). The direct-push wells were located in the area of the expected range of influence of the GCW. The contaminant distribution indicated a capturing of a part of the contaminant plume by the GCW with concentrations of approximately 100 µg/L. The concentrations downstream the GCW along the centre-line of the plume (RP7 – RP17) and at CP2-3 indicated natural attenuation. The concentration of NSO-HET was reduced from 100 µg/L at the GCW to 80 µg/L at B98 80 m downstream of the GCW.

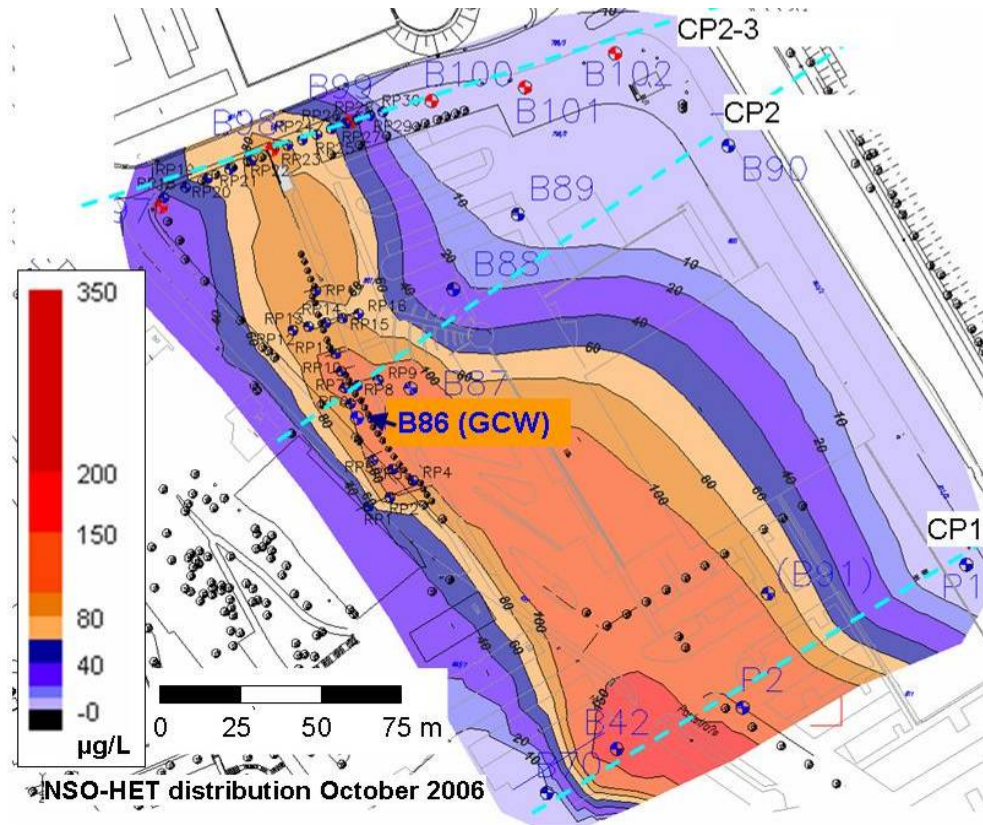


Figure 1: Contaminant distribution of NSO-HET before addition of H₂O₂

The GCW on the field site consisted of a lower filter section for groundwater extraction followed by a hydraulically inactive zone (packer) of 1 m length and an upper filter section for infiltration. Aquifer thickness is about 4 m. Fig. 2 illustrates how a spherical groundwater circulation flow is induced by the GCW between the extraction and infiltration filter section. In general the range of the induced circulation flow is the higher the mightier the aquifer, the higher the discharge and the larger the distance between extraction and infiltration sections. Initial flow simulation indicated a range of influence of 10 m width for a discharge of the GCW of 12 m³/h.

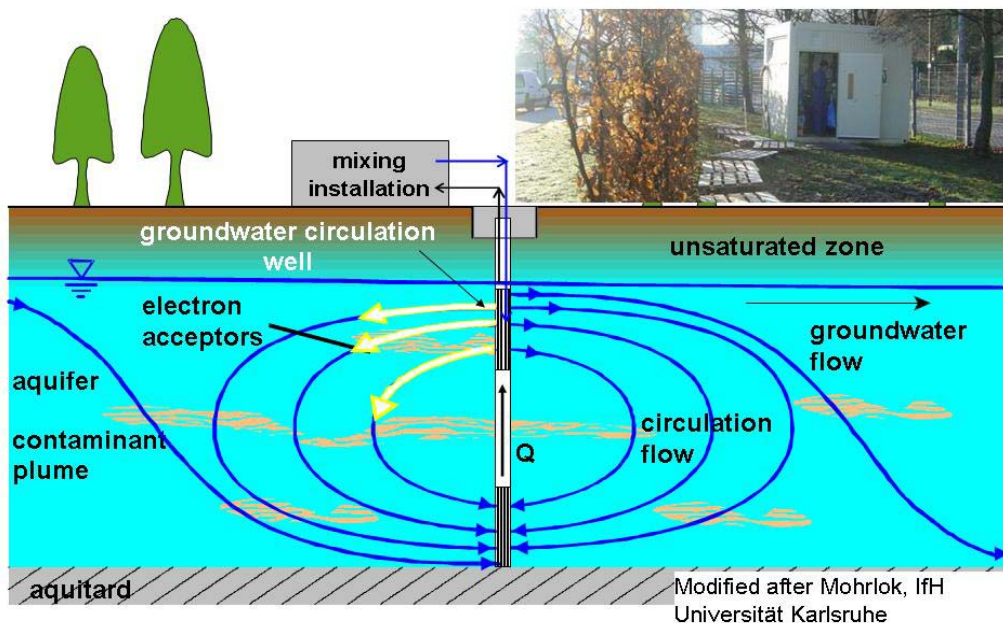


Figure 2: Scheme of GCW and process container

The plant for mixing hydrogen peroxide and air (oxygen) was equipped with sand filters to minimize the infiltration of generated iron (III) and manganese (IV) compounds. Air was added to the infiltrated groundwater by means of an injector pump, hydrogen peroxide by means of membrane pumps.

Tracer tests using fluorescent Uranine AP

During step 3 of the pilot application three tracer tests were conducted to determine the capturing zone of the GCW, as well as the downgradient flow pattern of the aerated groundwater.

Uranine was injected (Dirac pulse) at three different 1"-monitoring wells and with a time offset of the tracer pulse of one month each. These wells were located in a distance of 25 m upstream the GCW and along a line transversal to the groundwater flow direction. The tracer was captured by the GCW for low discharges of 4 m³/h and a transversal distance of 8.5 m between the infiltration well and the GCW. The groundwater capture zone ranged between 12 m width for a flux of 1.5 m³/h and 20 m width for a flux of 8 m³/h.

The numerical flow model was calibrated according the results of the tracer tests. The anisotropy (K_{hor} / K_{vert}) of aquifer matrix and the effective porosity were changed. Downgradient movement of the tracer followed the regional groundwater flow direction (NNW) following the selected orientation of the center-line (GCW → B98).

The groundwater velocity was determined as 1.6 m/d. The width of detectable tracer at CP2-3 of 60 m indicated an increase of transverse dispersion by the GCW. Effective porosity was determined as 0.17 and average hydraulic conductivity estimated as 1.6×10^{-3} m/s for a gradient of 0.0016.

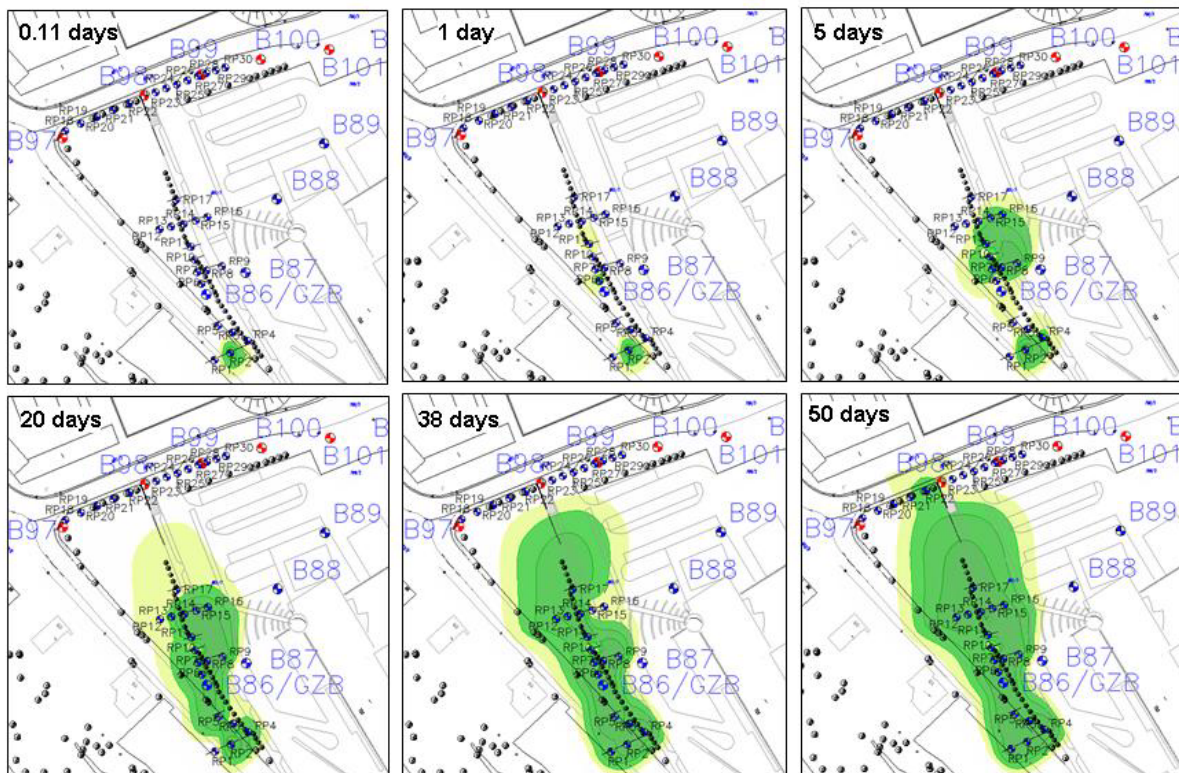


Figure 3: Tracer propagation TFS for adding in RP2

Initial mixing of air, formation of iron ochre in GCW and intermittent ENA

During the initial aeration of the aquifer air was mixed in the circulation flow of the GCW. The concentration reached approximately 4.5 mg/L of oxygen, meaning 0.8 kg/d of oxygen release. After one week of operation an increase of oxygen in the groundwater of 1.5 to 4.4 mg/L was detected only in the close vicinity of the GCW (RP6, RP7, RP8, RP10). At the same time a reduction of NSO-HET concentration from initial 30 – 90 µg/L to 0.3 – 7 µg/L was measured.

During mixing of air the groundwater level in the filter annulus of the GCW slowly increased. After nine days of operation an outflow of groundwater at the well head was observed, meaning a local water

level increase in the aquifer of about 3 m. Massive formation of iron ochre due to the oxidation of Fe(II) was found in the upper part of well's annulus and in close vicinity to the well. Installed sand filters were not able to separate the generated iron hydroxide from the circulating groundwater flow. Therefore, an additional filtration unit (using dead-end filtration (500-200-50 μm filters)) was installed before starting the following aeration by hydrogen peroxide. The filtration unit led to a mass flux reduction of 80% of total iron content (15 mg/L \rightarrow 3 mg/L).

Due to the formation of iron ochre aeration was stopped and the well had to be regenerated by acid flushing (H_2SO_4). After the successful acid flushing GCW was operated with a flux of 4 m³/h. To simulate an intermittent ENA for the next 2 months, the GCW was operated without mixing of electron acceptors. During this anaerobic phase the biological degradation decreased. NSO-HET and PAH concentration increased to a level comparable to the period before starting aeration.

Mixing of hydrogen peroxide and resulting change of the hydraulic regime

The concentration of H_2O_2 in the infiltrated groundwater was adjusted at 50 mg/L to ensure the oxidation of iron (II) and a remaining high concentration of more than 30 mg/L for the oxygen supply of the bacteria. The effective dosage was between 0.1 and 0.25 kg/h hydrogen peroxide, resulting in an oxygen infiltration of 1.1 to 2.8 kg/d. The daily mass of iron hydroxide separated by the filtration unit was about 800 g. Thus, the pressure losses on the filters increased rapidly and caused instable fluxes of the GCW and the dosage of H_2O_2 .

In the beginning of February 2007 the hydraulic system was changed which led to a stable operation of the GCW and the mixing unit. After dosage of H_2O_2 and separation of iron hydroxide approximately 50% of the extracted groundwater was infiltrated into a satellite well (RP6, 1"). RP6 was located downstream of the GCW in the range of the groundwater circulation flow. Due to this modification the flux of the GCW was kept at 1.2 m³/h for the next 5 months without significant problems of flooding of the GCW. The validated numerical flow model indicated a capture zone of 12 m width and a range of infiltration of 14 m in the new system (Figure 4).

- extraction GCW (lower filter): 1.2 m³/h
- infiltration GCW (upper filter): 0.5 – 0.6 m³/h
- infiltration RP6: 0.6 – 0.7 m³/h

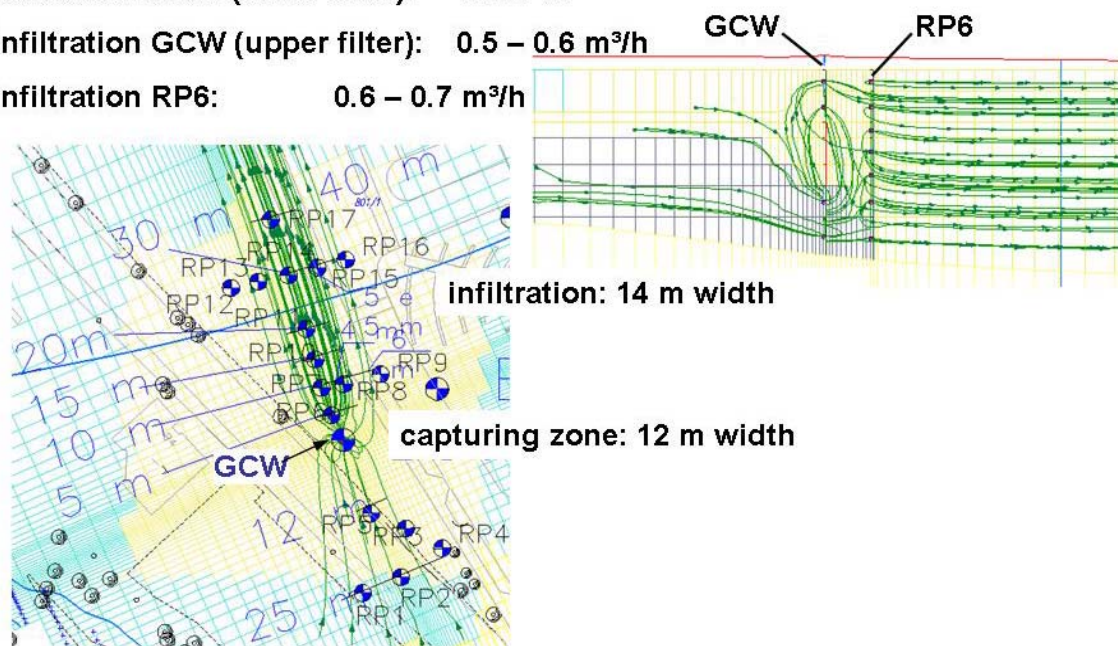


Figure 4: Numerical simulation of GCW after change of hydraulic system

After changing the hydraulic system the infiltration of H_2O_2 was reduced since a maximum oxygen content of 20 mg/L were measured on the circulation flow and down-gradient distribution of oxygen (Figure 5) indicated aerobic conditions. Approximately 0.15 kg/h of H_2O_2 , meaning 1.7 kg/d oxygen were infiltrated instead of 2.8 kg/d.

At a distance of 25 m downstream the GCW the oxygen concentration in the groundwater ranged between 1.5 and 16 mg/L. At the control plane RP12 – 16 (30 m downstream of the GCW) the oxygen

concentration were constantly below 1.5 mg/L, meaning nearly anaerobic conditions. In these monitoring wells precipitating Fe(III) was observed leading to the assumption of a “Fe(III)-wall” formation in the aquifer.

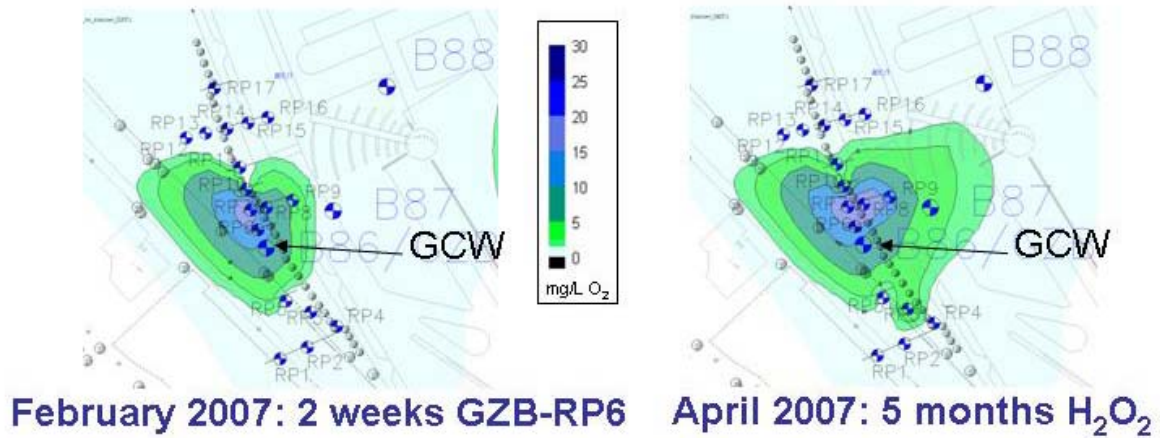


Figure 5: Development of oxygen distribution in the vicinity of GCW

Aerobic biological degradation of NSO-HET and PAH

After two weeks of adding H₂O₂ the NSO-HET concentration in the close vicinity (RP6 – 11; 5 – 20 m) of the GCW were reduced by more than 65 % (average values: 107 µg/L → 35 µg/L), (Figure 6). Further downstream (RP12 – 17; 30 and 40 m) the NSO-HET concentrations were reduced by approx. 40% (72 µg/L → 42 µg/L). Two months after changing the hydraulic system the NSO-HET in the vicinity of the GCW were found to be further degraded (35 → 25 µg/L), (Figure 6, bottom left).

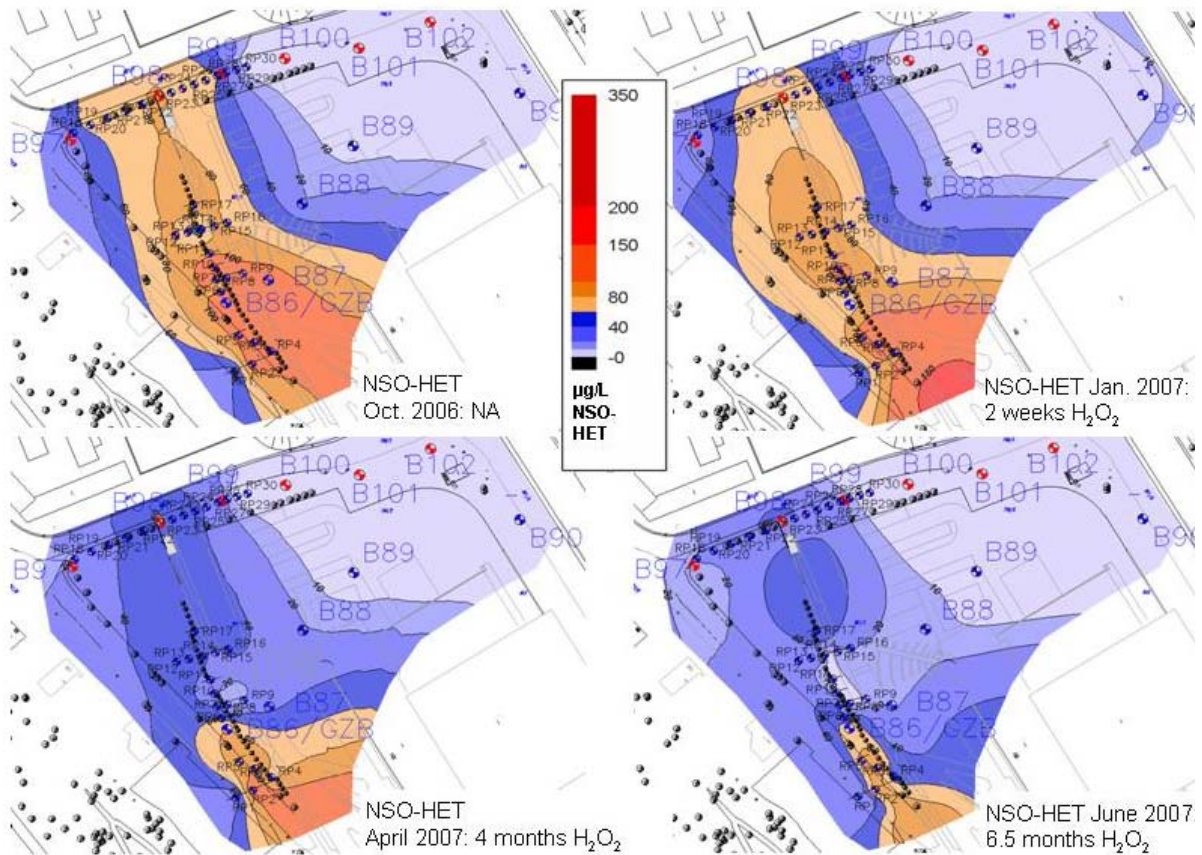


Figure 6: Development of NSO-HET distribution during ENA

During the following two months the degradation of NSO-HET was further enhanced and the concentrations measured downstream of the GCW (10 – 40 m) ranged between 1.5 and 52 µg/L; 23 µg/L in average. At a distance of 80 m down-gradient of the GCW the concentration ranged between 1 and 41 µg/L, and the contaminant plume was focussed on a width of 60 m around B98. The NSO-HET concentration in the GCW ranged at that time between 70 and 88 µg/L.

A similar degradation of PAH and its dominant contaminant acenaphthen was observed. After four months of hydrogen peroxide dosage the concentrations in the vicinity of the GCW ranged between 0.7 – 45 µg/L (average 17 µg/L) while the PAH content in the GCW was approximately 109 µg/L. Further downstream (RP12 – RP16) the PAH concentration was 60 µg/L in average. After another two months of ENA the concentrations at this control section were reduced to 42 µg/L (in average). The PAH concentration of the GCW ranged between 135 – 147 µg/L while the contaminant concentration at the site border (B97- RP18 – RP30 – B99) ranged between 0.1 and 62 µg/L, in average 24 µg/L. Figure 7 illustrates the development of PAH distribution during ENA.

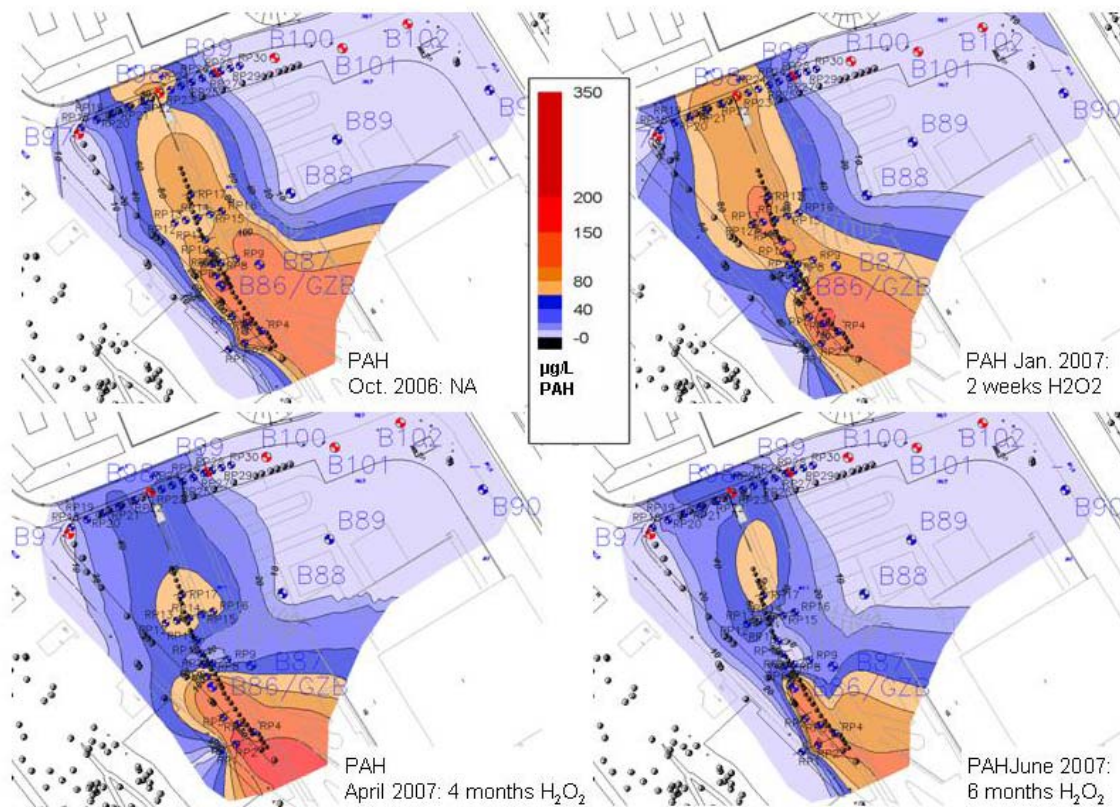


Figure 7: Development of PAH distribution during ENA

Microbial community analysis

The number of microorganisms in the groundwater at the several monitoring wells was screened regularly (MPN method). In addition to the total number of aerobic heterotrophs (GKZ), aerobic contaminant degrading bacteria, iron(III)-, sulphate- and nitrate reducing bacteria were determined.

After starting the addition of H₂O₂ there was a significant decrease of microbial numbers in the inlet and outlet flow of the GCW as compared to the situation before H₂O₂ addition. This indicated a toxic effect of hydrogen peroxide on non acclimated bacteria. During ENA, the microbial numbers increased down-gradient the GCW, e.g. in the groundwater of the monitoring well RP7. This well is located 10 m downstream the GCW and had the highest oxygen concentrations (Figure 8).

In the same zone, the number of aerobic contaminant degrading bacteria increased significantly. 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 effect is promising since enhanced biodegradation with Fe(III) might be possible also during periods of limited oxygen supply.

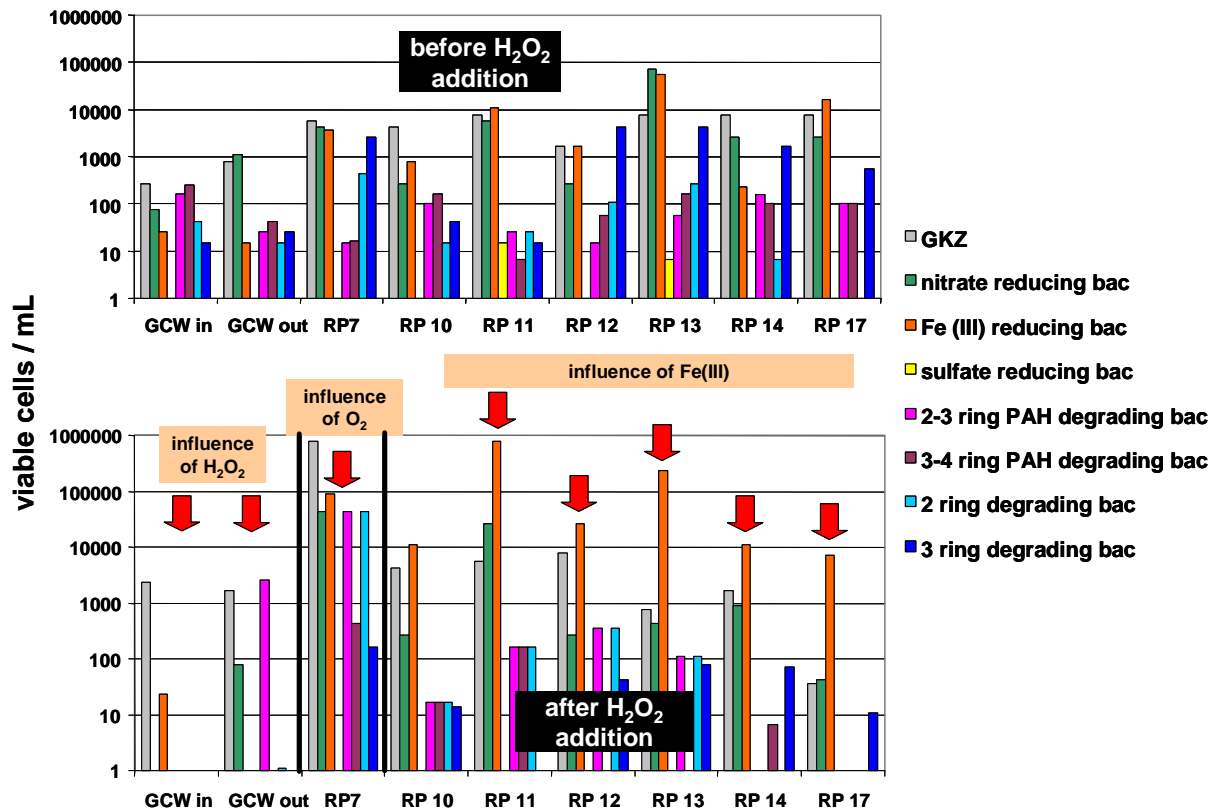


Figure 8: Microbial numbers (MPN test) before and after the addition H₂O₂

Financial aspects

The initial operation of GCW was cost intensive with respect to personal and material expenses. Due to the unexpected high amount of iron in the zone of B86 up to three times per week maintaining works and filter change was required. Initial technical problems in dosing of hydrogen peroxide, the precipitation of iron (III) and the filtration of iron had to be solved. The hydraulic system of the GCW using a single well appeared to be very sensitive with respect to ochre formation. The usage of “satellite wells” was a reasonable option to maintain a stable cost efficient long term operation of groundwater circulation technique. With regard to the future use of the technology at the site a different, cost-effective technology for the separation of iron (III) using sand filtration, automatic back-flushing and sedimentation is proposed.

Based on the costs of the pilot application (personnel, analytics, chemicals and consumables) and the potential cost reduction due to an automatically working iron filtration the yearly costs to continue the ENA measure with a range of influence of 40 % of the contaminant plume were estimated to be 40,000 EUR. For an extension of the range of application to ensure the capturing of more than 80% of the plume the yearly costs of the ENA measure were also estimated.

Table 1: cost evaluation pilot application and cost estimation of ENA TFS

	Pilot application net costs [EUR / month]	Field application net costs [EUR / year]
Personnel costs: Surveillance, operation and maintenance	2,800	22,500 (material)12,600
Operation costs: chemicals	450	17,500
Operation costs: electric power	220	4,500
Investment costs drilling, plant installation, piping work		Total: 159,000 EUR
Analytical costs incl. sampling	-	11,200
Investment costs (amortisation of 10 years)	260	16,000
sum EUR net costs	3,730	84,300

The cost estimation ranges between 80,000 and 100,000 EUR per year. The estimation includes the extension of the treated area by the installation of additional wells, a continuously working iron separation unit, enlarged hydrogen peroxide storage and dosage unit and subsurface field piping work. To determine the yearly costs it was assumed that one time yearly the biological degradation is monitored by sampling at the control planes CP1, CP2, CP2-3 and CP3.

Summary and conclusion

ENA of NSO-HET using hydrogen peroxide as oxygen releasing compound and a groundwater circulation well for the effective transversal mixing of the electron acceptor into the contaminated groundwater was effectively realised during a pilot application. The methodology of selecting the most appropriate electron acceptor, the most appropriate infiltration technique for the given site, the combination of Integral Pumping Test and the installation of small direct push wells (Centre line method) to monitor and control the effectiveness of the measure were basis of the success. The aim of a significant and constant biological degradation of the contaminants was reached during six months of operation. The concentration of the contaminants PAH and NSO-HET was reduced by 55 to 80% in the range of influence of the GCW (20 – 25 m width).

In general, high iron contents in the groundwater are causing systematic problems for the application of a GCW and other infiltration technologies using hydrogen peroxide, oxygen or air as electron acceptor. The formation of iron ochre in well annulus and the aquifer in close proximity to the well lead to a reduction of the infiltrated flux by a factor of 10 during the pilot application. Using small satellite wells for the infiltration located within the range of the groundwater circulation flow was a practicable, low cost solution to maintain a wide capturing zone for a minimised infiltration rate.

The yearly cost to treat about 40% of the plume are estimated to be between 40,000 and 50,000 EUR, whereas the treatment of about 80% of the plume should be possible with 80,000 to 100,000 EUR per year.

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