Natural Attenuation of Hydrocarbon Compounds in Groundwater

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Contents

Abstract

Natural attenuation (NA) is a widely used strategy for the risk-based management of groundwater contaminated with hydrocarbons. New process-based conceptual models highlight the spatial distribution of biodegradation processes in plumes, controlled by microbial activity, electron acceptor bioavailability, and aquifer properties, as a key control on NA performance. The plume fringe is identified as a critical interface for enhanced microbial activity and biodegradation of hydrocarbons in plumes. Mass transport and process heterogeneity in aquifers must be adequately resolved to ensure reliable estimates of hydrocarbon attenuation. The adoption of mass discharge as a performance measure and use of high-

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resolution multilevel monitoring devices is recommended to address these issues. These concepts are illustrated with a case study example. Stable isotope methods are important tools in NA assessments and, when combined with hydrochemical analyses, offer new possibilities to characterize contaminant sources, biodegradation pathways, redox processes, element cycling, the relative contribution of different attenuation processes, and quantify biodegradation of hydrocarbons in groundwater.

1   Introduction

Natural attenuation (NA) of polluted subsurface environments refers to naturally occurring physical, chemical, and biological processes which occur in situ and act, in isolation or combination, without human intervention to reduce the mass, toxicity, mobility, flux, volume, or concentration of contaminants in soil and groundwater (Wiedemeier et al. 1995; ASTM 1998; U.S. EPA 1998a, b; Environment Agency 2000; McLaughlan et al. 2006). These in situ processes include biodegradation, abiotic degradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction (U.S. EPA 1999; Wiedemeier et al. 1999; McLaughlan et al. 2006; Rivett and Thornton 2008). The technical application of NA processes for the management of soil and contaminated groundwater is termed *monitored natural attenuation* (MNA). This emphasizes rigorous performance assessment of NA using appropriate monitoring strategies and analytical tools to demonstrate an acceptable reduction in environmental risk at a specific compliance point or receptor within a reasonable timeframe (U.S. EPA 1998a; Environment Agency 2000; Rügner et al. 2006). Example receptors include humans (by direct exposure), potable water supply wells, and surface water bodies, whereas the legal boundary of a site is a typical compliance point, although many other examples may be identified in specific circumstances. Different receptors may be identified at various stages in the management of a contaminated site, during future site development or use and for different contaminants, according to their properties. While NA can be implemented to manage inorganic contaminants in both soil and groundwater, this chapter describes the theoretical concepts and practical application for hydrocarbon compounds in groundwater. These are illustrated by reference to petroleum hydrocarbons, a common pollutant in groundwater, but also underpin the implementation of NA for other similar organic compounds (e.g., polyaromatic hydrocarbons, diesel, phenols, coal tar compounds). The reader is referred to other texts for the assessment of NA in soils (Mulligan and Yong 2004; Khan et al. 2011), for chlorinated organic compounds (RTDF 1997; U.S. EPA 1998b; Environment Agency 1999; Wiedemeier et al. 1999) and for inorganic compounds (U.S. EPA 2007a, b).

Scientifically and operationally NA is distinct from bioremediation in that only biological processes are considered in bioremediation, whereas these contribute with many other nonbiological processes to NA (Alvarez and Illman 2006; U.S. EPA

2006; Rivett and Thornton 2008). The key technical components underpinning the implementation of NA for groundwater are (i) a site-specific risk assessment, (ii) development of a conceptual model which describes NA processes and translation of this understanding into a mathematical model for prediction, and (iii) demonstration and performance assessment of NA against stated site management and remediation objectives (Wiedemeier et al. 1999; Environment Agency 2000; Alvarez and Illman 2006; McLaughlan et al. 2006). The risk assessment seeks to identify the relevant contaminant linkage(s) in terms of the source-pathway-receptor (or target) framework (Environment Agency 2006). Characterizing the source (e.g., type, form, distribution, quantity of contaminants) and quantifying NA processes along the pathway (e.g., aquifer) are critical to the robust prediction of potential impacts on receptors, risk reduction, and effectiveness of NA in groundwater. If this analysis indicates remediation is necessary at a site, then the identified risks can be mitigated to an acceptable level by reducing the source mass or concentration, and/or reducing the flux of contaminants or preventing migration along the pathway, and/or removing or isolating the receptor. In most cases source reduction measures will be required to support the implementation of NA for contaminated groundwater, to ensure the achievement of remediation objectives in reasonable timescales (Environment Agency 2000; Chapelle et al. 2003).

2 Conceptual Model for Natural Attenuation of Hydrocarbons in Groundwater

Groundwater contamination by hydrocarbons originates from sources (e.g., leaking underground storage tanks, pipeline distribution systems, refining facilities, coal-gasification and chemical manufacturing plants, fuel transportation, and waste disposal practices) that release pure or dissolved phase hydrocarbon compounds to soil or the unsaturated zone. The dissolved phase compounds migrate to the water table in recharge water, which infiltrates the unsaturated zone. Pure liquids move under gravity to the water table, where they either form an immiscible phase in the capillary fringe if less dense (light nonaqueous phase liquid, LNAPL) than water (e.g., petroleum fuel) (CL:AIRE 2014), or migrate below the water table if more dense (e.g., coal tar) (Environment Agency 2003). The constituent compounds also dissolve into groundwater, limited thermodynamically by their effective solubility in the mixture (Thornton et al. 2013).

A general conceptual model of a contaminant plume formed in groundwater from a release of hydrocarbons is shown in Fig. 1. The plume is shown within the Source-Pathway-Target risk assessment framework. It is created by the continuous dissolution of organic compounds from the hydrocarbon source and transport of these to the water table, where groundwater advection and dispersion distribute the mass down hydraulic gradient of the release point. The plume source geometry and composition, ambient flow field, physical heterogeneity of the aquifer, and availability of electron acceptors for biodegradation exert an important control on the spatial and temporal distribution of hydrocarbon compounds in groundwater. Volatilization may reduce
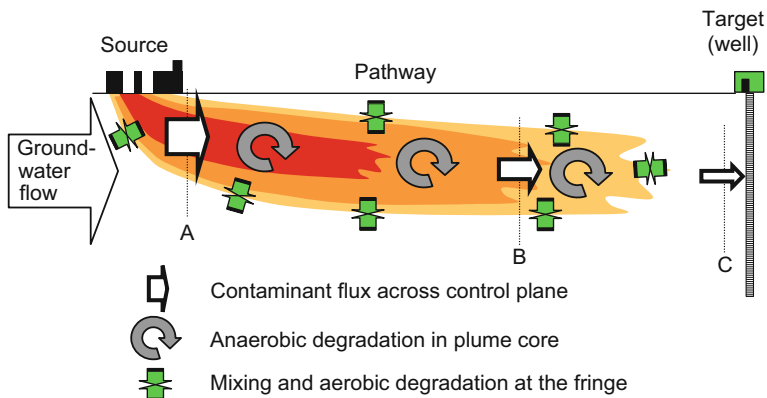
Fig. 1 Conceptual model for natural attenuation of hydrocarbon compounds in groundwater, in which contaminant fluxes are reduced during flow from a source along the aquifer pathway to a receptor by a combination of spatially distributed aerobic and anaerobic biodegradation processes, as shown

the concentration of dissolved contaminants in groundwater, where the plume is located at the water table (CL:AIRE 2014). Other abiotic processes such as sorption contribute to the attenuation of hydrocarbon compounds by slowing (retarding) their migration in the plume, according to the contaminant-specific properties (e.g., relative hydrophobicity) and the aquifer geochemistry (Schwarzenbach et al. 2003). When originating from a single source area, the plume boundary is usually sharply defined by transverse dispersion in the aquifer, a process which induces mixing of the contaminated and uncontaminated groundwater. Dispersion is controlled by the aquifer physical properties and is important in diluting the contaminant concentrations and supplying dissolved electron acceptors for biodegradation in the plume (Chapelle et al. 2003; McLaughlan et al. 2006). In most cases, biodegradation of hydrocarbons at the plume fringe will largely be limited by the small magnitude of transverse dispersion in aquifers (Lerner et al. 2000; Thornton et al. 2001a, b; Rahman et al. 2005; Watson et al. 2005; Gutierrez-Neri et al. 2009). However, in general biodegradation is usually more important than either physical or chemical processes for the natural attenuation of hydrocarbon compounds in groundwater.

Contaminated groundwater is transported from the source at A, through the plume B, to the receptor at C. If the flux and concentration of pollutants measured across the *control planes* is reduced sufficiently to make the risks to the receptor acceptably low, then NA is considered to be successful. The control planes are virtual points of reference, used at different locations along the plume flowpath to estimate the change in contaminant concentration or flux over the distance between them. This measure is used in more sophisticated monitoring strategies to assess the performance of NA for site management (see Sect. 5). Biodegradation of the organic contaminants by aerobic respiration, nitrate reduction, and sulfate reduction using dissolved electron acceptors (O_2, NO_3, SO_4) will occur at the periphery or *fringe* of the plume, driven by mixing between the plume and background groundwater (Lerner et al. 2000; Thornton et al. 2001a; Bauer et al.

2008; Gutierrez-Neri et al. 2009; Eckert et al. 2015). Slower anaerobic biodegradation by manganese reduction, iron reduction, and methanogenesis will occur inside the plume core, using mineral Mn and Fe oxide fractions on the aquifer sediment and fermentation processes. Generally, microbial activity and biodegradation processes at the plume fringe are more important for attenuation than processes occurring in the plume core (Thornton et al. 2001b; McLaughlan et al. 2006; Tuxen et al. 2006; Bauer et al. 2008; Tischer et al. 2013; Eckert et al. 2015). The plume will increase in length until a steady state is reached, in which the contaminant flux from the source is balanced by the rate of attenuation from the combined fringe mixing-controlled and the slower internal reactions (Chapelle et al. 2003; Gutierrez-Neri et al. 2009). Source management measures are typically implemented with NA to both reduce the duration and steady-state length of the plume (McLaughlan et al. 2006). If the source is depleted (e.g., by natural weathering) or removed through source management measures (e.g., remediation), the plume may become detached from the source and migrate down hydraulic gradient as a separate entity (Wiedemeier et al. 1999).

3 Sorption of Hydrocarbon Compounds in Groundwater

Sorption of dissolved hydrophobic hydrocarbons in groundwater is generally well described by the partitioning of the organic compound within the particulate organic matter fraction of the aquifer sediment (Schwarzenbach et al. 2003; Chapelle et al. 2003). At the low dissolved concentrations of organic chemicals typically found in most plumes, this process can be described by a linear isotherm and estimated from laboratory batch sorption tests or using empirical relationships (McLaughlan et al. 2006):

$$K_d = K_{oc} \cdot f_{oc}$$

where K_d is the distribution coefficient of the organic chemical between the groundwater and aquifer at equilibrium (L^3/M), K_{oc} is the distribution coefficient of the organic chemical normalized to the total organic carbon content (L^3/M), and f_{oc} is the fraction of organic carbon present in the aquifer material (fraction). Other relationships have been developed to estimate K_d according to the fundamental properties of the organic chemicals, such as their octanol-water partition coefficient, K_{ow} (Fetter 2001), and also extended to predict sorption at higher concentrations using Freundlich and Langmuir isotherms (Schwarzenbach et al. 2003). The transport of organic chemicals in a plume can then be estimated according to the following relationship:

$$R_f = 1 + \frac{\rho_b K_d}{\theta}$$

where R_f is the retardation factor for the organic chemical, relative to the groundwater velocity [dimensionless], ρ_b is the bulk density of aquifer material (M/L^3), and θ is the porosity of the aquifer material (fraction).

Table 1 Relative mobility of common organic chemicals in groundwater

Compound	Solubility (ppm)	K_{oc}	Mobility class
Acetone	Miscible	1	Very high
2-Methylphenol (*o*-cresol)	31,000	15	Very high
4-Methylphenol (*p*-cresol)	24,000	17	Very high
2,4-Dimethylphenol (2,4-xylenol)	17,000	21	Very high
Phenol	82,000	27	Very high
2-Chlorophenol	11,087	27	Very high
Benzene	1,780	97	High
Toluene	500	242	Moderate
o-Xylene	170	363	Moderate
p-Xylene	156	552	Low
m-Xylene	146	588	Low
Ethylbenzene	150	622	Low
3,5-Dimethylphenol (3,5-xylenol)		1,038	Low
2,6-Dimethylphenol (2,6-xylenol)		1,060	Low
Naphthalene	32	1,300	Low
Phenanthrene	1.3	23,000	Immobile

Data source: Fetter (2001)

Sorption results in retardation of contaminants relative to the groundwater velocity and limits plume migration until it reaches steady state (Chapelle et al. 2003). It can be important for the NA of more hydrophobic hydrocarbon compounds in aquifers with relatively higher particulate organic carbon (e.g., alluvial and carbonaceous materials). Table 1 compares the relative mobility of organic chemicals in groundwater, according to their solubility and respective K_{oc} value. More soluble organic chemicals (e.g., phenol and cresols) are highly mobile in groundwater and typically migrate further from the point of release, whereas polyaromatic hydrocarbons (e.g., naphthalene and phenanthrene) have relatively limited mobility and may be restricted to the plume source area. This knowledge helps inform monitoring programs for NA, by identifying the expected type and spatial distribution of organic chemicals which may be present in groundwater, according to the known source composition (e.g., a release of coal tar vs. gasoline).

4   Biodegradation of Hydrocarbon Compounds in Groundwater

Biodegradation of hydrocarbon compounds in groundwater occurs by aerobic and anaerobic pathways, coupled to the reduction of dissolved electron acceptors (oxygen, nitrate, sulfate, and carbon dioxide) and mineral oxidants (manganese and iron oxides) on the aquifer sediment (Chapelle 1993; Borden 1994). In most cases, biodegradation of these compounds occurs through primary metabolism, in which the microorganisms use the hydrocarbon compounds as carbon and energy sources

(Wiedemeier et al. 1999), although co-metabolism is also important (Borden 1994; Alvarez and Illman 2006). The various pathways by which hydrocarbon compounds can be biodegraded in groundwater to organic intermediates or mineralized to carbon dioxide and the microorganisms responsible have been extensively studied. A detailed analysis of these is outside the scope of this chapter, but can be found in many excellent reviews (Smith 1991; Cerniglia 1992; Harayama and Timmis 1992; Haritash and Kaushik 2009). This section describes the biogeochemical processes which develop in hydrocarbon-contaminated groundwater as a basis to interpret and predict the natural attenuation of these compounds.

Molecular oxygen is used by aerobic bacteria as the terminal electron acceptor for respiration, whereas both facultative and obligate anaerobic microorganisms can facilitate anaerobic oxidation of hydrocarbons (Borden 1994). For a given oxidizable substrate (i.e., hydrocarbon compound), these electron acceptors are typically consumed in the order oxygen, nitrate, Mn-oxide, Fe-oxide, sulfate, and carbon dioxide, according to the decreasing energy yield to microorganisms mediating the reactions (Chapelle 1993; Reinhard 1994). The microorganisms release this energy by coupling the oxidation of an electron donor (the hydrocarbon compound) with the reduction of an electron acceptor in a redox reaction. The specific energy yield of a redox reaction can be quantified using the Gibbs free energy of the reaction (ΔG_r^o). Calculated values of ΔG_r^o for selected electron acceptor and electron donor (hydrocarbon compound) half-cell reactions are shown in Table 2 and expressed per mole e- transferred. Coupled redox reactions are expected to occur in the order of their thermodynamic energy yield, provided microorganisms facilitating each reaction are present and there is adequate supply of electron acceptors for biodegradation. For a given redox condition and availability of electron acceptors, this implies a preferred order of hydrocarbon biodegradation in mixtures. For example, aerobic respiration of BTEX would theoretically occur in the order B > T = E > X, although other factors (e.g., presence of competing substrates and viable microorganisms supporting biodegradation) may affect this sequence (Environment Agency 1999; Wiedemeier et al. 1999; Spence et al. 2005).

In hydrocarbon-contaminated aerobic groundwater, these microbially mediated reactions create a characteristic sequence of spatially and temporally dynamic redox processes, comprising successive zones of predominantly aerobic respiration, denitrification, Mn/Fe-reduction, sulfate reduction, and methanogenesis along the flowpath from the plume source (Chapelle 1993; Borden 1994; Williams et al. 2001). Characteristically this creates steep biogeochemical gradients across the plume fringe, driven by microbial activity and consumption of electron acceptors, where hydrocarbon biodegradation is enhanced (Thornton et al. 2001a; Thornton et al. 2014; Tuxen et al. 2006; Prommer et al. 2009; Tischer et al. 2013). The development of these redox zones (Fig. 2) is sustained by the supply of hydrocarbon (and other oxidizable) compounds from the plume source and the availability of both dissolved and mineral-based electron acceptors in the aquifer. This is critical for the natural attenuation of hydrocarbons in groundwater, given that biodegradation of specific compounds may only occur under specific redox conditions (Borden et al. 1997; Wiedemeier et al. 1999; Banwart and Thornton 2003, 2010; Wilson et al. 2004).

Table 2 Gibbs free energy of reaction for electron donor and electron acceptor half-cell reactions for selected hydrocarbon compounds

Species	ΔGro (kJ/mol e$^-$)	Electron donor half-cell reaction[a]	Species	Electron acceptor half-cell reaction[b]	ΔGro (kJ/mol e$^-$)
Benzene	−29.44	$C_6H_6 + 12H_2O > 6CO_2 + 30H^+ + 30e^-$	Hexachlorobenzene[c]	$2e^- + H^+ + C_6Cl_6 > C_6HCl_5 + Cl^-$	−39.33
Toluene	−28.91	$C_7H_8 + 14H_2O > 7CO_2 + 36H^+ + 36e^-$	Tetrachlorobenzene[c]	$2e^- + H^+ + C_6H_2Cl_4 > C_6H_3Cl_3 + Cl^-$	−36.40
Ethylbenzene	−28.91	$C_8H_{10} + 16H_2O > 8CO_2 + 42H^+ + 42e^-$	Trichlorobenzene[c]	$2e^- + H^+ + C_6H_3Cl_3 > C_6H_4Cl_2 + Cl^-$	−34.73
m-Xylene	−28.62	$C_6H_4(CH_3)_2 + 16H_2O > 8CO_2 + 42H^+ + 42e^-$	**Redox process[d]**		
1,2,4-Trimethylbenzene	−28.43	$C_6H_3(CH_3)_3 + 18H_2O > 9CO_2 + 48H^+ + 48e^-$	Aerobic respiration	$4e^- + 4H^+ + O_2 > 2H_2O$	−77.40
Phenol	−30.81	$C_6H_6O + 11H_2O > 6CO_2 + 28H^+ + 28e^-$	Denitrification	$5e^- + 6H^+ + NO_3^- > N_2 + 3H_2O$	−70.71
Naphthalene	−28.82	$C_{10}H_8 + 20H_2O > 10CO_2 + 48H^+ + 48e^-$	Mn(IV) reduction	$2e^- + 4H^+ + MnO2(s) > Mn^{2+} + 2H_2O$	−36.03
Tetrachlorobenzene[c]	−51.86	$C_6H_2Cl_4 + 12H_2O > 6CO_2 + 26H^+ + 4Cl^- + 22e^-$	Fe(III) reduction	$e^- + 3H^+ + FeOOH > Fe^{2+} + 2H_2O$	−64.62
Trichlorobenzene[c]	−44.49	$C_6H_3Cl_3 + 12H_2O > 6CO_2 + 27H^+ + 3Cl^- + 24e^-$	Sulfate reduction	$8e^- + 8H^+ + SO_4^{2-} > S^{2-} + 4H_2O$	22.45
Dichlorobenzene[c]	−38.41	$C_6H_4Cl_2 + 12H_2O > 6CO_2 + 28H^+ + 2Cl^- + 26e\text{-}$	Methanogenesis	$8e^- + 8H^+ + CO_{2(g)} > CH_{4(g)} + 2H_2O$	24.95
Chlorobenzene[c]	−33.51	$C_6H_5Cl + 12H_2O > 6CO_2 + 29H^+ + Cl^- + 28e^-$			
Carbohydrate	−41.84	$CH_2O + H_2O > CO_2 + 4H^+ + 4e^-$			

[a]Electron donor half-cell reactions define the relevant species which will be oxidized in a redox reaction involving an electron acceptor

[b]Electron acceptor half-cell reactions define the relevant species which will be reduced in a redox reaction involving an electron donor

[c]Chlorobenzene compounds are chlorinated aromatic hydrocarbons which can be biodegraded and biotransformed in redox reactions as an electron donor or electron acceptor, according to the relative oxidation status of the compound

[d]Common redox processes in hydrocarbon-contaminated aquifers, presented as generic electron acceptors which participate in the reduction of organic and inorganic electron donors
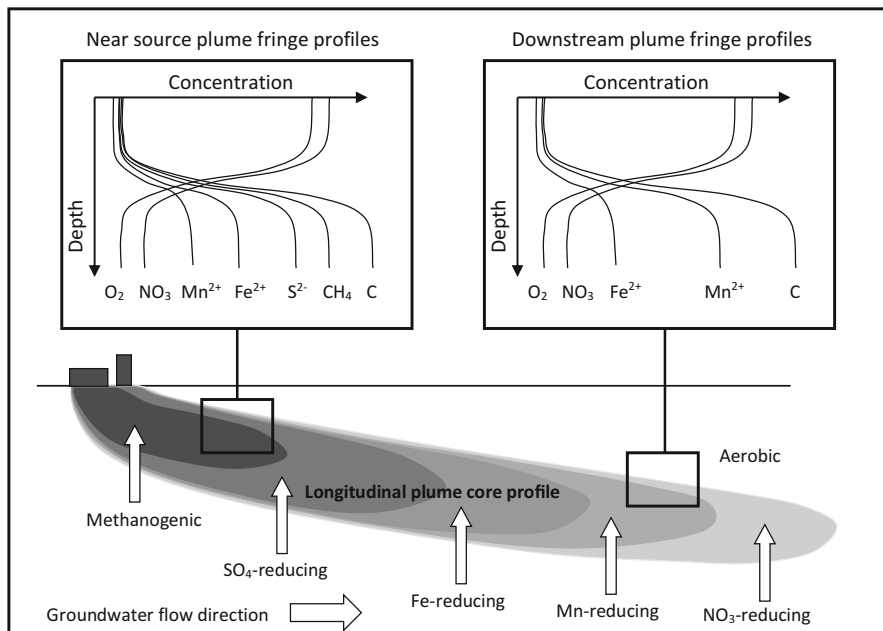
Fig. 2 Idealized conceptual model in longitudinal section and vertical profile of redox zone distribution in groundwater for a typical plume of oxidizable hydrocarbon compounds

The aquifer oxidation capacity (OXC) provides a convenient measure of the total reservoir of electron acceptors from all sources that can support hydrocarbon biodegradation in a per unit volume of aquifer (Heron et al. 1994). This is given by:

$$OXC = 4[O_2(aq)] + 5[NO_3(aq)] + 2[MnO_2(s)] + [FeOOH(s)] + 8[SO_4(aq)] + 8[CO_2(aq)]$$

where [ ] denotes concentration or mass in moles, (aq) denotes aqueous concentration, and (s) denotes solid mineral species. A key assumption of this analysis is that all electron acceptors are available for biodegradation. However, biodegradation using dissolved electron acceptors is potentially limited by the relatively low solubility of oxygen or rate of mass transfer of oxygen, nitrate, and sulfate into the plume by dispersion (Thornton et al. 2001a, b; 2014). Moreover, while aquifer sediments typically have a significant reservoir of mineral-bound electron acceptors as Mn- and Fe-oxides, only the easily reducible amorphous forms will contribute oxidation capacity for hydrocarbon biodegradation in groundwater (Borden 1994; Wiedemeier et al. 1999; Banwart and Thornton 2003; Thornton et al. 2011). Estimates of OXC therefore represent an upper limit on the maximum concentration of hydrocarbons that can be biodegraded according to the theoretical consumption of the total mass of electron acceptors in the aquifer.

5   Performance Assessment of Natural Attenuation for Hydrocarbon Compounds

The performance assessment of natural attenuation for hydrocarbons in groundwater aims to (i) characterize the nature and spatial extent of in situ biodegradation processes for the hydrocarbons, (ii) estimate hydrocarbon biodegradation rates, and (iii) confirm NA occurs at a rate which will reduce environmental risk, protect identified receptors, and achieve site management/remediation objectives. It also identifies the need for additional measures if NA will not achieve remediation requirements in isolation. These aims are fulfilled through an intensive long-term monitoring program of groundwater quality and source composition, supported by a technically rigorous evaluation of the site investigation and groundwater quality data, as documented in relevant technical protocols and guidance (AFCEE 1995; Buscheck and O'Reilly (1995); ASTM 1998; Environment Agency 1999, 2000; U.S. EPA 1999; Wiedemeier et al. 1999; CGER 2000). Current best practice for the performance assessment of NA may involve the integrated analysis of hydrochemical, isotopic, microbiological, and other data using a wide range of qualitative and quantitative techniques (reviewed in Bombach et al. (2010) and Hunkeler and Aravena (2010)) at different scales (Table 3) to document the occurrence and extent of hydrocarbon attenuation by in situ processes.

This analysis is formalized within a "lines of evidence" framework, which includes the collection of different types of information (AFCEE 1995; ASTM 1998; U.S. EPA 1998a, b; Wiedemeier et al. 1999; Environment Agency 1999, 2000; National Academy of Sciences 2000; Alvarez and Illman 2006; McLaughlan et al. 2006):

- **Primary line of evidence**: Field time-series data showing a consistent reduction in the contaminant concentration or flux over time at one or more points along the source-pathway-receptor linkage, typically used to deduce the status of the plume (i.e., expanding, stable or shrinking), relative to predictions of groundwater flow
- **Secondary line of evidence**: Field data demonstrating in situ biodegradation of hydrocarbons in the plume, typically based on the consumption of dissolved (e.g., O_2, NO_3, SO_4) and mineral phase (e.g., MnO_4, FeOOH) electron acceptors in the aquifer and corresponding increase in organic metabolites, inorganic reaction products (e.g., Mn^{2+}, Fe^{2+}, HS^-), and other chemical species (e.g., dissolved CO_2 and CH_4) that verify different biodegradation processes
- **Tertiary line of evidence**: Supporting evidence related to the verification of natural attenuation processes, such as laboratory microcosm studies to quantify biodegradation rates, confirmation of biodegradation mechanisms and pathways using stable isotope analysis, or the use of molecular biological techniques to demonstrate the activity of appropriate hydrocarbon-degrading microorganisms

Not all lines of evidence are required in every case, but rather an appropriate level of data collection and interpretation will apply. However, this analysis will typically include mathematical modeling studies to verify the site conceptual model

Table 3 Data collection and analysis typically used for the performance assessment of hydrocarbon natural attenuation in groundwater

Indicator or measurement	Basis for performance assessment
Hydrochemical-based	
Decreased electron acceptor concentration	Utilization by microorganisms during biodegradation of specific hydrocarbons
Increased inorganic carbon concentration	Production from biodegradation and mineralization of hydrocarbon compounds and organic metabolites
Stoichiometry and mass balance between reactants and products	Balanced consumption of electron acceptors and organic compounds (hydrocarbons and relevant organic metabolites) during biodegradation under specific redox conditions
Increased concentrations of intermediate-stage and final products	Identification of specific biodegradation pathways and transformation for hydrocarbons
Increased ratio of transformation products to parent compounds	Progressive biodegradation of parent compound to metabolite over space and time
Decreased ratio of reactant to inert tracer	Preferential biodegradation of hydrocarbon species relative to a nonreactive species in the same mixture, accounting natural attenuation due to abiotic processes
Relative rates of transformation of different hydrocarbons consistent with laboratory data	Independent confirmation of biodegradation potential at field-scale based on controlled laboratory studies
Stable isotope-based	
Changes in carbon, chloride, and hydrogen isotope ratios of specific organic contaminants (depending on respective chemical group), and isotope ratios of electron acceptors and inorganic carbon in CO_2 and CH_4	Biodegradation of specific organic compounds (if based on compound-specific isotope analysis, CSIA), biodegradation of nonspecific compounds (if based on total dissolved carbon isotope ratios), and specific redox processes (if based on isotope ratios of electron acceptors)
Microbiological-based	
Increased number of (live/active) bacteria in hydrocarbon plume	Increase in size of viable microbial community for in situ biodegradation
Increase in relative abundance of known degraders in hydrocarbon plume	Increased contribution of specific microorganisms within community with capability for hydrocarbon biodegradation
Increase in abundance of genes associated with biodegradation in hydrocarbon plume	Development of metabolic pathways in microorganisms which enable biodegradation of specific hydrocarbons

underpinning the interpretation and to predict the long-term behavior of the plume for site management. Primary and secondary lines of evidence are obtained from the distribution of dissolved reactants along the plume flowpath, using groundwater samples collected from monitoring wells in the plume source area, uncontaminated and contaminated sections of the aquifer. The plume is presumed to have a center-line, characterized by the monitoring wells, for this analysis. Visual, graphical, and quantitative methods, including regression techniques, statistical analyses, and mass

balances (e.g., Table 3), are available to interpret these data using concentration versus time and concentration versus distance plots (see Wiedemeier et al. 1999; Environment Agency 2000; Alvarez and Illman 2006 for summary). An important objective is the estimation of plume-scale contaminant biodegradation rates from this analysis, often assumed to follow first-order kinetics for mathematical simplicity and use in numerical reactive transport codes (Buscheck and Alcantar 1995; Suarez and Rifai 1999; Beyer et al. 2007). Similarly, the maximum steady-state plume length and time to plume stabilization must also be predicted, usually to evaluate receptor impacts and remediation timescales. Various mathematical approaches and modeling tools have been developed to undertake this for hydrocarbons plumes, based on different conceptual models of plume development, substrate mixtures, and biodegradation processes (Chapelle et al. 2003; Atteia and Guillot 2007; Gutierrez-Neri et al. 2009).

A relatively sophisticated site assessment and monitoring program is required to verify the effectiveness of NA for hydrocarbons in groundwater (Wiedemeier et al. 2006). This is because the technical appraisal relies primarily on the evaluation of subsurface transport and biodegradation processes using the aquifer characteristics and groundwater quality data. However, data quality can be strongly influenced by heterogeneity in the spatial and temporal distribution of contaminants, geological and hydrogeological properties, and biodegradation processes, which must be resolved for correct performance assessment of NA. These issues are incorporated in the concepts of *mass transport heterogeneity* and *process heterogeneity*, which must be resolved in NA assessments.

5.1   Mass Transport Heterogeneity

Mass transport heterogeneity results from the spatial and temporal variability in contaminant distribution and plume development due to the combined effects of variation in plume source term (composition and location) aquifer properties (geological structure, stratigraphy and geochemistry) and hydrogeology (recharge, groundwater flow direction). The effect of these factors on plume development is illustrated by considering a series of generic plume scenarios (not exhaustive of all possible scenarios), shown in Fig. 3. If the plume has a unique or representative centerline that can be identified (Fig. 3a), then centerline monitoring may be possible and a pseudo-first-order contaminant biodegradation rate estimated from the contaminant concentration versus distance profile (Buscheck et al. 1995; Wiedemeier et al. 1999). However, where a plume has a single dominant flowpath (i.e., a centerline), it may be missed by monitoring wells installed using an assumed, but incorrect, groundwater flow direction or if there is periodic lateral migration of the plume due to seasonal (or induced) variations in groundwater flow direction (Fig. 3b). Furthermore, macroscale physical heterogeneity (e.g., buried stream channels) may result in a "centerline" that deviates according to the subsurface geological structure (Fig. 3c) (Mackay et al. 2001). Rather than follow a unique centerline, contaminants may be transported along a "flowpath" within a series of relatively discrete plumes of
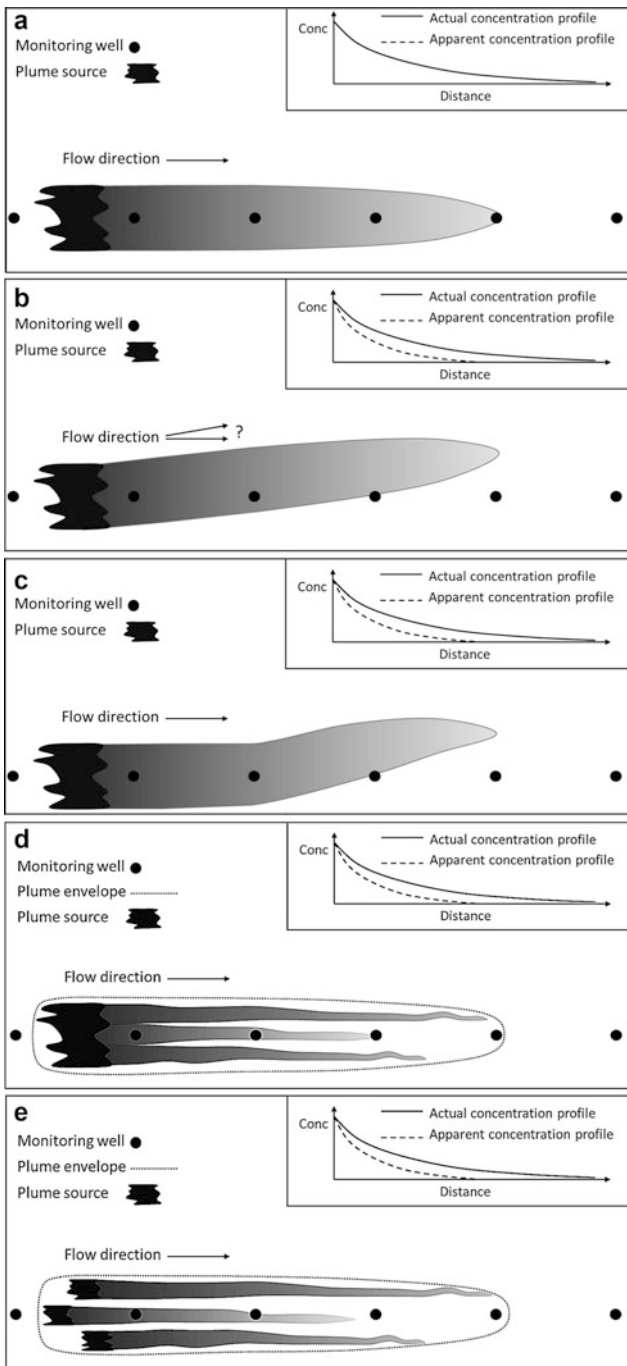
Fig. 3 Conceptual diagrams illustrating problem in establishing and instrumenting representative centerline monitoring in different scenarios: (**a**) uniformly distributed plume in homogeneous,

varying strength and/or migration rate (Jankowski et al. 1997; Lee et al. 2001). This can reflect preferential pathways due to heterogeneity in the aquifer hydrogeology, for example, layers with different permeability, cross-bedding or discontinuities (Fig. 3d) or distributed sources (Fig. 3f).

Hydrocarbon releases from source zones may also vary temporally as the source term naturally weathers or is depleted in more soluble components (Thornton et al. 2013), or due to water table fluctuations, recharge variations, and changes in groundwater flow direction (McMahon and Bruce 1997; Davis et al. 1999; McGuire et al. 2000; Mackay et al. 2001; Wilson et al. 2002). This variability may occur on a scale of weeks to months (water table, recharge and flow direction changes) or years (source term aging and compositional changes). Therefore, centerline monitoring typically requires more detailed site characterization to accurately define the spatial-temporal variation in plume flowpath.

The effect of mass transport heterogeneity on NA assessments is potentially significant. The assumption of a fixed centerline for a plume can mean that the primary pathway contributing most to contaminant migration can be missed. When the monitoring wells which intersect the plume are sampled, this can result in an apparent longitudinal contaminant concentration profile, which is less than the actual profile (Fig. 3a–c). A misleading interpretation of a much shorter plume length and overestimation of hydrocarbon attenuation along the flowpath would then arise.

An alternative approach is to use changes in contaminant *mass discharge* and *mass flux* through a series of monitoring wells set transverse to the plume flowpath (i.e., functioning as control planes) and capturing the full depth and width of the plume for performance assessment of NA (Kao and Wang 2001; Wilson et al. 2004; Alvarez and Illman 2006; ITRC 2010). Mass discharge and flux estimates quantify source or plume strength at a given time and location (ITRC 2010). *Mass flux* is a rate measurement specific to a defined area, which is usually a subset of a plume cross section, and expressed as mass/time/area. *Mass discharge* is an integrated mass flux estimate, representing the sum of all mass flux measures across an entire plume. It therefore gives the total mass of any solute transported in groundwater through a defined plane. If the total mass discharge of contaminants migrating through successive control planes decreases over time, NA is evident (Alvarez and Illman 2006).

The mass discharge of hydrocarbons (or any other dissolved chemical species) can be estimated from (API 2003; ITRC 2010):

Fig. 3 (continued) isotropic media, (**b**) uniformly distributed plume in homogeneous, isotropic media where hydraulic gradient is inaccurately defined or is temporally variable, (**c**) uniformly distributed plume in media with undetected macroscale heterogeneity (e.g., buried stream channel), (**d**) nonuniformly distributed plume migrating along preferred pathways in heterogeneous media within plume envelope, (**e**) nonuniformly distributed plume generated from heterogeneously distributed sources within plume envelope. Insert diagrams show resulting apparent and actual contaminant concentration-distance profiles

$$M_d = \sum_{i=1}^{i=n} C_i q_i A_i$$

where M_d is the total hydrocarbon mass discharge from the plume source that passes a given control plane (M/T), C_i is the concentration of a specific hydrocarbon measured at the flow area within the given control plane (M/L^3), q_i is the specific discharge (L/T), and A_i is the flow area associated with specific hydrocarbon measurement within the control plan (L^2). The value of q_i can be calculated from:

$$q_i = K.i$$

where K is the hydraulic conductivity of the flow area (L/T) and i is the aquifer hydraulic gradient (L/L).

Flux planes can capture spatially and temporally variable contaminant distribution, as well as estimate biodegradation rates using different methods, such as the sampling of a dense monitoring array (Borden et al. 1997; Kao and Wang 2001; Béland-Pelletier et al. 2011), control plane pumping of a more sparse array (Bockelmann et al. 2003; ITRC 2010; Béland-Pelletier et al. 2011), or a passive flux meter approach (Hatfield et al. 2004; ITRC 2010). In addition to defining the source strength and plume attenuation rate, mass flux estimates can identify areas of a plane through which most contaminant mass is moving. This helps target monitoring and remediation efforts (e.g., amendments to enhance NA) to optimize treatment. As such, flux-based methods provide a superior analysis of NA performance compared with methods based on assumed centerlines of plumes, by integrating results from many monitoring wells and accommodating plume heterogeneity in estimates of mass loss (API 2003; Wilson et al. 2004; Alvarez and Illman 2006; Beyer et al. 2007). However, this approach requires a higher density of groundwater monitoring wells or sampling stations, ideally using higher resolution MLS, to characterize the contaminant and hydraulic conductivity distribution in sufficient detail (API 2003; Alvarez and Illman 2006; ITRC 2010).

5.2 Process Heterogeneity

Process heterogeneity refers to the spatial and temporal distribution of biodegradation processes that occurs in plumes. As biodegradation is the most important attenuation mechanism for hydrocarbon compounds in groundwater, monitoring should focus on deducing the type and location of biodegradation processes in plumes from the groundwater chemistry and other data. This information is necessary to estimate biodegradation rates (Thornton et al. 2001b), and experience shows that contaminant biodegradation is strongly influenced by the evolution in redox conditions (Lyngkilde and Christensen 1992; Lerner et al. 2000; Cozzarelli et al. 2001; Thornton et al. 2001a), contaminant concentrations (Pickup et al. 2001; Wu et al. 2006; Baker et al. 2012) and microbial communities (Elliott et al. 2010;

Rizoulis et al. 2013) in plumes. While the characteristic longitudinal development of redox zones resulting from biodegradation of hydrocarbon compounds in groundwater (Fig. 2) has long been known (Champs et al. 1979; Barcelona et al. 1989; Chapelle et al. 2002), the importance of biodegradation at the plume fringe is now increasingly recognized as a major contribution to overall biodegradation in organic contaminant plumes (Pickup et al. 2001; Anneser et al. 2008; Prommer et al. 2009; Tischer et al. 2013; Thornton et al. 2014). However, weak vertical dispersive mixing means that the plume fringe zone may be less than 1 m thick (Davis et al. 1999; Schreiber and Bahr 1999; Cozzarelli et al. 1999; Cozzarelli et al. 2001; McGuire et al. 2000), with steep gradients in chemical species, such as electron acceptors, electron donors, and metabolites (see profiles in Fig. 2), and microorganisms supporting biodegradation (Tuxen et al. 2006).

The challenge of monitoring process heterogeneity in hydrocarbon plumes is therefore to adequately resolve the spatial and temporal distribution of biodegradation processes. This objective can only satisfactorily be achieved using high-resolution multilevel sampling (MLS) devices (Thornton et al. 2001a; Einarson and Cherry 2002; Spence et al. 2005; Anneser et al. 2008). Figure 4 shows vertical profiles of phenol and selected redox-sensitive chemical species across the plume fringe at two locations in an aromatic hydrocarbon plume, obtained from a MLS (1 m sampling interval), with black bars indicating the lengths of single screen monitoring wells typically used at the site. (Thornton et al. 2001b). It is evident that neither the vertical distribution of chemical species in the plume nor the steep gradients in these across the plume fringe can be adequately discriminated with the single screen monitoring wells, which straddle multiple redox zones and induce dilution, mixing, or averaging of dissolved chemical concentrations within the borehole, destroying any gradients. This artifact can result in erroneous interpretation of dominant biodegradation processes in hydrocarbon plumes and underestimation of biodegradation capacity (Martin-Hayden and Robbins 1997; Schreiber and Bahr 1999).

The MLS devices provide superior understanding of the chemical framework needed to quantify contaminant biodegradation and predict the bioattenuation potential of the plume as a whole. At the study site, they suggest that simultaneous aerobic respiration and NO_3^- and Fe^{3+} reduction occurs over a narrow 1 m mixing zone at the plume fringe. Further illustration is provided in Table 4, which shows a depth-integrated electron acceptor and carbon mass balance for the plume, estimated from the MLS at locations A and B using the methodology developed by Thornton et al. (2001b). The mass balance compares total electron acceptor consumption with contaminant consumption and production of organic and inorganic metabolites. It shows that aerobic respiration and denitrification at the plume fringe account for significantly greater biodegradation and carbon turnover than anaerobic biodegradation processes in the plume core, apart from fermentation (Table 4). This mass balance was also used to estimate. An overall plume-scale pseudo-first-order biodegradation rate of 0.005 year^{-1} was estimated from this mass balance, two orders of magnitude lower than that obtained using data from the single-screen monitoring wells.
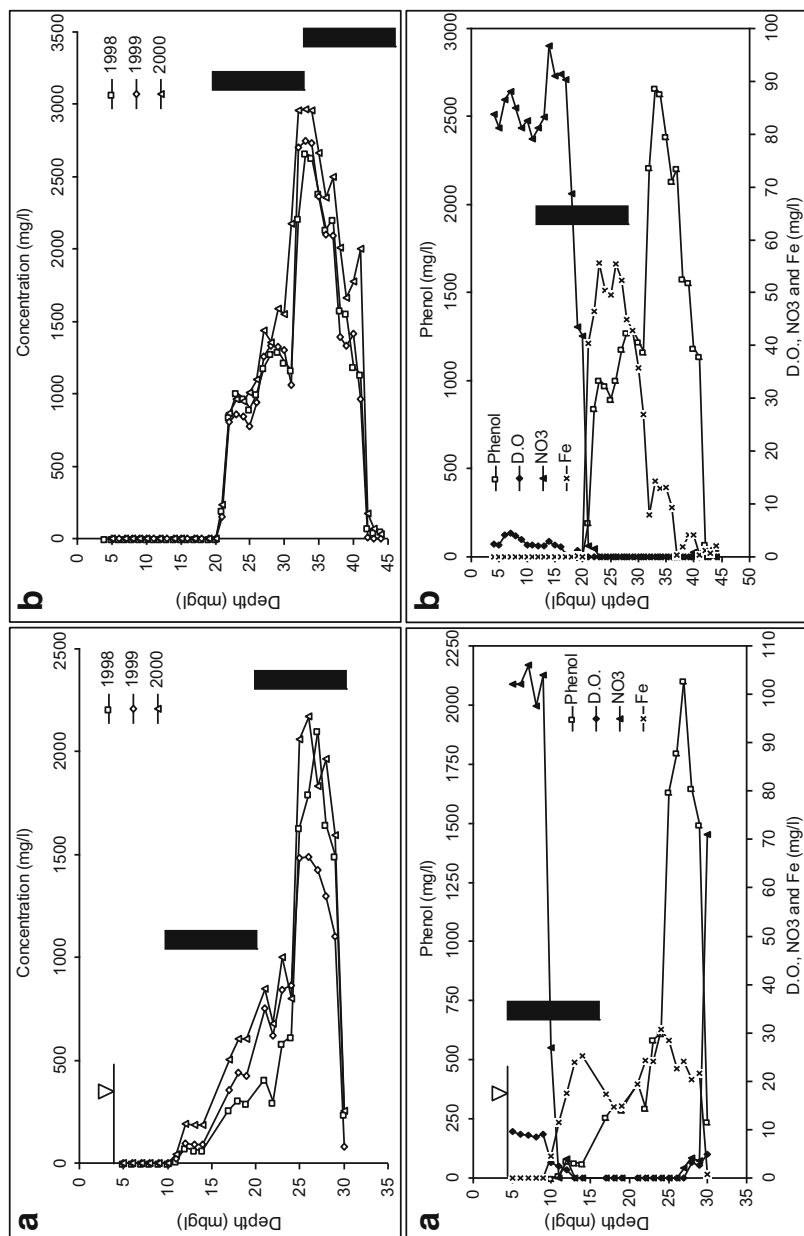
Fig. 4 Vertical profiles of phenol (successive annual surveys) and selected redox-sensitive chemical species (1998 survey) at near source MLS (**a**) and downstream MLS (**b**) in an aromatic hydrocarbon plume. *Black* bars are typical screen lengths for single screen monitoring wells at the site

Table 4 Contaminant carbon and aquifer oxidant consumption estimated from MLS vertical profiles at locations A and B

Species	Oxidant consumption $(kg \cdot m^{-2})$[a]		Contaminant consumption (kg phenol-C$\cdot m^{-2}$)[a, b]			
	Borehole A	B	A	Residual phenol-C	Borehole B	Residual phenol-C
O_2	0.42	0.21	0.14		0.066	
NO_3	4.67	4.2	0.97		0.87	
SO_4	0.0016	0.001	0.00034		0.00022	
MnO_2	0.041	0.24	0.0032		0.018	
FeOOH	0.15	0.24	0.0056		0.009	
Acetate[c]			0.31		0.19	
Total	5.28	4.89	1.43	7.18	1.15	15.5

[a]Values are integrated over the depth of the MLS profile

[b]Consumption is presented in terms of equivalent phenol carbon and by assuming that all contaminants are present as phenol

[c]Acetate is assumed to be produced by fermentation of the hydrocarbon compounds

5.3   Stable Isotopes

Measurements of hydrochemical species in groundwater will not always provide conclusive proof of hydrocarbon biodegradation for NA assessments (Borden 1994; Hunkeler and Aravena 2010). For example, biodegradation of specific hydrocarbon compounds in mixtures can be difficult to deduce if common pathways exist, when organic metabolites are similar to potential parent compounds, or if analytes are present at trace levels that are difficult to quantify (Alvarez and Illman 2006; Spence et al. 2005). Also changes in redox conditions which are attributed to hydrocarbon biodegradation in groundwater can also arise from metabolism of other co-contaminants, including natural substances, confounding quantitative interpretation, and mass balances at the plume scale.

Many of these problems can be addressed using natural abundance and compound-specific stable isotope analysis (CSIA) of H, C, N, O, S, and Cl in hydrocarbon compounds, their biodegradation metabolites, and the respective elements in NO_3^-, SO_4^{2-}, CO_2, CH_4. The fundamental principles and environmental applications of stable isotope analysis have been extensively reviewed (Meckenstock et al. 2004; Hunkeler and Elsner 2010; Elsner and Imfeld 2016). With respect to the natural attenuation of hydrocarbons in groundwater, stable isotope analysis can be used to (i) identify the source(s) and origin (e.g., via biological or abiotic transformation) of a compound (both organic and inorganic) released to or formed in a given environment; (ii) deduce specific pathways and redox processes (e.g., aerobic vs. anaerobic) for biodegradation; (iii) assess the contribution of biotic and abiotic transformation processes affecting contaminants during subsurface transport; (iv) quantify the extent of biodegradation; (v) verify reactive transport models for prediction of environmental impacts, remediation system design, and treatment

timescales; and (vi) understand element cycling in natural and contaminated systems using isotope-labeled compounds (Höhener and Aelion 2010).

More recent development of stable isotope methods include the use of dual isotope analysis to interpret in situ biodegradation processes for aromatic hydrocarbons and other organic contaminants. Attention has mainly focused on understanding the reaction mechanisms and enzymes involved (Morasch et al. 2001), relevant metabolic pathways (Mancini et al. 2003; Fischer et al. 2008), characterizing the physiological groups of microorganisms facilitating biodegradation (Kümmel et al. 2015), deducing the dominant redox processes supporting biodegradation (Spence et al. 2001, 2005; Feisthauer et al. 2012; Thornton et al. 2014), and quantifying biodegradation at field scale (Hunkeler et al. 2001; Mancini et al. 2002, 2003; Richnow et al. 2003; Griebler et al. 2004; Meckenstock et al. 2004; Spence et al. 2005; Fischer et al. 2007; Hunkeler and Aravena 2010; Thornton et al. 2011; Lesser-Carillo 2014).

6   Research Needs

The process-based conceptual model which describes the spatial distribution of microbiological activity and biodegradation potential in hydrocarbon plumes is increasingly recognized as a fundamental biogeochemical framework to understand and predict the natural attenuation of a wide range of aromatic hydrocarbon contaminants in groundwater. The steep gradients in biogeochemical processes which characterize the plume fringe interface provide a unique environment for the biodegradation of oxidizable organic chemicals. However, further research is needed in two areas to understand the complex relationships that exist within the microbial communities which develop at this interface and to interpret their interactions in response to changing environmental conditions.

6.1   Mechanistic Understanding of Microbial Community Interactions at Plume Interfaces

It is likely that the composition, function, and activity of specific populations within the microbial community at the plume fringe will be sensitive to selective pressures created by the availability of organic substrates and electron acceptors, which in turn are controlled by the aquifer properties and groundwater flow field. Both competitive and synergistic interactions between microbial populations may characterize the biodegradation of hydrocarbons under these conditions, but this is poorly understood. Moreover, little is known about the characteristic response times of the microbial community to temporal variations in plume conditions, such as those which occur by natural evolution in the source term composition and by engineered interventions (e.g., injection of amendments to increase microbial activity and contaminant turnover). The work of Thornton et al. (2014) highlighted the potential to increase rates of NA in such circumstances, but the response, in particular the

recovery timescales, of planktonic and attached populations in a hydrocarbon plume to such intervention must be qualified and formerly linked to the biogeochemical drivers controlling this behavior.

6.2 Quantitative Description of Microbial Interactions at Plume Interfaces

Datasets to quantitatively measure and interpret the microbial interactions which develop at the plume fringe, supported by a theoretical framework which enables these observations to be translated into predictions of NA performance at field scale. This necessarily requires the improved mechanistic understanding outlined above and new modeling tools which can represent such dynamic relationships across different scales (microscale to plume scale). The work completed in Watson et al. (2005) highlighted the importance of such adaptive modeling frameworks to scale biogeochemical processes across the plume fringe but also emphasized the conceptual and theoretical limitations of existing modeling approaches.

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