NanoRem 8
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CL:AIRE

NanoRem Bulletin

CL:AIRE's NanoRem bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater using nanoparticles. This bulletin describes a remediation pilot study using an iron oxide nanoparticle to treat groundwater contaminated with BTEX compounds.

NanoRem Pilot Site – Spolchemie II, Czech Republic: Remediation of BTEX compounds using Nano-Goethite

1. INTRODUCTION

This bulletin describes a pilot study to test an iron oxide nanoparticle (NP) called Nano-Goethite for enhancing the natural biodegradation of benzene, toluene, ethylbenzene and xylene (BTEX) compounds. It was undertaken as part of the NanoRem Project (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment), which was funded through the European Union Seventh Framework Programme.

The Spolchemie site (Czech Republic) was chosen as one of the NanoRem pilot sites to test two different nanoparticles (NPs): Nano-Goethite, the subject of this bulletin, and two nano-scale zero valent iron (nZVI) particles, which are described in NanoRem Bulletin #7. Nano-Goethite was applied for the remediation of BTEX compounds and nZVI for remediating chlorinated hydrocarbons (CHCs). Nano-Goethite is an iron oxide modified by humic substances, developed at the Helmholtz Centre Munich and the University of Duisburg-Essen. It was supplied as an aqueous suspension.

Nanoremediation was seen as giving an opportunity to enhance remedial works that have been ongoing at the site since 2005. The ongoing remediation approach for the BTEX compounds on site is the removal of free phase by skimming enhanced by groundwater pumping and treatment, followed by enhanced biodegradation. The main aim of this study was to assess the ability of Nano-Goethite to enhance the microbial activity in the pilot study area, in order to degrade BTEX compounds more effectively. The ferric iron mineral acts as an electron acceptor for microbial respiration [$Fe3^{+}$-reduction coupled to oxidation of the BTEX compounds] and can overcome limitations in electron acceptor availability. In addition migration characteristics and remedial efficiency of Nano-Goethite were evaluated using advanced procedures for monitoring both total iron and vertical stratification of BTEX.

2. SITE DESCRIPTION

Spolchemie is one of the leading synthetic resin manufacturers in Europe, located at Usti nad Labem, Czech Republic. The plant started to produce resins and freons based on tetrachloromethane and tetrachloroethene from the middle of the twentieth century. The production, treatment, storage and distribution of various raw materials and organic solvents (like toluene and xylenes) has led to extensive contamination by BTEX, which have dispersed widely from the original source areas.

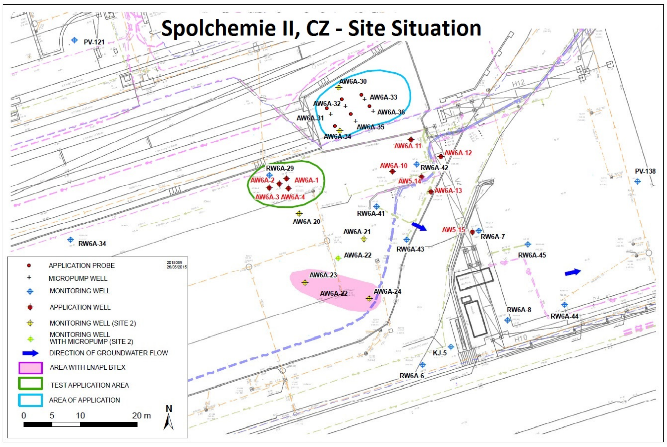

Figure 1. Site plan of the Spolchemie II site.

The pilot study area, named "Spolchemie II", is approximately 10 m x 10 m and is located in the middle of the southern border of the factory compound. Figure 1 provides a site plan of the site and shows the location of monitoring and injection wells and the area of BTEX impact in groundwater.

Figure 2 shows a cross-section of the site and the distance to the primary receptor, the river Bílina. The subsurface at this location consists of Quaternary sand and gravel with a thickness of approximately 10 m underlain by a clay aquitard. The Quarternary sand and gravel terrace is the only hydrogeologic unit where the BTEX detections have been found. The groundwater level is 4-5 m below ground level (bgl), thus the unconfined aquifer has a saturated thickness of 6-7 m. The groundwater flows in a south-easterly direction and has a velocity of approximately 0.9 m/d.

Figure 3 gives an example of the proportion of the different BTEX compounds on site (mainly xylenes, then toluene and ethylbenzene) and their vertical distribution in groundwater. The highest total BTEX concentration was found in groundwater at 5 m bgl (up to 90,000 μg/l), in contrast, the total concentration of BTEX at 8 m bgl was only 15,000 μg/l.

Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment.
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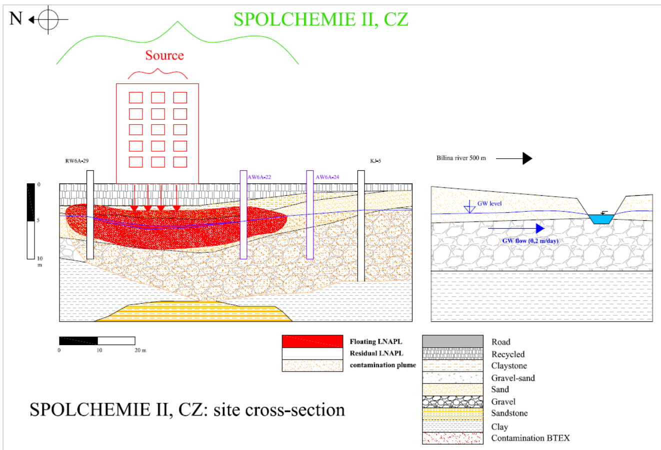

Figure 2. Cross-section of the Spolchemie II site.

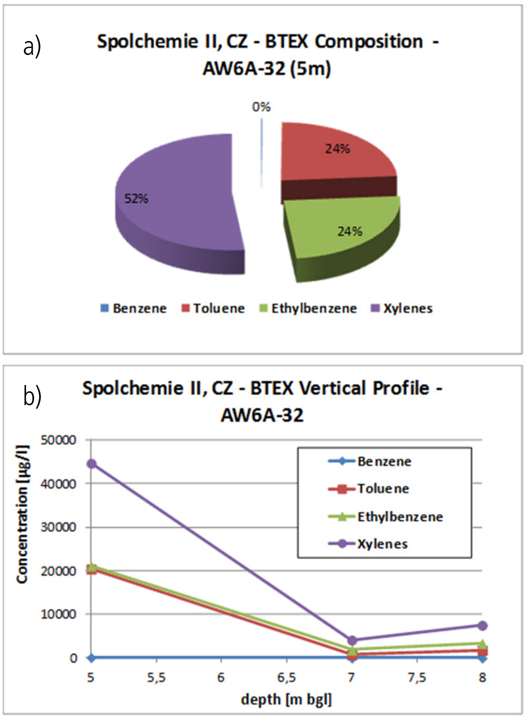

Figure 3. a) Relative proportions of BTEX and b) vertical concentration profile of contaminants on the Spolchemie II site. Low benzene concentrations (max.170 µg/l) were recorded in other wells.

Within the pilot study area there is residual light non-aqueous phase liquid (LNAPL) in the central area, surrounded by a dissolved phase BTEX plume.

3. PROJECT MANAGEMENT

3.1 Project Team

The pilot study was managed by AQUATEST - a private company performing *in situ* remediation, and involved the successful cooperation of several NanoRem project partners: University of Duisburg-Essen - the producer of Nano-Goethite, VEGAS, University of Stuttgart - responsible for large-scale experiments with NPs, NMBU and University of Vienna – responsible for monitoring particle migration, and Technical University of Liberec - responsible for microbiological analyses.

3.2 Regulatory Approval

For the Spolchemie site, permission has been granted by the local authorities (Regional government of Ustí nad Labem region - Krajský úřad Ústeckého kraje) for the injection of three tonnes of iron NPs per year. AQUATEST is permitted to distribute this quantity across the whole Spolchemie site according to its needs.

4. DESIGN, INSTALLATION AND OPERATION

4.1 Monitoring System Design

The first Nano-Goethite pilot test application on the Spolchemie II site took place in October 2015 at which point the monitoring programme began and continues to date. Prior to the injection, seven new boreholes were drilled and five of them were installed with micro-pumps almost in the same position at depths 5, 7 and 8 m bgl. Two new monitoring wells (upgradient and downgradient) have common casing with an open interval (screens) between 4 to 8 m.

In addition to wells AW6A-31, AW6A-32, AW6A-32, AW6A-35 and AW6A-36 (15 sampling points) there are two new narrow-diameter monitoring wells AW6A-30 and AW6A-34 (diameter 45 mm, open screen) on the site and two other monitoring wells on the outflow from the site (RW6A-42 and RW6A-7). The locations of the wells is shown in Figures 1 and 4.

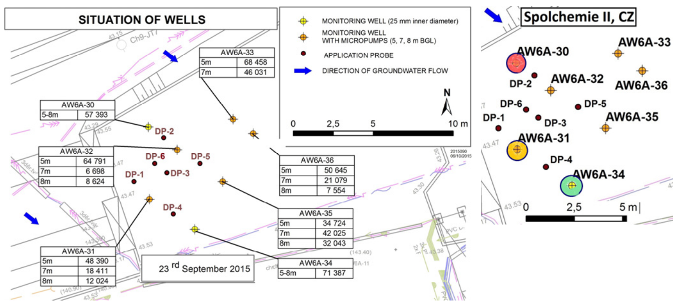

Figure 4: Test field for the injection of Nano-Goethite (left overview with initial concentration of BTEX (in µg/l), right details)

4.2 Injection of Nano-Goethite and Tracer

A preliminary test of the direct-push injection of Nano-Goethite was carried out in November 2014 with the aim of verifying the behaviour of Nano-Goethite during injection. This Nano-Goethite was provided by the Helmholtz Centre, Munich, Germany. The injection was performed in the northern part of the BTEX plume between wells AW6A-1, AW6A-2 and AW6A-4 (see "test application area" in Figure 1). In total, 60 kg of the nanomaterial was injected into the aquifer at a concentration of approximately 20 g/l, comprising 3 m3 of suspension. Two direct-push probes were situated in the centre of the monitoring system. A third was situated 1 m north in the upgradient direction. The application pressure of the fluid oscillated between 1 and 12 bars due to the variation in permeability in the zone of application. The application started at 4 m bgl and continued to 7 m bgl in 0.5 m increments (5 m, 5.5 m… …10 m, 10.5 m). The Nano-Goethite suspension was continuously stirred during the injection. Potassium bromide (KBr) was injected as a conservative tracer together with the NPs to make it easier to monitor their migration. In total, 1 kg of KBr was injected in the first cubic metre of the suspension. The monitoring points were the following wells: AW6A-1, AW6A-2, AW6A-3 and AW6A-4. Samples were taken from these points in 16 monitoring rounds during a 4 week period.

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After evaluation of the preliminary pilot test results, a new area was chosen for the main pilot test, for which a detailed monitoring system was emplaced, including the installation of new wells for assessing the vertical extent of BTEX impact. These wells contained micro pumps especially installed for monitoring NPs in the field. Nano-Goethite was supplied by the University Duisburg-Essen, Germany, and was injected again via direct-push in October 2015. 300 kg of Nano-Goethite was injected at a concentration of 5 g/l: in total 60 m^3 of suspension of Nano-Goethite stock solution in technological water (filtrated water from Elbe river) were injected. Again, the suspension was stirred continuously during the injection. 3 kg of KBr tracer was diluted in the injected volume. The injection parameters are shown in Table 1 and the set up of the injection system is shown in Figure 5.

Table 1: Injection parameters for Nano-Goethite and KBr tracer

Well	Date	NP conc (g/l)	Vol. (m³)	Q (m³/h)	NP (kg)	KBr (g)	Inj. Pressure (bar)	Inj. Depth (m bgl)
DP-2	20.10.15	5	12	1.8	60	600	1-12	5.8
DP-1	21.10.15	5	10.2	1.8	51	510	1-12	5.8
DP-5	21.10.15	5	11.7	1.8	59	590	1-12	5.8
DP-6	22.10.15	5	6	1.8	30	300	1-12	5.6
DP-4	22.10.15	5	9.1	1.8	45	450	1-12	5.8
DP-3	23.10.15	5	11	1.8	55	550	1-12	5.8
Total	20.10.15-23.10.15	5	60	1.8	300	1000	1-12	5.8

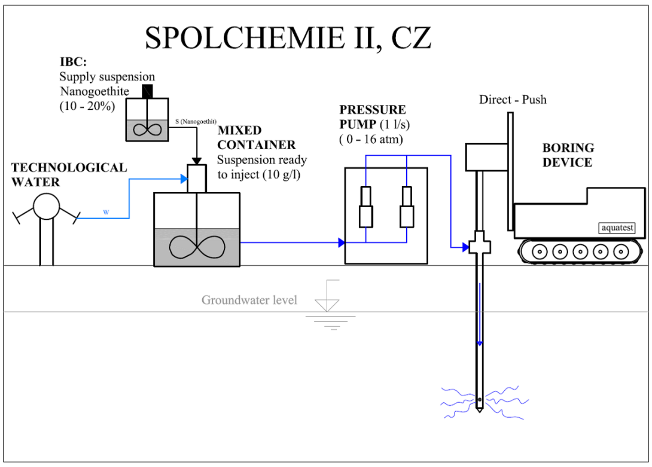

Figure 5. Set up of Nano-Goethite direct-push injection.

5. RESULTS AND DISCUSSION

5.1 Nano-Goethite Preliminary Injection

Tracer test and total iron content

Figure 6 shows the results of the tracer test executed during the injection and total iron content analyses. For interpretation purposes, the wells AW6A-1, AW6A-2, AW6A-3, AW6A-4 can be divided into two pairs: AW6A-1 and AW6A-4 have a lower saturation of iron and lower concentrations of bromide; AW6A-2 and AW6A-3 are much more saturated (10 times more) by iron and the concentration of bromide is more then one order of magnitude higher compared to AW6A-1 and AW6A-4. In fact, all the wells in the area showed a significant increase of tracer concentration and total iron content immediately after injection of NPs.

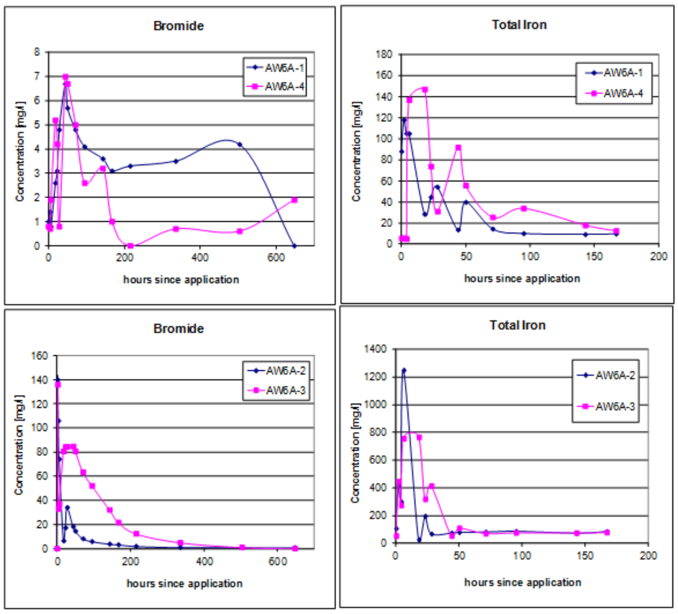

Figure 6. Tracer and total iron concentrations for the preliminary injection at the Spolchemie II site.

BTEX concentrations

Baseline monitoring took place 7 days before injection of NPs. The groundwater level was measured before sampling. All 4 wells were sampled under dynamic conditions. Redox potential was measured during the sampling. Samples of groundwater were analysed for BTEX compounds. Two rounds of post-application monitoring took place 23 and 123 days after the injection and the same sampling procedures as above were followed.

Figure 7 displays the results of total BTEX concentration after injection and shows that the concentrations vary greatly from well to well. Each well is very close to one another (1.5 m); with three direct push injection probes the creation of a temporal underground reactor would be expected to have similar properties in its whole volume. Instead Figure 7 shows an increase of BTEX concentration in well AW6A-4 of two orders of magnitude – from 2000 µg/l to 291,000 µg/l (probably due to mobilisation of NAPL from the capillary fringe zone). In contrast AW6A-2 displays an inverse behaviour with BTEX concentration decreasing from 261,000 µg/l to 18,000 µg/l. These contradictory results are most likely the effect of induced movements of groundwater and NAPL under high pressure associated with the direct-push injection rather than of

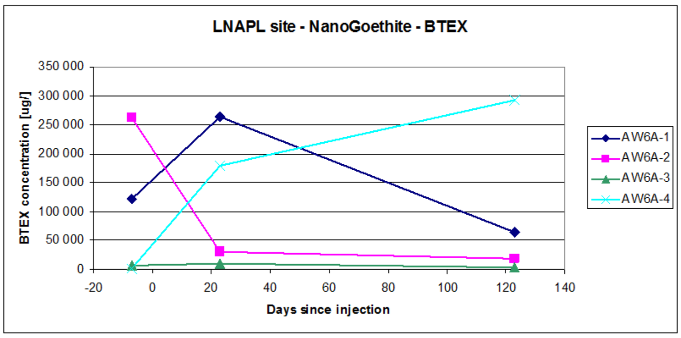

Figure 7. BTEX concentrations for the preliminary injection at the Spolchemie II site.

bioremediation induced by Nano-Goethite. Daylighting[1] was also observed along the casing of wells AW6A-2 and AW6A-4 during the pressure infiltration. These effects combined to change the BTEX concentrations and these observations could be significant for future microbiological analyses.

5.2 Nano-Goethite Pilot Study Injection

Tracer, total iron and ferrous iron concentrations

Figure 8 shows the results from the injection of the potassium bromide tracer in addition to the measurements of total and ferrous (Fe^{2+}) iron content.

The injection of Nano-Goethite caused a significant increase in total iron content (more than 300% of the original concentration) in all micro-pump horizons of well AW6A-31, in the well AW6A-32 at 5 and 8 m bgl and in AW6A-35 at 7 m bgl. In all the other monitoring points an increase of 50-70% of total iron content compared to the concentrations before the NP injection was observed. The increase of total iron concentration lasted only 8-15 days since the start of the injection (or 4-11 days after its end), indicating that the nanoparticles were immobilised in the ground of the application area after this period.

The concentration of bromide increased significantly immediately after the injection of NPs and tracer in all monitoring points. Compared to the increase in total iron concentrations, the increase in bromide concentration lasted for a longer time (48 days or longer after NP injection), due to better migration properties of the bromide ion.

An important conclusion of the tracer test on the Spolchemie II site is that the site was saturated with the Nano-Goethite suspension in the most permeable zones . Contact between contaminated groundwater and NPs was proved at every monitoring point.

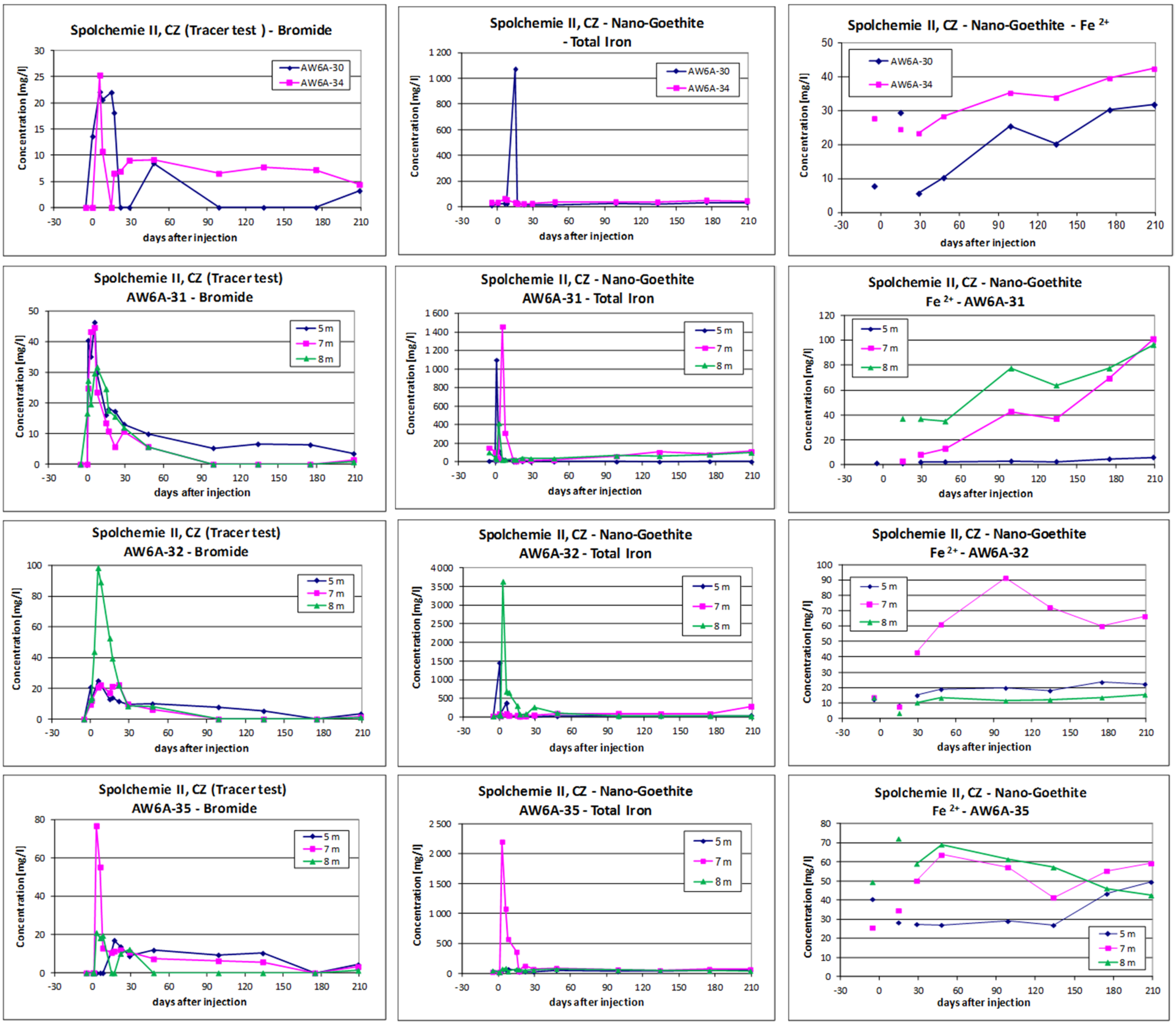

Figure 8. Bromide, total iron and Fe^{2+} concentrations at the Spolchemie II site.

[1] 'Daylighting' is a term used in the direct injection of substances into ground, in which the substance takes a preferential pathway to the surface (instead of being laterally distributed from the point of injection), either directly up through the borehole in which it is being injected (i.e. along the side of the injection rod) or up through an adjacent borehole or well (i.e. it progresses laterally from the injection point then upwards once the injected substance meets the well or borehole).

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The time from injection to the peak concentration of iron content (1450 mg/l) in AW6A-32 (5 m bgl) was only 4.5 hours. The distance between the application probe and this monitoring point was 1 m. It is possible to conclude from this observation that groundwater flow can be induced which moves NPs of Nano-Goethite at least 0.2 m/hour at a pressure of 1-12 bars. This calculation is based on sampling undertaken during the tracer test.

The concentration of bromide ion during pilot tests is not only important for tracing the injected agent, but also an important parameter for estimating dilution effects. Figure 8 shows that the injected suspension with high bromide concentrations was completely replaced after more than 30 days in all monitoring points, except AW6A-34. Around all of the monitoring points a minor amount of injected liquid still remains.

BTEX response post Nano-Geothite injection

Figure 9 shows that concentrations of BTEX in the inflow wells (AW6A-30 and AW6A-32) increased after 15 days and 30 days respectively after an initial decrease following the injection of Nano-Goethite particles to the subsurface. The increase is very likely caused by unsaturated and capillary fringe zone washing after a groundwater level increase during the infiltration. Groundwater levels also increased during winter 2015/2016 and the spring 2016 after a very dry summer 2015 (Figure 10). The higher relative increase of BTEX was monitored in the less contaminated horizons (7 and 8 m bgl). This increase was caused by direct push injection of a high volume of the aqueous Nano-Goethite suspension. The concentration of BTEX in the outflow line (AW6A-35 at 5 m bgl) of the pilot application decreased significantly during the first 90 days after injection. This was followed by an increasing trend from 134 days after application. This fact indicates the ongoing process of microbial degradation of BTEX and a rebound to the original BTEX dissolution from the source area after the mobilisation by the injection.

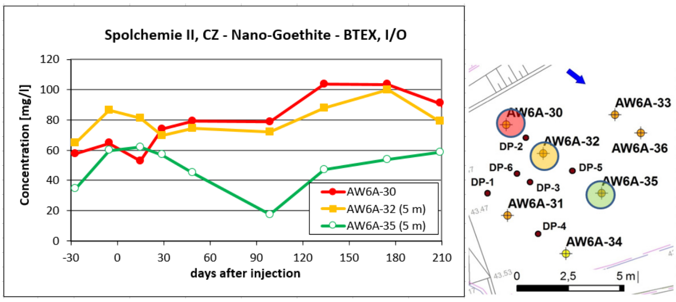

Figure 9. Development of BTEX concentrations after injection of Nano-Goethite on the Spolchemie II site.

Nevertheless, bioremediation is a slow remediation process, especially under anoxic/anaerobic conditions (iron reducing conditions) and the concentrations of contaminants are still very high on the site.

Figure 11 shows the total removal of BTEX in the subsurface created after the Nano-Goethite application. Although the concentrations of BTEX are still very high, even on the wells of outflow line, the difference between the wells in the inflow and outflow areas are evident and the trends are confirmed by long term monitoring.

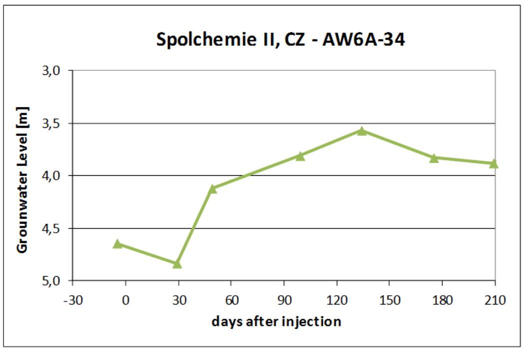

Figure 10. Groundwater level monitoring at the Spolchemie II site.

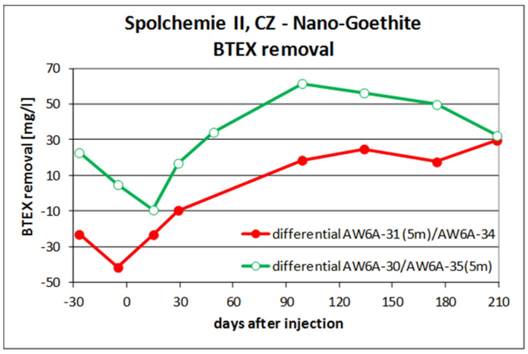

Figure 11. Differntial BTEX concentrations between inflow and outflow wells.

The biodegradation of the BTEX and existing organic matter content is documented also by a clear difference (increase) of Total Inorganic Carbon (TIC) in inflow and outflow areas (between AW6A-30 and AW6A 34 wells), see Figure 12.

The use of Nano-Goethite as an electron acceptor for biodegradation has been confirmed by a clear increase of dissolved Fe^{2+} ions and dissolved carbonate in the groundwater (data not shown).

The differences of BTEX concentration between wells in the inflow area (AW6A 30 and AW6A 32 in the northeast part, AW6A-31 in the southwest part) and outflow line (AW6A-35, AW6A-34) zone of the pilot site are clearly visible not only in the layer with maximum groundwater velocity speed (Figure 11) but also in all of the monitored depths (Figure 12).

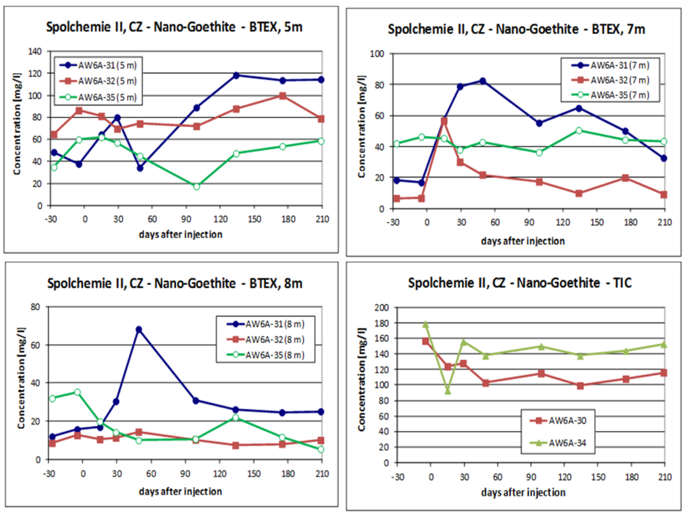

Figure 12. BTEX and Total Inorganic Carbon concentration development at the Spolchemie II site.

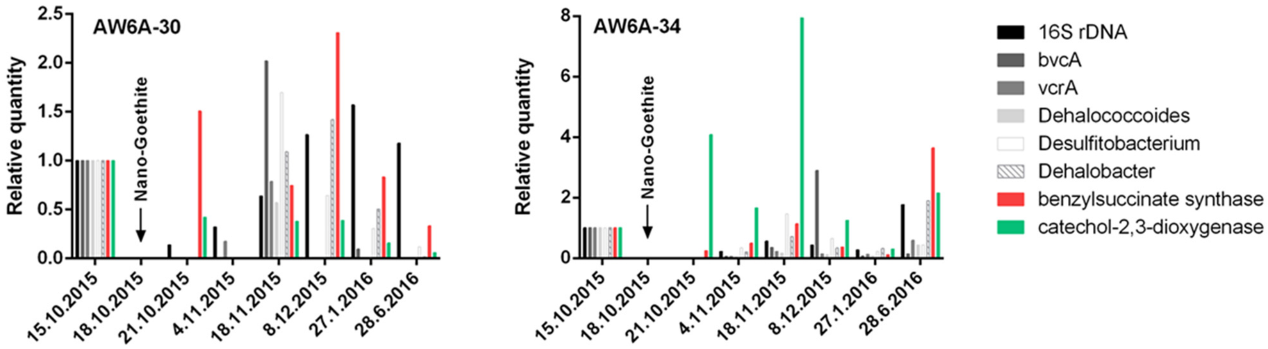

Figure 13. Relative quantification of total bacterial biomass, organohalide-respiring bacteria, vinyl chloride reductase genes and BTEX degrading enzymes in wells AW6A-30 and AW6A-34 before and after Nano-Goethite injection.

Microbial activity monitoring

Water samples taken before and after the Nano-Goethite application were sent to TUL for analysis of indigenous microbial communities. Specifically, samples were obtained from AW6A-30 and AW6A-34 before the Nano-Goethite injection, and 3 days, 2 weeks, 1 month, 2 months, 3 months and 8.5 months after the injection (Figure 13).

Samples were processed and DNA was isolated. qPCR with specific primer sets was performed to monitor changes in the quantity of total bacterial biomass (16S rDNA), enzymes involved in BTEX degradation - benzylsuccinate synthase (anaerobic pathway) and catechol-2,3-dioxygenase (aerobic pathway) and were also analysed for different organohalide-respiring bacteria, and vinyl chloride reductase genes level (vcrA and bvcA), because the chlorinated ethenes are also present in low concentration (units of mg/L) on the site.

The Nano-Goethite application had an immediate inhibitory effect on organohalide-respiring bacteria in well AW6A-30, then all the monitored parameters increased again after 1 month, and slowly decreased until the end of the sampling period (Figure 13). Benzylsuccinate synthase gene levels were slightly affected (increased) by the application and remained rather stable throughout the experiment but the level of the enzyme for the aerobic BTEX degradation pathway, catechol-2,3-dioxygenase, remained low even after 8.5 months after Nano-Goethite injection.

Colonisation of well AW6A-34 developed differently. After Nano-Goethite application, growth of organohalide-respiring bacteria and bacteria with anaerobic BTEX degradation enzyme benzylsuccinate synthase were inhibited, while the level of aerobic catechol-2,3-dioxygenase level increased. This is in agreement with CFU determination – aerobic bacteria were increasing from 1.9×10^3 CFU/ml right after injection to 3.6×10^6 CFU/ml 90 days after injection. All monitored bacterial groups and enzymes were detected 8.5 months after the application.

Thus, it seems that the suspended microbial community in the water phase did not react significantly to the ferric iron injection. The great majority of the microorganisms are attached to the sediment, thus changes in the microbial community composition are not immediately reflected in the water phase.

6. CONCLUSIONS AND LESSONS LEARNED

This pilot study resulted in the successful application of Nano-Goethite to groundwater contaminated with BTEX on the Spolchemie II site. Interpretation of the data collected provides the following conclusions:

- The tracer test results confirmed that the Nano-Goethite suspension was injectable into the sand and gravel aquifer; contact between contaminated groundwater and NPs was proved at each monitoring point.
- BTEX removal was inferred from a decrease in BTEX concentrations between the wells in the inflow and outflow areas and the trends were confirmed by long term monitoring, although the concentrations of BTEX at the outflow are still very high.
- The use of Nano-Goethite as an electron acceptor for biodegradation was confirmed by a clear increase of dissolved Fe^{2+} ions and dissolved carbonate in the groundwater (downgradient).
- Microbiological analyses confirmed that the microbial community in the water phase did not react significantly to the ferric iron injection. Since the majority of the microorganisms are attached to the sediment, changes in the microbial community composition are not immediately reflected in the water phase.
- The use of micro-pumps for groundwater sampling proved very effective and are considered an effective technology providing representative groundwater samples in vertical profile and time. Vertical profiling of groundwater contamination is a must during every *in situ* injection.

For further information on NanoRem please visit www.nanorem.eu

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