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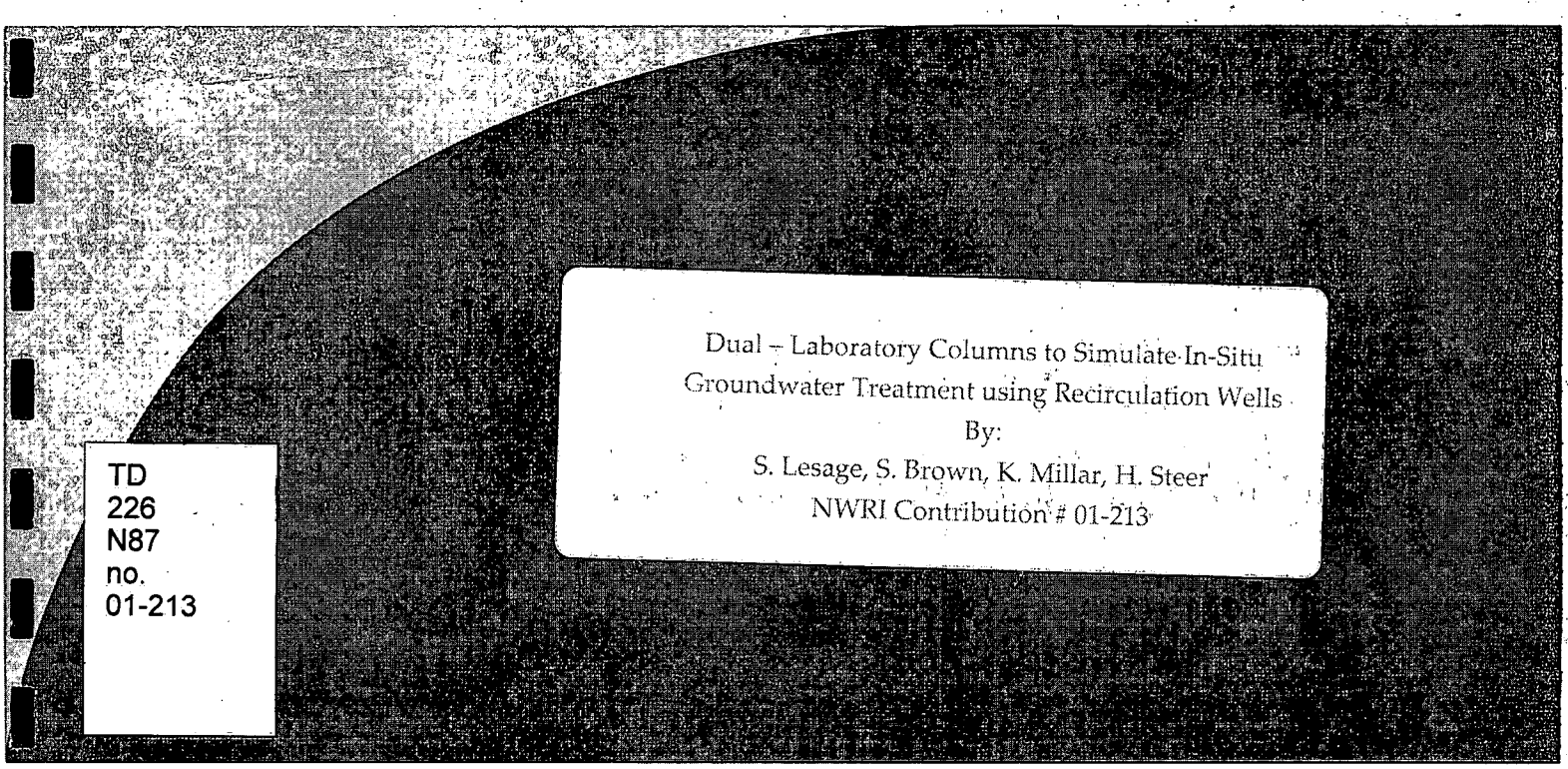

Dual – Laboratory Columns to Simulate In-Situ Groundwater Treatment using Recirculation Wells

By:
S. Lesage, S. Brown, K. Millar, H. Steer

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DUAL - LABORATORY COLUMNS TO SIMULATE *IN-SITU* GROUNDWATER TREATMENT USING RECIRCULATION WELLS.

Suzanne Lesage, Susan Brown, Kelly Millar and Helena Steer, National Water Research Institute, Environment Canada

ABSTRACT

This paper describes a dual-column laboratory set-up that was used to evaluate an *in-situ* groundwater treatment. The apparatus was designed to simulate a groundwater recirculation well as an *in-situ* reactor and injection well. The treatment was a vitamin B12 concentrate consisting of a buffered mixture of titanium (III) citrate and vitamin B_{12}. One column, made of glass replicated the well, whereas the second one was made of stainless steel, filled with aquifer material and instrumented with in-situ Eh probes. This was found to be a very efficient way of monitoring the redox conditions which were expected to be influenced by the addition of titanium (III) citrate. The apparatus was used to determine appropriate reagent concentrations in order to achieve the desired degradation rate. The redox measurement showed that although the sand contained large quantities of iron oxides, the oxidation rate was relatively slow and the titanium solution remained reduced for some time in the aquifer, continuing to react with the contaminants.

Management Perspective

This paper describes an ingenious experimental set-up that was used in the laboratory as a tool to evaluate the reaction conditions that would be used subsequently in the field for the application of vitamin B12 and titanium citrate for the degradation of a mixture of chlorinated solvents in groundwater. A detailed report has been produced in the past for the client, the US Army at Aberdeen Proving Grounds, but because the results could have wider application, this article should be published in the scientific literature.

INSTALLATION DE LABORATOIRE À DOUBLE COLONNE SIMULANT LE TRAITEMENT *IN SITU* D'EAUX SOUTERRAINES DANS UN PUITS DE RECIRCULATION

Suzanne Lesage, Susan Brown, Kelly Millar et Helena Steer

RÉSUMÉ

Cet article décrit une installation de laboratoire à double colonne utilisée pour évaluer un traitement *in situ* d'eaux souterraines, à l'aide d'un appareillage composé d'un réacteur *in situ* et d'un puits d'injection, de façon à simuler un puits de recirculation des eaux souterraines. L'eau était traitée par un concentré de vitamine B_{12} constitué d'un mélange tamponné de citrate de titane (III) et de vitamine B_{12}. Pour simuler le puits, on utilisait une colonne de verre et une colonne d'acier inoxydable remplie de matières d'aquifère et pourvue de sondes Eh *in situ*. On a constaté qu'il s'agissait d'une façon très efficace de surveiller les conditions d'oxydo-réduction qui, selon les prévisions, devaient changer après l'addition de citrate de titane (III). On a utilisé cet appareillage afin de déterminer la concentration appropriée de réactif nécessaire pour obtenir le taux de dégradation souhaité. La mesure de l'oxydo-réduction a montré que, malgré la présence d'une grande quantité d'oxyde de fer dans le sable, la vitesse d'oxydation était relativement lente et que la solution de titane restait à l'état réduit pendant un certain temps dans l'aquifère et continuait à réagir avec les contaminants.

Sommaire à l'intention de la direction

Cet article décrit un dispositif expérimental ingénieux utilisé en laboratoire pour évaluer les conditions réactionnelles pour le traitement *in situ* vitamine B_{12} - citrate de titane utilisé pour dégrader un mélange de divers solvants chlorés dans les eaux souterraines. On a déjà rédigé un rapport détaillé pour le client, les Forces terrestres des États-Unis au polygone d'essais d'Aberdeen Proving Grounds, qui nous ont recommandé de publier un article dans une revue scientifique.

DUAL - LABORATORY COLUMNS TO SIMULATE *IN-SITU* GROUNDWATER TREATMENT USING RECIRCULATION WELLS.

Suzanne Lesage, Susan Brown, Kelly Millar and Helena Steer, National Water Research Institute, Environment Canada

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This paper describes a dual-column laboratory set-up that was used to evaluate an *in-situ* groundwater treatment. The apparatus was designed to simulate a groundwater recirculation well as an *in-situ* reactor and injection well. The treatment was a vitamin B12 concentrate consisting of a buffered mixture of titanium (III) citrate and vitamin B_{12}. One column, made of glass replicated the well, whereas the second one was made of stainless steel, filled with aquifer material and instrumented with in-situ Eh probes. This was found to be a very efficient way of monitoring the redox conditions which were expected to be influenced by the addition of titanium (III) citrate. The apparatus was used to determine appropriate reagent concentrations in order to achieve the desired degradation rate. The redox measurement showed that although the sand contained large quantities of iron oxides, the oxidation rate was relatively slow and the titanium solution remained reduced for some time in the aquifer, continuing to react with the contaminants.

INTRODUCTION

Innovative groundwater remediation methods are commonly developed initially at a very small scale in the laboratory. Bioremediation is tested in static microcosms containing aquifer material, water from a contaminated site, nutrients and a carbon source, with an eventual bacterial inoculum. Some research groups have also added soil columns to their battery of tests (Bagley et al. 2000; Kaseros et al. 2000) to follow bioremediation with distance. However, to our knowledge, in laboratory investigations, nobody has looked at what happens in the well where treatment is injected and in a recirculation well where partially treated water is mixed with untreated water. Therefore a two column system was designed consisting of a glass column, representing an injection well, attached to a second column filled with aquifer material. The effluent from the soil column was mixed with untreated water and used to feed the glass column (representing an injection well), thus replicating a recirculation well system. A diagram of the experimental set-up is shown on Figure 1, whereas the field scenario that it is meant to represent, is shown on Figure 2. In the field, the reagent concentrate is injected at the bottom of the recirculation well where water infiltrates through the screen. An in-well pump moves the water upward through the well and the treated water exits via the upper screen. The flow lines as drawn show that some of the water exiting the upper screen is recaptured at the bottom of the well.

While many groundwater remediation applications use injection/withdrawal systems to introduce chemicals into the ground, a recirculation well is beneficial for two reasons (Herrling and Stamm, 1992). The first one is mixing. When a treatment is introduced into an injection well, a typical "oval pancake" plume is formed. Therefore, to treat a substantial volume of water several injection and withdrawal wells are needed. The recirculation system pulls water into the treatment zone and mixes it with reagents before re-injecting it in the aquifer, forming a circular zone of influence. The other major advantage is that the well becomes an in-situ reactor, where minimal contact with the aquifer material occurs. When the treatment involves oxidants or reductants that can react not only with the contaminant, but with the aquifer material, providing a period of reaction in the absence of interaction with the aquifer, can significantly enhance the reaction rate.

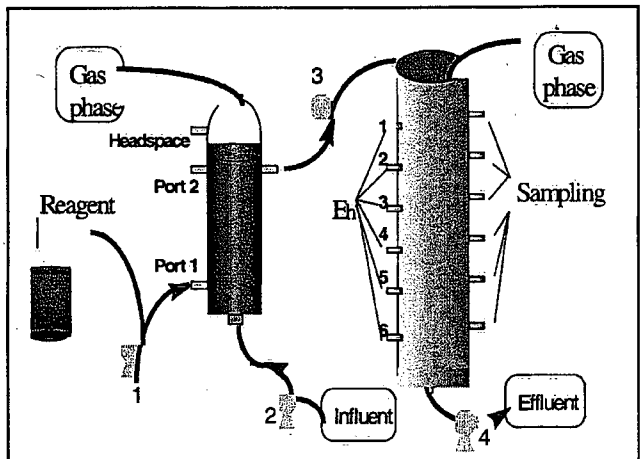

Figure 1. Setup for the column experiment. The sampling points were as indicated: the influent bag, the bottom port (1), the top port (2), the headspace, and the effluent from the soil column. Eh probes were inserted and remained *in-situ* for the duration of the experiment

Because of the importance of the geochemical reactions in evalutating the long-term effectiveness of an injected reducing agent, a series of redox probes were installed in the soil column. The in-situ platinum wire probes (Swerhone et al., 1999) were monitored continuously using a data-logger. This provided a much more accurate picture of the *in-situ* reactions than taking water samples would. Indeed, in a previous study with an in-ground column (Sorel et al, 1998), while Eh had been found to be a good indicator of reactivity, many technical difficulties were encountered in obtaining accurate readings from small water samples.

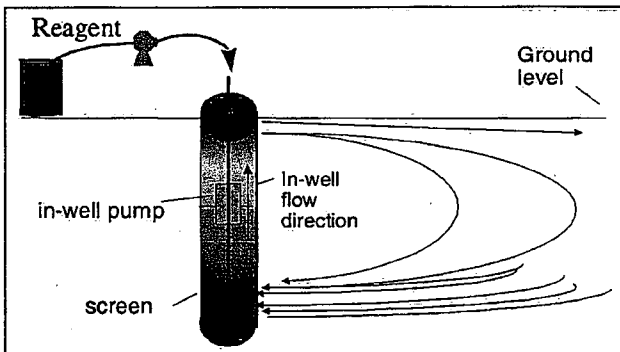

Figure 2 Recirculation Well Conceptual Model

The treatment that was tested in this case was the use of vitamin B12 and titanium citrate for the reductive dechlorination of chlorinated solvents (Lesage et al. 1997). While it had been successfully used in the laboratory to treat tetrachloroethylene (PCE; Burris, D.R et al., 1996; Lesage, S., et al.. 1996; Lesage, S. and S.J. Brown. 1997)) and many other chlorinated solvents individually (Krone, U.E., et.al. 1989; Krone, U.E. and R. K. Thauer. 1991; Gantzer, C.J. and L.P. Wackett. 1991; Shanke, C.A. and L.P. Wackett. 1992; Holliger C. et al. 1992; Assaf-Anid et al. 1994; Chiu, P.-C. and M. Reinhard. 1995) only one pilot scale field

application had been done on a mixture of PCE and 1,1,1-TCA (Sorel et al., 1998; Sorel et al., 2001). This study followed a series of microcosms that were designed to delineate the abiotic versus the biological reactions and the role of each of the ingredients in the mixture (Millar et al..2001). These tests were part of a feasibility study for an eventual field demonstration at Aberdeen Proving Grounds (Dames and Moore 1999).

Groundwater at Graces Quarters, Aberdeen Proving Grounds (APG), is contaminated with chlorinated volatile organic compounds (VOCs). The most abundant compounds at the site are 1,1,2,2-tetrachloroethane (TeCA) and carbon tetrachloride (CT), with peak dissolved phase concentrations on the order of 2,000 to 4,000 μg/L. Concentrations of trichloroethene (TCE) are below 500 μg/L, and chloroform (CF) and tetrachloroethene (PCE) concentrations are less than 100 μg/L.

EXPERIMENTAL SECTION

Aquifer material and contaminated groundwater were obtained from the Graces Quarters site at Aberdeen Proving Grounds in Maryland. The aquifer material was a quartz sand containing large amount of iron oxides and no carbonate mineral. Water was obtained from two piezometers labeled Q52 and Q14, respectively and representing two levels of contamination. The pH of the water as received was 4.5, attesting to the low-buffering capacity of the aquifer.

Tracer test

After the soil column was packed with sand from the site, a tracer test was conducted to measure the pore volume and the hydraulic conductivity of the system. A mixture of sodium bromide (100 mg/L) and lissamine (10 mg/L) was introduced at the top of the column. The appearance of bromide was measured by conductance of the effluent using an electrode and a Delta data logger. Lissamine was measured manually using a fluorescence detector. Although the sand that was obtained from the site did not contain much organic carbon, some retardation of lissamine was observed (R_f: 1.3). The pore volume of the column was estimated to be 4.2 L, only slightly more than the volume in the glass column (3.8 L). With a flow rate of 3.8 L/day, the linear velocity in the column was 0.9 m/day. At the slower pumping rate, designed for a 5-day retention time in the

glass column, a linear velocity of 18 cm/day was achieved. These represent velocities that would be observed some distance away from a recirculation well (30-40 m) depending on the specific design of the well and its flow rate.

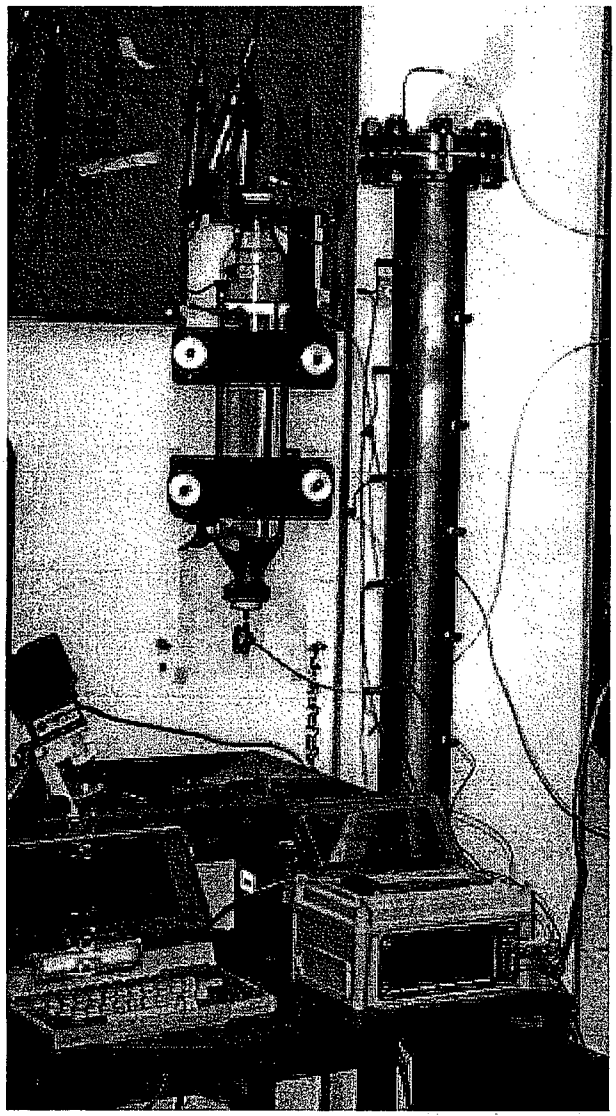

Figure 3. Photograph of setup showing lack of mixing at the top of the glass column.

Preliminary microcosms

The microcosm study (Millar et al. 2001) had been designed to maximize reaction rates: therefore titanium citrate was used at 30 mM and vitamin B12 at 10 mg/L. The purpose of the dual column study was to replicate the field application, where cost of reagents would be an important design factor. In order to determine the optimal reagent concentration, another series of microcosms were run, with site water only. From these tests (data not shown), we concluded that if the goal in the first treatment was to completely degrade TeCA, CT and PCE in one day, 4 mM titanium citrate and 3 mg/L vitamin B12 would be an effective concentration for the lesser contaminated site water. If the goal was to have TCE also below the maximum acceptable concentration (MAC), a residence time of 5 days would be required and the reagent concentrations would have to be increased to at least 5 mg/L vitamin B12 and 10 mM titanium citrate. The only expected products left would be *cis* and *trans*-DCE and VC. The concentration

of glucose was reduced from 10 to 1 g/L, thus reducing the amount of CO_2 produced and alleviating some of the gas pressure problems encountered in the microcosms.

Week 1 - Glass column only

The glass column (Figure 3) was filled with 3.7 L of site water (from piezometer Q52), leaving 300 mL of headspace. For the first two days, treatment was introduced by pumping a concentrate of the reagents for 6 hours each day and site water at the rate of 3.8 L/day, such as to produce a concentration of 4mM titanium citrate, 3mg/L vitamin B12 and 1g/L invertose (commercial glucose) in the glass column.

This was done to confirm whether the concentrations that were determined from the microcosm study were adequate to completely convert CT and TeCA, based on a one-day residence time. Samples were taken at the bottom (Port 1, Figure 1) after one day to monitor the concentration of titanium and glucose achieved. The concentration of the contaminants and their degradation products were measured in the influent bag and at the top (Port 2, Figure 1). After two days, because degradation was rapid and the water removed from the top of the column was partially reinjected (75% column top, 25% untreated water), the amount of reagent added was reduced in half.

Week 2-3 - Both columns - One day residence time.

At the beginning of the second week the effluent from column 1 was introduced into the soil column. The rest of the schedule is summarized in Table 1. The effluent of the soil column was collected in a 3 L Tedlar bag, and, after taking a subsample for analysis, was mixed with site water (3:1) to become the next glass column influent. For the first 2 days, the same amount of reagent as that of the previous week was added. However, because the effluent from the soil column was untreated water, it was necessary to resume pumping reagents for six hours to achieve the target Eh (< 300 mV).

Table 1 Vitamin B12/Titanium Concentrate Log						
	Date pumped	hours pumped per day	ml/min flow rate	B12 (mg/L)	titanium (mM)	Invertose (g/L)
Week 1						
	Jul-20-21	6	0.27	3	4	1
Pumps stopped for weekend	Jul-22-23	3	0.27	1.5	2	0.5
	Jul-27-28	3	0.27	1.5	2	0.5
Column pale	Jul-29	7.5	0.27	3.75	5	1.25
Pumps stopped for weekend	Jul-30	6	0.27	3	4	1
Week 3	Aug-04-05	6	0.27	3	4	1
5 day started	Aug-06	6	0.27	3	4	1
	Aug-07	2	0.27	5	10	1
Week 4	Aug-10-12	3	0.27	5	10	1
	Aug-13	3	0.27	5	10	2
Week 5	Aug-14	9	0.27	5	10	2
	Aug-17-19	3	0.27	5	10	2
	Aug-20	9	0.27	5	10	2
Changed to Q14						
	Sep-08-10	6	0.7	5	10	2
5 day started	Sep-11	3.5	0.7	5	10	2
	Sep-14-17	1.16	0.7	5	10	2
	Sep-18	3.5	0.7	5	10	2
	Sep-21-24	1.16	0.7	5	10	2
	Sep-25	3.5	0.7	5	10	2

Week 4-5 -Both columns - Five day residence time

After three weeks, the overall pumping rate was reduced such as to have an effective five-day residence within the glass column. The concentration of B12 was increased to 5 mg/L and that of titanium to 10 mM. After two days, the concentration of glucose (as invertose) was increased to 2g/L because the citrate concentration had decreased in the glass column, indicating that after a five-day acclimation period all the glucose had been used by the bacterial population.

Second Phase - Q14 water

The glass column was emptied and cleaned before changing to the high concentration site water. During that period the water in the soil column was recirculated completely without the addition of reagents. As planned, for the first day, the treatment (5 mg/L B12 , 10 mM titanium and 2g/L glucose) was pumped through the glass column only to ensure that no untreated water would be

transferred to the soil column. The first week the water was pumped to provide a one-day residence time and starting on the second week, the pumping rate was reduced to provide a five-day residence time. No further changes were made during that period.

Chemical Analyses

Water samples (50 mLs) were placed in a 60-mL serum bottle. The analysis was done by injecting a sample of the headspace after equilibration to room temperature into an SRI Gas chromatograph with ECD and FID detectors. PCE, TCE, TeCA, CT, CF and DCM were measured by ECD, whereas *cis* and *trans*-DCE, and VC results are reported using the FID.
Glucose was measured using a glucometer (Encore™, Bayer). Titanium was measured as titanium IV sulfate colorimetrically at 400nm on a Varian Carey 3 spectrophotometer. The bright yellow solution was obtained by acidification with sulfuric acid and the addition of hydrogen peroxide. Volatile fatty acids were measured by ion-exclusion chromatography using a Waters IC-Pak column with 1 mM HCl as eluent at 1 ml/min, and a Waters Model 430 conductivity detector.

RESULTS

Week 1 - Glass column only

The purpose of only using the glass column in the first week was to verify whether the chosen concentrations would produce the expected rate of reaction and whether the amount of glucose added (1 g/L), would suffice to prevent citrate degradation and titanium precipitation in the column.

The degradation of TeCA, CT, and CF was complete (Figure 4, 7/20 to 7/27). PCE was degraded to below its MAC (1 μg/L). The concentration of TCE did not vary much, partially because some of it is formed from PCE, and also because its degradation rate is much slower than that of the other compounds present in site water. As was observed in the microcosms, *cis* and *trans*-DCE and vinyl chloride (VC) were formed and not degraded (no measurable ethene).

One interesting feature was that, during this short period and in the absence of soil, no glucose degradation was observed. Because there was no CO_2 produced to induce mixing, the top 2 cm in the column, above the sampling port, remained untreated (Figure 3). The concentration of VOCs in the headspace were similar to those of the untreated site water and no products were observed. This is representative of the lack of mixing that can occur in groundwater and supports the usefulness of recirculation wells as reactors to maximize treatment distribution.

Week 2-3 - Both columns - One day residence time.

During the second and third weeks of treatment (weeks beginning July 27 and August 4), the water was pumped from the top port of the glass column to the top of the soil column. The data for samples taken at the top of the glass column shows that all the TeCA and CT were degraded within the one-day residence time (Figure 4). A sudden increase in the influent concentration of TeCA, carbon tetrachloride and PCE is evident on July 29. This is because the influent was changed at this point from treated water from the top of the glass column to soil column effluent, which contained untreated site water.

The colloid present in the effluent from the soil column caused cloudiness in the glass column. It seemed that the iron oxide floc was not being reduced and dissolved by the titanium treatment, at least not during the one-day retention period. After the first week, substantial biomass could also be seen in the glass column. After August 4, the glucose level started to drop, but enough titanium citrate remained in solution to sustain the dechlorination reaction. One of the effects of the biomass was the production of CO_2 which induced mixing in the system and the transfer of some of the VOCs to the headspace. During this period, concentrations of TCE, *cis* and *trans*-DCE and VC were essentially identical before (Top-2) and after the soil column, indicating that there was no significant degradation in the soil column.

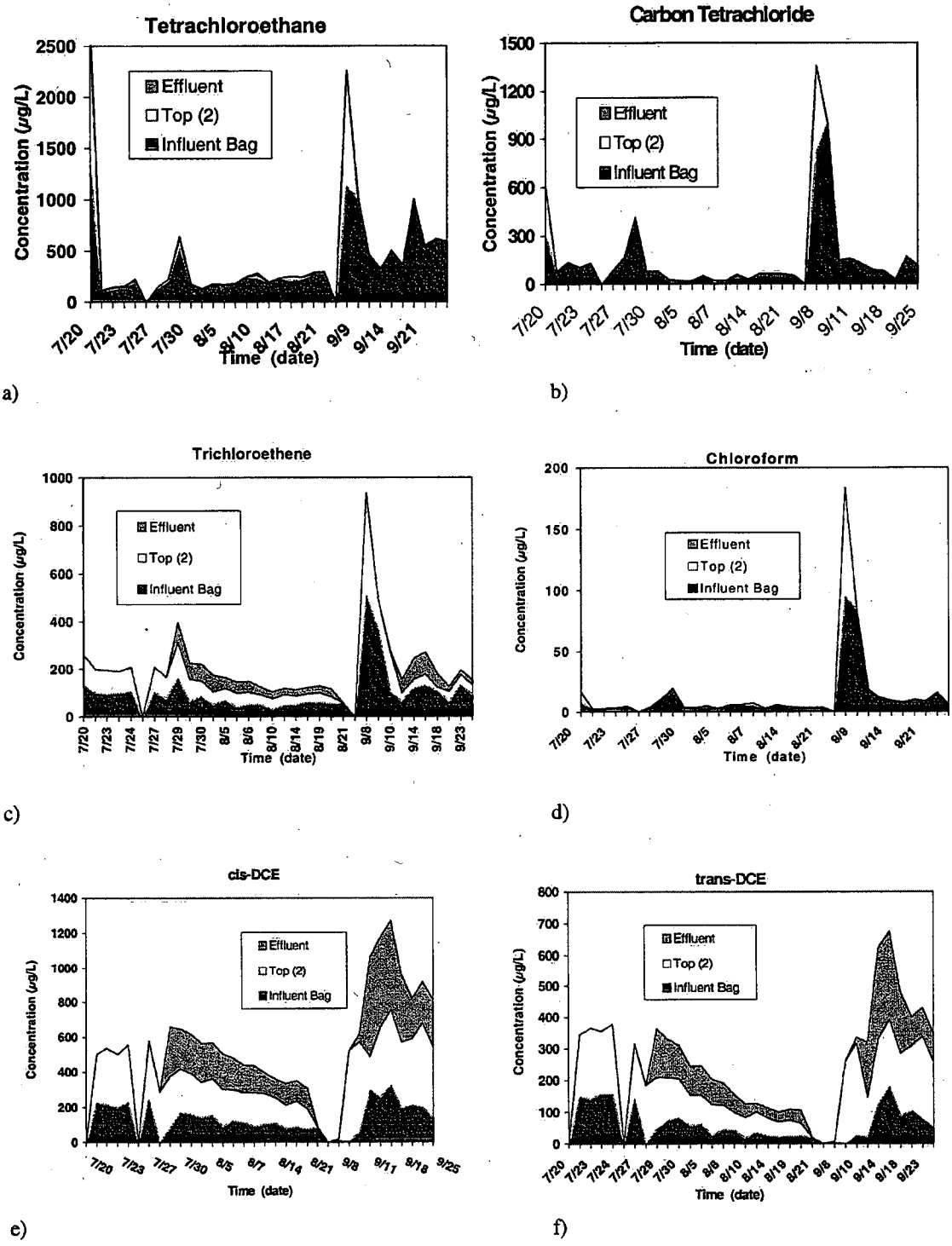

Figure 4 Concentrations of the main VOCs under different pumping regimes. First week – glass column only. Starting in September – Q14 water.

August 7- August 24 -Both columns - Five day residence time

The purpose of this phase was to determine whether it was possible to completely degrade TCE within the glass column, by increasing the residence time. Also, a slower flow rate would allow a longer time for the oxidation of titanium(III) citrate, providing an indication of reactivity in the field at the furthest distance from the well, where the velocity of the water would approach background. Therefore, on August 7, the pumping rate was reduced to produce a five-day retention within the glass column and a linear velocity of 18 cm/day within the soil column. The concentration of reagents was increased to 5 mg/L B12,10 mM titanium citrate and 2g/L glucose, because the extensive biomass that had formed led to glucose degradation within two days.

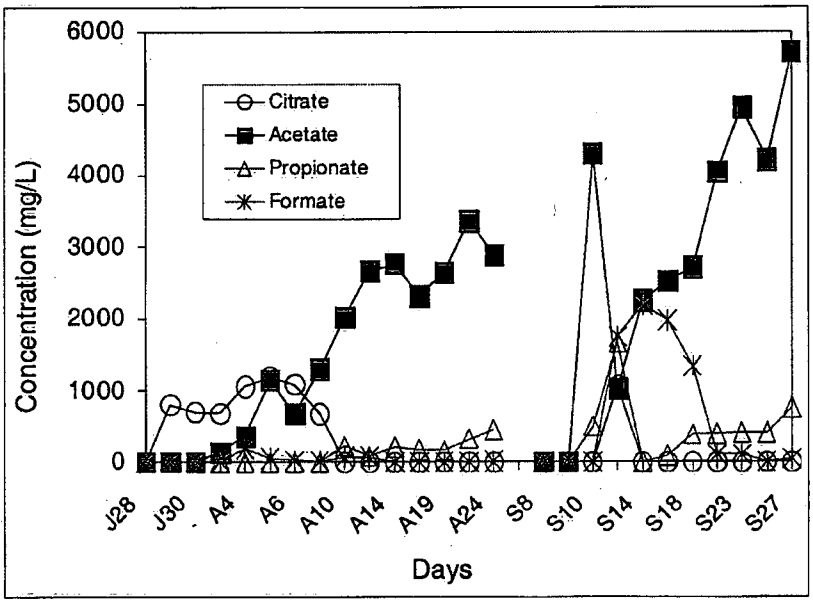

Figure 5 VFAs in Soil Column Effluent.

The concentration of acetate (Figure 5) increased significantly and propionate became measurable. Even though, the Eh increased in both the glass and the soil columns, the degradation of TeCA, CT and CF was sustained within that period. It is important to note that the reagent concentrate was added for three hours each day at port 1 and that the measurements for titanium, glucose and Eh were taken a day later out of the same port, before the addition of the

fresh reagent. Therefore, suitable conditions were probably prevalent long enough for the degradation to occur in the glass column.

The effluent concentrations of *cis* and *trans*-DCE were lower than those at the top port (Figure 4). When comparing individual points on the graph, it is important to remember that a five-day period elapsed between the influent and the top and another five days between the top and the effluent, making point to point comparisons difficult. However, when considering the overall downward slope of the lines in the graph, it is very apparent that some degradation of *cis* and *trans*-DCE must have been occurring, otherwise their concentration would remain constant throughout the period. Similarly, the amount of VC was reduced to below detection limit (data not shown). TCE also exhibited a decreasing trend, although not as pronounced as with *cis* and *trans*-DCE. The amount of PCE was also very low, such that even the influent concentration was below the MAC. Towards the end of the period, the concentration of methane in the effluent could no longer be accounted for by the amount of CT degraded, indicating methanogenesis in the column.

At this point, the system was shut down for maintenance and changeover to Q14 site water. However, the effluent was entirely recirculated through the soil column, to prevent stagnation and possible bio-clogging.

Q14 (high concentration site water)

September 8- September 25 - Q14 water

The glass column was cleaned thoroughly and filled with fresh untreated Q14 water. The treatment was started at the faster pumping rate (1 day retention time). The concentration of B12 was 5 mg/L and that of titanium citrate was 10 mM.

The degradation of TeCA with the concurrent formation of *cis* and *trans*-DCE in a ratio of 2:1, was similar to that observed for the Q52 water and indicative of the vitamin B12-catalysed

reaction (Millar et al. 2001). Similarly, all CT, CF and PCE were rapidly removed from the water. In the case of TCE, between September 11-18, the concentration in the effluent was still higher than that at the top, reflecting the concentrations five days earlier at the top of the glass column. However, as treatment progressed (after Sept 21) the effluent concentration of TCE decreased to about 20 μg/L. Selected results of TCE degradation are shown in Table 2 with the calculated rate constants. Because the overall retention time in the system was 10 days and the column was run at that rate for two weeks, only few data points are available. They show an increase in rate constant with time, which is potentially indicative of biological degradation starting to occur.

Table 2. TCE degradation in both columns, five day retention time Q14 water. Concentrations in μg/L. Rate constants- first order.

Date In	Influent	Top 5 days later	k ($days^{-1}$) Influent to top	Effluent 5 more days	k ($days^{-1}$) Top to Effluent
9/10	104	49	0.15	19	0.19
9/16	129	44	0.22	21	0.29

Cis and *trans*-DCE concentrations trends were similar to those with the low concentration water. For the first week, the effluent concentrations were almost identical to those at the top of the column (again taking the column retention time into account). However, in the last week, the concentrations of *cis* and *trans*-DCE in the effluent decreased to about half of that at the top (Table 3). The *cis:trans* ratio increased from 2:1 at the top to 3:1 in the effluent, indicating that biodegradation was occurring. These results are different than those observed in the field by Lorah and Olsen (1999) in an area contaminated with both TeCA and TCE where the proportion of trans was much higher (*cis:trans* ratio ranging from 0.4:1 to 1.5:1.0) but closer to those observed by Chen (2.4:1.0) on the degradation of TeCA only (Chen, 1996). The effluent concentration of VC decreased to between 3 and 6 μg/L. In the case of these compounds, it is not possible to calculate a meaningful rate constant in the glass column, because the compounds were both formed and degraded. Calculated degradation rates in the soil column are shown in Table 3. The fact that the rate constant were in the same order of magnitude for all four

compounds also supports the fact that the degradation was mediated by bacteria, because the vitamin B12 catalyzed dechlorination rates drop dramatically with successive dechlorinations.

Table 3. *Cis* and *trans*-DCE and VC degradation in the soil column, five day retention time Q14 water. Concentrations in μg/L. Rate constant – first order.

	Cis-DCE			Trans-DCE			VC		
Date In	Top	Effluent 5 days later	k ($days^{-1}$) Top to Effluent	Top	Effluent 5 days later	k ($days^{-1}$) Top to Effluent	Top	Effluent 5 days later	k ($days^{-1}$) Top to Effluent
9/16	433	231	0.13	213	92	0.17	10	6	0.10
9/18	376	236	0.09	197	92	0.15	11	5	0.16
9/21	378	275	0.06	205	88	0.17	14	3	0.31

During this phase, the soil column was overwhelmingly methanogenic. Because of the recirculation, methane was also transferred to the influent. Methanogens started to establish themselves towards the end of the first period where Q52 was pumped slowly and where the Eh was far from being at its lowest. It is possible that there was only small methanogenic zones, in the heart of the column at port 3 and 4. At the startup with Q14, the influent was pumped fast for three days, then slowly. This was enough to cause a rapid drop in Eh, that slowly recovered upwards when the pumping rate was reduced. The best degradation of *cis* and *trans*-DCE and of VC was in the latter part of the treatment, where the Eh readings were back up into the -200 mV range.

When considering the products of bacterial activity, depending on the phases, different species of bacteria were present. Unlike what was seen with Q52, no lactate was detected in spite of the fact that glucose was being degraded in the glass column. Citrate was conserved in the glass column, but completely utilized in the soil column. Large amounts of acetate were formed in both the glass and the soil column, presumably from glucose in the first instance and from citrate in the second. Some acetogens must also therefore be present in addition to the methanogens. Propionate, which is produced by some anaerobic glycolytic strains such as *Clostridia sp and Propriniobacterium sp.*, (Jurstshuk, 1996), was also formed in the latter part of the study within the soil. Formate was formed in the glass column and used in the soil column. All these products

are typical of anaerobic systems. Therefore, the further degradation of the chlorinated ethene metabolites was occurring under anaerobic conditions.

Redox

In-situ Eh probes were used to monitor the redox status of the soil column. In a previous field investigation (Sorel et al., 2001), the addition of titanium citrate to an *in-situ* vertical column in the up-flow mode resulted in a dramatic reduction of the aquifer material (down to – 600 mV) within the first 20 cm above the injection point, but 50 cm higher the Eh did not get lower than -300 mV. This is due to the aquifer oxidation capacity (Barcelona and Holm, 1991; Heron et al. 1994). In this experiment, the addition of the reductive treatment solution resulted in a rapid drop in Eh throughout the entire soil column (Figure 6). The lowest Eh was observed at ports 2, 3 and 4, in the middle of the column. As the pumping rate was decreased, the Eh increased, because there was more time for the redox exchange to occur.

The aquifer material from this site is mainly a medium quartz silica sand with metal oxides, primarily iron. As the aquifer material became reduced, an orange colloid collected in the effluent, which was attributed to mobilized Fe(II) that was reoxidized when passing through lower zones (ports 5 and 6). This data was very valuable in the design a future field test, because this showed that titanium (III) citrate could travel a significant distance from the well before being oxidized. Therefore it is important to consider not only the oxidation capacity of an aquifer, but also the chemical availability and reactivity of the species involved. In a flowing system, kinetics are very important. This dual column experiment allowed us to capture this difference and to design the field demonstration more effectively.

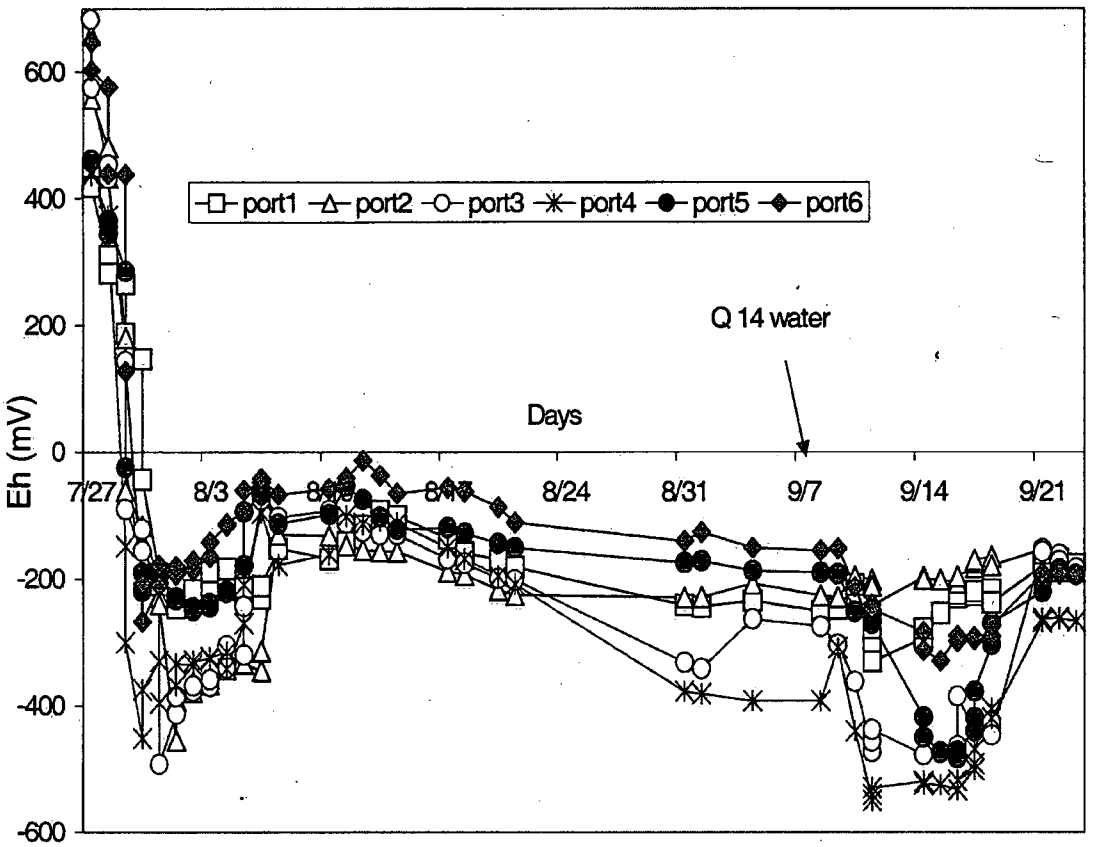

Figure 6. Eh fluctuations in soil column - Pt electrode readings -not corrected.

IV. Conclusions

The two-column study was a very effective way to gain further insight into the possible behavior of the vitamin B12/titanium citrate reagent in a recirculation well system. The results obtained with the two concentrations of contaminants were essentially similar. The presence of the *in-situ* Eh probes provided data on the degree of equilibrium between redox active species that occurs at different pumping rates in the system. These pumping rates were used to represent the situation in the soil at increasing distances from the well. This showed that, close to the well, the water flow rate would be such that equilibrium with the soil solids would not be attained, i.e. the Eh would remain close to that in the well. This is positive in terms of well design constraints,

because this means that the reaction time with titanium citrate and B12 would be the well residence time, plus the travel time in the soil, up to the point where the water slows down to a linear velocity below one meter per day.

The second important conclusion is that it is probably not necessary to add any other means of treatment. It appears that with time and distance, different bacterial populations that are capable of completing the degradation of the chlorinated ethenes could establish themselves. These populations are anaerobic, but do not require extreme conditions.

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REFERENCES

Assaf-Anid, N., K.F. Hayes, and T.M. Vogel. 1994. Reductive Dechlorination of carbon tetrachloride by cobalamin (ii) in the presence of dithiotreitol: Mechanistic studies, effect of redox potential and pH. *Environmental Science and Technology* 28: 246-252.

Bagley, D.M., M. Lalonde, V. Kaseros, K.E. Stasiuk and B.E. Sleep. 2000. Acclimation of Anaerobic Systems to Biodegrade Tetrachloroethene in the Presence of Carbon Tetrachloride and Chloroform, Water Research. **34**, 171-178.

Barcelona, M.J. and T.R. Holm. 1991. Oxidation-reduction capacities of aquifer solids. *Environmental Science and Technology* 25: 1565-1572.

Burris, D.R., C.A. Delcomyn, M.H. Smith, and A.L. Roberts. 1996. Reductive dechlorination of terachloroethylene and trichloroethylene catalyzed by vitamin B12 in homogeneous and heterogeneous systems. *Environmental Science and Technology* 30, No. 16: 3047-3052.

Chen, C., J.A. Puhakka and J.F. Ferguson. 1996. Transformations of 1,1,2,2-tetrachloroethane under methanogenic conditions. *Environmental Science and Technology* 30:542-547.

Chiu, P.-C. and M. Reinhard. 1995. Metallocoenzyme-mediated reductive transformation of carbon tetrachloride in titanium(III) citrate aqueous solution. *Environmental Science and Technology* 29: 595-603.

Dames and Moore 1999. Installation Restoration Program, Graces Quarters, Aberdeen Proving Ground, Edgewood MD, Treatability Study Report, Primary Test Area.

Gantzer, C.J. and L.P. Wackett. 1991. Reductive dechlorination catalyzed by bacterial transition-metal coenzymes. *Environmental Science and Technology* 25: 715-722.

Herrling, B. and J.Stamm. 1992. Groundwater Circulation Wells (GZB) for the Realization of In-Situ Bioremediation. In " In-Situ Bioremediation Symposium'92" Proceeding of the Symposium held at Niagara-on-the-Lake, Ontario, September 1992. S. Lesage Editor. Pages 251-253.

Heron, G., T.H. Christensen, and J.C. Tjell. 1994. Oxidation capacity of aquifer sediments. *Environmental Science and Technology* 28: 153-158.

Holliger C., G. Schraa, A.J. Stams, and A.J.B. Zenhder. 1992. Evidence for the involvement of corrinoids and factor F_{430} in the reductive dechlorination of 1,2-dichloroethane by *Methanosarcia barkeri*. *Journal of Bacteriology* 174: 4427-4434.

Jurstsuk, P. jr . 1996. Bacterial Metabolism. In Medical Microbiology, Samuel Baron, Ed. Fourth Edition. Chapter 4. Available at http://gsbs/utmb/edu/microbook/ch004.htm.

Kaseros, V., B.E. Sleep and D.M. Bagley. 2000. Column Studies of Biodegradation of Mixtures of Tetrachloroethene and Carbon Tetrachloride, *Water Research*, **34**, 4161-4168.

Krone, U.E., R.K. Thauer, and H.P.C. Hogenkamp. 1989. Reductive dehalogenation of chlorinated C_1- hydrocarbons mediated by corrinoids. *Biochemistry* 28: 4908-4914.

Krone, U.E. and R. K. Thauer. 1991. Reductive formation of carbon monoxide from CCL4 and FREONs 11, 12 and 13 catalyzed by corrinoids. *Biochemistry* 30: 2713-2719.

Lesage, S., S.J. Brown, and K.R. Millar. 1996. Vitamin B12-catalysed dechlorination of perchloroethylene present as Residual DNAPL. *Ground Water Monitoring and Remediation*. Fall 1996: 76-85.

Lesage, S., S. J. Brown and K.R. Millar."Method for Dehalogenating Contaminated Water and Soil" U.S. Patent 5,645,374. Date of issue: July 8, 1997.

Lesage, S. and S.J. Brown. 1997. Biochemical degradation of perchloroethylene using generator columns containing residual DNAPL. *Journal of Environmental Science & Health* A32: 241-257.

Lorah, M.M. and L.D. Olsen. 1999. Natural attenuation of chlorinated compounds in a freshwater tidal wetland: Field evidence of anaerobic degradation. Water Resources Research. 35: 3811-3827.

Millar K. R., S. Lesage, S.J. Brown, H. Steer. 2001. Remediation of Groundwater Contaminated with a Mixture of Chlorinated Methanes, Ethanes, and Ethenes using Vitamin B_{12}-Catalyzed Dechlorination. NWRI Report 01-207. In submittal.

Shanke, C.A. and L.P. Wackett. 1992. Environmental reductive elimination reactions of polychlorinated ethanes mimicked by transition-metal coenzymes. *Environmental Science and Technology* 26: 830-833.

Sorel, D., J.A. Cherry, and S. Lesage. 1998. In-situ vertical circulation column. *Ground Water Monitoring and Remediation* 18, No. 1: 114-125.

Sorel, D., S. Lesage, S. Brown and K.R. Millar. 2001. Vitamin B12 and Reduced Titanium for the Remediation of Residual Chlorinated Solvents: Field Experimentation. Groundwater Monitoring and Remediation. 21 (4). 140-148.

Swerhone, G.D.W., J.R. Lawrence, J.G. Richards and M.J. Hendry. 1999. Construction and testing of a durable platinum wire Eh electrode for in situ redox measurements in the subsurface. Ground Water Monit. Remediat. Spring: 132-136.

Vogel, T.M. and P.L. McCarthy. 1985. Biotransformation of tetrachloroethylene, trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. *Applied Environmental Microbiology* 49, No. 5: 1080-1083.

Zehnder, A.J.B. and K. Whurmann. 1976. Titanium(III) citrate as a nontoxic oxidation-reduction buffering system for the culture of obligate anaerobes. *Science* 194: 1165-1166.

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