Bioremediation and Sustainable Environmental Technologies—2017. Fourth International Symposium on Bioremediation and Sustainable Environmental Technologies (Miami, FL; May 2017). ©2017 Battelle Memorial Institute, Columbus, OH, www.battelle.org/biosymp. A. Barton and S. Rosansky (Chairs)

Wind-Powered Constructed Wetland for PCE Dechlorination

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ABSTRACT: Full perchloroethylene dechlorination has been demonstrated in a tailored self-sustaining constructed wetland in a field experiment. Straw had been added to the wetland as slow release compound for dissolved electron donor to enhance reductive dechlorination and a wind pump was used for contaminated groundwater extraction from the subsurface. During the field experiment tracer tests showed a residence time of 10 to 14 days where up to 93.5% of the contaminant load had been fully dechlorinated within the wetland through trichloroethylene, 1,2-dichloroethylene, vinyl chloride to ethene and ethane. Constructed wetlands in combination with wind pumps seem to have great potential for sustainable contaminated groundwater treatment, due to low maintenance and relatively low construction and operation cost.

INTRODUCTION

At Amersfoort central station in The Netherlands a perchloroethylene (PCE) groundwater contamination is situated at a former workshop for assembly and welding on rail carriages. The PCE was most likely dumped at the backdoor when its degreasing capacities declined after usage. The volume of the contaminated area is estimated at approximately 90.000 m^3 with a footprint around 10.000 m^2, with a groundwater fringe around 2 meter below ground surface (mbgs). To prevent further spreading of PCE to the surroundings, the contaminated soil was largely excavated in 2007, but pockets of contaminated soil remained from 3.5 to 14.0 mbgs at the bottom of the dugout pit. After completion of the excavation work, 14 m^3/hr of contaminated groundwater was extracted by a pump and treat (PAT) system over a period of 3 years. In the first 12 months of operation PCE-concentrations in the influent dropped from ±1000 µg/L to ±100 µg/L, but the effectiveness of the PAT system decreased. After one year of operation no further reduction of the PCE-concentration in the monitoring wells was observed. This was explained by rebound of PCE from semi-permeable layers in the subsurface (Drenth and Lindeman, 2012) The PAT system had limited success over a short period of time and was found to be a rather intensive measure and relatively expensive to its environmental efficiency output. Therefore, the PAT was stopped in 2011 but on going clean-up measures needed to continue in order to manage rebound due to regulation demands.

The objective of the current study is to develop a low maintenance, self-sustaining ecological engineered alternative to conventional PAT, where on a long-term basis, PCE is removed from the aquifer by a ‘green remediation’ solution.

Over the past decades several biological concepts for PCE dechlorination have been used, for example bioaugmentation (Van Bemmel et al., 2007), increasing the temperature in the subsurface, addition of electron donor, and phytoremediation. Phytoremediation of PCE was demonstrated by the infiltration of polluted groundwater in a constructed wetland, or helophyte filter (Chen et al., 2012) In a constructed wetland the presence of different redox zones and the availability of organic compounds that can be utilized as electron donor stimulate dechlorination of higher chlorinated hydrocarbons. In the pilot study of Chen et al., removal of PCE was successful, however the toxic metabolites cis-1,2 dichloroethene (DCE) and vinyl chloride (VC) accumulated because of the high sulfate concentration originating in the pumped groundwater from the contaminated location. Sulphite formation inhibited further dechlorination at anaerobic or aerobic conditions, created by the release of oxygen by the helophyte plant roots. Apart from the incomplete dechlorination of PCE, continuous energy was required for pumping for groundwater extraction and infiltration into the constructed wetland.

Phytoremediation of contaminated groundwater can be an interesting option for green remediation of PCE, but transport of polluted groundwater from the subsurface into a constructed wetland at ground surface requires continuous energy input. In the concept of this

study a wind pump is used to extract groundwater from the PCE-contaminated aquifer. The extracted groundwater flows then into the constructed wetland, tailored for anaerobic degradation of PCE. This paper evaluates the efficiency of this green remediation concept.

MATERIALS AND METHODS

Design and Construction of the Wetland, in Combination with a Windpump. Through a tailored design that suits local circumstances, a pilot scale constructed wetland was developed, built and maintained. The wetland contained a variation in plants, porous materials and a slow release electron donor compound and contaminated groundwater was infiltrated with a wind pump.

The wetland was constructed with a 3 mm polypropylene (PP) liner as an impermeable layer, with dimensions of 30 m x 5.5 m x 2.1 m (length x width x depth). The wetland is divided in four compartments, separated by PP sheeting in the upper 0.9 m of the system, allowing a connection of the compartments at the lower 1.2 m to keep the water flowing at anaerobic circumstances. The wetland was filled from bottom to top using: 0.1 m gravel, 0.3 m porous basaltic rock, also known as scoria, 1.15 m with a mixture of scoria + straw, 0.15 m gravel and on top 0.1 m water. The compartments were randomly implanted at a density of 10 plants/m^2 with three types of helophytes: *Phragmites australis*, *Juncus effuses* and *Scirpus lacustris* (Figure 1).

Within the system 25 monitoring wells were installed with filter depths at 1.7 – 2.1 m and 1.2 – 1.35 mbgs, respectively, distributed over the four compartments (Figure 2). The filters of the monitoring wells can also be used for addition of extra electron acceptor or donor, when needed.

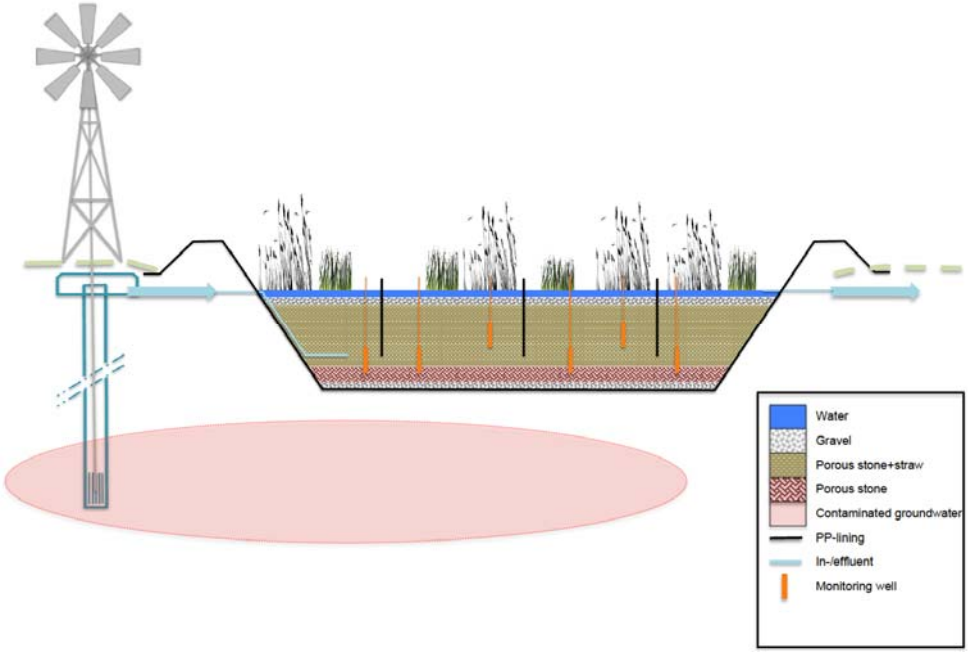

FIGURE 1. Schematic overview of the design of the constructed wetland and wind pump to treat the PCE polluted groundwater.

A wind pump (WK 225-46/6, rotor diam. 225 cm., pump diam. 46 mm, tower height 6 m., avg. capacity of 200 L/hr.) was installed to extract the groundwater from the subsurface and infiltrate it into the constructed wetland. To prevent PCE from spreading by groundwater transport from rebound at least 600 L per day should be extracted from a well south of the source zone area.

During the field experiment, the water flow and distribution through the constructed wetland was tested by use of two tracers: fluorescein and bromide. Fluorescein was used as

an optical tracer and samples were analysed on light extinction by a spectrophotometer at 500 nm. Bromide as an analytical tracer was analysed by ion chromatography. 50 L of fluorescein (1 g/L) was added instantaneous to the influent of the constructed wetland. Shortly after, 20 L sodium bromide solution (35 g/L) was pumped into the wetland at a rate of 0.1 L/h. Tracer concentrations of fluorescein and bromide were monitored over a period of 19 days at an interval of 1 to 3 days, at varying positions of the constructed wetland.

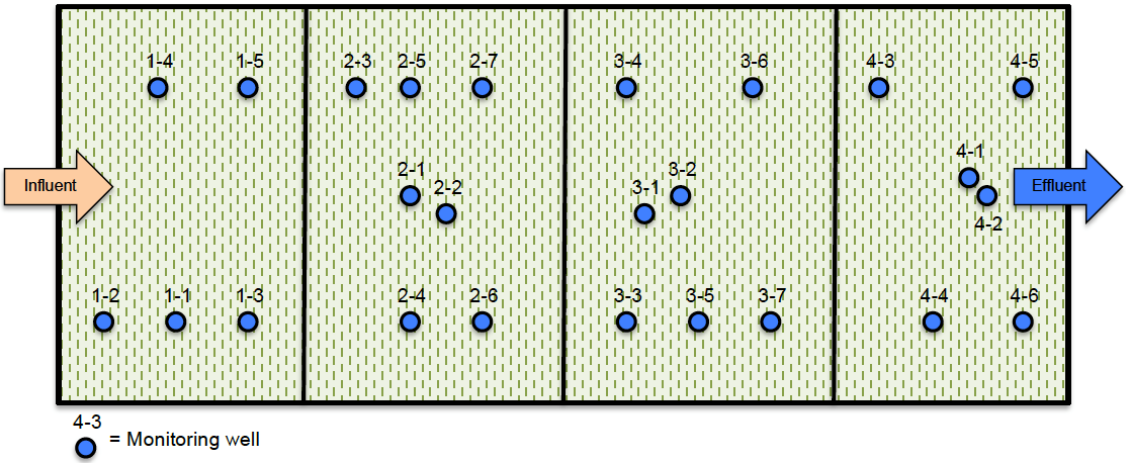

FIGURE 2. Schematic overview of the constructed wetland and monitoring well positions.

Operation and monitoring of the green remediation pilot test. After completion of the constructed wetland, groundwater was infiltrated by the wind pump. To assess PCE dechlorination and effects on the contaminant plume, frequent monitoring (at intervals of 1 - 3 months) in the constructed wetland and in the subsurface was performed.

The quantity of water flowing through the constructed wetland was continuously monitored at the influent by a flow meter. Redox potential (in mV), electric conductivity (in µS/cm), temperature (in °C) and pH were monitored by hand held sensors (Eijkelkamp, the Netherlands) in a flow cell during sampling of the monitoring wells. Samples for PCE-concentrations and its potential metabolites trichloroethene (TCE), cis/trans-DCE, VC, ethane and ethane, Dissolved Organic Carbon (DOC), electron acceptors and reductive dechlorinating bacteria were sampled from the monitoring wells in the constructed wetland and transported to the laboratory for further analysis.

Samples for PCE-analysis and its potential metabolites were taken in the field by pumping the monitoring wells where samples were collected in 20 mL glass vials, capped with PTFE lined silicone septa, fixated with 1 g/l $HgCl_2$ and stored until analysis within 10 days at 4ºC. The analysis was done at an Agilent using a Gas Chromatograph with a Porabond-Q 25 m, 0.32 mm diameter and 5 µm film thickness column and a FID-detector. Temperature program started at 40°C for 1 min followed by the 5 temperature increasing steps: from 20°C/min. to 100°C; 10°C/min. to 160°C; 2°C/min. to 180°C; 10°C/min. to 210°C and 80°C/min. to 250°C. This temperature is maintained for 2 minutes.

DOC samples were collected in the field from the monitoring wells, filtrated over a 45 µm membrane filter and pipetted in a 30 mL glass vials, capped with PTFE lined silicone septa. The sample was acidified by adding 30 µl 2 M HCl per 30 ml and stored until analysis at 4ºC. Within 10 days the samples were analysed using non-purgeable organic carbon method on a Shimadzu TOC-5050A analyser. Before analysis, samples were purged for 6 minutes with synthetic air at a rate of 150 mL/min.

Samples for potential present electron acceptors nitrate and sulfate were collected in 1.5 mL glass vials, capped with PTFE lined silicone septa and fixated with 1 g/l $HgCl_2$ and stored at 4ºC until analysis within 10 days on a Dionex ICS-1500 ion chromatograph. The Dionex ICS-1500 was equipped with an Ionpac AS14 anion-exchange column and an A SRS-Ultra 14-mm suppressor (Dionex Corp., Sunnyvale, CA). The eluent (2.0 mM Na_2CO_3 and 0.75 mM $NaHCO_3$) flow rate was 1.0 ml/min. The injection needle was preflushed with 100 µl of MilliQ

water, and 50 µl samples were injected. External standards at six different concentrations from 0 to 250 mM were used for calibration.

Total amount of bacterial 16S rRNA genes, *Dehalococcoides spp*. specific 16S rRNA genes, vinyl chloride reductase genes (*vcrA*), and epoxyalkane coenzyme M transferase genes (*etnE*) were quantified by quantitative real-time PCR (qPCR) on a CFX96 PCR system (Bio-Rad) based on presence of their DNA. Samples for DNA analyses were collected in sterile 1 L glass bottles from the monitoring wells, directly cooled at 4ºC and filtrated within 24 hrs over a 0.2 µm cellulose membrane filter. Filters were stored at -20 ºC for maximum one month until DNA extraction. DNA was extracted from the filter by using Qiagen SYBR® Green PCR kit. qPCR assays were performed as described before in (Van Der Zaan et al., 2010) and (Liu and Mattes, 2016).

RESULTS AND DISCUSSION

Flow Conditions. The constructed wetland holds a volume of 154 m^3 which mostly consists of scoria with a typical porosity range of 50 - 80% and permeability k range of 1.10^{-11} - 1.10^{-13} per m^2 (Saar and Manga, 1999) 4.5 – 5.0 % of the wet volume is straw which has an estimated porosity of 96% (Bouasker et al., 2014) The combined volume of the materials has an estimated average porosity of 0.65, which implicates a wet volume of ±100 m^3. Due to large variations in porosity and permeability of the applied materials, a tracer test was done to assess distribution of water entering, flow properties and residence time of the system.

From the tracer test, it was concluded that the residence time within the constructed wetland ranged between 10 and 14 days. The relation between wind velocity and water flow created by the wind pump was determined during the tracer test (Figure 3). There was a clear relationship between the wind power and the water flow. By fluctuation in wind velocity, the influent water flux varied within a range of 52 to 1198 L/h (1.2 to 28.7 m^3/d), with an average of 125 L/h (3 m^3/d) during a period of 19 days. This indicates that insight in the local wind circumstances is important before designing a constructed wetland.

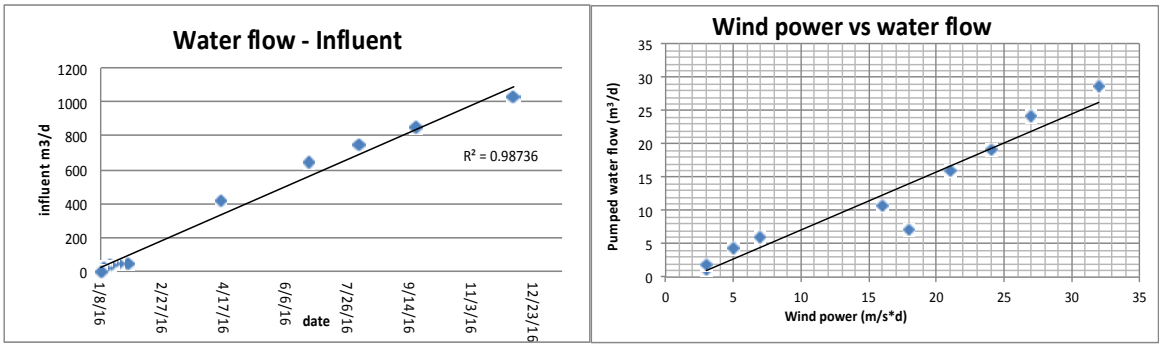

FIGURE 3. Relation between wind power and amount of water pumped from the subsurface to the constructed wetland (left panel) and water flow, generated by the wind pump, through the constructed wetland during the field experiment (right panel).

Based on the average monitored water flow (3 m^3/d) and a total wet volume of the constructed wetland (100 m^3), the residence time was calculated at 33 days. This is almost 3 times higher than the residence time determined with the tracers (fluorescein and bromide). Therefore, it is concluded that the influent water passes through the constructed wetland along a preferential flow path and therefore the flow design of the wetland can be improved to optimize its efficiency.

During the 11-month field experiment, which followed directly after the tracer test, the water flowed at an average rate of 3 m^3/d through the wetland. This is similar to the flow rate during the tracer test. The wind pump generated relatively stable flow rate through the constructed wetland, in spite of the daily fluctuations in the wind velocity.

Dissolved Organic Carbon. After 6 months from the start of the field experiment, the DOC concentration in the constructed wetland was higher than 14 months earlier (Figure 4). Furthermore, during the field experiment, the DOC concentration in the wetland was higher than in the influent water. This may reflect the release of organic matter from the straw and helophytes in the constructed wetland, but also increased DOC concentrations in the extracted groundwater over time.

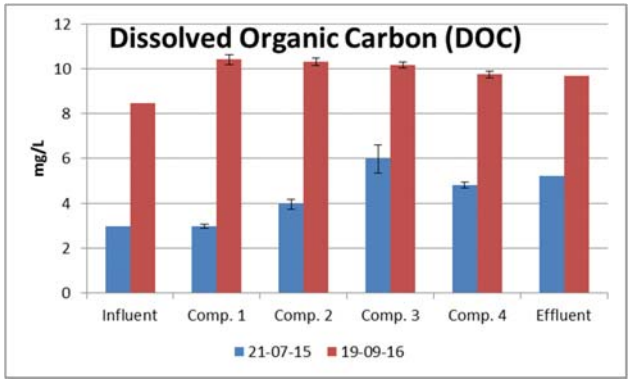

FIGURE 4. DOC concentrations (mg/L) in the constructed wetland, and influent and effluent water, directly after the construction of the wetland (blue bars) and 6 months after start of the field experiment (red bars). The data are average values of the different monitoring wells per compartment. The error bars reflect the standard error of the data.

Nitrate and Sulfate. In the influent water extracted from the subsurface, 15.4 ± 1,8 mg/L nitrate and 64.3 ± 0.9 mg/L sulfate was present. During the field experiment nitrate was found only once in the first compartment of the constructed wetland, but was not present in the water of the other compartments or in the effluent (data not shown). Sulfate was detected in the water of all four compartments during the field experiment. The concentrations decreased with distance from the influent to the effluent. The sulfate concentration in the effluent water was 1.6 mg/L in summer period (August and September) and 20.5 mg/L in December. The absence of nitrate and low concentrations of sulfate (<1 mg/L) are favourable for reductive dechlorination. Sulfate was present during the whole field experiment in higher concentrations. Although it cannot be excluded that micro niches with lower sulfate concentrations are present, further reduction of the sulfate concentration would create more favourable conditions for the reductive dechlorination of chlorinated ethenes. The increase of methane concentrations in the monitoring wells up to 18 mg/L indicated the development of methanogenic conditions in the wetland, favorable for reductive dechlorination. The differences in nitrate and sulfate concentrations between the compartments reflect the heterogeneity of redox-conditions in the constructed wetland.

Microorganisms. Table 1 shows the number of bacteria and genes found in the constructed wetland and influent and effluent water prior to pumping into the wetland and 6 months after the start of the field experiment (19-9-2016). Before start no genes of chloroethene degrading bacteria were detected. After start of the field test >1000 16S rRNA gene copies / ml water of *Dehalococcoides* spp. and vinyl chloride reductase (*vcrA*) genes were present in the constructed wetland and the effluent water. In parallel to reductive dechlorination capacity, also >100 gene copies / ml of the key enzyme for the aerobic degradation of VC (*etnE*) was present in compartments 2, 3, and 4 of the constructed wetland. This highlights the degradation potential for chlorinated ethenes via anaerobic and aerobic pathways is simultaneously present in the constructed wetland.

TABLE 1. Gene copy numbers of total bacteria 16S rRNA, Dehalococcoides spp. specific 16S rRNA, vinyl chloride reductase (vcrA) and epoxyalkane coenzyme M transferase (etnE) genes before (21-10-2014) and 6 months after start of the field test.

		Total bacteria	*Dehalococcoides* spp.	*vcrA*	*etnE*
		Gene copies/mL groundwater			
Influent	21-10-'14	880000	<400	<250	-
	19-09-'16	105000	88.7	<3	<135
Comp. 1	21-10-'14	-	-	-	-
	19-09-'16	-	1720	548	0
Comp. 2	21-10-'14	28100000	<750	<400	-
	19-09-'16	-	3940	1300	249
Comp. 3	21-10-'14	29900000	<625	<350	-
	19-09-'16	-	5730	3470	187
Comp. 4	21-10-'14	38400000	<625	<350	-
	19-09-'16	-	4240	3470	544
Effluent	21-10-'14	45700000	<2500	<1400	<1750
	19-09-'16	-	5810	5400	69.6

Biodegradation Process. The concentrations of PCE and its dechlorination products TCE, cis-DCE, VC, ethene and ethane were monitored over time in the different monitoring wells in the constructed wetland (Figure 5).

The concentration of PCE in the influent water was relatively constant at about 100-200 µg/L. A small amount of TCE and/or cis-DCE was found in the extracted groundwater as well during the last 3 months of the field experiment. In the constructed wetland itself, the PCE concentration in compartment 1 was up to 50 mole % of the influent concentration, 10 mole % in compartment 2 and <1 mole % in compartments 3 and 4. Vinyl chloride was found in all compartments, and in the effluent water of the constructed wetland. With distance from the influent to the effluent, the relative amount of ethane and ethane increased, showing complete PCE dechlorination in the constructed wetland.

The recovery of the total amount of PCE and the sum of its potential dechlorination products decreased with distance from the influent. In September only 1 mole % of the PCE load into the system was recovered as VC in the effluent stream. In compartment 4 the dechlorination products recovery was 30 mole % of which 66% was identified as ethene. The maximum removal of chlorinated ethenes was 93.5%. With an average residence time of 10-14 days, the maximal observed PCE dechlorination rate was 15.5 mg/L PCE per day.

The performance of the constructed wetland in the winter (December) was a bit lower than in the summer, as TCE was identified into compartment 3 and cis-DCE was found in compartment 4. However, even under those lower temperature conditions, more than 60 mole % of the detected (chloro)ethenes was ethene at a recovery of 16%. Seasonal variation can be explained by both variation in wind velocity and temperature, where increased wind velocity is negatively correlated to the residence time in the constructed wetland. In the present study, the monitoring frequency did not allow to identify the direct relation between wind velocity and dechlorination day by day. However, optimisation of the residence time to the local wind circumstances would make it possible to further improve the biodegradation process.

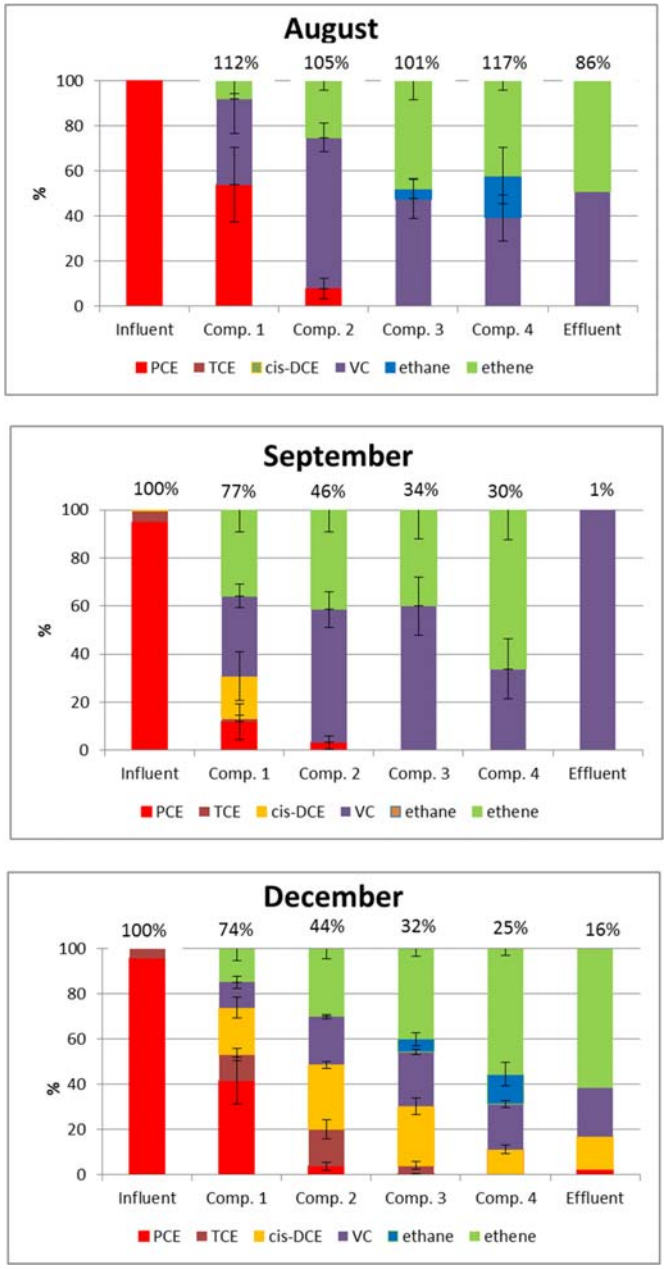

FIGURE 5. Relative amount of PCE and its dechlorination products in August, September and December 2016 in the influent, effluent and the four compartments of the constructed wetland. The percentages are relative to sum of the molair concentrations of PCE, TCE, cis-DCE, VC, ethene and ethane. Error bars represent the standard error based on the 6-7 individual monitoring wells per compartment. The numbers above the bars represent the recovery compared to the Influent concentration.

CONCLUSION

The self-sustaining wind powered constructed wetland at the former welding workshop of Dutch rail is capable of complete dechlorination of PCE in contaminated groundwater. PCE was degraded via TRI, cis-DCE, VC to ethene and ethane up to 93.5% at the effluent. Seasonal variation of temperature and wind seem to affect the efficiency of the system. The wind pump provided sufficient groundwater flow over the test period of 11 months. Local wind variations are of importance in dimensions of the tailored design. The DOC from the straw added to the system as a slow release electron donor compound most probably caused stimulation of PCE dechlorination within the constructed wetland. At the optimal residence time of 10-14 days in a period with wind abundance, biodegradation showed to be sufficient for PCE dechlorination to ethene and ethane. Constructed wetlands in combination with wind pumps seem to have great potential due to low maintenance and relative low construction and operation cost. Tailoring the design to local circumstances is key to its success.

Further improvement and development of this bioremediation approach may include:

- Optimizing flow paths within the wetland, to decrease its footprint
- Exploring possibilities to evolve the concept for application with other contaminants
- Optimisation of the dimensions of the system for local wind conditions
- Applying different carbon release compounds in addition to straw such as wood chips, saw dust or compost
- Re-injection of effluent water within the contaminated zone to stimulate *in situ* degradation

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