

# 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 Carbo-Iron<sup>®</sup> nanoparticles to treat groundwater contaminated with chlorinated hydrocarbons.

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## NanoRem Pilot Site – Balassagyarmat, Hungary: *In Situ* Groundwater Remediation Using Carbo-Iron<sup>®</sup> Nanoparticles

### 1. INTRODUCTION

This bulletin describes a pilot study of *in situ* remediation using Carbo-Iron<sup>®</sup> nanoparticles (NPs) to treat a groundwater plume contaminated with chlorinated hydrocarbons (CHCs). 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.

There were no specific remediation targets for the CHCs at the site. Nevertheless, and in accordance with the NanoRem project, the major objectives of the pilot study involved:

- testing of emerging NP applications at the pilot site;
- optimisation of NPs and tools via feedback from pilot sites;
- application of appropriate injection technologies for varying hydrogeology; and
- alleviating the current lack of validated field scale performance data for end-users and regulators.

Carbo-Iron<sup>®</sup> is an air-stable powder developed at The Helmholtz Centre for Environmental Research - UFZ and commercially available from SciDre GmbH. Carbo-Iron<sup>®</sup> consists of activated carbon colloids which are doped inside with nanoiron structures and can be used to target halogenated organic contaminants or heavy metals in groundwater. The results of previous field applications of Carbo-Iron<sup>®</sup> are summarised in Mackenzie *et al.* (2016).

### 2. SITE DESCRIPTION

The pilot site is located in the outskirts of the city of Balassagyarmat, Hungary. Balassagyarmat has 16,000 inhabitants and is located approximately 80 km (50 miles) north of Budapest (Figure 1, indicated by red star).

Between 1970-1994, the industrial site south of the demonstration area was used for producing electrical components for industry. In

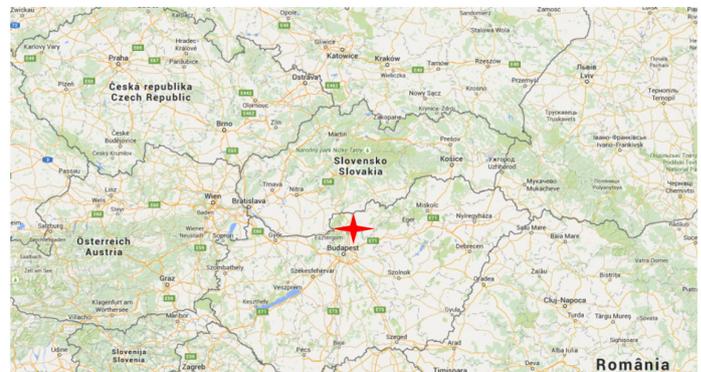


Figure 1. Map showing location of pilot site.

1994, production ceased and the buildings were removed. Currently, the pilot site area is an industrial brownfield, with some remaining foundations and roads. The southern part of the site is mostly abandoned land exhibiting the contaminant source in the groundwater, whereas the northern part of the site is used as a soccer pitch with adjacent residential areas and weekly market activities. The contaminated area is approximately 250 m wide (E-W) and 700 m long (N-S) and the pilot test area was located next to the soccer pitch (see red star in Figure 2).



Figure 2. Photograph showing the contaminated area and location of the Carbo-Iron<sup>®</sup> injection (red star).



Taking **Nanotechnological Remediation Processes** from Lab Scale to End User Applications for the Restoration of a Clean Environment.  
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Preliminary site investigations were undertaken in 2005 to gather subsurface data on the suspected groundwater contamination on site. Detailed information on general site conditions, the site geology, hydrogeology, hydro-/geochemistry, and the local groundwater model were compiled from additional subsurface investigations in 2013.

The site is primarily contaminated with CHCs such as perchloroethylene (PCE), trichloroethylene (TCE) and dichloroethylene (DCE). The contaminated plume is estimated to contain 15 kg CHC (95% PCE), and the volume of contaminated groundwater is estimated to about 190,000 m<sup>3</sup>. The highest contaminant concentrations, between 15-20,000 µg/L CHC, were identified in the sandy gravel layer between 12-13 m below ground level (m bgl).

In 2014, four Continuous Multilevel Tubing (CMT) monitoring wells (CMT1 – CMT4) were installed with three sampling intervals (in general 4.0-5.0 m bgl / 8.2-9.2 m bgl / 13.5-14.5 m bgl) including one at the most contaminated gravel layer above the sandstone bedrock. Another four monitoring wells (CMT5, CMT6, M1 and M2) were installed in 2015 with only one sampling interval at the most contaminated gravel layer. The parameters of the CMT wells were determined according to the geological information and groundwater contamination recovered during the site investigations. The CMT1 – CMT6 wells were deepened using sonic drilling with continuous soil core sampling. Injection was conducted at three different points (I-1, I-2, I-3) at a depth of 13 m bgl using direct push technology and injection probe rods in September 2015 and was followed by seven groundwater monitoring periods until late 2016. The M1 and M2 monitoring wells were deepened using auger drilling rig and were developed with 125 mm PVC casing. A data logger was installed in monitoring well M2 to provide continuous monitoring of the geochemical parameters.

Based on the geochemical parameters measured in the monitoring wells the dissolved oxygen (DO) concentration is low (below 2.0 mg/L), and anaerobic conditions are assumed in the aquifer (ORP < 0 mV).

A Conceptual Site Model (CSM) was devised (Figure 3) which outlines the risks associated with the subsurface contamination transport of CHCs towards different receptors in the pilot site test area. Within the CSM contaminant sources released into subsurface during former industrial usages, pathways and associated risks (migration in aquifer, ingestion of local vegetables and fruit irrigated by contaminated groundwater, inhalation of indoor and outdoor air) were identified and receptors (uncontaminated groundwater, water (irrigation) wells, residents, workers and users of soccer pitch, market workers and users) outlined. However, the usage of the groundwater was prohibited by the Local Municipality in the surrounding properties.

A general sustainability assessment was performed by NanoRem partners addressing social, environmental and economic indicators and initially discussed during a NanoRem workshop in 2015.

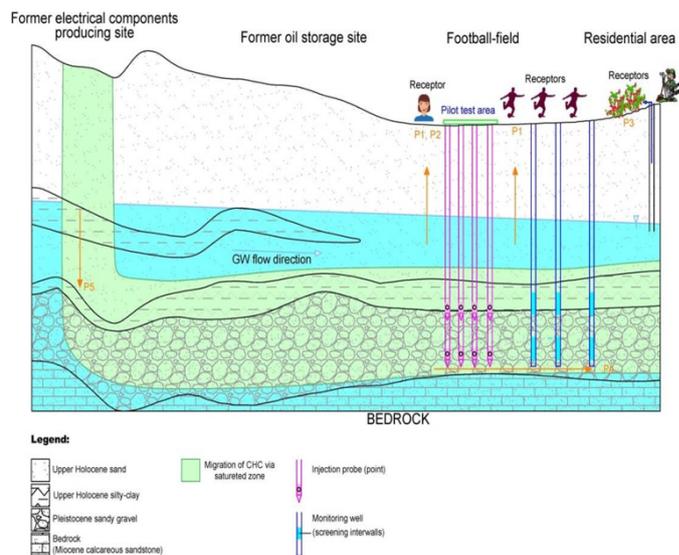


Figure 3. Conceptual site model.

## 3. PROJECT MANAGEMENT

### 3.1 Project Team

Golder Associates GmbH was responsible for the general project management. The selection and preparation of the pilot site, including well installation, Carbo-Iron<sup>®</sup> injection and monitoring was performed by Golder Hungary, with groundwater samples analysed by an accredited laboratory in Hungary (Wessling Laboratory Ltd). Golder had previous comparable field experiences in Germany and Hungary and applied conceptual and hydraulic modelling prior to and after Carbo-Iron<sup>®</sup> injection. Carbo-Iron<sup>®</sup> was supplied by SciDre GmbH from Dresden, Germany.

Project support was gathered from, among others, results of lab-scale testing from associated NanoRem work package (WP) groups (e.g. UFZ Leipzig and VEGAS, University of Stuttgart).

On demand, soil and groundwater samples were also sent to selected project partners before injection and during the post-injection monitoring campaign: Technical University of Denmark (DTU), Norwegian Institute of Bioeconomy Research (NIBIO), Technical University of Liberec (TUL), University of Manchester (UMAN), University of Vienna and UFZ Leipzig.

### 3.2 Regulatory Approval

The historical source and the groundwater contamination is well known in the town. The site (also known as "Köporc") is listed on the OKKP (Országos Környezeti Kármentesítési Program – National Program for Remediation) but no remediation process/obligation has been started yet. An application document including a site investigation plan, description of planned tasks and a chemical characterisation for Carbo-Iron<sup>®</sup> was sent to the regional regulator "Middle - Danube - Valley Environmental, Nature and Water Inspectorate" in 2013 and approved by the competent authority in 2014.

In addition, representatives of the Balassagyarmat Municipality and the facility manager of the sports field gave their permissions to conduct the pilot test at the site.

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## 4. DESIGN, INSTALLATION AND OPERATION

### 4.1 Laboratory Testing

Carbo-Iron<sup>®</sup> needs to be stabilised in a suspension using a specific kind of carboxymethyl cellulose (CMC) defined in the handling instructions of the Carbo-Iron<sup>®</sup> producer. Nevertheless, suspensions using CMC from other distributors were also tested in the laboratory at Golder Budapest. The stability of the suspension to be injected using a Pagani Penetrometer with injection heads (Figure 4) was chosen as the criterion for the CMC selection. In laboratory tests at Golder Budapest, Carbo-Iron<sup>®</sup> and different CMCs were mixed using UFZ/Golder experience from previous field and lab tests to select a feasible, water soluble CMC (molar mass 50,000 – 100,000 g/mol) to be injected together with the Carbo-Iron<sup>®</sup>. Unfortunately transport tests in columns were not conducted with this Carbo-Iron<sup>®</sup> / CMC combination. In future this would be strongly recommended prior to field injections (see section 6, Conclusions and lessons learned).



Figure 4. Injection Penetrometer.

### 4.2 Implementation

The injection of the Carbo-Iron<sup>®</sup> / CMC suspension was conducted on September 15-16, 2015 in three injection points (I-1; I-2; I-3) using injection probes and the selected Penetrometer. Beforehand the suspension was prepared on site in IBC tanks equipped with a disperser pump. CMC and Carbo-Iron<sup>®</sup> mixed with oxygen-free (tap) water was pumped from the tank to the injection rod using a hydrosleeve pump (Figure 5). The suspension was injected at 13 m bgl at each injection point with specific bar pressure and flow and analysis according to the parameters listed in Table 1.

Groundwater sampling at the monitoring events (-5 to 360 days) was conducted at the CMT1/2, CMT1/3, CMT2/2, CMT2/3, CMT 3/2, CMT 3/3, CMT4/2, CMT4/3, CMT5, CMT6, M1, M3, 14/04 wells upgradient and downgradient of the injection area with the intention to verify contaminant mitigation due to Carbo-Iron<sup>®</sup> injection into the aquifer. Groundwater analysis focused on the parameters listed in Table 2.

Table 1. Injection parameters.

Parameter	Dimension
Amount of Carbo-Iron <sup>®</sup>	176.8 kg
Amount of CMC	21.2 kg
Amount of oxygen-free tap water	12.35 m <sup>3</sup>
Carbo-Iron <sup>®</sup> concentration	~10-15 g/L
CMC concentration	~1.5 g/L
Injection pressure	0.5-5 bar
Injection flow rate	20-30 l/min
Injection depth at each injection point	13 m bgl
Soil porosity	30%



Figure 5. Equipment to prepare Carbo-Iron<sup>®</sup> suspension (prior to mixing).

Table 2. Analytical parameters for laboratory and field sample (significant indicators are highlighted in bold).

Groundwater Analysis	Components
Laboratory analysis:	pH, Conductivity 25°C, Permanganate index, p-alkalinity, m-alkalinity, Hydrogen carbonate, Carbonate, Hydroxide, Fluoride, <b>Chloride</b> , Bromide, Nitrate, Sulphate, Orthophosphate, Nitrite, Ammonium, <b>Iron</b> , Manganese, Sodium, Potassium, Calcium, Magnesium, Total hardness.
Laboratory analysis:	1,1-Dichloroethylene, <b>cis-Dichloroethylene (cis-DCE)</b> , trans-Dichloroethylene, Dichloromethane, 1,1,2-Trichlorotrifluoroethane (Freon 113), 1,1-Dichloroethane, 1,2-Dichloroethane, Trichloromethane (Chloroform), 2-Chloroethanol, 1,2-Dichloropropane, 2,3-Dichloropropene, Bromodichloromethane, <b>Trichloroethylene (TCE)</b> , Epichlorohydrin, 2-Chloroethyl vinyl ether, cis-1,3-Dichloropropene, trans-1,3-Dichloropropene, 1,1,2-Trichloroethane, Dibromochloromethane, 1,2-Dibromoethane, <b>Tetrachloroethylene (PCE)</b> , 1,1,2,2-Tetrachloroethane, <b>Sum of CHC (23)</b> , Vinyl chloride, Hexachlorobutadiene, <b>Ethane</b> , <b>Ethylene</b> .
Field analysis:	Groundwater level, Temperature, <b>pH</b> , <b>Dissolved Oxygen</b> , <b>Redox Potential</b> , <b>Electrical Conductivity</b> (continuously in data loggers M1, M2 and 14/04, periodically in all other wells).

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## 5. RESULTS AND DISCUSSION

Golder carried out scheduled groundwater sampling campaigns related to the injection at the site (-5, 0, 7, 36, 85, 160, 360, 540 days; Chemical parameters: CHC, BTEX, TPH, ethane, ethene, chloride, Fe). Three sensors were installed in the 14/04, M1, M2 monitoring wells which provided continuous groundwater data from the site (EC, temperature, groundwater level). Nine CMT and two common monitoring wells (M1, M2) were installed. The groundwater samples were analysed by an accredited Hungarian laboratory. Monitoring was performed in all relevant aquifer layers.

Based on the results gained until January 2016 Golder decided to install an additional three monitoring wells (CMT7, CMT8, CMT9) very close to the injection points to get more information about the migration of Carbo-Iron®. The layout of monitoring wells and injection points is shown in Figure 6. Monitoring well parameters are summarised in Table 3.

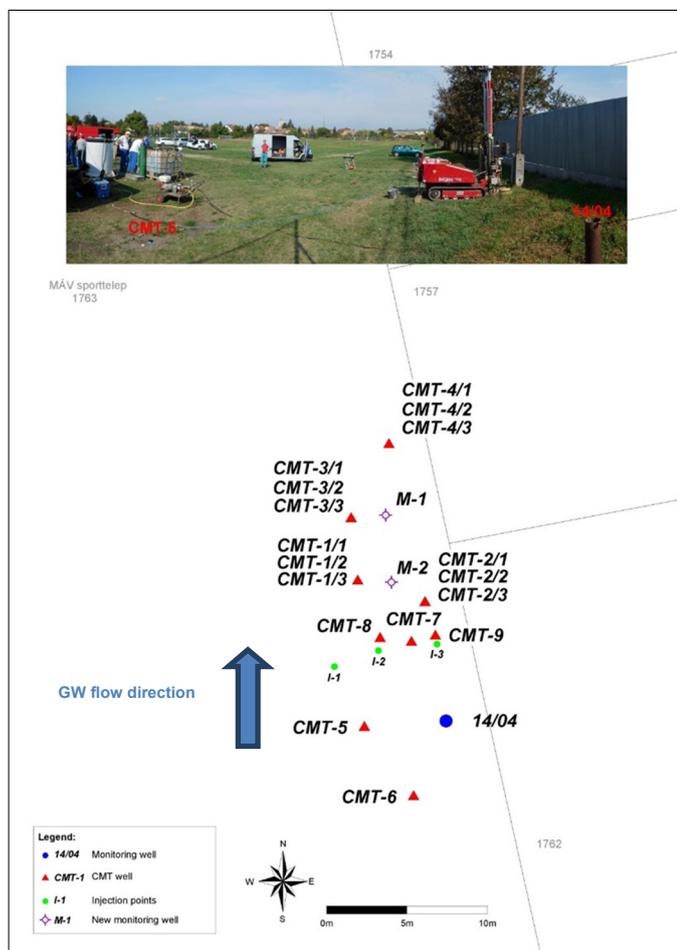


Figure 6. Location of injection points, monitoring wells and data loggers at the pilot site.

In addition to the groundwater sampling there was an opportunity to take soil samples during the installation of the new wells, when continuous core sampling was performed (23/02/2016). Based on the on-site observation and the laboratory results only a limited migration of Carbo-Iron® particles could be detected at the site. At CMT-9 drilling point, at the depth from 12.8 m bgl to 13.7 m bgl, an indication of the presence of Carbo-Iron® particles was observed only 0.5 m from the I-3 injection point (Figure 7).

Table 3. Monitoring well parameters.

Well ID	Diameter (mm)	Depth (m bgl)	Screened interval (m)
CMT-1/1 CMT-1/2 CMT-1/3	CMT wells with ID 9.5 mm at each	15.5	4.0 – 5.0 8.2 – 9.2 13.4 – 14.4
CMT-2/1 CMT-2/2 CMT-2/3	CMT wells with ID 9.5 mm at each	16.8	4.0 – 5.0 8.6 – 9.6 13.4 – 14.4
CMT-3/1 CMT-3/2 CMT-3/3	CMT wells with ID 9.5 mm at each	15.0	4.0 – 5.0 8.2 – 9.2 13.6 – 14.6
CMT-4/1 CMT-4/2 CMT-4/3	CMT wells with ID 9.5 mm at each	16.1	4.0 – 5.0 8.4 – 9.4 13.5 – 14.5
CMT-5	ID 18 mm	15.0	13.5 – 14.5
CMT-6	ID 18 mm	15.0	13.5 – 14.5
CMT-7	ID 18 mm	15.0	13.5 – 14.5
CMT-8	ID 18 mm	15.0	13.5 – 14.5
CMT-9	ID 18 mm	15.0	13.5 – 14.5
M1	ID 120 mm	15.0	13.5 – 14.5
M2	ID 120 mm	15.0	13.5 – 14.5
14/04	ID 110 mm	15.6	10.9 – 15.6

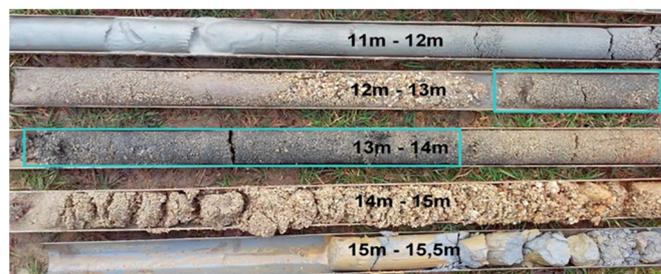


Figure 7. Soil samples from CMT-9 well.

According to the results the dispersion of the CHC contaminants was identified along the cross-section between CMT-6 (upgradient) and CMT-4 (downgradient). It is likely that the injected particle suspension is migrating from the injection points (I-1, I-2, I-3) to the direction of monitoring well CMT-4.

Figure 8 shows the concentration of CHCs in four monitoring wells (three downgradient of injection points CMT-2, CMT-4 and M-2, and one upgradient CMT-5). The decrease in concentration of CHCs were detected after the injection downgradient, along the migration pathway. The most significant effect of the above mentioned degradation was detected in the lowest screened section of monitoring well CMT-2(CMT-2/3). A significant reduction of PCE and enhanced microbiological degradation/chemical reduction in the monitoring wells closest to the injection points was detected but ethene and ethane concentrations, as indicators for CHC abiotic reduction were only detected in low concentrations right after the injection (22/09/2015, 21/10/2015, data not shown). In addition, a small increase of TCE, cDCE and VC concentration was detected compared to the change detected in PCE concentration (Figure 8).

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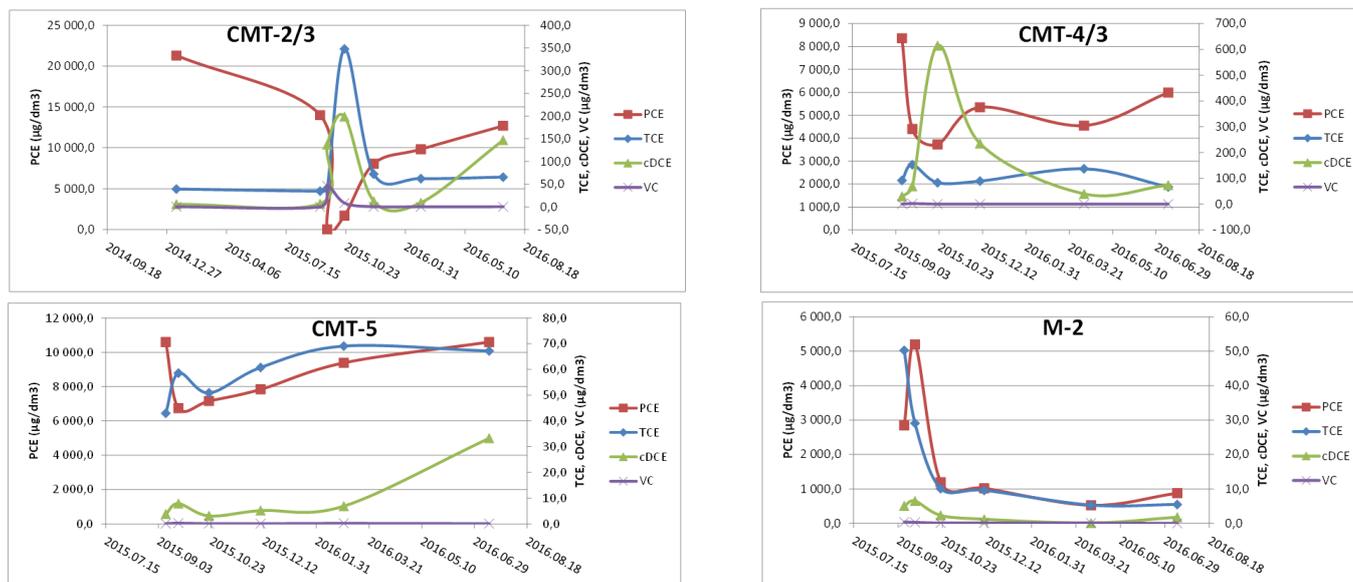


Figure 8. CHCs concentration in four monitoring wells. Injection date was 15/09/2015.

There could be several explanations of the different effects on the contaminant concentrations that were detected according to the distance from the injection points.

According to the analytical results it is likely that there are preferential migration pathways in the aquifer and due to the overpressure that was used for injection Carbo-Iron® migrated through these routes.

The high pressure (generally 5 bar overpressure was measured at the pump) could indicate pore blockages during injection. Moreover the injection of a Carbo-Iron® suspension into columns packed with site sediment and saturated with site water under similar conditions as used on site confirmed a reduced spreading of particles. This may be attributed to a fine grain content higher than expected from field investigations and to partially insoluble CMC, which in hindsight could explain the unexpected migration behaviour.

It is very likely that portions of Carbo-Iron® bypassed the target zone (due to the preferential pathways or to the blockage) and thus did not participate in the contaminant reduction. This has been also concluded from the non-representative degradation and sorption effects on the aquifer contaminants.

A rebound effect was detected in the closest well to the injection (CMT-2) and also in the CMT-4 well, but the concentration of the contaminants was well below the concentration detected before the injection. The presence of cDCE could be either attributed to intermediate formation in the abiotic degradation pathway or indicates microbial activity beyond the sphere of action in the periphery area represented by CMT-4. The effect of the injection was also detected in the upgradient monitoring well CMT-5 but the results of the long term monitoring might be determined mostly by the natural fluctuation of the contamination and the geochemical parameters of the groundwater upgradient. CMT-5 is located upgradient, between the source (the former plant, Köporc) and the pilot site.

Figure 8 displays a significant decrease in the PCE concentration in monitoring well M-2, located only 4 m from the closest injection point and no TCE, cDCE products nor rebound effect was detected. The PCE concentration stabilised around 1 mg/L.

No significant daughter products (TCE, cDCE) were detected in the well CMT-5 (compared to the concentration of the primary contaminant (PCE)); the immediate decrease of the concentrations after the injection can be attributed to dilution due to the injected volume. All the 13 injection events that were carried out in 2 days (September 2015) were registered by the data loggers installed both in M-1 (downgradient) and 14/04 (upgradient) monitoring wells (Figure 9).

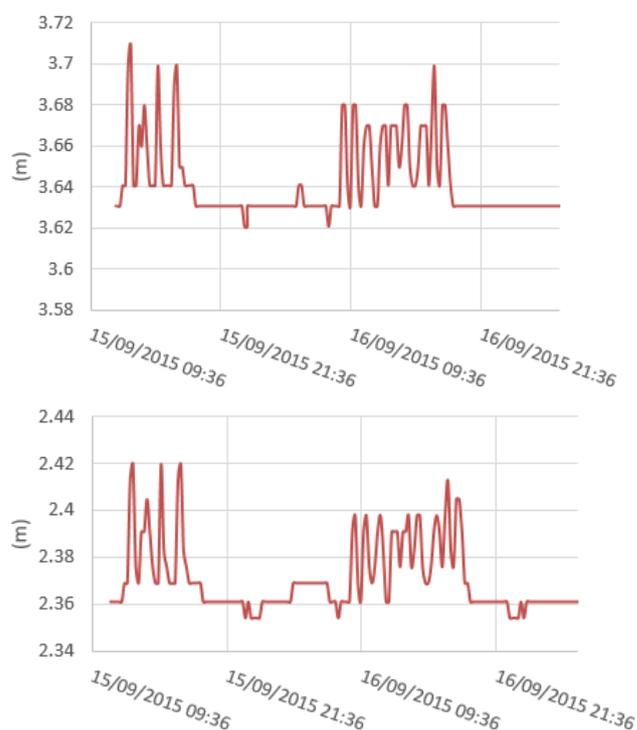


Figure 9. Groundwater level at 14/04 (top) and M-1 (bottom) monitoring wells during the injection (15/09/2016-16/09/2016).

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During the injection and right after the injection a significant decrease of the ORP and an increase of the total dissolved iron was measured only in the closest wells (CMT-2, Figure 10). This confirms the observation during the injection and the continuous core sampling in February 2016 that the Radius of Influence (ROI) and the direct effect of the injection was very limited.

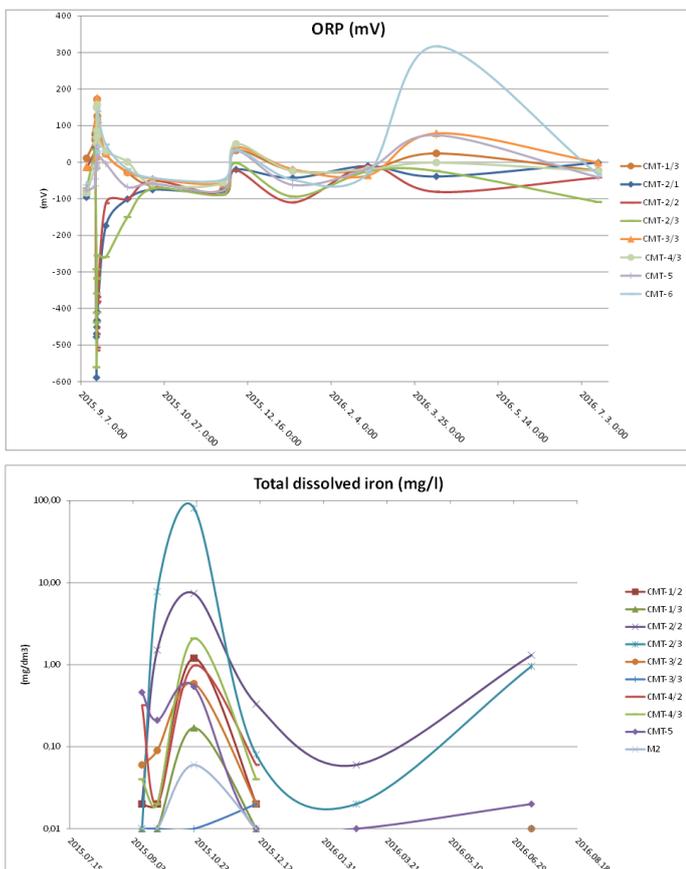


Figure 10. ORP and dissolved iron measurements in CMT-2.

## 6. CONCLUSIONS AND LESSONS LEARNED

A significant decrease of the primary contaminant (PCE) was detected in the monitoring wells closest to the injection points. The ROI was limited and traces of the injected Carbo-Iron® were observed only in very close proximity to the injection points.

According to the on-site measurements and the laboratory analyses it was presumed that Carbo-Iron® migration could be very significant right after the injection. The aquifer porosity ( $n_{eff} \sim 0.3$ ) and the low sorption potential of the gravelly layers could bring about the fast transport (advection/dispersion) of injected materials.

Due to the heterogeneity of the aquifer and the pressure needed for the injection it is very likely that the reactive barrier could not be formed in its designed extension. Particle transport in an aquifer which might be at the injection area more heterogeneous than

previously determined was found to be insufficient. Rather particles remained close by the place of injection and/or presumably migrated in preferential flow paths bypassing the target zone, thus hindering an effective retardation and degradation of the contaminants.

A lesson learned is that the stabiliser needs to be chosen very carefully, especially according to the site specific conditions (soil mechanical parameters, TOC, heterogeneity etc.). If replacing the stabiliser suggested by the producer it has to be ensured that the material is fully soluble and fits with the geological and hydrogeological conditions of the injected layers. It is highly recommended to conduct detailed laboratory tests (e.g. column tests with NPs plus CMC and different aquifer materials) before pilot testing. This is a necessary requirement to create a permeable reactive zone and utilise the full potential of Carbo-Iron® with respect to sorption and abiotic CHC degradation.

Modelling is also recommended. Migration of the injected materials can be predicted by measuring the on-site parameters and chemicals and it is recommended to build a hydraulic and transport model prior to the injection and make calculations regarding to the potential pathways during the injection. The model should be validated by on-site measurements, particle tracking (e.g. using some tracers according to the site specific parameters and the injected solvents) that could help to design the parameters (injection depth, injecting amount, overpressure, monitoring network etc.) during and after the injection.

The on-site activities (dispersing Carbo-Iron® and adding CMC) before the injection needed careful preparation and made the process quite slow at the site. In future, site preparation could be enhanced by using on-site equipment to disperse the materials to be injected (e.g. built in containers, dispersers, mills etc.) as used at a field site in Lower Saxony, Germany (Mackenzie *et al.*, 2016).

## REFERENCE

- Mackenzie K., Bleyl S., Kopinke F-D., Doose H., Bruns J. 2016. Carbo-Iron as improvement of the nanoiron technology: From laboratory design to the field test. Science of the Total Environment. Vols. 563–564, Pages 641–648

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