

## **IN SITU REACTIVE ZONE (IRZ) – INJECTION OF MOLASSES TO PROMOTE MICROBIAL IN SITU DEGRADATION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS (CVOCs)**

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### **INTRODUCTION**

The number of long-lasting groundwater remediation measures that are evaluated via a cost-effectiveness analysis is increasing. Most often the outcome of this analysis is that a 10 to 15-year-old concept of applying hydraulic remediation has to be revised. Meanwhile more efficient and consequently more cost-saving technologies have been developed and applied in Europe.

Pump-and-treat is capable of removing the mass of hydraulically available contaminants which can be seen by the initially rapid decrease in aqueous contaminant concentration; however, it is not suitable for a complete elimination of contaminants from the aquifer. Due to a continuous recharge of contaminants from the pool of soil-bound contaminants, residual phases, and hydraulically inaccessible zones (silt lenses, micropores), even after several years of pump-and-treat operation the aqueous concentration of the contaminants is still on a relatively high level (i.e. significantly higher than the remediation target) and is only slowly decreasing (asymptote value).

This remaining concentration value is characterised by a dynamic equilibrium, i.e. the contaminant mass hydraulically removed equals the contaminant mass recharged by the processes described above. The transition of the contaminants into an accessible form for hydraulic measures is a slow process, which determines the required time to reach target concentrations. After shut-down of a pump-and-treat measure, the groundwater flow velocity and consequently the removal of the contaminants are reduced, resulting in concentration increases as long as there is a remaining pool of contaminants in the aquifer. As soon as a pump-and-treat stops showing a significant mass removal it should be replaced by other remediation measures that overcome these natural limitations.

In the case of a groundwater contamination with chlorinated volatile organic compounds (CVOCs) the application of the *In Situ* Reactive Zone (IRZ) technology is suitable. In IRZ technology substrates, chemicals, nutrients, and other amendments are injected into the groundwater via conventional (monitoring) wells and are transported by the natural groundwater flow. Since especially the biodegradation of the higher chlorinated hydrocarbons requires strongly reducing conditions, an organic carbon-based substrate ( $C_{org}$ ) is used. The microbial consumption of this substrate creates a

biogeochemical environment in the subsurface which stimulates the reductive dechlorination of CVOCs. For the creation of a reducing IRZ for CVOC dechlorination soluble substrates like e.g. molasses, lactate, and ethanol as well as insoluble slow-release substrates like e.g. Hydrogen Release Compound (HRC®) can be used; however, insoluble substrates require different application techniques. Suspended food-grade oil represents an intermediate which can be delivered via regular wells but acts as a long-term  $C_{org}$ -reservoir due to its low solubility. The most extensive experiences have been made using molasses as a substrate.

Beside anaerobic IRZs aerobic applications are also implemented. Here hydrogen peroxide (with the addition of nitrate where appropriate) is injected to serve as electron acceptor for the aerobic biodegradation of contaminants.

**KEY-WORDS:** CVOC contamination, pump-and-treat, microbial in situ remediation, molasses, contaminant desorption

### **GEOLOGICAL AND HYDROGEOLOGICAL SITE CHARACTERISATION**

The contaminated site is located approximately 200 m north of the east harbour of Frankfurt, Germany at an elevation of 99 m asl, while the river Main, representing the receiving water for the groundwater, exhibits a water level at a height of around 94 m asl.

The site is mostly sealed by buildings, roads, and yards due to its use as industrial area. The surface sealing is underlain by an upper backfilling layer consisting of sandy gravels, gravely sands, slag and building rubble. Below is another backfilling layer consisting of slightly sandy to sandy, partially slightly gravely silts of stiff consistency, mixed with anthropogenic deposits (building rubble, sherds). This filling partly consists of resedimented alluvial clay sediments of the River Main. The layer thickness varies between 0.5 m and 2.1 m. Due to construction measures the lower backfilling layer is replaced by material of the upper backfilling layer in several places.

The lower backfilling is underlain by a sand/gravel-layer (the river terrace of the Main) with a minor fraction of fine grain (< 3%). This layer represents the upper (contaminated) aquifer. The medium

depth of the upper layer boundary is ca. 2 m b.g.l., the thickness of the sand/gravel-layer varies between 3 and 5 m. The hydraulic conductivity was determined based on sieve analyses and ranges from  $0.5 \cdot 10^{-4}$  m/s to  $2.0 \cdot 10^{-3}$  m/s, which indicates a good permeability of the upper aquifer. A silt/clay layer (Rupelian clay) serves as the aquiclude with an upper boundary layer of 6 to 7 m b.g.l. The surface relief is characterised by several relatively small scaled dells and channel-like depressions.

Due to the proximity of the receiving water the local groundwater depth is only 2.5-3.0 m and is anthropogenically influenced by groundwater extractions and infiltrations. This leads to temporary changes in groundwater flow direction, which is generally directed south to southwest (see Figure 3). The groundwater flow velocity strongly varies between 1 and 35 cm/d.

## CONTAMINATION, SITE HISTORY AND FIRST REMEDIATION ACTIVITIES

The 7.000 m<sup>2</sup> large industrial site in Frankfurt has been used since ca. 1950 for the production of automotive parts. In 1988 analyses of the soil, soil vapour, and groundwater showed contaminations of the subsurface with CVOCs, primarily chlorinated ethenes. The contaminations were attributed to the operation of a washing plant for metal degreasing over a period of 22 years. The maximum CVOC concentration in 1989 was ca. 70,000 µg/L (B 1/88, see Figure 4). Perchloroethene (PCE, 66%) and trichloroethene (TCE, 32%) were the dominating components, whereas *cis*-1,2-dichloroethene (cDCE) was only present in low concentrations. Vinyl chloride (VC) was not analysed.

The site is located within an area of several other industrial activities, which caused an additional CVOC burden of the groundwater. Analyses of the CVOC isotopic fingerprints proved several external contaminations adjacent to the site. These contaminations lead to an influx of CVOC contaminated groundwater to the site. According to the CVOC influent concentration of the groundwater a remediation target level of 80 µg/L was negotiated with the regulators.

In November 1989 a hydraulic containment measure (pump-and-treat) with a maximum extraction rate of 12 m<sup>3</sup>/h and subsequent water purification via stripping and activated carbon was put into operation. The groundwater was extracted at the wells B 1/88, B 2/88, B 4/88, B 6/88 (intermittent), and B 42B, treated and re-infiltrated in the wells B 5/88, B 20/90, and B 21/90 (see Figure 4). Within the first year of operation more than 200 kg CVOC were removed from the groundwater and the CVOC concentration in the water treatment inlet decreased from initially 11,000 µg/L to 1,500 µg/L. In June 1996 a new plant with one sand filter, activated carbon adsorbers and a lower flow rate of 6 m<sup>3</sup>/h was put into operation. The influent concentration had dropped to < 400 µg/L. By this time the efficiency of the CVOC removal had decreased significantly. Between 1996 and 2000 only 7 kg CVOC per annum could be removed from the groundwater (see Figure 2).

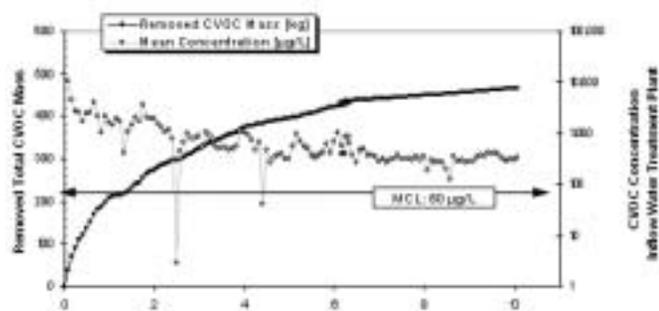


Fig. 1 - CVOC concentrations at the inflow of the water treatment plant and removed total mass

Linear regression of the influent analyses showed that the CVOC concentration decreased by only 8.2 µg/L per annum. Consequently, at least another 40 years would have been required for the pump-and-treat measure to meet the remediation target. In the course of a revision of the remedial actions until 2002, ARCADIS recommended to replace the hydraulic remediation by the IRZ technology using molasses. The biogeochemical conditions seemed to be favourable since the transformation products cDCE and VC were already detectable at the site.

## PRINCIPLES OF THE IRZ TECHNOLOGY

The IRZ technology is a passive *in situ* remediation. Many CVOC contaminated sites show natural anaerobic biodegradation; however, the degradation rate without anthropogenic intervention is usually not high enough to allow for complete contaminant removal within a reasonable time frame. This is usually due to a suboptimal biogeochemical environment as well as to lacking auxiliary substrates. The goal of the IRZ technology is to overcome these limitations. For that a suitable substrate (e.g. molasses) is delivered applying pulsed injections or continuous infiltration via conventional groundwater wells. The distribution within the aquifer proceeds passively and is supported by the natural groundwater flow. Especially when complex migration pathways exist, the advantage of this passive transport is that the infiltrated substrates take the same way as the contaminants. In contrast to the contaminants, most of the substrates are not retarded by the aquifer matrix; thus they will be transported to the location of the contaminants where they promote the microbial degradation. Only in the case of very extended contaminations closed infiltration loops are required to allow appropriate distribution of the substrate.

The organic substrate serves as electron donor for the autochthonous microorganisms. During substrate mineralization the electron acceptors competing with CVOC degradation are consumed. Due to thermodynamic reasons dissolved oxygen is primarily consumed; after that NO<sub>3</sub><sup>-</sup>, Mn(VI), Fe(III), and SO<sub>4</sub><sup>2-</sup> are reduced before eventually strongly reducing methanogenic conditions are created which preferentially allow for the reductive microbial dechlorination (FREEDMAN & GOSSETT, 1989, DE BRUIN *et al.*, 1992). In this biogeochemical environment e.g. PCE is degraded via the sequence:

PCE ♦ TCE ♦ cDCE ♦ VC ♦ Ethene/Ethane ♦ CO<sub>2</sub>. The final mineralization to CO<sub>2</sub> requires a more oxidising redox potential. The reductive dechlorination is primarily catalysed by the so called dehalorespiring bacteria which in most cases use CVOCs as the exclusive electron acceptors.

The substrate used to promote reductive dechlorination, molasses, is the final syrup in sugar production and allows no further economic yield of sugar by crystallisation. Molasses consists of > 47% total sugars in different forms and bindings, approximately 30% non-sugar organics (proteins and other nitrogen-free organic compounds, inorganic nutrients) as well as other nutrients (SCHWECK, 1995). The rest of molasses is water. Thus molasses is an ideal growth substrate for microorganisms and animals and is therefore used in feed industry. Under anaerobic conditions molasses is fermented by complex microbial consortia leading to the production of molecular hydrogen (H<sub>2</sub>) and acetate which serve as electron donors for the dehalorespiring microorganisms (MCCARTY, 1997).

Besides the substrate delivery the injection of molasses provides one more decisive advantage: an enhanced desorption of organic contaminants from the soil matrix (SUTHERSAN *et al.*, 2002). This can be recognized by means of a typical increase in the concentrations within the initial remediation phase. The reasons therefore are:

The distribution equilibrium of organic contaminants between soil and groundwater depends on the organic carbon content of both solid and aqueous phase. After injection of molasses the concentration of the organic carbon in the aqueous phase is increased significantly which results in desorption of the soil bound contaminants.

During sequential microbial degradation of the CVOCs lower chlorinated metabolites are formed which have a lower adsorption strength (K<sub>OC</sub>).

Simplified, microorganisms are only able to degrade contaminants dissolved in water. To enhance the bioavailability of the substrates they form biotensides.

During the degradation of molasses polar transformation products such as alcohols are produced which additionally serve as a solubiliser.

The increase in contaminant bioavailability caused by microbial action leads to a decrease in soil-bound contaminant mass. Usually the elimination of this mass determines the time required for site remediation. Hence, it is evident that the IRZ technology can reduce the remediation time substantially compared to other technologies.

#### ADDITIONAL SITE INVESTIGATION AND PILOT TEST

The concern of uncontrolled dissolution and spreading of contaminants after shut-down of a pump-and-treat measure and replacement by alternative remediation technologies causes some problems. In this case it was agreed with the regulators to shut down pumping of groundwater for a limited time frame (3 months) and to monitor the contaminant dissolution rates under natural hydrogeological conditions. The groundwater treatment plant was kept ready for service. A higher biodegradation rate (to be determined in a pilot test) com-

pared to the dissolution rate had to be shown as a proof that no contaminated groundwater may migrate downgradient from the site.

During this 3 months investigation phase the monitoring wells were sampled in four-week intervals. The results showed nearly constant TCE/PCE- and PCE/cDCE-ratios indicating a very slow natural biotransformation. Hence biodegradation could be neglected for the calculation of the dissolution rate. With the data gained a mean specific dissolution rate of 0.2 µg CVOC per litre soil and day could be derived.

From former construction measures at the site, one area of the aquifer with a groundwater monitoring well was hydraulically isolated by cut-off walls. Upon request of the regulators the area was used for the IRZ pilot test carried out over a period of 6 months. Since the hydraulic isolation allowed no groundwater flow, the pilot test was conducted as a single-well push-and-pull test. This means that for the injection of molasses as well as for the monitoring a defined volume of the groundwater had to be pumped out avoiding aeration. After addition of molasses and/or sampling the water was re-infiltrated. Molasses was added on the 1<sup>st</sup> and on the 70<sup>th</sup> day of the test. The results are summarised in Figure 2. In the beginning of the test the groundwater was moderately reducing it (-18 mV) and showed a low DOC content (1.5 mg/L). Among the analysed redox indicators (O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Fe-II, Mn-II, sulfate) only iron (5 mg/L) and sulfate (51 mg/L) could be detected. The concentration of the CVOCs was 251 µg/L. The groundwater monitoring on day 70 revealed a complete consumption of sulfate as well as the methanogenic environment required for reductive dechlorination. After each injection of molasses the decrease in pH as well as the increase in electrical conductivity showed that the molasses had been degraded to low molecular weight organic acids. From the subsequent recovery of both parameters to initial values it could be concluded that the acids had been mineralised to the final products H<sub>2</sub> and CH<sub>4</sub> (HELD & BURDICK, 2003).

The concentrations of PCE and TCE decreased continuously from the beginning of the pilot test to the end (30 µg/L ♦ 0.7 µg/L and 80 µg/L ♦ < 1.4 µg/L, resp.). The concentration of cDCE increased – as expected – within the first two months from 110 µg/L to 490 µg/L and subsequently decreased to 14.8 µg/L until the end of the test. The initial increase in concentration is due to the mobilisation of soil bound CVOCs. The concentration of VC decreased from 23 µg/L to 5.7 µg/L; hence, no significant accumulation of VC occurred during the CVOC dechlorination. It is remarkable that complete mineralization first started after the DOC concentration had dropped to relatively low values. In accordance with literature reporting, this is due to the fact that at low DOC and respective H<sub>2</sub> concentrations dehalorespiration is thermodynamically preferred over methanogenesis (BALLAPRAGADA *et al.*, 1997). From the results of the pilot test a first-order *in situ* biodegradation rate for total CVOCs of 0.018 d<sup>-1</sup> could be derived, proving that stimulated biodegradation was substantially higher than the dissolution rate. Consequently an uncontrolled migration of the contaminants downgradient could be excluded.

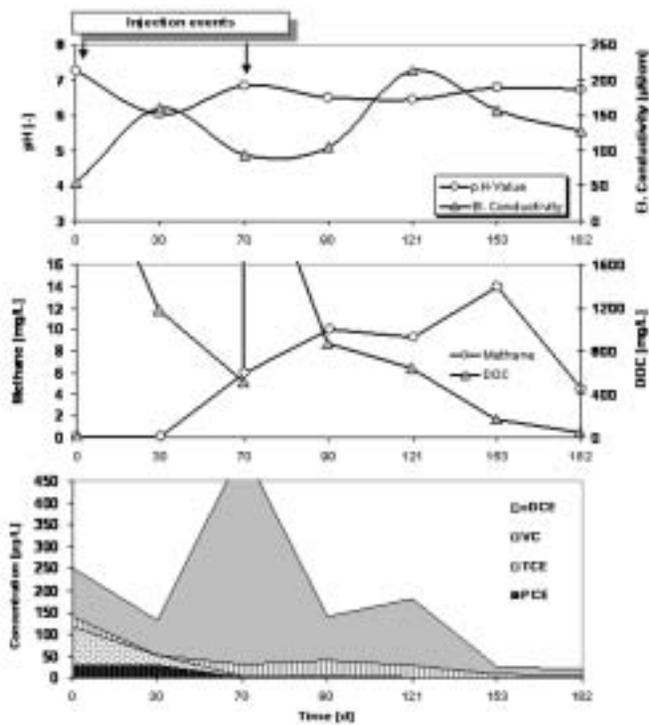


Fig. 2 - Parameters analysed during the half-year pilot test

After the successful pilot test on microbial *in situ* degradation of the chlorinated ethenes with the help of molasses injections it was decided by the regulators to finally shut down the hydraulic containment measure and to establish a full-scale IRZ at the site. Based on the data acquired during the pilot test a required remediation time of 3 years was derived.

### FULL SCALE IRZ REMEDIATION

After shut-down of the pump-and-treat measure as well as a baseline monitoring of the groundwater, the regular injections in all available monitoring wells started in May 2002. Since a high density of groundwater wells already existed at the site, the entire aquifer could be supplied with nutrients using pulse injections. Initially the pulse injections were conducted every 4 months. In the beginning of the second year during optimisation of the remediation, additional injections were carried out in the upgradient wells in order to sustain the highly reducing conditions in the aquifer continuously. The injections in the upgradient wells (B 5/88, B 20/90, B 21/90, B 7/88 und B 8/88, see Figure 4) were conducted every 6 weeks. Every 6 months (directly before the injections) groundwater samples were taken and analysed for CVOCs, degradation end products and redox indicators. Redox mapping is a simple but very effective method to evaluate if and how long after a molasses injection a suitable biogeochemical environment prevails. For this purpose the oxidation redox potential (ORP) was measured at different times in all groundwater wells *in situ*. With

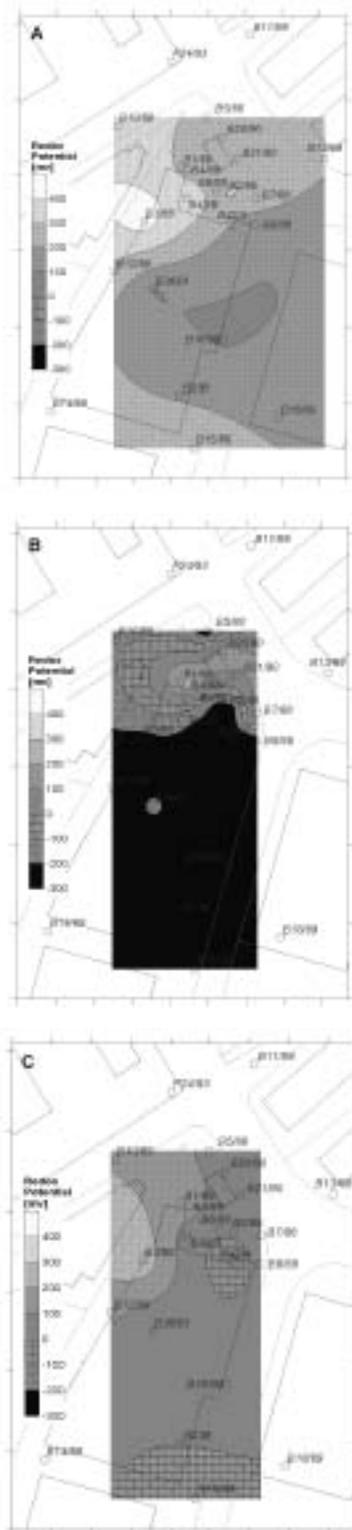


Fig. 3 - Redox mapping (a) before, (b) 3 days after, (c) and 3 months after an injection event at the entire site (top is north)

the help of a computer program (SURFER®) the measured values were presented graphically. This is shown exemplarily in Figure 3. It can be concluded that from north to north-west groundwater with an ORP of +200 mV enters the remediation area (Figure 3a). Accordingly the ORP within the contaminated site is in an oxidizing range. Shortly after the injection of molasses strongly reducing conditions was observed at the entire site (with the exception of a small area around B 1/88), promoting reductive dechlorination (Figure 3b). When the subsequent injection of molasses is not conducted in time, oxidized water will flow into the remediation area again (Figure 3c).

The results of the redox mapping were used to determine the frequency of molasses injection. In addition the analyses of the redox indicators were used to evaluate the biogeochemical environment. In the area directly influenced by the injection a complete consumption of the competing electron acceptors like dissolved oxygen, nitrate,

Mn-IV, Fe-III, and sulfate occurred simultaneously with the consumption of DOC.

Prior to the initiation of the IRZ remediation the maximum CVOC concentration at the site was 1,430 µg/L. The parental substance PCE represented the predominant compound of the contamination (63%), but the concentrations of the other compounds (16% TCE, 21% cDCE) showed that under natural conditions a reductive biological dechlorination process had already begun. Figure 4 shows the distribution of the CVOC contamination at the site immediately before the first molasses injection (Figure 4a) as well as at the end of the remediation (Figure 4b). Whereas in the beginning high contaminant concentrations were observed especially in the source area around B 4/88, about half a year before the scheduled end of the remediation 15 out of 17 groundwater wells showed a residual contamination below 30 µg/L and thus concentrations significantly below the maximum contaminant level (MCL) of 80 µg/L. In eight of these wells the CVOC concentrations were even below the determination level, only two wells revealed concentrations above the MCL. The highly contaminated well B 4/88 still showed a residual concentration of 91.2 µg/L. By the end of the remediation (i.e. after 3 years) the CVOC concentration in B 4/88 could be reduced to 79.0 µg/L (see Figure 4).

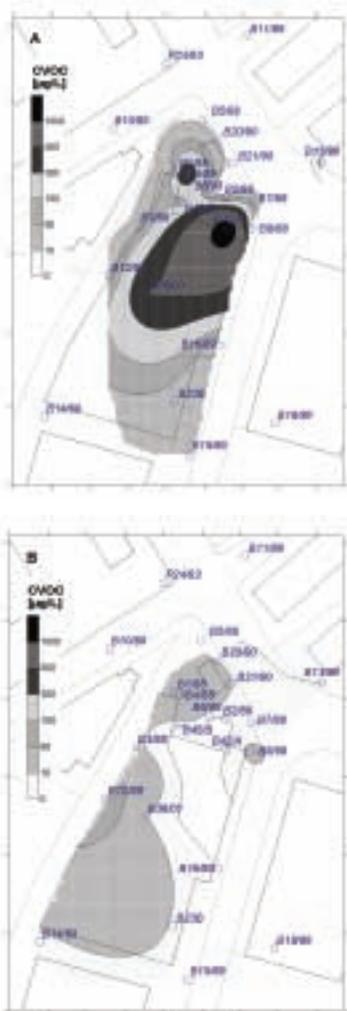


Fig. 4 - Distribution of the contaminants (sum of CVOCs in µg/L) (a) before and (b) after IRZ remediation

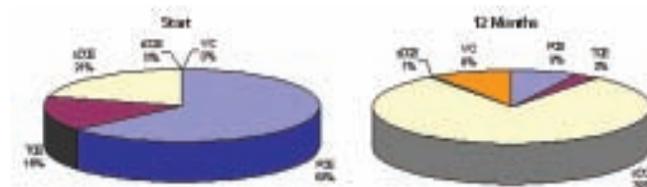


Fig. 5 - Comparison of the CVOC pattern (mean values over all monitoring wells, excluding the unchlorinated end products ethene and ethane)

Figure 5 shows that PCE and TCE accounted for 79% of the contamination. Only 12 months after the start of the *in situ* remediation (i.e. when the CVOC concentration had reached its highest value) the distribution of individual compounds had shifted to cDCE as the predominant compound (79%; the end products ethene and ethane were not taken into account). The distribution pattern found after 12 months did not change until the end of the remediation although the total concentrations decreased substantially. The fact that PCE was still detectable at the end of the remediation shows that during the entire remediation desorption of soil bound contaminants as well as solubilisation of residual phase droplets (so called blops) must have occurred.

Besides CVOCs and methane the end products of the reductive dechlorination, ethane and ethane, were also analysed in selected wells. Both compounds could be found in high concentrations (max. 800 µg/L and max. 900 µg/L, resp.). Thus complete reductive dechlorination was proven.

The CVOC concentrations are shown as mean values over all monitoring wells in Figure 6. The desorption of contaminants after

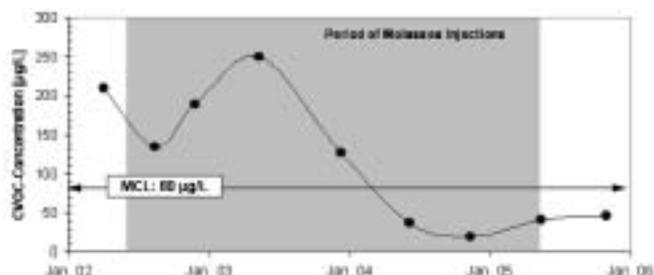


Fig. 6 - Mean CVOC concentrations during IRZ remediation

the injection of molasses can be derived from this graph. After optimisation of the injection volumes and frequencies the mean concentration increased from 128 µg/L in August 2002 to 236 µg/L in May 2003 and then decreased continuously to 19 µg/L in November 2004.

In June 2004, some two years after the start of the *in situ* remediation, the mean CVOC concentration of 36 µg/L was already below the MCL of 80 µg/L. The remedial action (i.e. injection of molasses) was terminated in spring 2005. Since then the site is monitored every six months for two years in order to determine possible rebound effects. In case no significant rebound of the CVOC concentrations will occur it can be concluded that the mass of soil bound CVOC has been depleted. Preliminary data showed that the CVOCs at the site could obviously be completely degraded. Hence, the remediation of the site can be regarded as successfully closed.

The mean annual costs for the IRZ remediation were in the range of 1/3 of the annual costs for the pump-and-treat measure run in previous years. Additional cost savings could be achieved by substantially reducing the required remediation time.

## CONCLUSION

The discussed remediation is – according to the knowledge of the authors – the first successfully closed site in Germany remediated with the IRZ or a related technology. In the United States more than 150 sites are treated by ARCADIS, corresponding to an enormous experience. This resulted in the publication of a technical protocol on

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As the documentation of the Frankfurt site shows, the IRZ represents an attractive, sustainable *in situ* technology for the decontamination of CVOC contaminated soils and groundwater. The analyses and evaluation of the experience collected at the site proved that the injection of a carbohydrate like molasses can both promote the dechlorination of chlorinated ethenes and enhance the desorption of soil bound contaminants. This leads to a reduction of the required time for the remediation from the estimated value of 40 years for pump-and-treat to only 3 years. The microbial *in situ* remediation technology applying molasses injections is thus superior to conventional technologies with respect to both environmental and economic aspects.

Furthermore the IRZ technology features a high degree of flexibility and a straightforward operation at the same time. An adequate arrangement of conventional groundwater monitoring wells is needed, which can also be used as injection wells. The injected molasses is transported (passively) by the natural groundwater flow and is consumed slowly due to its high content of polymeric substances, thereby revealing a high longevity. The injections can be optimised regarding the volume, concentration, frequency, and location. It is therefore possible to treat isolated, heavily contaminated areas individually.

Meanwhile several IRZ pilot tests in Germany have been conducted to investigate the feasibility and the limitations of this *in situ* technology. Complete microbial dechlorination of CVOCs could be achieved at several sites under varying biogeochemical and hydrogeological conditions, including a bedrock aquifer of variegated sandstone. Beside chlorinated ethenes other CVOCs such as chlorinated ethanes, methanes, and phenols can be biodegraded. In addition the IRZ technology can be used for *in situ* denitrification or for *in situ* detoxification and immobilisation of the carcinogenic chromate. The presented technology has also been successfully applied by ARCADIS for the *in situ* immobilisation of other metals like nickel, cadmium, zinc, and radionuclides.