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Abstract:

BTEX is a chemical contaminate found in gasoline. The chemical is a common pollutant found at underground storage tank sites. Due to health concerns caused by high solubility of the compound much effort and energy has gone into developing methods of treating contaminated sites. Several technologies have been studied and tested these include in situ aerobic bioremediation, in situ anaerobic bioremediation, in situ chemical oxidation and ex situ bioremediation. Each technology has its own advantages and disadvantages. This paper will look at some of the technologies and how they are being used to treat sites contaminated with BTEX. This paper will also examine the advantages and disadvantages of each technology.

Keywords:

BTEX, enhanced aerobic bioremediation, enhanced anaerobic bioremediation, chemical oxidation, Adsorption

Introduction:

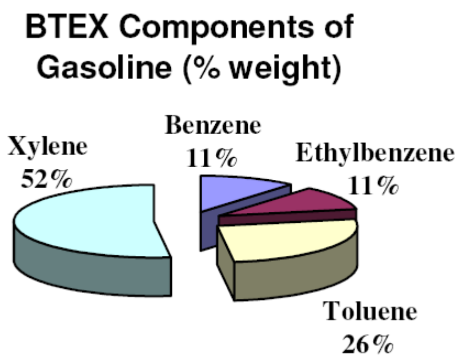
BTEX is the acronym for benzene, toluene, ethylbenzene and xylene. These compounds are volatile organic compounds found in petroleum products such as gasoline and other hydrocarbons. Benzene is used in the production of many synthetic products some examples of these are plastic, rubber, nylon and synthetic paints. Toluene is a solvent used on paint and oils. Ethylbenzene is a fuel additive, it is also used in the production of styrene which is a plastic. Xylene is a solvent used in the printing, leather and rubber production industries. There are many sites across the USA contaminated with BTEX, the majority of these sites are old petroleum production and underground storage sites. The major concerns for BTEX are ground water and soil contamination. There are many different methods of treating contaminated sites. There is in-situ, where the contaminated material is left where it is and treated at that location and ex-situ methods, where the material is moved to another treatment location. Chemical oxidation is where chemicals are used to convert contaminates to less harmful products. Free product recovery, a physical treatment where contaminates that are lighter than water are pumped out of the ground and treated or disposed of. Aerobic and anaerobic treatments can both be used, aerobic requires the presence of oxygen anaerobic is without oxygen.

Health risks:

BTEX exposure can result from ingestion, inhalation and skin adsorption. Known long term health problems associated with BTEX are respiratory disease, kidney, liver and blood problems. BTEX is also known to cause sensory irrigation and central nervous system depression. Benzene is a known human carcinogen. The majority of people showing signs of illness caused by BTEX were exposed in an occupational setting. Occupational workers that were exposed to BTEX had higher incidences of leukemia. (NIEHS) The maximum contaminant level (MCL) for benzene is 5 parts per billion for drinking water.

Properties:

BTEX is a volatile organic compound that is soluble in water. Gasoline that contains BTEX has a water solubility of 100-200 mg/L. Benzene has a water solubility of 1780 mg/L. (*Zogorski et al., 1997)* Because of the high solubility of BTEX, cleaning contaminated sites becomes more difficult since the free product can't simply be sucked up and pumped into a treatment system. Bioremediation is an option for treating contamination at the site of contamination. Many contaminated sites have large plumes that have migrated over time. Because of this it is often too expensive to use ex situ methods of treatment.

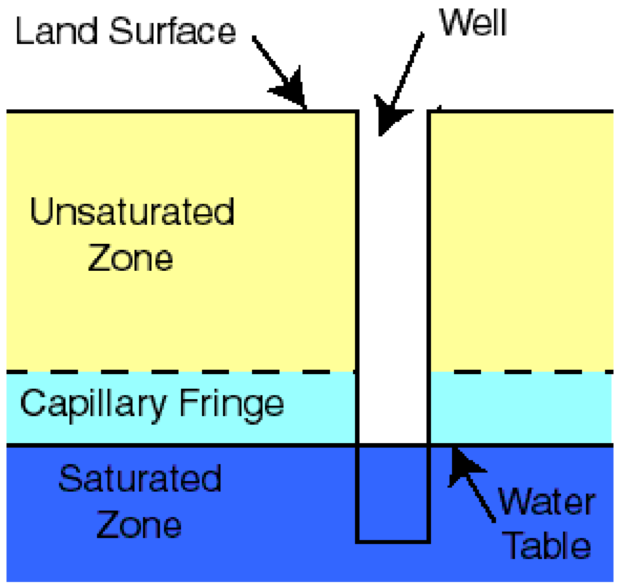


There are many methods of treating contaminated sites. Most sites use a combination of method to reach a satisfactory level. Any time there is a large plume that contains BTEX it is likely that several methods will be needed to clean the site. If free product is present it will need to be removed first. After the free product is removed the aerobic and anaerobic processes technologies can then be applied to remove the remaining dissolved contaminates. Site conditions will also play a large role in determining which technologies are the best choices for any particular site. Soils that have low permeability are particularly difficult to remediate. However the contaminate plume for UST's in soils with low soil permeability will not migrate as fast, leaving contaminates relatively localized. These conditions must be taken into account when determining which methods of bioremediation to use.

Determining in-situ or ex-situ bioremediation will require a cost analysis. Ex situ bioremediation is capable of achieving better results however it is the more expensive of the two options. Ex situ methods include landfilling contaminated soils. The soil is excavated and transported to a landfill. The method can be very expensive for large sites. Excavation will not be able to effectively treat large contaminations plumes. Pump and treat methods are capable of striping voc's from contaminated water, this method requires a significant energy input. Pump and treat methods also have a larger capital investment because of the physical nature of the treatment processes. In order to capture contaminates that are lighter than water and depression cone must be created by constantly pumping ground water. The depression cone reverses the flow of the contaminate plume by drawing contaminates to the pumping well. From there contaminates that are lighter than water can be pumped out with a separate pump and the water can be treated. The Pump and treat method is an effective way to remove large amounts of free product.

Understanding the different zones of contamination is important so that the best methods of remediation can be selected. The main zones of contamination are the unsaturated zone the saturated zone and the capillary fringe. The unsaturated zone begins at the soil surface and extends to the edge of the capillary zone. In the unsaturated zone both water and air molecules can be found in the soil. (Heath 1983) The saturated zone is below the water table. This zone has only water between soil molecules. The capillary fringe is area above the water table where water seeps upward due to capillary action to fill the area between pores. The capillary fringe includes the tension saturated and unsaturated portions of the zone. The size of the capillary fringe depends on the size and shape of soil particles. If the soil particles are small and roughly the same shape then the capillary zone can extend several feet above the water table.

When the particles are large and irregular shape the capillary fringe might only extend a few inches above the water table. (Wikipedia)

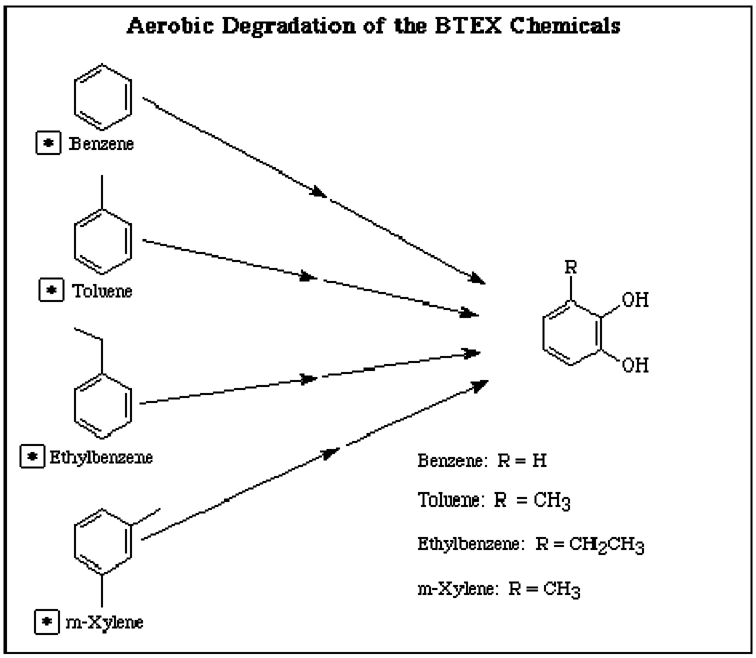


Enhanced aerobic bioremediation:

Enhanced Aerobic bioremediation is the process of increasing the amount of dissolved oxygen in the groundwater and subsurface soil to stimulate microorganism growth. In order for aerobic bioremediation to talk place there must be sufficient nutrients, energy in the form of carbon, BTEX, and terminal electron acceptors. There are naturally occurring microorganisms that can be found in the soil, these organisms will degrade hydrocarbons and BTEX over time by breaking the bonds of BTEX and metabolizing the carbon. The limiting factor for the naturally occurring microorganism is most often oxygen. (Duffy 2001) Occasionally nutrients are the limiting factor if this is the case nutrients will also be added. There are several different methods of applying enhanced aerobic bioremediation technology. These are bioventing, biosparging, pure oxygen, hydrogen peroxide and ozone injection. The goal of all of these methods is to increase the amount of oxygen in the environment. The microorganisms use the oxygen to convert the hydrocarbons and BTEX into carbon dioxide water and biomass, from cell growth. Generally bioremediation is used to treat areas that do not have any free product on top of the water table or heavily contaminated areas.

Bioventing is used to target contaminates in the unsaturated zone. (Bioventing EPA 1994) The unsaturated zone is the area between the contaminate plume and the soil. The purpose of bioventing is to add just enough oxygen to promote sufficient growth of biodegrading microorganisms. This is done either by injecting air from the atmosphere or by extracting soil air. The low airflow reduces the need for a SVE system. Bioventing does not work well with low permeable soil conditions because the micro organism will not receive enough oxygen. Bioventing is an inexpensive way to reduce contaminates in the unsaturated zone. Bioventing works well with other bioremediation techniques.

Biosparging is like bioventing it involves injecting oxygen into contaminated areas. The main difference is that biosparging is used to treat the saturated zone compared to bioventing that treats the unsaturated zone. The saturated zone is the area between the contaminate plume and the ground water or the interface. (Biosparging EPA 1994) If there are insufficient nutrients in the contaminated soil nutrients will be added to promote microorganism growth, added nutrients and added oxygen increase the number of biodegrading microorganisms in the water. If the desired level of efficiency is not being reached, introducing microorganisms that are known to be able to metabolize BTEX can be helpful. By introducing the microorganism you can kick start the bioremediation process. Often times the two methods are used simultaneously to treat the saturated and unsaturated zone.



Another method of increasing the oxygen in ground water is using permeable barrier treatment system. A permeable barrier experiment was done by a group scientist and explained for the EPA. (Borden et al 1996) This method involves drilling a series of ground water monitoring wells perpendicular to the flow of ground water. The wells consist of PVC pipes with filters at the bottom where the wells meet the ground water. The wells are then filled with a solid peroxide concrete sock; MgO_2, CaO_2 at different concentrations and in different forms were used in the experiment listed above. Several other concretes were tested but none of them had desirable The concrete socks are placed in the wells, when water flows past the wells the MgO_2 reacts with water releasing the oxygen into the water promoting microorganism growth. Microorganisms then can use that oxygen to break down organic compounds like BTEX. Sodium nitrate can be added to the concrete mix to improve the results. The main obstacle for this method of enhanced bioremediation is maintaining the condition of the monitoring wells, clogging is the main problem. When the wells become clogged water will not come in contact with the concrete inhibiting the chemical reactions. When this happens the chemical reaction that releases oxygen into the ground water will slow or stop, reducing efficiency. (Borden et al) This method of remediation alone isn't enough to reach desired reductions of BTEX, however due to its low cost it could be used with other technologies. This method is a relatively new technology and more research needs to be done to improve performance.

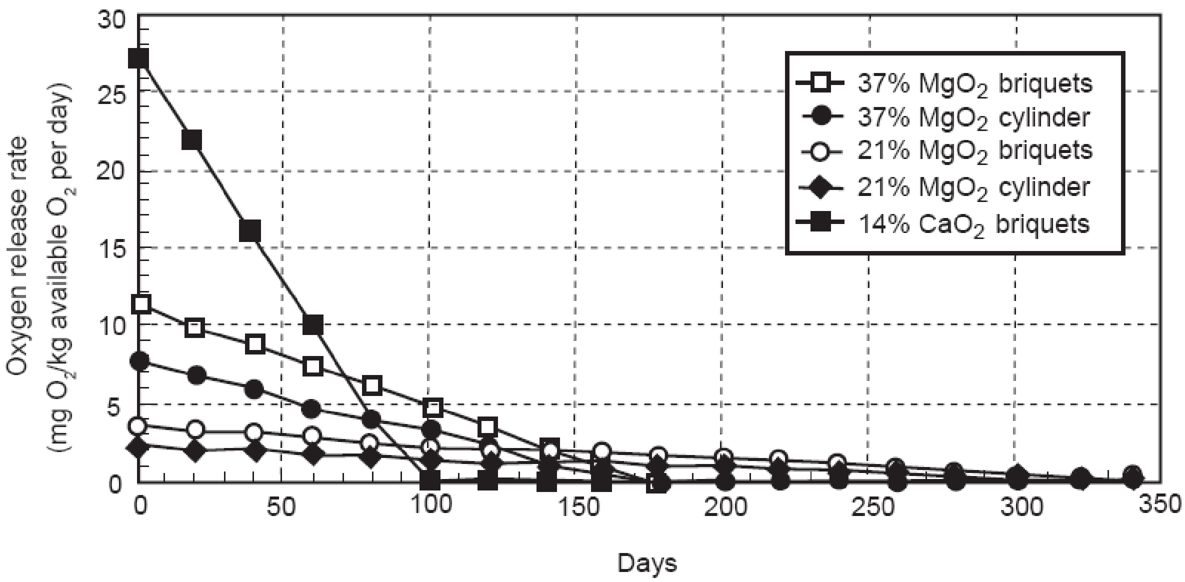


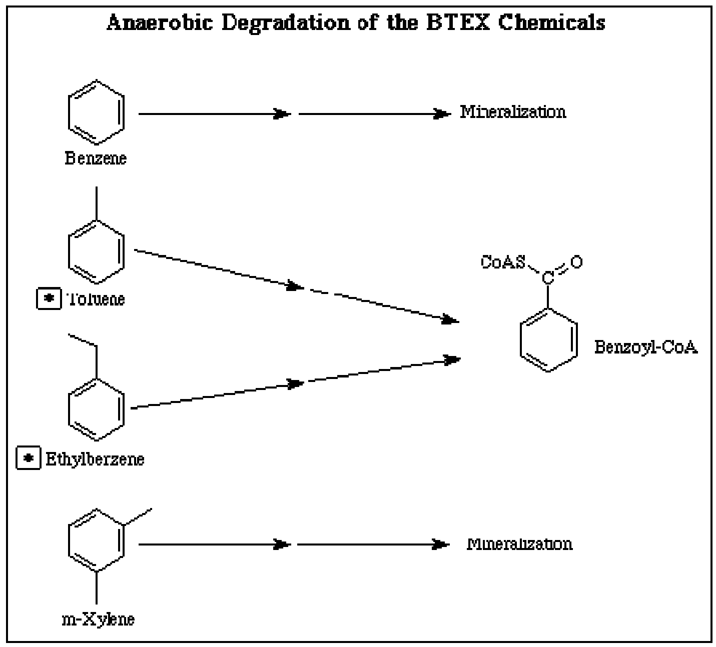
Figure 1. Best fit estimated lines showing variation in oxygen-release rates with time for magnesium peroxide and calcium peroxide concrete mixes.

Enhanced anaerobic bioremediation:

Enhanced anaerobic bioremediation is the process of removing contaminates in the absence of oxygen. Often times anaerobic condition are formed when contaminated ground water consumes its oxygen supply. Anaerobic bacteria will degrade BTEX by using enzymes that can overcome high activation energy. In an anaerobic process that biodegrades BTEX the contaminates are reduced as opposed to oxidized. (Heider 1997) In the absence of oxygen either Fe(III), nitrate or sulfate act as electron acceptors. (D R Lovely 1997). There are not many studies that have been able to quantify the effectiveness.

Initially at a contaminated site under anaerobic conditions the majority of BTEX mass loss occurred due to iron reducing conditions.(Botton 2006) Under anaerobic and iron reducing conditions benzene and toluene are degraded concurrently however no degradation of ethylbenzene and xylene was observed. (Botton 2006) After the iron has been depleted methanogenesis plays the more important role.

Experiments have been done to determine the effectiveness of nitrate as an electron acceptor. These tests were conducted under anaerobic conditions to determine if BTEX can be biodegraded using nitrate as an electron acceptor. When oxygen isn't available certain anaerobic bacteria are capable of using nitrate to stimulate growth and degrade organic compounds. (Schreiber 2002) In the experiment conducted by Schreiber and Bahr levels for toluene, ethylbenzene and xylene showed reduction in concentrations. Benzene was not biodegraded by the addition of nitrate. In the experiment the amount of nitrate added did not correlate to an equivalent drop in concentrations that would be expected based on stoichiometric calculations. The calculations and predictions for the amount of biodegradation that will occur do not match because simultaneous oxidation reduction reactions occurring in the soil at the same time. Other organics and being oxidized (Schreiber 2002)



Chemical Oxidation:

Chemical oxidation is a process of forcing oxidizing chemicals into contact with hydrocarbons, BTEX. The process can convert BTEX and other VOC's into carbon dioxide and water in a relatively short period of time.(Chemical Oxidation EPA 2004) The process is in-situ, injection wells are drilled and the chemicals are pumped into the wells or they can be injected at high pressures. The use of a soil vapor extraction system is often used as a concurrent treatment method. Soil vapor extraction applies a vacuum to wells in the contaminated zone. The vacuum has the capability to remove many volatile compounds in the soil. The SVE is important because when chemical oxidation is used there is a possibility of gases forming.

There are numerous chemicals used for chemical oxidation, the most common is hydrogen peroxide. (Huling 1990) Hydrogen peroxide will destroy hydrocarbons by providing contaminates with oxygen that will break the chemical bonds thereby degrading contaminates to less harmful products. Hydrogen peroxide is often used with a ferrous catalyst known as Fenton's reagent. With the addition of ferrous iron in the form of Fe^{2+} hydrogen peroxide will react with the iron to form ferric iron (fe^{3+}) hydroxyl radicals (OH) and hydroxyl ions (OH^-). The hydroxyl ion is a very strong oxidizing chemical that react with organic compounds. The hydroxyl radicals can break the bonds of hydrocarbons and rapidly break down the compounds into water and carbon dioxide.

Hydrogen peroxide will decompose into oxygen and water. This causes the dissolved oxygen in the water to rise to the solubility limit of water (9 mg/L). (Water chemistry Snoeyink, Jenkins) The increase in dissolved oxygen can enhance the growth of aerobic bacteria and improving aerobic bioremediation.

There are two methods used to inject hydrogen peroxide into contaminated plumes. Pressure injection, sparged air forces the chemicals into the injection wells. This method allows for rapid injection of large quantities of chemicals in a short time. The site conditions must be evaluated first to determine if this method can be used. The site should have high permeable soil conditions. Gravity injection relies of hydrogeolic conditions of the existing site. Smaller volumes of the chemicals are pumped into wells. The slower application allows for sites with lower permeable soils to be treated with this method.

There are limitations with chemical oxidation. Using hydrogen peroxide can be a very expensive treatment option. The cost of the chemicals can be high since thousands of gallons can be used at one site. Hydrogen peroxide must be monitored while it is being injected into the ground water. Many conditions must be monitored including temperature and pH. In order to use chemical oxidation an analysis of the soil conditions must be done. Soils with low permeability are not suitable for chemical oxidation because contaminates that are in the low permeable soils will not come in contact with the oxidizing chemical. In order for chemicals oxidation to work there must be sufficient contact between the chemicals and contaminates. The formation of secondary products that can be toxic must be monitored. The movement of VOC's into adjacent buildings must be monitored in order to ensure there are no spontaneous explosions. (XIII-7) This can happen in underground parking garages and in basements of buildings. An area of concern in these buildings is elevator shafts. This is because there is often low air circulation.

Adsorption:

Adsorption of BTEX is a relatively new technology that is being applied to industrial wastewater. (Lin 1999) The idea is that you can absorb BTEX with macroreticular resin, ambersorb 563, 572, and 600. In an experiment conducted by department of Chemical Engineering, Yuan Ze University the effectiveness of adsorption was studied. The properties of the ambersorp are as follows.

Table 1. Properties of the Ambersorb resins

Property	Ambersorb 563	Ambersorb 572	Ambersorb 600
BET surface area, m^2/g	580	1100	550
Microporosity (<40 A), ml/g	0.22	0.41	0.23
Mesoporosity (50–500 A), ml/g	0.17	0.19	0.14
Macroporosity (>500 A), ml/g	0.21	0.24	0.23
Particle size, mesh	20–40	20–50	20–50
Bulk density, g/ml	0.54	0.49	0.53

Samples of BTEX solutions were prepared and standardized to determine the exact equilibrium or adsorption capacity. Each of the different ambersorbs was tested and results for the reduction of each compound are shown (fig 2 and fig 3 below). The results below indicate that xylene and ethylbenzene can be completely absorbed in less than 400 minutes. Benzene and toluene require much more time to be completely absorbed. Benzene wasn't completely absorped after 600 minutes. The adsorption of BTEX can be done in either a batch or continuous reactor. (Lin 1999) Results were investigated theoretically and exponentially. The results were close indicating the adsorption can be an effective method for removal of BTEX and that it is possible to predict the amount of BTEX that will be removed.

This system does not work in situ. The process requires that the contaminated water be pumped from the ground and treated in the adsorption column. There will be energy input into the system to pump the water to the treatment equipment. There are also costs associated with the resin used as the adsorption material. It is best to use adsorption when there the concentration is so high that the contaminates act as inhibitors to biodegrading microorganisms. Another reason that adsorption is a popular method of removing BTEX from water is because it can be recovered. This is important because in many industries the BTEX can then be reused. When the BTEX is recovered costs are recovered for the industries that are using BTEX.

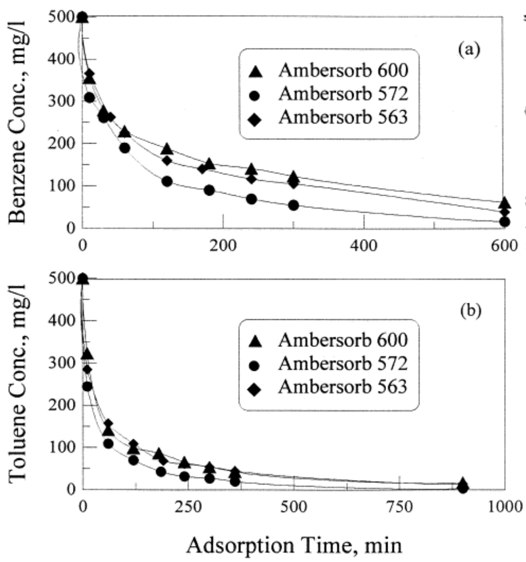


Fig. 2. Benzene (a) and toluene (b) adsorption by Ambersorb resins with 0.5 g adsorbent, 500 mg/l inlet concentration and at 30°C.

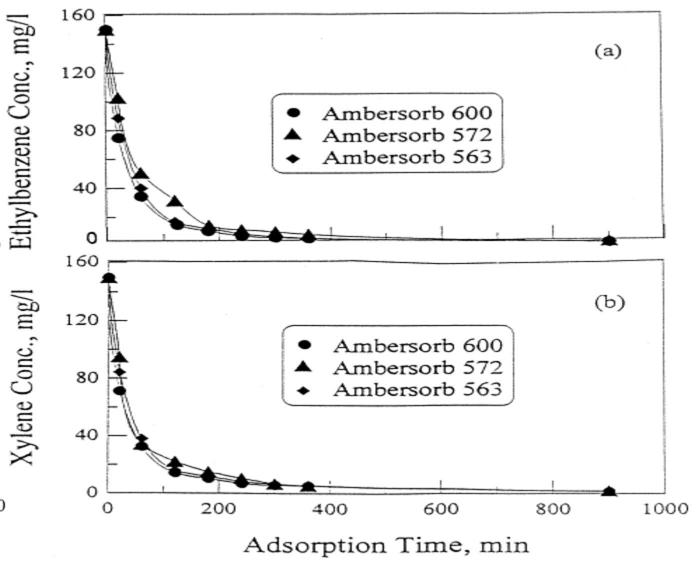


Fig. 3. Ethylbenzene (a) and xylene (b) adsorption by Ambersorb resins with 0.5 g adsorbent, 150 mg/l inlet concentration and at 30°C.

Conclusion:

There are numerous methods of removing BTEX from contaminated soil and ground water sites. These methods include enhanced aerobic bioremediation, enhanced anaerobic bioremediation, chemical oxidation and adsorption. Enhanced aerobic bioremediation includes bioventing, biosparging, SVE and permeable barrier systems. Each of these methods is used for all the different circumstances discussed above such as soil conditions concentration levels and locations of contaminates (saturated versus unsaturated zone). Enhanced anaerobic bioremediation requires the absence of oxygen. During anaerobic bioremediation iron, nitrate or sulfate can be used as electron acceptors. Under anaerobic conditions contaminates are reduced as opposed to oxidized. It is difficult to determine the effectiveness of anaerobic bioremediation because it is very difficult to accurately recreate natural anaerobic conditions. More research is needed to better understand the entire process. Chemical oxidation is where chemicals are introduced to contaminated sites. These chemicals can directly oxidize contaminates or they can break down into oxidizing chemicals. Usually the chemicals will break down releasing oxygen into oxygen deficient environments. A bonus of chemical oxidation is that excess oxygen will dissolve in the contaminated water promoting bioremediation. Adsorption is the process of removing contaminates by absorbing them.   macroreticular resin or granular carbon can be used. This process provides an opportunity for the contaminates to be recovered.

Each method for treating BTEX contaminated sites provides its own advantages and disadvantages. Site investigations that determine levels of concentration and soil conditions are important in determining which methods are best. Economics can also come into play. Ex situ methods can be very effective but will likely cost more. It is up to the engineer to determine which method or combination of methods can best cleanup the site while still being economically viable.

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