HYDROGEOLOGICAL DATA REQUIREMENTS FOR ASSESSMENT OF NATURAL ATTENUATION.

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ABSTRACT

The use of natural attenuation of dissolved organics is becoming more and more an alternative remedial approach for sites where groundwater is contaminated with aromatic or chlorinated hydrocarbons. However before proceeding to natural attenuation as remedial approach for a specific site, a thoroughly assessment of natural attenuation should be performed. This paper intends to give an overview of data requirements for this assessment to emphasise on the importance of hydrogeological and geochemical data for evaluation of natural attenuation.

INTRODUCTION

Dissolved organic contaminants in groundwater result mostly from the dissolution of Nonaqueous Phase Liquids (NAPLs) in the subsurface. NAPLs are generally classified by specific gravity (density relative to water) into light NAPLs (LNAPLs) or dense NAPLs (DNAPLs). LNAPLs will have a density less than water, and will float on the watertable. The more dense DNAPLs can move downward past the water table and penetrate deep into the saturated zone. Figure 1 shows conceptual models for LNAPL and DNAPL release. Both type of NAPLs give rise to a dissolved organic contaminant plume. Experience with and studies have shown that many active remediation technologies to cleanup NAPL contaminated sites, are not as effective as once thought. One of the most difficult problems with NAPL contamination is the residual NAPL that serves as a continuing source of contaminants in groundwater, undermining aquifer restoration efforts. This is one of the factors why natural attenuation (NA) has emerged as a plume management technique. The term natural attenuation refers to (EPA), 1999)'natural occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in those media'. In practice, natural attenuation is also referred to as intrinsic remediation, intrinsic bioremediation, natural restoration, or passive bioremediation. It is a remediation approach that relies on naturally occurring processes such as dispersion, sorption and especially microbially mediated biodegradation to control the migration of contaminants dissolved in groundwater. The term monitored natural attenuation (MNA) is referred to by the U.S. EPA (EPA), 1999) as the use of natural attenuation as a remedial approach and implies a plume management approach that involves long-term monitoring of the plume.
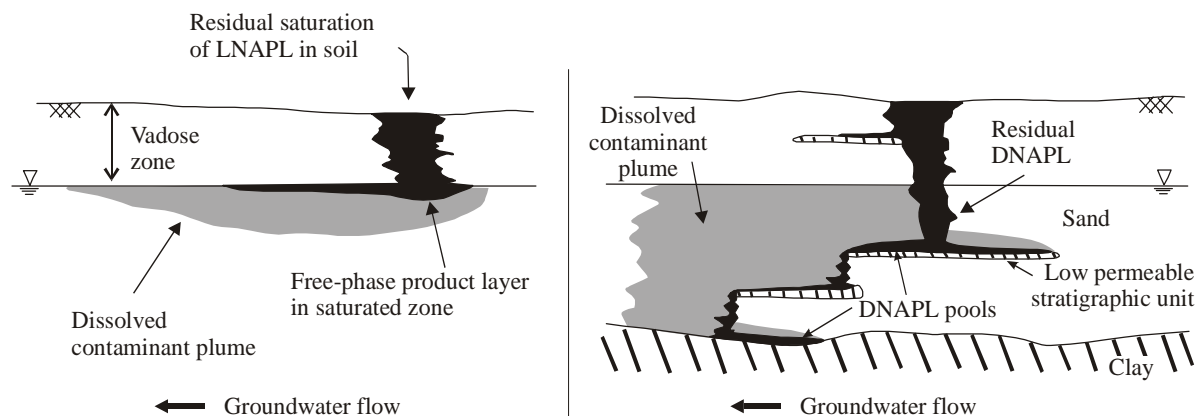

Figure 1: Conceptual model for LNAPL (left) and DNAPL (right) release. After (Bedient et al., 2000).

For a good knowledge of the data requirements for the assessment of natural attenuation a basic insight in the patterns of natural attenuation is required. Figure 2 shows the general geochemical evolution of groundwater when contaminated by organic carbon that can be oxidised by microorganisms. The hypothetical aquifer initially contains dissolved oxygen, nitrate, biologically available iron (III), sulphate, carbon dioxide, all necessary nutrients and has a positive oxidation-reduction potential (oxidising). Shortly after the introduction of the organic carbon in the aquifer, aerobic bacteria start biodegrading soluble organic carbon. Because of the low solubility of dissolved oxygen in water and the abundance of aerobic bacteria, the aquifer soon becomes anoxic. When concentrations of dissolved oxygen fall below 0.5 mg/l and nitrate is present in the groundwater, denitrification will start. During denitrification, the concentration of nitrate will decrease to the point where denitrification no longer can be supported. Hydrogen concentration will be poised during denitrification resulting in a plateau of hydrogen concentration. After nitrate is consumed, the dissolved hydrogen concentration will begin to increase until bacteria capable of reducing iron (III), iron (III) reducers, can be supported. The dissolved hydrogen concentration again reaches a plateau, during which iron (III) reducers will utilise organic carbon which results in an increase of iron (II) in the groundwater. If all bioavailable iron (III) is consumed, dissolved hydrogen concentration will rise again, now until sulphate reducers start with the consumption of organic carbon. A by-product of this electron-acceptor reaction is hydrogensulphide which will increase during sulphate reduction. Finally the dissolved hydrogen concentration will grow again after the sulphate in the groundwater is exhausted and will reach a plateau when methanogenesis can be supported. Methanogenesis is a combination of fermentation and respiration during which organisms use hydrogen and acetate as metabolic substrates and produce methane, carbon dioxide and water.
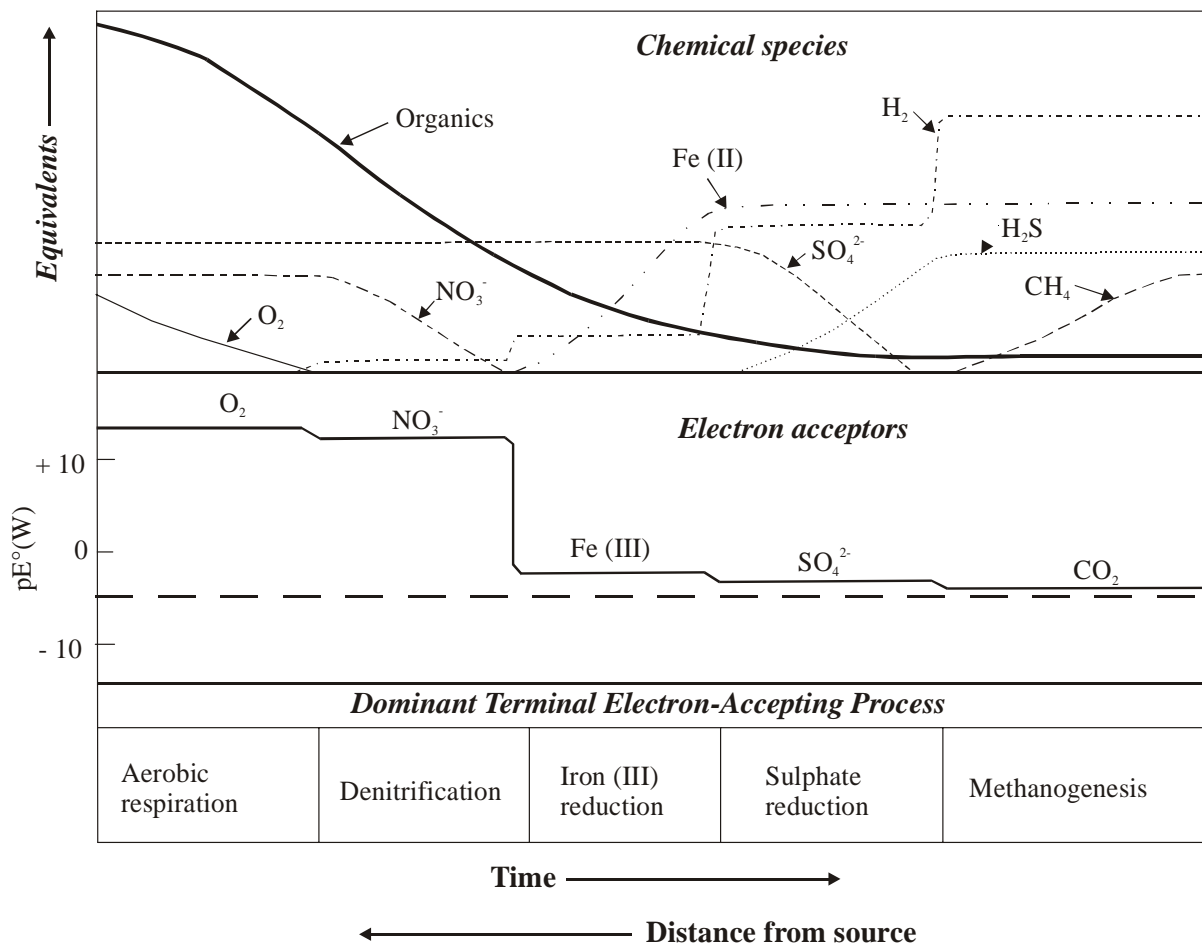

Figure 2: Geochemical evolution of groundwater contaminated by degradable organics. Source: (Weidemeier, 1997).

The above described geochemical evolution is an ideal case, in practice the geochemical evolution can start e.g. with sulphate reduction when the pristine aquifer has a high organic carbon content and consequently dissolved oxygen, nitrate and iron (III) is already been used up before the contamination with anthropogenic organic carbon. A terminal acceptor process (TEAP) can also be skipped when the electron acceptor is not available in sufficiently high concentrations in the aquifer.

DATA REQUIREMENT FOR DEMONSTRATING/EVALUATING NATURAL ATTENUATION

A precise methodology for demonstrating natural attenuation at any site does not exists and will vary from site to site, but nevertheless some actions will be similar at all sites and existing protocols for the evaluation of potential applicability of natural attenuation as remedial approach contain a lot of common features (Sinke and Hecho, 1999). An overview of protocols and guidelines can be found in (Sinke, 2001).
All the protocols have similar recommendations regarding data requirements. First of all a sufficient number of observation wells should be placed at the site to delineate the areal and vertical extent of the groundwater contamination and to determine the hydrostratigraphic units. In the US, ASTM (1998) developed guidelines that suggest that at least 6 wells or data points are required as generalised in figure 3a: one well in the source area, one upgradient well, one downgradient well, one lateral well of the plume and at minimum two wells located within the groundwater plume. The final number and location of observation wells will depend on many factors, including but not limited to the size of the spill, the hydrogeological complexity of the site, and the distance and potential pathways to sensitive receptors. Professional experience and judgment for the placement of these observation points are indispensable. Figure 3b shows an example of sampling locations in the horizontal as well as vertical directions.
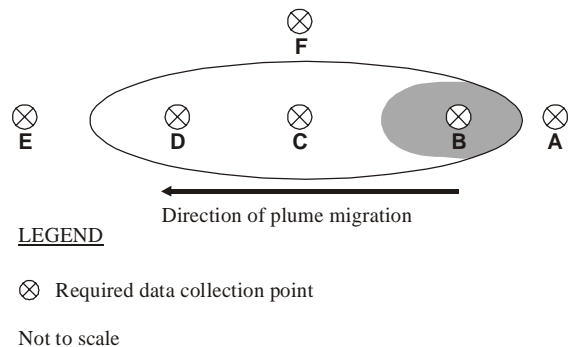

Figure 3: Minimum data requirements for evaluation of natural attenuation. After (Weidemeier, 1997)
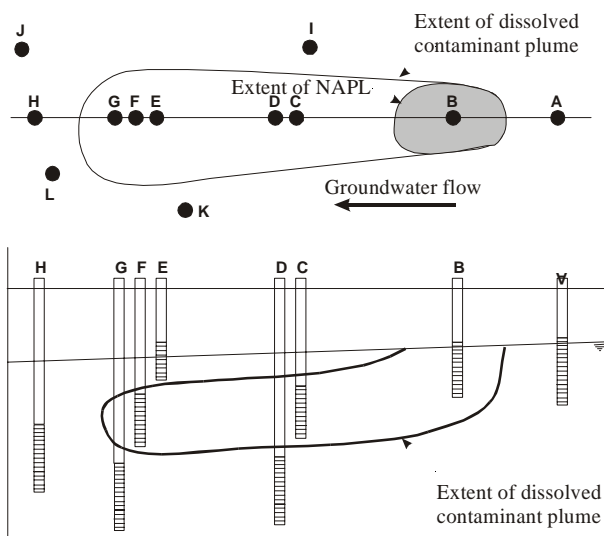
Figure 4: An example of data points for a contaminant plume. After (Weidemeier, 1997)

Accurate and reliable data are also needed for the hydrogeological characterisation of the site, since this will the basis for every site-specific conceptual model. Data requirements include measuring of water levels in the monitoring wells, creating a potentiometric surface map, determining the hydraulic gradient, determining the distribution of the hydraulic conductivity via slug tests or pumping tests and determining presence of potential receptors. Using the hydraulic conductivity data, hydraulic gradient data and estimates of aquifer porosity, the direction and velocity of groundwater flow can be estimated. Without this characterisation it is impossible to perform any assessment for natural attenuation at a site and thus care should be taken when this part is executed.

Beside hydrogeological data, (bio)geochemical data are needed for the process of evaluating natural attenuation. This include measurements of concentration of contaminants, inorganic acceptors, and metabolic by-products both in space and time. An example of groundwater analytical parameters useful for evaluating natural attenuation is listed in table 1. The geochemical data should be taken from at least four general areas (figure 3): the source area (B), an area downgradient (C) but still in the dissolved contaminant plume and an area downgradient (C) and upgradient (D) of the contaminant plume. It should be mentioned that figure 3 is very simplified for generalisation and in reality plumes will be 3-dimensional and can be located in different hydrostratigraphic strata. The geochemical data from the source zone are used to determine the dominant terminal electron acceptor process in this area. In combination with the data downgradient in the dissolved plume, it can be determined if degradation is occurring or not. The downgradient observation points in and outside the dissolved plume help to determine the distribution of electron acceptors along the flow path. The upgradient and lateral geochemical data are used for delineation of the plume and the determination of background concentrations of electron acceptors and electron donors.

All the above mentioned data are needed in the process of evaluating natural attenuation as a possible remediation process. Several tools exists for this evaluation, from pure statistically methods, e.g. Mann-Kendall test (Bedient et al., 2000), over analytical models such as BIOSCREEN (Newell et al., 1996) or BIOCHLOR (Newell et al., 2000) to numerical models as among others RT3D (Clement, 1998), BIOPLUME III (Rifai et al., 1997), etc. These tools are used in the evaluation at different stages and contribute all to the final decision to use natural attenuation as a remedial approach.

TABLE 1: GROUNDWATER ANALYTICAL PARAMETERS (FROM (Wiedemeier et al., 1999)).

Analysis	Data Use	Field or Fixed-Base Laboratory
Aromatic and chlorinated hydrocarbons (benzene, toluene, ethylbenzene and xylene (BETEX); chlorinated compounds)	Method of analysis for BETEX and chlorinated solvents/ daughter products, which are the primary target analytes for monitoring natural attenuation; method can be extended to higher-molecular-weight alkylbenzenes; trimethylbenzenes are used to monitor plume dilution if degradation if primarily anaerobic.	Fixed-base
Dissolved oxygen	Concentration below about 0.5mg/l generally indicate an anaerobic pathway. Measurements made with electrodes; results are displayed on a meter; protect samples from exposure to oxygen during sampling and analysis.	Field
Nitrate	Substrate for microbial respiration in the absence of oxygen.	Fixed-based
Mn(II)	Indication of Mn(IV) reduction during microbial degradation of organic compounds in the absence of dissolved oxygen and nitrate.	Field
Fe(II)	Indication of Fe(III) reduction during microbial degradation of organic compounds in the absence of dissolved oxygen, nitrate and Mn(IV).	Field
Sulfate (SO_4^{2-})	Substrate for anaerobic microbial respiration.	Field
Hydrogen sulfide	Metabolic by-product of sulfate reduction. The presence of H2S suggests organic carbon oxidation via sulfate reduction.	Field
Methane, ethane, and ethane	The presence of methane suggests organic carbon degradation via methanogenesis. Ethane and ethane data are used where chlorinated	Fixed-base

	solvents are suspected of undergoing biological transformation.	
Carbon dioxide	Carbon dioxide is produced during the biodegradation of many types of organic carbon.	Field
Alkalinity	General water quality parameter used (1) to measure the buffering capacity of groundwater, and (2) as a marker to verify that all site samples are obtained from the same groundwater system.	Field
Oxidation-reduction potential (ORP)	The ORP of groundwater reflects the relative oxidizing or reducing nature of the groundwater system. ORP is influenced by the nature of the biologically mediated degradation of organic carbon; the ORP of groundwater may range from more than 800 mV to less than –400 mV. Measurements made with electrodes: results are displayed on a meter; protect samples from exposure to oxygen. Report results against the hydrogen electrode (Eh) by adding a correction factor specific to the electrode used.	Field
pH	Aerobic and anaerobic processes are pH sensitive.	Field
Temperature	Well development.	Field
Conductivity	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system.	Field
Major cation	Can be used to evaluate other remedial actions.	Field
Chloride	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system. Final product of chlorinated solvent reduction.	Fixed-base
Total organic carbon (TOC)	Used to classify plume and to determine it cometabolism is possible in the absence of anthropogenic carbon.	Fixed-base
Hydrogen (H_2)	Sampled at well head requires the production of 100 ml/min of water for 30 min. Equilibration with gas in the field. Determined with a reducing gas detector.	Field
Biologically available iron (III)	Optional method that should be used when petroleum hydrocarbons or vinyl chloride are present in the groundwater to predict the possible extent of removal of petroleum hydrocarbons and vinyl chloride via iron reduction.	Fixed-base

CONCLUSIONS

This paper gives an overview of data requirements for evaluating natural attenuation. It is clear that when natural attenuation is considered as a possible remediation approach, a thoroughly site characterisation, geochemically as well as hydrogeologically has to be performed in order to evaluate this possibility.

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