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Managing risks from contaminated groundwater using natural attenuation

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Contaminated soil and groundwater can cause detrimental effects to human health, the wider environment and quality of water resources, as well as having major socio-economic impacts. There are many thousands of potentially contaminated sites across Europe where remediation is required, with associated annual management costs that run into several € billion. Common sources of groundwater contamination include releases from industrial facilities *e.g.* chemical manufacturing, processing and storage facilities, distribution and waste disposal facilities, coal mine sites, and agricultural practices. While aromatic hydrocarbons, halogenated compounds and phenols represent the majority of organic contaminants from these sources, inorganic compounds (*e.g.* heavy metals and nutrients) are also important.

Many engineered remediation methods are available to clean-up contaminated sites with the objective of managing associated risks to receptors such as humans, wells, groundwater and surface water. In contrast, natural attenuation (NA) refers to the use of naturally occurring *in situ* physical, chemical, and biological processes which act in isolation or combination, without human intervention, to reduce the mass, toxicity, mobility, flux, volume or concentration of contaminants in soil and groundwater. These *in situ* processes include biodegradation, abiotic degradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction. Monitored natural attenuation (MNA) is the application of NA processes for the management of soil and contaminated groundwater. MNA provides a rigorous performance assessment of NA using appropriate monitoring strategies to demonstrate an acceptable reduction in environmental risk at a specific compliance point or receptor within a reasonable timeframe.

Conceptual model for natural attenuation of hydrocarbons in groundwater

The processes of natural attenuation for a hydrocarbon release to groundwater are shown schematically in **Figure 1**. Contaminated groundwater is transported from the source at A, through the plume (B), to the receptor at C. MNA is considered successful if the flux and concentration of pollutants is reduced such that the risk to the receptor is acceptably low. Biodegradation of organic contaminants by aerobic respiration, nitrate reduction and sulfate reduction using dissolved electron acceptors (O_2, NO_3^-, SO_4^{2-}) will occur at the periphery or fringe of the plume, driven by mixing between the plume and background groundwater. Slower anaerobic biodegradation by reduction of manganese or iron and methanogenesis will occur inside the plume core, using mineral Mn and Fe oxide fractions in 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. The plume will grow until the contaminant influx at A is balanced by the rate of destruction of the combined fringe mixing-controlled and the slower internal reactions. Source management measures are typically implemented with NA to reduce the duration and steady-state length of the plume.

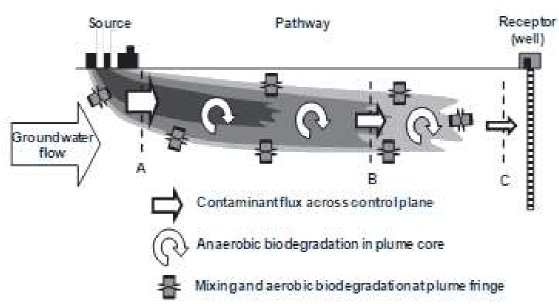

***Figure 1.** Conceptual model for natural attenuation of hydrocarbon compounds in groundwater.*

Implementation and performance assessment

Technical guidance is available to support the implementation and performance assessment of NA at sites for different types of contaminants. NA is implemented within the context of the Source-Pathway-Receptor framework (**Figure 1**). This emphasizes detailed characterisation of the contaminant source (supporting plume development) and quantification of NA processes along the plume pathway (aquifer) to predict impacts on receptors. Performance assessment of NA for organic contaminants seeks to (i) characterize the nature and spatial extent of *in situ* biodegradation processes for the contaminants, (ii) estimate 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. This may involve the integrated analysis of hydrochemical, isotopic, microbiological and other data using a wide range of qualitative and quantitative techniques at different scales to document the occurrence and extent of attenuation. This analysis is formalized within a "lines of evidence" framework, which includes the collection of different types of information:

- 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 contaminants in the plume, typically based on the consumption of dissolved (*e.g.* O_2, NO_3^-, SO_4^{2-}) and mineral phase (*e.g.* MnO_4^-, FeOOH) electron acceptors in the aquifer and a 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 NA, 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 microorganisms able to degrade the contaminants

Data analysis and interpretation

Mathematical models are typically used to verify the site conceptual model underpinning the interpretation for NA and to predict the long-term behaviour of the plume for site management. Primary and secondary lines of evidence are obtained from the distribution of dissolved reactants along the plume flow path, using groundwater samples collected from monitoring wells in the plume source area and both uncontaminated and contaminated sections of the aquifer. The plume is presumed to have a centreline, characterized by the monitoring wells, for this analysis. Visual, graphical, and quantitative methods, including regression techniques, statistical analyses, and mass balances are available to interpret these data using concentration versus time and concentration versus distance plots, although flux-based approaches are preferred.

An important objective of this analysis is the estimation of plume-scale contaminant biodegradation rates – often assumed to follow first-order kinetics for mathematical simplicity – to use in numerical reactive transport codes. 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 modelling tools have been developed to undertake this for hydrocarbon and chlorinated solvent plumes, based on different conceptual models of plume development, contaminant mixtures, and biodegradation processes.

References

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