RegenOx™

Advanced Chemical Oxidation

Treatment of Petroleum Hydrocarbons: When to use RegenOx™ vs. ORC Advanced®

Introduction

The in-situ treatment of petroleum hydrocarbon contamination in soil and groundwater presents a unique set of conditions. This is due not only to the variability and complexities inherent in the subsurface environment, but also to the variable nature of the contaminants themselves. When one refers to contamination generally as "petroleum hydrocarbons," they are referring to a very broad range of chemicals including very short- to very long-chain alkanes, and single-ring, soluble aromatic structures to multiple-ring, less soluble polyaromatic structures. It is important to understand what specific range of hydrocarbons is to be the target of an in-situ treatment program and to select a remedy that best achieves the overall goal of the remediation.

Total Petroleum Hydrocarbons

The term "total petroleum hydrocarbons" or "TPH" does not describe a compound, but theoretically describes a group of chemicals. TPH is also an acronym used to describe a group of analytical methods used in the environmental industry to measure the entire suite of petroleum-derived compounds potentially available in one sample. Laboratories perform TPH analyses differently depending on their location, applicable regulatory requirements, sample type, and client preferences.

Unfortunately, TPH analyses often measure not only the petroleum-derived compounds present, but also natural background organic matter in the sample (containing organics such as organic acids). Sometimes a "silica gel cleanup" of the sample is performed prior to the analysis to minimize the effects of naturally occurring organic matter. Employing this technique results in a more accurate estimate of the petroleum-derived compounds. (A more detailed description of TPH analysis is presented in the Regenesis Technical Bulletin 10.0 TPH Analysis: Analytical Challenges and Recommendations)

Biodegradation: Use of ORC Advanced®

ORC Advanced® stimulates the in-situ aerobic biodegradation of petroleum hydrocarbons. This approach is a well-documented, robust treatment that efficiently degrades bio-available (soluble) contaminants dissolved in the groundwater and sorbed onto soil in contact with groundwater. The use of ORC Advanced on a complex mixture of hydrocarbons, as measured by TPH analysis, will degrade the more bio-available contaminants in contact with groundwater, leaving the more insoluble fractions behind after the oxygen release is complete. Serial applications of ORC Advanced at a site will continually degrade the more soluble fractions of contaminants, leaving less and less soluble fractions evident by the results of TPH analysis.

The use of ORC Advanced to stimulate the in-situ biodegradation of short- to moderate-chain alkane-type TPH-range contaminants (gasoline-diesel range) is a very sound approach when low to moderate concentrations of these contaminants are present in the groundwater, and when the sorbed mass of these contaminants (the source of the dissolve contaminants) is thought to be low. Where high concentrations of contaminants are sorbed to the subsurface soil (either because of the adsorptive capacities of the soil matrix or because the TPH contaminants are long-chained, slower-to-desorb compounds), the use of ORC Advanced may require too much time and expense to treat by biodegradation compared to other remedial alternatives.

Chemical Oxidation: Use of RegenOx

Chemical oxidation of gasoline or diesel fuel contamination using any oxidation reagent is a very complex phenomenon, resulting in a myriad of partial oxidation products and contaminant mass equilibrium shifts (from sorbed to dissolved phase). Certain species, such as the aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylenes [BTEX], polyaromatic hydrocarbons [PAHs]), are rapidly activated and oxidized partially, if not entirely. Conversely, alkanes are slower to activate and oxidize, leaving a greater proportion of partially oxidized alkanes present. As a result of oxidation and pH shifts, as well as changes in contaminant and soil matrix chemistry, a temporary increase in the soluble fractions may occur post-application.

From an analytical standpoint, if one were simply focusing on the benzene and toluene constituents within a gasoline spill in groundwater subjected to RegenOx treatment, one could expect to see a rapid degradation of the target constituents. RegenOx, in adequate supply, would activate and oxidize the more easily degraded benzene and toluene. A scan of the aromatic fractions by typical volatile organic compound (VOC) methods (e.g., USEPA Method 8260-GC/MS) usually shows a decrease in BTEX compounds.

If, instead, one were to measure the same treatment results using a TPH-type analysis of groundwater, a much different result could be obtained. The TPH-type analysis, instead of showing degradation of the dissolved benzene and toluene, could show an increase in the total dissolved mass of "total petroleum hydrocarbons." The increase in TPH would likely be due to partial oxidation of sorbed contaminants bound to the soil matrix that were transformed via RegenOx (or another chemical oxidant) to more soluble hydrocarbons in groundwater. This results in the increase in soluble compounds measured by the TPH-type analysis.

For project sites where TPH-type analyses are to be used to measure remediation performance, some adjustments to customer expectations should be made. First, the customer should be made aware of the vagaries of typical TPH analyses and how they are impacted by RegenOx chemistry. Second, because RegenOx (or any chemical oxidant) is best used to reduce sorbed or soil-matrix-bound contaminant mass, soil samples should be analyzed as well as groundwater. By employing RegenOx, the sorbed contamination is oxidized (for some constituents more than others) and drawn into the dissolved phase by increasing the solubility. Once in the soluble, more-bio-available state, the partially oxidized contaminants are readily biodegraded given adequate remaining oxygen from the RegenOx application and/or from a subsequent ORC-Advanced application. This will take time, possibly months, depending on site conditions. Therefore, monitoring both soil and groundwater for several months after RegenOx treatment may be required to accurately assess treatment performance.

Product Recommendation

When treating petroleum hydrocarbons in groundwater, each site has specific conditions and project goals. There are no hard-and-fast rules for when to use RegenOx™ and when to use ORC-Advanced™ for these sites. However, based on sound science and project experience, Regenesis has developed the following recommendations for the use of its products for petroleum hydrocarbon remediation.

Recommended Product Selection
Based on Groundwater Contaminant Concentrations (mg/L)

	ORC Advanced	RegenOx and ORCAdvanced
BTEX (C6-C12)	≤20	>20
TPH-low (<C12)	≤20	>20
TPH-high (>C20)	≤10	>10
PAH (>C10; e.g., phenanthrene, etc.)	≤1	>1

For more information on RegenOx or a free application design and cost estimate contact Regenesis at 949-366-8000 or visit www.regenesis.com.