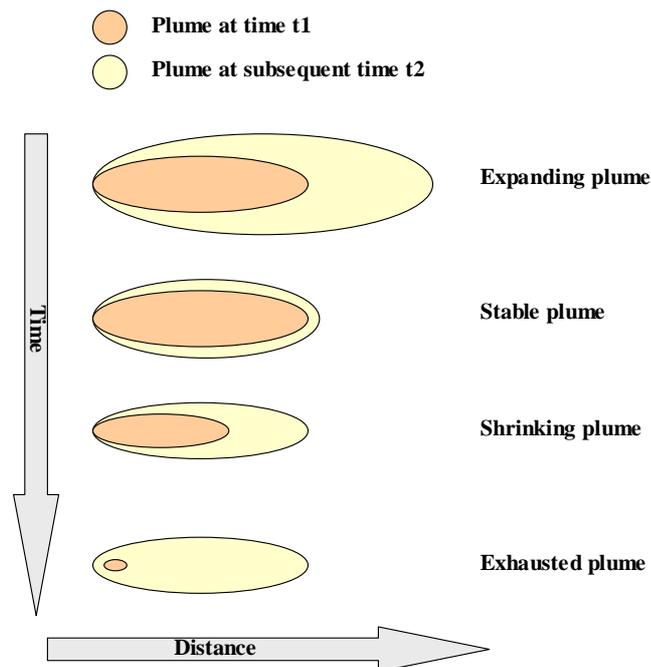




Qualitative, quantitative, and visual methods to assess natural attenuation

Environmental Protection Programme

Internal Report IR/04/169



BRITISH GEOLOGICAL SURVEY

ENVIRONMENTAL PROTECTION PROGRAMME

INTERNAL REPORT IR/04/169

Qualitative, quantitative, and visual methods to assess natural attenuation

M Lelliott and G Wealthall

The National Grid and other Ordnance Survey data are used with the permission of the Controller of Her Majesty's Stationery Office.
Ordnance Survey licence number
Licence No:100017897/2004.

Keywords

Natural attenuation, lines of evidence, assessment methods.

Front cover

Types of naturally attenuating plumes.

Bibliographical reference

LELLIOTT, M., WEALTHALL, G. 2004. Qualitative, quantitative, and visual methods to assess natural attenuation. *British Geological Survey Internal Report*, IR/04/169. 28pp.

Copyright in materials derived from the British Geological Survey's work is owned by the Natural Environment Research Council (NERC) and/or the authority that commissioned the work. You may not copy or adapt this publication without first obtaining permission.

Contact the BGS Intellectual Property Rights Section, British Geological Survey, Keyworth, e-mail ipr@bgs.ac.uk You may quote extracts of a reasonable length without prior permission, provided a full acknowledgement is given of the source of the extract.

© NERC 2004. All rights reserved

Keyworth, Nottingham British Geological Survey 2004

BRITISH GEOLOGICAL SURVEY

The full range of Survey publications is available from the BGS Sales Desks at Nottingham, Edinburgh and London; see contact details below or shop online at www.geologyshop.com

The London Information Office also maintains a reference collection of BGS publications including maps for consultation.

The Survey publishes an annual catalogue of its maps and other publications; this catalogue is available from any of the BGS Sales Desks.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects. It also undertakes programmes of British technical aid in geology in developing countries as arranged by the Department for International Development and other agencies.

The British Geological Survey is a component body of the Natural Environment Research Council.

British Geological Survey offices

Keyworth, Nottingham NG12 5GG

☎ 0115-936 3241 Fax 0115-936 3488
e-mail: sales@bgs.ac.uk
www.bgs.ac.uk
Shop online at: www.geologyshop.com

Murchison House, West Mains Road, Edinburgh EH9 3LA

☎ 0131-667 1000 Fax 0131-668 2683
e-mail: scotsales@bgs.ac.uk

London Information Office at the Natural History Museum (Earth Galleries), Exhibition Road, South Kensington, London SW7 2DE

☎ 020-7589 4090 Fax 020-7584 8270
☎ 020-7942 5344/45 email: bgs london@bgs.ac.uk

Forde House, Park Five Business Centre, Harrier Way, Sowton, Exeter, Devon EX2 7HU

☎ 01392-445271 Fax 01392-445371

Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS

☎ 028-9066 6595 Fax 028-9066 2835

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

☎ 01491-838800 Fax 01491-692345

Sophia House, 28 Cathedral Road, Cardiff, CF11 9LJ

☎ 029-2066 0147 Fax 029-2066 0159

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk

Contents

Contents.....	i
1 Introduction	1
2 Primary lines of evidence.....	1
2.1 Graphical techniques	2
2.2 Visual techniques.....	5
3 Secondary lines of evidence	6
3.1 Graphical	6
3.2 Biodegradation.....	12
4 Tertiary lines of evidence.....	17
5 Optional lines of evidence	18
5.1 Solute fate and transport modelling.....	18
5.2 Demonstration of assimilative capacity of aquifer	18
6 Natural attenuation assessment method summary	20
References	22

FIGURES

Figure 1: Types of naturally attenuating plumes (adapted from Agency, 2000)	2
Figure 2: First order decay for contaminants of concern (COC)	3
Figure 3: Centreline concentration plot for average COC concentrations over time for a stable plume, or individual monitoring event for a shrinking plume.....	4
Figure 4: Comparison of contaminant concentrations (after Agency, 2000).....	4
Figure 5: Comparison of contaminant/tracer ratio	5
Figure 6: Determining concentration versus time rate constant (K_{point}).....	6
Figure 7: Determining concentration versus distance rate constant (k).....	7
Figure 8: mass flux calculations using flux planes	11
Figure 9: Immission pumping technique to determine mass flux of COC.....	12
Figure 10: Comparison of degraded COC with breakdown products (after Agency, 2000)	13
Figure 11: Comparison of COC and breakdown product ratios.....	13
Figure 12: Evaluating degradation of TCE using SEQUENCE radial diagram software (www.waterloohydrogeologic.com).....	15
Figure 13: Evaluating redox indicators using SEQUENCE software (www.waterloohydrogeologic.com).....	15

TABLES

Table 1: Natural attenuation method assessment summary	20
--	----

EQUATIONS

<i>Eqn 1: Differential first-order decay</i>	3
<i>Eqn 2: First-order decay</i>	3
<i>Eqn 3: Time to reach remedial target</i>	7
<i>Eqn 4: Bulk attenuation rate constant</i>	7
<i>Eqn 5: Attenuation travel time</i>	8
<i>Eqn 6: Attenuation travel distance</i>	8
<i>Eqn 7: Buscheck & Alcantar biodegradation rate</i>	8
<i>Eqn 8: Conservative tracer correction</i>	9
<i>Eqn 9: Conservative tracer biodegradation rate</i>	9
<i>Eqn 10: Mass balance</i>	10
<i>Eqn 11: Mass flux</i>	10
<i>Eqn 12: Aquifer assimilative capacity</i>	19
<i>Eqn 13: Total biodegradation capacity</i>	19

1 Introduction

Monitored natural attenuation (MNA) is increasingly becoming accepted as a viable, cost effective option for managing the risks posed by contaminated groundwater in certain situations (Agency, 2000). In order for MNA to be approved as a viable option it has to be demonstrated that natural attenuation (NA) is occurring and that it is sufficiently effective to cause no unacceptable risk to receptors, and that remedial measures can be met within a reasonable timeframe.

Natural attenuation is demonstrated using three lines of evidence (R&D 95). Primary lines of evidence involve the use of historical contaminant data to demonstrate a trend of reduced pollutant concentrations down-gradient of the source, along the groundwater flow path. This form of evidence shows that attenuation is taking place, but fails to establish if contaminant mass is being destroyed by biological or non-biological degradative mechanisms. Secondary lines of evidence involve measuring changes in chemical and geochemical analytical data to prove a loss of contaminant mass. Two approaches are available (Agency, 2000):

- Using chemical and geochemical analytical data in mass balance calculations to show that decreases in parent contaminant and/or election acceptor/donor concentrations can be directly correlated to increases in metabolic by-products and/or daughter compounds;
- Using historical chemical data, complemented, if necessary, by biologically recalcitrant tracer testing, to demonstrate that the plume is shrinking, stable or expanding at a rate slower than predicted by conservative groundwater velocity calculations.

Tertiary lines of evidence use data from laboratory microbiological testing to show that indigenous bacteria are capable of degrading site contaminants. This line of evidence should be used when the first two are inconclusive. Optional line of evidence (ASTM, 2004) may be used to more rigorously interpret data developed as secondary lines of evidence.

The clear presentation of data is an important component in setting out the evidence in support of natural attenuation (Agency, 2000). The data can be displayed qualitatively (e.g. graphically), quantitatively (e.g. mass balance calculations), or visually (e.g isopleth maps). This report details the methods available for presenting data to support natural attenuation for each level of lines of evidence. The methods presented are not exhaustive, but do represent the principal methods employed.

2 Primary lines of evidence

The primary line of evidence (i.e. loss of contaminants) is typically documented by reviewing historical trends in contaminant concentration and distribution in conjunction with site geology and hydrogeology to define whether the plume is stable, shrinking, or expanding (ASTM, 2004) (Figure 1). A shrinking plume is evidence of natural attenuation, and indicates that the natural attenuation rate exceeds mass loading of contaminants of concern (COC) to groundwater (exhausted plume if no source remains). A stable plume is also evidence of natural attenuation, and indicates that the natural attenuation rate is approximately equal to the mass loading of COC's to groundwater. In the case of an expanding plume the mass-loading rate of COC's to groundwater exceeds the natural attenuation rate. MNA is likely to be only accepted for an expanding plume where it can be demonstrated that there will only be minimal expansion before the plume stabilises and shrinks (Agency, 2000). The natural attenuation rates are not quantified at this stage. The historical trends in contaminant concentration and distribution can be evaluated using qualitative (graphical) and visual (contour/isopleth plots) techniques. An additional technique is to evaluate tabulated COC concentrations, however this technique is not discussed further.

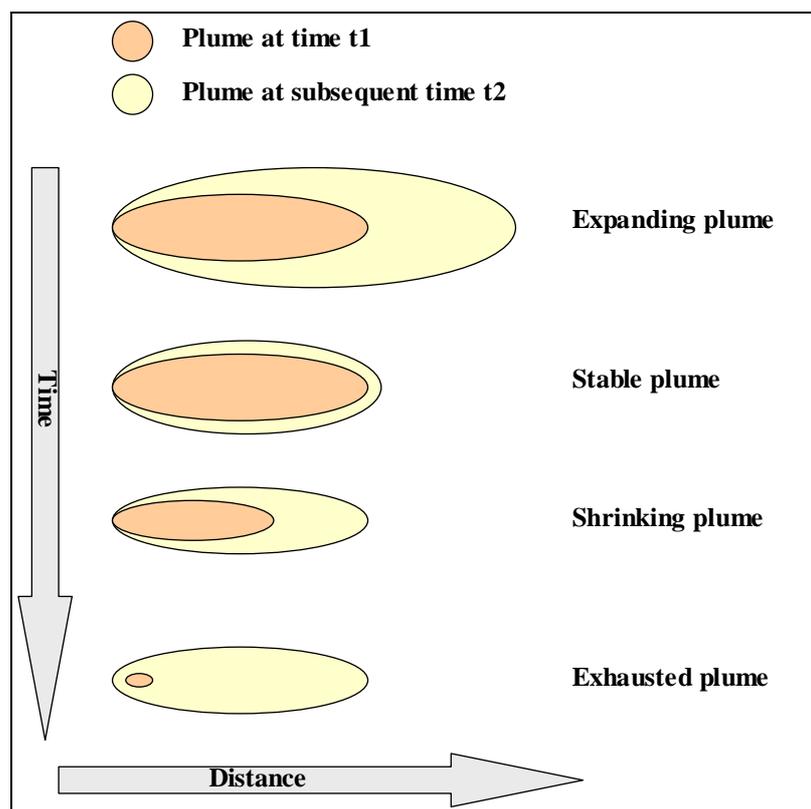


Figure 1: Types of naturally attenuating plumes (adapted from Agency, 2000)

2.1 GRAPHICAL TECHNIQUES

The change in contaminant concentration with distance or time will typically be a function of dilution, dispersion, sorption and natural degradation (Agency, 2000). Evidence for natural attenuation can be obtained by plotting well concentration plots (concentration versus time), centreline concentration plots (concentration versus distance), or by comparison of contaminant ratios.

2.1.1 Well concentration plots

This method evaluates the temporal changes in concentration of COC's at a single well, or to identify source history changes. Single well analysis identifies trends at one point within the plume, therefore it is necessary to use multiple wells within the plume to define whether trends are consistent throughout the plume.

As with a large number of processes, the change in solute concentration in the groundwater over time often can be described using a first-order decay rate constant (Wiedemeier, et al. 1999). In one dimension, first order decay is described by the ordinary differential equation:

$$\frac{dC}{dt} = -kt$$

Eqn 1: Differential first-order decay

Where: C = concentration at time t [M/L^3]

k = overall attenuation rate (first-order rate constant) [$1/T$]

Solving this differential equation yields:

$$C = C_0 e^{-kt}$$

Eqn 2: First-order decay

If the COC concentrations adhere to the first-order decay constant then plots of concentration over time can be expected to be exponential on a normal concentration scale, or linear on a logarithmic concentration scale (Figure 2).

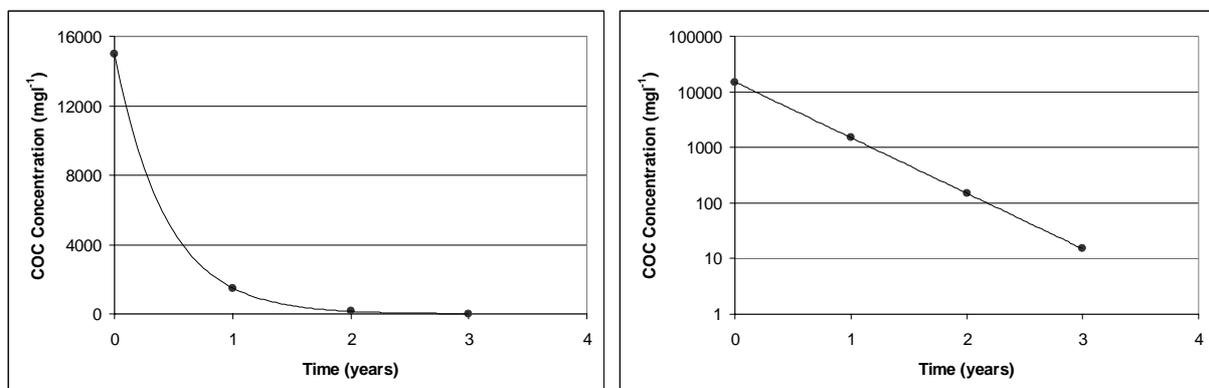


Figure 2: First order decay for contaminants of concern (COC)

The advantage of using the natural log of well concentrations is that stable or decreasing trends can be clearly differentiated from random concentration fluctuations (ASTM, 2004). A negative relationship for concentrations plotted on a logarithmic scale, as shown in Figure 2, is indicative of a shrinking plume, whereas a positive relationship indicates an expanding plume. Where the plume is stable then concentrations will be approximately constant and will plot accordingly.

2.1.2 Centreline concentration plots

This method identifies how COC's concentrations change along the centreline of the plume for a given time period and typically plot as a straight line on a log-linear plot due to first order decay (Agency, 2000). This method is only really applicable to stable or shrinking plumes (Agency, 2000). A plume is defined as stable where dissolved contaminant concentrations remain stable

over time in individual monitoring wells. Short-term variations in monitoring well concentrations due to water table fluctuation, variability in groundwater flow direction, sampling variability, and analytical uncertainty should be distinguished from statistically significant concentration changes (ASTM, 2004). If data from multiple sampling events are available for a stable plume, the concentrations plotted should be the average concentration for each well over time (ASTM, 2004). Centreline plots for a shrinking plume, where concentrations decrease with time at individual monitoring wells, can only be plotted for individual monitoring events due to the decrease in concentration at individual monitoring wells, and possibly the relative rate of decline between monitoring wells. An example of a centreline concentration plot is given in Figure 3. The centreline plot method is reliant on the availability of monitoring wells along the centreline of a plume, with deviations likely to cause erroneous results.

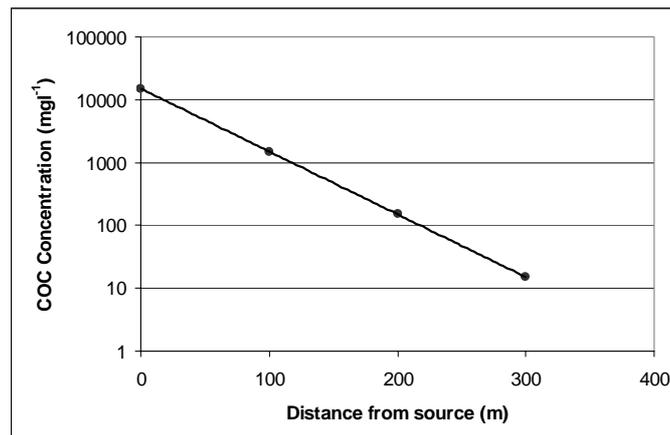


Figure 3: Centreline concentration plot for average COC concentrations over time for a stable plume, or individual monitoring event for a shrinking plume

2.1.3 Comparison of contaminant ratios

Evidence for natural attenuation and degradation can be obtained by comparing contaminant concentration or ratios along the flow path (Agency, 2000). For primary lines of evidence, plots can include log-normalised concentrations of contaminants with distance, and ratios of contaminant concentrations with distance. Comparison of normalised concentrations for a conservative contaminant to other contaminants can be used to identify different rates in migration due to sorption or degradation (Figure 4).

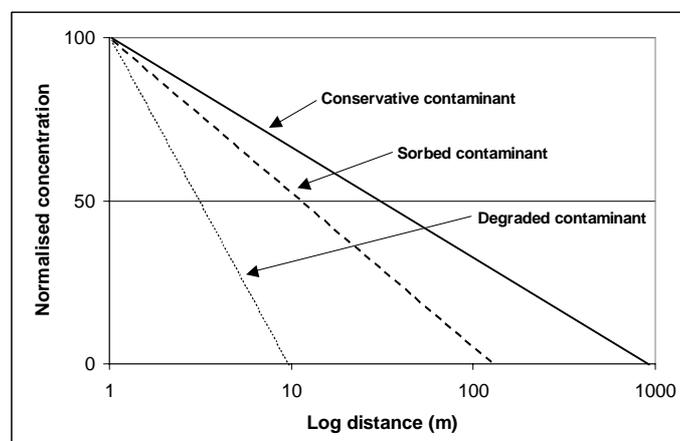


Figure 4: Comparison of contaminant concentrations (after Agency, 2000)

This can also be displayed graphically by comparing the ratio of a contaminant to a conservative contaminant (tracer) (Figure 5). A decline in ratio with distance indicates attenuation due to either sorption and/or degradation.

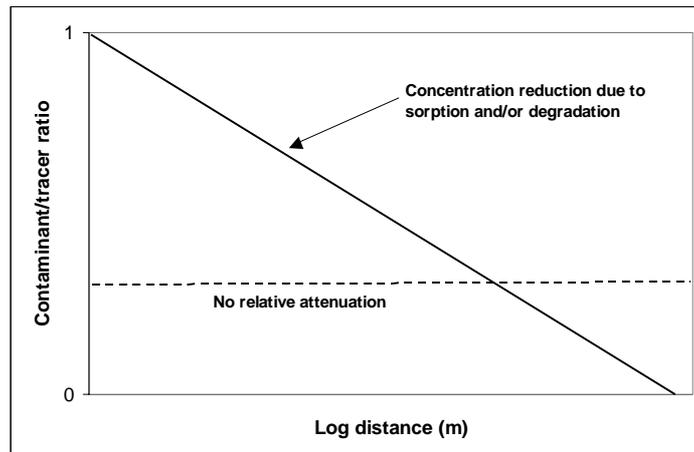


Figure 5: Comparison of contaminant/tracer ratio

In using this technique it is essential that the tracer utilised constitutes part of the contaminant source, and was released at the same time.

2.2 VISUAL TECHNIQUES

Plume contour (isopleth) plots are the most common visual method to identify whether a plume is stable, shrinking, or expanding over time. These can either be in plan view, or as a cross-section through the centreline of the plume. Plan-view contour plots, for different time intervals, give an immediate impression of the plume status (stable, shrinking or expanding), and can also be used to compare the plume shape and orientation to the groundwater flow direction. Contour plots of COC's should include a non-detect or compliance level contour for ease of comparison and to identify likely at risk receptors.

Cross-section contour plots are orientated along the centreline of the plume and are used to give an indication of the vertical variation in contaminant concentration. This method is only applicable where suitable multi-level monitoring boreholes are positioned along the plume centreline.

Contour plots are a good clear visual method to delineate plume edges, however, it is important to remember that creation of a contour plot is a subjective process as it requires interpolating (e.g. Krigging) the chemical distribution between monitoring wells (Carey, et al. 2003). Contour plots should be used with caution where there is not a high-density monitoring network, however are necessary so that contaminant concentrations can be gridded and used for input into numerical modelling (Weidemeier, et al. 1999).

Demonstration of natural attenuation using primary lines of evidence (identification of plume status) gives medium confidence of the applicability of monitored natural attenuation (MNA) as a remedial strategy (Agency, 2000), however it is likely that further lines of evidence will be required to further demonstrate natural attenuation.

3 Secondary lines of evidence

Secondary lines of evidence involve measuring changes in chemical and geochemical analytical data to prove a loss of contaminant mass. This can be demonstrated by estimating the natural attenuation rate, or by using geochemical parameters that serve as indicators of naturally occurring biodegradation (ASTM, 2004). The natural attenuation rate can be assessed using graphical regression techniques for well concentration and centreline concentration plots, or by a mass balance or mass flux approach. Indicators of naturally occurring biodegradation include correlating a decrease in parent contaminant, and/or electron donor, concentrations with an increase in metabolic by products and/or daughter products (Agency, 2000).

3.1 NATURAL ATTENUATION RATE

Rate calculations can be used as part of MNA studies to evaluate the contribution of attenuation processes and the anticipated time required to achieve remediation objectives (Newell, et al. 2002). The graphical methods outlined for primary lines of evidence (well concentration plots, and centreline concentration plots) can be utilised to determine rate constants, assuming first-order decay.

3.1.1 Well concentration rate constant

The attenuation rate constant is applicable to shrinking plumes only and is derived from the slope of the natural log concentration versus time curve measured at a selected monitoring location (Figure 6). The well concentration plot rate constant is K_{point} (first order attenuation rate constant (see Eqn 2)) and represents mass loss from all processes rather than true degradation rate and has units of inverse time (e.g. per day). The rate constant does not account for any changes in attenuation processes, particularly dual-equilibrium desorption (availability), which can reduce the apparent attenuation rate at lower concentrations (Kan, et al. 1998).

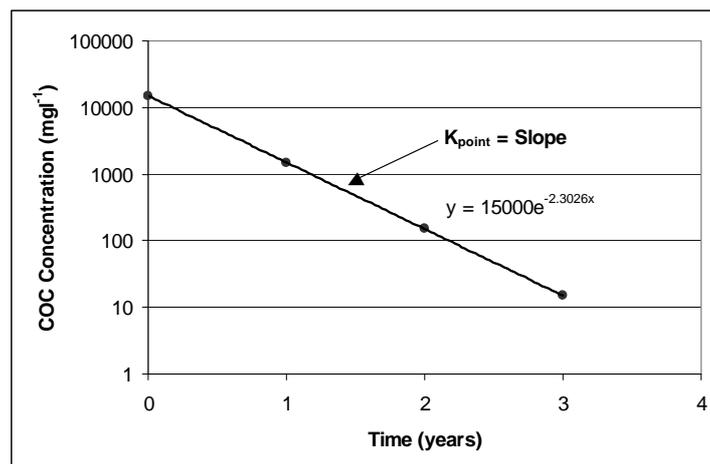


Figure 6: Determining concentration versus time rate constant (K_{point})

The time (t) to reach a remediation target concentration (C_{target}) at the point where K_{point} was calculated can be determined using Eqn 3.

$$t = \frac{-\ln \left[\frac{C_{\text{target}}}{C_{\text{start}}} \right]}{K_{\text{point}}}$$

Eqn 3: Time to reach remedial target

A rate constant derived from a well concentration plot provides information regarding the potential plume lifetime, or time to reach a remedial target, at that location, but cannot be used to evaluate the distribution of the contaminant mass within the groundwater system (Newell, et al. 2002). The entire plume can be assessed by determining rate constants in a number of boreholes throughout the plume. It is common for the rate of attenuation in the source area is slower than the rate of attenuation of materials in groundwater, and concentration profiles in plumes tend to retreat back to the source over time (Newell, et al. 2002). In this instance the lifetime of the plume is controlled by the attenuation of the source, and can be predicted by determining a well concentration constant in the most contaminated wells.

3.1.2 Centreline concentration rate constant

The attenuation rate constant is derived, for first-order decay, by plotting the natural log of the concentration versus distance along the centreline of a plume and calculating the rate as the product of the slope and the groundwater velocity (Figure 7). The centreline concentration constant serves to characterise the distribution of contaminant mass within space at a given point in time, and projects how far along a flow path a plume will expand. A single centreline concentration plot provides no information of dissolved contaminant mass over time, and cannot be used to estimate the time required for the dissolved plume concentrations to be reduced to a target concentration, but does identify how quickly dissolved contaminants are attenuated once they leave the source (plume trend evaluation). The rate constant incorporates all attenuation parameters (primarily sorption, dispersion, biodegradation).

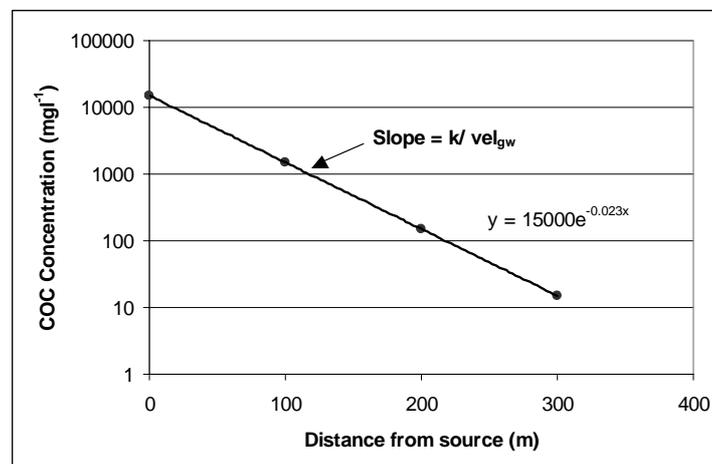


Figure 7: Determining concentration versus distance rate constant (k)

The bulk attenuation rate constant, k , (units of inverse time) is calculated by multiplying the negative of the slope of the regression ($-\text{Slope}_{\text{centreline plot}}$) by the contaminant velocity. The contaminant velocity equals the groundwater velocity (Vel_{gw}) divided by the retardation factor (R). This is summarised as:

$$k = -\text{Slope}_{\text{centreline plot}} \left[\frac{\text{Vel}_{\text{gw}}}{R} \right]$$

Eqn 4: Bulk attenuation rate constant

The first order rate constant can be displayed as a half-life by 0.693 divided by the rate constant. The half-life is for the dissolved contaminant phase only, and does not relate to the source zone.

The travel time required (t_t) for the contaminant concentration to attenuate to a target concentration can be calculated using Eqn 5.

$$t_t = \frac{-\text{Ln} \left[\frac{C_{\text{target}}}{C_{\text{start}}} \right]}{k}$$

Eqn 5: Attenuation travel time

The distance (L) that the dissolved constituents will travel as they are attenuating can be calculated by summation of contaminant velocity (groundwater velocity divided by retardation factor) and travel time (t_t):

$$L = t_t \left[\frac{\text{Vel}_{\text{gw}}}{R} \right]$$

Eqn 6: Attenuation travel distance

3.1.3 Biodegradation rate constants

The attenuation rate constant groups all processes acting to reduce contaminant concentrations and includes mainly advection, dispersion, dilution from recharge, sorption, and biodegradation. To determine the portion of the overall attenuation that can be attributed to biodegradation, these effects must be accounted for, and subtracted from the total attenuation rate (Weidemeier, et al. 1999). A method derived by Buscheck and Alcantar (1995) identifies the contribution of biodegradation, for a steady-state plume by coupling the regression of contaminant concentration versus distance downgradient (centreline concentration plot) to an analytical solution for one-dimensional, steady-state, contaminant transport that includes advection, dispersion, sorption, and biodegradation (Weidemeier, et al. 1999). For a steady-state plume, the first order decay rate is given by (Buscheck & Alcantar, 1995):

$$\lambda = \frac{v_c}{4\alpha_c} \left[\left[1 + 2\alpha_x \left[\frac{k}{v_x} \right] \right]^2 - 1 \right]$$

Eqn 7: Buscheck & Alcantar biodegradation rate

Where: λ = first-order biological decay rate [t^{-1}]

v_c = retarded contaminant velocity in the x-direction [Lt^{-1}]

α_x = dispersivity [L]

k/v_x = slope of line formed by making a log-linear plot of contaminant concentration versus distance down-gradient along flow path

The first-order biological decay rate can also be calculated by correcting the contaminant for a conservative tracer. The tracer has to be recalcitrant, and behave otherwise similar to the contaminant. The concentration of a contaminant at a point down-gradient of the source can be

corrected for the effect of dispersion, dilution and sorption using the following equation (Agency, 2000):

$$C_B C_{orr} = C_B \left[\frac{T_A}{T_B} \right]$$

Eqn 8: Conservative tracer correction

Where: $C_B C_{orr}$ = corrected concentration of contaminant at point B [M/L³]

C_B = measured concentration of contaminant at point B [M/L³]

T_A = measured concentration of tracer at point A [M/L³]

T_B = measured concentration of tracer at point B [M/L³]

By plotting corrected contaminant distribution on a log-linear plot of corrected concentration against down-gradient travel time along the flow path the degradation rate can be calculated using:

$$\lambda = -\frac{1}{t} \ln \frac{C_B}{C_A}$$

Eqn 9: Conservative tracer biodegradation rate

Where: λ = first order degradation rate [t⁻¹]

C_B = tracer corrected contaminant concentration at time t at down-gradient point B

C_A = measured contaminant concentration at upgradient point A

t = travel time between points A and B where $t = x/u$ (x = distance between A and B, u = retarded solute velocity)

The two methods, analytical solution and conservative tracer, provide comparable results (Weidemeier, et al. 1999), however it should be noted that the Buscheck and Alcantar method removes the effects of longitudinal dispersion, but does not remove the effects of transverse dispersion, and is essentially a hybrid between k and λ .

The first order biodegradation rate can also be calculated by calibration of a solute transport model to field data (Newell, et al, 2002). Models that can be used include BIOSCREEN, BIOCHLOR, BIOPLUME III, or MT3D, however it is necessary to ensure that the lines-of-evidence are available to substantiate the derived biodegradation rate (Odencrantz, et al. 2002) and that the biodegradation rate has not been derived purely to fit the model (other variables may be wrongly measured or estimated).

3.1.4 Mass balance method

The degradation rate can be estimated from the change in dissolved mass of COC's within a plume over time (Agency, 2000). This method is most applicable to situations in which the plume is stable or shrinking (ASTM, 2004). The mass of contaminant can be estimated as follows:

$$\text{Dissolved mass (M)} = C_{av} b n A$$

Eqn 10: Mass balance

where: M = dissolved mass [M]
 C_{av} = average plume concentration [M/L³]
 b = aquifer or plume thickness [L]
 n = porosity
 A = plume area [L²]

Calculated dissolved mass estimates can be compared over time to identify the rate of change of mass, and therefore the rate of degradation. A more exact calculation is to contour contaminant concentrations and to calculate the area between each contour (Agency, 2000).

As this method is time dependent it is reliant on many measurements over time, and also a relatively dense monitoring network that fully characterises the plume.

3.1.5 Mass flux method

The mass flux method can be used to demonstrate changes in flux, and consequently mass loss, at one or several distances along the plume over time. One approach is to monitor across the cross-sectional area of the plume, normal to flow, at one or more control planes and to determine the distribution of contaminant concentrations and groundwater flow at each control plane once or repeatedly (Barker et al, 2000). This approach will establish the flux of contaminant across each control plane. Evidence for mass loss would be a decline in flux at a control plane over time and/or decline in flux at down-gradient fences compared to an upgradient fence (Figure 8). The total contaminant flux across a control plane is given by:

$$\text{Flux} = \sum \left[C_{av} W v n D \right]_{\text{For each depth interval}}$$

Eqn 11: Mass flux

Where: Flux = summation of flux for each depth increment
 C_{av} = average contaminant concentration for depth increment [M/L³]
 W = width of plume [L]
 v = groundwater velocity [LT⁻¹]
 n = kinematic porosity
 D = depth increment for each average concentration, or plume thickness [L]

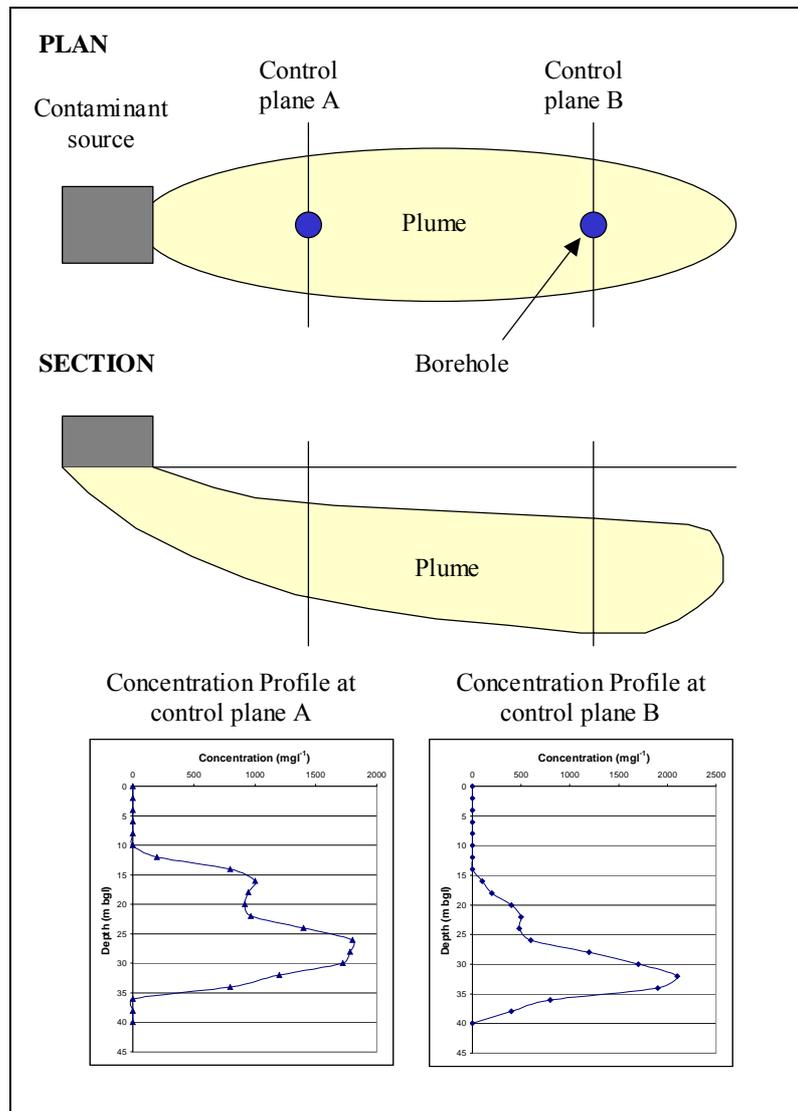


Figure 8: Mass flux calculations using flux planes

This method assumes that the lateral COC concentration is consistent at each depth interval, and is likely to be a gross simplification of the contaminant concentration distribution in the plume. The flux can be refined further by use of multiple boreholes along a control plane, however there is still a certain degree of uncertainty associated with point measurements even if the number of monitoring wells is relatively high (Rugner & Teutsch, 2001). An alternative approach is to use immission pump tests (Teutsch et al, 2000). This approach is also based on flux control planes orientated perpendicular to the plume, where the contaminant mass flux at a defined control plane is determined by immission pumping tests. The location of groundwater wells, the pumping rates and times are chosen in a way that the complete contaminant plume is recorded, and thus the mass flux can be determined across the entire plume (Rugner & Teutsch, 2001) (Figure 9). The concentration versus time is measured during the pumping test for one or more COC's. Based on a common groundwater flow and transport model the contaminant mass flux across the plume is determined using a numerical inversion of the time concentration curves (Schwarz et al, 1998).

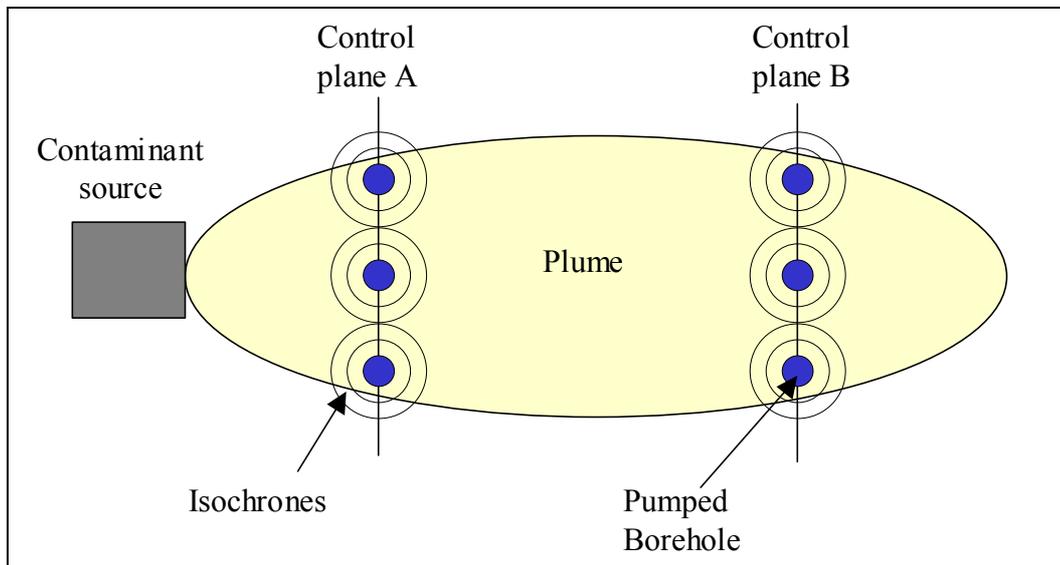


Figure 9: Immission pumping technique to determine mass flux of COC

The technique further allows the determination of the mean and maximum concentration at the control plane (Rugner, 2001), and can also be coupled with measurement of redox sensitive parameters and degradation products in order to provide further information on the degradation processes in the aquifer. By comparing the contaminant mass fluxes across several control planes the degradation rates at the site can be determined.

3.2 BIODEGRADATION INDICATORS

Geochemical data that serves as indicators of naturally occurring biodegradation can be used as secondary line of evidence. Biodegradation is the process in which naturally occurring subsurface micro-organisms biodegrade contaminants (ASTM, 2004). Evaluating indicators specific to the biodegradation process is of critical importance when presenting secondary lines of evidence for natural attenuation. Indicators of biodegradation can be identified graphically (contaminant/daughter product ratios), quantitatively (mass balance and mass flux), or visually (contour/isopleth plots, radial diagrams).

3.2.1 Contaminant ratio plots

Evidence of biodegradation can be obtained by comparing COC and breakdown product concentrations or ratios along the flow path (Agency, 2000). Examples of these methods are shown in Figure 10 and Figure 11. A decrease in COC concentration with an associated increase in breakdown product concentration, or an increase in the ratio of breakdown product to parent contaminant concentration, is indicative of biodegradation.

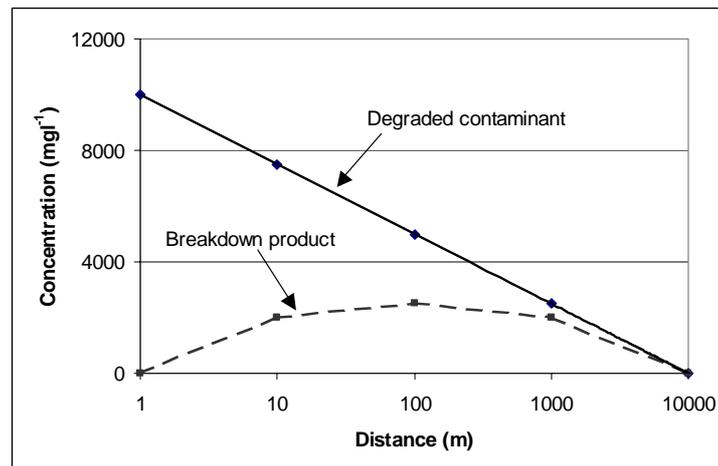


Figure 10: Comparison of degraded COC with breakdown products (after Agency, 2000)

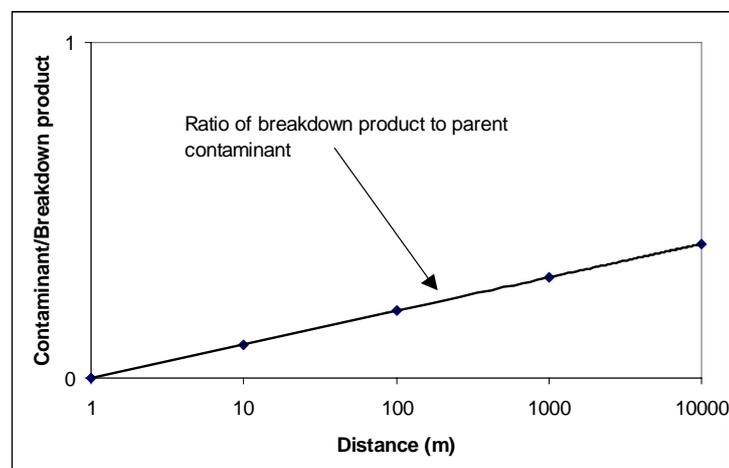


Figure 11: Comparison of COC and breakdown product ratios

In assessing contaminant ratios it is important to identify if the breakdown product is present in the source zone, or introduced as a separate incident (multiple sources or contaminant releases), as this could give a false indication of biodegradation.

3.2.2 Mass Balance/mass flux

The mass balance, mass flux method, as detailed in sections 3.1.4 and 3.1.5, can also be used to monitor the change in mass of COC breakdown products. An inverse relationship is expected between concentration changes for COC's and associated breakdown products.

3.2.3 Contour/isopleth plots

Biodegradation can be assessed visually using contour/isopleth plots for breakdown products, electron acceptors/donors, and hydrochemical indicators. Contour plots can be used to indicate the areal extent of indicators, or the vertical distribution and should be for different time periods to identify changes in indicator concentrations.

Contour plots of COC breakdown products provide visual evidence of where biodegradation is occurring, and there should be an inverse relationship between COC and breakdown product concentration. Breakdown products can often be more hazardous than the parent contaminant, and need to be considered within the monitored natural attenuation programme. It is important to identify if the breakdown product is present in the source zone, or introduced as a separate

incident (multiple sources or contaminant releases), as this could give a false indication of biodegradation.

Contour plots for electron acceptors, including dissolved oxygen, nitrate, manganese, iron, and sulphate, give an indication of biodegradation. During aerobic biodegradation, dissolved oxygen concentrations will decrease to levels below background concentrations (Wiedemeier, et al. 1999). After dissolved oxygen concentrations have been depleted (typically considered <0.5 ppm) nitrate, if available, may be used as an electron acceptor for anaerobic biodegradation and an inverse relationship between the COC and nitrate should be expected (ASTM, 2004). The use of Mn^{+4} as a terminal electron acceptor yields water soluble Mn^{+2} , therefore, under suitable redox conditions and where Mn^{+4} is present, there should be a positive correlation between the COC and Mn^{+2} . The same relationship is expected, under suitable redox conditions, where Fe^{+3} is used as a terminal electron acceptor and reduced to water soluble Fe^{+2} . Under strongly reducing conditions, after oxygen, nitrate, and ferric iron have been consumed, sulphate can be utilised as a terminal electron acceptor (ASTM, 2004). Sulphate consumption should yield an inverse relationship to COC degradation. Under extreme reducing (methanogenic) conditions CO_2 can be used as a terminal electron acceptor by methanogens to produce methane. Under methanogenic conditions a positive relationship is expected between the COC and methane concentration. Contour/isopleth plots for electron acceptors provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various electron acceptors (Wiedemeier, et al. 1999).

Contour/isopleth plots of various additional hydrochemical indicators can also be used to give a visual indication of biodegradation, including oxidation-reduction (redox) potential and alkalinity. The redox potential of groundwater is a measure of the relative tendency of a solution to accept or donate electrons (ASTM, 2004). Redox reactions in groundwater are usually mediated by micro-organisms and, therefore, redox potential can strongly depend on biodegradative processes (redox potential can also strongly influence these processes). Zones of low redox potential, relative to background measurements, can indicate areas where biodegradation is occurring. Respiration of dissolved oxygen, nitrate, iron (III), and sulphate tend to increase the total alkalinity of groundwater (Weidemeier, et al. 1999). Thus, the total alkalinity inside the contaminant plume generally increases to levels above background and can be used as indirect evidence for biodegradation (Agency, 2000).

3.2.4 Radial diagrams

A radial diagram visualisation approach allows simultaneous comparison of spatial and temporal trends for multiple chemicals on one map. This allows the direct comparison of source COC and sequential breakdown products, or redox indicators. Radial diagrams can be produced in software packages such as SEQUENCE (Carey, 1999). Figure 12 presents an example of a SEQUENCE radial diagram showing the COC's and sequential breakdown products for TCE and how the relative concentrations change along the contaminant plume. The outer data series (indicated by the purple line) represents the concentration levels for each of these contaminants as they are measured at the source of contamination. The inner data series (indicated by the red line) represents the concentrations of these contaminants measured at the monitoring wells located down-gradient from the contaminant source. This diagram shows decreasing concentrations of contaminants down-gradient of the source (primary lines of evidence), and the increased concentration of breakdown products (e.g. vinyl chloride and chloride) provide evidence of intrinsic biodegradation (secondary lines of evidence) of the COC's.

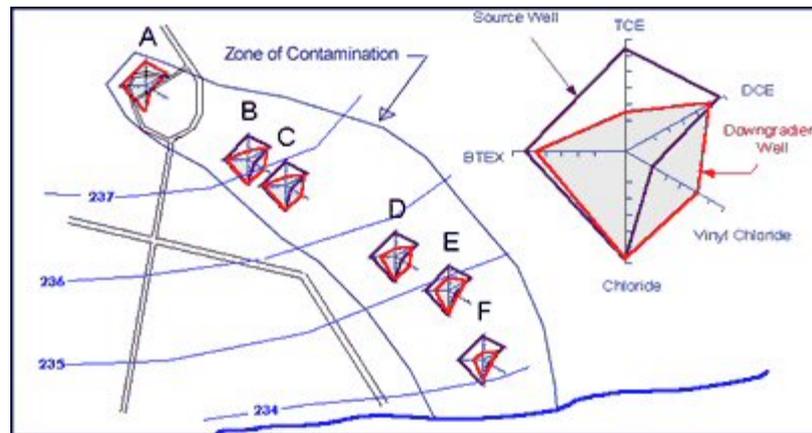


Figure 12: Evaluating degradation of TCE using SEQUENCE radial diagram software (www.waterloohydrogeologic.com)

Figure 13 is an example of a SEQUENCE-Redox map showing the change in concentration of biodegradation indicator species down-gradient from a fuel supplies. The axes of the radial diagram are arranged in the sequence in which these redox indicators are influenced during the biodegradation process (oxygen, nitrate, iron, sulphate, methane) (Carey, 2003). Manganese is not included in this example, however, the number of axes can be adjusted to fit parameters available. The direction of increasing indicator concentration for each axis in a radial diagram is specified such that background concentrations for the redox indicators appear outer-most on each axis, and the concentrations representing a zone where biodegradation is occurring appear toward the inner extent of each axis (Carey, 2003). For example electron acceptors typically decrease during the biodegradation process, therefore axis representing oxygen, nitrate, and sulphate are orientated so that concentrations decrease inward. Whereas, metabolic byproducts, such as manganese, iron, and methane, typically increase in concentration during the biodegradation process, hence axes increase towards the origin. A reduction in the size of the polygon representing plume conditions (Figure 13) relative to the background redox conditions provides an effective illustration of the degree of biodegradation occurring at each sampling location (Carey, 2003).

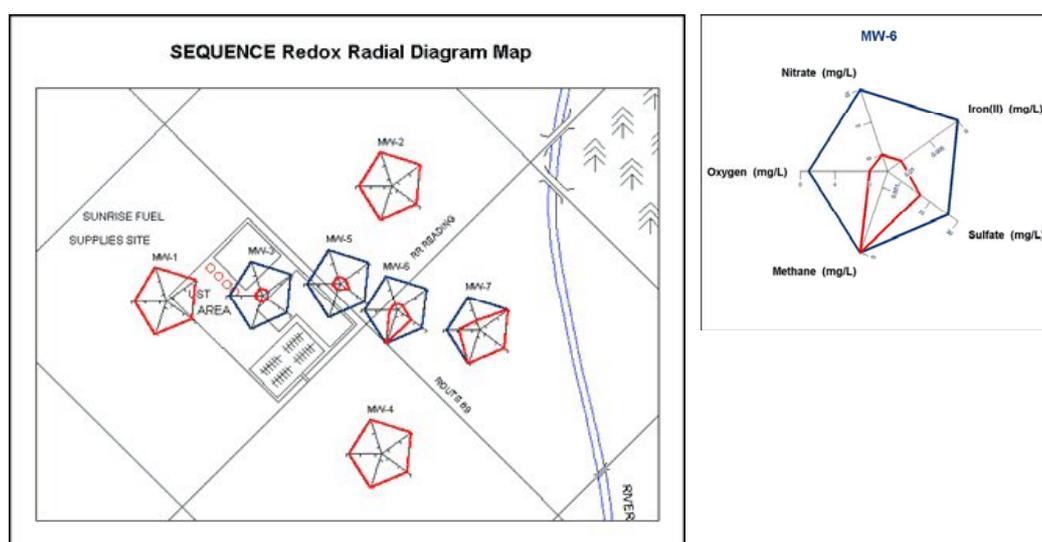


Figure 13: Evaluating redox indicators using SEQUENCE software (www.waterloohydrogeologic.com)

The use of radial diagrams allows clear comparison of multiple related chemical parameters (i.e. parent and breakdown products, sequential redox indicators) at individual monitoring wells, and also between monitoring wells. Radial diagrams also do not involve any data interpolation and are based on real chemical concentrations.

4 Tertiary lines of evidence

Tertiary lines of evidence use data from laboratory microbiological testing to show that indigenous bacteria are capable of degrading site contaminants (Agency, 2000). This line of evidence is only required when primary and secondary lines of evidence are inconclusive. A brief summary only is given for tertiary lines of evidence. Microbiological testing comprises mainly microbial counts and microcosm studies. Microbial counts of both heterotrophic bacteria and contaminant specific degraders can be used as an indication of biodegradation whereby the ratio of contaminant specific degraders to total heterotrophic bacteria should increase in aquifer zones where biodegradation is occurring (ASTM, 2004). However, microbial counts are often an unreliable indicator of biodegradation.

Microcosm studies are the only line of evidence that allows an unequivocal mass balance on the biodegradation of environmental contaminants (Wiedemeier, et al. 1999), however this has to be balanced with the likely cost and time implications of such an assessment. A microcosm study involves the measurement of the change in carbon substrate, terminal electron acceptors, and reduction product concentrations over time in a column comprising aquifer material and groundwater (ASTM, 2004). It is essential that the microcosm study is properly designed, and aquifer material and groundwater samples are collected appropriately, as detailed in Wiedemeier, et al (1999).

5 Optional lines of evidence

Optional lines of evidence may be used to more rigorously interpret data developed as secondary lines of evidence, particularly if the primary and secondary lines of evidence are inconclusive (ASTM, 2004). Optional lines of evidence include solute fate and transport modelling and estimates of assimilative capacity.

5.1 SOLUTE FATE AND TRANSPORT MODELLING

Analytical and numerical solute fate and transport models may complement the lines of evidence approach by (Agency, 2000):

- highlighting the differences between observed and predicted contaminant concentrations, which it may be inferred is attributable to attenuation;
- estimating the relative importance of various attenuation mechanism;
- testing the accuracy of model input data by comparing observed concentrations against those predicted by transport and fate modelling.

A detailed assessment of solute and fate transport modelling is outside of the remit of this report, however a brief summary is given.

Analytical transport models provide an exact solution to the equations that describe the migration of contaminants subject to advection, dispersion, linear sorption and degradation such as Ogata-Banks equation (time variant, constant source) or Domenico equation (time variant, declining source) (Agency, 2000). Analytical models are typically only appropriate to simple flow systems due to assumptions made regarding the nature of the aquifer, groundwater flow and attenuation mechanisms. These models are simple to use and have limited data requirements, but could give incorrect results for complex aquifer systems.

Numerical models provide an approximate solution to equations governing contaminant transport and allow more complex aquifer systems to be represented (Agency, 2000). This method has greater data requirements than analytical transport models, and requires technical expertise to develop.

Models may be deterministic (single value for each parameter resulting in a single value) or probabilistic/stochastic (parameter value defined by a range of values and yields a range of output values).

It is important to realise that models rarely provide an exact answer, and that inappropriate use of models can lead to erroneous results. Solutions to models are rarely unique, and there may be a number of parameter values that yield the same result. It is therefore essential that values used in the model are both accurate and representative. Additionally the user should be aware that calibration of the model to fit field data by the adjustment of values (e.g. rate coefficient) could require the use of unrealistic values (Odenchantz, et al. 2002).

5.2 DEMONSTRATION OF ASSIMILATIVE CAPACITY OF AQUIFER

The natural attenuation assessment will need to demonstrate that the assimilative capacity of the aquifer is sufficient to protect the identified receptors in the future (Agency, 2000). The assimilative capacity of an aquifer is determined by an electron-mass balance calculation based on measured changes in groundwater chemistry at a site together with a stoichiometric relationship describing the amount of contaminant degraded through oxidation/reduction

reactions. The amount of a contaminant that can be theoretically degraded by a electron accepting process can be estimated as follows (Agency, 2000):

$$BC = \sum \left[\frac{C_B - C_P}{F} \right]$$

Eqn 12: Aquifer assimilative capacity

Where: BC = biodegradation capacity [M/L³]
 C_B = average background concentration of electron acceptor or metabolic by-product [M/L³]
 C_P = lowest measured electron acceptor or metabolic by-product concentration within plume [M/L³]
 F = contaminant utilisation factor [MM⁻¹] (mass of COC degraded per unit mass of electron acceptor and metabolic by-product produced)
 Σ = sum of electron acceptors and metabolic by-products that contribute to degradation

The biodegradation capacity is the amount of contaminant that electron acceptors can assimilate or degrade based on the electron-accepting capacity of the aquifer. This is a function of groundwater flow below the contaminant source, and recharge/infiltration over the contaminant source area. The total biodegradation capacity (TBC) of the system can be estimated as:

$$TBC = 1000 \cdot Q \cdot BC$$

Eqn 13: Total biodegradation capacity

Where: TBC = total biodegradation capacity [MT⁻¹]
 Q = groundwater flow through plume [L³T⁻¹]
 BC = biodegradation capacity [M/L³]

This calculation can be used to determine whether the biodegradation capacity of the system is sufficient to have degraded the mass of contaminant, and indicate the relative importance of different electron acceptors or metabolic by-products to degradation (Agency, 2000). This method is purely qualitative due to uncertainties regarding the cause of the oxidation/reduction reaction (e.g. naturally anaerobic aquifers and mixed organic plumes).

6 Natural attenuation assessment method summary

The methods detailed in this report to assess natural attenuation are summarised in Table 1.

Table 1: Natural attenuation method assessment summary

N°	Assessment method	Type			Applicable determinands				Used for	Limitations
		Q	Qt	V	C	B	E	H		
1	1° lines of evidence									
1.1	Well concentration plots								Temporal change in COC concentration at a single well over time. Indicates if plume stable, expanding, or shrinking at one point.	Require use of multiple wells to identify if trends are consistent throughout the plume.
1.2	Centreline concentration plot								Spatial changes in COC concentrations along plume centreline (multiple wells). Indicates change in concentration of COC along plume. Plots for different times can indicate if plume stable, expanding, or shrinking.	Require monitoring wells to be located directly on plume centreline.
1.3	Contaminant ratios								Compare contaminant concentration or ratios to a conservative tracer along plume centreline.	Requires tracer to be recalcitrant but have similar other properties to the COC, and be part of the original spill incident.
1.4	Contour/isopleth plots								Cross section or plan view contours of COC at different time intervals to identify if plume is stable, expanding, or shrinking.	Subjective process with interpolation between wells. Requires high density monitoring network.
2	2° lines of evidence									
	<i>Natural attenuation rate</i>									
2.1	Well concentration rate constant								Attenuation rate constant (K_{point}) used to determine plume lifetime or time to reach remedial target at one well.	Only suitable for shrinking plumes. Represents mass loss from all attenuation processes. Assesses plume lifetime at one point only.
2.2	Centreline concentration rate constant								Attenuation rate constant (k) used to project how far along a flow path a plume will expand at a given point in time (plume trend evaluation).	Only suitable for stable or shrinking plumes. Represents mass loss from all attenuation processes. Does not show change in COC mass over time.
2.3	Biodegradation rate constant								Identifies biological decay rate, from all other attenuation mechanisms, for COC using Buscheck & Alcantar (1995) method or correction to a conservative tracer.	Buscheck & Alcantar method does not remove effects of transverse dispersion. Conservative tracer must be recalcitrant but have similar other properties to the COC, and be part of the original spill incident.
2.4	Mass Balance method								Calculation of the degradation rate from the change in dissolved mass of COC's within a plume over time.	Applicable where the plume is stable or shrinking. Requires that plume is fully characterised (i.e. all COC mass identified).
2.5	Mass flux method								Demonstrate change in mass flux, and hence mass loss, at one or several control planes normal to flow over time. Comparing of mass fluxes across several control planes used to determine degradation rates.	Uncertainty regarding point measurements of COC concentration to determine flux. The use of immission pump tests can resolve this issue.

N°	Assessment method	Type			Applicable determinands				Used for	Limitations
		Q	Qt	V	C	B	E	H		
<i>Biodegradation</i>										
2.6	Contaminant ratio plots								Comparison of ratios of COC's and COC breakdown products. An increase in the breakdown product to COC ratio is indicative of biodegradation.	Important to identify if the breakdown product is present in the source zone, or introduced as a separate incident as could give a false indication of biodegradation.
2.7	Mass balance								Mass balance (as detailed in 2.4) for COC breakdown products.	Breakdown products same requirements as 2.6.
2.8	Mass flux								Mass flux (as detailed in 2.5) for COC breakdown products.	Breakdown products same requirements as 2.6.
2.9	Contour/isopleth plots								Cross-section or plan view plots for breakdown products, electron acceptors/donors and hydrochemical indicators. Indicate areal extent of indicators and changes in concentrations over time.	Subjective process with interpolation between wells. Requires high density monitoring network. Hard to compare between multiple contour plots.
2.10	Radial diagrams								Simultaneous comparison of spatial and temporal trends for multiple chemicals on one map (SEQUENCE).	Do not give a quantifiable measurement of biodegradation.
3	3° lines of evidence									
3.1	Microbial counts								Comparison of total heterotrophic microbial counts to contaminant specific degraders to indicate where biodegradation likely to be occurring.	Microbial counts are often unreliable indicators of biodegradation.
3.2	Microcosm studies								Provide unequivocal mass balance on biodegradation of contaminants by assessing change in carbon substrate, terminal electron acceptors, and COC concentrations over time.	Microcosm study requires proper design, is costly, and time consuming.
4	Optional lines of evidence									
4.1	Solute fate & transport modelling								Modelling of contaminant migration. Can be used to predict plume trends.	Rarely provide an exact answer, and are reliant on the parameter values utilised. Calibration of the model to fit field data can lead to use of unrealistic parameter values.
4.2	Assimilative capacity of aquifer								Identify whether the biodegradation capacity of the system is sufficient to have degraded the mass of contaminants and indicate the relative importance of different electron acceptors or metabolic by-products to degradation.	Purely qualitative due to uncertainties regarding the cause of the oxidation/reduction reaction.

Q	Qualitative method
Qt	Quantitative method
V	Visual method

C	Contaminant of concern (inc tracers)
B	Breakdown products

E	Electron acceptors/donors
H	Hydrochemical indicators

References

- AGENCY. 2000. *Guidance on the assessment and monitoring of natural attenuation of contaminants in groundwater*. R&D Publication 95. Environment Agency, Bristol
- ASTM. 2004. *Standard guide for remediation of ground water by natural attenuation at petroleum release sites*. ASTM International. E 1943-98
- BARKER, J.F, BELAND-PELLETIER, C, BLAINE, F, DEVLIN, J. F, KING, M, W, G, SCHIRMER, M. 2000. Monitored natural attenuation – can mass flux through monitoring fences document mass loss in groundwater plumes?. *Groundwater Research*. 311-312
- BUSCHECK, T. E. AND ALCANTAR, C. M. 1995. *Regression techniques and analytical solutions to demonstrate intrinsic bioremediation*. Proceedings of the 1995 Battelle International Conference on In-Situ and On Site Bioremediation. April 1995
- CAREY, G. R. 1999. *The MoNA Toolkit – SEQUENCE, BioTrends, BioTracker – Users Guide*. Conestoga-Rovers & Associates and Waterloo hydrogeologic
- CAREY, G.R, VAN GEEL, P. J, WIEDEMEIER, T. H, MCBEAN, E.A. 2003. A modified radial diagram approach for evaluating natural attenuation trends for chlorinated solvents and inorganic redox indicators. *Groundwater monitoring and remediation*. 23, 4, 75-84.
- KAN, A. T, FU, G, HUNTER, M, CHEN, W, WARD, C. H, TOMSON, M. B. 1998. Irreversible sorption of neutral hydrocarbons to sediments: Experimental observations and model predictions. *Environmental Science and Technology*. 32: 892-902.
- NEWELL, C. J, RIFAI, H. S, WILSON, J. T, CONNOR, J. A, AZIZ, J. A, SUAREZ, M. P. 2002. *Calculations and use of first-order rate constants for monitored natural attenuation studies*. United States Environmental Protection Agency. Ground Water Issue. EPA/540/S-02/500
- ODENCRANTZ, J.E, VARLJEN, M. D, VOGL, R. A. 2002. Natural Attenuation: Is dilution the solution?. *LUSTLine*, Bulletin 40. 8-12.
- RUGNER, H, & TEUTSCH, G. 2001. *Literature Study: Natural attenuation of organic pollutants in groundwater*. Integrated concepts for groundwater remediation. WP6a
- SCHWARZ, R, PTAK, T, HOLDER, H, TEUTSCH, G. 1998. Groundwater risk assessment at contaminated sites: A new investigation approach. *Groundwater Quality: Remediation and Protection*. IAHS Publication 250
- TEUTSCH, G, PTAK, T, SCHWARZ, R, UND HOLDER, T. 2000. Ein neues Verfahren zur Quantifizierung der Grundwasserimmission. *Theoretische Grundlagen. Grundwasser* (eingereicht)
- WIEDEMEIER, T. H, WILSON, J. T, KAMPBELL, D. H, MILLER, R.N, HANSEN, J.E. 1999. *Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. Volume 1*. Air Force Centre for Environmental Excellence (AFCEE)
- www.waterloohydrogeologic.com. SEQUENCE: a modified radial diagram approach.