

Remediation of CHC by Reductive Dechlorination in Germany: A Full-Scale Approach

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ABSTRACT: A high permeable sandy gravelly aquifer at an industrial site in northern Germany was contaminated with a complex mixture of petroleum hydrocarbons and chlorinated solvents. The total concentrations prior to remedial activities reached 30,000 µg/l. At a first stage of groundwater remediation, enhanced reductive dechlorination was chosen as the main remedial strategy. As electron donor HRC[®] of Regenesis was selected. The monitoring data show, that within the plume the reductive dechlorination was effective and capable to reduce the CHC concentrations sufficient to prevent further migration downgradient. Within a reaction zone of approximately 15 m a CHC degradation of one order of magnitude was observed. However, in the source area the high amount of sorbed or free phase product replenished the contaminants, which were removed by in situ biodegradation, from the source material. To reduce the time of remediation activities a source area excavation was realized 10 month after HRC[®] injection and additional e⁻ donor material was introduced. The ongoing monitoring data show that the dechlorination of the CHC's progresses and leads to an efficient mass removal of contaminant remains in the core area as well as downgradient in the plume.

INTRODUCTION

A high permeable sandy gravelly aquifer at an industrial site in northern Germany was contaminated with chlorinated hydrocarbons (CHC) such as Perchloroethene (PCE), 1,1,1 Trichloroethane (TCA), Trichloroethene (TCE) and cis-Dichloroethene (cDCE). The source of the groundwater contamination was a complex mixture of petroleum hydrocarbons (PHC) and CHC, situated under an occupied maintenance shop of a production plant for drilling tools. The size of the oil-saturated core area was approximately 20 m in diameter and reached down to 5 m in depth. The CHC plume, released from this source area, extends more than 1,000 m in length and reaches a residential area approximately 80 m downgradient of the source area.

The impacted aquifer has a heterogeneous permeability of in average 5×10^{-4} m/s. The dissolved-phase CHC-contamination was concentrated in the upper 10 m of the aquifer, where total CHC concentrations prior to remedial activities reached 30,000 µg/l. It was possible to separate two hydrogeological units with differential flow patterns within the contaminated section of the aquifer. These separation was based on petrography and hydraulic conductivity. The upper part consists of medium to fine grained sand and has a lower permeability than the lower part, which is dominated by coarse grained sand with intercalations of gravelly, sandy layers and channels. This layers and channels lead to preferential flow paths within the lower unit. The groundwater table is in average 1.5 - 2 m below ground surface (bgs). Depending of the aquifer depth, different patterns of reductive degradation were found. Degradation ranged from a high

amount of cDCE in the upper part to nearly 100% of PCE in the lower part of the impacted aquifer.

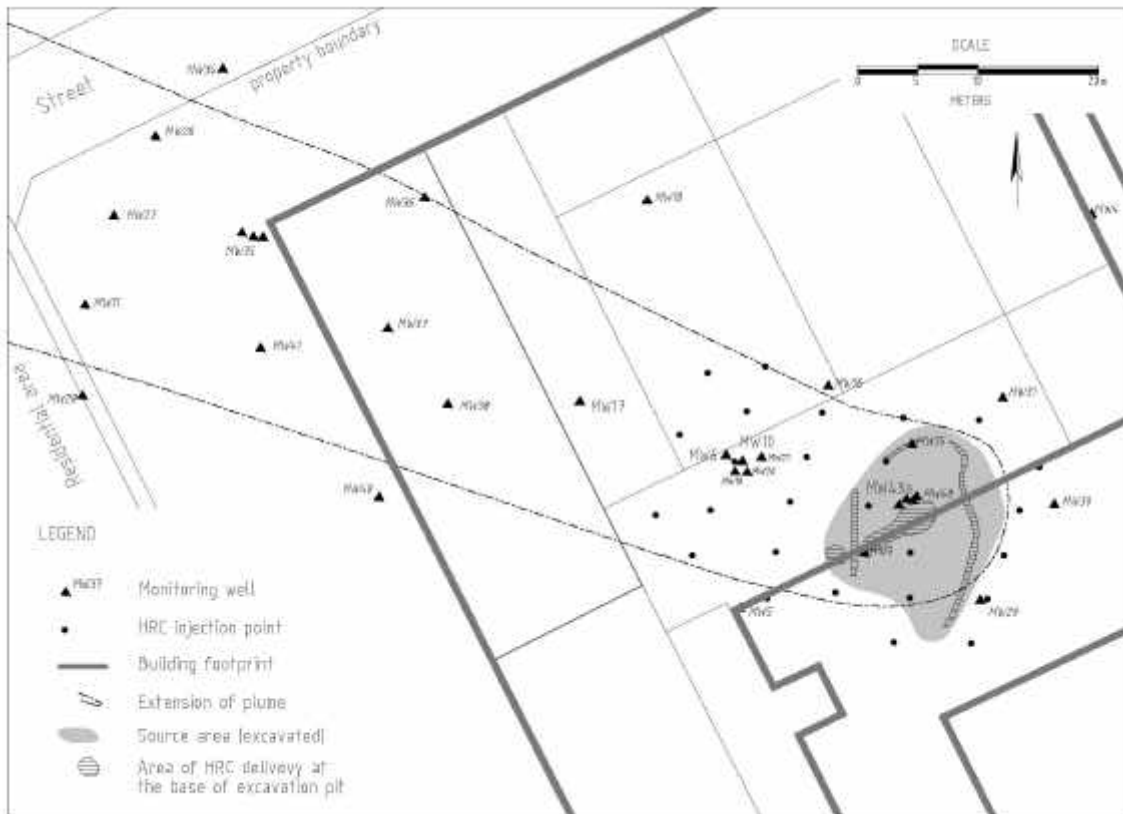


FIGURE 1. Site Map showing the extend of the Groundwater Plume and the Core Area of Soil and Groundwater Contamination prior to Remediation Activities

At a first stage of groundwater containment and remediation, enhanced reductive dechlorination through injection of electron donor material was chosen as the main remedial strategy for the plume directly downgradient of the source area, including the source area itself. At a second stage an excavation of the contaminated soil inside the source area was scheduled to shorten the time of remediation activities and to prevent further solution of CHC's from the oil-contaminated soil. Depending on the working activities inside the shop, the excavation could not get started until 9 month after electron donor injection. The open pit was used for additional supply of electron donor material into the subsoil during the backfill activities.

MATERIALS AND METHODS

Electron Donor Material. HRC[®] of Regenesis was chosen as electron donor material. HRC[®] is a polyacetate ester, designed to provide a carbon energy source and to create anaerobic, reducing conditions in groundwater to stimulate reductive dechlorination of CHC such as PCE and TCE. Introduced in the saturated zone, HRC[®] releases lactic acid. The lactic acid and its metabolites acitic, butyric, propionic and pyruvic acid ferment

over time, which causes a time-release of hydrogen at moderate concentration levels. The calculated amount of the injected material was based on contaminant concentrations, electron acceptor concentrations such as sulfate, iron reduction potential and nitrate as well as hydrogeological data obtained from former investigation activities.

Electron Donor Injection. The initial injection event was conducted in June and July 2001. A bottom-up injection with hollow direct push rods was chosen as the standard method to deliver the material into the subsurface. The rods were pushed or driven by percussion, using a track mounted all terrain drilling and sounding rig with a hydraulic power source. To avoid high pressures at the outlet of the injection rods, a bigger than normal diameter of the injection rods was used. The injection pressure was controlled by a control-unit at the pump and adjusted as low as possible to prevent preferential flow path of the injected material by fracturing of the surrounding soil. At the end of the rods an expandable injection probe with lateral borings and a sealing below was used. By this method the material was delivered into the aquifer material by pressure as low as required. The injection points were arranged in a grid-like pattern, consisting of 5 rows, throughout the core area of groundwater contamination and the area directly downstream. The spacing between the points in each row was 4 m and the spacing between the rows was 6 m. In total 25 injections were performed. The depth of injection reached from 2 m bgs to 10 m bgs. During a period of 5 days a total amount of 3,000 kg of HRC[®] was injected.

Excavation and HRC[®] Application. In May 2002 a restructuring of work processes inside the occupied building above the treated source area lead to the opportunity to excavate the oil-contaminated soil, which in turn released the mass of the CHC's. The high groundwater table of up to 1.5 m bgs and the depths of the contaminated soil made it necessary to temporarily lowering the groundwater by pumping and treatment activities. After the soil-excavation additional 500 kg of HRC[®] was delivered into the bottom of the open pit, by pouring the material into trenches and by mixing it with the backfilled sandy soil. In the central area of the source zone the contamination extended to a depth below 4.5 m bgs and could therefore not be excavated. This area was treated with a special amount of HRC[®].

Monitoring. The site monitoring started concurrently with the initial injection event, included monthly sampling of various monitoring wells. Later the sampling was extended to bimonthly intervals. Monitoring parameters used for this site included: CHC concentrations; HRC[®] component concentrations (metabolic acids); potential electron acceptors (sulfate, nitrate, iron); dissolved organic carbon (DOC); endpoint gases (methane, ethane, ethene); field parameters (DO, Eh, pH).

RESULTS AND DISCUSSION

Source Area Results. In the area of core contamination the monitoring of data from wells screened within the shallow zone of the aquifer did not show any clear evidence of a rapid enhancement of dechlorination processes throughout a period of 9 month after HRC[®] injection. From the beginning the CHC molar-ratios in this area showed a high

percentage of cDCE (up to 90 %) with no trend in total concentrations. The sulfate concentrations were found at high levels between 60 mg/l and 100 mg/l. Dissolved iron concentrations were low with maximum values of 20 mg/l. A low amount of organic acids was monitored and the aquifer seemed not to be in favorable conditions for effective reductive dechlorination. This was interpreted as the result of competing electron acceptors flowing into the system and into the HRC[®] application zone from areas upgradient of the contamination site. In addition the residence time of VOC's within the HRC[®] reaction zones could have also been of influence.

The special features of the source zone can give a further explanation of these observations. In this area an assumed amount of 6,000 kg PHC's were present before the core area was excavated. It is assumed that the CHC's were entrained within the free phase PHC. This could have created an on-going CHC-concentration issue allowing to maintain relatively high CHC's over an extended period of time. In a mixture of chemical components like here, it is virtually always expected to find a halo of dissolved components around the sorbed or phase liquids and there has to be a concentration gradient from the high concentration surface to essentially zero concentration at some distance away. Somewhere within this concentration range or halo is a concentration present, which is favorable for microbial growth wherein the indigenous population of microbes can utilize the substrate which leads to biodegradation of the CHC's. However, if sorbed or free phase product is still available in the subsurface as a source material, the contaminants removed by in situ biodegradation will be replenished from the source material. The system is simply trying to maintain equilibrium between phase and dissolved contaminants and the ongoing dechlorination process can not be proven by monitoring data. The enhancement of the dechlorination process was better recognizable in the aquifer beneath and directly downgradient of the PHC-contamination. The data collected from monitoring well (MW) 43a, located directly beneath the core contamination and screened in a depth from 5 to 7 m, show clearly the shifting of the aquifer into appropriately reducing conditions (sulfate reducing to methanogenic).

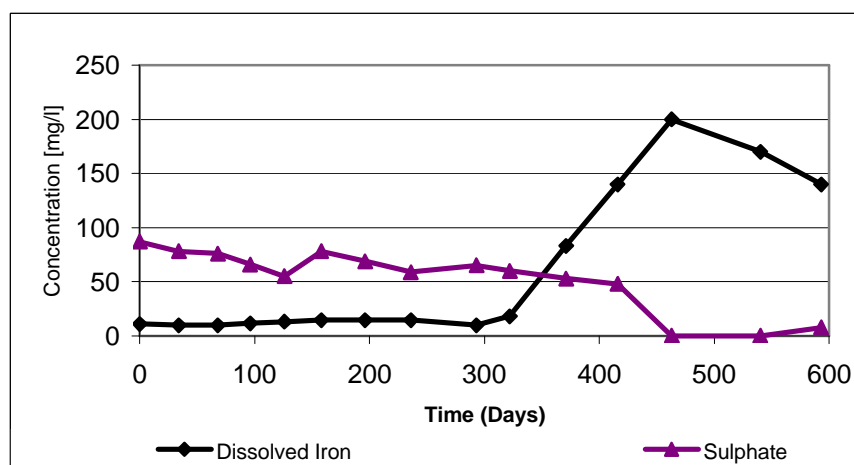


FIGURE 2. Changes in e^- acceptor concentrations in MW 43a

This is evidenced by the steady decline of sulfate in this well over time (refer to figure 2). This process was forced by the removal of the source material (day 300) compared with additional HRC[®] delivery. Immediately after the excavation activities a high increase of dissolved iron and a decline of sulfate to non-detectable levels was observed.

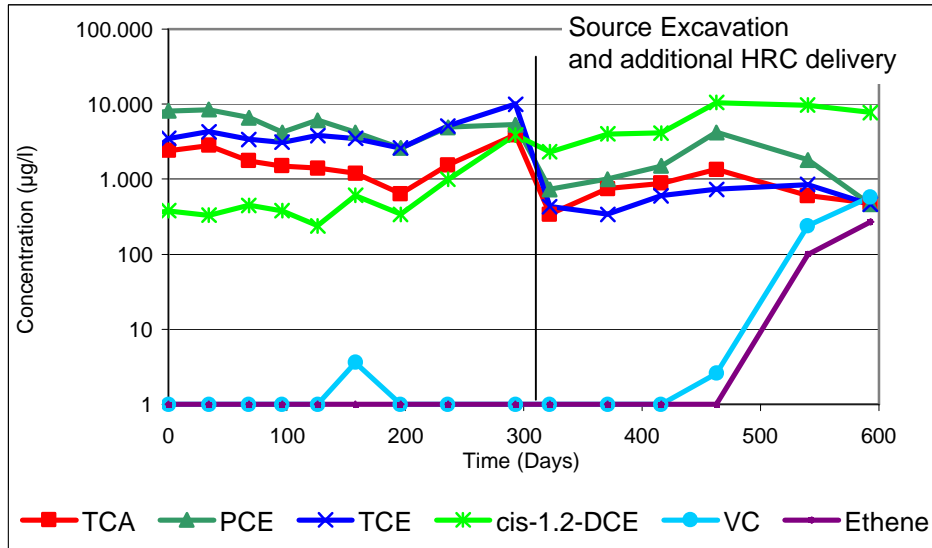


FIGURE 3. CHC concentration trends in MW 43a

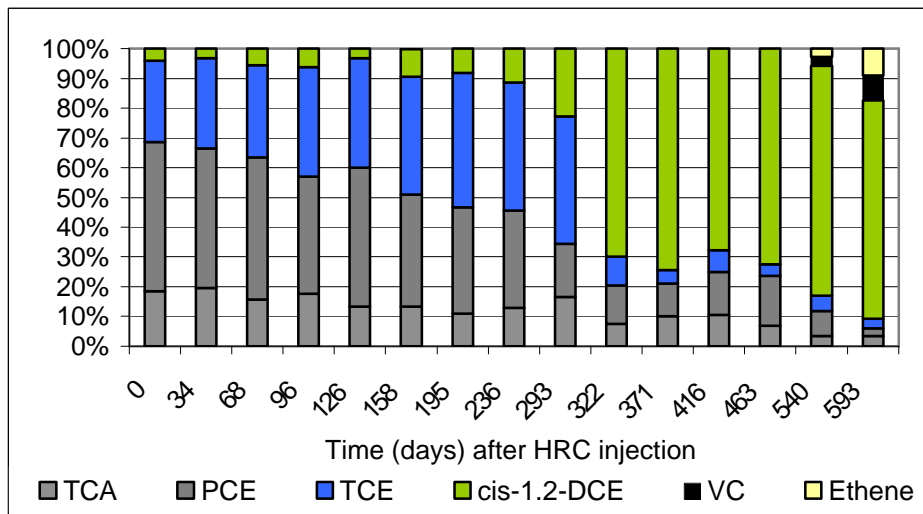


FIGURE 4: CHC Molar-Ratios in MW 43a

The CHC data (Figure 3) prior to source zone removal show a moderate degradation pattern at high concentration levels. Immediately after the excavation, a rapid decline of total concentrations was observed. However, after a short period of time the CHC-concentrations increased, caused by remnants of contaminated soil, which could not be removed by the excavation activities. The removal of the mass of source material and the additional delivery of HRC[®] lead to a fast degradation of chloroethenes

which is demonstrated by the trend of the molar-ratios (Figure 4). The cDCE percentage increased rapidly and remained high. With the last sampling events an increase of VC and the appearance of ethene could be observed, showing a complete degradation of chloroethenes. Further the last sampling events show a decline of PCE and it is expected, that the amount of remained CHC phase is going to be degraded over time.

Results downgradient of the Source Zone (lower vertical section of the aquifer).

The groundwater downgradient of the source area is monitored by the well MW 10 which is located 15 m downgradient of MW 43a in the center line of the plume (refer to Figure 1). The collected database shows clear evidence of a preferential flow path within the aquifer between the source area (MW 43a) and MW 10. Therefore the data of MW 10 are related to groundwater, which originated from the vicinity of MW 43a, and passed a reaction zone of 15 m. From the beginning of groundwater monitoring at the site, MW 10 showed a different pattern of parent / daughter ratios as the monitoring wells, which were screened in the upper vertical section of the contaminated aquifer. The molar percentage of PCE reached 90% and there was nearly no evidence that reductive dechlorination occurred. Approximately three month after the initial HRC[®] injection the aquifer started to shift into more reducing conditions. This is shown by the change of electron acceptor concentrations (Figure 5).

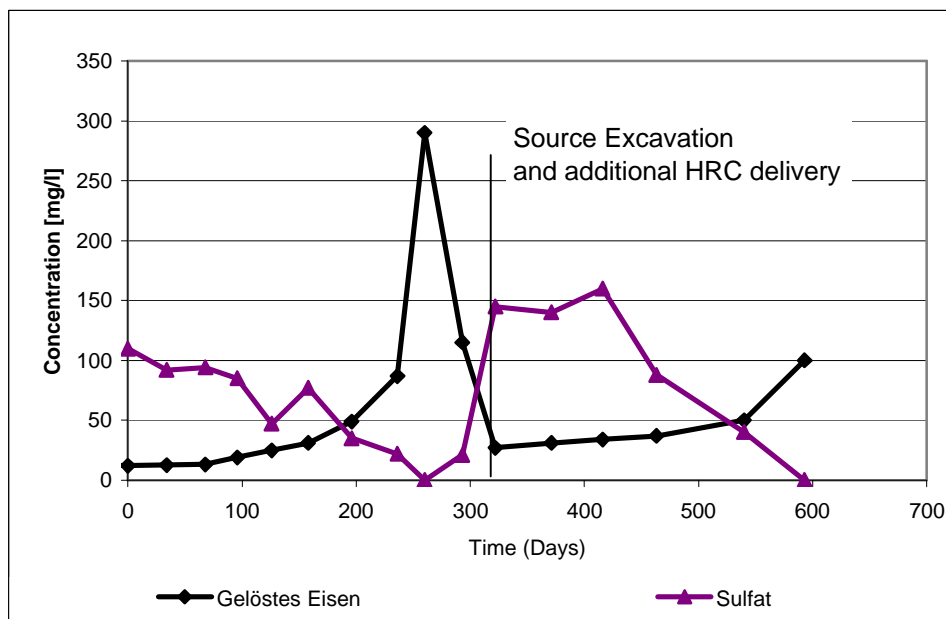


FIGURE 5: Changes in e^- acceptor concentrations in MW 10

The sulfate concentration decreased steadily down to non-detectable after a period of 9 month. Simultaneously the concentration of dissolved iron increased dramatically and peaked at a concentration of nearly 300 mg/l. The chloroethenes (Figure 6) showed a rapid degradation of PCE, starting at the time when beginning sulfate reduction was observed. TCE increased only to relatively low concentrations and peaked after 3 month. However, a steep rising of cDCE concentration occurred, which

could not be explained by the degradation of PCE and TCE. Therefore it is assumed that microbiological activity released additional CHC's in the source zone. The dissolved contaminants were degraded during their migration-way downstream.

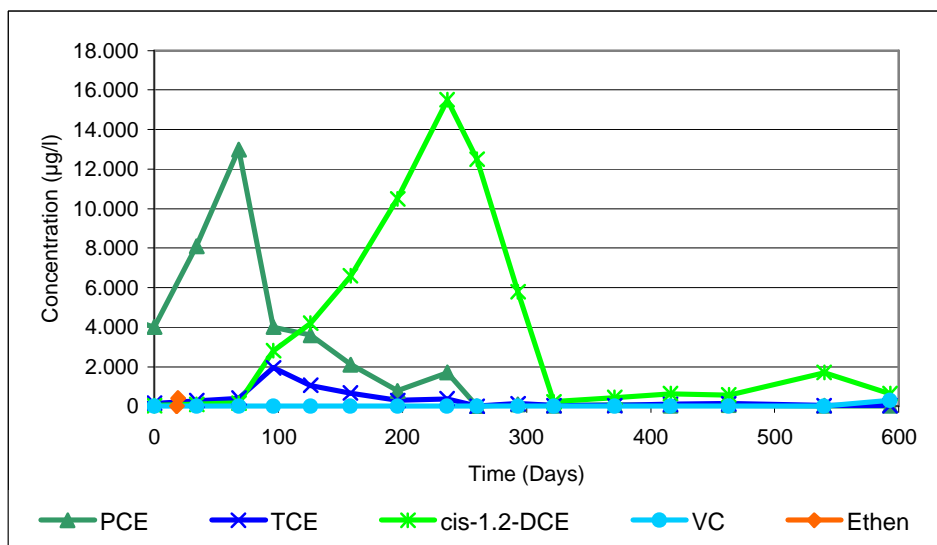


FIGURE 6: CHC concentration trends in MW 10

The cDCE concentration peaked at a time of 9 month after HRC[®] injection. At the same time PCE and TCE as well as sulfate were degraded to non-detectable levels and dissolved iron peaked at the highest concentration. Under this high reducing aquifer conditions an effective degradation of cDCE without accumulation of VC got started and continued until day 300 when the excavation activities began. After a period of nine month the injected HRC[®] created conditions which were favorable to dechlorinate CHC concentrations up to 20,000 µg/l (PCE) in the source zone to non detectable levels (PCE and TCE) or 2,000 µg/l (cis-DCE) respectively after a reaction zone of 15 m. Even though a rapid degradation of cDCE occurred, VC could not be observed at concentrations higher than 2 µg/l.

During the soil excavation the geochemical conditions within the aquifer changed completely because of the massive disturbance of the hydraulic system by pumping activities to lower the groundwater table. After the shut down of the pumping system the aquifer shifted back to aerobic conditions and the dechlorination process stopped. It took about four month until the additional delivered HRC[®] started to shift the aquifer back to sulfate and iron reducing conditions. This trend is expressed in Fig. 5 by the constant decrease of sulfate and the increase of dissolved iron. Simultaneously the cDCE concentrations were rising as they did before soil excavation, when the aquifer was in similar conditions. The diagrams shows that the cDCE and the dissolved iron peaked at the time when the sulfate was reduced to non detectable levels. Afterwards a rapid decline of cDCE can be assumed. The data of MW 10 indicate, that an effective and complete degradation of CHC's without an accumulation of the daughter product cDCE in this part of the aquifer will not occur until the sulfate, as a competing electron acceptor, is reduced completely (refer to figure 7 as well).

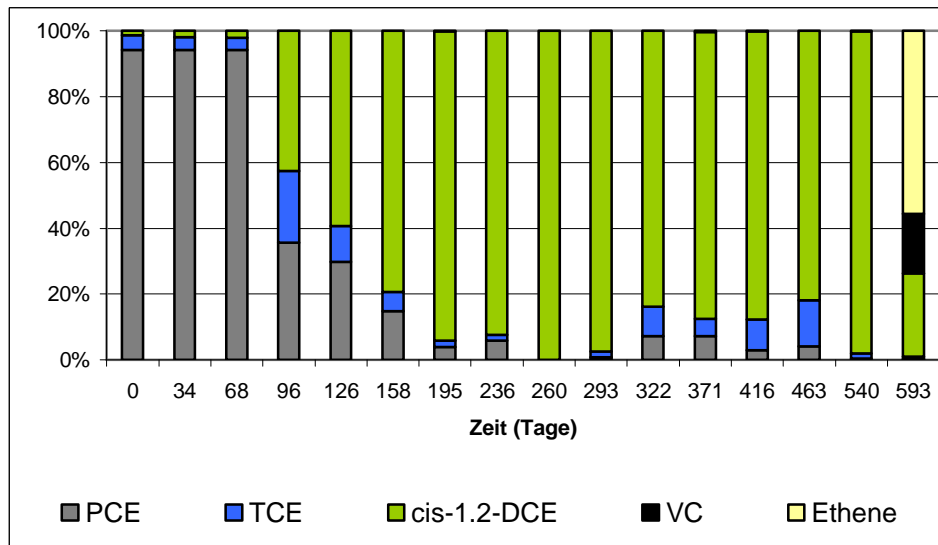


FIGURE 7: CHC Molar-Ratios in MW 10

CONCLUSIONS

The data of the intensive groundwater monitoring process prove that the provision of electron donor material was appropriate to enhance the reductive dechlorination of the CHC-contamination at the site. This process was effective and capable within the plume of dissolved contaminants to reduce the CHC-concentrations sufficiently to prevent further migration downgradient. Once the aquifer had been shifted into the appropriate conditions, the dechlorination process started and was maintained by the added HRC[®]. A CHC degradation of one order of magnitude was observed within a reaction zone of approximately 15 m. Therefore the enhanced reductive dechlorination can be seen as an effective containment strategy to prevent further migration of contaminants. Still after 9 month of monitoring, the data in the source area of the contamination site did not show clear results about the effectiveness of the dechlorination process. It can be assumed that a degradation of CHC's occurred together with a mass removal. However, because of the high amount of sorbed or free phase product in this area, the contaminants removed by in-situ biodegradation were replenished from the source material and the ongoing dechlorination process could not be proved by monitoring data.

The source zone excavation was found to be the most cost effective remediation strategy for the core area of contamination, considering the massive PHC contamination, and compared to the cost for a potential number of re-injection campaigns, which would have had to be realized to reduce the total mass of CHC's. Nevertheless, the additional HRC[®], which was poured at the base of the excavation pit, and the remaining depot of injected HRC[®], were capable to shift the aquifer back into appropriate conditions. The HRC[®] restarted and maintained the dechlorination process after the disturbance of the aquifer by pumping activities. The ongoing monitoring of data indicates that the dechlorination of the CHC's progresses and leads to an efficient mass removal of contaminant remains in the core area as well as in the plume.