ORC TECHNICAL BULLETIN #2.2.3.1

Oxygen Release Compound, ORC®

Potential for the Bioremediation of Methyl Tertiary Butyl Ether (MTBE)

The Problem:

The gasoline oxygenate, methyl tertiary butyl ether (MTBE), presents a serious complication in the remediation and closure of properties contaminated with fuel hydrocarbons. Several factors contribute to this complexity:

1. MTBE degrades very slowly under aerobic conditions.
2. MTBE is not recognized as an anaerobically degradable compound.
3. Unlike BTEX, MTBE is highly soluble and does not retard on the aquifer matrix. The compound in therefore capable of rapid and pervasive dispersion in groundwater.
4. The toxicity and carcinogenicity of MTBE have not been established.
5. Taste and odor thesholds for MTBE are very low.
6. Although MTBE is extremely volatile, when dissolved in water it is difficult to strip which complicates sparging and pumping options. In the latter case pumped water may have to be treated in bioreactors.

Just when a coherent and manageable protocol for BTEX remediation is being formed by consultants and regulators (Risk Based Corrective Action - RBCA), the MTBE "wild card" has threatened to change the tenor of the issue. In the words of one national clean-up manager for a major oil company, "We have come so far in managing thousands of our sites and now I feel like I'm back to square one with the MTBE problem."

A Solution in Development - ORC Enhanced Bioremediation

About a year ago, Regenesis began to notice that in wells containing ORC socks MTBE was disappearing at an unusually high rate. Data was sparse as MTBE was rarely measured and reported, however, an intriguing trend was emerging. In some cases the removal rates for MTBE, presumed to be a function of biological degradation, were extremely high. The literature reports aerobic degradation rate constants in a range of .0231 to .0038 (half-life of 30 to 182 days). In the Regenesis data from 11 wells across three diverse oil company sites (CA, MI and NJ), degradation rate constants were in a range of .1447 to .0112 (half-life of 5 to 61 days). The question then became - "What is the role of ORC in this process?"

Figures 1 to 3 present examples of BTEX and MTBE degradation in a single representative well for each of the three sites referenced above. Each example also reflects a low, moderate and high background level of BTEX. We believe that the presence of background hydrocarbons can interfere with the metabolism of MTBE by competent microorganisms. Thus, the documented impact of ORC on BTEX is an important factor in MTBE bioremediation.

This important hypothesis evolved as a result of sharing the data with other researchers in the field. Regenesis has since gathered evidence that supports the concept that in a mixed contaminant system BTEX is consumed preferentially to MTBE. This is not a competitive inhibition—in that different enzyme systems are responsible for the metabolism of each compound—but rather is a pattern of preferential consumption (BTEX> MTBE). It can be clearly seen in Figures 2 and 3 that there is a lag in degradation of MTBE relative to BTEX. In Figure 1, where BTEX is almost non-existent, MTBE is readily degraded from the outset.

Follow-up laboratory experiments further clarified the issue. Using microbial isolates that use MTBE as a sole carbon source, Regenesis has shown the metabolism of MTBE can be largely inhibited by the addition of BTEX - causing it to fall behind in the preferential sequence of degradation. Furthermore, MTBE metabolism can be predictably modulated by the BTEX, such that when BTEX is removed from the culture MTBE degradation resumes.

Regenesis is now in the process of funding more involved column bioreactor studies which will elucidate the inhibition of MTBE by background hydrocarbons. More importantly, this work will establish a mass balance for the process and identify other important co-factors that may be operating in the system. The first experiments will correlate an increase in CO_2 with a decrease in MTBE to establish that bioremediation is the primary mechanism of removal. Subsequent experiments will employ radioactively labeled MTBE and follow the appearance of various intermediates.

Figure 1

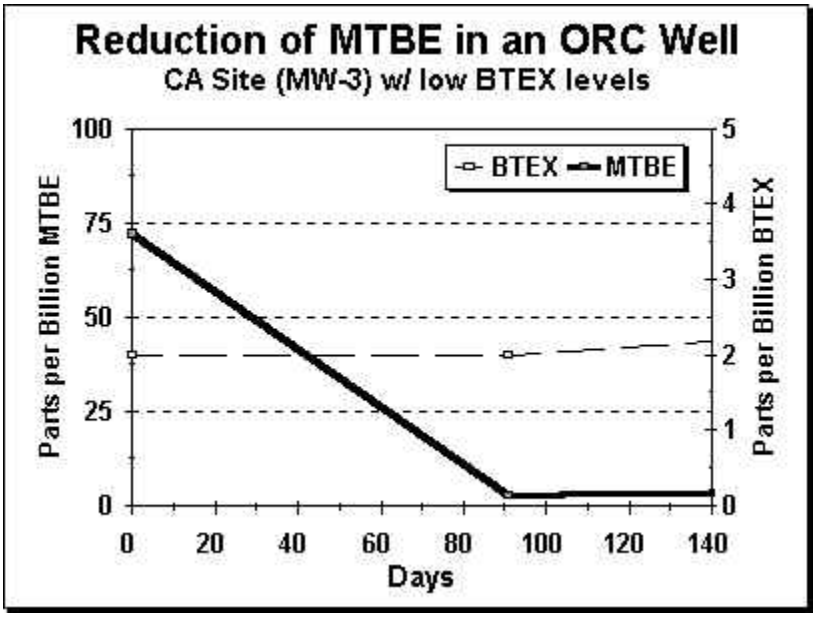


Figure 2

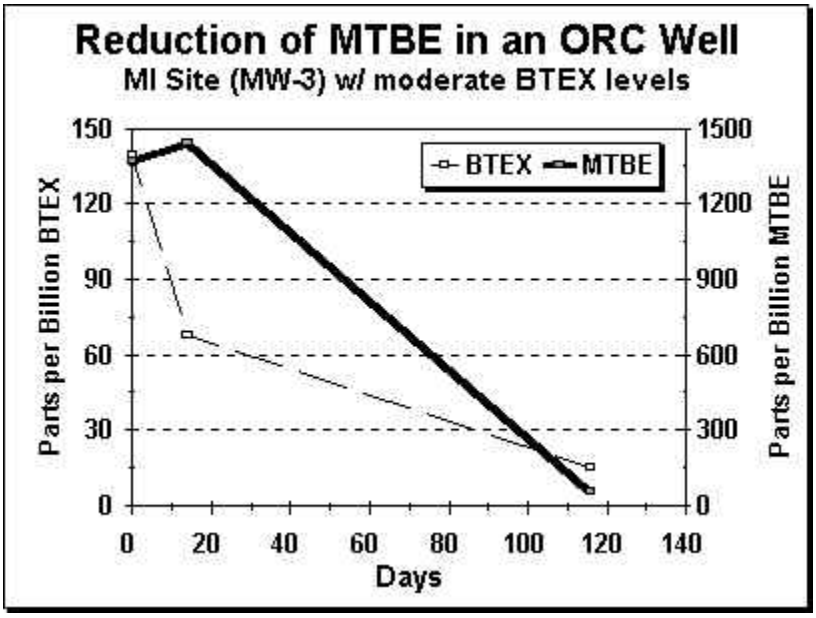
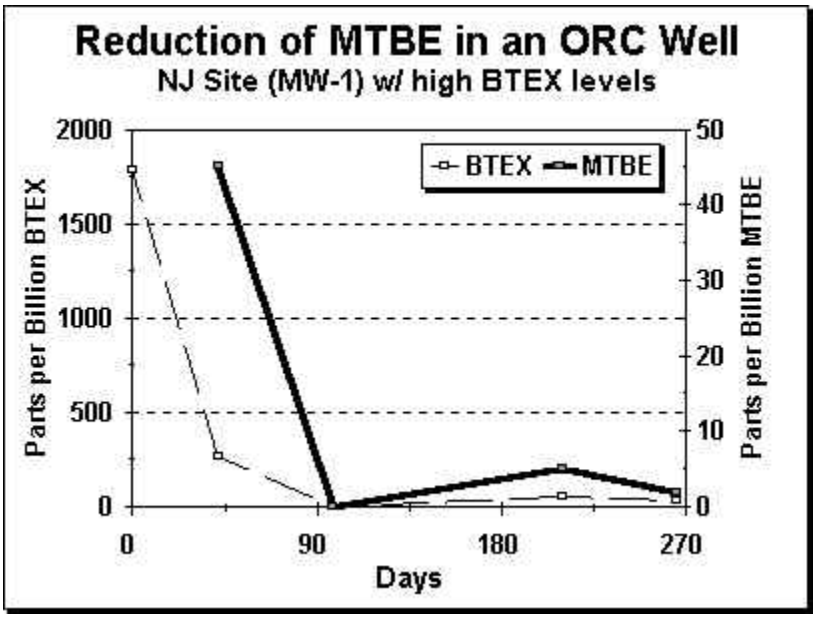


Figure 3



In addition to the commercial features of the project, establishing the relationship between ORC and MTBE bioremediation, the isotope study will also be fundamental to the basic science of MTBE degradation pathways as very little is known about the subject at this time.

Another possible explanation for the higher degradation rates is that MTBE degrading microorganisms, normally slow to metabolize the substrate, do so at greater efficiency in higher oxygen concentrations. This theory will also be tested in the bioreactor experiments. There are examples in the literature, specifically with PCP degrading fungi, that establish a relationship between high oxygen concentrations and high rates of degradation. This is important because ORC, as a pure oxygen source, is capable of generating dissolved oxygen levels in excess of those achieved by air saturation.

Encouraging results were obtained from a recent data set showing MTBE degradation outside an area that was source treated with ORC slurry injections. In Wisconsin, after about four months, the degradation rate in a well five feet downgradient of the treated area was .0434 (half-life of 25 days). This is presented in Figure 4. Note that these are not measurements from a well with ORC socks; the well is downgradient from an ORC source injection zone and was exposed to oxygenated groundwater derived from the injection array.

Earlier we stated that the biological degradation mechanisms were putative. Several other abiotic explanations must be considered and systematically eliminated; the following dialogue is intended to anticipate the appropriate questions.

Q. Is MTBE being absorbed by ORC? Does ORC chemically destroy MTBE?

A. No. Experiments in the laboratory have shown that there is no chemical or physical reaction between ORC and MTBE. This eliminates the possibility that any type of absorption by ORC or direct chemical oxidation is occurring.

ORC particles are insoluble and, when applied in filter socks, will not migrate from the application well. Groundwater samples were collected by standard purge methods (three to five casing volumes). Any chemical reactions occurring on the surface of ORC particles in the source well would therefore be diluted out, particularly on the sites in question which have low ground water velocity.

Furthermore, the new data show positive results at a distance from the ORC source wells. The fact that oxygen is slowly diffusing from ORC, which in turn is stimulating bioremediation of MTBE and competing species such as BTEX, remains the most the likely mechanism of action.

Q. Is the MTBE being volatilized from the well?

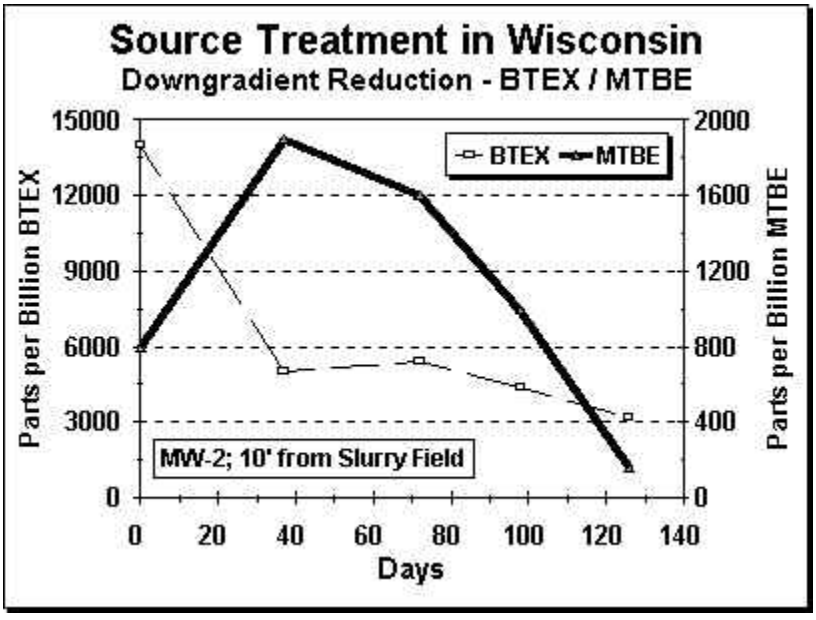
A. This is highly unlikely, although experiments are being planned to account for this. For the moment, one must realize that MTBE does not readily strip and that the release of oxygen from ORC is not forceful like air sparging. If MTBE were being stripped from a well volume, that stripped groundwater would experience the previously mentioned dilution in sampling. In addition, the results in Figure 4, which were derived from a downgradient monitoring point, provide good initial evidence that that MTBE is not being stripped.

Q. Is the MTBE moving through the well zone over time and only appear to be degrading?

A. The fact we have seen the same pattern in multiple wells makes this explanation unlikely. Also, if the rates of MTBE degradation were as dramatic as illustrated in Figures 1-4, then MTBE plumes would become infinitely diluted in short period of time which obviously is not the case.

In conclusion, it appears that MTBE is biodegradable and the application of ORC may be an approach to enhance the bioremediation of MTBE. Given the fact that an MTBE plume will move farther downgradient than the more highly retarded BTEX components, barriers of different configurations are likely required. A tight series of direct push injections to form an ORC "slurry wall," in combination with the use of MTBE degrading microorganisms, will soon be the subject of an investigation by a major oil company. Oxygen barriers using ORC filter socks in wells are also a reasonable approach to cutting off the leading edge of an MTBE plume. Otherwise, standard direct push injections in the core of the plume will address the problem at the source.

Figure 4



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