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Pilot-Scale Evaluation of a Permeable Reactive Barrier with Compost and Brown Coal to Treat Groundwater Contaminated with Trichloroethylene

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Abstract: This study evaluates, under field conditions, the efficiency of a permeable reactive barrier (PRB) with compost and brown coal to remove trichloroethylene (TCE) (109 μg/L) from contaminated groundwater. Three stainless steel boxes (1.2 × 0.5 × 0.5 m) with the brown coal-compost mixture at three different mixing ratios of 1:1, 1:3, and 1:5 (by volume) were installed to simulate the PRB. Groundwater from the TCE-contaminated aquifer was pumped into the system at a flow rate of 3.6 L/h. Residence times in the boxes were of: 25, 20, 10 h, respectively. Effluent samples were analyzed for TCE and its daughter products: dichloroethylene (DCE), vinyl chloride (VC) and ethane. During the 198-day experimental period TCE concentrations in groundwater decreased below ≤1.1 μg/L, i.e., much lower than groundwater and drinking water standards in Poland. After 16 days cis-1,2-DCE was monitored indicating possible reductive dechlorination of TCE. However, complete transformation of TCE into non-toxic byproducts was not evidenced during the time of experiments, indicating that reductive dechlorination slowed down or stopped at DCE, and that the designed residence times were not long enough to allow the complete dechlorination process.

Keywords: brown coal; compost; groundwater; field test; permeable reactive barrier; TCE

1. Introduction

Chlorinated solvents are contaminants frequently found in aquifers in the USA [1] and Europe [2]. Their removal is challenging as they are difficult to locate when they are present as dense non-aqueous phase liquids (DNAPL) [1], recalcitrant to biodegradation [3], and pose a potential and actual health hazard [4–6]. Evidence suggests that chlorinated solvents can be removed from groundwater via multiple mechanisms that include chemical oxidation-reduction, physical sorption, and anaerobic degradation via reductive dechlorination [7].

Reductive dechlorination is considered to be the most important mechanism for the bioremediation of highly chlorinated solvents like trichloroethylene (TCE). During reductive dechlorination, chlorine atoms are replaced by hydrogen atoms, resulting in sequential dechlorination from TCE to dichloroethylene (DCE), vinyl chloride (VC) and ethane [8]. TCE can be degraded into three different isomers of DCE—cis, trans, and 1,1-DCE; however, cis-1,2-DCE is the dominant product [9]. Reductive dechlorination of chlorinated aliphatic hydrocarbons (CAHs) is carried out by several different bacteria, in particular, cultures containing Desulfitobacterium, Dehalobacterrestrictus, Desulfuromonas, Dehalospirillum multivorans, and Dehalococcoides. However, Dehalococcoides are the only microorganism known capable of complete dechlorination of TCE to ethylene [10–16].

The use of permeable reactive barriers (PRB) to remove chlorinated solvents from groundwater has proven to be effective and has increased considerably during the past years [17]. The technology was first applied to remediate groundwater contaminated with chlorinated solvents using zero valent iron (ZVI) as a reactive material [18]. Currently, PRBs application is broadened to a wide range of both: contaminants and reactive materials [19]. While at the beginning most PRBs applications focused on the use of a single material, typically to treat a single contaminant plume; currently, combinations of reactive materials are frequently used in single or multi-barrier systems to address mixed contaminants by the occurrence of various removal processes simultaneously [20]. For instance, Ma and Wu [21] used a combination of ZVI and microbial community to treat tetrachloroethylene (PCE) and observed the higher removal efficiency for the combination of ZVI and the microbial community than for ZVI alone. Likewise, Henry et al. [22] evaluated a field-scale PRB with compost and mulch to remove TCE and noted 98% reduction of the contaminant concentration after 3 months of operation.

The use of compost in PRBs to treat TCE has been broadly documented [13,23–25]. Compost has shown to facilitate TCE reductive dechlorination by improving the conditions for microbial growth, and to provide a suitable environment for creating a bioactive zone capable of decomposing TCE in groundwater [25]. Brown coal waste materials have been widely used in remediation for years, especially for their ability to immobilize heavy metals [26–30], nonetheless their ability to retain organic and less polar organic contaminants (chlorophenols, nitrophenols) has also been demonstrated [31,32]. Although the efficiency of the proposed reactive materials to remove TCE has been demonstrated [22,25,32,33], they have not been studied in combination in a single PRB and under field conditions so far. Although to date over 200 pilot scale and field-scale PRBs have been constructed in North America and Europe [17,20,34], still most studies to treat chlorinated solvents focus on the use of ZVI and only few of them are carried out under field conditions.

This study was performed to evaluate the effectiveness of a mixture of two low-cost reactive materials like compost and brown coal waste to treat groundwater contaminated with TCE. Results from this study provide guidelines for the design of a full-scale PRB at the selected contaminated site. The main design parameters of a PRB to be determined during a field test include [35]:

PRB residence time. It is required to achieve site-specific remedial goals. Insufficient residence time will result in contaminant breakthrough in the barrier. The time required for the treatment together with the expected groundwater flow velocity can be then used to determine PRB barrier thickness.

Removal efficiency. Effectiveness of the reactive materials to remove the target contaminant from groundwater.

Hydraulic performance. It assesses the ability to provide the influent groundwater with the desired residence time in the reactive medium. Selection of the particle size of the reactive medium (mixtures) should take into account the trade-off between reactivity and hydraulic conductivity. Generally, higher reactivity requires lower particle size, whereas higher hydraulic conductivity requires larger particle size.

2. Materials and Methods

2.1. Site Description

The contaminated site is located in Southeast Poland in the vicinity of the town of Nowa Dęba and covers an area of approximately 30 km^2. The aquifer is mainly composed of quaternary alluvial and terrace deposits of sand, silt, clay and gravel with depths up to 30 m below the ground surface (bgs). The unconfined aquifer lies on an impervious layer of Miocene clay deposits and Carboniferous rocks that extends hundreds of meters bgs. The water table is located 1–9 m bgs. The groundwater flows in a northwest direction at a velocity of 0.4 m/d [36].

The contamination at the site originates from a metalwork facility and the plume extends to the extraction wells of a waterworks located 1600 m down gradient the source (Figure 1). The concentrations of TCE (up to 6130 μg/L) and Fe^{2+} (up to 59,730 μg/L), Ni^{2+} (up to 993 μg/L), Al^{3+} (up to 2530 μg/L) in groundwater exceed the maximum concentration limits (MCL) in Poland (10 μg/L for TCE; 200 μg/L for Fe; 50 μg/L for Ni and 500 μg/L for Al) [37].

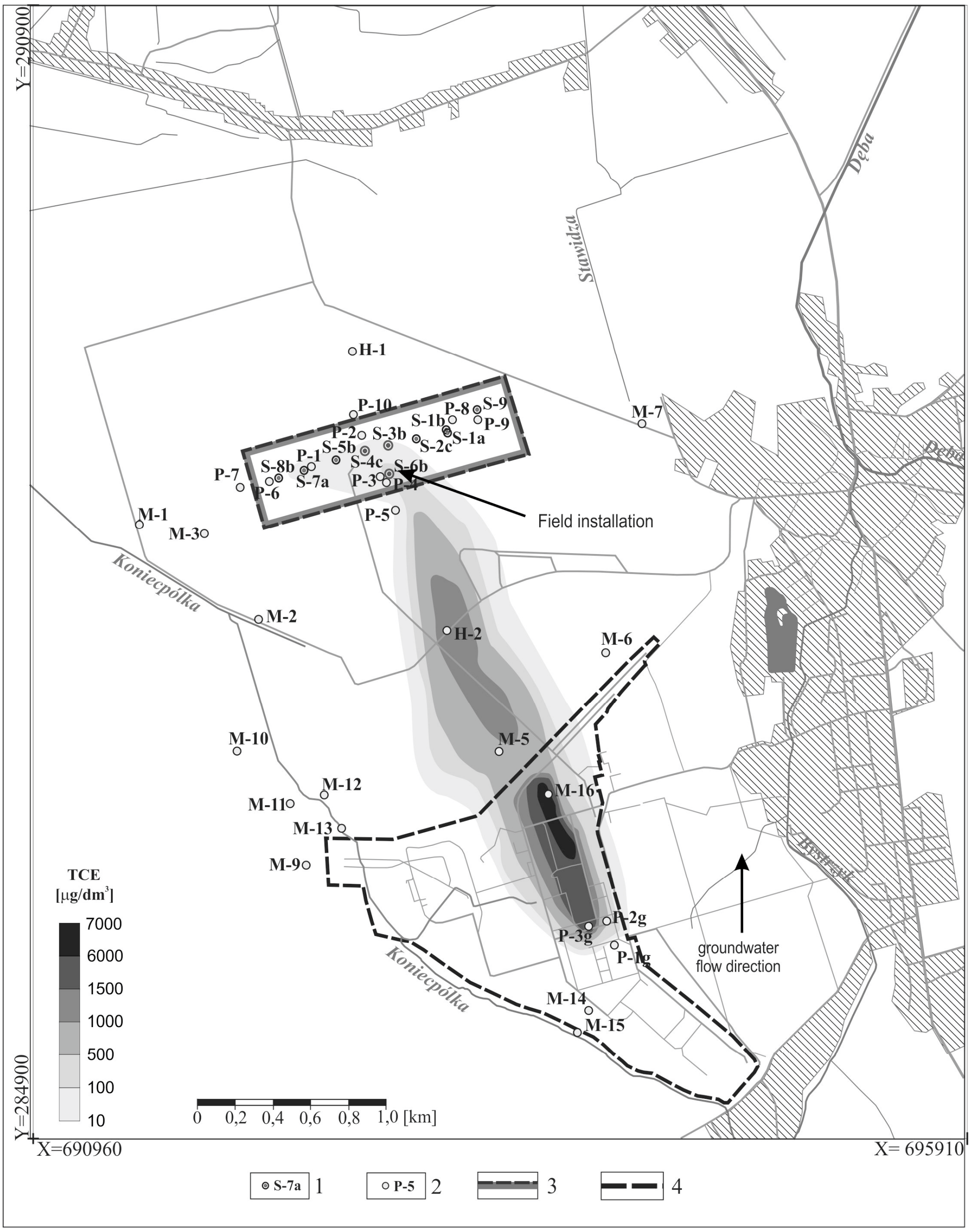

Figure 1. Overview map of the contaminated site including the location of metal-works factory, the affected waterworks and the estimated extent of the contaminant plume. Notation: 1—extraction wells; 2—piezometers; 3—waterworks area; 4—metal-works area.

Since 2010, field investigations have been conducted to delineate the plume and several remediation strategies have been evaluated. Initially, natural attenuation (NA) was assessed but the results suggested that intrinsic biodegradation of TCE via reductive dehalogenation was not enough for risk reduction, and that there was a limited potential for NA as a remediation alternative [38]. Currently, the installation of a PRB filled with a mixture of compost and brown coal is being evaluated as a long-term alternative.

2.2. Reactive Material Selection

The selection of appropriate filling reactive materials is a critical step in the design of a PRB. Factors considered in the selection of the materials included: removal efficiency, hydraulic properties, availability and costs. Four reactive materials and four materials mixtures (i.e., brown coal, compost, zeolite, diatomaceous earth, and mulch-compost, mulch-diatomaceous earth, zeolite-compost and brown coal-compost; Supplementary Material, Figure S1) were evaluated in a series of step-wise batch and column experiments to select the best candidate to treat TCE in a PRB [39]. Results of these tests showed that brown coal presented the highest TCE removal efficiency (97%) of all individual materials tested, followed by compost (86%). Moreover, the removal efficiency of the brown coal-compost mixture was of 86%, while in the case of the other mixtures it was below 50% (Supplementary Material, Figure S2). Therefore, in the present pilot-scale study only brown coal, compost and the brown coal-compost mixture were evaluated as the most suitable to treat TCE. In addition, also the hydraulic conductivity was increased by one order of magnitude when the materials were used in combination (Supplementary Material, Table S1). Finally, both brown coal and compost are inexpensive and readily available materials in the region. The main physico-chemical properties of the studied reactive materials are presented in Table 1 (procedures for measuring physico-chemical properties are referred to in Supplementary Material, Section 1.4).

Table 1. Physico-chemical properties of studied reactive materials.

Materials	**pH (1:2.5) ***		**ρb (g/cm^3)**	**Water Content (%)**	**CEC (mmol/kg)**	**TOC (%) LOI**	**Nutrients Content (mg/kg)**			
	H_2O	**1 M KCl**					**K**	**P**	**Ca**	**Mg**
Compost	8.05	7.39	0.69	44.4	480	34.9	7.40	2.53	9.40	2.15
Brown coal	4.91	4.56	1.13	16.2	n.d	64	-	-	-	-

Notation: ρb—bulk density, CEC—cation exchange capacity, TOC –total organic carbon, LOI—loss on ignition, MC—moisture content, n.d.—not determined. * The pH of the materials was determined in water and 1M KCl at a solid to liquid ratio of 1:2.5.

2.3. Pilot Installation for Field Demonstration

The design parameters of the pilot installation (Table 2) were based on the results gained from laboratory studies [39]. The pilot PRB was installed in the premises of the waterworks affected by the TCE plume. Three stainless steel boxes of 1.20 m long, 0.5 m wide and 0.5 m deep were constructed to represent a PRB. To guarantee a homogeneous flow distribution throughout the box, a 0.1 m wall of gravel was placed at each end of the box and separated from the reactive material by a metallic mesh. Contaminated groundwater was pumped uninterruptedly from a well and fed to each box at an inflow rate of 3.6 L/h using Viton tubing and fittings. In order to control the flow and the pressure of water coming from the well, flow-reducing valves were installed at two points of the system, as well as at the inlet of each box (Figure 2).

Table 2. Design parameters for the pilot field installation.

Parameter	**Value**
TCE input concentration	109 μg/L
MCL for drinking water in Poland	5 μg/L
Residence time in the boxes	
BC-C ratio of 1:1 *	25 h
BC-C ratio of 3:1 *	20 h
BC-C ratio of 5:1 *	10 h
Feed flow rate	3.64 L/h
Hydraulic conductivity—aquifer	1.9 m/d
Hydraulic conductivity—BC-C (ratio 1:1)	2.4 m/d
Hydraulic conductivity—BC-C (ratio 3:1)	2.9 m/d
Hydraulic conductivity—BC-C (ratio 5:1)	14 m/d

* BC-C: brown coal-compost mixing ratio by weight.

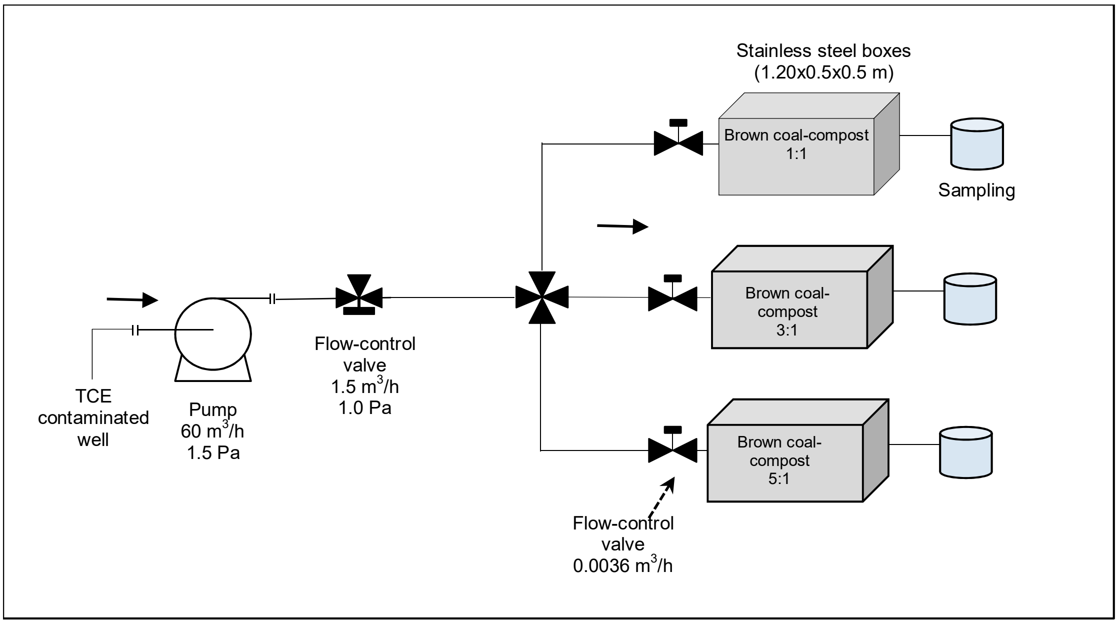

Figure 2. Schematic representation of the pilot brown coal-compost permeable reactive barrier (PRB) installation at the site.

The reactive material placed in the boxes was composed of a mixture of brown coal and compost at three different volumetric mixing ratios of 1:1, 1:3 and 1:5. Finally, the boxes were completely sealed to simulate an anaerobic environment.

In addition, hydraulic conductivity (K) of the reactive materials in each box was determined using the constant head permeability method (ASTM D2434 method). pH and Eh of the solution were measured using a multifunction computer meter (Elmetron, model Cx-742, Poland).

2.4. Determination of TCE Removal

The evaluation of the PRB was made during a period of 198 days. Since the dechlorination of TCE was anticipated, concentrations of TCE, as well as daughter products 1,1 DCE, cis-DCE, trans-DCE, VC, ethane in effluent from each box were measured periodically using gas chromatography (PN-EN ISO 15680:2008). Removal efficiency (E%) was calculated as the change in concentration between the influent and the effluent (Equation (1)), where: E is the removal efficiency (%); C_0: is the initial concentration (mg/L); and C_i is the final concentration (mg/L):

$$E = [(C_0 - C_i)/ C_0] \times 100 \quad (1)$$

3. Results & Discussion

3.1. TCE Removal from Groundwater

Figure 3 presents cumulative TCE removal during 182 days of the experiments. TCE concentrations in the effluents from three boxes decreased rapidly, and after only 8 days of operation the TCE removal efficiencies were of: 74% (ratio 1:1), 83% (ratio 1:3) and 49% (ratio 1:5). Within 52 days of operation, maximum TCE removal efficiencies of 94% for the mixing ratio 1:1, and 99% for the ratios of 1:3 and 1:5 were reached. Nonetheless, a notorious increase in TCE concentrations was observed in the effluents from all boxes after approximately 64 days of the experiments (Figure 4) resulting in final removal efficiencies of: 81%, 72% and 59% (Table 3). The box with the brown coal-compost mixture (mixing ratio 1:5) attained the overall lowest removal of contaminant.

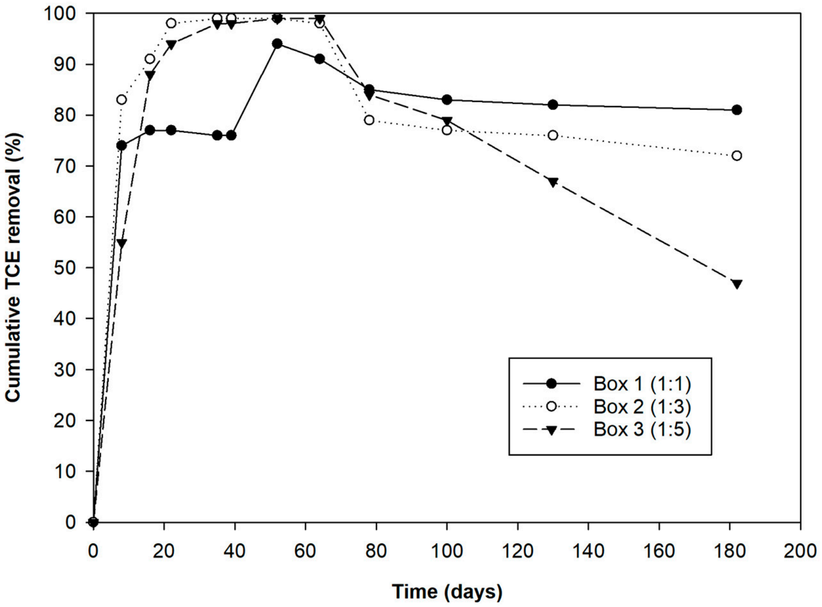

Figure 3. Cumulative trichloroethylene (TCE) removal during the time of the experiments.

The pH slightly rose from 5.9 to 6.2 (ratio 1:1), 6.03 (ratio 1:3) and 6.09 (ratio 1:5) during the first days of operation. After 16 days pH increased to 7.2 (ratio 1:1), 6.87 (ratio 1:3) and 6.75 (ratio 1:5), and maintained stability without any major fluctuations in all boxes for the remaining time of the experiment. The redox potential dropped from −16 to −186 mV (ratio 1:1), to −154 mV (ratio 1:3) and to −127 mV (ratio 1:5) after 16 days of the experiment and stabilized in this range. The decrease in Eh indicates that redox conditions were reached to a level considered appropriate for TCE reductive dechlorination. After pH and Eh stabilization the generation of DCE followed.

Table 3. Final concentrations and removal efficiency of TCE.

	Box 1 (1:1)	Box 2 (1:3)	Box 3 (1:5)
TCE initial concentration	109	109	109
TCE Final concentration (μg/L)	21.1	30.4	58.2
TCE maximal removal efficiency (%)	94	99	99
TCE overall removal efficiency (%)	81	72	47

The increase in TCE concentrations suggests desorption of the contaminant from the reactive material matrix. The amount of contaminant desorbed for studied mixing ratios was of 14.92 μg/L (ratio 1:1), 29.3 μg/L (ratio 1:3) and 57.1 μg/L (ratio 1:5). The more brown coal was present, the higher TCE removal was attained and the greater the amount of contaminant desorbed (ca. 50% of the initial concentration for the mixing ratio of 1:5). Such TCE desorption events have often been observed in granular media such as zeolite [40] and granular activated carbon (GAC) [41,42] but with little understanding of the mechanisms involved. Desorption experiments are usually performed in conjunction with adsorption studies to determine the reversibility of adsorbed compounds onto the soil matrix. However, the time frame and conditions usually encountered in the field are not adequately represented in the laboratory. Some studies have shown that adsorbed organics can be released from solid media when the concentration of the contaminant was reduced in order to reach equilibrium [42,43]. In addition, Zytner [42] also found that the organic carbon content of the solid media is an important controlling factor of adsorption and desorption. This means that materials with high organic carbon content are effective in adsorbing and retaining dissolved TCE. Brown coal used in this study contains high amounts of organic constituents (ca. 64%), mainly humic acids that represent a source of organic matter (Table 1). Our results indicate strong adsorption affinity of brown coal towards TCE but not as strong resistance to its desorption. Other authors have indicated that TCE resistance to desorption increases with the residence time and is independent of the material properties, like the organic carbon content [44–46]. Our results suggest that the organic carbon content of the material has a minor influence on the resistance to desorption whereas the residence time plays a greater role.

In addition, it has been postulated by many researchers that adsorption of contaminants will result in a reduction of the overall rate and degree of biodegradation [47,48]. The adsorbed contaminant is unavailable for biodegradation unless it desorbs. Therefore, desorption of TCE from the brown coal-compost mixture can benefit the rate of biodegradation, if enough residence time is allowed for complete transformation of TCE into less hazardous compounds like ethane.

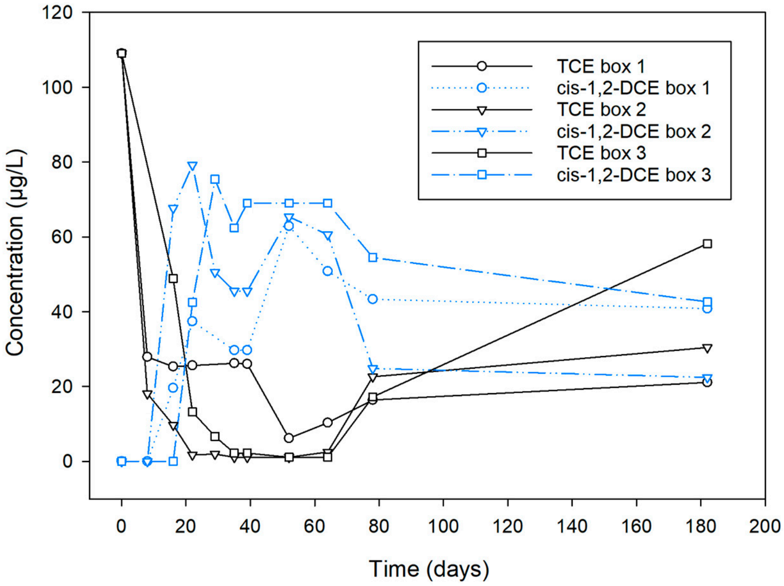

Figure 4. Concentrations of TCE and cis-1,2-DCE versus operation time of the experiments.

3.2. TCE Biodegradation Products

After 16 days of the experiment DCE (cis-1,2-dichloroethene) has been recorded in the three boxes effluent (Figure 4). As the initial concentration of DCE was zero, it is clear that its presence was due to TCE degradation. The trend of increasing DCE concentrations was observed in all boxes until day 29 when a slight reduction of DCE concentration was observed followed by an increase soon after. A final decrease in DCE concentration was noted on day 78 and from then concentration stabilizes until the end of the experiment. However, the conversion of DCE to VC and non-toxic by-products (ethane) did not occur during the time of the experiment indicating that reductive dechlorination slowed down or stopped at DCE. The initial steps in reductive dechlorination are generally more rapid than the final steps. Consequently, DCE and VC tend to accumulate at contaminated sites [49]. The effectiveness of chlorinated solvents to serve as electron acceptors is proportional to the number of chlorine molecules attached [8]. For example, TCE is more likely to serve as an electron acceptor and lose a chlorine atom through reductive dechlorination than is DCE, or VC. Nonetheless, field studies on dechlorination of chlorinated solvents have demonstrated the complete transformation of TCE into non-toxic products, if enough residence time is allowed in a PRB [22,25]. The incomplete removal of TCE observed in our experiment is likely associated with the short residence time of the contaminant in the reaction zone. A drop in pH can also slow dechlorination rates but during our experiments pH values remained close to 7, values which are considered optimal for dechlorination.

In addition, further dechlorination of DCE may have been inhibited by desorbed amounts of TCE still present in the barrier. Some authors have reported that higher chlorinated ethenes can inhibit the degradation of less chlorinated ethenes [50–54]. This means that TCE inhibits degradation of DCE and VC, and DCE inhibits degradation of VC. Nonetheless, concentrations of TCE in those studies were significatively higher than the concentration in our study. Studies reporting inhibition with concentrations similar to that of our studies have not been reported.

Furthermore, the presence of dissolved iron (Fe^{2+}) in the treated groundwater indicates that iron reduction may be taking place. Iron reduction might have played an additional inhibitory role, since iron respiration is suspected to be competitively inhibitory to reductive dechlorination, especially for less chlorinated compounds like DCE [55]. Since H_2 is the ultimate electron donor for dehalorespiring microorganisms, iron-reducer communities, among other microbial communities compete with Dehalococcoides species for H_2 and may inhibit the dechlorination process in TCE-contaminated aquifers [56,57]. Kean et al. [58] investigated the accumulation of DCE at a site undergoing reductive dechlorination and observed that geochemical conditions are dominant and influence the progression of the dechlorination process. Groundwater conditions suggest that iron reduction, sulfate reduction, or methanogenesis could all influence the accumulation and persistence of DCE. Although, at some contaminated sites the presence of dissolved iron is thought to negatively impact the dechlorination [23], it has also been documented by Paul et al. [57] that inhibition of microbial dechlorination of trichloroethylene by Fe^{3+} reduction depends on Fe mineralogy of iron oxides and hydroxides. In contrast, Wei and Fedelman [59] demonstrated that the reduction of Fe^{3+} did not inhibit dechlorination of TCE. Atashgahi et al. [60] observed that the type of substrate determines the degradation pattern of chlorinated compounds and stimulation of specific dechlorination microorganisms like Dehalococcoides mccartyi and methanogens. Lignocellulosic materials, a long-term electro-donor, exhibited higher amounts of D. mccartyi. These organisms can sustain reductive dechlorination over time due to its ability to survive in low H_2 conditions, giving it a competitive advantage over other H_2 consuming organisms like iron reducers and methanogens. On the other hand, shrimp waste, a source of rapidly degradable organic acids and alcohols, evidence a predominance of methanogens and as a result a reduced degradation of chlorinated compounds compared to lignocellulosic materials.

An additional common environmental phenomenon is the competitive adsorption of cis-DCE and TCE. The adsorption of several contaminants with different adsorption parameters to a limited reactive surface causes interspecies competition. DCE is the solute with the weaker adsorption affinity, and declines its sorption when TCE with higher adsorption affinity is present. This phenomenon is observed during the sorption of multiple species on microporous materials like activated carbons and zeolites [61] but also on sediments and wood materials [62].

3.3. Implications of The Field-Test Performance to The Full-Scale PRB Design

The brown coal-compost mixture is a promising combination of reactive materials to remove TCE from groundwater (99% maximal removal). Nevertheless, results for the studied materials mixtures illustrate the interference of compost and brown coal specific processes. TCE can be degraded by microorganism present in the compost, or adsorbed onto brown coal and its removal efficiency is governed by degradation rates and adsorption parameters. Therefore, the efficient groundwater treatment in a PRB can be achieved only if both: desorption effects and the formation of intermediate biodegradation products are carefully taken into account.

Compost fermentation can lead to the production of electron donors that serve for the TCE reductive dechlorination. This process was demonstrated by the production of the TCE degradation product (DCE). As the degradation of TCE was observed to be considerably faster than the degradation of DCE and VC; TCE is unlikely to limit the system performance unless it is present in groundwater at very high concentrations. Our results show that DCE and VC may be the most problematic contaminants for the proposed PRB application, even if they do not occur within the contaminant plume. Both are highly toxic, and have therefore to be limited to a rather low target concentration after leaving the barrier. In addition, they have lower sorptivity than TCE.

The designed residence times of 10, 20 and 25 h were not enough to allow the complete transformation of TCE into less harmful products. DCE was accumulated in the system and was not further dechlorinated. Consequently, DCE and VC degradation rates will determine the required residence time and therefore the barrier thickness. Although the required residence time for the complete transformation of TCE into ethane was not determined in this study, a close approximation can be achieved using the removal rates for DCE and VC reported in the literature and supported by numerical modeling. In addition, when determining the barrier thickness a safety factor to account for desorption should be incorporated anyway.

This study demonstrates the importance of field evaluation of reactive materials and the significant role that aquifer geochemistry plays in the microbial processes that occur. The results from this study where DCE accumulated and failed to be further dechlorinated suggests that geochemical conditions are an important factor influencing the progression of the dechlorination process. Groundwater conditions suggest that iron reduction could be influencing the accumulation and persistence of DCE. The specific contribution of each microbial process in the interference with DCE dechlorination cannot be determined from this work. Microcosms studies to establish the precise microorganisms participating in the TCE degradation and the role they play in each of the steps of the reductive dechlorination process should be subject to future research.

The mixing ratio of the reactive materials should be selected based on contaminant removal and hydraulic properties. Higher amounts of compost in the mixture could benefit reductive dechlorination and prevent the accumulation of toxic byproducts but at the same time lead to the reduction of the barrier's permeability. Our results indicate that the mixing ratio of 1:3 represent a good compromise between contaminant removal and hydraulic performance as it exhibited a high TCE removal efficiency (99% maximal removal and 78% overall removal; Table 3), while the hydraulic conductivity is still higher than that of the surrounding aquifer (2.9 m/d; Table 2), a suggested requirement for the full-scale barrier installation [35].

The results here presented cannot replace site-specific tests but reveal important features of the main processes influencing the performance of combined compost-brown coal PRBs. In this way, these types of experiments definitely hold potential for predicting TCE removal behavior under field conditions, and provides practical hints for the design of such barriers, even if flow patterns in a full-scale PRB may differ significantly from flow through a pilot installation like the one presented here. For the full-scale application, however, further research has to be performed focusing on: long-term performance of the reactive material, kinetic studies for TCE, daughter products DCE and VC degradation to determine barrier thickness, and microcosms studies to establish the microorganisms participating in the TCE biodegradation.

4. Conclusions

The effectiveness of a PRB with a brown coal–compost mixture at three different mixing ratios (1:1, 1:3, 1:5) was evaluated under field conditions. From this study, it can be concluded that compost fermentation can lead to the production of electro donors that serve to the TCE reductive dechlorination. TCE reductive dechlorination was demonstrated by the depletion of TCE (99% removal) and the production of degradation products (DCE). However, complete TCE dechlorination into non-toxic byproducts was not evidenced during the duration of the experiments. Anaerobic reductive dechlorination of TCE is a complex process that can be influenced by multiple factors like retention time and biogeochemical conditions. In this study, the designed residence time was not enough to allow the complete transformation of TCE into innocuous end products. The inhibitory degradation of less chlorinated ethenes by higher chlorinated ethenes, and the competitive adsorption of cis-DCE and TCE were theorized as important factors influencing the progression of the dechlorination process but were not demonstrated. Significant TCE removal from this system indicates that the proposed combination of reactive materials have the ability to decrease TCE concentrations from groundwater, but their potential to be applied to other chlorinated solvents sites needs further study on the production of daughter products, as well as on the effects of contaminant desorption from the reactive material.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/11/9/1922/s1, Figure S1: Reactive materials tested, Figure S2: TCE removal efficiency for each reactive material during batch test, Table S1: Hydraulic conductivities for the individual materials and the mixtures.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Stroo, H.F.; Unger, M.; Ward, C.H.; Kavanaugh, M.C.; Vogel, C.; Leeson, A.; Marqusee, J.; Smith, B.P. Remediating chlorinated solvent source zones. *Environ. Sci. Technol.* **2003**, *37*, 224A–230A. [CrossRef] [PubMed]
2. Panagos, P.; Van Liedekerke, M.; Yigini, Y.; Montanarella, L. Contaminated Sites in Europe: Review of the Current Situation based on data collected through an European network. *J. Environ. Public Health* **2013**, 1–11. [CrossRef] [PubMed]
3. Kao, C.M.; Chen, S.C.; Wang, J.Y.; Chen, Y.L.; Lee, S.Z. Remediation of PCE-contaminated aquifer by an in situ two-layer biobarrier: Laboratory batch and column studies. *Water Res.* **2003**, *37*, 27–38. [CrossRef]
4. Agency for Toxic Substances & Disease Registry (ATSDR). *Toxicological Profile for Trichloroethylene*; U.S. Public Health Service, U.S. Department of Health and Human Services: Atlanta, GA, USA, 1997.
5. United States Environmental Protection Agency (USEPA). *Toxicological Review of Trichloroethylene (CAS No. 79-01-6)*; Summary Information on the Integrated Risk Information System (IRIS): Washington, DC, USA, 2011.
6. Chiu, W.A.; Jinot, J.; Scott, C.S.; Makris, S.L.; Cooper, G.S.; Dzubow, R.C.; Bale, A.S.; Evans, M.V.; Guyton, K.Z.; Keshava, N.; et al. Human health effects of trichloroethylene: Key findings and scientific issues. *Environ. Health Perspect.* **2013**, *121*, 303–311. [CrossRef] [PubMed]
7. McCarty, P.L. Groundwater Contamination by Chlorinated Solvents: History, Remediation Technologies and Strategies. In *In Situ Remediation of Chlorinated Solvent Plumes*; Stroo, H.F., Ward, C.H., Eds.; Springer: New York, NY, USA, 2010; pp. 1–28.
8. Vogel, T.M.; McCarty, P.L. Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. *Appl. Environ. Microbiol.* **1985**, *49*, 1080–1083. [PubMed]
9. Brown, R.; Mueller, J.G.; Seech, A.G.; Henderson, J.K.; Wilson, J.T. Interactions between biological and abiotic pathways in the reduction of chlorinated solvents. *Remediat. J.* **2009**, *20*, 9–20. [CrossRef]
10. Cupples, A.M.; Spormann, A.M.; Perry, L.; Mccarty, P.L. Growth of a Dehalococcoides-like microorganism on vinyl chloride and cis-dichloroethene as el Butler ectron acceptors as determined by competitive PCR growth. *Appl. Environ. Microbiol.* **2003**, *69*, 953–959. [CrossRef]
11. Cupples, A.M.; Spormann, A.M.; McCarty, P.L. Comparative evaluation of chloroethene dechlorination to ethene by Dehalococcoides-like microorganisms. *Environ. Sci. Technol.* **2004**, *38*, 4768–4774. [CrossRef]
12. Révész, S.; Sipos, R.; Kende, A.; Rikker, T.; Romsics, C.; Mészáros, E.; Mohr, A.; Táncsics, A.; Márialigeti, K. Bacterial community changes in TCE biodegradation detected in microcosm experiments. *Int. Biodeterior. Biodegrad.* **2006**, *58*, 239–247. [CrossRef]
13. Katsenovich, Y.; Öztürk, Z.; Allen, M.; Wein, G. Evaluation of soil solid amendments for TCE biodegradation in a biobarrier system. *Remediat. J.* **2007**, *17*, 67–80. [CrossRef]
14. Lu, X.; Wilson, J.T.; Shen, H.; Henry, B.; Kampbell, D. Remediation of TCE-contaminated groundwater by a permeable reactive barrier filled with plant mulch (Biowall). *J. Environ. Sci. Heal. Part A Toxichazardous Subst. Environ. Eng.* **2008**, *43*, 24–35. [CrossRef] [PubMed]

15. Henry, B.M. Biostimulation for anaerobic bioremediation of chlorinated solvents. In *In Situ Remediation of Chlorinated Solvent Plumes*; Stroo, H.F., Ward, C.H., Eds.; Springer: New York, NY, USA, 2010; pp. 357–423.
16. Delgado, A.G.; Fajardo-Williams, D.; Popat, S.C.; Torres, C.I.; Krajmalnik-Brown, R. Successful operation of continuous reactors at short retention times results in high-density, fast-rate Dehalococcoides dechlorinating cultures. *Appl. Microbiol. Biotechnol.* **2014**, *98*, 2729–2737. [CrossRef]
17. Bone, B.D. Review of UK Guidance on Permeable Reactive Barriers. In Proceedings of the 2012 Taipei International Conference on Remediation and Management of Soil and Groundwater Contaminated Sites, Taipei, Taiwan, 30–31 October 2012; pp. 611–768.
18. O'Hannesin, S.F.; Gillham, R.W. Long-Term Performance of an In Situ "Iron Wall" for Remediation of VOCs. *Ground Water* **1998**, *36*, 164–170. [CrossRef]
19. Obiri-Nyarko, F.; Grajales-Mesa, S.J.; Malina, G. An overview of permeable reactive barriers for in situ sustainable groundwater remediation. *Chemosphere* **2014**, *111*, 243–259. [CrossRef] [PubMed]
20. Interstate Technology & Regulatory Council (ITRC). *Permeable Reactive Barrier: Technology Update (No. Report PRB-5)*; Interstate Technology Regulatory Council: Washington, DC, USA, 2011.
21. Ma, C.; Wu, Y. Dechlorination of perchloroethylene using zero-valent metal and microbial community. *Environ. Geol.* **2008**, *55*, 47–54. [CrossRef]
22. Henry, B.M.; Goodspeed, M.; Gonzales, J.R.; Haas, P.E.; Oakley, D. Permeable mulch biowall for enhanced bioremediation of chlorinated ethenes. In Proceedings of the Seventh International In Situ and On-Site Bioremediation Symposium, Orlando, FL, USA, 2–5 June 2003; Magar, V.S., Kelley, M.E., Eds.; Battelle Press: Columbus, OH, USA, 2003; p. K03.
23. Air Force Center for Environmental Excellence (AFCEE). *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents (TR-2250-ENV)*; Defense Technical Information Center: Port Hueneme, CA, USA, 2004.
24. Öztürk, Z.; Katsenovich, Y.; Tansel, B.; Laha, S.; Moos, L.; Allen, M. Enhancement of TCE Attenuation in Soils by Natural Amendments. *Soil Sediment Contam.* **2009**, *18*, 1–13. [CrossRef]
25. Öztürk, Z.; Tansel, B.; Katsenovich, Y.; Sukop, M.; Laha, S. Highly organic natural media as permeable reactive barriers: TCE partitioning and anaerobic degradation profile in eucalyptus mulch and compost. *Chemosphere* **2012**, *89*, 665–671. [CrossRef]
26. Butler, C.J.; Green, M.; Chaffee, L. MTE water remediation using Loy Yang brown coal as a filter bed adsorbent. *Fuel* **2008**, *87*, 894–904. [CrossRef]
27. Dębska, B.; Maciejewska, A.; Kwiatkowska, J. The effect of fertilization with brown coal on Haplic Luvisol humic acids. *Rostlinna Vyroba* **2002**, *48*, 33–39. [CrossRef]
28. Karczewska, A.; Chodak, T.; Kaszubkiewicz, J. The suitability of brown coal as a sorbent for heavy metals in polluted soils. *Appl. Geochem.* **1996**, *11*, 343–346. [CrossRef]
29. Leszczyńska, D.; Kwiatkowska-Malina, J. Effect of organic matter from various sources on yield and quality of plants on soils contaminated with heavy metals. *Ecol. Chem. Eng. S* **2011**, *18*, 501–507.
30. Skłodowski, P.; Maciejewska, A.; Kwiatkowska, J. The effect of organic matter from brown coal on bioavailability of heavy metals in contaminated soils. In *Viable Methods of Soil and Water Pollution Monitoring, Protection and Remediation*; Twardowska, I., Allen, H.E., Häggblom, M.M., Stefaniak, S., Eds.; NATO Science Series IV—Earth and Environmental Sciences 69; Springer: Dordrecht, The Netherlands, 2006; pp. 299–307.
31. Hobday, M.D.; Li, P.H.Y.; Crewdson, D.M.; Bhargava, S.K. The use of low rank coal-based adsorbents for the removal of nitrophenol from aqueous solution. *Fuel* **1994**, *73*, 1848–1854. [CrossRef]
32. Janos, P.; Zavodska, L.; Lesny, J.; Krizenecka, S.; Synek, V.; Hejda, S.; Kubu, M. Young brown coals for environmental applications: Composition, acid-base, ion-exchange, and sorption properties of selected central european coals. In *Coal Extraction*; Stewart, J.J., Ed.; Nova Science Publishers, Inc.: Hauppauge, NY, USA, 2011; pp. 71–90.
33. Erto, A.; Andreozzi, R.; Lancia, A.; Musmarra, D. Factors affecting the adsorption of trichloroethylene onto activated carbons. *Appl. Surf. Sci.* **2010**, *256*, 5237–5242. [CrossRef]
34. Birke, V.; Burmeier, H.; Jefferis, S.; Gaboriau, H.; Touze, S.; Romain, C.; Harald, B.; Stephan, J.; Herve, G. Permeable reactive barriers (PRBs) in Europe: Potentials and expectations. *Italy J. Eng. Geol. Environ.* **2007**, *1*, 1–8.
35. Gavaskar, A.; Gupta, N.; Sass, B.; Janosy, R.; Hicks, J. *Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation*; Battelle Press: Columbus, OH, USA, 2000.

36. Szklarczyk, T.; Kret, E.; Grajales-Mesa, S.J.; Kiecak, A.; Malina, G. Multilayer numerical groundwater flow model in the area of Nowa Deba waterworks. In *Water Supply and Water Quality*; Lemański, J.F., Sergiusz, Z., Eds.; PZITS: Poznań, Poland, 2012; pp. 411–431.
37. Kret, E.; Kiecak, A.; Malina, G.; Szklarczyk, T. Evaluation of Quaternary Chemical Status Exploited by Waterworks in Nowa Dęba. *Biul. Państwowego Inst. Geol.* **2011**, *445*, 23–29.
38. Kiecak, A.; Kret, E.; Cichostępska, M.; Malina, G. Assessment of intrinsic biodegradation potentials in an aquifer contaminated with chlorinated ethenes in the vicinity of Nowa Deba. *Ecol. Chem. Eng. S* **2013**, *20*, 265–278. [CrossRef]
39. Grajales-Mesa, J.; Malina, G. Screening reactive materials for a permeable barrier to treat TCE contaminated groundwater: Laboratory studies. *Environ. Earth. Sci.* **2016**, *75*, 1–14. [CrossRef]
40. Hawley, H.A.; Bergendahl, J.; Thompson, R. An Equilibrium Study on Trichloroethylene Adsorption and Desorption from ZSM-5 in Water. *Energy Environ. Eng.* **2013**, *1*, 5–9.
41. Bold, S.; Kraft, S.; Grathwohl, P.; Liedl, R. Sorption/desorption kinetics of contaminants on mobile particles: Modeling and experimental evidence. *Water Resour. Res.* **2003**, *39*, SBH31–SBH39. [CrossRef]
42. Zytner, R.G. Adsorption-Desorption of Trichloroethylene in Granular Media. *Water. Air. Soil Pollut.* **1992**, *65*, 245–255. [CrossRef]
43. To, P.C.; Mariñas, B.J.; Snoeyink, V.L.; Ng, W.J. Effect of Pore-Blocking Background Compounds on the Kinetics of Trace Organic Contaminant Desorption from Activated Carbon. *Environ. Sci. Technol.* **2008**, *42*, 4825–4830. [CrossRef] [PubMed]
44. Pavlostathis, S.G.; Jaglal, K. Desorptive behavior of trichloroethylene in contaminated soil. *Environ. Sci. Technol.* **1991**, *25*, 274–279. [CrossRef]
45. Pavlostathis, S.G.; Mathavan, G.N. Desorption kinetics of selected volatile organic compounds from field contaminated soils. *Environ. Sci. Technol.* **1992**, *26*, 532–538. [CrossRef]
46. Lee, S.; Kommalapati, R.R.; Valsaraj, K.T.; Pardue, J.H.; Constant, W.D. Rate-limited desorption of volatile organic compounds from soils and implications for the remediation of a Louisiana Superfund site. *Environ. Monit. Assess.* **2002**, *75*, 87–105. [CrossRef] [PubMed]
47. Alvarez-Cohen, L.; McCarty, P.L.; Roberts, P.V. Sorption of trichloroethylene onto a zeolite accompanied by methanotrophic biotransformation. *Environ. Sci. Technol.* **1993**, *27*, 2141–2148. [CrossRef]
48. Scow, K.M.; Fan, S.; Johnson, C.; Ma, G.M. Biodegradation of sorbed chemicals in soil. *Environ. Health Perspect.* **1995**, *103*, 93–95. [PubMed]
49. Brusseau, M.; Arnold, R.; Ela, W. *Overview of Innovative Remediation Approaches for Chlorinated Solvents*; Arizona Department of Environmental Quality: Phoenix, AZ, USA, 2001.
50. Popat, S.C.; Deshusses, M.A. Kinetics and inhibition of reductive dechlorination of trichloroethene, cis-1,2-dichloroethene and vinyl chloride in a continuously fed anaerobic biofilm reactor. *Environ. Sci. Technol.* **2011**, *45*, 1569–1578. [CrossRef]
51. Haest, P.J.; Springael, D.; Smolders, E. Dechlorination kinetics of TCE at toxic TCE concentrations: Assessment of different models. *Water Res.* **2010**, *44*, 331–339. [CrossRef]
52. Yu, S.; Semprini, L. Kinetics and modeling of reductive dechlorination at high PCE and TCE concentrations. *Biotechnol. Bioeng.* **2004**, *88*, 451–464. [CrossRef]
53. Yu, S.; Dolan, M.E.; Semprini, L. Kinetics and inhibition of reductive dechlorination of chlorinated ethylenes by two different mixed cultures. *Environ. Sci. Technol.* **2005**, *39*, 195–205. [CrossRef]
54. Schaefer, D.; Koeber, R.; Dahmke, A. Competing TCE and cis-DCE degradation kinetics by zero-valent iron—Experimental results and numerical simulation. *J. Contam. Hydrol.* **2003**, *65*, 183–202. [CrossRef]
55. Majone, M.; Aulenta, F.; Rossetti, S.; Tandoi, V. Lab and Field Scale Investigations of Natural and Enhanced Biodegradation Processes. In *Assessment of Fate, Impact and Indicators, Proceedings of the WAPO2 International Conference on WAter Pollution in Natural Porous Media at Different Scales*; Candela, L., Fernández, L.V., Aagaard, P., Bedbur, E., Trevisan, M., Vanclooster, M., Viotti, P., López-Geta, J.A., Eds.; Instituto Geológico y Minero de España: Barcelona, Spain, 2007; pp. 59–84.
56. Lu, X.-X.; Tao, S.; Bosma, T.; Gerritse, J. Characteristic Hydrogen Concentrations for Various Redox Processes in Batch Study. *J. Environ. Sci. Heal. Part A Toxic Hazardous Subst. Environ. Eng.* **2001**, *36*, 1725–1734. [CrossRef]

57. Paul, L.; Herrmann, S.; Bender Koch, C.; Philips, J.; Smolders, E. Inhibition of microbial trichloroethylene dechorination by Fe (III) reduction depends on Fe mineralogy: A batch study using the bioaugmentation culture KB-1. *Water Res.* **2013**, *47*, 2543–2554. [CrossRef] [PubMed]
58. Kean, J.; Graves, D.; Lodato, M. Enhanced Reductive Dechlorination and the Relationship between cDCE Accumulation and Methanogenesis. In *In Situ and On-Site Bioremediation Symposium, Proceedings of the Seventh International*; Magar, V.S., Kelley, M.E., Eds.; Battelle Press: Orlando, FL, USA, 2003.
59. Wei, N.; Finneran, K.T. Influence of ferric iron on complete dechlorination of trichloroethylene (TCE) to ethene: Fe(III) reduction does not always inhibit complete dechlorination. *Environ. Sci. Technol.* **2011**, *45*, 7422–7430. [CrossRef] [PubMed]
60. Atashgahi, S.; Maphosa, F.; De Vrieze, J.; Haest, P.J.; Boon, N.; Smidt, H.; Springael, D.; Dejonghe, W. Evaluation of solid polymeric organic materials for use in bioreactive sediment capping to stimulate the degradation of chlorinated aliphatic hydrocarbons. *Appl. Microbiol. Biotechnol.* **2014**, *98*, 2255–2266. [CrossRef] [PubMed]
61. Avila, M.A.S.; Breiter, R. Competitive sorption of cis-DCE and TCE in silica gel as a model porous mineral solid. *Chemosphere* **2008**, *72*, 1807–1815. [CrossRef]
62. Ma, X.; Archer, T.; Wang, C. Concentration effects on competitive sorption of trichloroethylene and tetrachloroethylene to the roots of typha latifolia: Implications for phytomonitoring. *Water Air Soil Pollut. Focus* **2009**, *9*, 271–277. [CrossRef]