

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 pilot study to evaluate the nanoscale zero-valent iron remediation of chlorinated solvents in groundwater.

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NanoRem Pilot Site – Solvay, Switzerland: Nanoscale zero-valent iron remediation of chlorinated solvents

1. INTRODUCTION

This bulletin describes a pilot study of *in situ* nanoscale zero-valent iron (nZVI) remediation. 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 main objective of the test was to demonstrate how nZVI can be used in combination with an existing operational pump-and-treat installation to shorten the time-frame of remediation.

The selection of the test area was based on previous investigations, which identified a secondary source located downgradient of an impermeable underground wall. The target contaminants are perchloroethylene (PCE), trichloroethylene (TCE) and hexachloroethane (HCA); these contaminants are concentrated in the lower part of the aquifer at about 16 m bgl. In the aquifer mainly aerobic conditions prevail.

The area around the site is classified as water protection area A_{II} as defined in the *Swiss Waters Protection Ordinance*. As foreseen by the *Contaminated Sites Ordinance (CSO)* the site is listed in the public cantonal *Register of Polluted Sites*. The CSO states that there is a need for remediation to protect the groundwater if the concentration of contaminants exceeds some specified values. Concentration values applicable for this site are 20 µg/l PCE and 35 µg/l TCE. These values can be considered as the final remediation goal. A concentration value for HCA has yet to be defined.

2. SITE DESCRIPTION

The site, belonging to Solvay, is located in the north of Switzerland. The site is 200 m from the River Rhine and adjacent to the main road K131.

Until 2004 a mercury cell chlor-alkali electrolysis plant was operated at this site. Chlorinated solvents were produced from 1945 to 1976 in a dedicated production unit. The soil and groundwater around this production and storage unit were contaminated by chlorinated products accidentally spilled or by contaminated wastewater leached from the sewer. The main contaminants found are PCE, TCE and HCA. As pure HCA is solid and almost insoluble in water, it is assumed that the contamination with HCA is caused by HCA dissolved in PCE. After closedown of the electrolysis plant the site has turned into an industrial park where the former manufacturing buildings are reused.

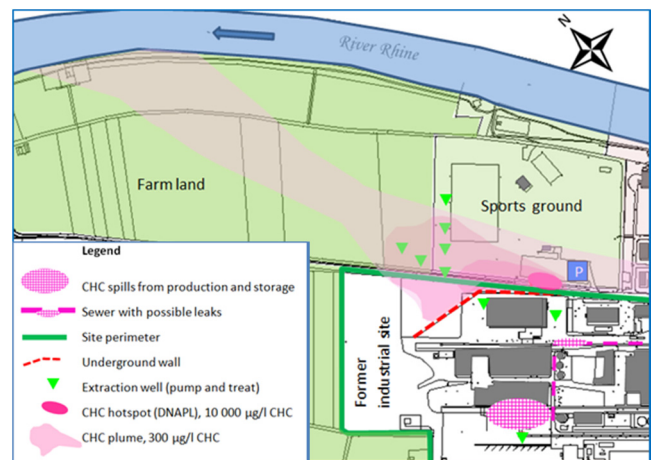


Figure 1. Map showing the localisation of the secondary source and the plume downgradient of the impermeable underground wall. (The plume from the primary source is not shown).

Within the site the groundwater flows to the north-east in the direction of the river. However, just outside the site the groundwater combines with the main body of groundwater flowing north and the plume of contaminants reaches a length of 600 m before entering the Rhine. Next to the site the land affected by the plume is used for parking and leisure activities, further downgradient there are agricultural fields. There are no water catchments and no residential areas affected by the plume.

To prevent the flow of contaminants towards the Rhine a hydraulic barrier was installed in the plume in 2001. Further migration of contaminants from the primary source to the area outside the plant is prevented by an underground impermeable wall which was constructed in 2008.

The test area ground consists of unconfined alluvial sediments of sand and gravel, but stones and boulders are also abundant. The marlstone bedrock (Opalinus Clay) is found at 16.5 m bgl and the average water table at 13 m bgl.

Before selecting nZVI technology for this pilot study alternative remediation technologies were evaluated. Soil vapour extraction and treatment was tested in the vicinity of the primary source where some contamination of the unsaturated soil is expected. However, in the area of the secondary source the contamination is concentrated in the lower part of the aquifer, therefore soil vapour extraction is not suitable.



NanoRem Bulletin

In situ chemical oxidation (ISCO) is an option for the remediation of sites contaminated with TCE and PCE. However, at this site HCA is an important contaminant, and it was estimated that the amenability of HCA to chemical oxidation is poor. *In situ* bioremediation has also been evaluated, but this option was not followed after the failure of preliminary tests.

3. PROJECT MANAGEMENT

3.1 Project Team

Four organisations from the NanoRem research project played a key role in the pilot study:

- Solvay (Schweiz) AG - the site owner, responsible for selecting the pilot test area, for obtaining the necessary permission from the regulator, for establishing the new wells and infrastructure needed. Solvay was also responsible for the monitoring and reporting.
- VEGAS, University of Stuttgart – a research facility, developed and installed the monitoring and sampling equipment used at the pilot site. In addition, some water samples were analysed by VEGAS.
- Aquatest a.s., Czech Republic - the consultant, designed the pilot test and carried out the injection of nZVI into the ground using its own equipment.
- UVR-FIA GmbH, Germany – an engineering company, developed and produced the milled nZVI (called FerMEG12) tested on site.

3.2 Regulatory Approval

According to the Swiss Contaminated Sites Ordinance (CSO) a site is in need of remediation if downgradient the site groundwater concentration of substances exceeds 50% of the concentration values defined by CSO. Thus, there is a need for remediation if the PCE concentration exceeds 20 µg/l or the TCE concentration 35 µg/l. For the Solvay site it was planned to achieve this goal with the combination of the impermeable underground wall along the border of the industrial site and the hydraulic barrier, which is placed 100-150 m downgradient of the source. After 13 years of pumping the annual quantity of TCE and PCE extracted from the plume has declined to 25% of the initial value, but the PCE concentration in particular is still far from the limit of 20 µg/l.

The cantonal authorities are closely following the progress of the remediation at the site and they are supportive of any activity which could shorten the remediation time-frame. After presenting the NanoRem project to them, permission for drilling and installation of the test wells was obtained. Then after their evaluation of the risks and sustainability of the method, permission for the NanoRem test was granted in September 2014.

4. SITE CHARACTERISATION

4.1 Use of Existing Wells

The test area was selected close to where the secondary source was assumed. A hypothesis was drawn up that the contaminants were pooled on top of the bedrock or even had diffused into the underlying marlstone (Opalinuston). The previous monitoring based on sampling with small submersible centrifugal pumps (Eijkelkamp) did not allow a verification of this theory. Thus well logging of existing boreholes close to the selected test area was performed to clarify the regime of groundwater flow in the wells. A strong vertical (upward) flow as well as flow direction were detected. It was also shown that the clay content within the gravel was reduced below the water table.

After the well logging, micropumps were installed at different levels in two existing wells (B139 and B140), and the vertical flow in these wells was prevented by installation of packers. During the following months the monitoring confirmed that the concentration of contaminants

increased with depth. Based on this result, the target for the injection of nZVI was defined as the layer just above the marlstone. Correspondingly the injection wells were only screened over a short interval at the bottom. The arrangement of injection and monitoring wells in the test area is shown in Figure 2.

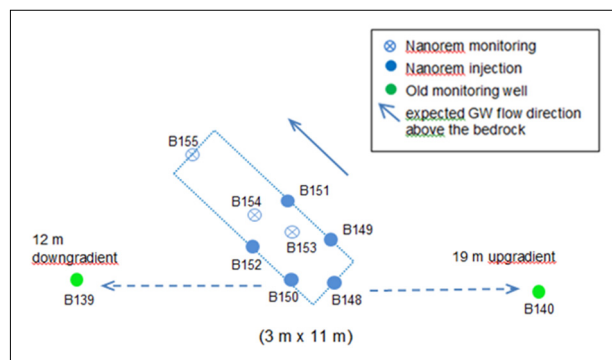


Figure 2. Layout of NanoRem test area relative to existing wells.

4.2 Installation of New Wells

The new injection wells were constructed of 50 mm ID polyvinylchloride (PVC) pipe with a screened interval of 75 cm at the bottom of the aquifer. The screen slot size is 1 mm. The space around the screen was filled with gravel (2/3.2 mm). From the gravel pack and up to the water table the annulus was sealed with Compaction pellets.

The micropumps installed at three pre-defined levels in each monitoring well use compressed nitrogen for the transport of water. The micropumps are constructed in a way to minimize the loss of contaminants by evaporation. The maximal pumping capacity is 2-3 l/h. After installation of the micropumps and iron sensors the protecting pipe was removed and the soil was allowed to collapse around the installed equipment.

Samples collected from the drill cores showed that the contaminants were concentrated in the upper 10 cm of the marlstone and in a thin layer of weathered marlstone between the alluvial sediment and the black marlstone. Whereas up to 20 g/kg of chlorinated hydrocarbon (CHC) was found in this region in B149 to B154, the samples from B148 and B155 were significantly less contaminated. The results are summarised in Table 1.

Table 1. Average concentration of CHC and relative concentration of contaminants found in the upper 10 cm of black marlstone layer and in the thin intermediate layer of weathered marlstone.

Borehole	Average Σ CHC (g/kg)	TCE % relative	PCE % relative	HCA % relative
B148, B155	0.2	17	68	16
B149-B154	12	6	60	34

The aquifer was found to be composed of 60-80% gravel (0.5–5 cm) in silty-sandy matrix intersected by a 1 m thick layer with gravel and stones and little sand (1%). Figure 3 illustrates the position of sampling points/iron sensors in the new monitoring wells and filter screen of the injection wells relative to the different geological layers of the aquifer.

The new injection and monitoring wells were placed between the old monitoring wells B139 and B140. These wells, the further downgradient wells B114, B8, B120 and the pumping well F4 are distributed over a length of 140 m along the main road K131. By comparing the profiles of the new wells with the profiles of the existing wells pronounced variations in the level of the bedrock surface were identified. The bedrock surface appeared to form a groove in the area near the new

NanoRem Bulletin

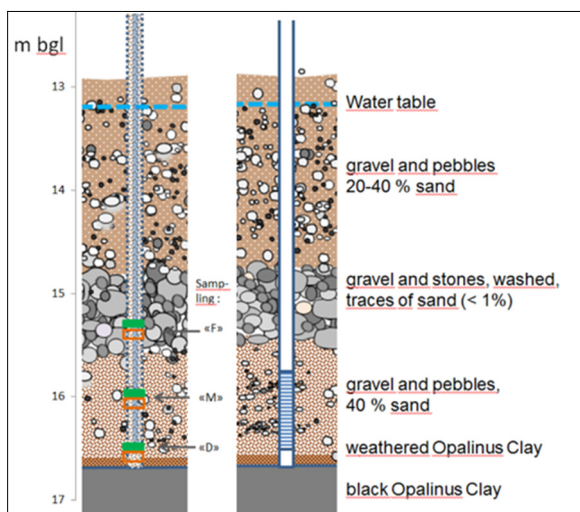


Figure 3. Left: Monitoring “well” with the position of the sampling equipment relative to the different aquifer layer shown. Right: Injection well with screened section.

wells. The existence of a groove can explain the accumulation of contaminants found in the upper layer of the opalinuston and the observation of a free phase in B149. The lower concentration of contaminants found in B148 is in agreement with the latitude of the bedrock head. B155 is situated 5 m downgradient of the injection zone. As only moderate contamination was found in B155, this point is probably situated outside the pool formed near B149 to B154.

4.3 Baseline Monitoring

Groundwater samples were taken by means of the installed micropumps. Dissolved oxygen, pH, ORP and electrical conductivity were measured on site (flow through cell in the sampling line). Samples for head space GC analyses of volatile components and for further parameters were collected directly in vials or in air free glass bottles. After drilling of the new wells in May 2014 baseline monitoring was continued until injection of FerMEG12 took place in March 2015.

5. INJECTION OF NANOPARTICLES

The nZVI used for the test was a suspension of iron (FerMEG12) in monoethylene glycol which was delivered in 15 litre containers and poured into a premixer. In a dosing unit tap water and lithium were added to give final concentrations of 10 g/l iron and 3.2 mg/l lithium. With a high pressure pump and a packer system placed 50 cm above the bottom of the well, the liquid was injected with 5 bar pressure at a rate of 50 l/min. A total of 100 kg iron (in 10 m³ of water) was injected into each well (in the sequence B149, B150, B151, B152 and B148).

During the three days of injection, sampling from the monitoring wells B153-B155 was carried out frequently. There was no evidence of preferential flow paths as lithium was detected at equal concentrations at 0.1 m (level D) and 0.75 m (level M) above the bedrock surface whereas the maximum lithium concentration at 1.5 m (the upper sampling level F) appeared with some delay. In the case of the remote sampling point B155 the lithium concentration in the upper sampling level remained low compared to the lower sampling levels.

In view of the large volume of liquid injected some upward flow was expected. After the injection the decrease in lithium was much faster in the upper sampling level than in the lower levels, reflecting the better permeability in the upper strata. The concentration of total organic carbon (TOC) (from monoethylene glycol) correlated with the lithium concentration.

A travel distance for the FerMEG12 particles of at least 2 m was confirmed as black water was collected from the two monitoring wells closest to the injection zone. At the sampling point B155, which was 5 m further downgradient, lithium was detected but not FerMEG12.

6. MONITORING RESULTS

The results shown in Table 1 for the new boreholes indicate that the boreholes B149-B154 are located in or near the DNAPL source zone, whereas B148 and B155 are at the border of this zone. This means that there are two monitoring wells, B153 and B154, situated within the source zone **and** within the nZVI reactive zone; whereas possibly B155 and B139 are located downgradient of the source zone. However, there is some evidence, that only B139 but not B155 is situated in the plume from the source zone. The monitoring results from B155 are therefore evaluated separately.

6.1 Monitoring of Borehole B155

The baseline concentration of contaminants in groundwater sampled from B155 (shown in Figure 4) was found to be one order of magnitude smaller compared to B139 and two orders of magnitude smaller than the concentrations found in B153 and B154. It is remarkable, that in B155 the concentrations of HCA and PCE are similar whereas the relative concentration of TCE is very low. A possible explanation is that a residual source around B155 has been depleted in PCE and especially in TCE, due to their higher solubility. As PCE dissolves faster than HCA, crystals of HCA might be formed¹. Only the additional dissolution from a solid phase can explain why the concentration of HCA is higher than expected from the solubility of HCA in PCE. At 10 °C the solubility of HCA is 270 g/kg PCE.

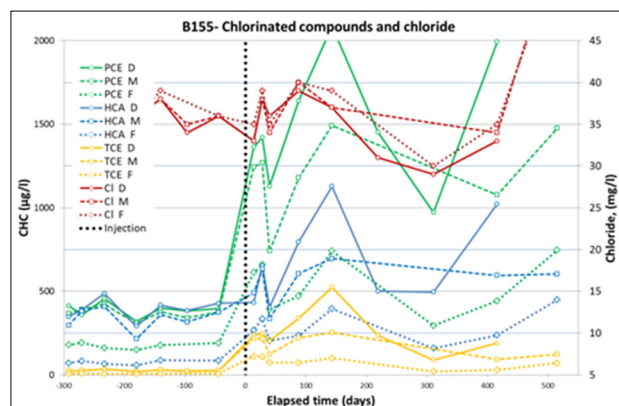


Figure 4. Concentration of chlorinated compounds and chloride in monitoring well B155 outside the nZVI reaction zone. The increase in concentrations after injection is most likely related to displacement of residual phase during injection of the FerMEG12 suspension. [Key: “D” refers to water samples collected 0.1 m above bedrock surface, “M” is 0.75 m and “F” is 1.50 m above “D”].

After the injection of FerMEG12 an increase in the concentration of contaminants was observed in B155. As the lithium-tracer was detected in B155 during injection, the increase is probably caused by flooding of contaminants from the injection zone. The stable concentration of chloride and the lack of other degradation products confirm that this monitoring well is not situated downgradient of the nZVI reaction zone. Ten months after the injection the concentrations have nearly returned to the initial concentration, the mass transport increased by the flooding is neither significant nor permanent. The assumption that B155 is located outside the nZVI radius of influence was also supported by the

¹ This assumption was supported by the observations of white crystals in soil samples, especially in the layer at the bottom of the aquifer referred to as “modified opalinuston”.

NanoRem Bulletin

drop in the concentration of dissolved oxygen and ORP which was observed at all levels of this well but only for a very short period after injection.

6.2 Monitoring of Reactive Zone and Downgradient Plume (B153, B154, B139)

The results of the monitoring before and after the injection of FerMEG12 for HCA, PCE, TCE and chloride for boreholes within and downgradient of the reactive zone are illustrated in Figure 5. Additional monitoring data collected three months after injection are presented in Table 2.

After three months a significant decrease in HCA concentration of 57-99% was found. The best results are obtained in B139 and in the upper level (F) of B153 and B154. The PCE concentration in B153F was reduced by 49% and in B154F by 89% whereas a significant increase was observed all other sampling points. As PCE is the first intermediate in the dechlorination of HCA, the increase in PCE is (at least partially) related to the decline in HCA. For TCE the best results were also obtained in B153F (81% reduction) and in B154F (97% reduction). A TCE increase was only observed in B154D. Glycol is known to have a solubilising effect; this might also have contributed to the increase in the concentrations of PCE and TCE after the injection.

The degradation products cis-DCE and trans-DCE were not detected in B153F and B154F. The highest concentrations were found 2 weeks after injection in B153D (270 µg/l cis-DCE and 130 µg/l trans-DCE). In general, the concentration of cis-DCE was approximately twice the concentration of trans-DCE.

Iron was determined as total iron. In the downgradient well B139 iron was not detected (detection limit 0.05 mg/l) during the first six weeks of monitoring. The appearance of iron in B139 seems to be related to a strong increase in the concentration of ethane, TCE, PCE and chloride, whereas ORP and the concentration of HCA decreased.

Nitrate was completely reduced in B139. This indicates that B139 is situated in the downgradient plume from the nZVI reactive zone.

The TOC concentrations are related to the concentration of monoethylene glycol. The slow decrease of TOC values in the sampling level D of B153 and B154 indicates a slow flow of groundwater at the bottom of the aquifer.

The measurement of dissolved oxygen and ORP indicates the presence of nZVI (or other reducing substances). Hydrogen is formed by the reaction of nZVI with water, thus it is an indicator for the longevity of reactive nZVI. Hydrogen was still detected 3-5 months after injection.

The increase in chloride concentration after injection of FerMEG12 might originate from the degradation of the chlorinated products. However, high chloride concentrations were also observed for a long period after installation of the new wells. In this case it is assumed that the chloride originates from pore water of the marlstone bedrock (opalinuston) as the upper layer of the marlstone was penetrated by drilling the new wells.

Three months after the injection ethane is the final degradation product and only traces of ethene are detected. 1 mg ethane is produced by total dechlorination of 7.8 mg HCA or 5.5 mg PCE. The amount of ethane produced indicates that not only is HCA degraded to PCE, but a considerable amount of PCE or TCE has also been further degraded.

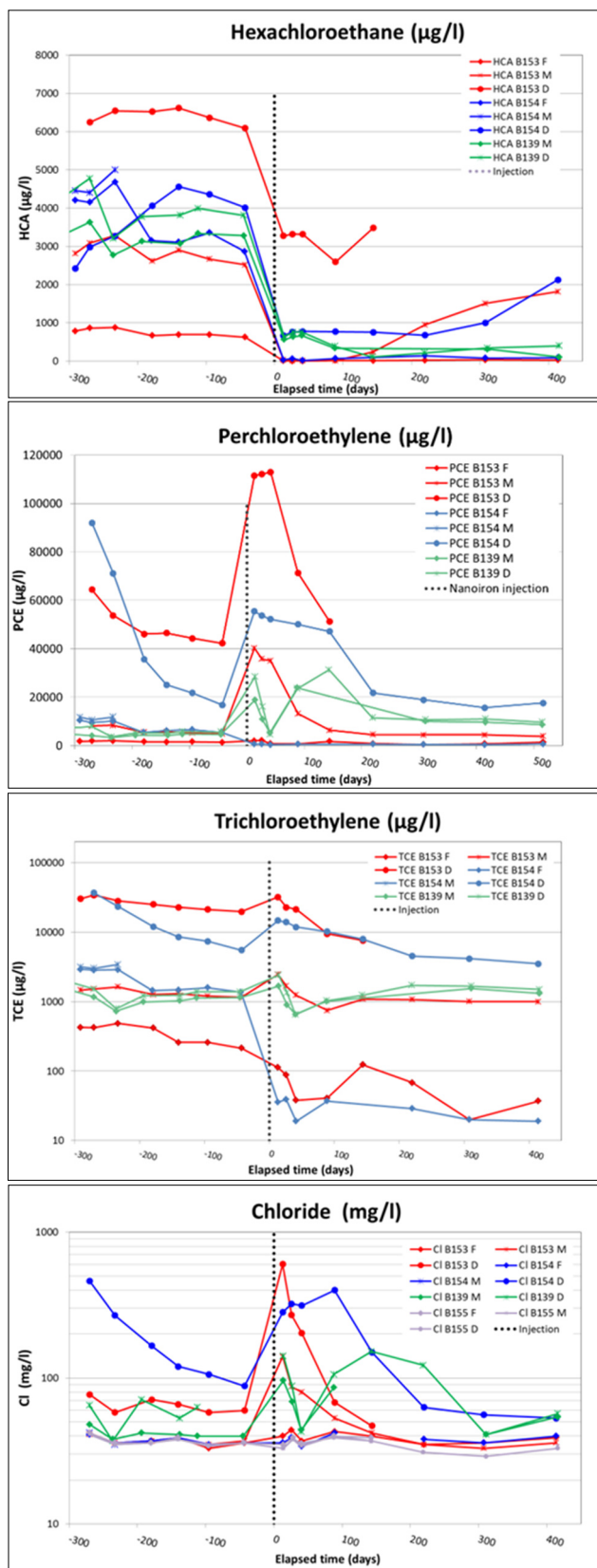


Figure 5. Long term monitoring results from nZVI reactive zone and downgradient plume.

The concentration of TCE in the nearest extraction well F4 is about 1% of the concentration of TCE in B139. If all TCE in F4 comes from the area around B139, then still only 10 % of PCE in F4 can be accounted for. The contribution from the area around B139 to the quantity of contaminants extracted in F4 is therefore not significant.

NanoRem Bulletin

Table 2. Monitoring results before (baseline) and three months after application of FerMEG12.

Parameter	Borehole Depth above bedrock ^a	B153			B154		B139	
		F	M	D	F	D	F	D
HCA	baseline (µg/l)	630	2500	6100	2900	4000	3300	3800
	3 months post inj. (µg/l)	20	14	2600	69	770	340	390
	relative change (%)	-97	-99	-57	-98	-81	-90	-90
PCE	baseline (µg/l)	1400	4800	42000	5500	17000	4600	5700
	3 months post inj. (µg/l)	710	13300	71000	610	50000	24000	23500
	relative change (%)	-49	177	69	-89	194	422	312
TCE	baseline (µg/l)	220	1200	20000	1400	5500	1150	1380
	3 months post inj. (µg/l)	41	750	9500	37	10200	1020	1030
	relative change (%)	-81	-35	-52	-97	85	-11	-25
cis-DCE	3 months post inj. (µg/l)	<5	<5	61	<5	<5	<5	<5
trans-DCE	3 months post inj. (µg/l)	<5	<5	22	<5	<5	<5	<5
Fe (total)	baseline (mg/l)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	3 months post inj. (mg/l)	62	12	7	6.9	2.3	0.44	0.74
SO ₄ ²⁻	baseline (mg/l)	30	29	32	-	-	31	31
	3 months post inj. (mg/l)	-	28	-	-	-	29	-
NO ₃ ⁻	baseline (mg/l)	17	17	17	-	-	17	17
	3 months post inj. (mg/l)	5.8	<0.1	1	-	0.1	<0.1	<0.1
pH	baseline	7.24	7.18	7.16	7.18	7.16	7.15	7.12
	3 months post inj.	7.35	7.42	7.18	7.28	7.40	7.21	7.22
Diss O ₂	baseline (mg/l)	6.12	7.52	6.25	6.5	5.48	6.76	7.2
	3 months post inj. (mg/l)	0.06	0.12	0.4	0.89	0.57	0.88	1.1
ORP	baseline (mV)	232	221	11	333	10	334	-269
	3 months post inj. (mV)	-235	-307	-270	-138	-337	-341	-
TOC	Last day of injection (mg/l)	5040	5250	3540	-	3700	-	-
	3 months post inj. (mg/l)	2.5	2.2	9.0	1.3	360	-	-
H ₂	3 months post inj. (mg/l)	0.02	0.78	0.36	0.69	1.26	<0.1	<0.1
Chloride	baseline (mg/l)	36	37	60	36	88	40	63
	3 months post inj. (mg/l)	43	53	68	42	399	86	106
	10 months post inj. (mg/l)	36	33	(<47)	36	56	41	41
Ethene	3 months post inj. (mg/l)	0.02	0.01	0.01	0.01	0.03	(<0.01)	(<0.01)
Ethane	3 months post inj. (mg/l)	0.43	1.7	1.9	0.37	4.5	3.0	3.1

^a For B153 and B154 "D" refers to water samples collected 0.1 m above bedrock surface, "M" is 0.75 m and "F" is 1.50 m above "D". In B139 "D" is placed 0.5 m above bedrock surface and B139 M is 1.0 m above D.

7. PERFORMANCE EVALUATION

Before installation of the monitoring and injection wells, the pilot site was expected to be situated in the plume from an upgradient secondary source. It was also anticipated that contaminants being slowly released from the underlying marlstone could contribute to the concentration of contaminants in the plume. The evidence of free phase in the lower part of the pilot site aquifer changed the main test scope from plume treatment to source treatment. The pronounced layered soil structure further complicates the interpretation of the test results.

Thus the monitoring wells B153 and B154 are situated in the reactive zone from the injection of nZVI, this reactive zone is also part of the source zone. The sampling point D is placed just above the marlstone bedrock, at this level the soil is composed of weathered marlstone. The permeability of the weathered marlstone is considered to be very low compared to the permeability of the alluvial sediment layer found at the higher sampling levels M and F.

NanoRem Bulletin

After injection of FerMEG12 the observations made at level D and M are comparable (Figure 6). The presence of reactive FerMEG12 reduces ORP and HCA is transformed to PCE by the first dechlorination step. However, the initial increase in the PCE and chloride concentrations is greater than the decrease in HCA concentration; the accumulation of PCE suggests that the initial dechlorination of HCA is faster than the further dechlorination of PCE.

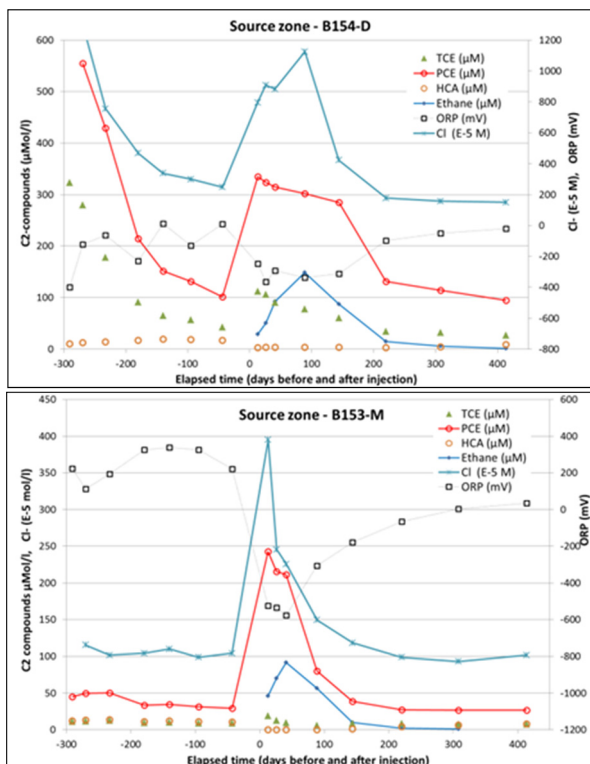


Figure 6. Long term monitoring results from boreholes B154D and B153M.

Approximately 200 days after injection of the FerMEG12 the concentration of chloride has returned to the pre-injection level. This indicates that dechlorination reactions have ceased – at this time the ORP has increased to around -100 mV. The termination of the dechlorination reactions is followed by an increase in the concentration of HCA (B154-D) or of HCA and TCE (B153-M).

The results from the sampling level F differ remarkably from the results at the lower levels M and D. After the injection of FerMEG12 a distinct ORP reduction was observed. However, the increase in the concentration of chloride and PCE was not significant compared to the background concentrations. In this case the elimination of HCA and TCE as well as the relatively high concentration of ethane proves that the dechlorination process takes place. Remarkably, at level F no rebound of HCA and TCE concentrations was observed even one year after the injection (Figure 7). This behaviour can be explained by a nearly complete elimination of the source of contaminants for this layer.

8. CONCLUSION

nZVI as FerMEG12 has been injected directly into a DNAPL secondary source zone where the contaminants are present in pools, as residual phase and more permanently adsorbed into the opalinuston. The remediation goal is to eliminate the plume by treating the source and thus shorten the operating time of the existing pump-and-treat installation.

Three months after the injection the concentration of contaminants at the sampling level F in the injection zone was reduced by 49-89 % for

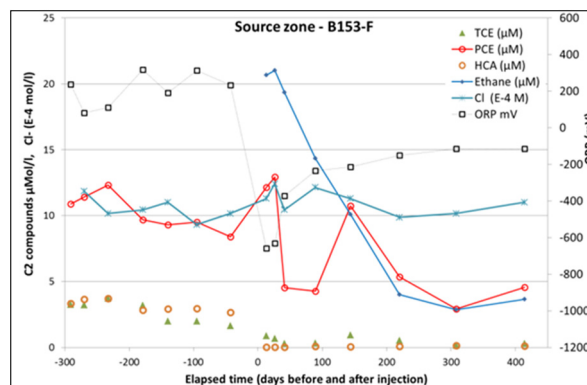


Figure 7. Long term monitoring results from borehole B153F.

PCE, 81-97 % for TCE and 97-98 % for HCA. A slight rebound was not observed until one year after the injection. The results from the sampling level F are considered to be a good measure for the performance of the test. The secondary source is concentrated in the lower part of the aquifer, which is characterised by low hydraulic conductivity and hence a low rate of groundwater flow (sampling level D and M). It is assumed that the main mass transport from the source zone to the downgradient plume takes place after dissolution, desorption and back diffusion into the groundwater flowing in the overlying and more permeable layer around sampling level F.

In the source area oxygen and nitrate have nearly completely been reduced by nZVI. The presence of high concentrations of ethane at the lower sampling levels D and M proves that the reduction of the chlorinated contaminants takes place in parallel. Due to the lack of a mass balance is it difficult to estimate the amount of contaminants eliminated. In addition, the injection of high volumes of FerMEG12 suspension probably caused a (lateral) spread of the source and increased the dissolution of contaminants into the groundwater. The presence of HCA (which degrades through PCE) also makes the interpretation of test results from the lower part of the aquifer difficult.

In the plume the concentrations of oxygen and nitrate are high compared to the concentration of contaminants. Thus the remediation of the plume with nZVI will be costly due to an excess consumption.

Even if the release of contaminants from the source was successfully reduced, this could not yet be verified in the groundwater extraction wells situated 120 m downgradient the source. Due to the age of the secondary source a major proportion of contaminants is probably released from the plume and only a minor part from the source. The effect of reducing the amount of contaminants released from the source will therefore appear with some delay.

The quantity of contaminant found in the test area (mainly in the deepest part) has exceeded what was expected, so to achieve a further elimination of PCE released from the source area as well as a reduction of the total mass of contaminants in the source a second injection of nZVI has been planned.

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

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