

## Sustainability of Natural Attenuation (NA) of Aromatics (BTEX)

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### Introduction

Natural attenuation (NA) is a risk management tool to reduce contamination and prevent migration, resulting in less remediation activities and costs [1]. Determination of the occurrence of NA and the sustainability of NA are important aspects: is NA indeed occurring for all contaminants present, will the required conditions for NA still be present in the future and will the assumptions used in modelling still be valid in five or ten years? This information is essential for a reliable extrapolation of future plume behaviour and to determine the applicability of NA.

The Dutch government and industrial partners developed a new protocol for the sustainability of NA of chlorinated ethenes in 2002 [2]. Aromatic hydrocarbons (BTEX) are another important group of contaminants frequently detected in groundwater plumes that could be considered for NA. NICOLE, together with Bioclear, Port of Rotterdam and Shell Global Solutions, has undertaken this project to develop a protocol to evaluate the occurrence, sustainability and applicability of NA for BTEX.

### Activities

Recent knowledge of BTEX degradation was collected and research results from various groups working on natural attenuation of BTEX were integrated. Specific measurements and tests were undertaken to confirm degradation under various conditions. Using these data and the experience gained from the sustainability protocol for chlorinated ethenes, the BTEX protocol was developed. The protocol gives information on the mechanisms of and prerequisites for NA, (analytical) tools to determine BTEX degradation and an approach to determine the sustainability and applicability of the NA processes at a site.

### First step of the protocol: determine the occurrence of NA of BTEX

In the first step of the protocol, the 'three lines of evidence', explained in more detail elsewhere [1], are used to demonstrate NA. In general, this approach consists of:

- primary lines of evidence that include data from historical groundwater and/or soil chemistry samples that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentrations at appropriate monitoring or sampling points;
- secondary lines of evidence that include geochemical and biochemical indicators that are indicative for NA processes. This line of evidence often includes a characterisation of the redox conditions in uncontaminated groundwater, the source zone and the plume and analyses on specific degradation products and/or compound-specific stable isotopes analyses (CSIA);
- tertiary lines of evidence that include data from field or laboratory microcosm studies (conducted in or with actual contaminated site samples) that directly demonstrate microbial activity in the soil or aquifer material and its ability to degrade the contaminants of concern. Also, molecular analyses targeted at the detection of specific micro-organisms involved in the degradation of contaminants can be used as a third line of evidence.

Based on the results of a Dutch SKB project [3] in which new innovative analytical techniques were evaluated (anaerobic laboratory microcosms, compound-specific stable isotopes analyses, analyses for specific degradation products of benzene and molecular analyses), the following strategy was proposed to investigate the natural attenuation potential at BTEX contaminated sites.

### **Proposed strategy to determine the occurrence of NA at BTEX contaminated sites**

To evaluate NA of BTEX at a contaminated site, a tiered approach is most common. The aim is to obtain a good estimation of the probability that NA is occurring, preferably as soon as possible and with as little expense as necessary. Typically, the first line of evidence is the starting point. Site-specific data concerning the history of activities (possible accidents, spillages), contaminants (time series), and (geo)hydrology is collected and evaluated. Data gaps can be identified and a plan for additional monitoring activities, if necessary, can be developed.

For the second line of evidence, analyses for redox conditions and non-specific and specific degradation products (alkalinity, phenols/benzoates) are performed. Mapping the redox conditions at a contaminated site and comparing the redox conditions in uncontaminated groundwater with the redox conditions in contaminated groundwater can be used to determine the use of suitable electron acceptors, which is evidence for the occurrence of degradation. CSIA are performed to confirm the degradation of the separate BTEX components.

Laboratory microcosms mentioned in the third line of evidence are considered optional and can be used to obtain additional information. The laboratory microcosms are a good alternative for CSIA if the prerequisites for the performance and interpretation of CSIA (data) are not met. These microcosms indicate that the potential for biodegradation exist in the aquifer.

The SKB project [3] also revealed that analyses for specific BTEX degrading micro-organisms are, at this moment, not sufficiently developed to be used as a conclusive line of evidence, since there are various microbial strains known or supposed to be involved in the (anaerobic) degradation of BTEX. Also, the use of degradation products that are supposed to be specific indicators for anaerobic benzene degradation (phenol, benzylsuccinate) could not be confirmed in this project and were not considered suitable to be used as a line of evidence for benzene degradation.

### **Second step of the protocol: determine the sustainability of NA of BTEX**

When the evidence shows that NA occurs, the results of field and laboratory activities are used for the second step. In this step, the ratio between electron acceptor (oxygen, nitrate, sulphate) and electron donor (BTEX contamination) is calculated for monitoring wells upstream, in the source zone and in the plume. If the ratio is larger than one, the score is positive, otherwise it is scored negative. The prerequisites for sustainable NA at site scale are assessed using the distribution of positive and negative scores over the site. Additional analyses downstream of the plume may be necessary to assess the contribution of bioavailable iron(III) or manganese(IV) to the degradation process. This tiered approach is presented in figure 1.

If this approach shows that NA is sustainable, a conceptual model can be used to determine if site specific requirements are met.

### **Third step of the protocol: determine the applicability of NA to achieve site specific requirements**

The conceptual model includes the three parameters that determine the evolution of the plume, namely the concentration of BTEX, its migration rate and the half life (degradation rate) of the contaminants. These three parameters, which can be quantified using field and laboratory measurements, literature and groundwater modelling, are closely related. The relationship between them can be plotted in a three-axis graph, as shown in figure 2.

To quantify the combined effect of natural attenuation rate, migration rate and the concentrations of the contaminants, groundwater modelling and contaminant transport modelling is necessary. In a model, these parameters are used as input and a plume prediction over time can be produced. For relatively simple situations, indicative calculations or two-dimensional models like Bioscreen or Webplume can be used. For more complex scenarios a 3-D model (for instance Visual Modflow with RT3D) is advised. In 3-D models, different soil layers with different redox conditions and related degradation and migration rates can be defined, resulting in a more reliable plume prediction.

Finally, a check list was formulated in order to highlight technical aspects that may influence the degradation process in the future and organisational aspects that determine monitoring requirements, acceptance and regulatory enforcement.

### **Possibilities for extensive stimulated biological degradation of BTEX**

It might be necessary to stimulate the degradation processes by the addition of a suitable electron acceptor. For instance, if natural attenuation is not occurring or the rates of NA are too low to meet site requirements. Addition of oxygen is a well-known remediation approach, but can have disadvantages like relatively high investment and operation costs (especially for deep groundwater contaminations), risks regarding settlement of the soil and the need to install a soil vapour extraction system to prevent volatilisation of BTEX to the atmosphere. In these cases, a stimulated bioremediation approach based on the addition of nitrate or sulphate can be considered. Both approaches have been shown to be effective.

An example of a remediation by enhanced natural attenuation using sulphate as electron acceptor is the Vries-4 site. At this site, the consumption of sulphate in the contaminated groundwater and the presence of intermediate products like benzoates and alkyl phenols indicated clearly the occurrence of natural attenuation. However, it was also shown that the biodegradation of BTEX was limited because of a lack of sulphate in the contaminated groundwater. This resulted in strongly reduced methanogenic conditions which are not favourable for the degradation of BTEX.

A relatively easy and effective remediation was performed by addition of sulphate using a temporary groundwater recirculation system. At the Vries-4 site, a one-time injection with sulphate was used to treat the benzene contamination with concentrations up to 10,000 µg/l. Within 2.5 years the benzene concentrations decreased to about 10 µg/l (figure 3).

### **Conclusions**

The developed protocol for BTEX and the existing protocol for chlorinated ethenes provide a structured approach to assess the feasibility of NA as a stand-alone option or an addition to active measures and help remove doubts of site owners and regulators. They deal with the most important groups of mobile contaminants in the groundwater. The protocol for BTEX is available via NICOLE ([www.nicole.org](http://www.nicole.org)). The protocol for chlorinated ethenes is available via the website of SKB ([www.skbodem.nl](http://www.skbodem.nl)).

If natural attenuation is not occurring or the rates of NA are too low to meet site requirements, degradation processes can be stimulated by the addition of a suitable electron acceptor. Oxygen is the most suitable and results in the highest degradation rates, but site characteristics can limit the applicability of a remediation approach based on aerobic processes. In these cases, addition of nitrate and/or sulphate can be considered as suitable alternative to stimulate NA of BTEX and to meet site requirements.

### **Recommendations**

At this moment, the described protocol is considered 'best practice' when a NA approach is considered at a site. However, the protocol could be improved when more knowledge is available. It is recommended to focus future research activities on the following topics:

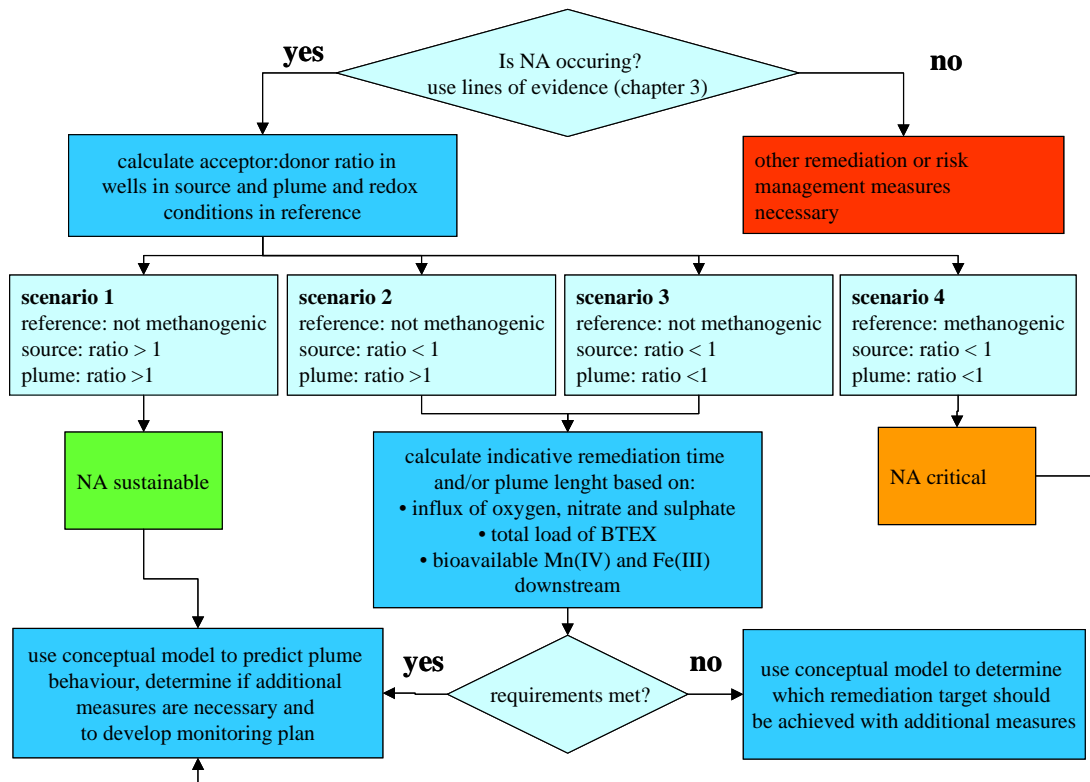
- molecular screening of the lifecycle of mineral oil/BTEX spills and plumes;
- which organisms/functional groups are associated with the redox shift in BTEX plumes and what is their natural function?

The study of these topics may lead to a more complete understanding of intrinsic bioremediation processes and therewith to a faster and more secure approach to the application of intrinsic bioremediation as a remediation strategy. Also, the knowledge gathered on these topics may lead to new stimulated bioremediation strategies.

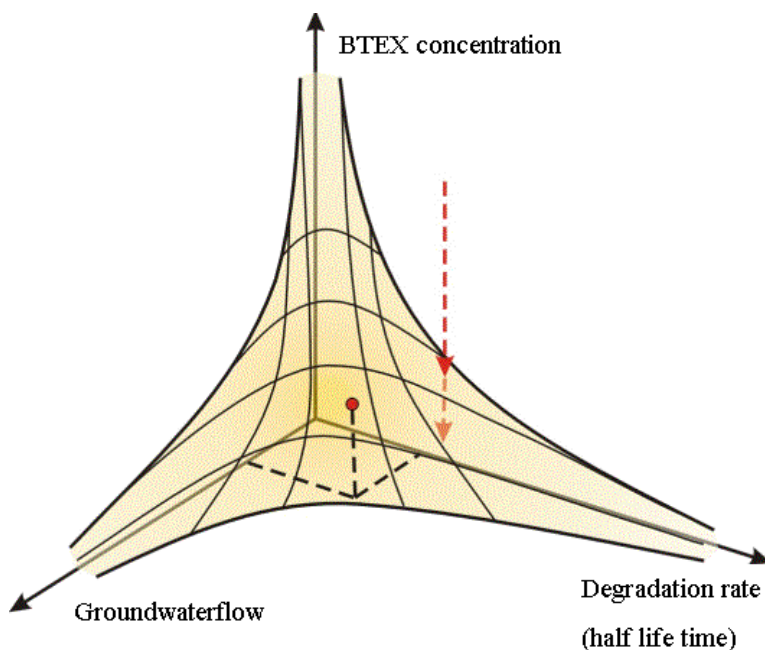
[1] H. Slenders, R. Jacquet and A. Sinke. Monitored Natural Attenuation: demonstration & review of the applicability of MNA at 8 field sites. NICOLE project, 2005.

[2] J.E. Dijkhuis, J.B.M. van Bommel, M.J.C. Henssen and R. van Lotringen. Protocol for the determination of the sustainability of the natural attenuation (S-NA) of chlorinated ethenes. SKB project SV-513, 2003.

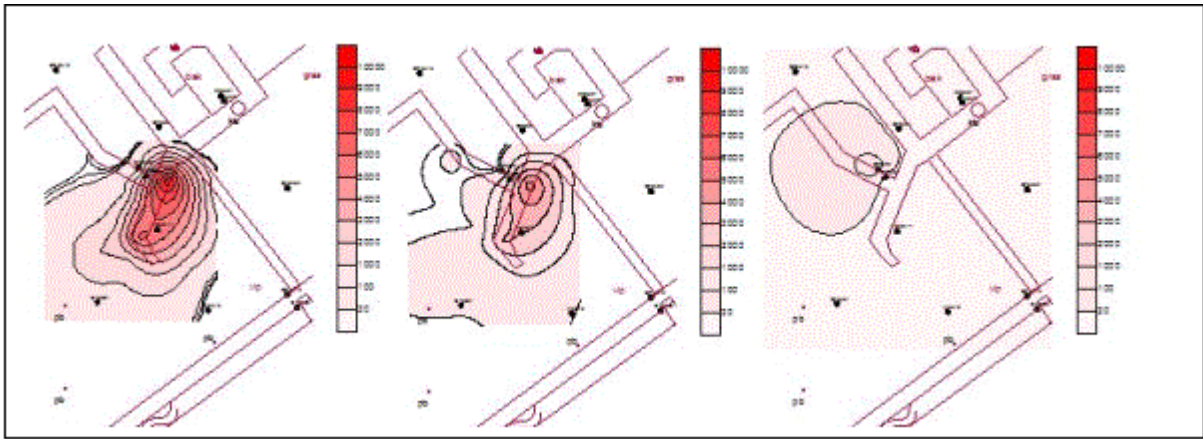
[3] A. Langenhoff en N. van Ras. Bewijsvoering anaerobe afbraak benzeen. Nieuwe technieken om het optreden van anaerobe biologische afbraak van benzeen aan te tonen. Bodem 5, oktober 2008 (in Dutch).



**Figure 1.** Flowchart to determine the sustainability of NA at a BTEX contaminated site



**Figure 2.** Model illustrating the interaction between BTEX concentration, groundwater flow and degradation rate



**Figure 3.** Results of anaerobic benzene degradation after addition of sulphate to stimulate the degradation process