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In Situ Destruction of Chlorinated Hydrocarbons in Groundwater Using Catalytic Reductive Dehalogenation in a Reactive Well: Testing and Operational Experiences

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Abstract

A groundwater treatment technology based on catalytic reductive dehalogenation has been developed to efficiently destroy chlorinated hydrocarbons *in situ* using a reactive well approach. The treatment process utilizes dissolved H_2 as an electron donor, in the presence of a commercial palladium-on-alumina catalyst, to rapidly reduce common chlorinated aliphatics such as trichloroethylene and tetrachloroethylene into non-chlorinated hydrocarbons such as ethane. Rapid reaction rates permit the deployment of a treatment unit within a dual-screened well bore, allowing contaminated groundwater to be drawn from one water-bearing zone, treated within the well bore, and discharged to an adjacent zone with only one pass through the system. A demonstration groundwater treatment system based on this concept was evaluated in a chlorinated hydrocarbon contaminated aquifer at a major Superfund site. The system rapidly destroyed a variety of common contaminants such as TCE and PCE and maintained its performance for a test period of one year. Operation of the treatment system was optimized to maintain catalyst activity and to prevent formation of intermediate compounds.

Introduction. Groundwater contamination by trichloroethene (TCE), tetrachloroethene (PCE), and other chlorinated hydrocarbons is a well-recognized environmental problem. Conventional treatment technologies such as air-stripping with activated carbon adsorption require the construction of surface treatment facilities and produce secondary waste streams.

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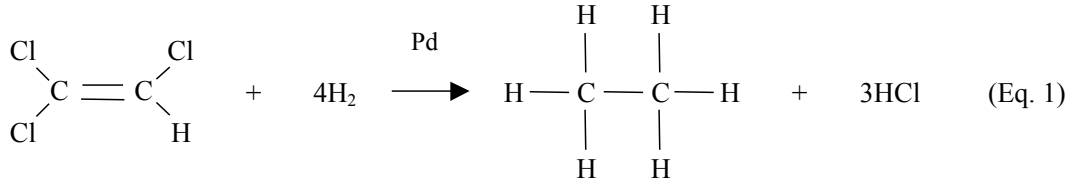
Alternative subsurface treatment techniques such as natural bioremediation or passive chemical filter walls may circumvent some of these problems but are subject to their own associated difficulties (e.g., sensitivity to the aquifer biogeochemistry, slow reaction rates, depth to contaminated zone). As a result, new treatment technologies are continually being sought.

Recent studies have indicated that a variety of halogenated hydrocarbons may be subject to reductive dehalogenation by dissolved H_2 in aqueous systems in the presence of metallic palladium acting as a catalyst. TCE, for example, is ultimately transformed by catalytic reductive dehalogenation into ethane and hydrochloric acid,



Schreier and Reinhard (*1*) observed the rapid transformation of TCE, PCE, *cis*- and *trans*-1,2-dichloroethene (*cis*- and *trans*-1,2-DCE), and vinyl chloride in batch systems using small quantities of palladium supported by alumina or carbon. Reductive dehalogenation by H_2 on palladium also appears to be effective in reducing 1,2-dibromo-3-chloropropane (*2*) and chlorinated aromatic compounds (*3*). Liang et al. (*4*) showed that a bimetallic treatment approach entailing palladium and iron led to faster reaction rates in the reductive dehalogenation of TCE than iron metal alone. Electrolysis cells featuring palladium cathodes have also been shown to be effective in reducing halogenated hydrocarbons, including 1,1,2-trichloro-1,2,2-trifluoroethane (*5*) as well as 2,4-D and other chloroaromatic pesticides (*6, 7*). McNab and Ruiz (*8*) employed a hybrid approach combining electrolytically-generated H_2 with a commercial catalyst material consisting of palladium supported on alumina beads in a flow-through column arrangement to dechlorinate PCE, TCE, 1,1-dichloroethene (1,1-DCE), and carbon tetrachloride.

Chloroform was also reduced in the same study, but at a slower rate, whereas 1,2-dichloroethane (1,2-DCA) did not suffer any appreciable reduction.

Treatment of contaminated groundwater by catalytic reductive dehalogenation would offer several advantages. First, reaction rates for a number of common chlorinated hydrocarbons in solutions containing dissolved H_2 and a supported palladium catalyst are relatively fast, with first-order half-lives on the order of seconds to minutes, depending on experimental conditions (*1*, *8*). Thus, short residence times within a reactor unit could permit a compact design for treatment within a well bore. In addition, the presence of dissolved O_2 does not stop the dehalogenation reactions through competition for H_2 (although reaction rates may be reduced). This result implies that catalytic reductive dehalogenation systems could be deployed in naturally aerobic aquifer settings without the need to remove O_2 from the influent stream prior to treatment. Finally, halogenated intermediate transformation products, which are a significant concern in biological systems, have generally not been observed in previous studies.

The purpose of the study described herein was to assess the suitability of catalytic reductive dehalogenation for well-bore treatment of chlorinated hydrocarbons at a site within Lawrence Livermore National Laboratory (LLNL), east of San Francisco, California. The particular location at the LLNL site required a novel treatment approach because tritium in the subsurface complicated the task of treating groundwater at the surface with conventional methods while other factors precluded alternative *in situ* techniques. A prototype well bore treatment unit was installed to assess performance under field conditions and to identify optimal operating conditions.

Field Testing

Hydrogeologic Setting. The LLNL site, located east of San Francisco, is underlain by Tertiary and Quaternary unconsolidated alluvial sediments derived from the California Coast Ranges.

Groundwater beneath the facility has been impacted by chlorinated hydrocarbons as a result of historical usage and disposal dating from the 1940s. Depth to groundwater is generally on the order of 20 to 30 m, depending on location. A number of distinct hydrostratigraphic units (HSUs), through which contaminants reside and migrate as groundwater plumes, have been identified by subsurface investigation activities (*9*). Groundwater across the site is aerobic, with very little organic matter present in the sediments. As a result, the chlorinated hydrocarbons do not appear to be undergoing any appreciable intrinsic reductive dehalogenation (*10*).

The test area of concern for this study at the LLNL site is characterized by relatively high concentrations of chlorinated hydrocarbons (up to 30 parts-per-million in some wells) as well as tritium (up to 20,000 picocuries/L) associated with waste disposal pits that were used between the 1950s and 1970s. The highest concentrations of both types of contaminants are located in one particular hydrostratigraphic unit, HSU 3. The presence of tritium in the groundwater complicates conventional pump-and-treat approaches to remediating the chlorinated hydrocarbon contamination because of the potential for accidental releases to the environment and because of the need to dispose of mixed wastes (tritiated spent activated carbon) generated from air-stripping. The aerobic groundwater environment precluded natural reductive dehalogenation as a means of remediation, while the depth to groundwater rendered the placement of passive treatment walls (e.g., using iron filings) impractical. Given these constraints, the decision was made to test the remediation of the chlorinated hydrocarbons within a flow through well bore, discharging the tritiated effluent back into the subsurface where it would self-remediate through radioactive decay. Previous subsurface investigations in the area had identified two separate sand units within HSU 3, separated by a clay layer, which would serve as a source of contaminated influent water and a discharge location for treated water, respectively. Both sands were characterized by similar contaminant chemical profiles: TCE, PCE, 1,1- DCE, chloroform,

carbon tetrachloride, and 1,2-DCA with a total concentration of chlorinated hydrocarbons of approximately 4,000 to 5,000 parts per billion. Tritium was also present in both sands at a concentration of approximately 8,000 picocuries/L. The background groundwater chemistry, which is typical of conditions across the LLNL site, is given on Table 1.

Design. The configuration of the pilot *in situ* treatment system is shown on Figure 1. The well-bore treatment system is designed to draw water from one water-bearing zone, destroy the chlorinated contaminants in the influent stream, and then discharge the treated effluent to an adjacent water-bearing zone. Given sufficient residence time within the treatment unit, high removal efficiency could be achieved on a single pass, so that multiple passes through the unit (i.e. a recirculating well) were not anticipated in the design of the unit. The major components of the treatment system included: (1) an H_2 injection and dissolution system, (2) two fixed bed catalyst columns, (3) a pumping system and associated plumbing, (4) a pneumatic packer assembly, and (5) sensors and instruments for controls, interlocks, and data acquisition. In-well equipment was placed in a 20.3-cm inner diameter PVC well casing with dual screened intervals.

Hydrogen Supply System. A module containing hydrophobic microporous hollow fiber membranes (Celgard, Inc.) was used to dissolve H_2 gas into the groundwater treatment stream. Hydrogen gas was supplied in bottled form. The hollow fibers, consisting of a bundle of 28-cm-long 300-μm-diameter filaments, provided a contact area between the gas and aqueous phases of approximately 1.4 m^2 per cubic cm of module interior space, allowing for rapid mass transfer. Transfer was effected by diffusion of H_2 across the membrane between the gas and aqueous phases, as opposed to direct injection of H_2 gas. Operation of the membrane system has been studied and modeled by hollow fiber membrane designers **(***11*).

Catalyst Beds. Two packed-bed catalyst beds were constructed as columns in series downstream of the H_2 injection module. The first column was designed to remove most of the chlorinated hydrocarbon mass, while the second column was intended to function as a polishing step. Both columns were constructed of stainless steel, 15 cm in diameter, with lengths of 2.5 m and 2.4 m, respectively, with stainless steel screens on the ends to support the catalyst material. The packed bed catalyst material, obtained from Prototech, Inc., consisted of uniform alumina (Al_30_2) spheres, coated with 1% palladium metal by weight, with a particle density of approximately 1.2 g/cm^3. The first column was packed with 30 kg of 0.32-cm nominal diameter spheres, while the second column was packed with 22 kg of 0.16-cm nominal diameter spheres. The deployment of different size catalyst beads in the two columns reflects a compromise between removal efficiency, which is higher in the presence of the smaller spheres as a result of greater surface area, and the need to maintain a relatively low pressure drop across the columns.

Other System Components. A centrifugal ten-stage 10-cm diameter pump (Goulds, Inc.) was used to direct water from the lower screened interval through 25-μm sediment filters, the H_2 injection module, and the two catalyst beds and then into the upper zone. A pneumatic packer was used to isolate the two screened intervals in the well to prevent flow short-circuiting. Sample ports were located in the influent reactor stream, after the H_2 injection module, and in the effluent streams of both catalyst columns. System performance was regulated by a combination of manual and automatic controls. Labview 5 (Labview, Inc.) software was used on a Microsoft Windows NT platform for data acquisition and system control. An Opto 22 controller was employed to process instrument analog and digital input and output signals. The system was designed to shut down automatically via interlock controls under abnormal operating conditions (e.g., pump failure/loss of flow, H_2 supply failure).

Operational Parameters. Aquifer testing of the reactive well prior to startup of the treatment system indicated that the well could sustain pumping rates on the order of 4 to 6 L/min. Thus, the treatment system was operated at 4 L/min to provide a margin of safety against de-watering, yielding residence times of approximately 5 min and 6 min within the first and second catalyst columns, respectively. An H_2 injection rate of approximately 120 mL/min at 3 atm pressure was applied to maintain saturation.

Previous bench-scale experiments by McNab and Ruiz (*8*) indicated that deactivation of the catalyst, which was expected to occur in the reactive well, could be reversed by periodically removing the H_2 supply. To address this issue, the initial phase of system testing involved operating the unit from four to eight hours per day. Water samples were collected from the influent sampling port as well as the effluent ports from both catalyst columns for chlorinated hydrocarbon and dissolved gas analyses.

Following shutdown of the unit each day, the catalyst columns were purged with three pore volumes of non-hydrogenated groundwater and then drained, exposing the catalyst beads to the atmosphere above the water level in the well. In addition, the catalyst columns were purged with deionized water at the end of each week of operation, drained, and left idle over weekends. The total elapsed time for the phase of testing reported in this paper was 76 days of operation.

Analytical Methods. Water samples for chlorinated hydrocarbon analyses were collected in 60 mL bottles with Teflon-coated caps, filling completely to exclude headspace, chilled on ice, and analyzed within 24 hrs using a modified EPA Method 601 **(***12*). Dissolved gases (H_2, N_2, O_2, and Ar) were analyzed using a custom membrane-inlet gas mass spectrometer (MIMS) following techniques outlined by Kana et al., (*13*). Water samples for dissolved gas analyses were collected in 75 ml valved, double-end, stainless steel bottles at the pressure present in the

system; no depressurization on sampling occurred. Samples were analyzed promptly (within 2 h of collection). System calibration was based on two standards: water in equilibrium with 1 atm of H_2 and water in equilibrium with 1 atm of air. A liquid nitrogen trap was used between the membrane-inlet and the mass spectrometer to eliminate water vapor and CO_2. The detection limit for H_2 and O_2 was approximately 0.1% of equilibrium solubility of pure gas.

Results

Results obtained from initial testing for operating periods of 4 h/day are shown in Table 2. Among the chlorinated hydrocarbons present in the influent stream, PCE, TCE, 1,1-DCE, and carbon tetrachloride were effectively remediated by the system, with most of the removal occurring across the first catalyst column. Daughter products of reductive dehalogenation of TCE (*cis*-1,2-DCE and vinyl chloride) were not observed, except for trace levels of cis-1,2-DCE which may have been present in the influent. Chloroform exhibited some resistance to the process but was still largely transformed. 1,2-DCA appeared to be highly resistant to the treatment process and passed through both catalyst columns without undergoing any significant reaction. For TCE and the other chlorinated ethenes, reaction half-lives across first catalyst column were on the order of 20 to 30 seconds for 30 kg of catalyst (300 g of Pd) in 19 liters of water. These results are consistent with laboratory results recently reported by Lowry and Reinhard (*14*).

After the first 20 days of initial testing, treatment time was increased to a period of approximately 8 hrs/day. After a subsequent 10 days, removal efficiency began to decline (Table 3). This change in system behavior was not only characterized by breakthrough of the original contaminants; vinyl chloride, an intermediate reductive dehalogenation product, began to be produced within the first catalyst column. To test whether or not the degradation in treatment system was reversible, the operating period was reduced back to approximately 4

hrs/day, with a number of days without operation. The result of this action was a recovery of treatment capacity (Figure 2). Toward the end of the experiment period, a daily operational duration of 5 to 6 h/day seemed to maintain stable performance. Vinyl chloride was not observed subsequently.

Concentrations of dissolved gases across the treatment system, essentially constant over the duration of the experiment, are given in Table 4. Both O_2 and H_2 appear to be removed across the first catalyst bed. Given the influent chlorinated hydrocarbon concentrations, approximately 15% of the H_2 loss can be explained by reductive dehalogenation, so it is likely that much of the remaining H_2 loss as well as the depletion in O_2 results from the recombination of H_2 and O_2 to form water on the catalyst. Although such a reaction is exothermic, the expected temperature increase, approximately 0.1 °C at the flow rates and concentrations present in the experiment, could not be readily distinguished from other effects (e.g., heats of adsorption of multiple adsorbates, frictional heating).

Chlorinated hydrocarbon concentrations measured in sampling ports across the treatment system indicated that almost all activity took place across the first catalyst column, thus the reaction capacity of the second column remained largely unutilized. At the same time, gas phase saturation measurements indicated that essentially no dissolved H_2 was reaching the second catalyst column. These results suggested the possibility that the second catalyst column was essentially inert in the bottom-up flow configuration (Figure 1), neither catalyzing reductive dehalogenation reactions nor deactivating in the presence of H_2. As such, a treatment regime in which the flow direction through the column assembly was alternated, offered the promise of a prolonged treatment period each day, since each column would be used (i.e., exposed to significant dissolved H_2 concentrations) for only half of the daily treatment cycle. To test this operating procedure, mechanical modifications to the column were made and a second testing

sequence was undertaken, with flow directed in a bottom-up fashion for 4 to 5 h, followed by a top-down flow regime for another 4 to 5 h each day. The resulting removal efficiency history, measured with reference to the bottom-up direction, are shown on Figure 3. A comparison of effluent TCE concentrations with those of the initial testing period with no flow direction switching (Figure 2) suggests significantly improved resilience in system performance in the face of increased operating hours per day.

Discussion

This study demonstrates the feasibility of groundwater treatment with catalytic reductive dehalogenation in a reactive well system. The advantages of such an approach for remediating groundwater include: (1) containment of the majority of the treatment system below ground, reducing the surface footprint and engineering costs, (2) providing a closed-loop treatment system that minimizes the potential for above-ground releases of undesirable species (e.g., tritium and other radioactive contaminants), (3) chemical destruction of chlorinated contaminants, eliminating the problem of secondary waste stream disposal, (4) independence of the catalytic dechlorination reactions of the background redox conditions, and (5) applicability to depths beyond the reach of passive trenching approaches.

Preliminary results suggest that catalytic activity, hence overall system removal efficiency, may be maintained over time with proper system management entailing periodic shut-off of the H_2 supply and aeration. However, the specific mechanism responsible for deactivation has eluded efforts at identification to date. Scanning electron microscopy and energy dispersive x-ray spectrometry studies have revealed subtle differences between fresh and used catalyst material (e.g., accumulation of trace amounts of aluminosilicate mineral phases), but no definitive candidate deactivation mechanisms. Significant relationships between the degree of deactivation and water chemistry are also not readily apparent **(***14*). Furthermore, potential

competition for H_2 by other electron acceptors such as NO_3^- or SO_4^{2-} has not manifested itself in terms of significant concentration reductions of these species across the catalyst columns. Indeed, the only significant adsorption appears to involve F^- and PO_4^{3-} present at trace levels in the influent (less than 1 mg/L). It may be that deactivation involves a transient side-reaction product such as formate produced by reduction of CO_2 **(***15*). The formation of palladium hydride (PdH_x) may also play some role (e.g., *16*). It is also conceivable that biological mechanisms may be involved. In the absence of clear candidates for the deactivation mechanism, improvements in the design of the treatment unit may be implemented using the empirical observations of this study as a guide. For example, by selectively utilizing some of the catalyst material while letting other portions sit idle or regenerate through aeration (perhaps housed in a series of modules), the operational period may be increased significantly.

In assessing the practicability and cost-effectiveness of applying catalytic reductive dehalogenation to cleanup chlorinated hydrocarbons in ground water in general, several factors must be considered. Current costs for the Pd/Al_20_3 catalyst used in this study are approximately $270/kg, or about $8000 for the material in the first catalyst column. At this cost, the long-term durability of the catalyst is an important issue. To date, the catalyst used in our experiments has maintained a consistent level of performance (Figure 4), provided that it is periodically aerated. However, this apparent resilience may be related to the site groundwater chemistry. Under highly anaerobic conditions, for example, poisoning of the ctalyst by sulfides present in the groundwater is a possibility. The local hydrogeology must also be considered in designing a deployment strategy, particularly in balancing the trade-off between reactor residence time and capture zone size time in terms of pumping rate. Innovative pumping strategies could also be called upon, such as having several reactive well operating together but pumping in different

directions (i.e., both upward and downward). Finally, system operational and maintenance costs must be compared to those of other approaches such as pump-and-treat with air-stripping.

Acknowledgments

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TABLE 1. Study Area Background Geochemistry.

parameter	concentration (ppm)
Alkalinity[a]	170
Ca^{2+}	51
Cl^{-}	44
F^{-}	0.54
Fe^{2+}	<0.10
Mg^{2+}	19
Mn^{2+}	<0.03
NO_3^{-}	21
pH	7.5
PO_4^{3-}	0.096
K^{+}	1.5
Na^{+}	39
SO_4^{2-}	11

[a]Alkalinity = bicarbonate alkalinity (as $CaCO_3$).

TABLE 2. Initial Test Results (ppb) at Sampling Points Within Treatment System, Initial 4 Hours/Day Operating Cycle.

compound	influent[a]	first catalyst column effluent[b]	second catalyst column effluent	system removal efficiency[c]
TCE	3612–3777	<0.4–0.9	<0.4–0.8	>99%
PCE	366–370	<0.4	<0.4	>99%
Chloroform	167–235	11–38	6.5-36	~91%
1,1-DCE	130–180	<0.4	<0.4	>99%
1,2-DCA	26–28	20–26	19–27	~0
Carbon tetrachloride	18–21	<0.4	<0.4	>98%
Cis-1,2-DCE	0.6–0.7	<0.4–1	<0.4–0.9	–
Vinyl chloride	<0.4	<0.4	<0.4	–

[a]Influent concentrations refer to range of values reported over the entire course of the experiment. [b]Effluent concentrations for both catalyst columns refer to range of values reported during the first 20 days of the experiment when operating time was less than 4 hours/day. [c]System removal efficiency estimated by R.E. = 1 – mean effluent concentration (second column)/mean influent concentration.

TABLE 3. Initial Test Results (ppb) at Sampling Points Within Treatment System, Initial 8 Hours/Day Operating Cycle.

compound	influenta	first catalyst column effluentb	second catalyst column effluent	system removal efficiencyc
TCE	3612–3777	163–254	227–260	~93%
PCE	366–370	42–75	59–74	~82%
Chloroform	167–235	71–81	71–103	~57%
1,1-DCE	130–180	4.1–7.7	6.3–7.1	~96%
1,2-DCA	26–28	16–37	14–26	~0
Carbon tetrachloride	18–21	<0.4	<0.4	>98%
Cis-1,2-DCE	0.6–0.7	1.3–2.2	1.7–2.2	–
Vinyl chloride	<0.4	3.7–7.4	4.6–8.2	–

[a]Influent concentrations refer to range of values reported over the entire course of the experiment. [b]Effluent concentrations for both catalyst columns refer to range of values reported during the first Days 20 and 34 of the experiment when operating time was approximately 8 hours/day. [c]System removal efficiency estimated by R.E. = 1 – mean effluent concentration (second column)/mean influent concentration.

TABLE 4. Dissolved Gases at Sampling Points Within Treatment System.

gas species[a]	influent	first catalyst column effluent	second catalyst column effluent
H_2	114.1%	0.1%	0%
O_2	109.8%	3.0%	3.4%
N_2	166.5%	221.0%	220.0%
Ar	139.5%	172.1%	170.7%

[a]Hydrogen saturation reported with respect to equilibrium with 1 atm H_2; all other gas saturations reported with respect to 1 atm of air.

Figure Captions

Figure 1. Reactive well configuration using catalytic reductive dehalogenation.

Figure 2. System performance over time during initial testing phase: relationship between removal efficiency, indicated by TVE breakthrough, and daily operating time. D.L. denotes analytical detection limit for TCE.

Figure 3. System performance over time during operational testing phase: relationship between removal efficiency, indicated by TCE breakthrough and daily operating time. D.L. denotes analytical detection limit for TCE.

Figure 4. Long-term system performance as quantified by destruction of TCE.

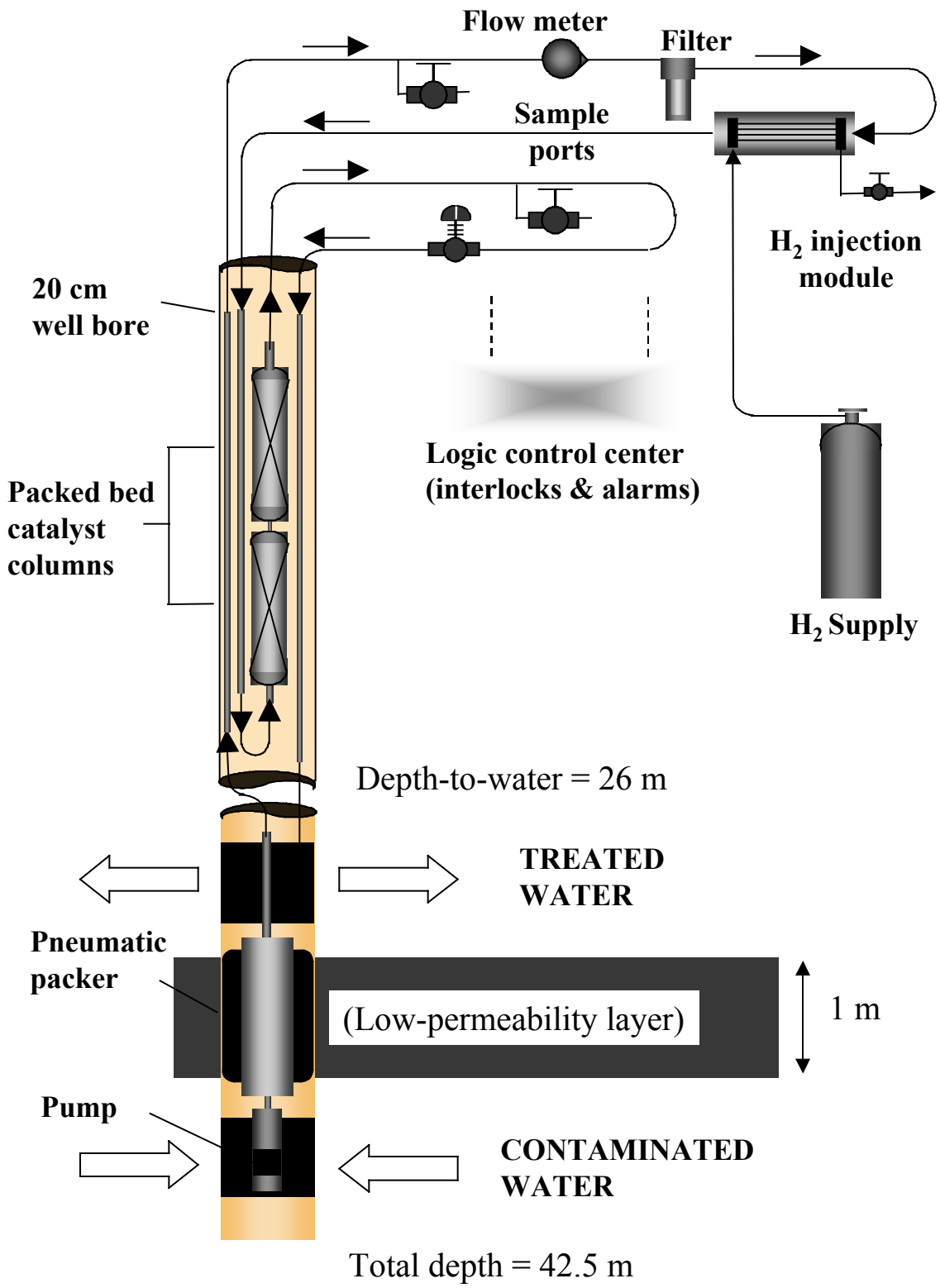
Flow meter
Filter
Sample ports
H_2 injection module
20 cm well bore
Logic control center (interlocks & alarms)
Packed bed catalyst columns
H_2 Supply
Depth-to-water = 26 m
TREATED WATER
Pneumatic packer
(Low-permeability layer)
1 m
Pump
CONTAMINATED WATER
Total depth = 42.5 m

Figure 1.

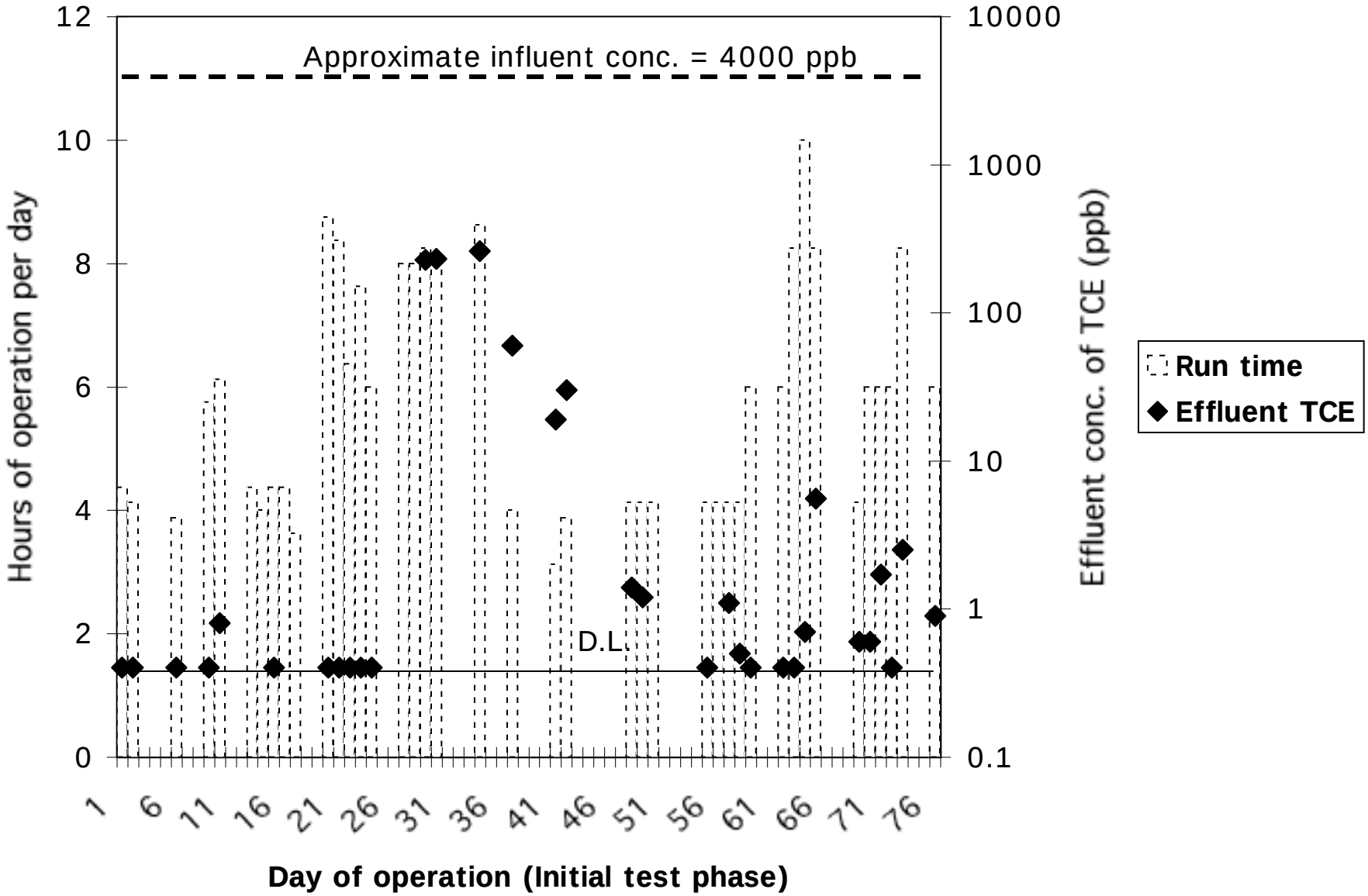
Approximate influent conc. = 4000 ppb
D.L.
Hours of operation per day
Effluent conc. of TCE (ppb)
Day of operation (Initial test phase)
Run time
Effluent TCE
12
10
8
6
4
2
0
10000
1000
100
10
1
0.1
1
6
11
16
21
26
31
36
41
46
51
56
61
66
71
76

Figure 2.

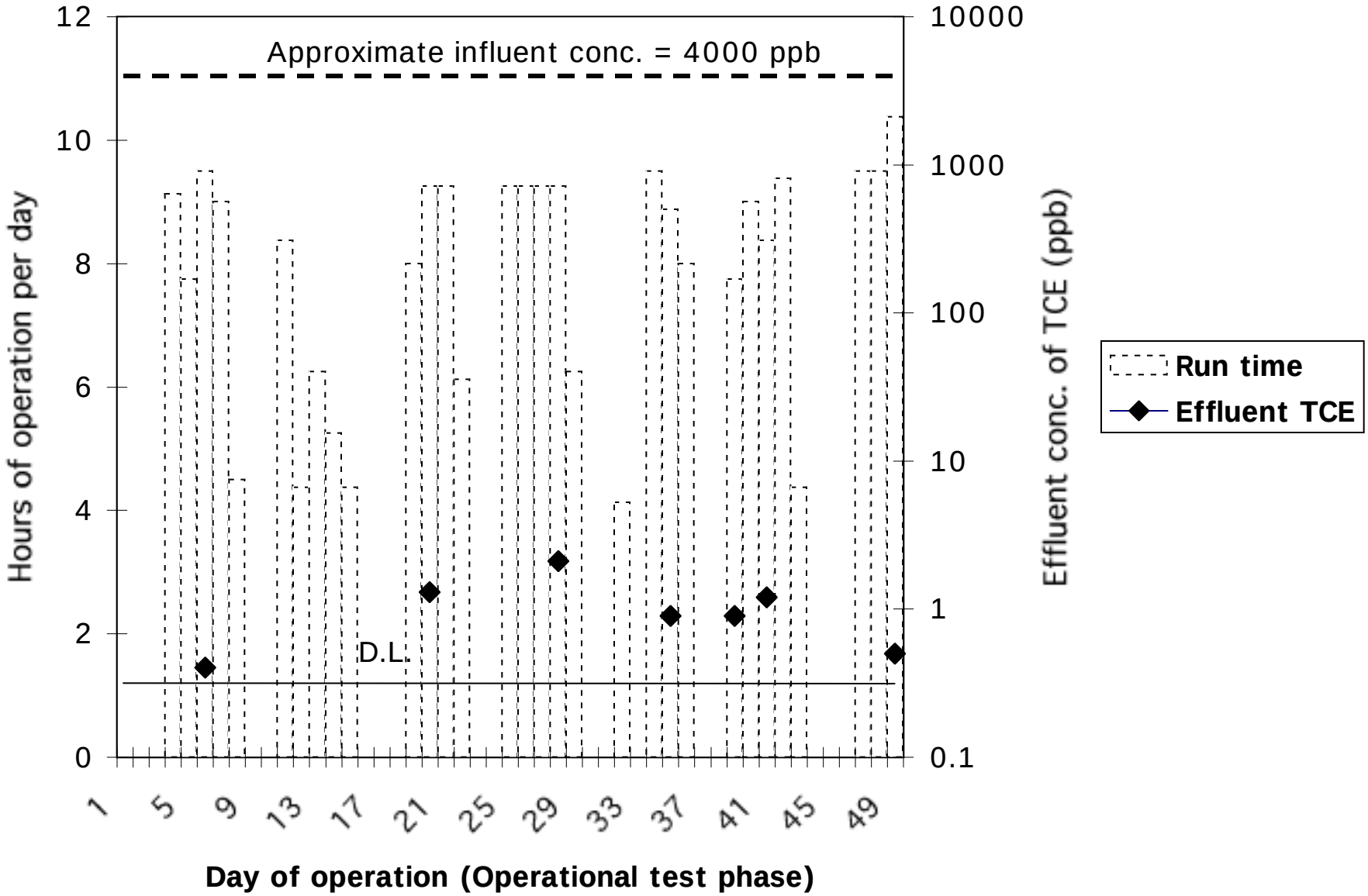
Approximate influent conc. = 4000 ppb
D.L.
Hours of operation per day
Effluent conc. of TCE (ppb)
Day of operation (Operational test phase)
Run time
Effluent TCE
0
2
4
6
8
10
12
0.1
1
10
100
1000
10000
1
5
9
13
17
21
25
29
33
37
41
45
49

Figure 3.

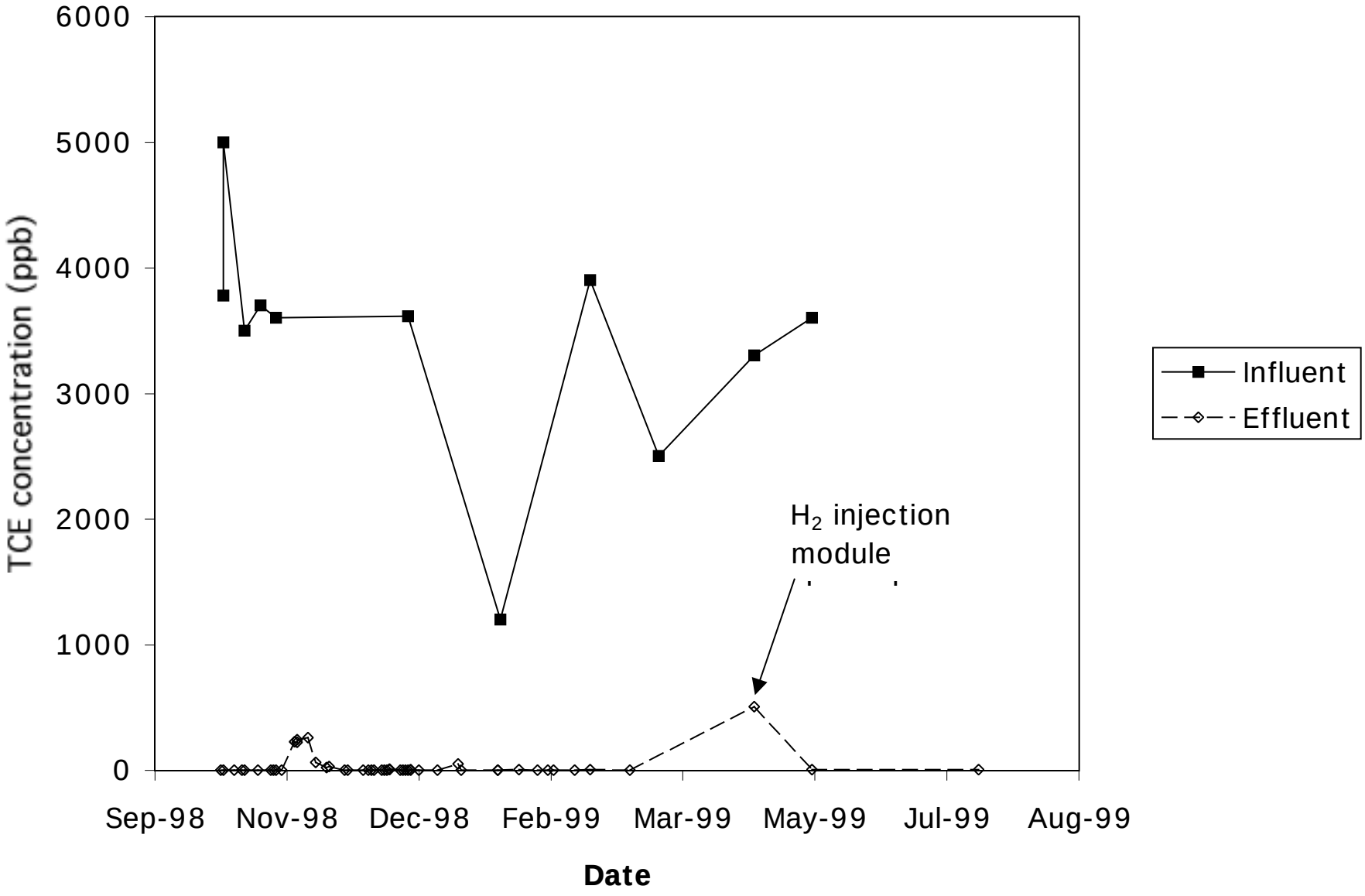
6000
5000
4000
3000
2000
1000
0
TCE concentration (ppb)
Sep-98
Nov-98
Dec-98
Feb-99
Mar-99
May-99
Jul-99
Aug-99
Date
Influent
Effluent
H_2 injection module

Figure 4.