

ENHANCED AEROBIC BIOREMEDIATION OF PETROLEUM UST RELEASES IN PUERTO RICO

Baxter E. Duffy, Inland Pollution Services, Inc., Elizabeth New Jersey
Gil Oudijk, Triassic Technology, Inc., Princeton, New Jersey
John H. Guy, Inland Pollution Services PR, Inc., Bayamón, Puerto Rico

Abstract: Releases of petroleum compounds from underground storage tanks (USTs) containing diesel fuel and gasoline are a serious and increasingly prevalent problem in Puerto Rico. Remediation of groundwater impacted by these releases utilizing common methodologies can be quite costly and require long periods of time to implement. Oxygen is often the limiting factor retarding optimal biodegradation of petroleum compounds in groundwater. The delivery of dissolved oxygen to impacted groundwater zones will enhance the biodegradation of dissolved phase benzene, toluene, ethyl benzene and xylene (BTEX) and total petroleum hydrocarbon (TPH) compounds by microorganisms which occur naturally in the subsurface. Oxygen Release Compound (ORC[®]) is an efficient and effective method of supplying dissolved oxygen directly to the impacted groundwater. In a pilot scale study, ORC was delivered to subsurface groundwater bearing zones of a gasoline service station in Puerto Rico by slurry injection with direct push equipment and by ORC socks. Concentrations of BTEX and TPH were found to decrease inversely to the increase in dissolved oxygen. Concentrations of BTEX were reduced by 89 to 90% and TPH concentrations were reduced by 75 to 96% within eight weeks of installing ORC into the subsurface water bearing zones.

INTRODUCTION:

BTEX and TPH contamination in groundwater caused by leaking USTs is a significant problem in Puerto Rico. The objective of this pilot study is to demonstrate the effectiveness of the use of ORC in increasing dissolved oxygen levels in groundwater thereby enhancing the natural biodegradation of BTEX compounds and petroleum hydrocarbon contaminants. The goal is to accomplish the introduction of ORC and effect the enhancement of natural biodegradation in a passive manner without altering groundwater flow or the installation of mechanical equipment.

Site Description. The site selected for the implementation of the pilot study is a Texaco Puerto Rico, Inc., Texaco Service Station, located in Toa Baja, Puerto Rico. There are three active underground storage tanks (USTs) at the operating service station. These USTs include two twelve thousand gallon capacity gasoline and one ten thousand gallon capacity diesel fuel tanks. USTs previously in service at this location were confirmed to have discharged gasoline and diesel fuel at the site.

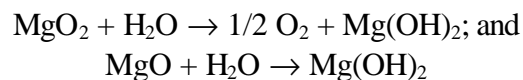
The site is primarily flat and level lying at approximately 33 feet above Mean Sea Level. There are no drainage features within the boundary of the site. The site lies on alluvial deposits of Pleistocene age consisting primarily of silt and clay with some sand

and gravel within the Rio Plata River's alluvial valley. During site activities, groundwater was observed to fluctuate from as shallow as 9.05' to 16.32'. The average groundwater level was 12.77'.

MATERIALS AND METHODS:

Two pilot scale test plots were established at the site. ORC was installed in an existing monitoring well utilizing ORC socks and in an "Oxygen Barrier" array at a second existing well location. At the location of existing well MW-1, a 2" diameter well 20' in total depth with 15' of screened interval, was fitted with seven, 2" diameter ORC Socks. A 1" diameter well point was installed down gradient from MW-1. At the location of existing well MW-4 a passive barrier of ORC was installed as a slurry by direct push techniques. A 1" diameter well point was installed between MW-4 and the oxygen barrier.

ORC is a patented formulation of magnesium peroxide, MgO_2 , produced by REGENESIS Bioremediation Products, which when hydrated releases oxygen slowly. The hydrated product is magnesium hydroxide, $Mg(OH)_2$. The basic chemistry of ORC is as follows: ORC is magnesium peroxide, "oxygenated magnesia", which gives off oxygen upon contact with water (at 3% moisture content). The magnesium peroxide is converted into magnesium hydroxide, $(Mg(OH)_2)$ as oxygen is released. This is also the fate of the magnesium oxide, which hydrates to form the hydroxide. The reactions are:



Therefore, the uniform end point of ORC, from both compounds, is magnesium hydroxide.

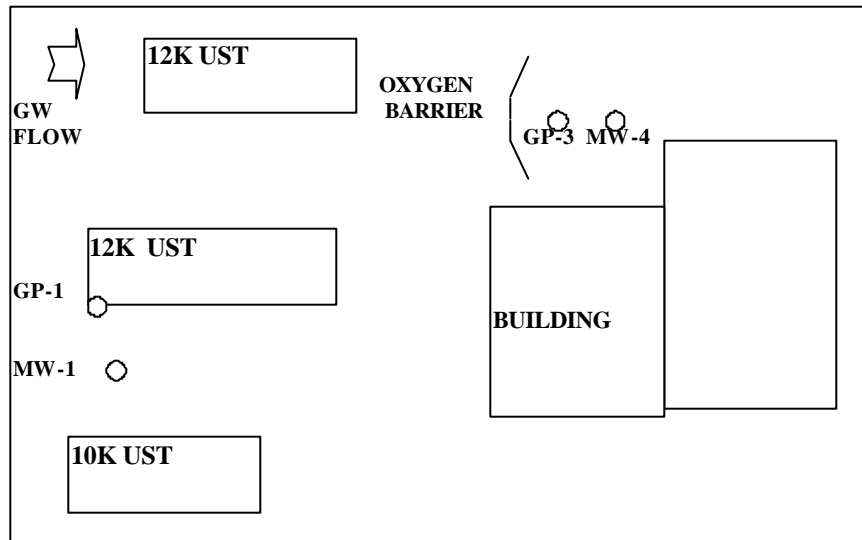
Existing Well ORC Sock Application. At MW-1, the existing 2" PVC monitor well was utilized and fitted with ORC socks. A monitoring point was installed approximately 3 feet from the well downgradient and designated as GP-1 (Figure 1). This monitoring point was constructed of 1" diameter schedule 40 PVC with .010" slotted screen installed in the aquifer to a depth of 16.3'.

Seven 2" socks were installed into the existing well MW-1. Each 2" sock is 12" in length and contains approximately 0.75 pounds of ORC. The total weight of ORC installed is approximately 5.25 pounds. Only those socks, which are suspended in water and hydrated, will provide dissolved oxygen to the subsurface.

Oxygen Barrier Installation. During the implementation of the ORC installation at MW-4, a series of five soil borings were installed to a depth of 19'. These borings lie along an arc aligned at an orientation as to surround the subject well from the source area at a distance of ten feet on center in relation to the well (Figure 1). These borings were designated as the oxygen barrier. ORC was injected into the borings as a slurry, composed of 150 pounds of ORC powder and approximately 42 gallons of potable

water divided evenly across the five boring locations. The slurry was pressure grouted into the borings from 14 to 19' below ground surface into groundwater utilizing direct push drilling equipment. A monitoring point was installed approximately 5 feet from the well between the well and the oxygen barrier and designated as GP-3 (Figure 1). This monitoring point was constructed of 1" diameter schedule 40 PVC with .010" slotted screen installed in the aquifer to a depth of 19'.

FIGURE 1. SITE PLAN



GROUNDWATER SAMPLING AND ANALYSIS:

In October of 1997, the study was initiated by collecting base line samples. Groundwater samples were collected from wells MW-1 and MW-4 along with GP-1 and GP-3. The reaction of BTEX, DO and CO₂ in groundwater at the monitoring point locations was monitored every two weeks and at the conclusion of the study (twelve weeks). TPH and pH were analyzed for at the base line sampling and final sampling events.

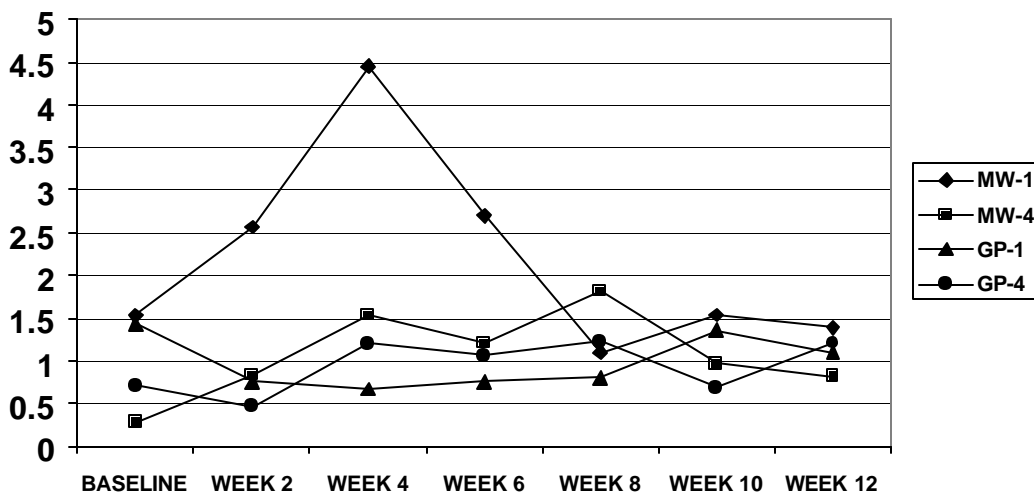
Groundwater grab samples were collected from the existing 2" monitor wells and 1" Geoprobe well points. Groundwater samples collected were analyzed for Total Petroleum Hydrocarbons (method 8015M), total BTEX (method 8020), DO (method 360.1), Alkalinity (method 310.2) (for CO₂), and pH (method 150.1).

The base line sampling was conducted in October of 1997. The six subsequent monitoring events were performed from November of 1997 to February of 1998 collecting samples every two weeks. The results for BTEX and DO are shown on Figures 2 and 3.

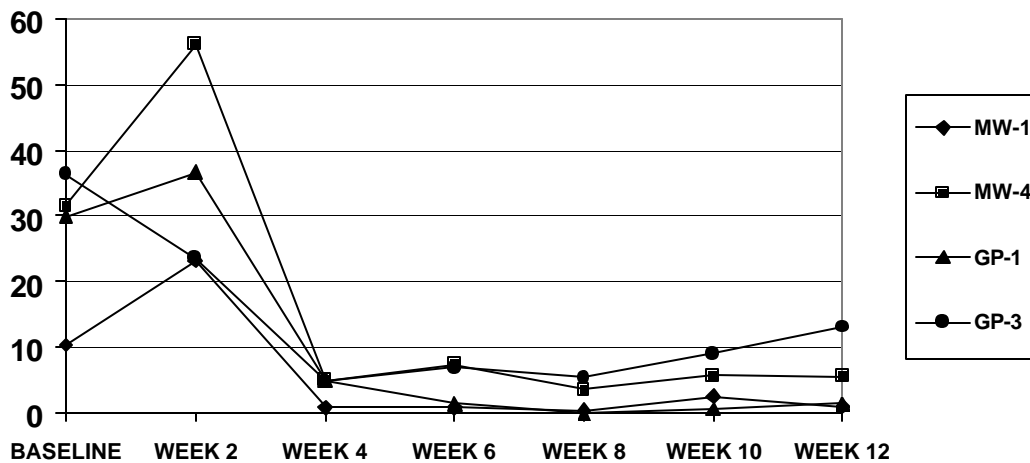
RESULTS AND OBSERVATIONS:

At MW-1, our base line sampling indicated concentrations of BTEX and TPH of 10.37 and 47.06 ppm respectively. No free phase product was observed in MW-1. At MW-4, At the location of existing well MW-4, base line sampling indicated concentrations of BTEX and TPH of 31.54 and 1,774.39 ppm respectively. No free phase product was observed in MW-4. On November 5, 1997, IPSI re-mobilized to the site to install the ORC in the test areas.

**FIGURE 2
DISSOLVED OXYGEN CONCENTRATIONS
(IN PPM)**



**FIGURE 3
BTEX CONCENTRATIONS (IN PPM)**



Benzene, Toluene, Ethyl Benzene and Total Xylenes. BTEX were tracked as the prime indicator at all monitoring points as this is commonly a wide spread contaminant on gas station sites and therefore easily observed. The results indicate a sharp rise in BTEX concentrations in the first monitoring event conducted two weeks following the installation of ORC. This trait has been observed by REGENESIS on many other sites and is attributed to biosurfactant production by the microbes caused by the sudden increase in the release of enzymes brought on by the proliferation of the native bacteria. The biosurfactant enzymes will act to desorb organics from the saturated soil matrix. If desorption rates are greater than the rate of biodegradation, an increase in dissolved BTEX concentrations will be observed. BTEX concentrations then decreased significantly in the following sampling event as the bioactivity increases. This response is exaggerated in the tropical environment by higher mean groundwater temperatures.

The BTEX concentrations continued to fall to the week eight sampling event. The dissolved oxygen levels also drop with the increased bacterial activity. At week ten, the levels begin to show a small rise in BTEX and dissolved oxygen indicating the beginning of the die off of the bacterial population stimulated by the addition of the ORC.

The overall reduction of BTEX compounds at MW-1 from base line sampling to week eight is 9.87 ppm from 10.37 to 0.5 ppm a reduction of 95%. The overall reduction of BTEX compounds at MW-4 from base line sampling to week eight is 27.93 ppm from 31.54 to 3.61 ppm a reduction of 89%.

Dissolved Oxygen. Dissolved oxygen is an important indicator of the effectiveness of the ORC itself as a source of dissolved oxygen, as well as the method of installation in terms of the dispersion of the ORC material. Dissolved oxygen was analyzed for and tracked throughout the study at all test locations and monitoring points. In the tropical environment, background DO levels are normally low as the solubility of oxygen in water decreases with higher temperatures. The results show the DO rising through weeks two and four from 1.53 to 4.45 ppm in MW-1 and 0.28 to 1.54 ppm in MW-4. The DO is then observed declining with the BTEX concentrations through week eight as the DO is consumed with the available BTEX (1.54 ppm at MW-1 and 0.97 ppm at MW-4). By week ten the DO begins to rise back near background concentrations with the die off of the bacteria population.

TPH, pH and CO₂. TPH compounds were analyzed as a base line indicator prior to the installation of ORC and at the close of the study to observe the effectiveness of ORC treatment on these compounds. The TPH concentrations responded to the increase in dissolved oxygen and resultant increase in microbial activity with decreasing concentrations. The concentrations of TPH dropped from 47.06 to 11.59 ppm at MW-1 from base line to week ten. A reduction of 75%. The concentrations of TPH dropped from 187.85 to 37.87 ppm at MW-4 from base line to week ten. A reduction of 80%. The concentrations of TPH dropped from 1,774.39 to 63.6 ppm at GP-3 from base line to week ten. A reduction of 96%.

pH was analyzed for as a base line indicator prior to the installation of ORC, at week four and at the close of the study to observe the impact of ORC treatment on pH values in the environment. The change in pH levels ranged from approximately 0.5 to 1.5 across the site during the study.

Carbon Dioxide (CO₂) is a by-product of microbial activity and is an indicator of the increase in such activity. As the microbial degradation increases, so should the concentrations of CO₂. To determine CO₂, Alkalinity in groundwater was analyzed for and tracked throughout the study at various test locations and monitoring points. These results were compared with concurrent pH results to calculate the CO₂ concentrations. Samples collected to determine CO₂ concentrations prior to installation of any ORC as a base line value was zero. All subsequent samples collected at two week intervals during the study and at the close of the study for CO₂ were zero. This is likely due to geochemical reactions, consuming CO₂ as it is generated. This indicates that the use of CO₂ as an indicator of biodegradation in tropical environments may not be reliable and, although costly, biological plate counts should be utilized in the future.

Conclusions: The sampling results show that as DO is supplied to the impacted zone by ORC, the BTEX compounds are first mobilized and then consumed by the proliferating naturally occurring bacteria. The levels of BTEX dropped by as much as 95% and TPH by 96% at test locations during the study.

As the ORC is hydrated, the DO rises above background concentrations and then fluctuates with the bacterial population. As the DO is exhausted, the bacterial population dies off and the BTEX levels rise again. The pH levels in groundwater rise as the ORC is hydrated. The overall increase in the pH level is between 0.5 and 1.5 across the study areas as expected. As the ORC is depleted, the pH levels begin to return to background levels immediately. The drop in pH levels occurs concurrently with the return of DO to near background levels and the rise in BTEX levels indicating that the amount of ORC provided in the pilot study has been exhausted. It is assumed that the lack of detection of CO₂ at any point of the study indicates a geochemical reaction may be masking any production of CO₂ at this site.

REFERENCES

Driscoll, F.G.. 1986. *Groundwater and Wells*. 2nd ed. Johnson Division, St. Paul, MN.

U.S. Geologic Survey. *Atlas of Ground-Water Resources in Puerto Rico and the U.S. Virgin Islands*. Water-Resources Investigations Report 94-4198.

Wilson, J.T. and M.J. Noonan. 1984. "Microbial Activity in Model Aquifer Systems." In G. Bitton and C.D. Gerba (Eds.), *Groundwater Pollution Microbiology*. John Wiley and Sons, NY, NY.