Remediation Techniques for BTEX Contamination of Groundwater- A Review

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Abstract—Groundwater contamination with BTEX compounds has become major concern because of their adverse effects on the environment and public health. Most common sources for BTEX-contamination of groundwater and soil are spills involving the release of petroleum products such as diesel fuel, gasoline and lubricating oil from leaking oil tanks. Serious risk of groundwater contamination is due to the high solubility of BTEX in water. Benzene is a known carcinogen. With the advent in the technology to remediate the contaminated sites many remedial techniques are developed. Recently developing remedial techniques for remediation of BTEX-contaminated groundwater are examined in this paper. It is observed from the review that bioremediation has become an emerging viable method because of its cost effectiveness, energy efficient, public acceptance and the ability to achieve the maximum possible destruction of organic contaminants.

Key words: BTEX (benzene, toluene, ethyl benzene and p-xylene); groundwater; bioremediation

1. INTRODUCTION

With growing population, industrialization and urbanization contaminated groundwater management has become an important and challenging environmental issue affecting the health of millions of people worldwide. Groundwater contamination with BTEX is increasing these days requiring an urgent development of methodologies that are able to minimize or remove the damages caused to the environment by these compounds.

Sources of BTEX: BTEX refers to the chemicals of benzene, toluene, ethyl benzene and xylene which occur naturally in crude oil and can be found in sea water in the vicinity of natural gas and petroleum deposits. BTEX compounds are created and used during the processing of petroleum products, adhesives, inks, cosmetics and pharmaceutical products. Leakage of gasoline from underground storage tanks causes groundwater contamination which is primarily due to the presence of BTEX. Because of their polarity and very soluble characteristics, the organic chemicals of petroleum products are able to enter the soil and groundwater systems and cause serious pollution problems. BTEX compounds are among the most abundantly produced chemicals in the world.

BTEX-Health Hazards:

- Benzene: Affects the nervous system, immune system and reproductive system and development. It causes aplastic anemia (damage to the bone marrow) and acute myelogenous leukemia.
- Toluene: Affects the nervous system, respiratory system, kidneys, reproductive system and development. It can cause unconsciousness and death.
- Ethyl benzene: Affects the nervous system, liver, kidneys, respiratory tract. It can cause eye irritation, irreversible damage to the inner ear and hearing. It may also be responsible for birth defects.
- Xylenes: Affects the nervous system, liver, kidneys, respiratory tract. It can cause eye, skin irritation, unconsciousness and death. It can also cause birth defects.

Kim et al. (2009) studied the health effects of exposure to BTEX in the Taean area in South Korea after the Hebei spirit spill and results showed the increased risk of health effects among pregnant women. There is an increasing demand in the development of more efficient contaminant minimization or removal methods. Main disadvantages of the conventional physical treatments are higher operational costs and removal of the contaminants from the environment without destroying or transforming them into harmless products and accumulating as toxic residues. Bioremediation which makes use of the biodegradation processes has become an emerging viable remediation technique because of its advantages of lower capital cost, in-situ operation, permanent elimination of contaminants and cost effectiveness (Shieh and Peralta, 2005).

II. REMEDIAL TECHNIQUES OF BTEX-CONTAMINATED GROUNDWATER

Due to the advent in technology many remedial techniques in removing the BTEX from contaminated groundwater are developed. Most popular BTEX removal methods are bioremediation, advanced oxidation technologies, phytocatalysis, sonolysis and radiolysis. Among these, bioremediation has received more attention due to its generally nontoxic attributes in comparison with others (Yen
et al 2010). In the present study certain efficient methods of BTEX removal are analyzed.

A. AIR SPARGING

Air sparging, a physical remediation technique, involves injecting a gas (usually air/oxygen) under pressure into the saturated zone to volatilize groundwater contaminants and to promote biodegradation in saturated and unsaturated soils by increasing subsurface oxygen concentrations (GWRTAC, 1996). Contaminants that are dissolved in groundwater are volatilized by the oxygen injected below the water table, existing as a separate aqueous phase and sorbed onto saturated soil particles. Volatilized contaminants are migrated upward into the vadose zone and are removed generally by using vapor extraction techniques. Air sparging reportedly can be more effective than pump-and-treat methods since “contaminants desorb more readily into the gas phase than into groundwater” and since increased volatilization can overcome the diffusion-limited extraction of VOCs from groundwater (GWRTAC, 1996). From the past 15 years air sparging has been used to address a broad range of volatile and semi volatile soil and groundwater contaminants including gasoline, associated BTEX components and chlorinated solvents. Figure 1 depicts the process of air sparging.

Johnston et al. (1998) examined the BTEX contaminated site at Kwinana in Western Australia to quantify the relative distributions of volatilization and biodegradation by employing the method of air sparging. Volatilization was found to be the dominant mechanism of dissolved organics by air sparging. Henry’s law of constant hierarchy was followed by the loss of particular compounds from groundwater. From the results it was found that rate of removal of dissolved organics was very rapid (removed within 3 days of the start of sparging). Presence of residual entrapped air in the aquifer and bulk movement of groundwater was found to be the source of uncertainty for biodegradation.

B. BIOREMEDIATION

Natural microbiological processes cause degradation and known quite far back in wastewater treatment (Baker and Herson, 1994). The new phenomenon is the application of this technology to in situ groundwater contaminants. In-situ bioremediation refers to the use of natural microbiological processes occurring in the subsurface environment to breakdown complex compounds into simpler, non-toxic compounds namely carbon dioxide and water without removal of aquifer material. Microorganisms (yeast, fungi and bacteria) just like humans eat and digest organics to acquire nutrients and energy. In chemical terms, organic compounds are those that contain carbon and hydrogen atoms. In-situ bioremediation offers attractive economics for remediation because it precludes the need for excavation and disposal costs. To enhance the bioremediation process, generally oxygen and other chemicals which activate the biological growth are injected into the contaminated site (Bedient et al, 1999). However the success of the system in removing the contaminants like petroleum hydrocarbons is directly related to the efficiency with which the electron acceptors and nutrients are delivered to the contaminated aquifer.

**Engineered In-situ Bioremediation:** This technique generally requires a mechanism for stimulating and maintaining the activity of micro-organisms which is usually a delivery system for providing one or more of the following: (a) an electron acceptor (oxygen, nitrate); (b) nutrients (nitrogen, phosphorus, calcium, magnesium, potassium, iron etc.); and (c) an energy source (carbon). In general electron acceptors and nutrients are the two most critical components of any delivery system. The process where the nutrients are injected through the injection wells is illustrated in Figure 2. This helps in enhancing the processes of remediation and the groundwater is extracted through the extraction wells. The monitoring wells examines the quality of extracted water which helps in assessing the contaminant removal efficiency.

![Air sparging with soil vapor extraction process](http://followgreenliving.com/cleaning-planet-bioremediation/)

![Process of Engineered In-Situ Bioremediation](http://followgreenliving.com/cleaning-planet-bioremediation/)
Shieh and Peralta (2005) developed a simulation-optimization (SO) model combining optimization which used a new hybrid method of Genetic Algorithm (GA) and Simulated Annealing (SA) with BIOPLUME III for optimizing in-situ bioremediation system design of hypothetical BTEX-contaminated site. The proposed design goal of minimizing the total system cost and time varying pumping strategy cost was achieved. The results showed that parallel recombinative simulated annealing performed better than simulated annealing and genetic algorithm for optimizing system design when installation cost is included.

Prasad and Mathur (2006) developed a methodology to optimize pumping rates in in-situ bioremediation system design of hypothetical BTEX-contaminated site with the aid of artificial neural network (ANN) and Monte Carlo approach. They adopted the non-derivative methods such as genetic algorithm to search for the optimal pumping pattern. The results showed that proposed approach can successfully identify potential well locations from a set of preselected well locations. Main advantage of this approach is that it reduces the size of problem considerably by eliminating redundant well locations and hence reducing the computational burden.

Schreiber and Bahr (2002) carried out the nitrate enhanced bioremediation technique in the BTEX contaminated site by conducting two natural-gradient pulse tracer tests and observed that within the portion of the aquifer that contains the highest contaminant concentrations, nitrate addition stimulated biodegradation of toluene, ethyl benzene, and m, p-xylene but not of benzene.

**Anaerobic Bioremediation:** As the result of microbial respiration consuming the low concentrations of oxygen that can dissolve in groundwater and because of low rates of re-oxygenation as a result of oxygen diffusion, significant portion of petroleum-contaminated aquifers are anaerobic. Within last decade it has become apparent that BTEX can be degraded in anaerobic zones and such anaerobic BTEX degradation may be responsible for significant removal of BTEX components from contaminated groundwater (Lovley, 1997). This process is technically difficult and expensive. However from recent studies it is understood that remediation of petroleum hydrocarbons (BTEX) is enhanced by adding Fe(III), nitrate and sulphate.

Lovley (1997) reviewed the literature of anaerobic degradation of BTEX and concluded that potential of degradation of all BTEX components can be achieved even in the absence of molecular oxygen by the addition of Fe(III), sulfate or nitrate as electron acceptors. The recent findings suggested that benzene; the most toxic compound which was not degraded in anaerobic conditions can be rapidly degraded under Fe(III) and sulphate reducing conditions. He suggested that focus should be more emphasized on the study of the organisms involved in the metabolism and the factors controlling their distribution and activity.

Cunningham et al. (2001) demonstrated an in-situ anaerobic biodegradation of BTEX compounds at a petroleum-contaminated aquifer in Seal Beach, California by combined injection of nitrate and sulphate. It was observed that nitrate was consumed in higher amount compared to sulphate. Additional benefit of this technique was the complete removal of xylene. Also they found that benzene degradation was stimulated by combined injection of nitrate and sulphate.

**Natural Bioremediation:** It is also known as natural attenuation or passive bioremediation which is an environmental site management approach that relies on naturally occurring microbial processes for petroleum hydrocarbon removal from groundwater, without the engineered delivery of nutrients, electron acceptors or other stimulants (Curtis and Lammey, 1998; Kao et al., 2006). Main advantage of this method is its cost effectiveness compared to engineered conditions. Disadvantage of this technique is that it takes more time for organic biodegradation.

**Permeable reactive barrier (PRB):** A PRB is a reactive treatment zone designed to intercept and transform or retain the contaminant through physical, chemical and biological reactions. Since the dissolved oxygen (DO) content is usually very poor within the groundwater (3 mg/l) the deficiency can be surmounted by using oxygen-releasing compounds (ORCs) which enhances aerobic conditions, thereby obtaining higher degradation efficiency in reactive barrier technology. Figure 3 depicts the process of remediation by PRB. In the last 15 years there has been an explosion in the development and implementation of PRB technology. Advantages of biological treatments over physiochemical treatments such as cost effectiveness and ability to transform the toxic compounds into less harmful compounds (CO2, water and methane) has led to its application through PRB which is commonly referred as permeable reactive bio barrier (PRBB). In this technique as the contaminated groundwater passes through the PRBB, micro-organisms convert the toxic compounds into innocuous compounds. Disadvantage of PRBB in removing the target contaminant is the occurrence of performance losses when there are discontinuous contaminants.

Yeh et al. (2010) conducted column experiments to obtain the maximum amount of dissolved oxygen from ORC’s (Oxygen Releasing Compound) and suggested the ratio of CaO2 in the ORC as 40% (w/w) which resulted in the highest average amount of dissolved oxygen of 5.08 mg/l. They have used a real-time PCR (polymerase chain reaction) and observed higher BTEX removal efficiencies and are consistent with the results obtained by Thiruvengadam et al. (2008). The results from their study can be useful in designing a PRB system for field remediation of petroleum hydrocarbons in contaminated groundwater.

Xin et al. (2013) developed bioaugmented permeable reactive barrier (Bio-PRB) system with Mycobacterium species CHXY119 and Pseudomonas species YATO411 immobilized bead to remediate the BTEX contaminated groundwater with about 100 mg/l concentration. From the developed Bio-PRB model, degradation rates of 97.8% for
benzene, 94.2% for toluene, 84.7% for ethyl benzene and 87.4% for p-xylene were achieved. Results from the Bio-PRB system have showed the efficiency increase of 37.8% for benzene, 14.2% for toluene and 9.4% for p-xylene as compared with the bio-stimulation results. They had observed from the Bio-PRB system that limited oxygen supply was required for the removal of higher amount of BTEX. Also the toxicity of groundwater fell by 91.2% after bioremediation by the bio-augmented PRB, proved its great potential in remediating high concentrated contaminants.

**Phytoremediation:** Bioremediation using plants is known as phytoremediation. Phytoremediation can be defined as the combined use of plants, soil amendments and agronomic practices to remove pollutants from the environment or to reduce its toxicity (Clemente et al., 2005). Most groundwater phytoremediation systems utilize hybrid poplar trees (Populus) or willow trees (Salix) because they grow quickly, have deep-rooting characteristics, and can use water directly from the saturated zone (Ferro et al., 2013).

Nicholas et al (2014) demonstrated phytoremediation site in North Carolina (USA) by planting 3,250 hybrid poplars, willows and pine trees from 2006 to 2008 over approximately 579,000 liters of residual gasoline, diesel and jet fuel. The results obtained from soil-gas analysis showed a 95% mass loss for total petroleum hydrocarbons and 99% mass removal for BTEX.

Barac et al (2009) performed phytoremediation at the site contaminated by BTEX plume which occurred as a result of leaking solvents and fuel storage tanks by planting 275 poplar trees. They observed that soon after the tree roots reached the contaminated groundwater zone the remediation process became active resulting in the complete removal of BTEX. Also it was found that rhizosphere and endophytic bacteria enrichment helped in degradation of toluene. A comparison of BTEX-contaminated groundwater remediation techniques is shown in table 1.
<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Remediation Technique</th>
<th>Nature of work</th>
<th>Results</th>
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<tbody>
<tr>
<td>Lovley</td>
<td>1997</td>
<td>Anaerobic bioremediation</td>
<td>Reviewed the literature of anaerobic bioremediation of BTEX contaminated sites</td>
<td>Potential benefits with Fe(III), nitrate and sulfate as electron acceptors</td>
</tr>
<tr>
<td>Johnston et al</td>
<td>1998</td>
<td>Air Sparging</td>
<td>Applied to site at Kwinana in Western Australia</td>
<td>Within 3 days, very rapid removal of dissolved organics</td>
</tr>
<tr>
<td>Cunningham et al</td>
<td>2001</td>
<td>Anaerobic in-situ bioremediation</td>
<td>Applied to site at Seal Beach, California</td>
<td>Complete removal of xylene and also observed that nitrate consumption is more than sulphate</td>
</tr>
<tr>
<td>Schreiber and Bahr</td>
<td>2002</td>
<td>Nitrate Enhanced bioremediation</td>
<td>Applied to the real site</td>
<td>In the zones of higher concentration nitrate addition enhanced the removal of TEX but not benzene</td>
</tr>
<tr>
<td>Shim et al</td>
<td>2002</td>
<td>Bioreactor technique</td>
<td>Performed laboratory experiments</td>
<td>100% removal efficiency for retention time greater than 1 hr</td>
</tr>
<tr>
<td>Shieh and Peralta</td>
<td>2005</td>
<td>Engineered in-situ Bioremediation</td>
<td>Developed simulation-optimization model of hypothetical site</td>
<td>Minimized total system cost by using parallel recombinative simulated annealing</td>
</tr>
<tr>
<td>Prasad and Mathur</td>
<td>2006</td>
<td>Engineered in-situ bioremediation</td>
<td>Developed simulation-optimization model of hypothetical site</td>
<td>Optimized total system cost and pumping rates with the aid of ANN</td>
</tr>
<tr>
<td>Yeh et al</td>
<td>2010</td>
<td>PRB( Permeable reactive barrier) system</td>
<td>Conducted lab experiments</td>
<td>Higher BTEX removal efficiencies and also can be applied to field remediation problems</td>
</tr>
<tr>
<td>Xin et al</td>
<td>2013</td>
<td>Bio-PRB( Permeable reactive barrier) system</td>
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</tr>
<tr>
<td>Nicholas et al</td>
<td>2014</td>
<td>Phytoremediation</td>
<td>Applied to site in North Carolina (USA)</td>
<td>95% mass loss for total petroleum hydrocarbons and 99% mass removal of BTEX</td>
</tr>
</tbody>
</table>
III. CONCLUSIONS

This study examines certain emerging remedial techniques in practice for BTEX-contaminated groundwater. Air sparging, a physical remediation technique is an innovative method employed in successful removal of BTEX compounds which has proved to be an excellent cost effective alternative to conventional groundwater pump and treat technology. Permeable Reactive Barrier system is also found to be efficient remedial technique because of its cost-effectiveness and ability to transmute toxic compounds into less harmful compounds. It is also observed that in some sites hybrid poplar trees are mostly preferred in phytoremediation process to maximize the BTEX removal efficiency. From the present study it is recommended that in-situ bioremediation has become an emerging viable technique which is most widely used because of lower capital cost, in-situ operation, permanent elimination of contaminants and cost effectiveness. Because of health concerns groundwater contamination from petroleum products (mainly BTEX) needs more focussed research for its efficient remedial techniques. Authors propose to use engineered bio-remediation technique involving finite element and particle swarm simulation optimisation model to achieve bioremediation of a synthetic confined aquifer.

IV. REFERENCES