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Methods for Investigation of Natural Attenuation and Modeling of Petroleum Hydrocarbon Contamination in Coastal Aquifers

Kıyı Akiferlerinde Petrol Hidrokarbon Kirliliğinin Doğal Gideriminin Araştırılması ve Modellenmesi Yöntemleri

Zübeyde HATİPOĞLU-BAĞCI[1], Louis H. MOTZ[2]
[1]*Jeoloji Mühendisliği Bölümü, Mersin Üniversitesi, Çiftlikköy, 33343 Mersin*
[2]*Department of Civil and Coastal Engineering, University of Florida, Gainesville, Florida 32611 U.S.A.*

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ABSTRACT

In this study research methods are assessed to determine the spatial distribution of petroleum hydrocarbon contamination in the coastal aquifers and to develop a groundwater flow and transport model that can be used to evaluate the level of natural attenuation that has occurred. The stages of this study include: 1) preliminary assessment and conceptual model including hydrogeologic characteristics of the site, the history of the site, and any past or current remedial activities, 2) field and laboratory investigations including soil and groundwater sampling techniques such as soil borings, multi-level monitoring well installation, aquifer tests and water quality sampling. Parameters to be measured, their measurement methods and use of these data should be explained in detail, 3) physical and geochemical characterization of the study area with the results of the field and laboratory investigations, 4) development of the groundwater model with selected software, 5) evaluation of monitored natural attenuation according to primary and secondary lines of evidence established during the investigation. The primary lines of evidence, which is a stable or shrinking plume rather than an expanding plume, will be the benzene, toluene, ethylbenzene and xylene (BTEX) contour maps prepared as a result of the groundwater sampling. Secondary lines of evidence, which include geochemical data that serve as indicators of naturally occurring biodegradation and estimates of natural attenuation rates, will be based on electron acceptor/reduction product concentrations measured within the BTEX plume. The results of the groundwater modeling are used to help decide whether the monitored natural attenuation process results in BTEX contaminant levels declining to acceptable levels within a specified time. If projections of contaminated levels indicate that natural attenuation is not enough for remediation, then additional remedial alternatives can be recommended for further investigation.

Keywords: BTEX, Groundwater, Monitored Natural Attenuation, Numerical Modeling, Petroleum contamination

ÖZ

Bu çalışmada, kıyı akiferlerinde petrol kirliliğinin yayılımını belirlemek ve bir akım ve taşınım modeli oluşturarak doğal giderimin derecesini belirlemek için uygulanacak araştırma yöntemleri değerlendirilmiştir. Böyle bir çalışma beş aşamadan oluşur; 1) Bölgenin hidrojelojik karekteristiklerini içeren kavramsal modelinin oluşturulması ve mevcut ve geçmişteki iyileştirme aktivitelerinin belirlenmesi 2) Detaylı saha araştırmaları ile çok seviyeli gözlem kuyularının kurulması, zeminden karot alınması yöntemleri kullanılarak arazi ve laboratuvar analizleri için zemin

Yazışma Yazarı / *Correspondence:* zubeyde11@gmail.com

ve yeraltısuyu örnekleri alınması. Ölçülecek parametreler, ölçüm yöntemleri ve bu parametrelerin hangi amaçla kullanılacağı ayrıntılı olarak belirtilmeli, 3) Arazi ve laboratuvar çalışmaları ile elde edilen sonuçlara göre fiziksel ve jeokimyasal karakterizasyon 4) Seçilen yazılım ile yeraltısuyu modelinin oluşturulması 5) Araştırma sırasında elde edilen birincil ve ikincil kanıtlara göre gözlenen doğal giderimin değerlendirilmesi. Kirlilik bulutunun duraylı veya büzülüyor olduğunu gösteren birincil kanıtlar yeraltısuyu örneklemesi sonucu oluşturulan benzen, tolüen, etilbenzen, ve ksilen (BTEX) kontur haritalarıdır. Doğal biyolojik parçalanmanın belirteçleri olan ve doğal giderim hızının belirlenmesinde kullanılan jeokimyasal verileri kapsayan ikincil kanıtlar ise BTEX kirlilik bulutu içindeki elektron alıcı/vericilerin derişimleridir. Yeraltısuyu modelleme sonuçları, doğal giderim sürecinin BTEX kirletici düzeylerinin belirli bir sürede kabul edilebilir seviyelere gerileyip gerilemeyeceğinin belirlenmesi için kullanılır. Bu sonuçlar doğal giderimin yeterli olmadığını gösterirse bu durumda yeraltısuyunun iyileştirilmesi için alternatif iyileştirme yöntemleri önerilir.

Anahtar Kelimeler: *BTEX, Yeraltısuyu, İzlenen Doğal Giderim, Sayısal Modelleme, Petrol Kirliliği*

INTRODUCTION

Flat topography, good transportation facilities and availability of water resources make coastal regions preferred areas for settlement and industrial activities. These characteristics have contributed to a rise in population density of coastal areas increasing the negative impact on the quality and quantity of groundwater. Due to the high population density, the use of petroleum hydrocarbons has also increased and become a major contamination source for groundwater (Mirzaee et al., 2017; Raynauld et al., 2016; Fiori and Zalba 2003; Teng et al., 2013; Van Stempvoort and Biggar 2008; Yu et al., 2003; Maric et al., 2015; Chiu et al., 2013; Banerjee et al., 2016). Hydrocarbons are toxic and hence cause to serious health and environmental problems (Chiu et al., 2013; Zheng, et al., 2016; Chiu et al., 2017). Monoaromatic hydrocarbons benzene, toluene, ethylbenzene and the three isomers of xylene which are abbreviated as BTEX have greatest interest from the environmental viewpoint, because of their mobility and toxicity (Coresuil et al., 2011; Fernandes et al., 2014). BTEX are commonly found together in crude petroleum and petroleum products such as gasoline (Chen et al., 2008). Human activities centered on oil production, transportation, and storage result in oil spillage into freshwater sources in the world. (Zheng et al., 2016; Raynould et al., 2016; Mukhopadhyay et al., 2017; Indumathi et al., 2017; Zhang et al., 2017; Ruggieri et al., 2017). With a widespread increase in contamination of water systems, effective contamination control and remediation is becoming a major technical problem (Mirzaee et al., 2017). Some technologies for control of environmental pollution have been described by various authors and have been converted into products that are being marketed for control of pollution. These technologies vary considerably in their cost and efficiencies and include the pump and treat method (considered to be cost-effective), in-situ soil vapor extraction, thermal enhancement systems, air stripping (Caetano et al., 2017), reactive barrier technology (Mcmurty and Elton, 1985; Guerin et al., 2002) and natural attenuation (Wiedemeier et al., 1996; U.S. EPA, 1999; Khan et al., 2004).

The remediation and control of pollution using natural attenuation process involves employing various mechanisms that may be biological, chemical or physical and include sorption, biodegradation, chemical decay, dilution, dispersion, volatilization, contaminant destruction, and biological stabilization (Wiedemeier et al., 1996; U.S. EPA, 1999; Neuhauser et al., 2009; Chen et al., 2010; Kamath et al., 2011; Declercq et al., 2012; Chui, et al., 2013; Chui 2017). Biodegradation is the exclusive natural process that can remediate contaminated soil and groundwater environment by transforming organic pollutants into inorganic substances (Wiedemeier et al., 1999b; Zheng et al., 2016). Biodegradation is also an attractive approach because of several other reasons. It is energy saving, economical, and an environmentally friendly method for reducing the impact of pollution for sites polluted by hydrocarbon products (Godeke et al., 2006; Chiu et al., 2017; Azubuike et al., 2016). Intrinsic biodegradation is a vital aspect in the removal of contaminants (Stasik et al., 2015; Davis et al., 2009) and breakdown of pollutants into products that are less harmful to the environment such as H_2O, CO_2, biomass, and salt (El-Naas, 2014; Chui, 2017).

This type of study includes a detailed site investigation for physical and geochemical characterization of the region. Soil and groundwater sampling techniques including soil borings, multi-level monitoring well installation and sampling are used to collect data for field and laboratory analyses. With soil sampling in the unsaturated zone and capillary fringe, mobile and residual light non-aqueous phase liquids (LNAPLs) that serve as source areas for the dissolved benzene, toluene, ethylbenzene and xylene (BTEX) contaminants in the underlying water-table aquifer are located. Soil samples are analyzed for total volatile and extractable hydrocarbons; aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylene (BTEX); total organic carbon (TOC), and moisture content. The subsurface distribution of hydro-stratigraphic units are determined. Multi-level monitoring wells are constructed to determine the three-dimensional characteristics of the BTEX and other plumes and the vertical distribution of chlorides and total dissolved solids (TDS), particularly in the vicinity of the seacoast. Groundwater samples are analyzed for total volatile and extractable hydrocarbons, aromatic hydrocarbons (BTEX), dissolved oxygen, nitrate, manganese, iron (II) (Fe^{+2}), sulfate (SO_4^{2}), methane, alkalinity, oxidation-reduction potential (Eh), pH, temperature, conductivity, chloride, and total dissolved solids (TDS). Two cycles of wet season-dry season sampling for a total sampling period of approximately 18 months is convenient. Slug tests, an aquifer pumping test, and permeameter tests can be conducted to determine the hydraulic conductivity of the water-table aquifer in the study area. The results of the field and laboratory investigations are used to prepare a physical and geochemical characterization of the site.

Monitored natural attenuation can be simulated using a solute fate and transport model. Based on the results of the physical and geochemical characterization of the area, RT3D (Clement, 1997; Lu et al., 1999) and other suitable codes such as PHWAT (Mao et al., 2006) can be considered for the groundwater model. The determination of whether natural attenuation can be considered appropriate for the study area are based on primary and secondary lines of evidence established during the investigation. The primary line of evidence is whether the BTEX plume is stable or shrinking, rather than expanding. Secondary lines of evidence, which include geochemical data that serve as indicators of naturally occurring biodegradation and estimates of natural attenuation rates, are based on electron acceptor/reduction product concentrations of oxygen, nitrate, manganese

(II), iron (II), sulfate, and methane measured within the BTEX plume. For example, depletion in dissolved oxygen, nitrate, and/or sulfate and increases in dissolved manganese, iron, and methane in the groundwater would indicate that biodegradation is occurring. The groundwater modeling results are used to help decide whether the monitored natural attenuation process will result in BTEX contaminant levels declining to acceptable levels within a specified time. If projections of contaminated levels based on the model results indicate that this objective cannot be met, then additional remedial alternatives can be recommended for further investigation.

DISTRIBUTION OF PETROLEUM HYDROCARBONS IN THE SUBSURFACE

Contaminants for sites contaminated by petroleum products occur in four different states (Beck and Mann 2010; Konecny et al., 2003) as shown in Figure 1. These states are;

1. Volatilized in soil vapors: in the unsaturated zone of the soil, hydrocarbons in volatile states decompose into gaseous phase as organic soil vapor and migrate into vapor phase,

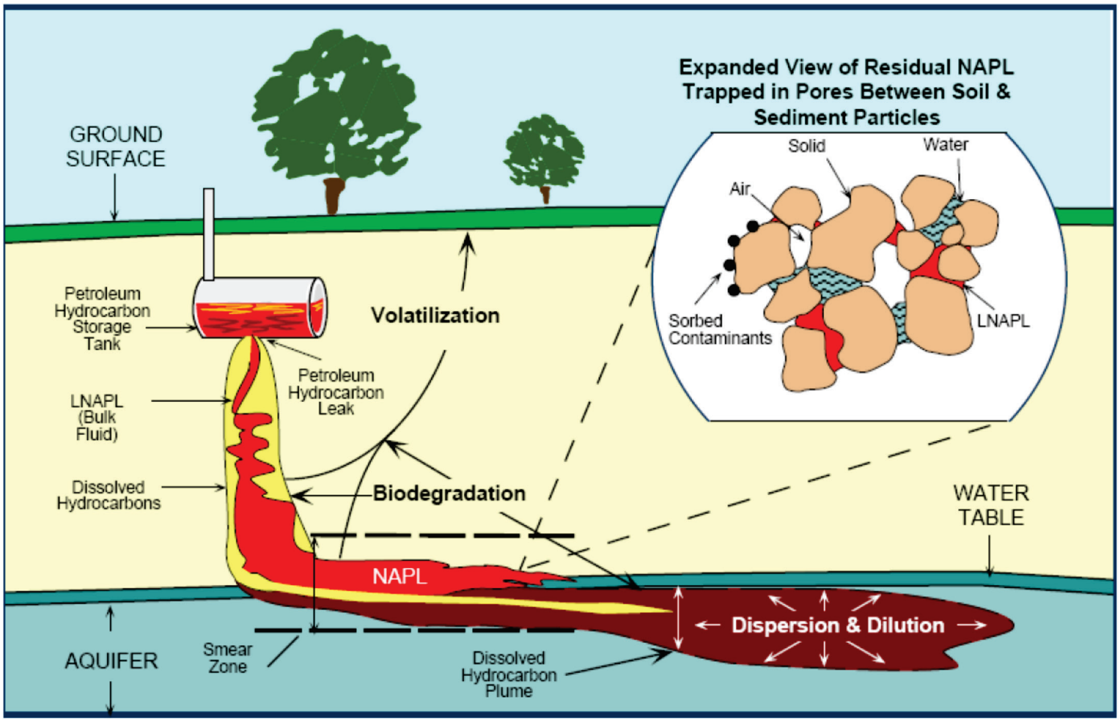

Figure 1. Schematic demonstration of how petroleum hydrocarbons distribution in a subsurface occurs after a site spillage (Department of Environmental Protection, 2004; Beck and Mann, 2010).

Şekil 1. Bir döküntü sonrası ortaya çıkan petrol hidrokarbonlarının yeraltında dağılımının şematik gösterimi (Department of Environmental Protection, 2004; Beck ve Mann, 2010).

2. Dissolved in groundwater: in vadose zone, petroleum compounds which are dissolved in percolating precipation, migrate into groundwater table with a concentration below the free phase solubility of the compound,
3. Sorbed onto matrix particles: the aquifer or the vadose zone matrix sorbs dissolved petroleum compounds into their matrix which has native organic carbon,
4. Non-aqueous phase liquids (NAPLs); these are organic, nondissolved liquids in the subsurface.

The majority of petroleum compounds in contaminated groundwater exist in the form of NAPLs. Introducing petroleum hydrocarbon NAPLs into unsaturated zone causes their movement down to the saturated zone. When reached at the water table, petroleum hydrocarbon NAPLs float on the water table as they are less dense than water and form a thin layer that spreads across the water table and capillary fringe. The resulting product is referred to as light NAPLs which are usually found as a mixture of chemicals although they also exist as single chemical (Wiedemeier et al., 1999a). More soluble aromatic hydrocarbons including benzene, toluene, ethylbenzene, and xylenes, popularly referred to as BTEX compounds dissolve from LNAPLs. Non-aqueous phase liquids that are denser than water are referred to as DNAPL. DNAPLs, unlike LNAPLs, after entering the saturated zone, descend vertically until residual saturation formation exhaust their volume. The presence of aquifer zones with lower permeability might disturb the vertical migration process and thus cause lateral migration (Konecny et al., 2003).

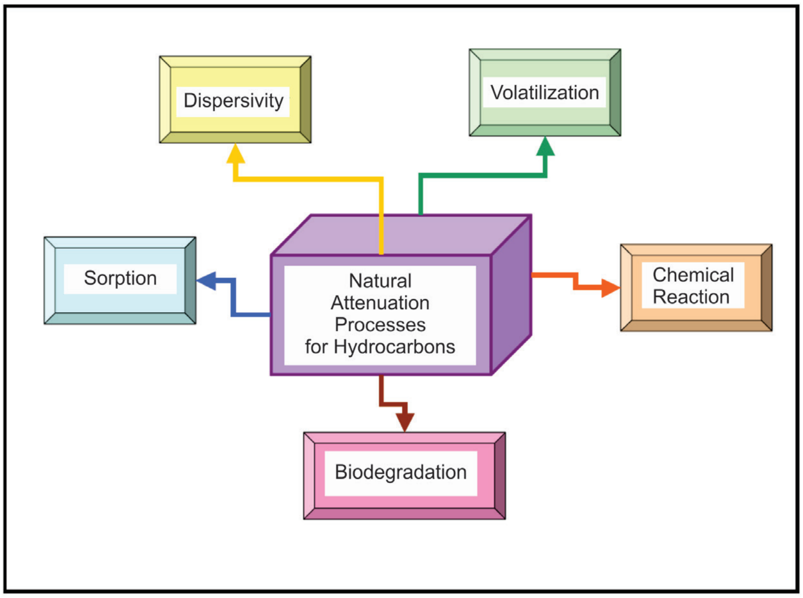

Figure 2. Schematic demonstration of how petroleum hydrocarbons are attenuated naturally (UK, EA, 2000; Beck and Mann, 2010).

Şekil 2. Petrol hidrokarbonlarının doğal gideriminin şematik gösterimi (UK, EA, 2000; Beck ve Mann, 2010).

The natural fate and transport process of soluble contaminants found in many areas contaminated with petroleum hydrocarbons includes dispersion, biodegradation, advection, sorption, chemical reactions, and volatilization (Figure 2) (Wiedemeier, et al., 1996; Kao and Wang 1999; Chen et al 2005; Bauer et al., 2008; Uçankuş and Ünlü 2008; Beck and Mann 2010; EPA, 2012; Chiu et al., 2017). Dispersion is the process, which a solute is diluted and thus reducing its concentration. Sorption refers to the process of partitioning of dissolved phase hydrocarbons into solid phase sorbents leading to their temporary or permanent immobilization through attachment to sites or sorption on solid surfaces in the subsurface matrix. On the other hand, volatilization is a mass-transfer process that causes the partitioning of dissolved constituents into vapor phase.

Biodegradation refers to mass transformation process in which petroleum hydrocarbons are broken down by microbially-facilitated chemical reactions and thereby reducing the concentration of contaminants and the amount of dissolved hydrocarbon in groundwater. Under some conditions, petroleum hydrocarbons may be broken down by some chemical reactions without the assistance of microorganisms. However, in dissolved phase biodegradation remains the dominant mass reduction process (Beck and Mann, 2010).

BIODEGRADATION OF BTEX

Biodegradation refers to the process by which chemical compounds are broken down by subsurface microorganisms. Through a biological activity, microorganisms break down hydrocarbons into water and carbon dioxide (Wiedemeier et al., 1996; ASTM 2010; U.S. EPA 2012; Banerjee et al., 2016). Once petroleum hydrocarbons intruduced into groundwater, an increase in the amount of organic carbon content will occur and the microorganisms in the contaminated environment will try to gradually adapt to this new environment (Su et al., 2013; Anderson and Lovely, 1997). The biodegradation intensity of contaminants by microorganisms is influenced by several factors that include oxygen, contaminant concentration and composition, nutrients, pH value, physical and chemical characteristics, and the history of the contaminated environment regarding pollution (Margesin and Schinner, 2001). By transforming hydrocarbons, microorganisms get energy and carbon which is crucial for their growth, reproduction, and survival. Microorganisms employ a series of catalyzed reactions by oxidative-reduction enzymes resulting to metabolic intermediates or water and carbon dioxide. Additionally, the oxidative reactions provide energy for growth and maintenance of microorganism cells. For the electrons to be passed through the steps that lead to the generation of energy, sink of an electron is required. Normally, the electron sink/acceptor is molecular oxygen and this process is referred to aerobic respiration. However, when molecular oxygen is lacking or insufficient, other compounds such as (NO_3), manganese (Mn^{+4}), ferric iron (Fe^{+3}), sulfate (SO_4^{-2}) or carbon dioxide (CO_2) act as terminal electron acceptors and this process is referred to as anaerobic respiration. The choice of these compounds occur in the order presented above (Wiedemeier et al., 1996; Skubal et al., 2001; Khan et al., 2003; Dyer, 2003; 2007; ASTM 2010; Su et al., 2013; Chiu et al., 2013; Chiu et al., 2017).

Aerobic and anaerobic metabolism of BTEX equations and resulting products are shown in following equations (Wiedemeier et al., 1999b):

Benzene oxidation/aerobic respiration

$$7.5O_2 + C_6H_6 \rightarrow 6CO_{2,g} + 3H_2O \tag{1}$$

Benzene oxidation/denitrification

$$6\,NO_3^- + 6H^+ + C_6H_6 \rightarrow 6CO_{2,g} + 6H_2O + 3N_{2,g} \tag{2}$$

Benzene oxidation/manganese reduction

$$30H^+ + 15MnO_2 + C_6H_6 \rightarrow 6CO_{2,g} + 15\,Mn^{2+} + 18H_2O \tag{3}$$

Benzene oxidation/iron reduction

$$60H^+ + 30Fe(OH)_3 + C_6H_6 \rightarrow 6CO_2 + 30\,Fe^{2+} + 78H_2O \tag{4}$$

Benzene oxidation/sulfate reduction

$$7.5H^+ + 3.75\,SO_4^{2-} + C_6H_6 \rightarrow 6CO_{2,g} + 3.75\,H_2S^0 + 3H_2O \tag{5}$$

Benzene is used in the equations, but the reactions can apply to all BTEX compounds. As illustrated in equations, while oxygen is consumed, the products of aerobic respiration are water and carbon dioxide. On the other hand, in anaerobic respiration, BTEX react with an electron acceptor and produces water, carbon dioxide, and a reduced electron acceptor. However, water is not produced in methanogenesis. For both aerobic and anaerobic processes lead to the attenuation of BTEX, the disappearance of dissolved oxygen and/or electron acceptors or the generation of electron-acceptor reduction products are indicators of biodegradation (Hunkeler et al., 1997; Van Stempvoort et al., 2008; ASTM, 2010; Robertson et al., 2012; Thapa et al., 2012; Yeung et al 2013; Chiu et al., 2013; Cassidy et al, 2015; Banerjee et al., 2016; Chiu 2017). Depletion of dissolved oxygen, nitrate and sulphate concentrations and increasing ferrous iron and methane concentrations indicate that anaerobic degradation is occurring (Naidu et al., 2012). However, the rate of degradation of BTEX under anaerobic respiration is slower as compared to that under aerobic respiration (Moreels et al., 2004; Kao et al., 2008; Kao, 2010; Silva and Corseuil, 2012).

The majority of electron acceptors and their products including O_2, NO_3, SO_4, Fe (II), Mn (II), CH_4 as illustrated in equations 1, 2, 3, 4 and 5 can easily be measured in water samples. By measuring these parameters, the impact of biodegradation on solute plume can be evaluated (ASTM, 2010).

Oxygen

Oxygen is the most favorable electron acceptor, and its presence facilitates rapid growth of aerobic bacteria given the availability of nutrients in polluted groundwater (Prommer et al., 1999; Wisconsin Department of Natural Resources, 2014). In zones where the concentration of BTEX is high, dissolved oxygen is depleted very fast as microorganisms use the oxygen to breakdown BTEX. Any oxygen that enters this zone is rapidly depleted as biodegradation of highly concentrated BTEX and other constituents requires a a high amount of oxygen. For this reason, an indication of biodegradation can be based on the inverse relationship of low dissolved oxygen and high hydrocarbon concentration (ASTM, 2010). For the degradation of the petroleum hydrocarbon using anaerobic reaction, electron acceptors such as nitrate, sulfate, ferric ions, and manganese are used by microorganisms (Washington State Department of Ecology 2005; Beck and Mann 2010).

Nitrate

Upon the depletion of dissolved oxygen in groundwater zone or the decreasing of its concentration to <0.5 ppm, nitrate will be used as an electron acceptor for anaerobic biodegradation (U.S. EPA 1999; ASTM 2010; Da Silva and Corseuil, 2012; Thapa et al., 2012; Fuentes et al., 2014). In groundwater zones with a high concentration of BTEX, the demand f nitrate by microorganisms that biodegrade BTEX may be high, and therefore this will lead to the decreasing of nitrate as compared to its concentrations outside the plume and upgradient zone. It is thus expected that there will be an inverse relationship between the concentration of BTEX and that of nitrate concentration (ASTM 2010).

Manganese

When oxygen and nitrates are depleted, microorganisms make use of manganese (Mn^{+4}) as a terminal electron acceptor to breakdown BTEX and generate reduced water soluble manganese (Mn^{+2}). In BTEX contaminated anaerobic groundwater zone, if Mn^{+4} (MnO_2) is available, it is expected that a positive relation between the concentration of BTEX and concentration of Mn^{+2}, which can be used as biodegradation indicator. Dissolved manganese (Mn^{+2}) has high sensitivity to oxidation (Zeeb and Wiedemeier, 2007; ASTM 2010; Beck and Mann 2010; Wisconsin Department of Natural Resources, 2014).

Iron

Microorganisms may also use ferric iron (Fe^{+3}) as electron acceptors and they produce water-soluble ferrous iron (Fe^{+2}). In BTEX contaminated groundwater zones, it is expected that a positive relationship between the concentration of BTEX and concentration of Fe^{+2}, which can be used as a biodegradation indicator (Zeeb and Wiedemeier 2007; ASTM 2010; Chiu et al., 2017).

Sulfate

When oxygen, nitrates, and ferric iron are depleted (strongly reducing conditions), microorganisms make use of sulfate as a terminal electron acceptor to breakdown BTEX to produce sulfide or ferrous sulfide precipitate. In groundwater with a high concentration of BTEX, the demand for sulfate by microbes that biodegrade BTEX may be high, and therefore this will lead to the depletion of sulfate as compared to its concentrations outside the plume and upgradient. In overall, it is expected that there will be an inverse relationship between the concentration of BTEX and that of sulfates in sulfate-reducing zones (Kao and Wang, 2000; Da Silva et al., 2005; ASTM 2010; Cassidy et al., 2015; Chui et al., 2017).

Methane

Methanogens produce methane under strongly reducing conditions by using CO_2 or cleave acetate as terminal electron acceptor. Methane, which is not found in fuels, can therefore be used as biodegradation indicator. The production of methane can be significant in high concentrations of BTEX and under methanogenic conditions. In these conditions it is expected that there will be a positive correlation between the concentration of BTEX and concentration of methane (Wiedemeier et al, 1996; Zeeb and Wiedemeier, 2007; ASTM 2010; U.S. EPA, 2012).

Oxidation-Reduction (Redox) Potential

The measure of relative tendency of a solution to accept or donate electrons is referred to as oxidation-reduction (redox) potential. Microorganisms act as important mediators of redox reactions in groundwater. For this reason, a biodegradative process strongly influences redox potential and vice versa. Redox potential in groundwater is between –400 and 800 mv. In this range, only specific biodegradative processes can operate as illustrated in Table 3. The zones where anaerobic biodegradation processes reduce the value of redox potential can be identified by measuring redox values of upgradient and within the plume (Wiedemeier 1999b; Washington State Department of Ecology, 2005; ASTM, 2010; Chiu et al., 2017). Table 3 presents a typical sequence of electron acceptors from both aerobic and anaerobic conditions (Washington State Department of Ecology, 2005; Beck and Mann, 2010).

GROUNDWATER PETROLEUM CONTAMINATION RELATED STUDIES IN TURKEY

There are very few studies about petroleum hydrocarbon contamination in groundwater in Turkey. Uçankuş and Ünlü (2008) used numerical simulation techniques for defining relationship between aquifer heterogeneity and the biodegradation rate of BTEX. Visual MODFLOW/RT3D was used for modelling of dissolved BTEX plume transport within heterogeneous aquifers. Kara (2006) evaluated the movement of petroleum plumes for city of Batman. The numerical simulations were performed using the BIOPLUME III program. Potential effects of the movement of petroleum plumes on drinking water quality simulations were explored. Akbulut (2009) measured physicochemical (pH, dissolved oxygen, Eh, temperature and electrical conductance) parameters in 212 wells and determined spatial distribution of natural attenuation indicators for Karaduvar (Mersin) aquifer which is heavily contaminated with petroleum hydrocarbons. She also determined BTEX concentrations, and designed a funnel and gate type permeable reactive barrier for remediation of the existing petroleum hydrocarbon pollution for the Karaduvar (Mersin) area, using MODFLOW software.

Table 3. Microbial reactions and geochemical indicators evaluation (⇓ = decreasing concentration, ⇑ = increasing concentration) (Washington State Department of Ecology, 2005; Beck and Mann, 2010).

Çizelge 3. Jeokimyasal indikatörlerin ve mikrobiyal reaksiyonların değerlendirilmesi (⇓= azalan konsantrasyon, ⇑ = artan konsantrasyon) (Washington State Deparment of Ecology 2005; Beck ve Mann 2010).

Type of Microbial Respiration	Electron Acceptor	Metabolic By-Product	Geochemical Indicator Response		Redox Potential Eh (mV @ pH, 25°C)	
Aerobic (Oxidation)	Oxygen	CO_2	O_2 ⇓	CO_2 ⇑	+820	Most preferred
Anaerobic (Reduction)	Nitrate (NO_3^-)	N_2	NO_3^- ⇓	CO_2 ⇑	+720	⇓
	Manganese (Mn^{4+})	Mn^{2+}	Mn^{2+} ⇑	CO_2 ⇑	+520	
	Ferric iron (Fe^{3+})	Ferrous iron (Fe^{2+})	Fe^{2+} ⇑	CO_2 ⇑	-50	
	Sulphate (SO_4^{2-})	H_2S	SO_4^{2-} ⇓	CO_2 ⇑	-220	Least Preferred
	Carbon Dioxide (CO_2)	Methane (CH_4)	CH_4 ⇑	CO_2 ⇑	-240	

Babaarslan (2001) investigated the biodegradation of BTEX compounds in a mixed culture obtained from the formation water which was produced from the petroleum wells of Turkey Petroleum Corporation (TPAO) in Adıyaman region (south-eastern Turkey).

PROCEDURES AND GUIDELINES

In a widely accepted guide for remediation of ground water by natural attenuation at petroleum release sites, ASTM (2010) describes typical site characterization, sampling parameters, methods, and special considerations for evaluating remediation by natural attenuation in groundwater for petroleum release sites. Wiedemeier et al. (1999b) prepared a technical protocol for support of intrinsic remediation of groundwater, contaminated with petroleum hydrocarbons. In this protocol, data collection and analyses are described for restoration of groundwater. Beck and Mann (2010) presented a technical guidance for the demonstrating of monitored natural attenuation for dealing with groundwaters impacted by petroleum hydrocarbons. Also, Wilson (2011) described a statistics-based approach for evaluating the progress of natural attenuation during long term monitoring and site characterization.

MODELING STUDIES

Clement et al. (1998) developed RT3D, a general purpose three-dimensional multispecies reactive transport code that uses MODFLOW to simulate groundwater flow and several MT3D sub-programs to simulate advection and dispersion. Modules of reaction are included in the code to simulate various types of multispecies reactive transport. Subsequently, Lu et al. (1999) used RT3D to model the natural attenuation of BTEX compounds dissolved in the groundwater migrating from a light nonaqueous phase liquid (LNAPL) source at Hill Air Force Base in Utah, USA. Suarez and Rifai (2004) simulated the fate and transport of fuel hydrocarbons in groundwater using the two-dimensional BIOPLUME III code (Rifai et al., 1996) code to model natural attenuation of BTEX and benzene. Prommer et al. (2003a) described the steps that are most often involved in numerical modelling of petroleum hydrocarbon contaminated sites and some of the most commonly used biogeochemical transport models and pre- and post-processing tools. As an example, the MT3DMS-based multicomponent transport code PHT3D was used to simulate the natural attentuation of a BTEX plume originating from a NAPL source. As described by Prommer et al. (2003b), PHT3D couples the transport simulator MT3DMS and the geochemical modeling code PHREEQC-2 (Parkhurst and Appelo, 1999) based on a split-operator technique. The PHT3D model was also used to simulate the mobilization of native metals in an aquifer, arsenic, under changing geochemical conditions, predominantly reduced dissoved oxygen (Wallis et al., 2011). Mao et al. (2006) described the development of PHWAT, which simulates multi-component reactive transport in variable density groundwater flow, by coupling the geochemical reaction model PHREEQC-2 with the density-dependent groundwater flow and solute transport model SEAWAT (Guo and Langevin, 2002) also using the split-operator technique. PHWAT was tested successfully for a one-dimensional case of freshwater flushing into a soil column saturated with brackish water and a two-dimensional case where seawater intrudes into a soil tank initially filled with freshwater and also was used to study a series of flow instability cases. In studies relevant to the saltwater intrusion that apparently has occurred at the Karaduvar site, Motz and Sedighi (2009 and 2013) used MODFLOW, MT3DMS, and SEAWAT to represent the coastal boundary condition and investigate saltwater intrusion and recirculation of seawater at a coastal boundary. Also, Çobaner et al. (2012) used SEAWAT to model seawater intrusion that occured in the Göksu Delta along the Mediterranean Coast at Silifke.

METHOD

Research of natural attenuation and modeling of petroleum hydrocarbon contamination can be divided into six tasks to achieve the purpose of the research:

Task 1. Preliminary Assessment and Conceptual Model
Task 2. Field and Laboratory Investigations
Task 3. Physical and Geochemical Characterization of the Study Area
Task 4. Development of the Groundwater Model
Task 5. Evaluation of Monitored Natural Attenuation

In the first three tasks, the hydrogeological structure and groundwater quality of the region is determined, and a realistic conceptual hydrogeological model is developed. In the fourth task, a groundwater flow and contaminant transport model representing dissolved BTEX compounds in the aquifer is developed. In the last two tasks, the groundwater modeling results are used to help decide whether the monitored natural attenuation process is resulted in BTEX contaminant levels declining to acceptable levels within a specified time. If the model results indicate that this objective cannot be met, then additional remedial alternatives can be recommended for further investigation.

In this context, the methodologies and procedures detailed below were compiled from Wiedemier et al. (1999b) and ASTM (2010). The proposed monitoring well network is based on Beck and Mann (2010).

Task 1. Preliminary Assessment and Conceptual Model

A preliminary conceptual model of the site is developed, including a preliminary assessment of the potential for monitored natural attenuation to occur. This includes describing hydrogeologic characteristics of the site, the history of the site, and any past or current remedial activities, based on reviewing existing literature, technical reports, and available site data.

Task 2. Field and Laboratory Investigations

A detailed investigation of the site is performed to determine the nature and extent of contamination and the potential for monitored natural attenuation to occur. Soil and groundwater sampling techniques including conventional soil borings, monitoring well installation, and water quality sampling, is used to collect data for field and laboratory analyses.

Soil Sampling

Soil sampling is carried out to determine of hydrostratigraphic units and mobile and residual distribution of LNAPLs in the unsaturated zone that serve as source areas for the dissolved BTEX contaminants in the underlying water-table aquifer. Soil samples are analyzed for total volatile and extractable hydrocarbons, aromatic hydrocarbons (BTEX), organic carbon content of saturated zone soils, and moisture content. Continuous soil sampling can be conducted with a soil coring kit for soil characterization and determining the location of LNAPLs.

Use of the collected data is as follows:

Total volatile and extractable hydrocarbons: Location, concentration, distribution and total mass of total petroleum hydrocarbons (TPH) sorbed to soils and mobile NAPL are used for contaminant partitioning calculations into groundwater from these phases. Knowledge of NAPL plume location is important to model applications for determinations of contaminant source area and boundary conditions of model.

BTEX: Data is used for determination of extent of soil contamination, presence of the contaminant mass, and thus the continuity of the BTEX plume and the necessity of source removal (Wiedemeier 1999b).

Moisture content: It is used for correction of soil sample analytical results such as dry weight of soil. (Wiedemeier 1999b).

Organic carbon content of saturated zone soils: These data is used to determine retardation factors of dissolved plume components and estimate transport rates (ASTM 2010).

Groundwater Sampling

Multi-level groundwater monitoring wells are constructed to determine the three-dimensional characteristics of the BTEX and other plumes and the vertical distribution of chlorides and total dissolved solids (TDS), particularly in the vicinity of the seacoast.

Groundwater samples are analyzed for total volatile and extractable hydrocarbons, aromatic hydrocarbons (BTEX), dissolved oxygen, nitrate, manganese, iron (II) (Fe^{+2}), sulfate (SO_4^{-2}), methane, alkalinity, oxidation-reduction potential (Eh), pH, temperature, conductivity, chloride, and total dissolved solids (TDS). Two cycles of wet season-dry season sampling for a total sampling period of approximately 18 months can be carried out. Groundwater sampling is conducted using the multi-level observation wells in contaminated area. Groundwater is sampled at a single level outside of the contaminated area. Use of the collected data during the groundwater sampling is as follows (compiled from ASTM, 2010):

BTEX: data of historical BTEX plume, which is a primary lines of evidence is utilized directly for the determination of whether plume is expanding, stable or shrinking.

Dissolved oxygen: the occurrence of aerobic biodegradation is indicated by an inverse correlation between the concentrations of dissolved oxygen to BTEX concentrations. The complete consumption of dissolved oxygen is expressed as depressed or nondetectable levels of dissolved oxygen throughout the plume.

Nitrate: the use of nitrate as an electron receptor for anaerobic breakdown of hydrocarbons will reduce the concentration of nitrate in the anaerobic portion of the plume.

Ferrous iron: the utilization of Fe (III) as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons will lead to increase in concentrations of Fe (II).

Manganese: increase in the level of Mn (II) is an indication of the utilization of Mn (IV) as a terminal electron receptor during anaerobic biodegradation.

Sulfate (SO_4^{-2}): the use of sulfate as an electron receptor for anaerobic breakdown of hydrocarbons will reduce its concentration in the anaerobic part of the plume.

Methane: the use of carbon dioxide as an electron acceptor for the anaerobic breakdown of hydrocarbons will elevate the concentration of methane.

Heavy metals: the presence of heavy metals such as selenium and zinc is important for the occurrence of biological processes. However, a high concentration of these metals is toxic to microorganisms that break down petroleum hydrocarbon compounds (Beck and Mann, 2010). Microbiological processes can also be impaired or eliminated by the presence of toxic metals such as cadmium and mercury. At sites where they occur naturally or develop anthropogenic impacts, inhibitor assessment is required.

Alkalinity: carbonate alkalinity is the major contributor to total alkalinity. Therefore, alkalinity can be considered as a measure of dissolved carbonate and bicarbonate.

Oxidation-reduction potential (Eh): Plume regions undergoing oxidation or reductions is defined using redox data. Redox data is also important for validating measurements of dissolved oxygen concentrations and evaluating the potential for biologically mediated redox reactions.

pH: the occurrence of biological activity may be indicated by the difference in pH between contaminated and uncontaminated groundwater.

Temperature: Groundwater temperature influences the solubility of oxygen, and therefore the rate of biodegradation is also affected by temperature. Within the plume of the solute, there may be an increase in temperature.

Conductivity: Conductivity can be used to indicate that samples are from the same hydrogeological zone though taken from different sampling points.

Chloride: concentration of chloride can be used as a proxy for fluid density and salinity.

Total dissolved solids (TDS): It can be used as the level of seawater intrusion.

Aquifer Test

Hydraulic conductivity is a significant parameter for the transport of the contaminants. Slug tests and aquifer pumping tests can be conducted to determine the hydraulic conductivity of the water-table aquifer in the study area. Hydraulic conductivity can also be measured in the laboratory with a permeameter on soils samples.

Observation Wells

The 3D characterization of petroleum contaminants in an aquifer is appropriately done using reliable and defensible data. Drilling of observation wells is needed for plume delineation (Figure 3). The properties of these observation wells are defined as follows (Beck and Mann 2010) (Figure 3):

1. Background well: For potential attenuation capacity and background groundwater chemistry, one or more wells can be chosen or drilled upgradient site of the contamination source. Natural hydrochemistry and concentrations of electon acceptors such as DO, NO_3, SO_4 in groundwater can be determined.
2. The maximum potential width of the plume can be established through the lateral delineation monitoring wells by drilling perpendicular to the flow direction of groundwater. In heterogeneous anisotropic system, lateral delineation can be highly variable.

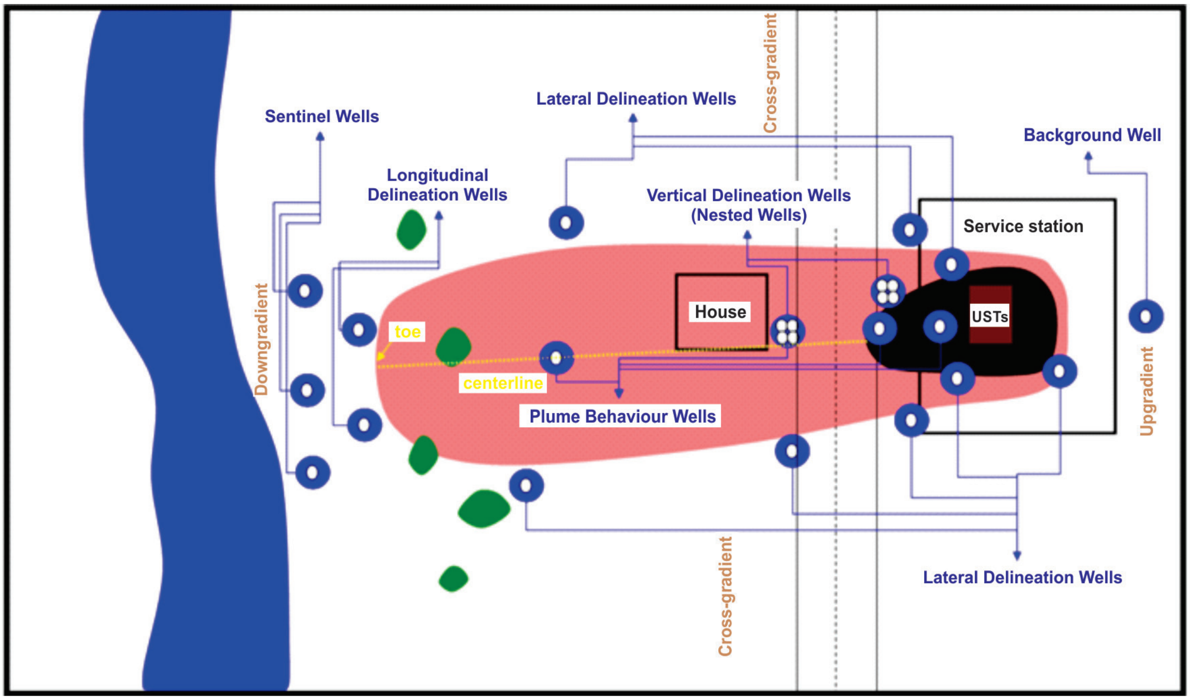

Figure 3. 3D delineation of the impact of petroleum hydrocarbon on groundwater sources using a typical observation well network (Beck and Mann, 2010).

Şekil 3. Petrol hidrokarbonunun yeraltı suyu kaynakları üzerindeki etkisinin tipik bir gözlem kuyu ağı kullanılarak 3 boyutlu olarak belirlenmesi (Beck ve Mann, 2010).

3. Plume centerline monitoring wells can be drilled from source to increasing distances on groundwater flow direction to assess changes of contaminant concentrations on down-gradient site of the source. These wells are located along the middle of the contamination plume, where the highest concntrations are expected.

4. Several source monitoring wells are drilled across the water table to allow screening and assessment of changes in mass loading and changes between trapped phase and free phase. This is controlled by several factors that include the velocity of the groundwater flow, product area, hydrogeochemical conditions, and mass loading and weathering.

5. The best location for drilling longitudinal delineation monitoring wells is contaminant plume toe in the direction of groundwater flow for determination of plume geometry changes and down gradient expands of the plume.

6. The best installation point for sentinel monitoring wells is near receptors, site boundaries or other designated compliance points. The implementation of the active remediation plans is made based on continuous detection of contaminant plume in these wells.

7. In case plume is suspected of sinking, vertical delineation monitoring wells can be drilled. This can be achieved using multi-level monitoring wells.

8. Other observation wells outside the contaminated area can be drilled for purposes of determining aquifer characteristics, groundwater sampling, and for groundwater level measurements.

Parameters and Their Measurement Methods

- Slug tests, pumping tests and permeameter tests for determining aquifer hydraulic characteristics;
- Grain size distribution analyses. Sieve analyses and hydrometer methods are used for determination of grain size distribution.
- Groundwater levels can be measured in observation wells at least for 4 rounds at approximately 6 months apart for fluctuations in groundwater elevation and flow direction.
- Major ion analyses of groundwater: These analyses can be conducted using Ion Cromotography.
- Heavy metals: These analyses can be conducted on selected samples using ICP-MS.

Determination methods of following parameters are compiled from ASTM 2010 and Wiedemeier, 1999b):

- Physical parameters of groundwater: Temperature, pH, electrical conductance (EC), dissolved oxygen (DO), and oxidation-reduction potential can be measured in the field in a flow-through cell which is a closed container with groundwater flowing in at the bottom and out at the top in such a way that no air is trapped inside (Weaver et al., 2007).
- Alkalinity: Alkalinity field test kit can be used.
- Background concentrations of electron acceptors: Mn^{2+}, NO_3, and SO_4 is determined in the field with colorimetric field kit.
- Metabolic byproduct Fe^{+2} is determined in the field with colorimetric method.
- Hydrocarbon analyses of groundwater and soil (BTEX): Purge and Trap Gas Chromotography is used for hydrocarbon analysis.
- Total organic carbon (TOC) of the soils aquifer matrix: Modified Mebius Procedure can be used for TOC.
- Methane: GC/FID method can be used for determination of methane contents.
- Sorption and retardation calculations: Organic carbon partitioning coefficient (K_{oc}) and total organic carbon (TOC) content of the aquifer matrix are used for contaminant sorption and retardation calculations.
- Contaminant sorption calculations can be made based on retardation coefficients (R_D), bulk density of the aquifer matrix, distribution coefficients (K_D) of contaminants, and aquifer porosity.
- Retardation coefficients (R_D): is determined based on bulk density, distribution coefficients K_D, and porosity.
- Bulk density: Bulk density of the aquifer matrix is determined based on laboratory samples and used in calculating retardation coefficients.
- Distribution coefficients (K_D) can be estimated from octanol-water partition coefficients (K_{oc}) and total organic carbon (TOC) content of the aquifer matrix.
- Octanol-water partition coefficients (K_{oc}) can be estimated from published values for individual contaminants.

- Porosity of the aquifer matrix is determined from laboratory samples and used in calculating retardation coefficients. Porosity will also be an input parameter in analytical and numerical models.
- Moisture content: can be measured using ASTM D-2216 method.

Task 3. Physical and Geochemical Characterization of the Study Area

The results of the field and laboratory investigations (Task 2) are used for physical and geochemical characterization of the site. Physical characteristics include topography and surface-water features, man-made features, and regional geology and hydrogeology. Site geology and hydrogeology will include lithology, stratigraphy, and grain-size distributions. Groundwater hydraulics will include water-table maps, flow directions and gradient, hydraulic conductivity, effective porosity, and specific yield for transient models, groundwater velocity, preferential flow paths, and groundwater use in the vicinity of the site. Climatological characteristics include evapotranspiration and rainfall for the site.

Geochemical characterization include delineating mobile and residual-phase LNAPLs that serve as sources of contamination dissolved in the groundwater. Groundwater chemistry includes dissolved-phase BTEX contaminants and inorganic and geochemical indicators of biodegradation. This include contour maps of BTEX, electron acceptors (dissolved oxygen, nitrate, manganese, and sulfate), metabolic by products (ferrous iron and methane), reduction/oxidation potential, alkalinity, pH, temperature, chloride, and total dissolved solids.

Calculations are made to investigate processes that affect contaminant concentrations and total mass of contaminants in the groundwater system. If LNAPLs remain at the site, fuel/water partitioning calculations is made to account for the partitioning from this phase into groundwater. Groundwater velocity calculations are made to account for the advective transport of dissolved contaminants. The mixing, i.e., hydrodynamic dispersion, that occurs downgradient from source areas in the direction of the advective velocity and also laterally and vertically to the direction of groundwater flow is investigated based on the plumes of BTEX contaminants and inorganic chemicals and geochemical indicators of biodegradation. Contaminant sorption and retardation calculations are based on aquifer matrix total organic carbon (TOC) content and the organic carbon partitioning coefficient (K_{oc}) for each contaminant. Biodegradation calculations are based on decay rates for aerobic respiration, denitrification, reduction of ferric (III) iron, sulfate and methanogenesis.

Task 4. Groundwater Model

Monitored natural attenuation can be simulated and evaluated using a solute fate and transport model. Analytical and numerical models that include the transport processes advection, dispersion, retardation, and biodegradation is used for this task. Appropriate analytical solutions is used for preliminary analysis of BTEX concentrations in the groundwater at the site; this involve consideration of one-dimensional (e.g., Bear, 1972; Van Genuchten and Alves 1982, and Wexler 1992), two-dimensional (Wilson and Miller, 1978), and three-dimensional (Domenico, 1987) analytical solutions to the contaminant transport equation. A three-dimensional numerical code such as RT3D (Clement, 1997) can be selected to develop a model of contaminant transport for the site.

This code was originally developed to support transport of contaminant modeling at natural attenuation demonstration sites (Lu et al., 1999; Clement et al., 2000), and the current version of this code is fully supported by the Pacific Northwest National Laboratory in Richland, Washington, USA. However, if it is determined that the advection and dispersion processes have been significantly affected by saltwater intrusion at the coastal boundary, resulting in a variable-density groundwater velocity flowfield, it may be necessary to consider using a more complex code such as PHWAT (Mao et al. 2006), which couples the variable-density transport code SEAWAT (Guo and Langevin, 2002) and PHREEQC-2 (Parkhurst and Appelo, 1999).

The hydrogeologic setting at the site is conceptualized and the groundwater model is constructed based on the conceptual model that was developed according to the characterization. Starting values for the groundwater model parameters is based on the field and laboratory investigations (Task 2) and the physical and geochemical characterization of the study area (Task 3). The three-dimensional distribution of mobile and residual LNAPLs will be delineated to define the source area(s) for the plume of BTEX contaminants dissolved in the groundwater. The groundwater model is calibrated by comparing observed and calculated values for hydraulic heads and plumes for BTEX and other constituents such as dissolved oxygen, nitrate, ferrous iron, sulfate and methane. A sensitivity analysis is conducted to determine the effects of the uncertainties in aquifer and geochemical parameters, particularly hydraulic conductivity and reaction rates, have on concentrations of BTEX and the other constituents.

Task 5. Evaluation of Monitored Natural Attenuation

The determination of whether natural attenuation is occurring at the aquifer is based on primary and secondary lines of evidence established during the investigation (ASTM, 2010). The primary line of evidence, which is a stable or shrinking plume rather than an expanding plume, will be the BTEX contour maps prepared as a result of the groundwater sampling. Secondary lines of evidence, which include geochemical data that serve as indicators of naturally occurring biodegradation and estimates of natural attenuation rates (Wiedemeier et al.,1996), is based on electron acceptor/reduction product concentrations of oxygen, nitrate, manganese (II), iron (II), sulfate, and methane measured within the BTEX plume. For example, depletions in dissolved oxygen, nitrate, and/or sulfate and increases in dissolved manganese, iron, and methane in the dissolved plume will indicate that biodegradation is occurring (Beck and Mann, 2010). The groundwater modelling results is used to help decide whether the monitored natural attenuation process results in BTEX contaminant levels declining to acceptable levels within a specified time. If projections of contaminant levels based on the model results indicate that this objective cannot be met, then additional remedial alternatives is recommended for further investigation. Along with continued intrinsic remediation, these additional alternatives would include options such as excavation of contaminated soils, complete LNAPL recovery, pumping and treating, bioslurping (vacuum-enhanced recovery), enhanced bioremediation (inducing air or oxygen into the unsaturated zone), air sparging (injecting air into contaminated groundwater), bioventing, and installation of reactive barriers.

CONCLUSION

Coastal regions have high population density which increase the use of petroleum products. The uses of petroleum products in these areas cause the contamination of groundwater sources and therefore posing a serious health and environmental problem. To address the pollution problem, several technologies have been developed. This paper focused on natural attenuation process.

Natural attenuation makes use of biological, chemical or physical processes to mitigate pollution by transforming organic pollutants into inorganic substances. Natural attenuation is energy saving, economical and environmentally friendly. Natural attenuation of BTEX compounds involves biodegradation in which petroleum hydrocarbons are broken down by microbially-facilitated chemical reactions to reduce their concentration in groundwater. Biodegradation involves either aerobic or anaerobic respiration. In aerobic respiration, the electron sink or acceptor is molecular oxygen. When molecular oxygen is lacking or insufficient, other compounds such as (NO_3), manganese (Mn^{+4}), ferric iron (Fe^{+3}), sulfate (SO_4^{-2}) or carbon dioxide (CO_2) act as terminal electron acceptors and facilitate anaerobic respiration of BTEX in the prescribed order. In aerobic respiration, BTEX react with oxygen and produces water and carbon dioxide only while in anaerobic respiration, BTEX react with an electron acceptor (NO_3, Mn^{+4}, Fe^{+3}, SO_4^{-2}, or CO_2) to produce water, carbon dioxide, and a reduced electron acceptor. Biodegradation of petroleum hydrocarbons in groundwater sources is influenced by other factors such as contaminant concentration and composition, nutrients, pH value, physical and chemical characteristics, and the history of the contaminated environment regarding pollution.

The paper describes the stages to determine the spatial distribution of petroleum hydrocarbon contamination and modeling. First stage includes realistic development of conceptual model of the site including hydrogeologic characteristics and contamination history of the site and applied past or current remedial activites. Second stage includes field and laboratory investigations to collect data for field and laboratory analyses with soil and groundwater sampling techniques including conventional soil borings, monitoring well installation, and water quality sampling to determine nature and extent of the contamination. Third stage includes physical and geochemical characterization of the site according to the result of the field and laboratory investigations. Site geology and hydrogeology is determined in detail. Dissolved phase BTEX contaminants and inorganic and geochemical indicators of biodegradation are defined. Calculations is made to investigate processes that affect contaminant concentrations in groundwater; fuel/water partitioning calculations is made to account for the partitioning; groundwater velocity calculations is made to account for the advective transport of dissolved contaminants, contaminant sorption and retardation calculations are made. Hydrodynamic dispersion is investigated based on the plumes of BTEX contaminants and inorganic chemicals and geochemical indicators of biodegradation. Fourth stage includes groundwater model. This stage describes simulation of the monitored natural attenuation using a solute fate and transport model. Analytical and numerical models are used including the transport processes advection, dispersion, retardation, and biodegradation. At the last stage monitored natural attenuation is evaluated. Primary and secondary lines of evidences are used for the determination of whether natural attenuation is occurring at the aquifer. BTEX contour maps are used for primary lines of evidence. If the plume is shrinking or stable, it indicates that biodegradion is occurring. Geochemical data is used for secondary lines of evidence. Depletions in dissolved oxygen, nitrate, sulfate and increases in dissolved manganese, iron, and methane in the dissolved plume indicate that biodegradation is occurring. The groundwater modeling results are used for whether the BTEX contaminant levels declining to acceptable levels with natural attenuation. In other case other remedial techniques should be considered.

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