



Evaluation of an Oxygen Injection Technology for In-Situ Hydrocarbon Bioremediation in a Fractured Bedrock Environment

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ABSTRACT

A field and modelling study was completed at a former gas station in Southern Ontario where the underlying dolostone aquifer is contaminated with petroleum hydrocarbons (PHCs). Oxygen addition is being considered at the site as a method to enhance PHC biodegradation. The objective was to better characterize the site and to evaluate how dissolved oxygen would behave in this type of fractured rock environment. The investigation included a dissolved oxygen injection test which was completed using inVenture Technologies' (iTi) gPro[®] oxygen injection technology. A three-dimensional numerical model was then developed and calibrated to the field conditions to assess the distribution of oxygen into the system.

RÉSUMÉ

Un aquifère fracturé, contaminé par des hydrocarbures sous une ancienne station de gaz dans le sud de l'Ontario, a fait l'objet d'une étude de caractérisation hydrogéologique et de modélisation numérique. L'addition de l'oxygène dissous est une des méthodes proposés pour faciliter la biodégradation des hydrocarbures. Les principaux objectifs de cette étude étaient de mieux caractériser le site et d'évaluer les processus de transport de l'oxygène dissous dans l'eau lors de son injection dans le milieu poreux fracturé. L'équipement connu sous le nom commercial gPro, développé par inVenture Technologies' Inc. (iTi), a été utilisé pour un essai d'injection de l'oxygène dissous. En outre, un modèle numérique tridimensionnel de l'aquifère fracturé a été ajusté aux données de terrain afin d'estimer le comportement de l'oxygène dissous dans ce système hydrogéologique.

1 INTRODUCTION

Petroleum hydrocarbons (PHCs) are a major source of groundwater contamination across North America and around the world. The rising costs and limitations of conventional methods for plume management and remediation have led to the development of a variety of in-situ remediation methods.

Oxygen addition has been shown to be an effective approach to enhance the bioremediation of PHC-contaminated groundwater (Landmeyer et al., 2003, Johnston et al., 1998, Arnon et al., 2005). However, to effectively deliver oxygen to a zone of petroleum hydrocarbons has proven difficult. This is especially true of complex hydrogeological systems such as fractured bedrock environments.

Numerous remedial strategies have been developed for use at PHC-contaminated sites that work by removing the oxygen limiting factors and encouraging efficient in-situ biodegradation. For example, the inVenture Technologies (iTi) gPro[®] unit is designed to increase the concentration of dissolved oxygen (DO) within a dissolved PHC plume.

To date, most applications of these technologies have been in porous media (e.g. alluvial aquifers). Research

into the injection of oxygen into fractured rock, and its subsequent distribution within discrete fractures zones has not been well reported in the peer-reviewed literature; these issues therefore form the focus of this investigation.

1.1 Site Background

The site selected for this study was a former gas station located within a small rural community in southwestern Ontario. The site operated as a fuel dispensing operation from the early 1970's until the mid 1990's during which time the groundwater became impacted by PHCs. The contamination zone is within the dolostone bedrock of the Guelph Formation.

1.2 gPro[®] Technology

iTi's High Pressure Gas Infusion Technology (gPro[®]) was selected for evaluation in this study. A mobile unit was constructed to fit into the back of a cargo van to facilitate moving on and off the site. The system design involved a 500 L holding tank with the discharge piped to the gPro[®] unit. The discharge pipe from the gPro[®] unit was attached to the top of a down-hole set-up that included an inflatable packer and sampling port.

1.3 Modelling Approach

The model chosen to simulate the oxygen injection test was the discrete fracture network model HEATFLOW/SMOKER (Molson et al, 1992; Molson and Frind, 2009). This model considers advective-dispersive transport of a dissolved phase component (or heat) within a porous matrix and/or within a discrete fracture network.

2 SITE CHARACTERIZATION AND SITE CONCEPTUAL MODEL

2.1 Initial Investigation

To characterize the bedrock and to establish a site conceptual model, a phased investigation approach was completed in which the results from each phase could be evaluated and used to design the following phase. The phases included borehole drilling and hydraulic testing (packer testing), multi-level well monitoring and sampling, digital borehole imaging, tracer testing and cross-borehole testing.

The bedrock was first characterized through the drilling of two open-hole bedrock test wells (TW1 and TW2) (Figure 1). The wells were located 3 m apart along the direction of groundwater flow.

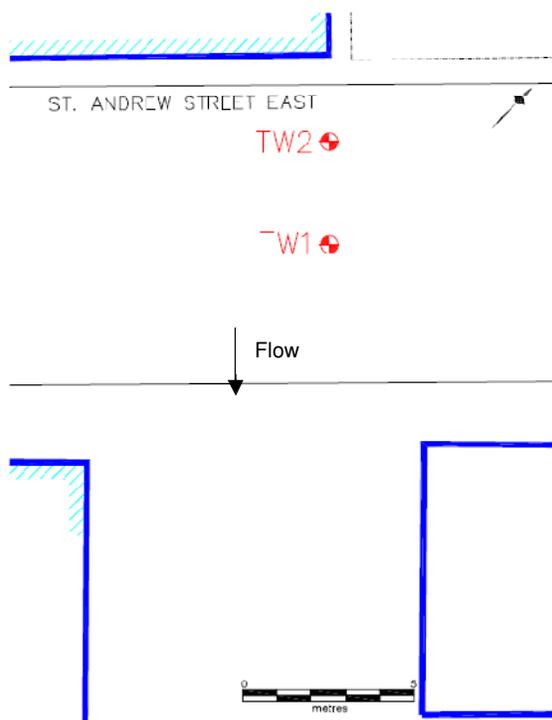


Figure 1. Location of injection well TW2 and down-gradient monitoring well TW1.

Packer testing of each borehole was conducted to obtain direct measurements of the bulk transmissivity of

the formation at 1 m intervals along the depth of the boreholes. Based on the hydraulically active zones in the rock as identified from the drilling and hydraulic testing, the down-gradient well (TW1) was instrumented with a Solinst CMT Multilevel monitoring system with seven isolated sampling intervals (TW1-1 to TW1-7) (Figure 2).

Digital borehole imaging was completed which allowed for the identification of discrete fractures and fracture features, and allowed for better characterization of changes in rock properties such as competency and matrix porosity.

Based on the results of the hydraulic testing and the digital borehole imaging, key fracture calculations were performed to determine the fracture spacing (2B), hydraulic fracture aperture (2b), and fracture velocity (v_f).

To confirm the hydrogeological properties of the aquifer and to identify and confirm flow paths between wells, a conservative tracer test was also completed. To evaluate the connectivity of fractures between the boreholes and to identify the most significant conductive fractures, a cross borehole hydraulic test was completed. The cross borehole test helped to determine the hydraulic connection between the up-gradient well (TW2) and the down-gradient monitoring points (TW1-1 to TW1-7).

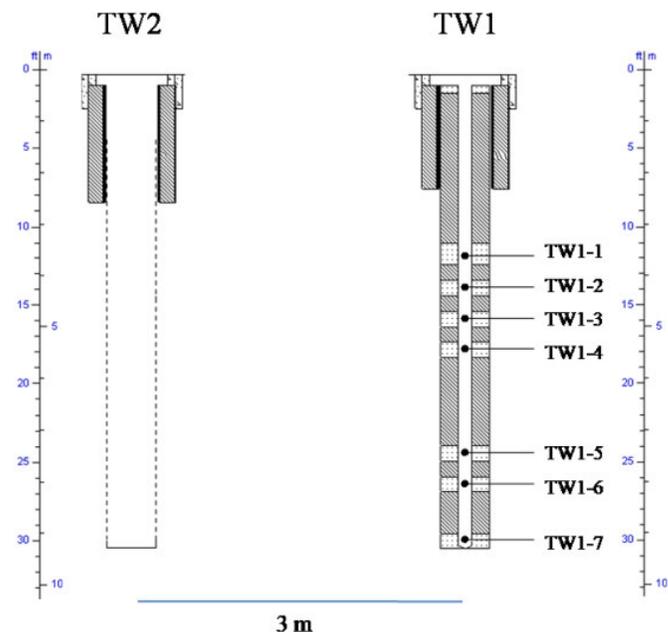


Figure 2. Instrumentation of TW1 (monitor well) and TW2 (injection well).

2.2 Site Conceptual Model

Based on the results of the initial investigation (borehole drilling and hydraulic testing, multi-level well monitoring and sampling, digital borehole imaging, tracer testing and cross-borehole testing), a site conceptual model was developed which is presented in Figure 3 and summarized below.

The site conceptual model divides the rock into four distinct units based on the rock properties: Zone 1, Zone 2a, Zone 2b and Zone 3.

The bulk hydraulic conductivity was identified for each of the 4 units (10^{-5} m/s, 10^{-5} m/s, 10^{-6} m/s, and 10^{-7} m/s, respectively). Zone 1 was found to be highly weathered and no direct hydraulic connection between the injection well and Zone 1 down-gradient (as seen in TW1-1) or with the lower zone (Zone 2a) was noted. Zone 2a contains discrete fractures at ~4.1, 4.7 and 5.2 m bgs (fractures 5, 6 and 7 - see Fig. 3). A strong hydraulic connection was confirmed across the unit based on the response between the injection well (TW2) and the down-gradient monitoring points completed in this unit (TW1-2, 3 and 4). Zone 2b contains discrete fractures at ~ 5.95, 6.45, 7.29 and 7.47 m bgs (1, 2, 3, and 4). No discrete fractures were noted within Zone 3 at the depths investigated. Based on the results of the cross-borehole testing, a strong hydraulic connection was noted between the injection well (TW2) and the down-gradient monitoring point (TW1-7) located within this zone. The observed hydraulic connection was likely a result of the injection under pressure and might not exist under natural conditions.

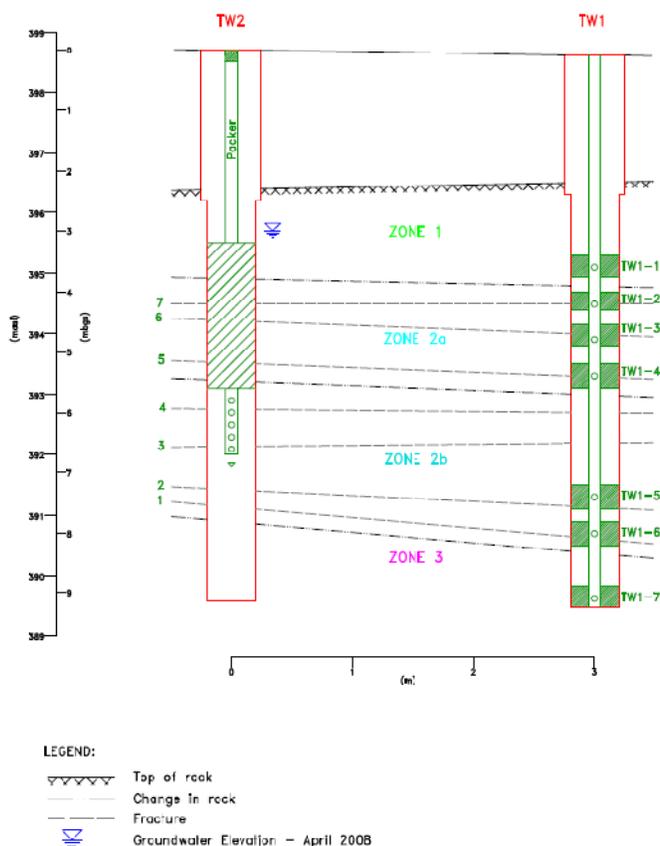


Figure 3. Site conceptual model showing injection well (TW2), the 7 monitoring points within the monitor well TW1, and the major fractures identified.

3 FIELD RESULTS AND INTERPRETATION

3.1 Injection Testing

The oxygen injection test was designed based on the site conditions using the gPro® technology. The objective of the test was to evaluate the delivery efficiency of the oxygenated water into the bedrock formation and to evaluate the distribution of injected water and oxygen within the discrete fracture zones.

The test interval in TW2, below 5.5 m bgs was first isolated using packers to assess the conditions within the discrete fractured zones (Zone 2a, 2b and 3) and to isolate the upper zone of highly fractured rock. Water was then injected in two 500 L batches pre-mixed with sodium bromide (bromide) (~ 688 mg Br/L) and treated using the gPro® technology prior to injection.

During the injection test, the treated water exiting the gPro®, with an average DO concentration (measured in the injection well) of 26.4 mg/L, was injected into TW2 at a rate of approximately 11 L/min for 44.2 minutes, then stopped for 29 minutes (to refill the tank), then injected again at 10.6 L/min for 37.8 minutes, for a total injection volume of 884 L. DO and bromide concentrations were measured in TW2 as often as possible and at least every 5 minutes during injection.

TW2 continued to be monitored for 212 hours (8.8 days) until oxygen and bromide concentrations had returned to background levels. DO and bromide concentrations were measured in TW2 during the injection to assess the temporal change in injection water and down-gradient in TW1 (TW1-1 to TW1-7).

3.2 Dissolved Oxygen Distribution

Breakthrough curves (concentration over time) were developed for oxygen at each monitoring point (Figure 4) to assess the distribution of oxygen within the system.

The breakthrough curves within the injection well (TW2) and at the down-gradient monitoring points located along the major fractures (at TW1-2, -3 and -4) are characterized by sharp peaks and diffusive-like tails, and are consistent with results seen at another fractured bedrock site within a similar dolostone unit (Novakowski et al., 1995).

The breakthrough curves suggest that a significant amount of oxygen has entered the matrix around the injection well, presumably due to advective transport under the high pressure gradients during injection. The diffusive-like tail noted on the breakthrough curves is a result of the back diffusion of the oxygen from the matrix. It should also be noted, however, that the migration of oxygen into the matrix is limited by the short injection time and possibly due to some loss of the injection pulse into the fractures.

Oxygen breakthrough was noted at the remaining monitoring locations (TW1-1, -6 and -7) but these results are not discussed as part of this paper. Bromide breakthrough is also not discussed, but further details can be found in Greer (2009).

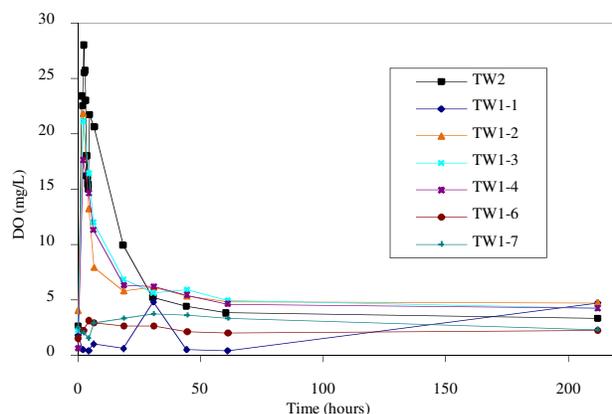


Figure 4. Oxygen breakthrough at the injection well (TW2) and down-gradient monitoring points.

4 NUMERICAL MODELLING

The oxygen injection experiment was simulated using the HEATFLOW/SMOKER model, a three-dimensional numerical model for groundwater flow and advective-dispersive transport within a discretely-fractured porous medium (Molson and Frind, 2009).

The objectives of the modelling were to validate the conceptual model for the site, simulate the oxygen distribution within the fracture network and porous matrix (including long-term oxygen concentration levels during and after injection), and finally to test the sensitivity of key parameters in order to improve the focus and/or optimize field investigations at other sites.

To achieve the objectives of the modelling, a field-based model was first developed using the observed site properties. The developed “field” model was then calibrated to the observed field conditions to obtain a best fit (base case). Sensitivity analyses were completed to test the model and to assess the sensitivity of the model parameters on the distribution and transport of oxygen within the system. Only the calibrated Base Case (Best Fit) results are discussed as part of this paper.

4.1 Model Development

The numerical model was developed based on the site conceptual model and using the parameters measured in the field (Figure 5). The injection site was simulated using a 3D grid oriented parallel to the groundwater flow direction. The injection well and the monitoring points were positioned on the grid relative to their position in the field and were assigned as breakthrough (monitoring) points in the model. The discrete fractures were positioned according to the site conceptual model and the fracture apertures were adjusted based on the model response.

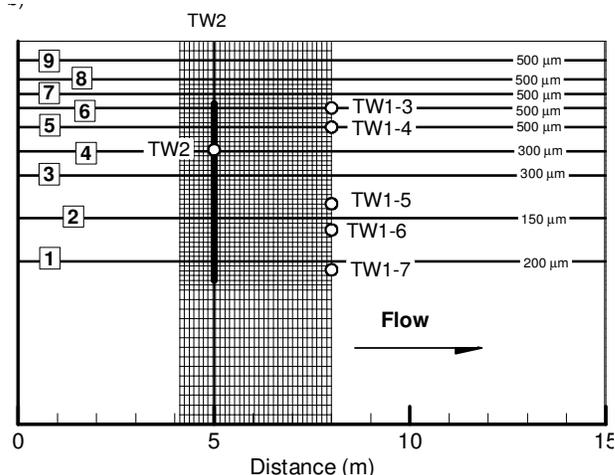


Figure 5. Model layout and input parameters showing transport domain with monitoring points and fracture apertures identified. Fracture numbers are shown at left; for clarity, only the central grid section is shown.

4.2 Base Case (Best Fit) Simulation

The calibrated base case model results were examined to provide insight into the oxygen distribution within the aquifer, with a focus on the fracture network and porous matrix.

The DO breakthrough curves from the calibrated base case (best-fit) model are consistent with those observed in the field (Figure 6). The simulated results show similar trends to those observed with an initial sharp peak in the injection well (TW2) of 26 mg O₂/L, followed by a tailing with a decrease in concentration over time to background levels after approximately 50 hours.

At the down-gradient monitoring locations TW1-3 and 4, similar trends were noted with simulated peak concentrations of 16 and 18 mg O₂/L, respectively; following injection, a rapid decline in concentration was noted before returning to background concentrations after approximately 20 hours.

Although the simulated responses at all monitor points provide a reasonably good match to the observed data (especially at the injection well), some variations in trends between the observed and simulated breakthrough curves from the calibrated (best-fit) base model were noted.

The most significant differences with the simulated results include a slightly delayed arrival time for the simulated peak DO concentrations at the down-gradient monitoring points (TW1-3 and 4) as well as a rapid, almost symmetrical decline (tail) at these points. The arrival curves here thus appear more pulse-like with limited evidence for diffusion-limited tailing. The relatively slower decline in the observed breakthrough curve could be the result, for example, of isolated highly-porous zones in the field that are not accounted for in the model. These zones would absorb oxygen, and then release it more slowly over time. On the other hand, the simulated oxygen

concentrations within the injection well were an excellent match to those observed.

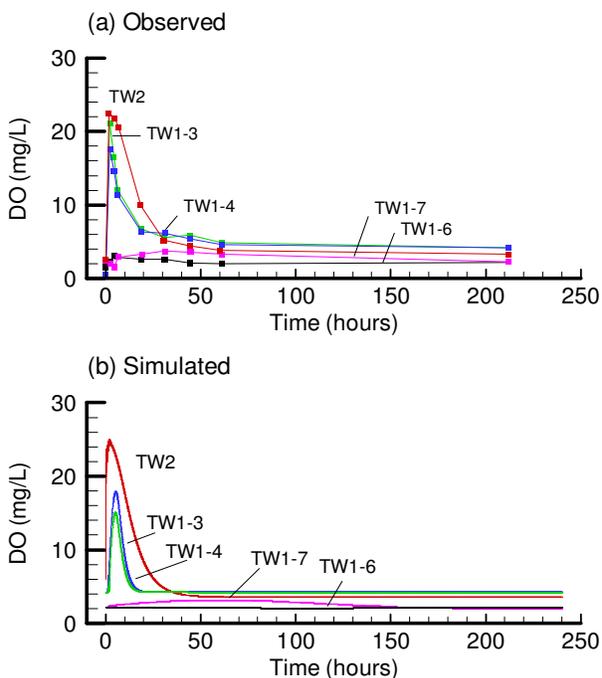


Figure 6. Breakthrough curves showing a) observed and b) simulated results for the base case.

The numerical model also allows for a visual depiction of the oxygen distribution over time and space (Figure 7). The oxygen concentration contour plots show that during the injection period, the oxygen is transported rapidly by advection into the matrix surrounding the injection well and fills the local intersecting fractures. Following the injection, the highest concentrations of oxygen are seen at the top of the injection interval (~30 mg O₂/L), but are quickly transported down-gradient through the fractures which are then rapidly flushed by the low-oxygen up-gradient water. Concentrations quickly decrease to background levels.

Within the lower discrete fractures, the dissolved oxygen is transported primarily under advection, migrating with time down-gradient even after the injection stops. The rate of transport is slower in these lower fractures because of their smaller apertures and hence lower velocities. Transport into the matrix along the fractures can also be seen with sharp concentration gradients along the fracture surface interfaces. Evidence of transport into the matrix can be seen by observing the concentration halos that form above and below the fractures as the dissolved oxygen is transported down-gradient and as the fracture water is replaced with relatively oxygen-free water. As the fractures are flushed with the natural low-oxygen water, the oxygen in the matrix back-diffuses into the fractures (due to a reversal in the concentration

gradients) which is likewise also transported down-gradient.

With time, the oxygen is flushed from the injection well preferentially into the fractures. This can be seen by the layers of higher concentrations above and below the fractures within the injection well and by lower concentrations centered on the discrete fractures.

The simulation verifies that the initial delivery of oxygen into the matrix surrounding the injection well was a result of high pressure gradients, resulting in the initial deep oxygen penetration around the injection well.

5 SUMMARY AND CONCLUSIONS

The injection test confirmed that oxygen can be successfully delivered into a fractured bedrock aquifer. The effectiveness of the delivery is shown in the breakthrough curves resulting from the injection test and confirmed by the groundwater model which was developed and calibrated to the observed field conditions.

The simulated distribution of oxygen within the system was consistent with the field conditions, with good agreement between the simulated and observed breakthrough curves.

The results have generally demonstrated that oxygen can be maintained at concentrations which are potentially sufficient to enhance aerobic biodegradation. Further model development is currently in progress to link hydrocarbon degradation and oxygen utilization within fractured systems.

ACKNOWLEDGEMENTS

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REFERENCES

- Arnon, S., E. Adar, Z. Ronen, A. Nejdat, A. Yakirevich & R. Nativ. (2005). Biodegradation of 2,4,6-tribromophenol during transport in fractured chalk. *Environmental Science & Technology*, 39: 748-755.
- Johnston, C.D., J.L. Rayner, B.M. Patterson, G.B. Davis. 1998. Volatilization and Biodegradation During Air Sparging of Dissolved BTEX-contaminated Groundwater. *The Journal of Contaminant Hydrology*.33. 377-404.
- Greer, K.D. 2009. Evaluation of an Oxygen Injection Technology for In-Situ Hydrocarbon Bioremediation in a Fractured Bedrock Environment. MSc Thesis, University of Waterloo.
- Landmeyer, J.E., P.M. Bradley. 2003. Effect of Hydrologic and Geochemical Conditions on Oxygen-enhanced Bioremediation in a Gasoline-contaminated Aquifer. *Bioremediation Journal*. 7: 165-177.

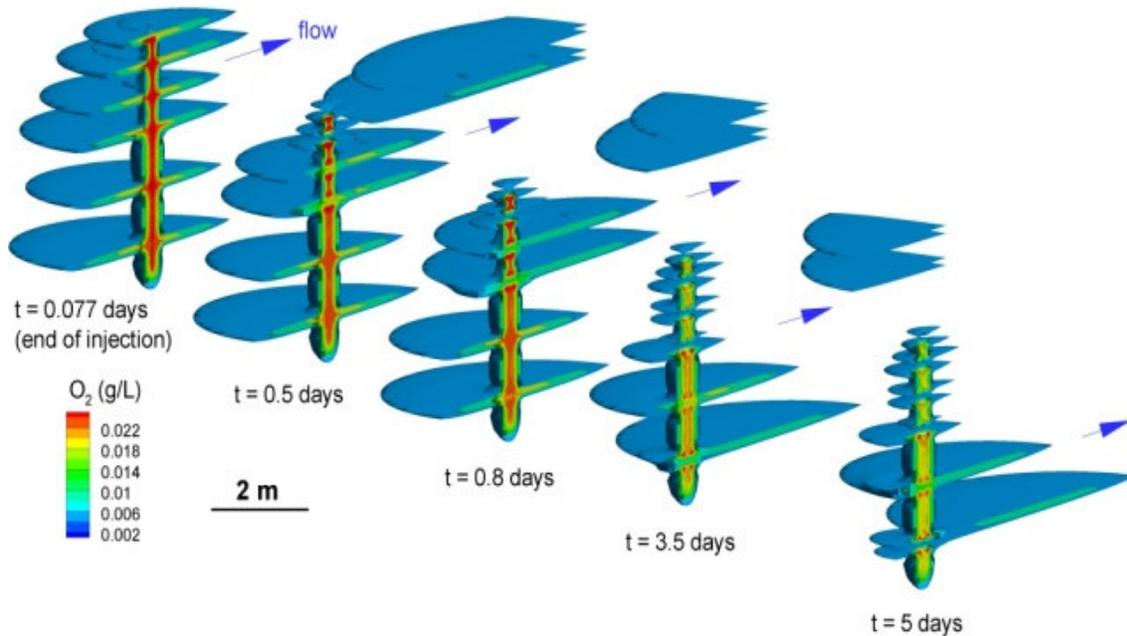


Figure 7. Simulated dissolved oxygen distribution at selected times, best-fit calibrated model.

- Molson, J.W., E.O. Frind, C. Palmer. 1992. Thermal Energy Storage in an Unconfined Aquifer 2. Model Development, Validation, and Application. *Water Resources Research*. 28: 2857-2867.
- Molson, J.W., E.O. Frind. 2009. HEATFLOW-SMOKER: Density Dependent Flow and Thermal Energy / Mass Transport Model in Three Dimensions, User Guide. Version 4.0, University of Waterloo & Université Laval.
- Novakowski, K., P. Lapcevic, G. Bickerton. 1995. Preliminary Interpretation of Tracer Experiments Conducted in a Discrete Rock Fracture Under Conditions of Natural Flow. *Geophysical Research Letters*. 22 (11): 1417-1420.