FINAL REPORT: PROJECT CU-1124

AN INNOVATIVE PASSIVE BARRIER SYSTEM USING MEMBRANE-DELIVERED HYDROGEN GAS FOR THE BIOREMEDIATION OF CHLORINATED ALIPHATIC COMPOUNDS

Performing Organization: University of Minnesota

Project Background

Contamination of soil and groundwater with halogenated organic solvents such as trichloroethene (TCE) is a significant problem in the U.S. and especially at U.S. Department of Defense sites **(1, 2)**. Some of the most appealing new remediation technologies for cleaning up such sites, because of their low cost and low impact, are *in situ* biological barrier systems. One biological barrier approach involves addition of electron donor to the contaminated aquifer. This stimulates the growth of indigenous microorganisms that are capable of using chlorinated ethenes as electron acceptors, resulting in the reductive dehalogenation of the contaminants to innocuous end-products. Electron donors that have been tested in such systems include lactate, butyrate, benzoate, and H_2 **(3)**.

As an electron donor H_2 is effective **(4),** significantly less expensive than alternative compounds, and generates less biomass in the subsurface per reducing equivalent than organic donors. Nevertheless, H_2 is a sparingly soluble gas that is difficult to distribute uniformly across a groundwater contaminant plume. Conventional gas transfer technologies such as sparging are problematic because they are inefficient and difficult to control. In addition, because H_2 is explosive, losses to the vadose zone because of channeling may be a cause for concern.

The problems associated with the use of H_2 can be overcome by taking advantage of recent advances in membrane gas transfer technology. This technology uses gas permeable membranes to dissolve H_2 directly into water without bubble formation and subsequent losses **(5-7)**. Depending on the mode of operation, these membranes can achieve up to 100% gas transfer efficiency **(7)**. In addition, the gas delivery rate can be controlled by adjusting membrane surface area and gas pressure **(8)**. Thus, this innovative gas transfer technology can deliver bio-available H_2 with a high degree of control and safety.

Objectives

The objective of this project was to examine the gas transfer behavior and performance of hollow fiber membrane passive barriers. The research assessed the suitability and effectiveness of membranes for delivering H_2 to accelerate the *in situ* remediation of chlorinated organic compounds such as TCE and perchloroethene (PCE).

The specific objectives and technical approach that was taken in this research, from the original proposal to the Department of Defense Strategic Environmental Research and Development Program, are presented below.

Technical Approach

1. Investigate the gas dissolution behavior of the membrane fiber under conditions of creeping flow.

The gas transfer behavior of the membranes under conditions of creeping flow has never been investigated. The low rates of gas delivery will necessitate the use of low gas pressures and the behavior of the membrane will be strongly influenced by the back-diffusion of dissolved gases. These effects need to be investigated to determine gas transfer rates as a function of gas pressure, groundwater velocity, membrane spacing, and hydrostatic pressure.

2. Characterize the impact of diffusion on the gas transfer behavior of the membrane.

The back diffusion of dissolved gases such as nitrogen and CO_2 into the membrane fibers has a profound effect on the gas transfer process **(7, 9)**. Condensation can also occur **(5)** and this can cause process failure. These effects are especially true at the low gas pressures that will be needed in this application. We need to characterize the impact of back diffusion accurately for scale up and for optimizing large scale operation. We also need to assess the impact of supplying H_2 with and without gas recirculation in the fibers.

3. Assess the effects of biofilm development and chemical reactions on the ability of membrane fibers to deliver H_2 at adequate rates.

If chemical precipitates or a biofilm develops on the outside of the fibers, then the gas transfer behavior of the membrane will be affected. The impact on gas transfer will be characterized by comparing the gas transfer behavior of the membrane in biologically and chemically reactive systems to the performance observed with clean water tests.

4. Characterize the transformation of dissolved chlorinated solvents in simulated groundwater systems using membrane delivered H_2.

The goal of this phase of the research is to demonstrate the ability of the gas permeable membrane system to deliver H_2 at rates that are suitable for effective dehalogenation without significant production of methane gas (CH_4) by methanogenic bacteria. In addition, another goal is to demonstrate the robustness of our membrane bioremediation system by evaluating solvent degradation performance for a range of aquifer conditions. Bench-scale flow-through column reactors fitted with a membrane H_2 delivery system will be used to simulate a remediation site. Column reactors will be filled with aquifer material obtained from at least three sites contaminated with chlorinated solvents (PCE and TCE). The ability to achieve effective dehalogenation using the various aquifer material sources will provide a proof of concept for the membrane treatment system and will demonstrate the need for further study, development, and scale-up of the system.

5. Model Simulation for Data Analysis.

A numerical model was developed to simulate non-steady-state substrate and biomass (both suspended and attached) profiles in porous media systems. This model incorporates the fundamental processes of microbial growth and decay, deposition, transport, and biodegradation **(10)**. The porous media biofilm model will be coupled with a membrane supported biofilm model to create a model that is capable of simulating biofilm accumulation, substrate (H_2) uptake, and contaminant dehalogenation throughout the experimental system (on the membrane

surface and on the porous media). The combined model will be used to evaluate the results obtained from the porous-media reactors operated in this research and will also be used to extend the experimental results to conditions that could not be evaluated experimentally due to time and cost considerations. The model will also be useful for the design of the pilot-scale studies discussed below and for the transition of the membrane-bioremediation technology to the field.

6. Pilot-Scale Studies for Assessing Factors Important for System Scale-up

Pilot-scale studies will be performed to assess factors important for scale-up of the passive barrier membrane system, such as membrane module design and installation. In addition, the pilot-scale studies will be used to test the performance of the system using conditions that are more representative of field-scale installations. Initial experiments will be performed to verify the clean water H_2 delivery rates observed from the bench-scale system. Experiments will also be performed to monitor contaminant dehalogenation in an aquifer material system to determine the effects of scale-up on system performance. The information gained from the pilot-scale studies will be useful for further system scale-up to field-scale installations.

Summary of the Final Deliverable

For the past four years we have investigated the use of gas permeable membranes for *in situ* H_2 delivery to stimulate the biodegradation of chlorinated ethenes. These laboratory, modeling, and pilot-scale studies have shown that membranes provide a reliable and effective means of delivering H_2 to groundwater. In addition, we have shown that the technology can be used to effectively stimulate biological reductive dehalogenation. This innovative technology appears to be ready to test under different installation and operation scenarios in the field.

Project Accomplishments

We successfully addressed each of the six specific objectives, as outlined below. The overall result of the research was the development of a H_2-delivery technology that is capable of delivering predictable quantities of H_2 to the subsurface (see Appendices A1, C1, C4 and C5) and is able to stimulate the reductive dechlorination of PCE and TCE (see Appendices A2, A3, A5, C3 and C4); complete dechlorination to ethene will occur if the appropriate microorganisms are present (see Appendices A5 and C4). A limited zone of influence around the membranes is a limitation of the technology, but experimental and modeling studies showed that an induced-gradient system could alleviate these problems (see Appendix C5). Fourteen publications (5 in print, 1 in press, 6 in review, 2 to be submitted) have or will result from this research. This research enabled the training of 7 students, resulting in 2 Ph.D. and 5 M.S. degrees. One post-doctoral research associate was also trained on this project and is now a faculty member at Texas A&M Kingsville.

1. Investigate the gas dissolution behavior of the membrane fiber under conditions of creeping flow.

The gas transfer behavior of the membranes under conditions of creeping flow was investigated. Membrane configuration (single-fiber and fabric) and membrane spacing did not affect gas transfer performance. The following dimensionless Sherwood number (Sh) correlation, expressed as a function of Reynolds number (Re) and Schmidt number (Sc), was obtained to

predict gas transfer under low-flow conditions ($0.0004<Re<0.6$): $Sh=0.824Re^{0.39}Sc^{0.33}$. These results are described in detail in Appendix A1.

2. Characterize the impact of diffusion on the gas transfer behavior of the membrane.
The back diffusion of dissolved gases, including water vapor, was evaluated computationally and experimentally. A numerical model to predict gas transfer and gas composition changes in membrane modules designed for passive groundwater treatment was developed and experimentally verified. Back diffusion of dissolved gases into the membrane lumen had a significant impact on gas transfer. The model was able to simulate both the dynamic and steady-state gas transfer behavior of the membranes under a variety of operating conditions, proving its utility for use in estimating gas transfer as a function of different membrane module design and operating parameters. These results are described in detail in Appendix C1. Experiments were also performed to investigate water vapor condensation inside the membrane fibers. These experiments showed that the gas in the membrane lumen is rapidly saturated with water when the membranes are submerged. This can lead to water condensation inside the membrane fiber. This condensation is predictable using a computational model developed as part of this work, but it cannot normally be avoided. Therefore, membrane module design and operation must consider the issue of condensate removal, for example, by using hydrophilic wicks potted into the base of a sealed-end module. These results are described in detail in Appendix C6.

3. Assess the effects of biofilm development and chemical reactions on the ability of membrane fibers to deliver H_2 at adequate rates.
The effect of iron sulfide minerals and biofilm development on gas transfer was studied with microporous polyethylene hollow-fiber membranes. In general, the membrane gas transfer coefficient decreased as the quantity of foulant accumulated on the membranes increased. Nevertheless, gas delivery continued under the conditions tested (Re from 650 to 5460) despite the accumulation of a thick (up to 100 μm) foulant layer comprised of microorganisms and iron sulfide minerals. More importantly, because of the dominance of the liquid film resistance in creeping flow, under typical groundwater flow conditions ($0.0004<Re<0.6$) this decrease would not have been noticable. These results are described in detail in Appendix A4.

The ability of membranes to transfer gas over time to water flowing through aquifer material was also studied in the field and laboratory. In a pilot-scale field study H_2 concentrations were measured in wells containing membrane modules made with silicone-coated hollow-fiber membranes. After 98 weeks in operation, the average H_2 concentration in the wells was 158 ± 5 μM. The predicted clean water H_2 concentration was 255 μM (based on the gas transfer correlation developed in objective 1). This indicates that the hollow-fiber membranes effectively delivered H_2 near the predicted level over an extended period of time (details are presented in Appendix C4).

Two column studies were performed, one with aquifer material from the Cape Canaveral Air Force Station (Cape Canaveral, Florida) using a membrane module comprised of microporous polyethylene membranes and the second with aquifer material from the Trio Solvents site (New Brighton, Minnesota) and a membrane module comprised of silicone-coated membranes. The polyethylene membrane fouled, accumulating a thick (approximately 125 μm) foulant layer and ceasing to transfer H_2 to the column after ~280 days of operation. The foulant was a phosphate-

rich mineral deposit containing high concentrations of Ca and lesser concentrations of Mg, Mn, and Fe. The fact that relatively large quantities of phosphoric acid (0.2 g/L) were used for pH adjustment in this study was likely an important contributor to the foulant accumulation. It was also thought that CO_2 stripping via the membrane and methanogenic activity close to the fibers could have caused a local increase in pH, exacerbating membrane fouling. In groundwater, the phosphate concentration is typically very low (approximately 0.01 mg/L) **(11)**; therefore, this type of membrane fouling is thought to be unlikely in a natural system. The silicone-coated membranes showed little evidence of either fouling or reduced gas transfer, even after 349 days of operation using the same phosphate-rich media. Taken together, these results suggest that the silicone-coated membranes are resistant to fouling and a subsequent decline in gas transfer ability, unlike the polyethylene membranes used in the study with the Cape Canaveral aquifer material. Therefore, because of their excellent resistance to fouling, the silicone-coated membranes are suggested for general field use. Details of these two column studies can be found in Appendices A5 and C3.

4. Characterize the transformation of dissolved chlorinated solvents in simulated groundwater systems using membrane delivered H_2.

Initial studies were performed using batch reactors containing membrane fibers through which gas could be delivered in a flow-through mode. Reductive dechlorination of PCE to *cis*-DCE could be sustained in reactors receiving H_2 (1% H_2 and 50% H_2), while negligible dechlorination was observed in control reactors (100% N_2). The 1%-H_2-fed reactor out-performed the 50%-H_2-fed reactor in an initial experiment, however, the dechlorinating performance in the two reactors was similar in a second experiment. Despite relatively high H_2 concentrations (4.6 to 178 μM) which led to H_2 consumption (and CH_4 production) by methanogens, dechlorination was effectively maintained for the duration of the experiments (35 to 62 days) (details are presented in Appendix A2). A second batch study investigated the impact of alternative electron acceptors on dechlorination. In these experiments, sufficient membrane-fed H_2 was supplied to completely degrade the alternative electron acceptors present (nitrate and sulfate) and initiate dechlorination. Nevertheless, nitrate and sulfate inhibited dechlorinating activity even when H_2 was not limiting. This suggests that if alternative electron acceptors are present, adequate H_2 must be supplied in the field to reduce compounds like nitrate and sulfate before substantial dechlorination will occur (details in Appendix A3).

Laboratory-scale column studies were performed as mentioned above with two aquifer materials (Cape Canaveral Air Force Station material and Trio Solvents site material). In the first study, two glass columns were packed with Cape Canaveral aquifer material and fed a minimal medium spiked with PCE (7 μM) for 391 days. The columns were operated in parallel, with one column receiving H_2 and a control column receiving no H_2. PCE was initially dechlorinated at a similar rate and to a similar extent in both columns, likely due to the presence of soil organic matter that supported dechlorination. After 265 days of operation, dechlorination performance declined in the control column and the benefits of membrane-supplied H_2 became evident. Although the membrane-supplied H_2 effectively stimulated PCE dechlorination, the system was inefficient in that only 5% of the supplied H_2 was used for dechlorination. Most of the remainder was used to support methanogenesis (94%). Despite the dominance of methanogens, complete dechlorination of PCE to ethene was observed in the H_2-fed column (details are presented in Appendix A5).

In the second study three columns were operated in parallel, with one column receiving H_2 continuously, one receiving H_2 in a pulsed mode (4 hours of H_2 followed by 20 hours of N_2), and a control column receiving only N_2. Dechlorination began first in the continuous H_2 column and then started in the pulsed H_2 column approximately 20 days later. Dechlorination in the control column began 84 days after it had started in the continuous H_2 column, again, supported by natural organic matter in the aquifer material. During stable operation, dechlorination was comparable in both the continuous and pulsed H_2 columns, however, adding H_2 in a pulsed manner decreased methanogenesis. CH_4 production was maintained below 40 μM in the pulsed H_2 column as opposed to 208 μM in the continuous H_2 column. No dechlorination beyond *cis*-DCE was observed in this experiment, suggesting that the soil from the Trio Solvents site lacked the essential population(s) to dechlorinate *cis*-DCE to VC and ethene. Details of this study are presented in Appendix C3. It is clear from these experiments that membrane-supplied H_2 supported dechlorination in two different aquifer materials and in a soil-free culture.

Work is continuing on the molecular analysis (using polymerase chain reaction-denaturing gradient gel electrophoresis) of the populations in all of these columns. It is expected that differences in the bacterial populations present will support the observations made during column operation (see Appendices A5, C3, and D1 for details).

5. Model Simulation for Data Analysis.

A one-dimensional contaminant fate and transport model was developed to simulate PCE dechlorination in the presence of membrane-supplied H_2. The model predicted that excellent dechlorination could be supported by providing H_2 at rates equal to the PCE demand. Supplying higher H_2 transfer rates was predicted to result in slightly lower dechlorination efficiencies and significantly lower dechlorination yields because of greater methanogenic growth and displacement of dehalorespirers away from the membranes. The model also predicted that high H_2-utilizing biomass concentrations would develop near the membranes, resulting in minimal H_2 dispersal. Model predictions were qualitatively similar to results attained in the column studies described above (see Appendix B1 for details).

The model is currently being improved by incorporating homoacetogenesis, acetotrophic dehalorespirers, and H_2 production via fermentation of biomass decay products. Results show that this improves the agreement between model simulations and the dechlorination patterns observed in the column studies described above (see Appendix D2 for details).

A mathematical model of an aquifer was also constructed using GMS software and verified with experimental results (see below) to evaluate the 2-dimensional (plan view) zone of influence of gas supplied by membranes. The model was calibrated and verified using experimental data from a pilot-scale system. The model was then used to compare passive versus pumped (at low flow rates) operation and to investigate various well configurations. Results showed that pumping could be used to increase the zone of influence of the dissolved gas plume, and that the increase was proportional to the pumping rate. In addition, the location of extraction and injection wells also had a significant effect on the zone of influence for equivalent pumping rates. Details concerning this work are presented in Appendix C5.

6. Pilot-Scale Studies for Assessing Factors Important for System Scale-up

A large groundwater flow system (2.5 m x 1 m x 1 m) was designed and constructed to evaluate the zone of influence of a membrane module operated in a passive mode or in an induced gradient system where water was pumped into the membrane-containing well. In addition to the physical experiments, GMS was used to model the groundwater flow in the system in two-dimensions and to simulate the transport of dissolved gases (see discussion above). For the passive addition of a conservative gas, the width of the downgradient plume was approximately 7.9 times the width of the well. Additional experiments were performed with groundwater pumping. These showed that with recycle flow rates of 16 and 32% of the total flow, the zone of influence increased to 11.8 and 15.7 times the width of the well. Thus, mild pumping was able to increase the zone of influence of the membrane module compared to passive gas addition (details are given in Appendix C5).

In addition to this large-scale experiment, a pilot-scale field study was also conducted. In this study, conducted at the Twin Cities Army Ammunition Plant site in New Brighton, Minnesota, hollow-fiber membrane modules were installed in the saturated zone of a TCE-contaminated aquifer and their effectiveness with respect to the *in situ* delivery of H_2 was evaluated. The extent of H_2-supported dechlorination at the site was also determined. The hollow-fiber membranes were able to effectively deliver H_2 for over 20 months. The dechlorination of TCE to VC and ethene was stimulated by the addition of H_2 to the groundwater at the site, despite the fact that microbial competition substantially decreased the quantity of H_2 used for dechlorination. Details of this study are presented in Appendix C4.

Action Items

The following were to be discussed in the final report:

1. The levels of H_2 employed in the study in terms of Lower Explosive Limit
2. The rationale and field practicability for use of oxygen as the tracer
3. "Acceptable" time delays for observing vinyl chloride and ethene production in the field and possible measures to expedite chlorinated solvent transformation

1. In the column studies and in the small pilot field study H_2 was typically fed at 100%. Lower partial pressures of H_2 could easily be fed instead, and modeling results suggest that this might be beneficial. Nevertheless, when 100% H_2 was fed to aquifer material, the highest H_2 concentrations measured in the water were on the order of hundreds of μM. If allowed to partition to the headspace, assuming an aqueous H_2 concentration of 200 μM, the headspace concentration would be 0.026%, compared to the Lower Explosive Limit for H_2 of 4.1% **(12)**. It is likely that sealed-end modules will be used in future field applications of this technology to avoid condensation problems. If open-ended modules were used, the low gas flow rate (1-5 mL/min) would result in the venting of very little H_2 mass to the atmosphere, again, remaining well below the Lower Explosive Limit of H_2. Engineers have designed systems for handling explosive gases for some time; therefore, this is not thought to be a great impediment for the use of H_2 to stimulate bioremediation *in situ*. More details on systems that could be used to handle H_2 for this application are provided in the transition plan below.

2. We believe that this statement refers to the large pilot-scale tank study that was conducted with oxygen as a gaseous tracer (as opposed to H_2). Oxygen was used for experimental convenience, as dissolved oxygen could be easily measured in situ with commercially available probes. The use of oxygen for this purpose is acceptable, as the results can be easily translated to what might occur with H_2 by correcting for the solubility of H_2 (as opposed to oxygen). An additional correction could be made to account for the approximately 40% greater diffusivity of H_2 as compared to oxygen. This correction, however, is deemed to be negligible as dispersion in aquifers is dominated by mechanical mixing and not diffusion.

3. "Acceptable" time delays for observing vinyl chloride and ethene production in the field would be determined through risk analysis performed by those remediating the site and the site owner. The time delay that can be tolerated will be dependent on the site characteristics, including the contaminants present, the geology of the site, and the organisms present. Microcosm studies would be conducted prior to the installation of a membrane system (see the transition plan); therefore, the likelihood that H_2 addition would stimulate dechlorination should be known prior to installation. It is likely that dechlorination to vinyl chloride and ethene should occur within several months of initiating H_2 addition, assuming that the microcosm studies showed that the site had the potential to completely dechlorinate PCE and TCE. One possible measure to increase the rate of dechlorination if passive H_2 addition alone is insufficient is to recirculate the water at the site to increase the H_2 zone of influence. The effectiveness of this measure requires additional testing.

Conclusions

SERDP funding was used to demonstrate the effectiveness of the membrane technology for providing sustained H_2 delivery to groundwater systems to support reductive dechlorination of chlorinated solvents. The key findings from this 4-year project, as described in peer-reviewed journal articles (Appendices A-D) are as follows.

- The rate of gas transfer from membranes to water flowing at slow (groundwater) velocities can be predicted using a Sherwood number correlation.
- Back diffusion of gases from the water into the membrane has a significant but predictable effect on transfer of the target gas.
- Transfer of water vapor into the membranes and subsequent condensation is an important issue that must be considered in membrane module design and operation. Sealed-end modules can be designed such that problems with water condensation do not occur.
- Silicone-coated Varflex membranes are more robust and resist fouling while polyethylene membranes appear to be unsuitable for use in groundwater systems.
- H_2 delivery from membranes supports reductive dechlorination of PCE, including complete dechlorination of PCE to ethene if the appropriate microorganisms are present.
- A one-dimensional finite difference model was developed for evaluating the effects of H_2 pressure in the membranes on the competition between dechlorinators and methanogens for H_2 and predicted that low H_2 partial pressures (~ 0.05 atm) will provide the most efficient use of H_2 for dechlorination.
- The zone of influence of a membrane module installed in a vertical well for passive operation can be expanded using water recirculation in a semi-passive operating mode. This presents

tradeoffs with respect to installation costs (determined primarily by well spacing) and operation and maintenance costs (determined primarily by groundwater recirculation rate).

Overall, these research findings indicate that this novel H_2 addition technology holds a great deal of promise for stimulating the *in situ* biological dechlorination of chlorinated solvents.

Transition Plan

A transition plan (presented in Appendix A) was constructed with the assistance of Daniel Sola, Wenck Associates Inc. to support the scale-up and implementation of this technology. An additional paper was written and submitted (see Appendix D2) comparing this technology to other known H_2-delivery technologies.

Recommendations

This novel technology is ready for scale-up and testing under different operating strategies at a field site. Specifically, the following should be investigated before large-scale implementation:

- the effects of operating the system in a semi-passive manner (intermittent groundwater pumping between membrane-containing wells) on well-spacing requirements and system performance;
- the effects of system operation on aquifer permeability (*i.e.* biofouling); and
- the effects of system operation on groundwater quality (*e.g.* pH, alkalinity, total organic carbon concentration).

After this has been completed, we feel that appropriate design criteria and costing information can be developed for technology implementation.

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Appendix A
Transition Plan

Appendix B
Papers in print

1. Fang, Y., Hozalski, R.M., Clapp, L.W., Novak, P.J., Semmens, M.J. 2002. Passive Dissolution of Hydrogen Gas into Groundwater using Hollow-Fiber Membranes. *Water Research*, 36:3533–3542.

2. Muenzner, H.D., Clapp, L.W., Hozalski, R.M., Semmens, M.J., Novak, P.J. 2002. Dechlorination of PCE by Mixed Methanogenic Cultures Using Hollow-Fiber Membranes. *Bioremed. Journal,* 6(4):337-350.

3. Nelson, D.K., Hozalski, R.M., Clapp, L.W., Semmens, M.J., Novak, P.J. 2002. Effect of Nitrate and Sulfate on Dechlorination by a Mixed Hydrogen-fed Culture. *Bioremed. Journal*, 6(3):225-236.

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5. Ma, X., Novak, P.J., Clapp, L.W., Semmens, M.J., Hozalski, R.M. 2003. Evaluation of Membranes for Hydrogen Delivery to Support Reductive Dechlorination in a Simulated Groundwater Environment. *Water Research,* 37(12):2905-2918.

Appendix C
Papers in press

1. Clapp, L.W., Semmens, M.J., Novak, P.J., Hozalski, R.M. 2003. Model for In Situ Perchloroethene Dechlorination via Membrane-Delivered Hydrogen. *Journal of Environmental Engineering,* in press.

Appendix D
Papers in review

1. Fang, Y., Clapp, L.W., Hozalski, R.M., Novak, P.J., Semmens, M.J. Membrane Gas Transfer Under Conditions of Creeping Flow: Modeling Gas Composition Effects, *Water Research,* submitted.

2. Semmens, M.J., Hozalski, R.M., Novak, P.J., Clapp, L.W., Sola, D.V. Hydrogen Delivery for Groundwater Remediation: Technology Review. *Groundwater Monitoring and Remediation,* submitted.

3. Edstrom, J.A., Semmens, M.J., Hozalski, R.M., Clapp, L.W., Novak, P.J. Stimulation of Dechlorination by Membrane-Delivered Hydrogen: Small Field Demonstration. *Environmental Engineering Science*, submitted.

4. Fang, Y., Novak, P.J., Hozalski, R.M., Cussler, E.L., Semmens, M.J. Condensation Studies in Gas Permeable Membranes. *Journal of Membrane Science*, submitted.

Appendix E
Papers in preparation

Note: copies of these papers will be mailed to SERDP at the time of their submission

1. Ma, X., Novak, P.J., Clapp, L.W., Semmens, M.J., Hozalski, R.M. Effect of Pulsed versus Continuous H_2 Supply on the Competition between Methanogens, Homoacetogens, and Dechlorinators in a Soil Column. To be submitted to *Water Research* in approximately one month.

2. Agarwal, N., Semmens, M.J., Novak, P.J., Hozalski, R.M. Zone of Influence of a Gas Permeable Membrane System for Delivery of Gases to Groundwater. To be submitted to *Environmental Engineering Science* in approximately one month.

3. Clapp, L.W., Semmens, M.J., Novak, P.J., Hozalski, R.M. Modeling Competition between Dehalorespirers, Methanogens, and Homoacetogens in a PCE-Contaminated Aquifer Supplied with Dissolved H_2 via Gas-Permeable Membranes. In preparation.

4. Ma, X., LaPara, T.M., Novak, P.J., Semmens, M.J., Hozalski, R.M. Community Distribution in Aquifer Material Fed H_2 via Hollow-fiber Membranes. In preparation.

Effect of Pulsed versus Continuous H_2 Supply on the Competition between Methanogens, Homoacetogens, and Dechlorinators in a Soil Column

Ma, X., Novak, P.J., Clapp, L.W., Semmens, M.J., Hozalski, R.M.

The main objective of this research was to compare the performance, in terms of methane production and PCE dechlorination, of aquifer columns fed H_2 continuously or in a pulsed manner via a hollow-fiber membrane. During this 349-day experiment, silicone membranes were more robust than previously investigated polyethylene membranes, delivering H_2 steadily over the entire experiment. During stable operation, dechlorination was comparable in both the continuous and pulsed H_2 columns, and was stimulated in comparison to the column fed only N_2 (control). Methane production was minimized when H_2 was added in a pulsed manner, averaging ≤ 40 μM in the pulsed H_2 column as opposed to ≈ 208 μM in the continuous H_2–fed column. Nevertheless, the dechlorinating population in the pulsed H_2 column seemed to be more susceptible to disturbance and less robust following unstable operation.

Zone of Influence of a Gas Permeable Membrane System for Delivery of Gases to Groundwater

Agarwal, N., Semmens, M.J., Novak, P.J., Hozalski, R.M.

One approach for cleaning up aquifers contaminated with organic chemicals is to stimulate biological degradation *in situ* by addition of gases such as oxygen or hydrogen. In this research, pilot-scale experiments and model simulations were performed to evaluate how the design and operation of hollow-fiber membrane gas transfer systems affect the zone of influence of the dissolved gas plume around a narrow-bore well in a sand aquifer. An "in-well" membrane module installed in a 2.54-cm inner diameter slotted well was operated with water recirculation (pumped) and without (passive) and an "external" module located above the ground surface was operated in pumped mode only. Most experiments and simulations were performed at an ambient groundwater flow velocity of 1 m/d. The zone of influence for the in-well module operated passively was 7.3 well diameters (18.6 cm) and increased to 11 well diameters (28.6 cm) with the introduction of recycle flow from a downgradient extraction well (40 mL/min/m well depth). The zone of influence for the external membrane module system increased from 2.4 to 15.8 well diameters with increasing pumping rate from 2 to 80 mL/min/m well depth. The simulated zones of influence from the calibrated MODFLOW-MT3D model were in good agreement (-1.3 to 14.4%) with experimental observations. Simulations of various well configurations (i.e. locations of extraction and injection wells) and dissolved gas consumption rates suggested that these factors can have a significant effect on the zone of influence. The combination of pilot-scale experiments together with model simulations is recommended for the design of the well array and development of the operational strategy of the membrane gas transfer system to provide effective low-cost remediation of contaminated aquifers.

Modeling Competition between Dehalorespirers, Methanogens, and Homoacetogens in a PCE-Contaminated Aquifer Supplied with Dissolved H_2 via Gas-Permeable Membranes

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Experimental results suggested that homoacetogenesis is an important phenomenon in a system to which H_2 is added. Therefore, an ongoing modeling study is being conducted to simulate competition between dehalorespirers, methanogens, and homoacetogens in a PCE-contaminated anaerobic aquifer supplied with H_2 via a gas-permeable membrane curtain. The new model simulates seven microbial populations: (1) H_2-utilizing PCE/TCE dechlorinators, (2) H_2-utilizing DCE/VC dechlorinators, (3) methanogens (hydrogenotrophic and acetoclastic combined, similar to *Methanosarcina* species), (4) H_2-utilizing homoacetogens, (5) syntrophic bacteria that utilize butyrate and produce H_2 and acetate (butyrate is assumed to be the "model" product of biomass decay), (6) acetate-utilizing PCE/TCE dechlorinators, and (7) acetate-utilizing DCE/VC dechlorinators. Both electron donor (H_2 or acetate) and electron acceptor (chlorinated ethenes) can limit dechlorinator growth and thus the dechlorination reaction rates are described by double-Monod-type kinetics. The model assumes that dechlorination cannot occur when H_2 and acetate concentrations decline to below threshold levels and that the dechlorinator populations undergo first-order decay, with the decay constants being proportional to the maximum growth rate constants. The decay of biomass is assumed to generate low concentrations of butyrate. The model assumes that there are separate H_2- and acetate-utilizing PCE/TCE dechlorinator populations, as well as separate H_2- and acetate-utilizing DCE/VC dechlorinator populations. The fate of eight solutes is simulated in this work: (1) H_2, (2) PCE, (3) TCE, (4) DCE isomers, (5) VC, (6) ethene, (7) CH_4, and (8) acetate. Solute transport is simulated with a traditional advection-dispersion equation with equilibrium adsorption to the soil (which is dependent on the soil f_{oc} value and the solute K_{ow} value). Finally, the model assumes that only H_2 is transferred through the membranes. The H_2 transfer rates are computed using an overall mass transfer coefficient derived from a dimensionless correlation for creeping groundwater flow conditions developed during the experimental H_2 transfer studies. Both lab- and field-scale experimental data have indicated that membrane-delivered H_2 is rapidly converted to acetate near the H_2-supply membranes. The ultimate purpose of the ongoing modeling study is to investigate if it is possible for this H_2-derived acetate to support significant downgradient dehalorespirer populations.

Community Distribution in Aquifer Material Fed H_2 via Hollow-fiber Membranes

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The literature concerning dehalorespirers suggests that the sequential dechlorination of PCE requires a diverse community of bacteria to achieve complete dechlorination. It is important not only to understand the genetic diversity of the bacterial population involved in the dechlorinating process, but also the potential syntrophic relationships with other consortia members, and the community response to changes in environmental conditions such as H_2 addition. One genetic fingerprinting technique, denaturing gradient gel electrophoresis (DGGE) of PCR-amplified ribosomal DNA fragments, is being used to analyze the bacterial community for both Cape Canaveral and Trio Solvents Site soil samples. DNA has been extracted from the samples of both columns. DGGE has been performed on PCR products from Cape Canaveral samples. Some distinct bands from DGGE gels, potentially representing unique bacterial populations, have been excised and purified. The purified DNA samples will be sequenced. PCR-DGGE will also be performed on the Trio Solvents Site samples. This work should result in a better understanding of the special distribution of bacterial populations in columns that have been fed N_2, H_2, or pulsed H_2 via hollow-fiber membranes. This will assist us in understanding how to best stimulate the desired organisms.