

Diffusive Oxygen Emitters for Enhancement of Aerobic In Situ Treatment

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Abstract

Aerobic biodegradation can be enhanced within contaminant plumes by elevating typically low dissolved oxygen (D.O.) levels using materials or devices that passively release oxygen. We have developed passive devices that provide a uniform, steady, long-term source of oxygen by diffusion from pressurized polymeric tubing and report test results under lab and field conditions. Lab flow-through reactor tests were conducted to determine the diffusion coefficient (D) of oxygen through four readily available tubing materials. Oxygen diffusion was greatest through Tygon[®] 3350 platinum-cured silicone ($D = 6.67 \times 10^{-7} \text{ cm}^2/\text{sec}$), followed by 2075 Ultra Chemical Resistant Tygon ($1.59 \times 10^{-7} \text{ cm}^2/\text{sec}$), 2275 High Purity Tygon ($5.11 \times 10^{-8} \text{ cm}^2/\text{sec}$), and low-density polyethylene (LDPE; $1.73 \times 10^{-8} \text{ cm}^2/\text{sec}$). Variable-pressure release tests with LDPE resulted in very close estimates of D , which confirmed that mass transfer is controlled by diffusion and that the concentration gradient is a valid approximation of the chemical potential driving diffusion. LDPE emitter devices were designed and installed in seven 8-inch-diameter well screens across a portion of a gasoline plume at a former service station. With the devices pressurized to 620.5 kPag (kilopascals gauge) late in the test, steady-state D.O. concentrations reached as high as 25 mg/L, comparing favorably to the value predicted using the mass-transfer coefficient estimated from the lab test (26.3 mg/L). The method can also be used to release other gases for other reasons: gaseous tracers (i.e., sulphur hexafluoride, helium, and argon), hydrogen (for reductive dechlorination), or light alkanes (for cometabolic biodegradation of methyl tertiary butyl ether [MTBE] or chlorinated solvents).

Introduction

It has been shown that some ground water contaminants naturally biodegrade at rates sufficient to make natural attenuation a viable remedial option (Barker et al. 1987; National Research Council 1993; Wiedemeier et al. 1999). This has certainly been demonstrated in the case of gasoline hydrocarbons, which have been shown to biodegrade under aerobic (Jamison et al. 1975; Atlas 1981; Alvarez et al. 1991), nitrate-reducing (with the possible exception of benzene) (Hutchins et al. 1991; Barbaro et al. 1992), iron-reducing (Lovley et al. 1989), sulfate-reducing (Edwards et al. 1992), and methanogenic (Grbic-Galic and Vogel 1987) conditions. Based on the thermodynamics of BTEX (benzene, toluene, ethylbenzene, and xylene) oxidation, aerobic degradation provides the greatest energy for microbes. Further, it has been generally observed that aerobic biodegradation rates are much greater than that of any of the anaerobic processes (Borden and Bedient 1986; Thierrin et al. 1995). Also, contaminants such as fuel oxygenates (MTBE, ETBE, TAME) and some chlorinated solvents (vinyl chloride and *cis*-1,2 DCE) are often recalcitrant under anaerobic conditions but may readily degrade aerobically (Davis and Carpenter, 1990; Semprini et al. 1991; Salanitro et al. 1994; Cowan and Park 1996; Mo et al. 1997). Often, however, contaminant plumes are anaerobic because background dissolved oxygen (D.O.) is depleted as the ground water migrates through the contaminant source area and because typically

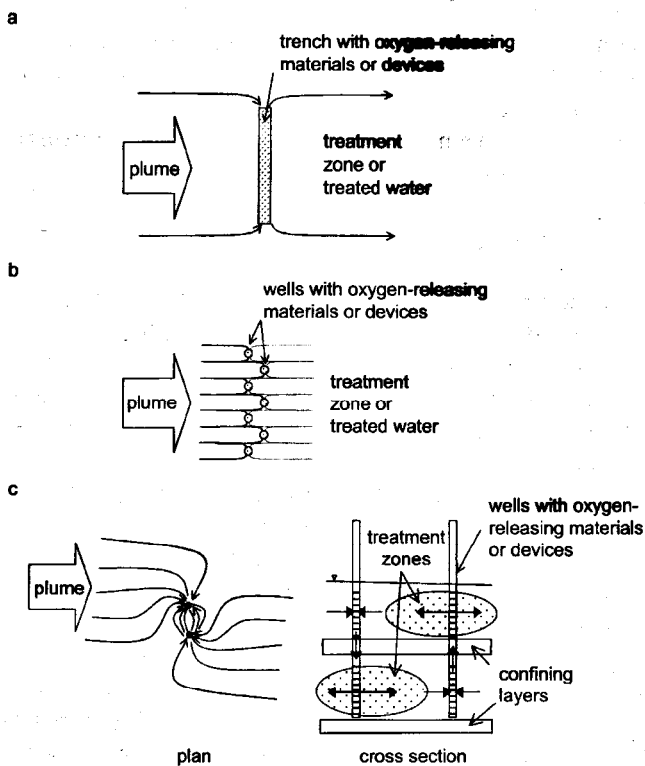


Figure 1. Conceptual schematic of (a) continuous permeable reactive barrier, (b) discontinuous permeable reactive barrier consisting of an array of un pumped wells, and (c) horizontal flow treatment well pairs.

weak transverse dispersion cannot efficiently reintroduce oxygen into the plume. This means that natural aerobic bioattenuation downgradient of the source area is often limited because the contaminants are migrating down an anaerobic "shadow," i.e., a zone invaded by the ground water made anaerobic by passage through the source zone. Therefore, to enhance the rate of in situ biodegradation of some contaminants, it may be necessary to increase D.O. concentrations within the plume.

Methods used in early attempts to enhance natural aerobic biodegradation were "active," i.e., involving the injection of fluids. These include injection of oxygenated/aerated water, hydrogen peroxide, microbubble foams (Spain et al. 1989; Wilson et al. 1994; Woodhull et al. 1997) and the injection of air/oxygen, also called sparging (Marley et al. 1992; Brown 1994). While these approaches succeed in introducing D.O. to the subsurface, they often may not achieve the intimate mixing of the D.O. with the ground water that is required to ensure uniform and reliable in situ remediation (Mackay and Cherry 1989; Johnson et al. 1993; Cherry et al. 1996). For example, injection of oxygenated liquids may result in the displacement of the contaminant in the vicinity of the injection and thus limit mixing of the added oxygen with the contaminated water. Injection of gases (sparging) may result in discrete channeling of the sparged gas and thus nonuniform introduction of D.O. into the plume (Johnson et al. 1993), or unintentional volatilization of volatile organic compounds into the atmosphere. Another concern about sparging is local "aquifer lockout"—a potential situation in which too much pore space becomes occupied

by the gas phase, reducing the local water permeability and resulting in diversion of the plume around the intended remediation zone. Furthermore, most of these methods carry a significant operation and maintenance burden. Nonetheless, these techniques are still extensively employed, due in part to the lack of effective and proven alternatives.

In recent years, new approaches have been developed to overcome or reduce the limitations just discussed. Two of these new approaches have been shown to successfully create in situ aerobic treatment zones (so called permeable reactive barriers or PRBs) using markedly different strategies. The "passive" approach involves the emplacement of oxygen releasing materials or devices across the path of the plume arrayed so that all or a portion of the plume is contacted. These PRBs are passive in that they rely on natural ground water flow to convey the plume to and through a treatment zone created in the subsurface. This strategy is intended to allow uniform plume/amendment mixing necessary for sustaining uniform in situ treatment. Passive PRBs may consist of continuous or discontinuous permeable devices installed across a plume (Figures 1a and 1b), each device containing a means to enhance D.O. concentrations. Wilson et al. (1997) outline the design principles of a discontinuous passive PRB, and various publications report successful field trials of the approach (Borden et al. 1997; Chapman et al. 1997; Gibson et al. 1998). Discontinuous PRBs could also be created using horizontal wells, which may be warranted where space permits their installation and the plume is relatively thin. In contrast to the passive approach, the "active" approach involves pumping to create a ground water circulation zone across the path of the plume into which oxygen is released. An example of the latter approach, using "horizontal flow treatment wells" (HFTWs), is illustrated schematically in Figure 1c. The HFTW method has been tried with success in a large-scale field experiment (McCarty et al. 1998) and the design principles have been discussed by Christ et al. (1999).

In previous work (Wilson and Mackay 1995), we described the theory and application of diffusive release through impermeable and semipermeable membranes for in situ passive amendment delivery, and presented experimental results of dissolved toluene, trichloroethylene, and bromide release. This paper extends that work to the release of gases, using oxygen as an example, evaluates the diffusion of oxygen through a number of different polymeric materials, and presents field test results of one possible emitter device design for long-term, steady, uniform, passive, in situ oxygen release. These diffusive oxygen emitters can be used in active or passive PRBs to create in situ aerobic treatment zones. The polymeric tubing on the emitter is pressurized with oxygen and the induced concentration gradient causes oxygen to diffuse out of the tubing and dissolve directly into the ground water flowing past the emitter. By avoiding the introduction of a gas phase (e.g., via sparging), this bubbleless transfer of oxygen to ground water is more efficient, wastes very little gas, does not strip contaminants out of

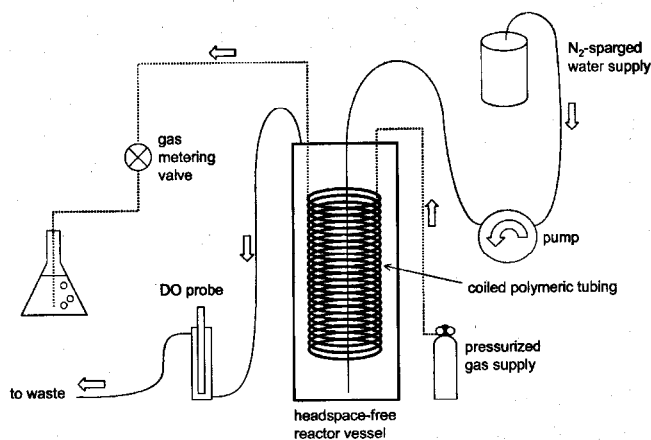


Figure 2. Schematic of lab test setup. Tubing details are compiled in Table 1. All tests were conducted at room temperature. Effluent water temperature varied by $<0.5^{\circ}\text{C}$. Water flow varied by $<3\%$ in each test.

the saturated zone, and may provide more predictable long-term delivery and distribution. At steady state, the rate of oxygen flux from the tubing matches the oxygen flux carried from the well by flowing ground water (assuming no oxygen is used within the well). The steady-state concentration is therefore dependent on the rate of ground water flow and oxygen mass flux from the tubing, which is in turn dependent on the concentration driving force (tubing pressure) and the length/wall thickness of tubing. Sanford et al. (1996) used this method to prepare solutions of dissolved inert gas tracers for lab column studies and to passively release helium and neon in a field tracer test. Gibson et al. (1998) also used devices based on this concept in a pilot test of a semiactive (limited pumping) treatment of a gasoline plume, but did not present any specific oxygen release data. In this paper, we summarize our investigations of the factors that influence oxygen release from polymeric tubing, provide results useful for designing field applications of the emitter technology, and report on one field application within a contaminant plume.

Theory

The oxygen emitters we are investigating consist of a continuous coil of polymeric tubing wound around a support and connected to a supply of oxygen (Figure 2). The wall of the tubing is in essence a polymeric membrane. The transport of fixed gases (e.g., oxygen, helium, nitrogen, and sulphur hexafluoride) through a polymeric membrane is a four-stage process (Gruenwald 1993): (1) adsorption to the polymer surface, (2) solubilization into the polymer, (3) mass transport through the polymer, and (4) desorption from the polymer surface.

It is well established that the mass transport of gases through polymeric materials is a diffusion-controlled process (van Amerongen 1946; Michaels and Bixler 1961a; Crank and Park 1968; Comyn 1985). Gas diffusion through polymers is known to be temperature dependent (Barrer 1937; van Amerongen 1946); e.g., Michaels and Bixler (1961a) observed that a 1°C rise in polymer

temperature resulted in a 7% increase in the diffusion coefficient of gases through low-density polyethylene (LDPE).

The diffusive mass flux of a gaseous species through a polymeric membrane is given by Fick's first law:

$$J = -D\delta c/\delta x \quad (1)$$

Strictly speaking, the force driving diffusion is not a concentration gradient (i.e., $\delta C/\delta x$), but rather a chemical potential gradient (Park, 1986). However, in this work, we have assumed that oxygen behaves as an ideal gas and that the driving force for diffusion can be approximated by the concentration gradient imposed across the membrane (i.e., across the tubing wall). The following development provides the rationale for this assumption. The driving force moving a molecule across a membrane of thickness δx is

$$[q - (q + \delta q)]/\delta x = \delta q/\delta x \quad (2)$$

where q is the mean energy per molecule. The mean energy per mole in a uniform system is the chemical potential, μ , and thus the mean energy per molecule is μ/N , where N is Avogadro's number. The driving force per molecule can therefore be defined as

$$F = - (1/N) \delta \mu/\delta x \quad (3)$$

The chemical potential of gaseous species can be defined in terms of fugacity, or under low-pressure conditions in terms of partial pressures (Stumm and Morgan 1996):

$$\mu = \mu^{\circ} + RT \ln(p/P^{\circ}) \quad (4)$$

where μ° is the standard potential and P° is a reference pressure (usually 1 atm). If it is assumed that the gas behaves ideally, partial pressure can be converted to mass-per-volume concentration using the ideal gas law and the molecular mass. The flux of molecules moving through a unit area of polymer in unit time is

$$J = v \times c \quad (5)$$

where v is mean molecular velocity defined as the driving force for movement (F) divided by resistance to that movement imposed by the polymer (τ):

$$v = - (\delta \mu/\delta x)/(N\tau) \quad (6)$$

Substituting Equations 4 and 6 into Equation 5 gives

$$J = - (RT/N\tau) \delta c/\delta x \quad (7)$$

Thus the diffusion coefficient is given by a constant term ($RT/N\tau$) and the driving force is approximated by a concentration gradient. Note that this derivation does not take into account the solubility of gases in, and sorp-

tion to, the polymer (steps 1, 2, and 4 previously noted). This is justified for two reasons: (1) while fixed gases such as oxygen are soluble in polymeric materials, they do not sorb significantly, and (2) the amount of gas dissolved in the polymer will rapidly reach a steady state in accordance with Henry's law partitioning. Thus, diffusion coefficients will be constant regardless of the concentration gradient imposed (Rogers 1985), and will be characteristic of the tubing material. If it is further assumed that pressurization of the tubing does not change the membrane properties, then an increase in pressure simply results in a proportional increase in the chemical gradient driving mass transfer.

Some other polymer characteristics should be detailed here, as they may affect oxygen release characteristics and tubing longevity, and may influence the choice of tubing for a given application. Rigid polymers (such as LDPE and PVC) contain both amorphous and crystalline polymer fractions (Michaels and Bixler 1961b). Diffusants are transported only through the amorphous fraction, and the crystalline fraction represents impedance to diffusion that is analogous to tortuosity found in porous media (Michaels and Bixler 1961a). For mass to diffuse through the tubing, there must be a continuous path of amorphous material extending from one side of the tubing to the other. The greater the number of these paths, the more mass will diffuse through the tubing. Diffusive mass transfer is therefore sensitive to wall thickness. The likelihood of continuous paths is greater in thin-walled tubing, and tortuosity effects are less than is the case with thicker walled tubing (assuming both have the same proportions of crystalline and amorphous fractions). This may mean that two samples of the same material with different wall thickness will yield different diffusion coefficient estimates.

Some polymer materials are naturally soft and flexible (e.g., silicone, natural rubber, and polyolefin), while others are made flexible through the addition of plasticizers (typically phthalate esters, which inhibit crystallization). An example of the latter is PVC. Rigid PVC has virtually no plasticizers, while flexible PVC formulations are roughly half plasticizers. Flexibility is a direct reflection of a higher fraction of amorphous polymer, and, in general, the higher the amorphous fraction, the higher the diffusivity. However, other manufacturing treatments may also influence diffusivity; e.g., fluorination renders otherwise gas-permeable polymers less so. Thus, the Teflon™ class of materials (including EFTE, PTFE, FEP, PFA, and PVDF) provide lower rates of diffusive oxygen release than similar nonfluorinated polymers. Another example is the range of diffusivities that are the result of the various proprietary treatments employed in the manufacture of different Tygon™ formulations (polyolefin-based). For example, the oxygen permeability estimates for seven formulations provided by the manufacturer vary over nearly two orders of magnitude.

Polymeric materials will sorb solvents (e.g., water and organic compounds) into their structure to varying degrees. In some cases this may cause the material to swell, but not necessarily dissolve because the polymer

chains are already fairly spread out and highly cross-linked (Gruenwald 1993). Swelling spreads the chains apart, opening "holes" in the amorphous fraction for the solvent to occupy. The resulting overall increase in amorphous volume may increase the diffusive flux of fixed gases (including oxygen, nitrogen, helium, and sulphur hexafluoride) because of their higher diffusivity in these solvents compared to that in the polymer (Gruenwald 1993). The degree of swelling (and increase in diffusion) depends on the solvent exposure level, the size of solvent molecules, the affinity the polymer has for that solvent, and the percentage of amorphous fraction. Even water can affect diffusivity. For example, while LDPE does not sorb much water (<0.1% v/v), nylon can take on as much as 10% v/v (Gruenwald 1993). In addition to the effect of solvents, there is the possibility that dissolved organic molecules (solutes), such as hydrocarbons, may be significantly soluble in and sorb to some polymers, but not cause swelling. In cases in which such molecules are able to diffuse through the polymer from the aqueous solution in contact with the polymer, the diffusion coefficient of the polymer may change as the diffusant concentration increases along the diffusion pathway (Vieth 1991). It is therefore possible that the diffusion of oxygen through some tubing may be increased as a result of exposure to dissolved organic contaminants (such as BTEX and chlorinated ethenes).

Many of the flexible polymer formulations (including silicone and Tygon) come with a manufacturer's recommendation to avoid exposure to either pure phase or high dissolved concentrations of organic compounds such as fuels or chlorinated solvents. While rigid polymers such as LDPE are rated to withstand higher concentrations and longer exposure times, exposure to some types of organic compounds may cause some materials to crack and/or prematurely fail (Gruenwald 1993). Polymer selection for a given site application should therefore take into account the types, phase, and/or concentrations of organic solvents that may be in the immediate vicinity of the intended installation. The long-term effect of these solvents on the fate of various polymeric materials is the subject of ongoing work.

Lab Release Experiments

Materials and Methods

Four types of tubing materials were selected for diffusive flux experiments: Tygon™ 3350 platinum-cured silicone, Tygon formulations 2275 and 2075, and LDPE. For the discussion that follows, the Tygon materials will be referred to as "2075" and "2275" for simplicity. A 7.0 L contactor vessel was constructed from a length of 15.24 cm diameter acrylic tube, to which a base and a flange top with a seated O-ring seal were solvent-welded. Stainless steel compression fittings were mounted on the outside of the top plate, and either compression or barbed fittings on the inside for oxygen (depending on tubing tested) and water conduction. A length of tubing to be tested was fixed to the inside oxygen influent and efflu-

Table 1
Tubing Statistics and Operating Conditions of Lab Diffusion Tests

Tubing Material	Inside Diameter (mm)	Outside Diameter (mm)	Wall Thickness (mm)	Tubing Length (cm)	Test Pressure (kPa gauge)	Maximum Rated Pressure (kPa gauge)	Average Water Flow Rate (L/day)	Average Contactor Residence Time (days)
Silicone	3.2	6.4	1.6	75	103.4	145	7.2	0.97
2275 Tygon	3.2	6.4	1.6	200	103.4	206	2.0	3.5
2075 Tygon	3.2	6.4	1.6	200	110.3	206	10.2	0.48
LDPE	4.8	6.4	0.8	300	*	758	10.3	0.48

LDPE: Low-density polyethylene. Tygon registered[®] Norton Performance Plastics Corp. Silicone: Tygon 3350 formulation, platinum cured.
*Pressure in the LDPE test was increased stepwise from 82.7, 124.1, 193.1, 330.9, to 465.4 kPag.

ent ports and the vessel was sealed, placed on a magnetic stirrer, and filled headspace-free with N₂-purged tap water. As shown in Figure 2, oxygen from a pressurized cylinder was conducted to and from the vessel through LDPE tubing connected to the vessel using standard compression fittings. N₂-purged water from a 20 L reservoir was metered via a peristaltic pump into the vessel and out through a small volume flow-through cell equipped with an Orion model 835 galvanic D.O. probe.

Water was allowed to flow for two to three days before starting oxygen release to stabilize flow and establish influent D.O. concentrations. At time zero, the tubing line was pressurized by opening the O₂ cylinder valve and setting the regulator to the desired operating pressure. Atmospheric gas was displaced from the tubing by venting O₂ through the line for three to four seconds. To maintain the set pressure and to ensure a uniform concentration gradient throughout each test, oxygen was slowly bled through the line using a metering valve at the end of the effluent gas line (Figure 2). Flow rates of the effluent water were gravimetrically determined daily during the tests. D.O. readings were collected frequently until the system approached a steady state, and less frequently thereafter until the test was terminated. The analytical range of the probe was 0 to 80 mg/L, with accuracy on the order of ±1%. Tubing parameters and experimental conditions are compiled in Table 1.

Results

According to the equations that describe the system shown in Figure 2 (Wilson and Mackay 1995), the concentration history observed in the contactor should describe a sinusoidal curve. At early time, the diffusant has not broken through the tubing wall and there is no increase in concentration in the contactor. After breakthrough, concentrations increase slowly as diffusive flux from the tubing starts to overcome the flux out of the contactor. As the diffusion gradient through the tubing approaches steady state, flux increases and concentrations in the contactor increase linearly. Once diffusion through the tubing has reached steady state, the flux from the tubing remains constant and concentration increase in the contactor slows. The whole system is at steady state when

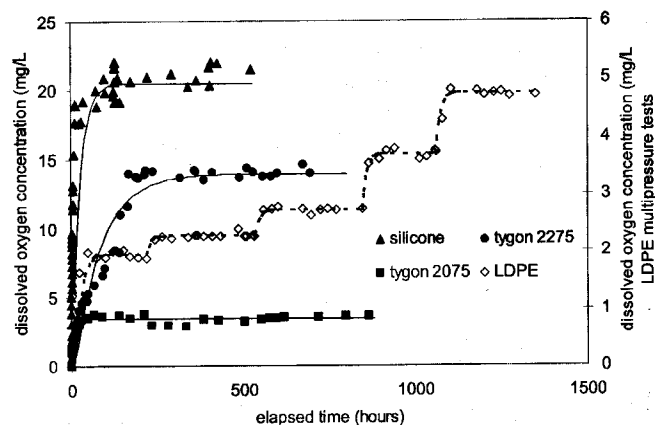


Figure 3. Oxygen concentration history and fit model curves in each of the four release tests. Symbols represent observed concentrations and the lines represent the model fits to those data. Diffusion coefficients fit at the five pressures in the LDPE test were, in order of increasing pressure ($\times 10^{-8}$ cm²/sec): 1.776, 1.776, 1.775, 1.645, and 1.666.

the diffusive flux from the tubing is equal to the flux out of the contactor.

Figure 3 shows the D.O. concentration histories of the four lab tests, each of which clearly exhibits the linear concentration increase and steady-state phases. The combination of thin tubing wall, small diffusant size, and large imposed concentration gradient resulted in rapid breakthrough and a very short early phase. After 200 hours, the pressure in the LDPE test was increased in several steps. Because oxygen was already at a diffusive steady state, onset of linear concentration increase was nearly immediate after each pressure increase. If our analytical resolution was much better and we sampled at much greater frequency shortly after increasing the pressure, we may have been able to discern this early phase. For various practical reasons, each material was tested under slightly different conditions (different tubing length, wall thickness, pressures, and/or pumping rates). In general, however, steady state in all the tests was achieved within six contactor residence times and concentrations varied thereafter by an average of 2.4%. The results were normalized by back-fitting oxygen diffusion coefficients (D) through each tubing (Table 2) using a simple computer

Table 2
Effective Diffusion Coefficients and Performance Characteristics

Tubing Materials	Mass-Transfer Coefficient (cm²/sec)	Tubing Cost Unit Length (US\$/m)	Length Required to Achieve 30 mg/L** (m)	Cost of Required Tubing Length (US\$)	Pressure Required to Achieve 30 mg/L*** (% of max rating)
Silicone	6.67×10^{-7}	4.86	8.9	43.24	20.0
2275 Tygon	5.11×10^{-8}	5.05	99.9	504.67	215.9
2075 Tygon	1.59×10^{-7}	4.40	32.0	140.64	33.3
LDPE	$1.73 \times 10^{-8*}$	0.49	51.55	25.26	84.6

Costs per unit length were taken from the same supplier, and are intended for comparative purposes only.

*Average of values fit to data collected at five different pressure settings (coefficient of variation: $\pm 3.8\%$).

** Steady-state concentration from 20.3 cm diameter by 1.52 m long well screen, with average ground water velocity of 10 cm/day, tubing pressurized to 80% of rated maximum ($100 \times \text{kPag}/\text{kPag}_{\text{max}}$).

***Steady-state concentration from same well as above, using 50 m of tubing (15 m in the case of silicone).

program incorporating the analytical solution presented by Wilson and Mackay (1995). The oxygen diffusion rate was found to be greatest through silicone, followed by 2075, 2275, and LDPE. Comparing the 2275 and 2075 concentration histories and diffusion coefficient estimates highlights the importance of this normalization. While the steady-state concentration was lower in the 2075 test, it was conducted at a higher water flow rate (lower residence time) and the estimated diffusion coefficient is actually greater than that for 2275 (Table 2). The closeness of fit in each of the five tests (Figure 3) suggests that the model accounts for all the significant variables in the system, and adequately describes all three phases of the concentration histories (Figure 3). This means that, given a diffusion coefficient, the model can be used to design field emitters and/or predict steady state oxygen concentrations under different operating conditions.

Recall that diffusion is a temperature-dependent process. During the course of these tests, effluent water temperature varied by less than 0.5°C and no trend was evident. This means that the error associated with coefficient estimates caused by temperature variation is estimated to be no more than 3% to 4%. Most of the deviation from the model curves is more likely attributable to fluctuations in gas pressure in the tubing and water flow rates through the contactor, especially at early time. These fluctuations were reduced after the first (silicone) test and model fit was improved.

During the LDPE test, pressure was increased four times (Table 1) to test the hypotheses that: (1) oxygen is transferred solely by diffusion, and (2) the chemical potential gradient driving diffusion is accurately approximated by the concentration gradient via the ideal gas law and pressure. The diffusion coefficients estimated from each segment of the release history were very similar ($1.73 \times 10^{-8} \pm 0.07 \text{ cm}^2/\text{sec}$), supporting the given hypotheses and further validating the curve-fitting model.

To test whether absorption of water may have affected diffusion, a 50 cm length of each material was weighed and the ends joined together with a short piece of 3.2 mm outside diameter (O.D.) tubing to form a closed loop with the

cut ends of the tested material touching. The loops were submerged in water and removed every five days over a 20-day period, dried, and weighed. The results from the water sorption tests (data not shown) indicate that none of the materials absorb detectable amounts of water. This result is not surprising given the hydrophobic nature of the materials.

Considerations for Tubing Selection

While offering the greatest oxygen mass flux, silicone is the second most expensive of the five materials (Table 2), and may be susceptible to swelling and/or failure in situations where petroleum hydrocarbons are present as a pure phase or at significant dissolved concentrations. We also had some concerns that the connection methods we used to plumb the soft tubing materials (hose barb fitting with ratchet tubing clamp) may not be robust enough for field application. After steady-state D.O. concentrations were reached in the silicone test, the oxygen pressure was increased in 34.5 kPag increments and left to equilibrate for at least 12 hours to evaluate tubing and connection competence. The tubing finally failed at 310.3 kPag, well above the maximum rating suggested by the supplier. The failure, a 1 cm long rupture parallel to the tubing axis, did not occur near either influent or effluent connection fitting. Although the barb/clamp connections themselves did not fail during this test, we are continuing to evaluate other soft-tubing plumbing methods to seek a more suitable approach for long-term application in the field. In applications where the concentration of dissolved organics is low, silicone may still be a good choice given the high oxygen diffusivity observed.

Tygon 2275 was found to have a diffusion coefficient roughly an order of magnitude less than silicone but greater than LDPE. However, limited working pressure range, high cost, low oxygen diffusivity, and general susceptibility to damage by organic solvents or high concentrations of dissolved organics suggests that 2275 may not be a suitable choice for many applications. The diffusion coefficient for 2075 was found to be roughly an order of magnitude greater than LDPE (Table 2). Despite

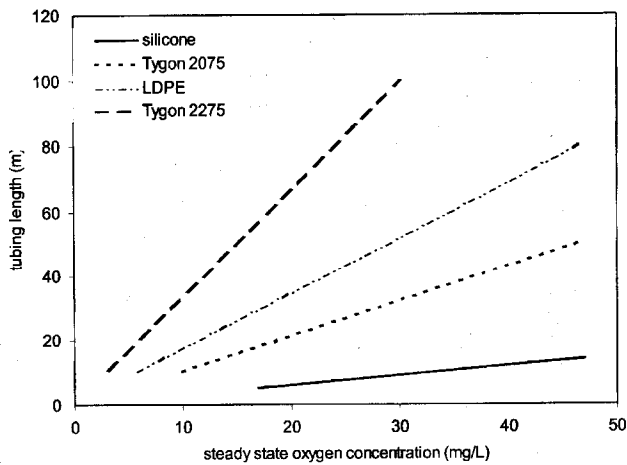


Figure 4. Relationship between steady-state oxygen concentration and tubing length. Operating pressure is assumed to be 80% of rated maximum, and temperature is constant.

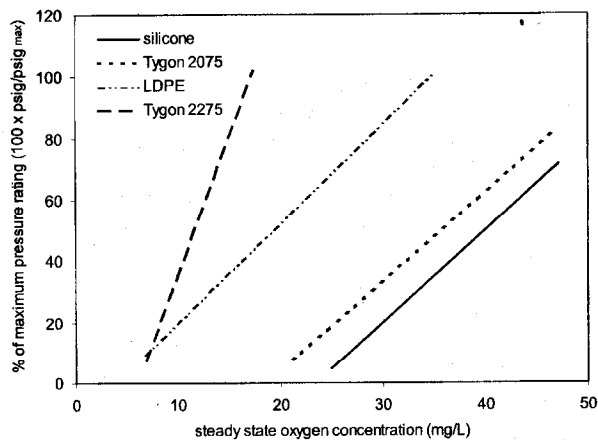


Figure 5. Relationship between steady-state oxygen concentration and operating pressure for fixed tubing lengths: 2075, 2275, and LDPE = 50 m, silicone = 15 m (the latter is based on observed diffusivity and availability). Temperature is assumed constant.

this, the total oxygen flux potential from the two materials is similar because the latter can be pressurized four times higher than the former (four times greater concentration gradient). Like 2275, the 2075 material is expensive and the manufacturer does not recommend prolonged exposure to either pure phase or high dissolved concentration of organic solvents. Nevertheless, 2075 may be a reasonable choice for field application where total organic contaminant loading is low. LDPE can be reliably plumbed using standard compression fittings that we have tested to 620.5 kPag in other work. Thus, in spite of the fact it has the lowest diffusion coefficient, it may still be useful in field applications given its low cost, chemical resistance, connection reliability, and wide working pressure range.

The relative differences between the four materials can be further demonstrated by considering a simple application scenario. Assume that an emitter is installed in a 20.3 cm diameter by 1.5 m long well screen emplaced within an aquifer with a ground water flow rate of 10 cm/d.

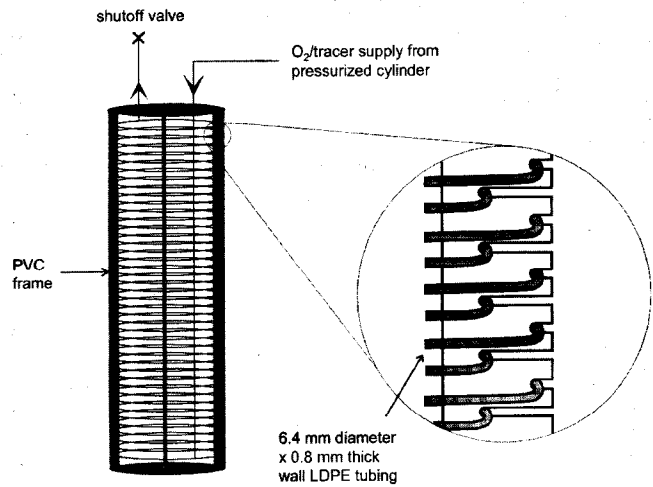


Figure 6. Schematic of passive oxygen emitter used in field trials. Device was 17.2 cm in diameter and 121.9 cm long. A 1.9 cm O.D. PVC pipe was threaded to the top of the frame to facilitate installation in the well, house gas supply and return lines, and allow access for sampling tubes.

The well screen is unpumped, serving solely as a permeable location for the ground water to contact the emitter. Theory suggests that the well screen will capture ground water flowing through an area roughly twice its own width (Drost et al. 1968; Halevy et al. 1967). Once a well (or other contactor) is installed, contactor volume is fixed and residence time is defined by the ground water flow rate. Tubing length and pressure are two design variables that are easiest to manipulate to achieve some delivery goal. The relationship between tubing length and steady-state D.O. concentration for emitters operated at a fix pressure (80% of maximum rating) is shown in Figure 4, whereas Figure 5 shows steady-state concentrations for fixed lengths of tubing operated at a range of pressures.

It is evident from Figure 4 that only very short lengths of silicone are needed to generate significant D.O. concentrations. However it is also evident that high D.O. concentrations can be achieved with polymers that have lower effective diffusion coefficients for oxygen provided they have a higher operational pressure range (e.g., LDPE). Table 2 lists the length of each tubing material required to generate 30 mg/L D.O., assuming the tubing was operated at 80% maximum pressure, along with the approximate cost for that length. Silicone and LDPE stand out as cost-effective alternatives. Alternatively, tubing length may be fixed by certain geometric constraints (chosen well diameter or emitter design). In Figure 5, we plot the steady-state D.O. concentrations for fixed lengths of tubing over a range of operating pressures (15 m for silicone. 50 m for the other materials). We have found in our own field experience that 50 m of tubing is a practical amount for an emitter designed for a 1.2 m long by 20.3 cm diameter well screen. The shorter length of silicone was used because of the high observed oxygen diffusivity, and as a practical matter silicone tubing is commonly available in 15 m lengths. Figure 5 also demonstrates the flexibility inherent in these diffusive emitters.

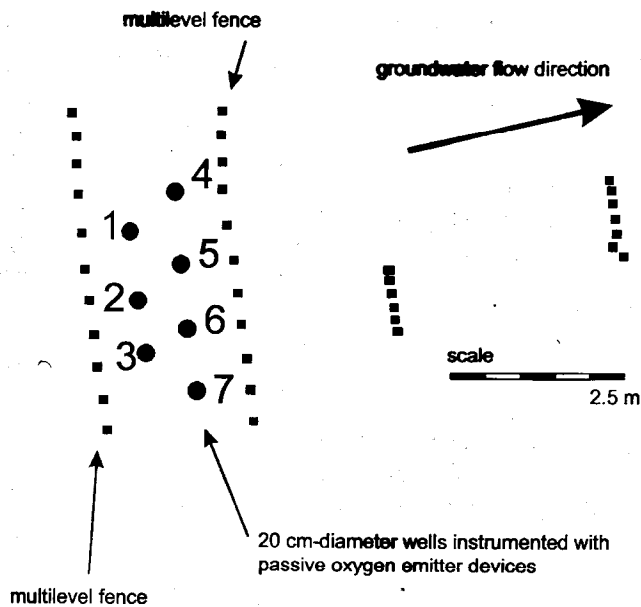


Figure 7. Approximate sketch map of the field test site showing location and layout of oxygen release wells and multilevel samplers in relationship to the plume. See Chapman et al. (1997) for details of multilevel and release well construction, and extent and composition of the plume.

Once installed, a range of D.O. concentrations is possible simply by adjusting the pressure (i.e., concentration gradient) that controls diffusive flux.

Field Release Experiment

Materials and Methods

Based predominantly on cost, reliability of pressure-tight connections, mechanical strength, and resistance to degradation by exposure to hydrocarbons, LDPE was selected for testing at the field scale (we are continuing to conduct tests with other materials). The basic design of the field-scale passive oxygen emitter involves a continuous coiled double loop of LDPE tubing (6.4 mm O.D. \times 0.79 mm thick wall) wound around an 18.4 cm diameter by 120 cm long PVC support frame (Figure 6). Tubing supports were machined in such a way as to maintain a constant spacing between the loops of tubing. Tubing was wound onto the inner support slots from the top down, and then onto the outer slots from the bottom up, resulting in a continuous run of approximately 40 m of tubing. Each emitter weighed approximately 4.5 kg. Sufficient tubing was left on the influent and effluent ends to run to the surface, where connection to the oxygen supply could be made and easily monitored for leaks.

Seven 20.3 cm diameter wells were installed within a gasoline plume at a former service station in Strathroy, Ontario, Canada. This is the site of our previous field evaluation of a solid oxygen release technology (ORC[™], Regenesys Bioremediation Products Inc., San Clemente, California). Chapman et al. (1997) describe the site in some detail, as well as the results of the prior evaluation. For the field work discussed here, two rows of wells were

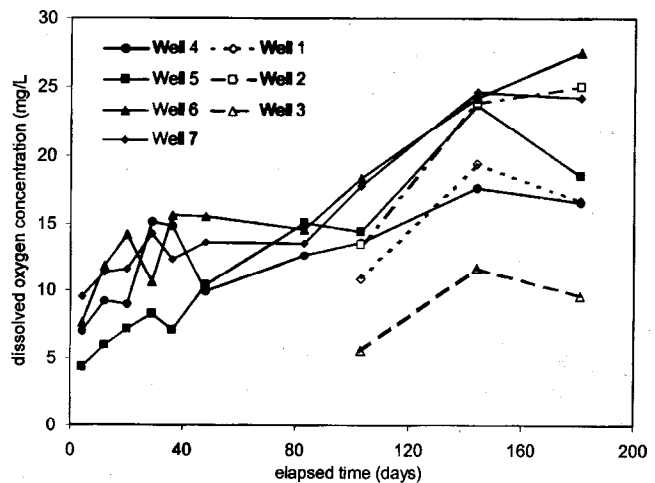


Figure 8. Dissolved oxygen concentration histories in the seven release wells at the Strathroy site. Emitters were operated at 50 psi for the first 80 days, then 90 psi for the remainder of the trial. Each emitter had approximately 40 m of LDPE tubing of the same diameter and wall thickness as that tested in the lab.

installed immediately adjacent to the previous study site by hollow-stem auger to a depth of 6.1 m and were screened over the bottom 1.4 m with #10 slot PVC wire-wrapped screen. The wells in each row were an average of 73 cm apart from center to center, with the second row staggered from the first (Figure 7). Limited available space forced the installation of the well array very close to the suspected NAPL source area. In fact, pure NAPL was encountered in some of the oxygen release wells and multilevel samplers during the test, and total BTEX concentrations influent to parts of the array were often in excess of 100 mg/L.

The wells were developed by repeated surging and purging using a surge block and high volume pump until no significant fines were produced. The oxygen emitters were installed in the wells across the screened interval. One end of the tube from each emitter was plumbed to a manifold that was in turn plumbed to a pressurized pure oxygen cylinder using compression fittings. The other end of each tube was plumbed to a dedicated solenoid valve controlled by a digital precision timer. Two sampling tubes were installed in each release well (one-third and two-thirds along the emitter length) to allow measurement of D.O. inside the well during the test. Prior to pressurizing the emitters, a D.O. snapshot was collected from each sample point to establish pre-release D.O. concentrations. The emitters in wells 4 through 7 were then pressurized to 344.7 kPag, and the tubing vented for three to four seconds to displace ambient air and ensure that the emitter tubing was full of oxygen. Oxygen release from wells 1 through 3 was initiated on day 80, when the whole system pressure was increased to 620.5 kPag. The tubes were vented four times daily for a total of two seconds to maintain optimal oxygen concentration gradient conditions. Dissolved oxygen concentrations were analyzed using a peristaltic pump and a flow-through cell fitted with an Orion model 835 D.O. probe (same as that used in the lab tests).

Results

The in situ contaminant treatment achieved by use of the oxygen emitters is the subject of an upcoming manuscript and will not be addressed here. Instead we focus on the oxygen release performance of the emitters under field conditions. Given the length, diameter, and wall thickness of tubing used to construct the emitters, the measured ground water flow rate and the intended operating pressures, the anticipated steady-state D.O. concentration was estimated using the effective diffusion coefficient determined in the lab. For the first 80 days, the system was operated at 344.7 kPag and then turned up to 620.5 kPag. The predicted D.O. concentrations for both periods (16.3 and 26.3 mg/L) compare favorably to the concentrations measured in the release wells (approximately 13 and 25 mg/L, Figure 8), in spite of the presence of degradable hydrocarbons. Note that emitter performance was not noticeably affected by exposure to NAPL (units 3, 6, and 7), although exposure time was at most two to three months. The weaker performance of the emitter in well 3 is likely the result of a pinch in the LDPE tubing that we subsequently discovered, which we surmise prevented adequate venting of that emitter. The concentration gradient was therefore not as high as it was for the other emitters. Pressure was maintained at the intended setting throughout the test, and no visible signs of polymer deterioration were observed when the emitters were removed.

All seven wells were slug-tested before and after the trial period to detect any changes in flow through the wells as a result of any chemical precipitation on or biofouling of the screens. Estimated hydraulic conductivities differed by less than 2% (data not shown), suggesting that the hydraulic performance of the wells did not change over the six-month trial period.

After reaching steady state, D.O. concentrations were relatively uniform during each three-month operational period. This demonstrates the steady and uniform nature of oxygen delivery possible with the diffusive emitters over long time frames. One other advantage of this method of oxygen release is that operation and maintenance demands are low. For the six-month test, only two tanks (approximately 22 kg) of industrial grade oxygen were needed. Furthermore, only a very minor amount of electrical power was required to operate the venting timer and solenoid valves; this could conceivably be supplied entirely by batteries in remote applications lacking line power. Uniform, steady oxygen release and low operation and maintenance demands can be contrasted to the results of the prior demonstration (Chapman et al. 1997) in which the oxygen concentrations released from the solid oxygen sources decayed exponentially from near saturation levels just after the start of the test to an average of roughly 2 mg/L on day 182. This nonsteady release suggests that at this and similar sites frequent replacement of the oxygen source would be necessary to ensure an adequate supply of oxygen to meet long-term plume demand.

Potential Field Applications

Diffusive oxygen emitters could be used in a number of scenarios. The field test described is an example of a

passive discontinuous PRB. These PRBs rely on the modest hydraulic capture of unpumped wells to direct plume into a treatment zone and thus require small spacing between wells. Emitters could also be installed at key points within other hydraulic management systems (e.g., funnel and gate systems or collector trenches with treatment at nodes) to minimize the number of emitters needed. Various semiactive schemes could be envisioned that all have the goal of increasing spacing of emitter locations, e.g., in-well recirculation or recirculation between two neighboring wells. The horizontal flow treatment well (HFTW) concept (Figure 1c) is an extension of the latter approach. In that method, wells can be placed much farther apart than they would in a passive PRB application. However, the pumping rate needed to achieve acceptable capture and recirculation would result in a significant reduction in contactor residence time, which in turn imposes a significant demand on the oxygen emitter. Nevertheless, based on the diffusion coefficients obtained in this work, it should be possible to derive an HFTW/emitter design combination that will result in sufficient oxygen delivery to a relatively large treatment zone using a small number of wells and emitters. For example, pairs of 10.2 cm diameter wells spaced on the order of 3 to 5 m apart and pumped at 2 to 5 L/min provide sufficient residence time to deliver sufficient oxygen to meet demand in some situations. In high demand situations, the interwell spacing would have to be reduced if emitters were the preferred method of oxygen release.

Summary

Natural attenuation is an aquifer restoration option that has gained favor recently. However, there are some sites where intrinsic processes do not reduce the flux of contaminants sufficiently to control risk. At such sites, some intervention is required. In the case of aerobically degradable contaminants, the efficient delivery of dissolved oxygen at concentrations adequate to sustain or enhance in situ biodegradation is a key requirement. The method described herein provides steady and uniform long-term release of oxygen from pressurized polymeric tubing. Mass transfer is controlled by diffusion through the tubing in response to the concentration gradient imposed as a result of pressurization. Of the four types of tubing material tested, platinum-cured silicone was found to have the highest oxygen diffusion coefficient, followed by 2075 Tygon, 2275 Tygon, and LDPE. The choice of tubing material for a given application will be defined by site conditions. High VOC loading may require the use of LDPE, which is the most chemically resistant of the materials tested. In cases where the risk of damage by VOC loading is minimal but high oxygen demand is imposed from other sources (dissolved or solid), silicone may be an appropriate choice. Other practical concerns may factor into the selection of a material. For example, LDPE is the least expensive of the group, and its rigid nature gives it superior mechanical strength. We are continuing to look at the release characteristics of other polymers, the effects of organic solvents on release behavior, and methods to release ionic solutes.

Diffusive oxygen emitter devices could be used in permeable reactive barriers, horizontal flow treatment well schemes, or a range of other hydraulic management systems incorporating a contactor suitable for the installation of one or more devices. The field trial described herein demonstrates that significant D.O. concentrations can be generated from an array of closely spaced wells containing emitters constructed of LDPE tubing. Once installed, steady and uniform diffusive release of oxygen can be maintained indefinitely (as long as the concentration gradient is maintained) with minimal maintenance. Operational cost is low. The concentration gradient may be provided by pressurized cylinders or, if economically warranted, by oxygen generators. The principal advantages of passive diffusive release of oxygen are in the simplicity of the release mechanism, the ability to control steady-state concentrations by changing tubing type, length or gas pressure, and the fact that mass transfer is bubbleless. Avoiding the introduction of a gas phase results in a very efficient transfer of oxygen to the water flowing through the well. Passive release also overcomes the problems of plume displacement and mixing that are typical of active injection methods of oxygen delivery.

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Editor's Note: The use of brand names in peer-reviewed papers is for identification purposes only and does not constitute endorsement by the authors, their employers, or the National Ground Water Association.

References

- Alvarez, P.J.J., P.J. Anid, and T.M. Vogel. 1991. Kinetics of aerobic biodegradation of benzene and toluene in sandy aquifer material. *Biodegradation* 2, 43-51.
- Atlas, R.M. 1981. Microbial degradation of petroleum hydrocarbons: An environmental perspective. *Microbiological Reviews* 45, no. 1: 180-209.
- Barbaro, J.R., J.F. Barker, L.A. Lemon, and C.I. Mayfield. 1992. Biotransformation of BTEX under anaerobic, denitrifying conditions: Field and laboratory observations. *Journal of Contaminant Hydrology* 11, no. 3-4: 245-272.
- Barker, J.F., G.C. Patrick, and D. Major. 1987. Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. *Ground Water Monitoring Review* 7, no. 1: 64-71.
- Barrer, R.M. 1937. Nature of diffusion in rubbers. *Nature* 140, 106.
- Borden, R.C., and P.B. Bedient. 1986. Transport of dissolved hydrocarbons influenced by reaeration and oxygen limited biodegradation: I. Theoretical development. *Water Resources Research* 22, no. 13: 1973-1982.
- Borden, R.C., R.T. Goin, and C.M. Kao. 1997. Control of BTEX migration using a biologically enhanced permeable barrier. *Ground Water Monitoring & Remediation* 17, no. 1: 70-80.
- Brown, R. 1994. Treatment of petroleum hydrocarbons in ground water by air sparging. In *Handbook of Bioremediation*, ed. R.D. Norris and J.E. Matthews, 61-85. Boca Raton, Florida: Lewis Publishers.
- Chapman, S.W., B.T. Byerley, D.J.A. Smyth, and D.M. Mackay. 1997. A pilot test of passive oxygen release for enhancement of in situ bioremediation of BTEX-contaminated ground water. *Ground Water Monitoring & Remediation* 17, no. 2: 93-105.
- Cherry, J.A., S. Feenstra, and D.M. Mackay. 1996. Concepts for the remediation of sites contaminated with dense non-aqueous phase liquids (DNAPLs). In *Dense Chlorinated Solvents and Other DNAPLs in Groundwater*, ed. J.F. Pankow and J.A. Cherry, 475-506. Portland, Oregon: Waterloo Press.
- Christ, J.A., M.N. Goltz, and J. Huang. 1999. Development and application of an analytical model to aid design and implementation of in situ remediation technologies. *Journal of Contaminant Hydrology* 37, no. 3-4: 295-317.
- Comyn, J. 1985. Introduction to polymer permeability and the mathematics of diffusion. In *Polymer Permeability*, ed J. Comyn, 1-10. London: Elsevier Applied Sciences.
- Cowan, R.M., and K. Park. 1996. Biodegradation of the gasoline oxygenates MTBE, ETBE, TAME, TBA, and TAA by aerobic mixed cultures. 28th Mid-Atlantic Industrial and Hazardous Waste Conference, Buffalo, New York, 523-530.
- Crank, J., and G.S. Park. 1968. Methods of measurement. In *Diffusion in Polymers*, ed. J. Crank and G.S. Park, 1-39. London: Academic Press.
- Davis, J.W., and C.L. Carpenter. 1990. Aerobic biodegradation of vinyl chloride in groundwater samples. *Applied and Environmental Microbiology* 56, no. 12: 3878-3880.
- Drost, W., D. Klotz, A. Koch, H. Moser, F. Neumaier, and W. Rauer. 1968. Point dilution methods of investigating ground water flow by means of radioisotopes. *Water Resources Research* 4, no. 1: 125-146.
- Edwards, E.A., L.E. Wills, M. Reinhard, and D. Grbic-Galic. 1992. Anaerobic degradation of toluene and xylene by aquifer microorganisms under sulfate-reducing conditions. *Applied and Environmental Microbiology* 58, no. 3: 794-800.
- Gibson, T.L., A.S. Abdul, and P.D. Chalmer. 1998. Enhancement of in situ bioremediation of BTEX-contaminated ground water by oxygen diffusion from silicone tubing. *Ground Water Monitoring & Remediation* 18, no. 1: 93-104.
- Grbic-Galic, D., and T.M. Vogel. 1987. Transformation of toluene and benzene by mixed methanogenic cultures. *Applied and Environmental Microbiology* 53, no. 2: 254-260.
- Gruenewald, G. 1993. *Plastics: How Structure Determines Properties*. Munich: Hanser Publishers.
- Halevy, E., H. Moser, O. Zellhofer, and A. Zuber. 1967. Borehole dilution techniques: A critical review. In *Isotopes in Hydrology*, 531-564. Vienna: International Atomic Energy Agency.
- Hutchins, S.R., G.W. Sewell, D.A. Kovacs, and G.A. Smith. 1991. Biodegradation of aromatic hydrocarbons by aquifer microorganisms under denitrifying conditions. *Environmental Science & Technology* 25, no. 1: 68-76.

- Jamison, V.W., R.L. Raymond, and J.O.J. Hudson. 1975. Biodegradation of high-octane gasoline in groundwater. *Developments in Industrial Microbiology* 16, 305-312.
- Johnson, R.L., P.C. Johnson, D.B. McWhorter, R.E. Hinchee, and I. Goodman. 1993. An overview of in situ air sparging. *Ground Water Monitoring & Remediation* 13, no. 4: 127-135.
- Lovley, D.R., M.J. Baedecker, D.J. Lonergan, I.M. Cozzarelli, E.J.P. Phillips, and D.I. Siegel. 1989. Oxidation of aromatic contaminants coupled to microbial iron reduction. *Nature* 339, 297-300.
- Mackay, D.M., and J.A. Cherry. 1989. Groundwater contamination: Pump-and-treat remediation. *Environmental Science and Technology* 23, no. 6: 630-636.
- Marley, M.C., D.J. Hazebrouck, and M.T. Walsh. 1992. The application of in situ air sparging as an innovative soils and ground water remediation technology. *Ground Water Monitoring Review* 12, no. 2: 137-145.
- McCarty, P.L., M.N. Goltz, G.D. Hopkins, M.E. Dolan, J.P. Allan, B.T. Kawakami, and T.J. Carrothers. 1998. Full-scale evaluation of in situ cometabolic degradation of trichloroethylene in groundwater through toluene injection. *Environmental Science and Technology* 32, no. 1: 88-100.
- Michaels, A.S., and H.J. Bixler. 1961a. Flow of gases through polyethylene. *Journal of Polymer Science* 50, 413-439.
- Michaels, A.S., and H.J. Bixler. 1961b. Solubility of gases in polyethylene. *Journal of Polymer Science* 50, 393-412.
- Mo, K., C.O. Lora, A.E. Wanken, M. Javanmardian, X. Yang, and C.F. Kulpa. 1997. Biodegradation of methyl t-butyl ether by pure bacterial cultures. *Applied and Environmental Microbiology* 47, 69-72.
- National Research Council. 1993. *In Situ Bioremediation. When Does It Work?* Washington, D.C.: National Academy Press.
- Park, G.S. 1986. Transport principles — Solution, diffusion and permeation in polymer membranes. In *Synthetic Membranes: Science, Engineering & Applications*, ed. P.M. Bungay, H.K. Lonsdale, and M.N. de Pinho, 57-108. NATO ASI Series C: Mathematical & Physical Sciences.
- Rogers, C.E. 1985. Permeation of gases and vapours in polymers. In *Polymer Permeability*, ed. J. Comyn, 11-73. London: Elsevier Applied Science Publisher.
- Salanitro, J.P., L.A. Diaz, M.P. Williams, and H.L. Wisniewski. 1994. Isolation of a bacterial culture that degrades methyl t-butyl ether. *Applied and Environmental Microbiology* 60, no. 7: 2593-2596.
- Sanford, W.E., R.G. Shropshire, and D.K. Solomon. 1996. Dissolved gas tracers in groundwater: Simplified injection, sampling, and analysis. *Water Resources Research* 32, no. 6: 1635-1642.
- Semprini, L., G.D. Hopkins, P.V. Roberts, D. Grbic-Galic, and P.L. McCarty. 1991. A field evaluation of in-situ biodegradation of chlorinated ethenes: Part 3, Studies of competitive inhibition. *Ground Water* 29, no. 2: 239-250.
- Spain, J.E., J.D. Milligan, D.C. Downey, and J.K. Slaughter. 1989. Excessive bacterial decomposition of hydrogen peroxide during enhanced biodegradation. *Ground Water* 27, no. 2: 163-167.
- Stumm, W., and J.J. Morgan. 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. New York: John Wiley and Sons.
- Thierrin, J., G.B. Davis, and C. Barber. 1995. A ground water tracer test with deuterated compounds for monitoring in situ biodegradation and retardation of aromatic compounds. *Ground Water* 33, no. 3: 469-475.
- van Amerongen, G.J. 1946. The permeability of different rubbers to gases and its relationship to diffusivity and solubility. *Journal of Applied Physics* 17, 972-985.
- Vieth, W.R. 1991. *Diffusion in and Through Polymers*. Munich: Hanser Publishers.
- Wiedemeier, T.H., H.S. Rifai, C.J. Newell, and J.T. Wilson. 1999. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. New York: John Wiley & Sons.
- Wilson, J.T., J.M. Armstrong, and H.S. Rifai. 1994. A full-scale field demonstration on the use of hydrogen peroxide for in situ bioremediation of an aviation gasoline-contaminated aquifer. In *Bioremediation: Field Experience*, ed. P.E. Flathman, D.E. Jerger, and J.H. Exner, 333-360. Ann Arbor, Michigan: Lewis Publishers.
- Wilson, R.D., and D.M. Mackay. 1995. A method for passive release of solutes from an unpumped well. *Ground Water* 33, no. 6: 936-945.
- Wilson, R.D., D.M. Mackay, and J.A. Cherry. 1997. Arrays of unpumped wells for plume migration control by semi-passive in situ remediation. *Ground Water Monitoring and Remediation* 17, no. 3: 185-193.
- Woodhull, P.M., D.E. Jerger, D.P. Leigh, R.F. Lewis, and E.S. Becvar. 1997. Field demonstration of oxygen microbubbles for in situ bioremediation. In *The Fourth International In Situ and On Site Bioremediation Symposium*, ed. B.C. Alleman and A. Leeson, 141-146. Columbus, Ohio: Battelle Press.

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