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Remediation of ground water containing chlorinated and brominated hydrocarbons, benzene and chromate by sequential treatment using ZVI and GAC

Abstract A laboratory experiment with two sequenced columns was performed as a preliminary study for the installation of a permeable reactive barrier (PRB) at a site where a mixed ground water contamination exists. The first column contained granular zero valent iron (ZVI), the second column was filled with granular activated carbon (GAC). Trichloromethane (TCM, 930 µg/l) and chlorobenzene (MCB, 260 µg/l) were added to the ground water from the site as the main contaminants. Smaller amounts (< 60 µg/l) of benzene, 1,2-dichloroethane, 1,1,2-trichloroethane (1,1,2-TCA), 1,1-dichloroethene (1,1-DCE), trichloroethene (TCE), tetrachloroethene (PCE), 1,2-dichloropropane (1,2-DCP), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM), vinyl chloride and chromate were also added to the water to simulate the complex contamination pattern at the site of interest. PCE, TCE, 1,1-DCE, DBCM, BDCM, TBM, MCB and chromate were remediated in contact with ZVI, while the remaining contaminants showed incomplete degradation. A fraction of 8–16.5% TCM was converted to dichloromethane (DCM). Remaining contaminant concentrations were efficiently sorbed by the GAC until breakthrough of DCM was observed after 1,230 exchanged pore volumes in the GAC. The results show that the complex mixture of contaminants can be remediated by a sequenced PRB consisting of ZVI and GAC and that DCM sorption capacity is the critical parameter for the dimensions of the GAC reactor.

Keywords Sequenced permeable reactive barriers · Zero valent iron · Granular activated carbon · Halogenated hydrocarbons · Benzene · Chromate

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Introduction and objective

Remediation of chlorinated ethenes, ethanes and methanes by zero valent iron (ZVI) is a well-known process which is now increasingly used for ground water clean-up with permeable reactive barriers (PRB). In some places, a mixture of these compounds with other contaminants is found which cannot be degraded through contact with ZVI, e.g. benzene, toluene, ethylbenzene and xylene compounds or chlorinated aromatic hydrocarbons such as chlorobenzene (MCB). It has already been demonstrated in several studies that in such cases, ZVI can be combined with other reactive media in a sequenced barrier to successfully remediate the mixed contamination. Examples of such studies include the combination of ZVI with granular activated carbon (GAC) (Köber et al. 2001a) for the sorption of compounds which show incomplete or no degradation by ZVI. Further, combinations of ZVI with bioreactive zones have also been demonstrated. The bioreactive zones were created through amendment with microorganisms and nutrients (Dries et al. 2003), or by the

addition of oxygen through sparging of oxygen (Morkin et al. 2000), or through the use of a mixture of ORC® ("Oxygen Release Compound") and quartz sand as a reactive barrier material (Köber et al. 2001b). ORC is a mixture of MgO_2 and MgO which has been amended with phosphate to ensure the slow release of oxygen in contact with water (Koenigsberg et al. 2000). Due to the complex reactions between ground water and reactive media, several authors (e.g. Gavaskar et al. 2000; Carey et al. 2002) recommend that laboratory column tests be performed for dimensioning purposes prior to the installation of a PRB. Although dimensioning experiments have been performed for ZVI PRB for a number of sites, there has been only a comparatively small number of publications reporting data from preliminary studies of sequenced PRB for the remediation of mixed contaminations (e.g. Köber et al. 2001a, b; Schäfer et al. 2002; Dries et al. 2003), and data from these studies cannot easily be generalised to predict the prospects for the degradation of other contaminant mixtures by similar remediation approaches.

The present work was performed as a preliminary dimensioning study for the possible installation of a PRB for the remediation of a mixed contamination at a chemical industry site. The contaminants found at the site include chromate, aromatic hydrocarbons (benzene and MCB), and a wide range of chlorinated and brominated aliphatic hydrocarbons, including trichloromethane (TCM), 1,2-dichloroethane (1,2-DCA), 1,1,2-trichloroethane (1,1,2-TCA), 1,1-dichloroethene (1,1-DCE), trichloroethene (TCE), tetrachloroethene (PCE), 1,2-dichloropropane (1,2-DCP), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM) and vinyl chloride (VC). The highest concentration of these compounds was found for TCM. It has already been demonstrated that PCE, TCE, 1,1-DCE, VC, TCM, TBM, 1,1,2-TCA and 1,2-DCP can be degraded through contact with ZVI (e.g. Powell et al. 1998; Gavaskar et al. 2000 and references therein), and that the degradation of halogenated hydrocarbons can in most cases be adequately described by pseudo first-order kinetics. Nevertheless, according to Gavaskar et al. (2000), the time scales required for remediation of individual compounds may differ by about three orders of magnitude, with half-lifes ranging from 2.5 min for TBM to 2,240 min for 1,1-DCE. In addition to halogenated compounds, Cr(VI) contaminations in ground water can be remediated by ZVI through the reduction of Cr(VI) to Cr(III) and its subsequent precipitation (e.g. Blowes et al. 2000; Schlicker et al. 2000). Not all halogenated hydrocarbons can be remediated by ZVI; for example, TCM is known to be dechlorinated to dichloromethane (DCM) through contact with ZVI. DCM is a compound which is recalcitrant to further degradation by ZVI (e.g. Gillham and O'Hannesin 1994; Matheson and Tratnyek 1994). Similarly, 1,2-DCA is

apparently not degraded by ZVI (Powell et al. 1998), and reduced aromatic hydrocarbons like benzene and MCB are not likely to be degraded through contact with ZVI. To our knowledge, kinetic data have only been published on the degradation of BDCM and DBCM through contact with a mixture of palladised iron and sand (Guasp and Wei 2003), and thus it was unclear as to which residence times would be required for the degradation of these compounds by ZVI alone. We anticipated that ZVI alone would not be sufficient to remediate the complex contaminant mixture, and thus a sequenced barrier concept was tested in a laboratory experiment using two sequenced columns. One column contained ZVI and the other GAC, which served to absorb those compounds which showed no degradation or incomplete degradation through contact with ZVI. The first aim of the experiment was to investigate whether the complex mixed contamination can be treated by a sequenced PRB. The second aim was to determine the residence time needed in the ZVI column for reductive dehalogenation of degradable compounds and the sorption capacity of the GAC for contaminants which are not, or only partially, degradable by ZVI. Additionally, a variety of geochemical parameters was monitored during the experiment to better understand the sequenced system and to recognise possible problems arising from the reactions between ZVI and site ground water and the subsequent effect these reactions could have on the GAC.

Materials and methods

Experimental

A laboratory experiment was conducted with two sequenced columns (Fig. 1). The first column (HDPE, *L*: 112 cm, Ø: 10 cm) contained cast iron (Gotthart Maier FG 300-2000 1×, grain size 0.3–2 mm), while the second column (Plexiglas®, *L*: 15 cm, Ø: 4 cm) was filled with GAC (Chemviron Carbon TL 830). Both columns contained a layer of quartz grains (10 cm in the column containing ZVI, 3.5 cm in the column containing GAC) at the bottom to ensure one-dimensional flow conditions in the reactive media. The columns were filled with water in increments of a few centimetres, after which either ZVI or GAC was added. In this way, they remained saturated with water throughout the process, thus preventing inclusion of air bubbles into the system. Porosities in the reactive media were determined gravimetrically from the amount of water which was filled into the reactive section (4.47 l in the column containing ZVI, 0.11 l in the column containing GAC, leading to total porosities of 0.56 and 0.76, respectively). The porosities thus determined are total porosities, which result in conservative estimates of exchanged pore
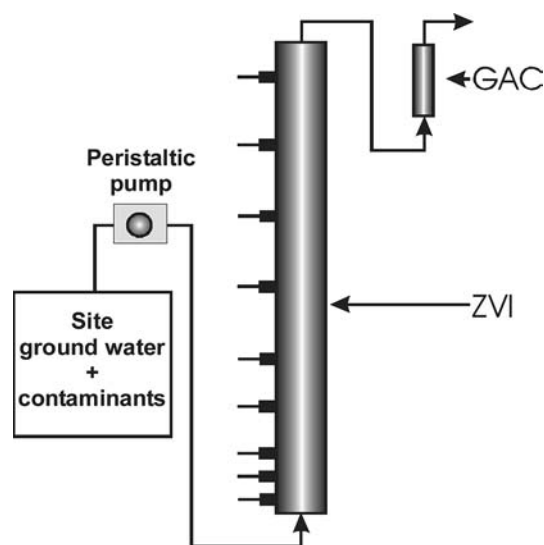
Fig. 1 Experiment setup

volumes (PV) and residence times in the reactive media as compared to effective PV which are lower. Samples were taken from the inflow and outflow of the two columns. Additionally, samples were removed from the pore water of the column containing ZVI through nine sampling ports fitted with stainless steel canulas. The sequenced columns were percolated with site ground water through viton tubing using a peristaltic pump.

Water from the contaminated site was filled into plastic canisters (30 l) on site and shipped to the laboratory, where it was stored under cool and dark conditions until it was used for the experiment. Analyses of the water showed that it had a considerable salt content (TDS approx. 8 g/l, Table 1) resulting mainly from high Na^+ and Cl^- concentrations. As contaminant concentrations found in the stored site water were lower than observed in the field, the water was then spiked with well-defined contaminant concentrations. For use in the experiment, site ground water was transferred in 30 l batches into collapsible Tedlar® bags which had proved, during previous experiments, to be sufficiently gas-tight to prevent volatilisation of volatile organic compounds. The water was subsequently spiked with adequate amounts of stock solutions to reach the desired contaminant concentration. For this purpose, separate stock solutions were prepared for each contaminant by adding an excess amount of the pure compound to a 50-ml vial which had been filled with deionised water and mixing on a magnetic stirrer for several hours. For chromate, a stock solution of 186.8 mg/l K_2CrO_4 was prepared. Subsequently, the individual stock solutions were added to the Tedlar bag in appropriate amounts to reach the desired concentration. The dilution effect due to the addition of the stock solutions to the site water (in total ca. 50 ml of stock solutions added to 30 l of site

water) was considered as negligible. TCM (approx. 930 µg/l) and MCB (approx. 260 µg/l) were added at the highest concentration levels, while benzene, 1,2-DCA, 1,1,2-TCA, 1,1-DCE, TCE, PCE, 1,2-DCP, BDCM, DBCM, TBM, VC and chromate were added in smaller amounts (< 60 µg/l, Table 1). BDCM was first added to the influent solution after 40 days running time.

The system was run at $20 \pm 3°C$ for 26 days at an average flow rate of 1.9 ml/min, then for 38 days at 3.0 ml/min, resulting in a total of 53 exchanged PV in the column containing ZVI and of 2,165 PV in the column containing GAC. In order to facilitate the establishment of sulphate-reducing bacteria often found in field applications of ZVI PRBs, the system was inoculated with sulphate-reducing bacteria after a running time of 7 days. For the inoculation, a syringe and a steel canula were used to remove ca. 100 ml of pore water from another column experiment where active sulphate reduction had been consistently observed. The water was subsequently injected into the influent of the column system.

During the first phase of the experiment, samples were taken after approximately 2 weeks (Table 2). After the flow rate had been increased (> 26 days running time), samples were taken about weekly. When DCM breakthrough was observed after 57 days, additional samples from the inflow and outflow of the GAC column were taken to improve the characterisation of the DCM breakthrough.

Samples for anion, cation and organic compound analysis were filtered through 0.2 µm cellulose acetate filters, and samples for cation analysis (with the exception of NH_4^+) were acidified with HNO_3 (65%, s.p.). For organic compound analysis and for analysis of dissolved H_2, 5 ml of the sample were transferred into glass headspace vials and sealed gas-tight with Teflon-lined caps. Triplicate samples were taken for quantification of organic compounds, and results for these compounds, presented in the following text, represent the mean concentration of the three measurements. All samples were stored under cool and dark conditions until they were analysed.

Analytical

Immediately after the samples were taken, pH was measured using a glass combination electrode. The alkalinity of the samples was determined by titration with HCl to pH 4.3. Concentrations of dissolved hydrocarbons were determined by GC headspace analysis on an HP 6890 + gas chromatograph, which was equipped with a headspace autosampler and a combination of flame ionisation detector and electron capture detector. Concentrations of dissolved H_2 were determined using an HP Micro GC, which was equipped with

Table 1 Composition of the influent solution (site ground water spiked with contaminants)

Parameter	Unit	Mean value	+/−	Minimum	Maximum
pH		7.49	0.23	7.18	7.82
Na	mg/l	2,750	170	2,540	2,950
K	mg/l	71.1	3.1	67.7	75.8
Ca	mg/l	145	16	126	164
Mg	mg/l	184	21	163	213
Fe	mg/l	<0.25	–	<0.25	<0.25
Mn	mg/l	0.14	0.222	<0.25	0.488
Cr	µg/l	24.6	18.4	7.4	53.2
Si	mg/l	2.29	0.64	1.72	3.13
NH_4^+	mg/l	<0.025	–	<0.025	<0.025
Alkalinity	mg/l HCO_3	470	11	460	490
Cl^-	mg/l	3,930	310	3,500	4,390
SO_4^{2-}	mg/l	620	60	564	711
NO_3^-	mg/l	26.8	22.6	14.8	72.8
Br^-	mg/l	15.4	0.6	14.4	16
TCM	µg/l	929	137	715	1,100
BDCM	µg/l	55.2	12.8	37.6	74
DBCM	µg/l	14.2	12.4	1.1	28.9
TBM	µg/l	24.7	13	13.6	48.2
1,2-DCA	µg/l	38.3	10.4	26.1	53.8
PCE	µg/l	18.8	2.6	14.9	22.8
TCE	µg/l	39.9	9.2	30.2	56.5
1,1-DCE	µg/l	26.2	7.7	17.7	37.3
VC	µg/l	21.1	1.6	18.3	22.8
1,1,2-TCA	µg/l	9.12	4.29	5.48	15.3
1,2-DCP	µg/l	25.1	14.9	<1.5	41.4
Benzene	µg/l	20.8	4.9	15.2	28.9
MCB	µg/l	260	149	158	559

a thermal conductivity detector. Total dissolved concentrations of Ca, Mg, Fe, Mn, Na, K and Si were determined using ICP-AES analysis (VARIAN VISTA AX). Due to high background Na concentrations, measurements were performed in tenfold diluted solutions. Ammonium concentrations were determined by photometric analysis (ZEISS PM2DL). Concentrations of Cl^-, Br^-, NO_3^- and SO_4^{2-} were determined by ion chromatography (Dionex DX 500). Due to the elevated concentrations of Cl^- and SO_4^{2-}, measurements were performed in 100-fold diluted samples for Cl^- and in tenfold diluted solutions for the other anions. Concentrations of total inorganic carbon (TIC) were calculated with sample data on alkalinity, anion and cation concentrations by geochemical equilibrium calculations using PHREEQC (Parkhurst and Appelo 1999). Cr concentrations were determined by ICP-MS analysis (Agilent 7500 ORS ICP-MS).

Results and discussion

pH and concentrations of inorganic water constituents

Due to anaerobic corrosion of ZVI, pH values increased in the column containing ZVI from 7.2–7.8 in the column inflow to 8.9–9.4 in the outflow over the course of the experiment (Fig. 2). With increasing running time in the experiment, a zone of relatively stable pH level developed near the column inflow, probably due to passivation of ZVI. Elevated concentrations of dissolved H_2 up to approx. 800 µmol/l indicated that a strongly reducing environment developed in the column containing ZVI. Concentrations of Ca and Mg decreased by 2.0–3.2 and 0.85–1.35 mM, respectively, through contact with ZVI. Together with the decrease in TIC (by 5.5–7.6 mM), this indicates that carbonates precipitated in the ZVI due to the increased pH. As the decrease in TIC exceeded that of the total Ca and Mg (approx. 2 mM) concentrations, carbonate containing Fe^{2+}, e.g. siderite, most likely contributed to carbonate precipitation. Precipitation of iron carbonates and of iron (hydr)oxides provides a possible explanation why elevated concentrations of dissolved iron (up to 10.8 mg/l) were found only in small areas near the column inflow where pH had not reached the high values which were observed after longer residence times with ZVI. Si (1.7–3.1 mg/l) was completely removed from the solution through contact with ZVI, most probably due to the formation of surface complexes at the particle–water interface (e.g. Davis et al. 2002). Initially, sulphate concentrations remained stable in contact with ZVI. In contrast, after 40 days and during later sampling events, a significant decrease of sulphate concentrations by max. 140 mg/l through contact with ZVI was observed. This is a strong indicator that the sulphate-reducing bacteria which were added to the system after a running time of 7 days established themselves, resulting in the partial reduction of dissolved sulphate. Nitrate (14–72 mg/l) was completely removed from the solution in contact with ZVI throughout the experiment. Initially, the greatest part of the nitrate concentration decrease (max. 68% after 15 days) was balanced out by the production of dissolved ammonium. During later sampling events, smaller amounts (e.g. 8 mol% after 61 days) of the decrease of nitrate concentration were balanced by ammonium production. This indicates a change of the reduction

Table 2 Sampling schedule for the columns containing ZVI and GAC

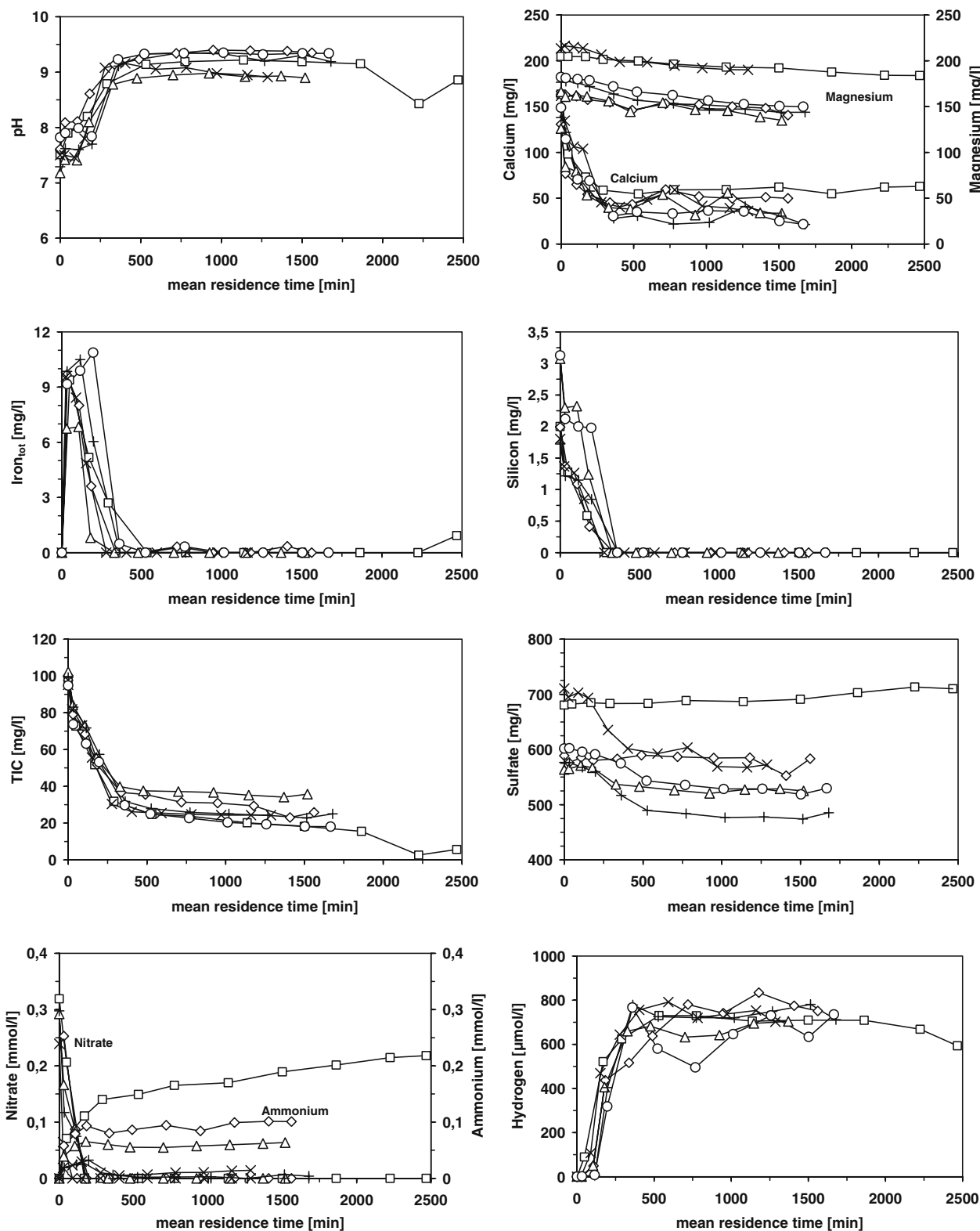| Running time (days)	15	29	40	47	54	57	61
Exchanged pore volumes ZVI	10	19	30	38	44	46	50
Exchanged pore volumes GAC	392	781	1,230	1,546	1,791	1,901	2,042
Samples ZVI	x	x	x	x	x		x
Samples GAC	x	x	x	x	x	x	x

Fig. 2 pH profiles and concentration profiles of Ca, Mg, Fe, Si, TIC, sulphate, nitrate, ammonium and dissolved hydrogen in the column containing ZVI during the sampling events after 15 days (-*open square*-), 29 days (-*open diamond*-), 40 days (-*open upper triangle*-), 47 days (-*times*-), 54 days (-*plus*-) and 61 days (-*open circle*-) running time. Note limited concentration scale range for sulphate

mechanism for nitrate from the abiotic reduction of nitrate by Fe^0, which leads to stoichiometric production of ammonium (Till et al. 1998), to the microbial reduction of nitrate to N_2 or N_2O by autotrophic bacteria. Consequently, nitrate-reducing and sulphate-reducing bacteria appeared to have established themselves by the end of the experiment, reflecting the microbial processes which are also expected for a field application. In contact with the GAC, changes of pH and concentrations of inorganic compounds were in general minor, with the most notable changes being a pH decrease of max. 0.3 units and a decrease of dissolved H_2 concentrations of max. 260 μmol/l (results not shown).

Contaminant degradation in contact with zero valent iron

Through contact with ZVI, TCM was completely degraded until low concentrations were detected in the ZVI outflow after 50 exchanged PV (Fig. 3). The results of linear regression analysis (Table 3) show that TCM half-lifes increased during the experiment from 92 to 221 min, indicating a loss of ZVI reactivity towards TCM. In total, 8–16.5% of the TCM was converted to DCM, which did not show significant further degradation through contact with ZVI. These results compare well with the results of Matheson and Tratnyek (1994), who also observed reductive dechlorination of TCM to DCM without apparent further DCM degradation, although these authors observed higher mole fractions (typically 50%) of DCM resulting from TCM degradation.

Compared to TCM, the brominated methanes TBM, BDCM and DBCM showed considerably faster degradation. Due to these fast degradation kinetics and the relatively low inflow concentrations of these compounds, they were not detected in the first sampling port (< 50 min residence time) during most sampling events (Fig. 3). Consequently, it was not possible to determine whether the kinetic behaviour of these compounds can be adequately described by pseudo first-order kinetics. Nevertheless, as TCM degradation kinetics could be adequately described by pseudo first-order degradation kinetics in the experiment, and Gillham and O'Hannesin (1994) observed pseudo first-order kinetics for TBM as well as for TCE degradation by ZVI in batch experiments, it is reasonable to assume that pseudo first-order kinetics can be used to describe the degradation of TBM, DBCM and BDCM through contact with ZVI in the present column experiment. Assuming pseudo first-order degradation kinetics provides estimated half-lifes for TBM, DBCM and BDCM of < 8 min.

PCE, TCE and 1,1-DCE concentrations were reduced to below detection limits through contact with ZVI (Fig. 4). VC was initially completely degraded through contact with ZVI. After 40 days running time, the VC degradation rate had slowed down, and 6.1–11.5 μg/l VC were observed in the column outflow from this time until the end of the experiment. Although for PCE, TCE and 1,1-DCE few data points were available for correlation analysis due to the low influent concentrations and the comparatively fast degradation kinetics of these compounds, their decrease of concentration could be approximated by pseudo first-order kinetics (Table 3). PCE exhibited longer half-lifes than TCE and 1,1-DCE. Although it is typically observed that the dechlorination rate of chlorinated ethylenes by ZVI increases with an increasing number of chlorine substituents, this comparatively slow degradation of PCE may be explained by predominance of an indirect mechanism of chlorinated ethylene reaction by hydrogen adsorbed to the iron surface under anodic iron corrosion control (Farrell et al. 2000). Other isomers of DCE, i.e. *trans-* and *cis-*1,2-DCE, which represent possible breakdown products of PCE and TCE, were not detected in any sample throughout the experiment.

1,1,2-Trichloroethane concentrations decreased to below detection limits through contact with ZVI (Fig. 5) until after 61 days running time, low concentrations (1.2 μg/l) were detected in the ZVI outflow. As expected, 1,2-DCA did not show any apparent degradation through contact with ZVI. The increased concentration in contact with ZVI observed after 19 PV had been exchanged in the ZVI (29 days running time) was most probably due to higher inflow concentrations than intended during the initial phase of the experiment. This led to comparatively high concentrations in the downgradient part of the column containing ZVI. 1,2-DCP was only partially degraded through contact with ZVI. Assuming that 1,2-DCP degradation followed pseudo first-order kinetics, half-lifes increased during the experiment from 788 min after 29 days to 3,520 min after 61 days running time. Consequently, 1,2-DCP exhibited the slowest degradation kinetics of the compounds which could be degraded through contact with ZVI. It would be the limiting factor for the dimensions of the ZVI reactor if complete dehalogenation of these compounds was required in the ZVI reactor.

Benzene concentrations initially decreased through contact with ZVI (Fig. 5) to below detection limits. After 40 and 47 days, benzene nearly unaffected passed through the ZVI, indicating that sorption to ZVI particle surfaces contributed to the initial benzene concentration decrease until a sorption equilibrium was reached. Later in the experiment (after 54 and 61 days), benzene concentrations decreased in a narrow zone between the inflow and the first sampling port by max. 17 μg/l. As reductive degradation of a reduced compound like benzene by ZVI is unlikely, this concentration decrease most probably can be attributed to
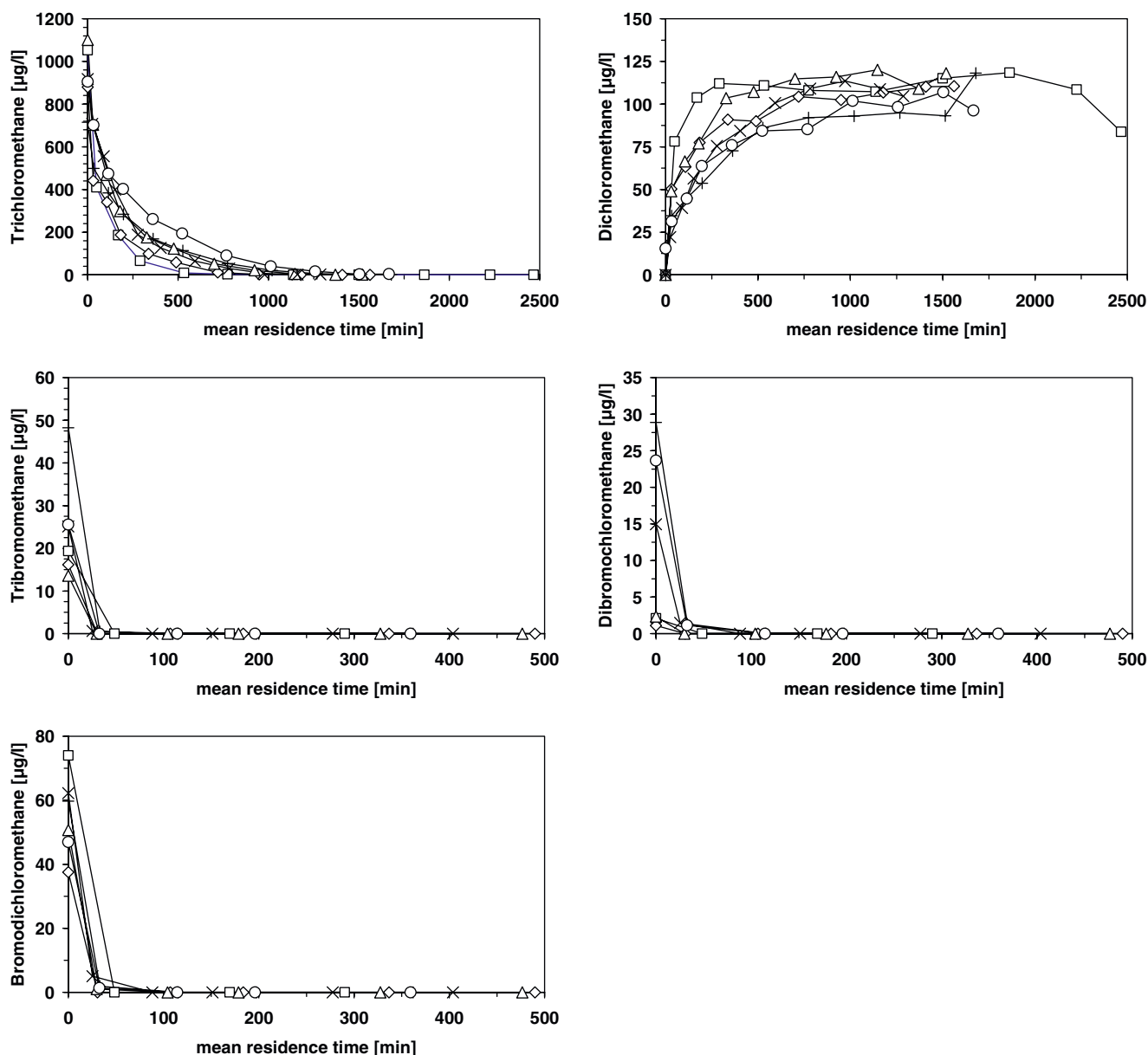
Fig. 3 Concentration profiles of halogenated methanes in the column containing ZVI during the sampling events after 15 days (-*open square*-), 29 days (-*open diamond*-), 40 days (-*open upper triangle*-), 47 days (-*times*-), 54 days (-*plus*-) and 61 days (-*open circle*-) running time. Note shorter residence time scale for brominated methanes

microbial aerobic degradation of benzene using dissolved oxygen which resulted from diffusion of small amounts of oxygen through the viton tubing during transport of the feed solution from the Tedlar® bag to the column system. Microbial benzene degradation, e.g. by sulphate-reducing bacteria (Wiedemeier et al. 1999), inside of the ZVI appears to be unlikely because the zone of sulphate reduction observed later in the experiment did not spatially coincide with the zone of benzene concentration decrease.

MCB concentrations decreased through contact with ZVI to below detection limit throughout the experiment. This result was unexpected, because degradation of MCB through contact with ZVI has been observed to be negligible (e.g. Wüst 2000). According to the same author, significant reduction of MCB as an intermediate product of dechlorination of 1,4-dichlorobenzene to benzene as a stable end product was only observed when more reactive materials, such as palladised ZVI, were used. Consequently, if MCB were reductively degraded

Table 3 Calculated half-lifes for pseudo first-order reductive dehalogenation by ZVI (n/a: no data available due to inflow concentrations deviating from those intended)

Running time (days)	15	29	40	47	54	61	Mean half-life (min)
	Half-life (min)	Half-life (min)	Half-life (min)	Half-life (min)	Half-life (min)	Half-life (min)	
TCE	50	68	67	84	100	83	75
1,1-DCE	58	89	85	86	169	151	106
PCE	93	92	122	142	171	164	131
TCM	92	118	149	138	177	221	150
1,1,2-TCA	n/a	375	496	363	454	699	477
VC	360	545	1,093	2,091	2,145	1,894	1,355
1,2-DCP	n/a	788	2,491	1,981	2,051	3,524	2,167

by the ZVI that was used in the present experiment, increased benzene concentrations should have been observable. However, such increased benzene concentrations were not observed. According to Dahmke et al. (1999), who observed a considerably higher sorption for MCB compared to benzene in an on-site column experiment with ZVI at a different site, one possible explanation for the sustained MCB concentration decrease through contact with ZVI is that MCB was sorbed to surfaces of ZVI or precipitates such as iron (hydr)oxides or carbonates which were freshly generated

during the experiment through ZVI corrosion and mineral precipitation. This would also explain why MCB concentrations decreased faster than benzene concentrations because MCB is a more hydrophobic substance than benzene (log $K_{OW} = 2.92$ for MCB and 2.13 for benzene, Schwarzenbach et al. 1993). An additional possible mechanism for MCB removal is the microbially catalysed degradation of MCB by nitrate-reducing bacteria, which has been previously demonstrated (e.g. Wünsche et al. 1999). Even under optimised conditions, however, such degradation occurs at con-
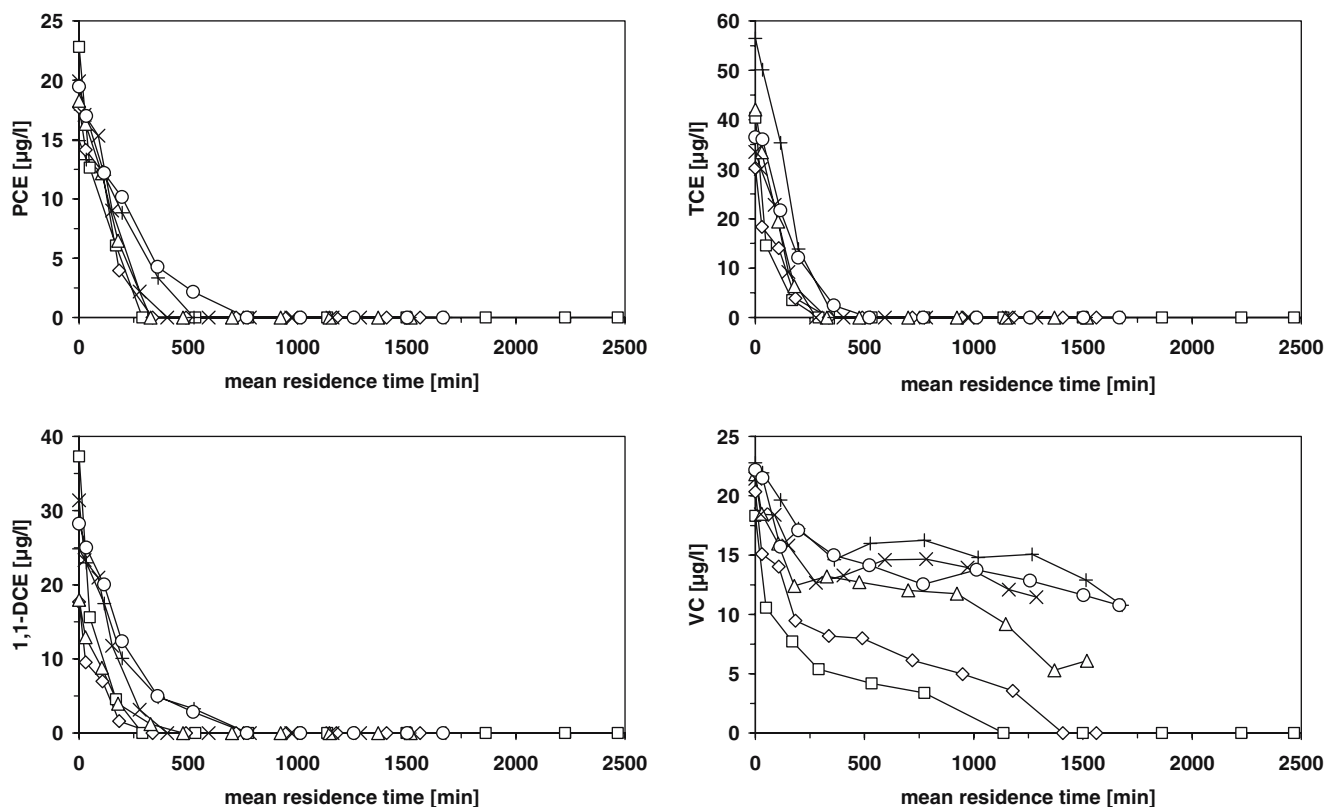
Fig. 4 Concentration profiles of chlorinated ethylenes in the column containing ZVI during the sampling events after 15 days (-*open square*-), 29 days (-*open diamond*-), 40 days (-*open upper triangle*-), 47 days (-*times*-), 54 days (-*plus*-) and 61 days (-*open circle*-) running time; *cis*-1,2 DCE and *trans*-1,2-DCE were not detected throughout the experiment
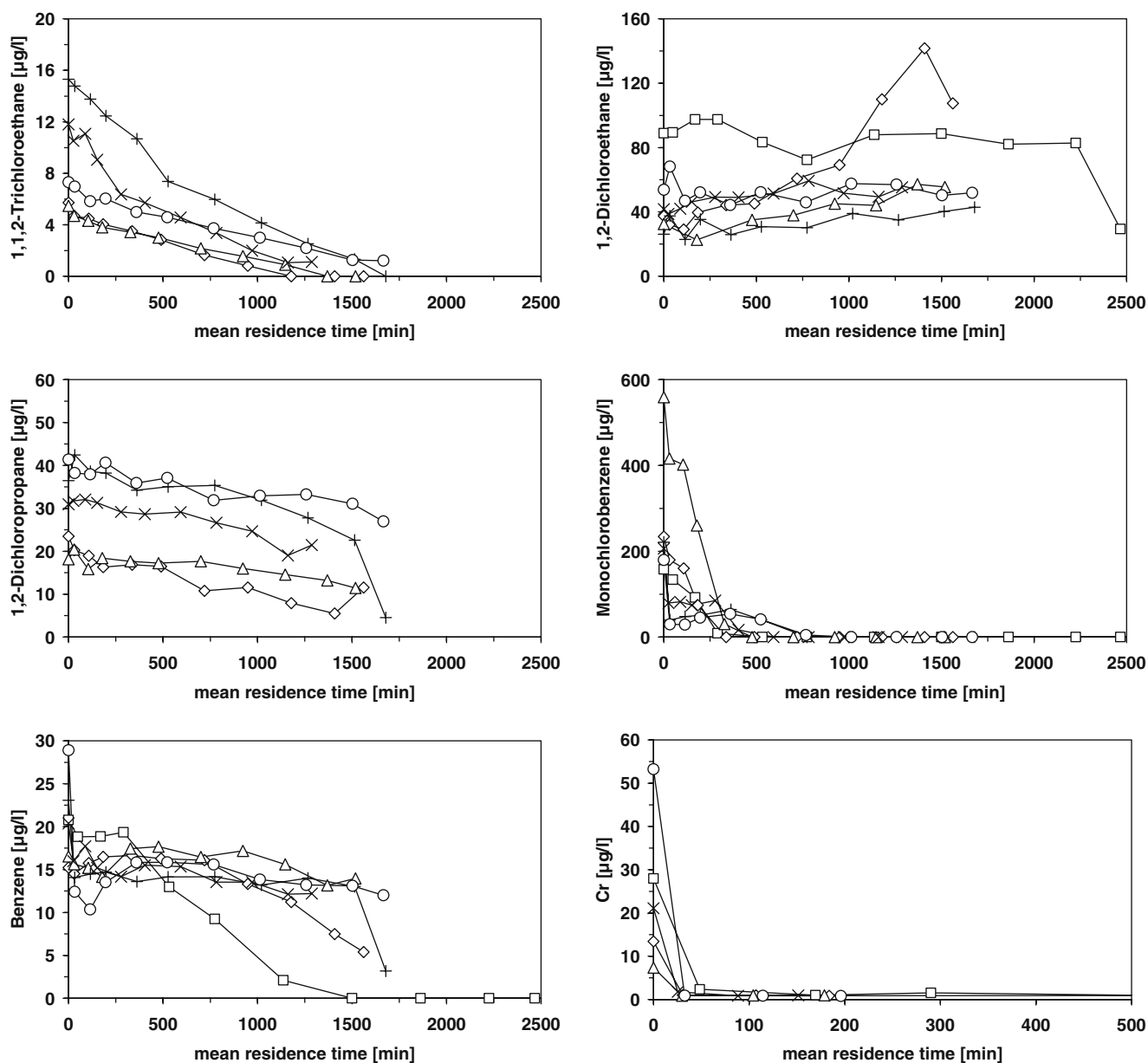
Fig. 5 Concentration profiles of 1,1,2-TCA, 1,2-DCA, 1,2-DCP, MCB, benzene and Cr in the column containing ZVI during the sampling events after 15 days (-*open square*-), 29 days (-*open diamond*-), 40 days (-*open upper triangle*-), 47 days (-*times*-), 54 days (-*plus*-) and 61 days (-*open circle*-) running time. Note shorter residence time scale for Cr

siderably slower rates than aerobic MCB degradation. Wünsche et al. (1999) also observed MCB degradation by sulphate-reducing bacteria. However, as the onset of sulphate reduction was later observed during this experiment, sulphate-reducing bacteria cannot account for the sustained MCB removal observed here. Starting after 29 days, an additional MCB concentration decrease was observed between the column inflow and the first sampling port, possibly indicating an aerobic

microbial MCB degradation in the tubing similar to that discussed above for benzene.

Chromium concentrations were reduced to < 2.5 µg/l after a reaction length of 2 cm through contact with ZVI throughout the experiment. This can be explained by the reduction of Cr(VI) to Cr(III) through contact with ZVI, with subsequent precipitation as Cr(III) hydroxide or sorption to iron (hydr)oxides (e.g. Kaesche 1990; Schlicker et al. 2000).

For all halogenated hydrocarbons which were degraded through contact with ZVI, half-lifes increased during the experiment (Fig. 6), indicating that ZVI reactivity with respect to these substances decreased over time. Further, the development of a zone without significant pH increase near the upgradient end of the column containing ZVI provides further evidence of a decrease in ZVI reactivity. Various processes may have contributed to this decrease of reactivity, including surface passivation of the ZVI either by precipitation of iron (hydr)oxides or carbonates or by formation of surface complexes with Si on the surfaces of ZVI particles. The establishment of sulphate-reducing bacteria after 40 days running time (30 exchanged PV in the ZVI) coincided with a distinct increase in half-lifes of TCM, PCE, VC and 1,2-DCP. This indicates that microbial sulphate reduction may decrease the reactivity of ZVI towards these substances by promoting surface passivation through precipitation of sulphide phases. While Cr precipitation or sorption may also lead to surface passivation of ZVI (Schlicker et al. 2000), it is unlikely that these processes significantly contributed to ZVI surface passivation at the low Cr concentrations which were added to the influent solution.

Contaminant sorption in contact with granular activated carbon

In the GAC column, DCM concentrations initially decreased to below the detection limit (Fig. 7). A breakthrough of DCM through the GAC was observed later in the experiment (1.4 µg/l in the outflow after 40 days, corresponding to 1,230 exchanged PV in the GAC). Using a mean DCM concentration of 106 µg/l in the GAC inflow, it can be calculated that 175 µg DCM/

g GAC had been sorbed at that time. After 61 days (2,040 exchanged PV in the GAC), the sorption capacity was exhausted, and no concentration decrease of DCM was observed through contact with GAC. The equilibrium sorption capacity was 245 µg DCM/g GAC. Remaining concentrations of 1,2-DCA, 1,2-DCP, benzene, VC, 1,1,2-TCA and TCM which had not been removed through contact with ZVI were reduced to below detection limits in the GAC column due to sorption throughout the experiment, with the exception of the sampling event after 57 days (1,900 exchanged PV in the GAC) when small MCB concentrations (3.6 µg/l) were detected in the column outflow (Fig. 8). Consequently, DCM sorption capacity limited the lifetime of the GAC, while the other compounds did not break through the GAC throughout the experiment. Nevertheless, in the long term a limiting influence of VC cannot be excluded, because VC exhibits a lower tendency to adsorb on organic phases than DCM (K_{OW} for VC = 0.60 and for DCM = 1.15, Schwarzenbach et al. 1993). The fact that VC did not break through the GAC earlier than DCM in the present experiment may be due to the initial phase of the experiment. During this phase, VC was completely degraded by ZVI and consequently did not enter the GAC, while DCM passed the ZVI unaffected and was sorbed to the GAC throughout the experiment. Over longer periods of time, if VC is incompletely degraded in the ZVI, elevated VC concentrations will be found in the ZVI outflow, and the VC sorption front might reach the preceding DCM sorption front in the GAC. One possible way of avoiding breakthrough would be to choose the dimensions of the ZVI reactor such that complete VC degradation can be assured even with a certain degree of ZVI passivation. Similarly, overdimensioning of the ZVI reactor in a sequenced PRB consisting of ZVI and GAC to overcome possible problems arising from unfavourable VC sorption properties on GAC has recently been proposed by Kouznetsova et al. (2003). Further, VC accumulation in the column outflow could be prevented by choosing another type of iron which shows faster degradation rates for VC than for PCE or TCE, such as described by Arnold and Roberts (2000) or Schäfer et al. (2003). As in previous studies (e.g. Köber et al. 2001a), negative effects of the sequential coupling of ZVI with GAC, such as possible decreases in porosity due either to precipitation of mineral phases or to bioclogging, were not observed during the course of the experiment.
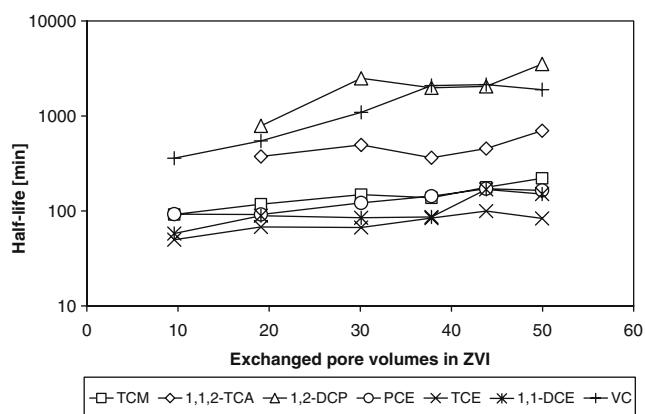

Fig. 6 Development of half-lifes for the degradation of TCM, 1,1,2-TCA, 1,2-DCP, PCE, TCE, 1,1-DCE and VC through contact with ZVI over experiment running time (expressed as exchanged pore volumes in the ZVI)

Conclusions

The results of the experiment described here show that the complex contaminant mixture containing halogenated aliphatic and aromatic hydrocarbons, benzene and chromate can be remediated by a sequenced PRB
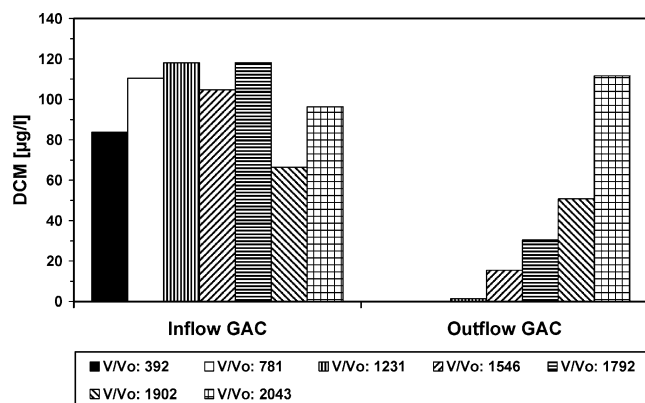
Fig. 7 DCM concentrations in the inflow (*left*) and outflow (*right*) of the column containing GAC

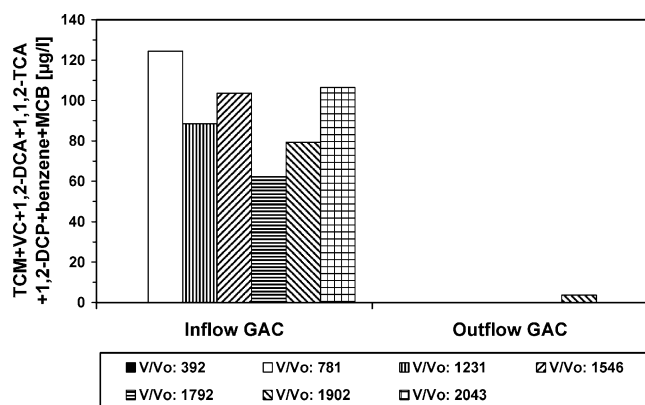**Fig. 8** Sum of TCM, VC, 1,2-DCA, 1,1,2-TCA, 1,2-DCP, benzene and MCB concentrations in the inflow (*left*) and outflow (*right*) of the column containing GAC

consisting of ZVI and GAC. As the degradation of TBM, DBCM and BDCM was observed to be consid- erably faster than the degradation of TCM, brominated methanes are unlikely to limit system performance un- less they are present in very high concentrations. To our knowledge, the degradation of DBCM and BDCM by nonpalladised iron was demonstrated in a column experiment for the first time. A range of halogenated compounds was degraded through contact with ZVI. The dimensions of the ZVI reactor will mainly be dominated by the economic trade-off between dehalo- genation of these compounds by ZVI and sorption to the GAC. The observed DCM breakthrough indicates that the DCM sorption capacity is the critical parameter for the dimensions of the GAC reactor, and in the case of a nonlinear (e.g. Freundlich) sorption isotherm, the GAC lifetime depends on the TCM fraction which is con- verted to DCM (observed 8–16.5%). Other compounds (with the possible exception of VC) will not limit the GAC lifetime unless they enter the activated carbon in concentrations which are considerably higher than ob- served in the present experiment. As in previous studies by other researchers, no negative effects of sequential coupling of ZVI with GAC were observed, indicating that such a combination is able to successfully remediate the mixed contamination which is found at the site. As a continuous decrease of reactivity of the ZVI was ob- served during the experiment, appropriate safety factors should be regarded for the dimensions of the ZVI reactor to ensure that residence times in contact with the ZVI are sufficient for the removal of the contaminants concerned (especially TCM and VC), even if half-lifes increase during operation of the PRB.

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