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O2Tube Sullivan Illinois Project Overview and Results

Illinois EPA Incident # 20020216

Environmental Consultant: United Science Industries, Inc., Wood lawn, Illinois 62898 Phone: (618) 735-7907

- Total BTEX reduced from 51,738 PPB to 2472 PPB - 95 % Reduction
- Total Benzene reduced from 24,212 PPB to 1690 - 93% Reduction
- Average DO increased from 3.2 PPM to 5.86 PPM at distances of 30 feet from well
- Average ORP increased from 152 mV to 450 mV at distances of 30 feet from well
- Nitrite and Nitrates were exhausted during study (a first in Illinois silty clay)
- pH steady at (7.2 - 8.0)

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Purpose

Demonstrate for the Illinois EPA that the O2Tube System can effectively remediate BTEX contamination in Groundwater flowing through Illinois silty clay.

Procedure

Eight four inch screened wells and vents were installed on 60 foot spacing over approximately ¾ of an acre so that two 16 amp O2Tube Systems can be operated over nine months. The nine month period is for comparison to chemical injection of Regenesis ORC®. In addition, sixteen monitoring wells were installed to collect samples for BTEX, ORP, DO, odor, color, Temperature, plate count and pH (see attached drawing).

Each test is essential for determining the effectiveness of any dissolved oxygen technology and must be understood with regards to the pilot studies short time duration. The O2Tube cell continually recirculates the groundwater in a doughnut shaped pattern around it's well. This recirculation of water creates a dynamic environment which must also be accounted for regarding each test. The following sections will help explain what each test adds to a full scale remediation plan.

BTEX - Benzene, Toluene, Ethylbenzene and Total Xylene

BTEX contamination is a multiphase problem (Brown, Loper, and McGarvey, 1986). BTEX contaminants in the subsurface can be present as three phases: mobile free phase, residually saturated soil (adsorbed phase), and contaminated groundwater (dissolved phase). The mobile free phase is toxic to hydrocarbon degrading bacteria and should have been removed or significantly reduced. The BTEX samples taken reflect the free phase contaminant in parts per billion.

While reducing the BTEX concentration is the main objective of any remediation project, it's a terrible indicator of bioremediation in a two month study because of the time required to build a significant bacterial colony. When dissolved oxygen is increased in groundwater at a contaminated site, the order of oxidation's is organic material, sulfides, iron, nitrates and finally bacteria. After the bacteria has access to dissolved oxygen, it must begin releasing enzymes to reduce the BTEX into smaller fractions which it can ingest and allow it to use the carbon and oxygen to produce more bacteria. This process repeats over and over until the BTEX is gone.

Since the groundwater is recirculating while using the O2Tube dissolved oxygen system, BTEX levels will fluctuate due to simple mixing, previously absorbed BTEX is released from soil by enzymes, and the rotating water tends to draw contaminants towards the O2Tube well (see O2Tube handout "What Happens After Starting an O2Tube Cell?").

Additionally, the well that contains the O2Tube cell will test negative for contaminants at any time that the system is operational because the electrochemical cell produces hydroxyl radicals at the surface of the cathodes that chemically oxidizes contaminants.

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ORP - Oxygen reduction potential

A useful concept for bioremediation is that the ORP is a measurement of electrons that are available to reduce contaminants in the same way that pH is the measurement of available protons. Oxygen is the preferred electron acceptor in aerobic respiration followed by nitrates, iron(+3), and sulfates. Therefor, the rate of hydrocarbon degradation increases with increasing ORP (Riser-Roberts, 1992).

At a contaminated site where the dissolved oxygen level in groundwater is low (0.5 ppm) and the ORP is low (50 mV) , degradation is occurring very slowly with the conversion of iron(+3) to iron(+2) is the dominant reduction reaction. Dissolved oxygen is still the preferred (and fastest) electron acceptor , but, there isn't enough oxygen to make a difference. As the dissolved oxygen level is increased and more oxygen is available to accept electrons, the potential for the oxygen to be reduced increases, and the ORP increases. The initial dissolved oxygen will be used to oxidize other materials before its available to the bacteria because of a greater difference in potential energy yield of the reaction. The preferred order of dissolved oxygen usage is decomposing organic matter (ORP -750 to -240 mV), oxidation of sulfides (ORP -600 to -150 mV), oxidation (rusting) of iron (ORP -550 to +50 mV), oxidation of nitrates (ORP -150 to +400 mV, and finally aerobic respiration (bacteria, ORP +100 to +800 mV).

The ORP looks at the total solutions potential and is a great indicator of oxygen being available for respiration. The ORP, however, cannot tell if the bacteria, contaminant, and oxygen are all in the same area so respiration occurs. Therefor, an abundance of centralized dissolved oxygen would generate a high ORP, even though the dissolved oxygen may be diffusing vertically upward to the vadose zone. An example would be oxygen diffusion or oxygen releasing chemicals (Regenesis ORC) that rely on groundwater movement for transport farther than what occurs by diffusion.

Because the O2Tube cell rotates the groundwater and thereby mixes the dissolved oxygen throughout the treatment area, ORP is a more accurate indicator of respiration than in diffusion limited methods like oxygen diffusion or oxygen releasing chemicals (Regenesis ORC).

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DO (Dissolved Oxygen) and pH

"Adding oxygen to the soils to enhance bioremediation is a proven technology" (Doug Clay, 2001)

"For those systems requiring aerobic microbial processes, oxygen is generally the limiting factor for in-situ treatment" (John T. Cookson, 1995)

"Aquatic environments with low concentrations of dissolved oxygen have lower degradation potentials" (Eve Riser-Roberts, 1992)

At pH between 5 and 9, mineralization of hydrocarbons in groundwater is highly dependent on oxygen availability . The ultimate oxygen demand, coupled with the rate of degradation, establishes the rate at which oxygen must be delivered. Oxygen supply should be balanced with oxygen demand to optimize the cleanup time for bioremediation. Too low an oxygen supply rate relative to the contaminant load results in extended remediation times. Too high a rate of oxygen supply results in elevated remedial cost and potential for soil gas binding. The theoretical oxygen requirements to remediate one gram of gasoline are 2.5 grams of dissolved oxygen to reduce the contaminant and 4.0 grams of oxygen for complete mineralization to carbon dioxide and water.

Dissolved oxygen should be maintained above the critical concentration for the promotion of aerobic activity, which ranges from 0.2 to 2.0 mg/l, with the most common being 0.5 mg/l (EPA, 1985). For example , hydrocarbon degrading bacteria in well-oxygenated groundwater containing 4 mg/l of molecular oxygen can degrade only 2 mg/l benzene.

The dissolved oxygen level information collected during the short pilot study is used to confirm oxygen plume migration and shape that can be used in the final remedial design. The fact that the water is circulating and mixing will increase the efficiency that the oxygen is utilized.

Odor and color

As dissolved oxygen levels increases in groundwater, hydrocarbon degrading bacteria will release enzymes. These enzymes will aid in the breakdown of the hydrocarbon chains that contain the carbon which the bacteria use as a food source. The bacteria will begin dividing and increasing in number while releasing carbon dioxide and water. At the point the free swimming bacteria reach a colony count of 10,000,000 bacteria per cc, the water will become opaque and the color of the dominant bacteria..

The groundwater contains millions of varieties of bacteria, algae and fungus that can use the hydrocarbon as a food source. They all use dissolved oxygen just like the bacteria. As different breakdown products form, different odors will be evident to the nose. An example would be when amines break down, the human nose will pick up a fish smell. The most important odor at a petroleum site is gasoline smells. A rule of thumb that is spread by chemical engineers is that the human nose can detect better than 5 ppm volatiles in samples. As the oxygen levels increase in the groundwater, strong gasoline odors will become weathered and finally not existent.

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The water in the O2Tube well will have whirlpool type odor from the trace sodium hyper chlorite that's formed while salts pass through the electrolysis cell. In groundwater that has high salt content, like next to a road that's salted in the winter, a activated carbon sock can be placed in the cell just ahead of the electrolysis cell.

Temperature and Plate Count

The temperature range for optimal bacterial growth in groundwater has been found to range from 68 to 99 degrees F (EPA, 1985). According to the "Q-10" rule, for every 10 F decrease in temperature in a specific system, enzyme activity is halved (Riser-Roberts, 1992).

The plate count is a value for the number of bacteria per cc of groundwater.

9 Month Full Scale Demonstration

The demonstration began on March 16, 2004 after samples from each well were tested for BTEX, DO, and ORP. The O2Tube systems were turned on and the airflow to each well was balanced. The Sullivan Pilot study startup was attended by representatives of Sullivan Park District, Illinois EPA, United Science Industries and O2Tube Technology. The remaining discussion of the work completed will be separated into the *beginning (Mar. 16 to May 22), middle (May 22 to Sept. 7), end (Sept. 7 to Dec. 28)*

Beginning (Mar. 16 to May 22 **)**

The O2Tube cells during this period are establishing a vertical recirculation around each well. The water movement around each well is maintained by constantly moving groundwater through the O2Tube cell and up the well where it mounds and flows out horizontally. This constant movement creates a recirculation that resembles an inverted bowl. The flow pattern at Sullivan was established in approximately 30 days given the stabilization of DO and ORP levels.

The DO stabilized at 3.23 PPM during this period with the ORP averaging 225 mV. The groundwater levels were fairly stable with the total BTEX (MW-10 is not included in the average because the it is between the still contaminated source and the treatment area) of 51,738 PPB.

Middle (May 22 to Sept. 7)

The O2Tube cells vertical recirculation around each well is established with DO being distributed throughout the site to accelerate bioremediation of the contaminants.

The average DO has increased from 3.23 PPM to 4.72 PPM during this period with the average ORP increasing from 225 mV to 258 mV. The groundwater levels increased by almost one foot due to heavy rain with the total BTEX (MW-10 is not included in the average because the it is between the still contaminated source and the treatment area) decreasing from 51,738 PPB to 17,006 PPB..

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<u>End</u> *(Sept. 7 to Dec. 28)*

The average DO has increased from 4.72 PPM to 5.86 PPM during this period with the average ORP increasing from 258 mV to 468 mV. The groundwater levels decreased by almost one foot due to little rain/snow with the total BTEX (MW-10 is not included in the average because the it is between the still contaminated source and the treatment area) decreasing from 17,006 PPB to 2972 PPB.

Discussion of Results and Conclusions

Over the nine months that the O2Tube Systems was operated:

- Total BTEX reduced from 51,738 PPB to 2472 PPB - 95 % Reduction
- Total Benzene reduced from 24,212 PPB to 1690 - 93% Reduction
- Average DO increased from 3.2 PPM to 5.86 PPM at distances of 30 feet from well
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The patented O2Tube cells successfully recirculated the groundwater in the low flow Illinois silty clay (1 x 10 -5 cm/s) while distributing dissolved oxygen which is generated from the groundwater via electrolysis.

The O2Tube cells slightly raise the pH of the surrounding groundwater by ½ to 1 pH unit, which is ideal for bioremediation as opposed to injection of chemicals like Regenesis ORC® which increase the pH to levels in excess of 9.5 which is toxic to bacteria.

The nitrate and nitrite nutrients were exhausted during the study, which was a first for the Illinois EPA. It appears that Illinois clay contains nutrients deep within its soil matrix that usually dissolve very slow because of poor water movement through the clays pores and are usually not a factor in bioremediation of groundwater until the O2Tube cell came along. Since the O2Tube pump creates a vertical recirculation around the well through the clays pores, deep embedded nitrogen is more available for use by the bacteria which accelerates the remediation process and may require additional nutrients be added which is simple with the O2Tube system. The electrolytic plates are turned off before water based nutrients are added to the wells that contain the O2Tube cells. The system is recirculated for three days before the electrolytic cells are turned back on. The ability to recirculate nutrients and amendments is unique to the O2Tube systems patented recirculation and oxygenation process.

The final point in regards to this demonstration is that after nine months, the O2Tube treated site is biologically optimized and to further reduce the contamination level, just let the system keep operating. With chemical injection of Regenesis ORC® or similar products, if the contaminant level needs to be further reduced, another costly injection is required which will raise the pH and kill active bacteria.