CoronaScreen: PROCESS-BASED MODELS FOR NATURAL ATTENUATION ASSESSMENT

Guidance for the application of NA assessment screening models

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Executive Summary

Conventional assessment of natural attenuation (NA) as a risk protection strategy relies on lines of evidence predicated on data collected along plume centrelines. The spatial variability inherent in most plumes makes accurate characterisation of longitudinal plume concentration profiles difficult at best. Where it is possible to collect sufficient spatial and temporal data, complex numerical models may be used to evaluate NA and allow prediction of key parameters such as maximum plume length and contaminant concentration at receptors. In many cases, however, it will not be possible to collect sufficient data to use a numerical model. If true, the user may be compelled to make assumptions that will lead to unacceptable uncertainty. Where data is scarce, acceptable first approximation of natural attenuation may be possible using a screening model – a simplified mathematical representation of a given site with inputs that capture key features of the plume. The screening models presented herein differs from available models in that they focus on quantifying biogeochemical processes rather than relying on spatial chemical data. The result is NA assessment on a par with or better than existing models using less spatial monitoring.

This document is intended as a companion to the CoronaScreen natural attenuation assessment modelling suite. It provides a *basic* overview of NA processes, assessment protocols and strategies, and demonstrates how and in what case scenarios CoronaScreen models should and should not be applied. Validation and input parameter sensitivity analysis are presented to demonstrate levels of confidence that can be ascribed to plume length and distance concentration estimates.

The document and model suite is intended for use by regulators and consultancies involved in the early stages of site assessment and/or engineered remediation design and implementation. The models are not designed to replace more complex deterministic numerical fate and transport models where use of such models is warranted.

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1. Natural attenuation in a site management context

1.1 General approach to site assessment

Ordinarily, assessment of contaminated sites begins with an examination of historical geological, hydrochemical and site use data to initiate the development of a conceptual model of the contamination scenario. Where contamination has impacted groundwater, it is often desirable (in many jurisdictions necessary) to conduct a risk assessment to evaluate potential impacts to sensitive receptors (water supply wells, surface water bodies, subgrade living/working airspace, etc). Integral to this risk assessment is often an evaluation of natural attenuation (NA), the most useful output of which is an estimate of either maximum plume length or the expected contaminant concentration at some point of interest along the flowpath.

Site risk assessment may be conducted in one or more stages of increasing complexity. The first stage typically involves a desk study of historical records and data from initial site investigations. If there is clear evidence that no there is no risk to any receptor (defined by local regulations), no further action may be necessary. In the event of some evidence of risk, a follow-on stage may involve either 1) more data collection to refine the conceptual model or 2) the design and application of some engineered remediation. Additional stages generally involve additional data collection and application of sophisticated numerical contaminant fate and transport models. Risk assessment is complete when it is proven that 1) there are no risk receptors, 2) natural attenuation is protective of risk or 3) NA is insufficient and engineered remediation is required. Even if NA is not protective of risk posed by prevailing contaminant mass flux, it may be protective if overall contaminant mass flux is reduced as a result of in situ remediation. Thus an estimate of natural attenuation rate may represent a key part of engineered remediation design, which purpose may be strategic reduction of contaminant mass flux rather than complete treatment.

1.2 When to apply screening level NA assessment models

Screening level NA assessment models are most appropriate in the early stages of site investigation. Indeed, because these types of models are constructed of simplified fate and transport relationships, the few data input requirements are those typically determined early in site investigations. Alternatively, estimates of key input parameters or literature values can be used to provide preliminary estimates of plume length or concentration at points along a flux path. Such estimates can be useful when designing or optimising monitoring well locations prior to invasive site investigations.

Screening level models may also be applied at later stages of site investigation/risk assessment, using refined parameters derived from more comprehensive site data. These simplified models run much quicker than complex deterministic numerical models, and thus can also be used in an iterative fashion to explore the sensitivity of key fate and transport parameters.

Because of simplifications and imbedded assumptions, screening models are not intended for comprehensive analysis of contaminated sites where complex biodegradation, sorption and transport processes occur. For such cases, a more sophisticated deterministic numerical model is recommended.

2. Natural attenuation of contaminants

It is not the purpose of this document to discuss in detail natural attenuation processes or site assessment protocols. For this, the reader is directed to more comprehensive reviews (e.g. Wiedemeier et al., 1999) or other references cited in Section 3.2. The aim here is to examine key natural attenuation processes, illustrating where those processes occur within a plume, and highlighting what processes dominate during various evolutionary phases of a plume.

2.1 Contributing processes

Natural attenuation can be viewed as a reduction in contaminant concentration along a flowpath as a result of volatilisation, dilution, retardation, dispersion, and biodegradation. The contribution these five processes make to overall natural attenuation depends on the nature of the contaminant(s), the characteristics of the aquifer, and the mode of contaminant release. Weakly attenuating contaminant species typically have low volatility, low retardation and are resistant to biodegradation. One example is MTBE, which attenuates primarily by dispersive mixing with uncontaminated water and dilution at receptors.

Natural Attenuation Processes

Volatilisation: partitioning of a contaminant from a separate organic liquid phase to soil gas.

Dilution: mixing of plume with uncontaminated water at e.g a river discharge or abstraction well

Retardation: reduction in contaminant velocity due to partitioning to aquifer matrix

Dispersion; mechanical and diffusive mixing of contaminant and background water during transport

Biodegradation: transformation of contaminants by indigenous microbes

Volatilisation: Air-Water Partitioning

Contaminants partition from the dissolved phase to air (soil gas) according to Henry's Law:

$$H_{cc} = {C_a}/{C_w}$$

where C_a is air concentration and C_w is water concentration (both in mass/volume, e.g. mg/L). In this form, H is dimensionless – beware of units in other forms. A more volatile contaminant will have a larger H_{cc} compared to a less volatile contaminant.

Volatilisation (partitioning of contaminants from the water phase to the gas phase) will make a more significant contribution to the attenuation of highly volatile contaminants (larger Henry's constant) relative to low volatility contaminants. Thus, it could be expected that volatilisation will be a more significant NA process for benzene (H_{cc}=0.24) than for MTBE (H_{cc}=0.023), even though both may be found in the same plume dissolving from a fuel hydrocarbon spill. Also, significant volatilisation can only occur at or near the water table and therefore will contribute more to the attenuation of plumes emanating from spilled petroleum fuel hydrocarbons (light non-aqueous phase liquids that float on the water table) than those emanating from a chlorinated solvent spill (a dense NAPL distributed to depth), even though both spills have constituents with similar Henry's constants.

Dilution occurs where a plume intersects a receptor (water supply well, river, etc). Since the plume represents only a fraction of the groundwater captured by the receptor, plume contaminant concentrations are diluted by contaminant-free water. The magnitude of dilution depends on the proportion of plume to clean water flux into the receptor. Thus, for a given receptor, plumes with a small cross-sectional area of flow will be diluted more than larger plumes. These issues are addressed by Einarson and Mackay, 2001).

Retardation attenuates contaminants by slowing transport velocity via the process of sorption. Contaminants that readily partition to organic carbon or ion exchange sites will migrate more slowly than those that weakly partition. For most of the common organic contaminants, the magnitude of sorption usually does not vary with contaminant concentration, meaning that retardation can be estimated using a simple partitioning relationship. If local contaminant concentrations are constant in space (i.e. the plume is at steady state; neither growing or shrinking), then retardation does not contribute to overall contaminant attenuation because solid-water partitioning is in equilibrium. Only when concentrations are not in equilibrium (during plume growth or decay) does retardation contribute to attenuation.

Sorption: Solid-Water Partitioning

Contaminants partition from the dissolved phase to the solid phase (i.e. aquifer media) according to a distribution coefficient (K_d):

$$K_d = C_s / C_w$$

where C_s is the concentration of contaminant on the solids. There are published K_d values and a number of semi-empirical methods to estimate it for most common contaminants. Solid-water partitioning slows contaminant transport velocity by a retardation factor:

$$R = \nu_w / \nu_c = 1 + \rho_b / \Theta \, K_d$$

where ν_c and ν_w are contaminant and water velocity, respectively, ρ_b is aquifer bulk density and θ is aquifer porosity.

Dispersion is the process responsible for mixing waters during transport. Dispersion has two additive components: advective and diffusive. The magnitude of the advective component of mixing is defined by groundwater velocity and an aquifer characteristic called dispersivity. Aquifers with a wide range of pore sizes (greater heterogeneity) typically have greater dispersivity. The diffusive component is driven by the chemical gradient between higher and lower concentration areas of the plume.

Biodegradation by indigenous microorganisms is the only NA process that results in the removal of contaminant mass, either via complete mineralisation or transformation to another specie. Because of this, NA assessments focus on collecting data to establish the rate of bioattenuation. While biodegradation is often a complex process involving interacting microbial consortia operating over a range of geochemical conditions, at the early stages of NA assessment it can be approximated by pseudo first order decay. In the case of contamination by hydrocarbons or their derivatives, decay is often rapid enough to be treated as effectively instantaneous (since groundwater velocities are typically small).

2.2 Plume development and life phases

If a sufficient mass of contaminant is released into the subsurface, some of that mass may be transported to the water table. The result is the generation of a groundwater contaminant plume. The manner in which the plume forms depends on the nature of the contaminant release. Some contaminants (e.g. ammonium and nitrate) are released as aqueous solutions, while others (petrol, chlorinated solvents, coal tar) enter the subsurface as non-aqueous phase liquids (NAPLs). Aqueous contaminants can be released below the water table or be flushed down to the water table by recharging water. Constituents dissolving from a NAPL located above the water table may also be flushed down to the water table to form a plume, or the NAPL itself may invade the water table and then generate a plume (see Figure 10 in Section 5.3). In either case, a plume of contamination will emanate from what is called a localised or point source area. Non-point sources of contamination are those that originate from more diffuse sources (i.e. from agricultural activity). Natural attenuation assessment of plumes derived from such sources can be performed, but because the source area may be many hectares in size and spatially complex, they must be treated at a very large scale. The various assumptions that must be made to simplify the source means any estimate of plume length will have a high degree of uncertainty.

2.2.1 Growth phase

Immediately after a source is introduced to the subsurface, a plume will begin to form in groundwater and be transported downgradient if contaminant concentrations are stoichiometrically greater than available electron acceptors (Figure 1). The rate at which a plume grows thus depends on groundwater velocity, sorption, and biodegradation: by estimating or measuring these parameters, it is possible to estimate the time required for a given plume to reach the end of the growth phase or attain its maximum plume length.

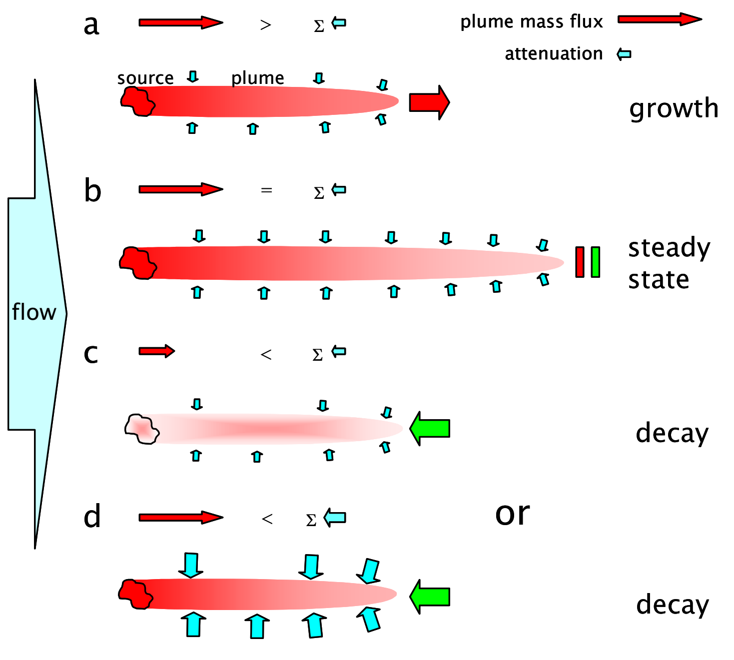

Figure 1. Plume life phases defined by the balance between plume mass flux and plume attenuation due to natural processes.

2.2.2 Steady-state phase

Once the rate of contaminant mass flux (cross-sectional plume area x plume velocity x contaminant concentration) is offset by the combined rate of mass attenuated by natural processes, the plume has reached steady state. As long as contaminant flux from the source area continues and the rate of attenuation does not change, the plume will remain at steady state. In the case of contamination by dissolved species (often of finite volume or mass), it is rare that the associated plume will reach a steady state condition. NAPL sources, on the other hand, may last for decades or centuries due to the low effective solubility of the dissolving plume constituents. Thus, the steady state phase of plumes emanating from NAPL sources may be of the same order.

2.2.3 Decay phase

When contaminant mass flux no longer matches the rate of attenuation (the source is exhausted or the rate of attenuation increases), the plume will begin to shrink or decay. If steady state is disturbed because the attenuation rate has increased, the plume may shrink until it achieves a new steady state length. Conversely, if the attenuation rate decreases for some reason (e.g. buildup of toxic microbial byproducts), the plume may grow until it again reaches steady state. If the source is exhausted, the plume will decay until it disappears. Note that the plume may appear to shrink in length for a period of time, but since attenuation occurs everywhere in the plume (at various rates), the plume will in fact effectively "dissolve" away. The length of the decay phase should theoretically be roughly equivalent to that of the growth phase.

2.3 Biodegradation in detail

Fortunately, many, if not most of the contaminants found in groundwater are amenable to microbially mediated degradation. There are two fundamental reaction types that contaminants can undergo: oxidation and reduction. Contaminants that are oxidised lose electrons, while those that are reduced gain electrons. The transfer of these electrons is regulated by microbial activity. These fundamental reaction types should not be confused with oxidising and reducing geochemical conditions, commonly expressed as redox, or oxidising potential. This is a measure of the tendency for the system to transfer electrons. As electron acceptors are consumed, the groundwater becomes more reducing and the redox potential of the groundwater decreases.

2.3.1 Oxidised contaminants

The vast majority of petroleum hydrocarbons (petrol, diesel, fuel oil, coal tar, etc) consist of compounds that contain carbon in a reduced state. Organisms that degrade these compounds do so by facilitating the exchange of electrons from the compound to an electron acceptor,

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

which is itself reduced in the reaction. Note that the oxidation of these compounds can occur under oxidising or reducing geochemical conditions, which is often a source of some confusion. For example, benzene can be biodegraded by organisms using oxygen as an electron acceptor (under aerobic or oxidising geochemical conditions. The half-cell reactions are:

$$C_6H_6 + 12H_2O \longrightarrow 6CO_2 + 30H^+ + 30e^-$$

Adding these yields the coupled reaction:

$$C_6H_6 + 7.5O_2 \longrightarrow 6CO_2 + 3H_2O$$

Benzene can also be oxidised by organisms that use sulphate as an electron acceptor (under moderately to strongly reducing geochemical conditions). The sulphate reduction half-cell reaction is:

$$8e^- + 10H^+ + SO_4^{2-} \longrightarrow H_2S + 4H_2O$$

Adding this to the benzene half-cell reaction above yields the coupled reaction:

$$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \longrightarrow 6CO_2 + 3.75H_2S + 3H_2O$$

In both cases, from the half-cell reactions it can be seen that benzene loses electrons (is oxidised) while the electron acceptor gains electrons (is reduced). It is important to note that the geochemical conditions under which each reaction occurs is mutually exclusive: aerobic reactions cannot happen under sulphate reducing conditions and sulphate reduction cannot occur under aerobic conditions.

2.3.2 Reduced contaminants

Halogenated aliphatics such as TCE (trichloroethylene), PCE (perchloroethylene or tetrachloroethylene), 1,1,1-TCA (trichloroethane), and DBE (dibromoethene) are common groundwater contaminants and are examples of compounds where carbon exists in an oxidised state. These compounds may be degraded by microorganisms via reductive dehalogenation: transfer of electrons from a donor (typically molecular hydrogen) to the contaminant. The half-cell reactions for the reductive dechlorination of TCE to cis-1,2 DCE are:

$$H_2 \longrightarrow 2H^+ + 2e^-$$

and

$$C_2HCl_3 + 2H^+ + 2e^- \longrightarrow C_2H_2Cl_2 + H^+ + Cl^-$$

yielding the coupled reaction:

$$C_2HCl_3 + H_2 \longrightarrow C_2H_2Cl_2 + H^+ + Cl^-$$

Thus TCE gains electrons (is reduced) while hydrogen loses electrons (is oxidised). The organisms that perform these reductive reactions require very strongly reducing conditions. Thus, the greatest rate of contaminant dehalogenation will occur near the core of the plume where the necessary conditions can manifest.

2.3.3 Biodegradation redox regimes

In the case where contaminants are oxidised, biodegradation reactions occur in a specific order defined on the basis of thermodynamics. More energy is available to organisms that degrade one mole of benzene aerobically (ΔG^o_r = -765 kcal) compared to that via sulphate reduction (ΔG^o_r = -123 kcal). In fact, the common electron acceptors are preferentially utilised in decreasing order of thermodynamic favourability – oxygen, nitrate, iron (III), manganese, sulphate, and carbon dioxide. The result of this is distinct zonation of bioreactions and therefore electron acceptor distributions, grading from carbon dioxide reducing (commonly referred to as methanogenic) in the plume core to aerobic at the outer fringe or corona (Figure 2). Because of the superior energy yield, aerobic reactions tend to be faster than methanogenic reactions, giving rise to a state where slow reactions are confined to the core while faster reactions are limited to the outer plume fringe. In most cases the plume travels slower than the reaction products (due to sorption of the former), meaning that once oxygen and nitrate are depleted at the leading plume edge, following contaminant flux travels in an electron acceptor depleted halo (Figure 2). The only way fringe reactions can be maintained is via mixing of outward dispersing plume constituents with inward dispersing electron acceptors. In many cases therefore, overall plume attenuation is controlled by this rate of mixing, which is influenced by horizontal and vertical transverse dispersion.

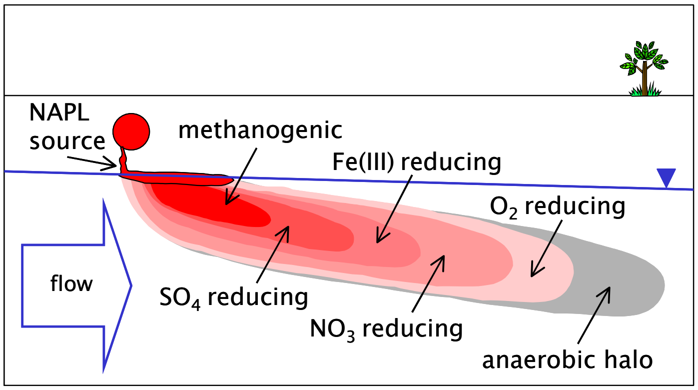

Figure 2. Distribution of redox zones in a typical naturally bioattenuating plume of dissolved oxidisable constituents.

3. Current NA assessment practices

3.1 NA assessment philosophy

The implementation of MNA as a remedial measure requires that natural attenuation occurs at a rate sufficient to achieve site-specific remedial targets within a reasonable time frame. Evaluation of MNA as a potential remedial approach requires the implementation of a reliable and acceptable technical protocol to confirm and quantify natural attenuation processes. A series of protocols and guidelines published in the mid to late 1990s (Table 1) have since gained acceptance among both practitioners and regulators. Consensus on the general approach, the data requirements and the evaluation process for determining the feasibility of MNA (Rittmann, 2000; Sinke, 2000; Small and White, 1998) make it logical to include NA assessment at the initial stage of site investigation.

Table 1. MNA protocols and guidelines

Protocol/guidance	Contaminant type
AFCEE, 1995	Petroleum hydrocarbons
*Wiedemeier et al., 1996	Chlorinated solvents
*ASTM 1998	Petroleum hydrocarbons
RTDF, 1997	Chlorinated solvents
*OSWER, 1997	General
*NOBIS, 1998	Chlorinated solvents and BTEX
UK EA, 2000)	General

* new, adapted, editions are available

Because it is relatively inexpensive compared to engineered remediation, MNA is the option to which others are compared from a technical and cost perspective. In some jurisdictions risk assessments frame the earliest investigations at a site, imbedded in which is an assessment of natural attenuation. Absence of risk generally means NA is sufficient to serve as a plume management option, but may or may not require monitoring.

3.2 Current NA practices

Current NA assessment often focuses on assembling lines of evidence to establish the presence and long-term viability of biodegradation by indigenous microorganisms. In current investigation protocols, there are three lines of evidence sought: 1) historical data indicating the plume has either reached steady state, is growing, or is shrinking, 2) geochemical data showing decrease in contaminant concentrations, decrease in electron acceptor or donor concentrations, increase in metabolic by-product concentrations, and increase in daughter product concentrations, and 3) microbiological data demonstrating the presence and activity of microorganisms capable of the required reaction.

3.2.1 Site investigation methods

Data are most often collected from monitoring wells that are intended to represent a contiguous flow path or plume centreline. Current protocols recognise that various bioattenuation reactions occur in specific zones within the plume, but do not advocate monitoring specifically designed to characterise these zones. More often than not, well screens that span more than one redox zone are installed, obscuring this important zonation. An example is given by one of the sites investigated as part of the CORONA project, located in the UK Midlands. A phenols plume was initially instrumented with long screened monitoring wells (2-5 m), and interpreted to have the structure shown in Figure 3a. Subsequently, high-resolution multilevel wells were installed, data from which yielded the plume interpretation shown in Figure 3b. Both the conceptual model and the apparent rate of plume attenuation are considerably different in that example.

3.2.2 Confounding effect of heterogeneity

Current protocols call for a series of monitoring wells (at least 4-6) to be installed along some flow path, ideally the plume centreline. However, in many cases aquifer heterogeneity results in spatially variable source distribution and/or contaminant transport along preferred (or spatially discrete) flux paths, resulting in plumes that lack a unique centreline (Wilson et al., 2004). Using data from wells that do not represent a centreline can lead to over- or underprediction of NA rates (Figure 4), and in any case a high degree of uncertainty in the delineation of the plume geometry, structure and temporal behaviour.

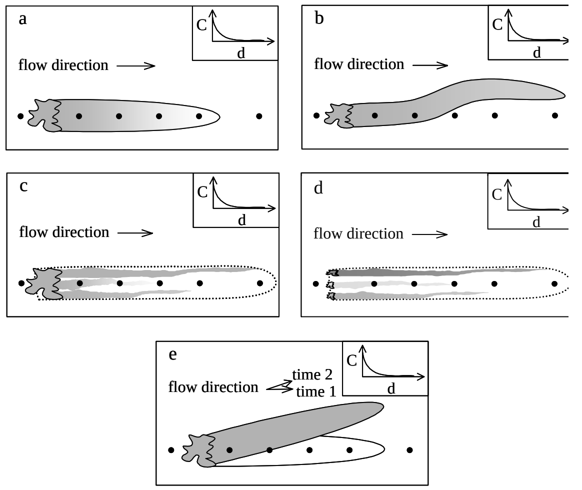

Figure 4. The effects of various forms of heterogeneities on assessment of natural attenuation.

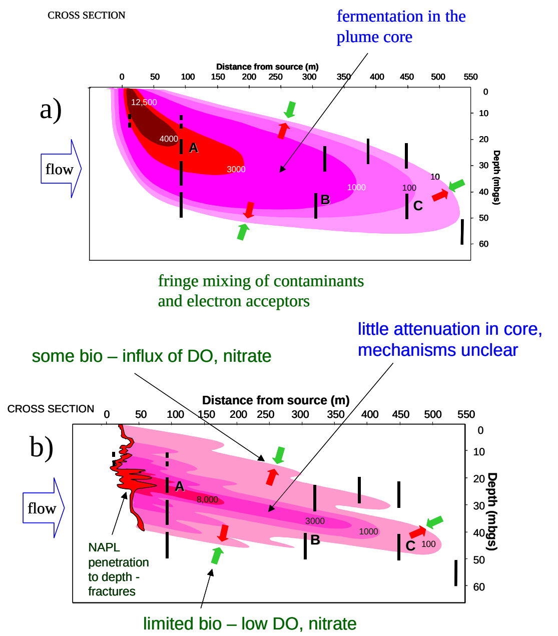

Figure 3. a) Long screen monitoring wells and resulting plume interpretation. b) high-resolution monitoring wells and revised interpretation of the same plume.

3.3 CORONA approach

The CORONA approach to NA assessment differs from the traditional approaches in that it does not seek to obtain plume centreline concentration data or gather lines of evidence. Rather, CORONA seeks to quantify and rank the key NA processes influencing plume transport. A conceptual model of the site should always be built, starting with comparison with plume analogues. For example, the maximum length of a plume degrading by oxidation will be controlled by mixing of electron acceptors at the plume fringe, which is impacted by vertical transverse dispersion. Monitoring well installation and data collection would be designed to obtain data to allow estimation of dispersivity, inward electron acceptor flux gradients, and outward contaminant flux gradients.

3.3.1 Core vs fringe controlled plumes

By focussing on process identification and quantification, the CORONA approach involves a determination of where within the plume the majority of contaminant biodegradation occurs. Generally, fringe processes control the attenuation of plumes consisting of contaminants that are oxidised (e.g. petroleum hydrocarbons), whereas processes occurring in the core control the attenuation of plumes comprised of reducible contaminants (Figure 5). It is important to note that the reactive fringe will become increasingly thicker along the plume flowpath (fringe thickness is a key input parameter for one of the CoronaScreen models). In some cases, both core and fringe processes may contribute significantly to overall mass degradation, so NA assessment should account for both. Plumes derived from coal tar NAPLs are an example of dual process systems because both oxidation and fermentation may contribute significantly to overall carbon turnover. Because chlorinated solvents degrade by reductive dechlorination (which requires highly reducing conditions), plume length is typically controlled by core processes only.

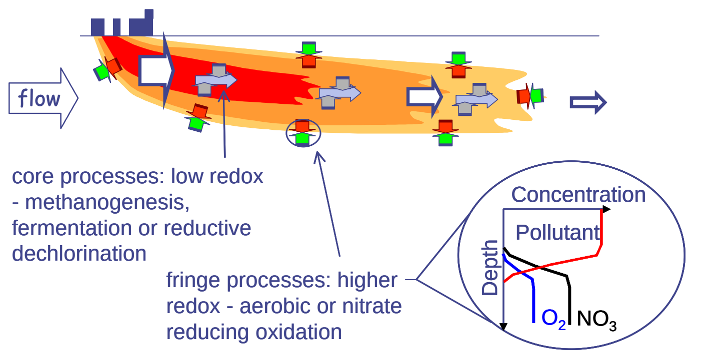

Figure 5. Schematic of a plume showing location of fringe and core processes.

3.3.2 Preferred site instrumentation

To obtain the data necessary to identify and quantify key processes, high-resolution (25 – 100 cm spacing) multilevel wells can be installed to allow quantification of dispersive electron acceptor and plume gradients at the plume fringe (in the case of oxidising plumes), and therefore transverse vertical dispersivity. Because the focus is on process quantification rather than spatial contaminant distribution, it should be possible to make a reasonably accurate estimate of NA performance from a fewer number of high-resolution multilevel monitoring wells.

4. Screening models in NA assessment

The first phase of NA assessment generally involves an assessment of historic site data. It is a step that often is overlooked, but one of the first tasks that should be started for a new site is the development of a conceptual site model. By comparing the site in question to similar sites (geology, contaminant, mode of contaminant release, etc), which, and where within the plume, attenuation mechanisms are likely to be important can be anticipated. This can influence where best to install monitoring wells and what kinds of monitoring devices to use (monitoring device and location guidance is presented in Appendix III). Conceptual models should be considered a living device that is constantly updated as new data is gathered.

In the early phases of investigation, it may be desirable to get a sense for risk that a given plume may pose. Two measures of risk are 1) estimates of how long the plume may be expected to grow and 2) what contaminant concentrations may manifest at certain points along the plume after a certain time. It is likely at this stage that insufficient data will be available to use a complex numerical model to simulate plume history. Groundwater velocity, flow direction, contaminant and background electron acceptor concentrations may be known from a few locations, but other key parameters such as dispersivity and sorption may have to be estimated. Simplified or screening level models may be a more appropriate approach because they require few input parameters.

Subsequent phases of site investigation result in the acquisition of data that help resolve the question of risk. These data can also be used to refine the conceptual model and improve parameter estimates for input to simplified (or complex) simulation tools.

4.1 Conceptual model development

There are a number of aspects of a conceptual model: geology, hydrogeology, geochemistry, microbiology and mode of contaminant release. Site records or local knowledge are often sufficient to build a basic geologic model. Refinements to the geologic part of the model will come from analysis of core, trial pits, or drill cuttings – this may be important if the site is comprised of highly heterogeneous sediments or fractured rock. The hydrogeological, geochemical and microbial components (water table maps, average water velocity) may be approximated from local or regional data, but site-specific data will almost certainly be required. If the mode of release is known (i.e. release of a known volume of NAPL with certain properties from a known location at a known rate), then an idealised source distribution model can be generated. However, given the complex nature of two-phase flow, the exact distribution of NAPL in the subsurface can never be known with certainty.

4.2 Application of screening models

Screening models that incorporate analytical solutions of the mass transport equation have been used to explore various basic characteristics of a plume. These models assume biodegradation proceeds at a uniform pseudo first order rate for all the electron donor/acceptor couples. Solutions are available for vertical and horizontal line, point and planar sources of finite, infinite or decaying duration. As such, a wide range of source/plume scenarios can be approximated by an analytical solution. Input requirements are generally limited to groundwater velocity, source geometry, source concentration, electron acceptor concentrations, and longitudinal and/or transverse dispersivity. These inputs could also be used in a numerical model, but simplified models are easier to operate and run quicker, and given similar levels of uncertainty may be a preferable means to explore aspects of a given plume (e.g. sensitivity of plume length to changes in groundwater velocity or dispersivity).

4.3 Available screening models

There are three screening models currently available: BioScreen (Newell et al., 1996), NAS (Chapelle et al., 2003) and BioChlor (Aziz et al., 2000). The first two are intended for use on oxidising plumes while the latter is for reductive dechlorination. All three models use a modified form of the Domenico, 1987) analytical solution for a degrading contaminant plume transported from a vertical plane source. From a relatively short list of input parameters (those for BioScreen are compiled in Table 2;

Table 2. Input parameters for BioScreen

Parameter
groundwater velocity [i]
longitudinal dispersivity
transverse horizontal dispersivity
transverse vertical dispersivity
retardation factor [ii]
1st order biodegradation constant [iii]
source area width and thickness
source contaminant concentration [iv]

i or hydraulic gradient, hydraulic conductivity and porosity

ii or bulk sediment density, fraction of organic carbon and water/solid partitioning coefficient

iii or electron acceptor concentrations in the case of instantaneous reactions

iv combined concentrations of all hydrocarbons in plume inputs for NAS are similar), a profile of contaminant concentrations along the theoretical oxidising plume centreline is calculated. From these profiles, the maximum plume length can be obtained. Alternatively, plume length (assuming it is known) can be input and dispersivities and/or decay rate can be estimated by curve fitting.

BioChlor is used in a similar manner, except individual 1st order decay rates and concentrations for parent and daughter products must be entered (i.e. for PCE, TCE, cis-1,2 DCE and VC in the case of chlorinated ethenes).

4.4 Advantages of existing screening models

There are a number of advantages of NA screening models. They typically run very quickly, allowing for output determination and sensitivity analysis in a matter of minutes. These models also require relatively few input parameters – mostly those that can be measured in the field or estimated from field data. Due to their simplicity, screening models do not require any special user expertise. They are usually based on spreadsheet applications, which make them relatively compact and easy to disseminate. These models are also cost-effective - a number are currently available freely from websites (e.g. BioScreen can be obtained from the USGS website).

4.5 Disadvantages of existing screening models

Parameters such as source concentrations, groundwater velocity, and retardation can be easily measured or estimated from semi-empirical relationships. However, dispersivities are difficult to measure, and source geometry requires a significant site investigative effort to establish. As such, estimates of plume length, etc., are subject to a degree of uncertainty that may be unacceptable. Indeed, the BioScreen model has largely fallen out of favour largely because it has been used without a clear understanding of the implications of inputting inaccurate estimates of key attenuation parameters. It is not necessarily a flaw with the underpinning analytical solution, but rather the NA assessment philosophy embodied in the model.

5. CoronaScreen NA models

The CoronaScreen models are predicated on the hypothesis that the identification and quantification of key attenuation processes will yield better NA assessment than evaluation of spatial concentration data. It was found during the CORONA project field investigations (6 different contaminant plumes in unconsolidated and rock aquifers), that processes contributed variably to natural attenuation. It follows that the parameters that have the most impact on plume length should be estimated with a greater degree of rigour. This differs from the conventional approaches embodied in the BioScreen model, which relies on concentration data collected along the plume centreline and estimates of dispersivity.

5.1 Output goals

As stated earlier, knowledge that is useful at the early stages of site management include some estimate of maximum plume length, concentration at key distances from source (compliance boundaries, receptors, sensitive monitoring locations), and the time it will take a plume to reach maximum length. The primary goal of a screening model is to obtain these useful estimates with as high a degree of accuracy as possible.

It should be understood that the outputs described below are calculated from the point where field data are collected. Therefore, if data are collected some distance downgradient of a source zone, the maximum plume length is the sum of that returned by the models ***and*** the distance from the source to the monitoring point. For example, if input data are collected from a monitoring point located 100 m downgradient of a petrol spill source, and the model returns a plume length of 500 m, the actual total maximum plume length is 600 m. The model automatically performs this calculation.

5.1.1 Maximum plume length

As described in Section 2.2, plume evolution involves growth, steady state and decay phases. A plume reaches steady state when contaminant mass flux downgradient is balanced by mass attenuated by natural processes, predominantly biodegradation. When at steady state, the plume will have reached its maximum length unless concentrations in the source area increase. Some estimate of this length is useful when considering impacts to potential receptors. For example, if a given plume is expected to migrate no more than 500 m from source, it will never impact an abstraction well 800 m away, and thus pose no risk.

Maximum plume length can be defined in a number of ways: maximum allowable concentration limit (e.g. 5 ug/L for benzene), analytical detection limit (varies with analytical method), or zero concentration (not attainable in a practical sense). Different regulatory systems may have unique criteria for defining plume boundaries: the user is referred to local or national regulations. Alternatively, a working definition may be negotiated with local authorities. Examination of numerical model results suggests that there is no significant difference in plume length for the different plume limit definitions. Nevertheless, the CoronaScreen models all define maximum plume length as the point where concentrations are reduced to zero, which provides the most conservative estimate.

5.1.2 Concentration at compliance

One of the analytical model outputs is concentration plotted along the plume centreline. From these plots, concentrations at a given distance from the source can be estimated. The analytical model can also output vertical concentration profiles of contaminant and electron acceptor at a user-defined distance from the source. These can also be used to indicate contaminant concentration at any point along the modelled plume travel path.

5.1.3 Time to reach steady state

If there is stoichiometrically more contaminant (electron donor) than electron acceptors, a plume will grow in length until attenuating mechanisms offset contaminant flux. An estimate of how long it will take for a plume to reach steady state (i.e. maximum plume length) may be useful in developing MNA sampling frequency and influence site management decisions. As an example, if a plume is estimated to require decades to reach steady state, it may be desirable to affect some engineered remediation, while a plume estimated to reach steady state in a few years might be left on its own.

5.2 Description of models

The CoronaScreen suite consists of three simplified reactive transport models that operate within an Excel spreadsheet environment (requiring Excel2000 or later). Data is input into topic-related section fields: each model extracts the required inputs (see Table 3), and performs the relevant calculations using VBA macros. Output is displayed as maximum plume length or concentration at a specified distance from source, and time to reach steady state. Contained within the spreadsheet is a database of common contaminants that can be added to the relevant input section. It is also possible to add contaminants to the database provided the user has a balanced half reaction equation. The Travelling 1-D model uses PHREEQC (geochemical speciation and reactive transport code), which is embedded in the CoronaScreen environment and automatically called when the Travelling 1-D model is used.

Table 3. Parameters required by the CoronaScreen models

Parameter	Travelling 1-D	Analytical	Electron Balance
Groundwater velocity	✓	✓	✓
Vertical dispersivity		✓	✓
Horizontal dispersivity		✓	✓
Longitudinal dispersivity		✓	
Plume width		✓	✓
Plume thickness		✓	✓
Plume fringe thickness		optional	✓
Background EA concentrations	✓	✓	✓
Plume EA concentrations	✓	✓	✓
Background ED concentrations	✓	✓	✓
Plume ED concentrations	✓	✓	✓
Porosity			✓
Aquifer bulk density			✓
Fraction organic carbon			✓
Distance: source to “source” well		✓	✓
Distance: source to MLS well		✓	✓

EA = dissolved electron acceptors or their redox couples: O_2, NO_3^-, SO_4^{2-}, Mn^{2+}, Fe^{2+}, CH_4

ED = electron donors (i.e. plume constituents)

MLS = multilevel sampling well

Each of the three models is predicated on a fundamentally different premise, providing the opportunity to assess NA from different theoretical perspectives. The analytical models are similar to that used in BioScreen and NAS, except that both electron acceptor and donor concentrations are converted to stoichiometric electron equivalents to implicitly represent multiple contaminants and electron acceptors consistent with reaction stoichiometry. This convention is also used in the Travelling 1D and Electron Balance models.

In some cases, especially early in a site investigation, field data to calculate the required input parameters shown in Table 2 will not be available. In these cases parameters may be estimated; the user is directed to Sections 5.2.1, 5.2.2, and 5.2.3 for a discussion of model sensitivity to various input parameters.

5.2.1 Analytical Model

The Analytical model is based on a closed-form analytical solute transport solution that simulates advection, dispersion, and biodegradation of a finite dimension continuous source emanating from a vertical plane. The model makes the following assumptions:

1) Biodegradation reactions are instantaneous, which for most groundwater velocity regimes is a valid assumption (Borden and Bedient, 1986; Gramling et al., 2002)
2) The plume is at steady state
3) Velocity is uniform and constant
4) Source is continuous and spatially/temporally uniform

See the appended Analytical Model User Guide for an explanation of the relevant equations.

Nearly all the required inputs are parameters that can be measured in the field (Table 2), with the possible exception of plume width. Vertical dispersivity can be either estimated based on literature values or calculated from reactive zone thickness derived from vertical concentration profiles obtained from multilevel wells or drive point profiling. This reactive zone thickness is a key input for the Electron Balance model, and is discussed in greater detail in section 5.2.3. Because the shape of vertical profiles will change with distance travelled, accurate estimation of vertical dispersivity requires that the profiles be adjusted for the distance between source and observation.

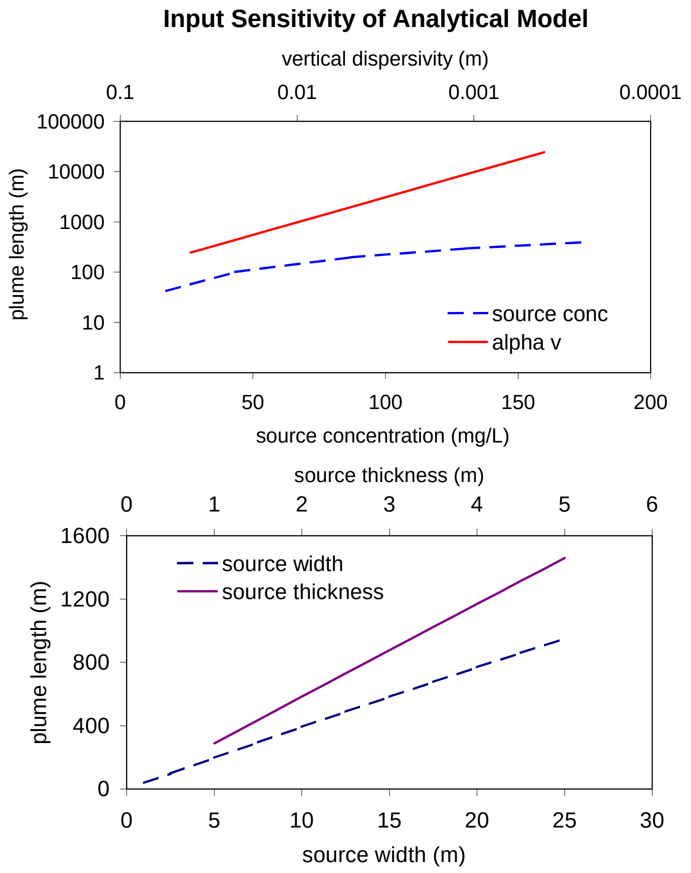

Figure 6. Sensitivity of the Analytical Model to various input parameters. See Appendix II for scenario details.

In addition to an estimate of plume length, the model calculates the time needed to reach steady state. Time to steady state is calculated using the input velocity, which is otherwise not used by the model (velocity is not needed to calculate plume length). A plot of contaminant concentration along the plume centreline is generated, from which concentration at some compliance point downgradient can be estimated. Vertical profiles of electron acceptors and contaminants at user-defined distances from the source are also generated, from which an evaluation of expected vs observed profiles could be performed to check or refine the site conceptual model.

The worked example found in Appendix II was used to assess parameter sensitivity for the Analytical and Electron Balance models. The Analytical model is particularly sensitive to vertical transverse dispersivity and source width (Figure 6), which both vary non-linearly with increasing width or decreasing dispersivity. Estimated plume is not particularly sensitive to source concentration, which means that it is not imperative to locate and sample the highest concentration in a source area to obtain a reasonable plume length estimate. It is clear from

Figure 5 that accurate estimate of vertical dispersivity and source width are integral to reliable plume length assessment, and thus any new data collection should be directed to refining estimates of these parameters.

5.2.2 Electron Balance Model

In the Electron Balance model adapted from Thornton et al., 2001), the plume is represented by a box with inwardly dispersing electron acceptors and outwardly dispersing electron donors on the lateral, top and bottom sides (Figure 7). The model compares the electron equivalents of acceptor and donors, and based on stoichiometric EA demands, iteratively increases plume length until both are in balance. At that point, there are sufficient acceptors to facilitate biodegradation of all the donors – i.e. the plume is at steady state and reached maximum length. The EB model has the most input parameter requirements of the three models. Because it considers dissolved inorganic carbon and methane in background and plume, the model can directly account for fermentation. This means that both fringe and core processes of oxidisable contaminants can be represented.

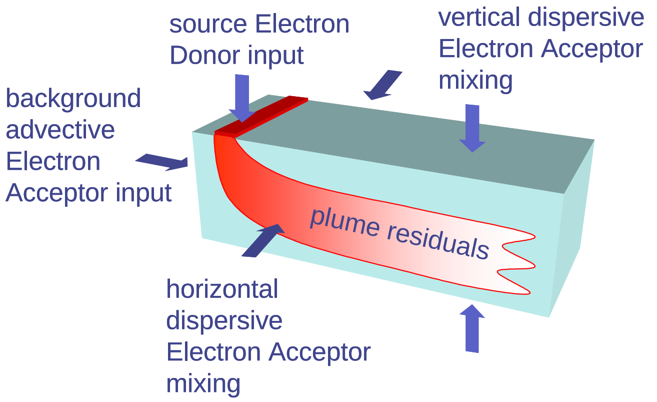

Figure 7. Schematic of plume representation by the Electron Balance model.

The EB model assumes that:

1) The source is infinite and temporally invariant
2) Plume velocity is uniform in space and time
3) Bioreactions are instantaneous
4) Reactive fringe thickness (RFT) does not change with travel distance

It is well accepted that horizontal transverse dispersion is greater than vertical transverse dispersion (generally assumed to be a factor of 10). It is therefore reasonable to assume that horizontal RFT will similarly be greater than vertical RFT. The EB model can convert vertical RFT (estimated from multilevel data) to vertical dispersivity using a simple equation derived by algebraic manipulation of the aforementioned analytical solution:

$$RFT = \left(1 - \frac{C_{EA_{\max}}}{C_{ED_{\max}} \left(1 + \frac{C_{EA_{\max}}}{C_{ED_{\max}}} \right)} \right) * \sqrt{\pi \alpha_{tv} L}$$

It then assumes that horizontal dispersivity is an order of magnitude greater than the vertical, and calculates horizontal RFT using the same equation. Of course, RFT increases with travel distance – the equation accounts for this by taking as input the distance between the source and

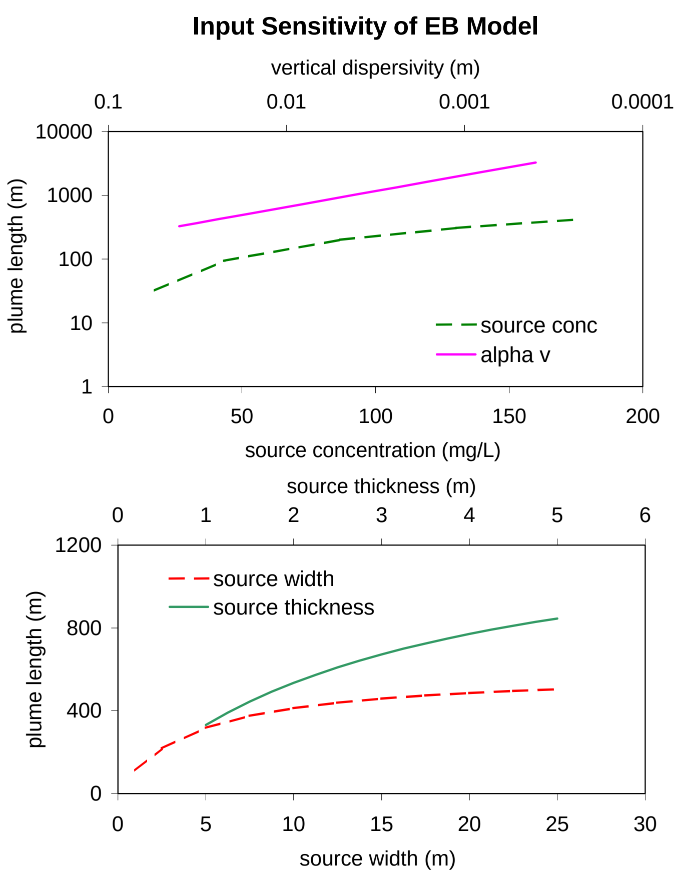

Figure 8. Input sensitivity of the Electron Balance model. See Appendix I for scenario details.

the observation point. Thus, uniform dispersivity, consistent with theory, is obtained from diferent ML data collected along a given plume.

It is important to note that assumption 4 (uniform RFT with distance) is in violation with the above. From the above equation, a dispersivity of 0.025 m, and the same EA/ED concentrations, the RFT 10 m from a source will be on the order of 0.85 m. The RFT 100 m downgradient would be 2.65 m. The plume length calculated by the EB model for the first validation example shown in Appendix I is 413 m for the former RFT and 1306 m for the latter. To obtain a conservative estimate of maximum plume length, it is advisable to obtain RFT estimates from as far downgradient as possible. Clearly, the EB model is sensitive to RFT (either as an input or derived from dispersivity). The model is also sensitive to source geometry and strength (Figure 8).

5.2.3 Travelling 1D Model

The Travelling 1D model uses PHREEQC to dispersively mix a one-dimensional column of water, oriented transverse to the plume axis, until fringe bioreactions reduce plume concentrations to zero. The time taken to reach this state is translated into distance (i.e. plume length) using site groundwater velocity (or plume velocity if the contaminant is retarded). Only the top plume fringe is modelled; it is assumed that the same fringe processes are occurring at the bottom fringe. Figure 9 shows conceptually how the model functions, although the user is reminded that the model does not actually simulate advection of the water column.

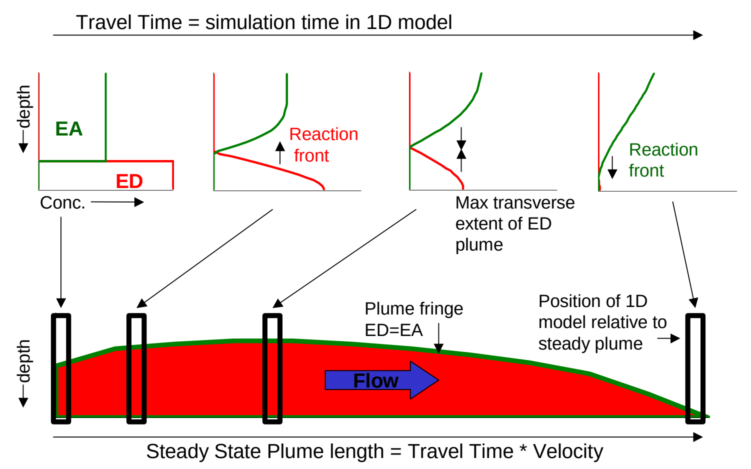

Figure 9. Conceptual diagram of how the Travelling 1-D model works. Transport is modelled only vertically.

Near the source, the water column is assumed occupied by electron acceptor(s) only above the background/plume interface and electron donor only below the interface (Figure 9). As time proceeds, donors and acceptors are consumed and the reactive front becomes less sharp. At steady state, there is only a dispersive profile of electron acceptors, contaminants having been completely consumed. The model assumes instantaneous reactions, and since initially electron donors are much greater than electron acceptors, the reaction front, i.e. plume fringe, moves outward from the plume core (Figure 9). Transverse mixing and reactions proceed until the plume reaches its maximum extent and the plume fringe retreats towards the plume centreline.

The model has four assumptions:

1) The source is continuous;
2) Velocity field is steady and uniform;
3) Reacting species (both contaminant and electron acceptor) are mobile and unretarded;
4) Longitudinal dispersion does not significantly influence maximum plume length.

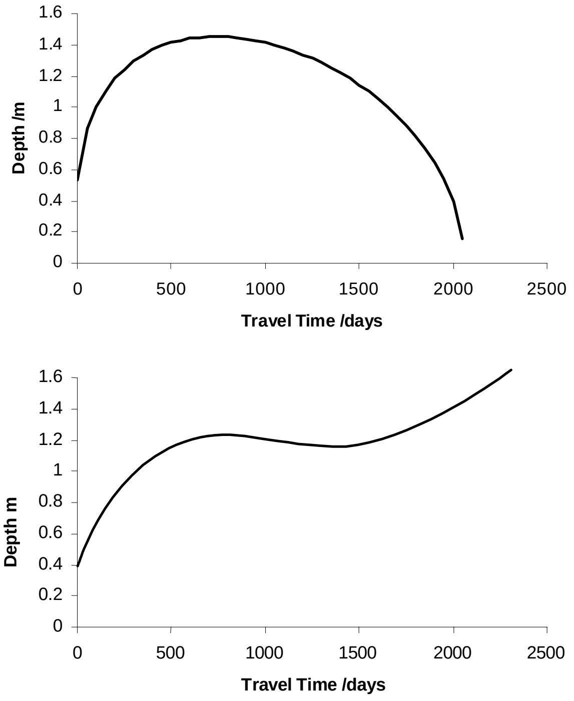

Figure 10. Example of Travelling 1-D model output: position of reactive fringe. a) where model has run to completion and fringe approaches plume centre. b) where model has run to completion but fringe diverges away from plume centre, indicating depletion of electron acceptors and unreacted upward dispersion of the plume.

Assumption 3 above means that reactions with immobile mineral phases (e.g. iron(III)) cannot be considered. While retardation cannot be included, it does not impact on maximum plume length (it does impact the time to reach steady state). Assumption 4 is valid provided the ratio of plume length to longitudinal dispersivity is greater than 30.

The Travelling 1-D model has the fewest input data requirements of the three CoronaScreen models (Table 3). However, the dispersion coefficient used to mix electron acceptors and plume is defined by the sum of mechanical mixing (velocity x transverse vertical dispersivity) and diffusion, and therefore the model is sensitive to vertical dispersivity. The user should be aware that the greater the coefficient of dispersion, the longer it takes for PHREEQC to converge for each time step. Therefore, run times can be quite long (> 1 hour) when dispersion exceeds 8.6E-04 m^2/day (mechanical mixing is dominant). Due to the complex nature of PHREEQC, certain inputs have been hardwired to allow ease of use for those not experienced in reactive geochemical modelling. However, access to the input files is possible for users experienced with PHREEQC.

On the Travelling1-D worksheet (via tab in upper right corner of the data input sheet), there is a tab to the raw output of model runs. This sheet shows a plot of the distance to the plume centreline (position of fringe) vs plume length (examples in Figure 10). Maximum plume length is where the reactive fringe horizon approaches the centre of the plume (see Figure 9). Because the boundary conditions of the 1-D column are fixed as closed flux, a simulation starts with finite electron acceptor and donor electrons (computed from input concentrations). For high concentration plumes (total EDs exceed the stoichiometric equivalent of EAs), electron acceptors are exhausted and the fringe horizon never approaches the plume centre (the plume continues to grow in length and thickness). So, while a given simulation may run through the user-specified time steps (shifts), only an inspection of the aforementioned plot will confirm whether the plume length reported in the Results section (data input sheet) is accurate.

5.3 When are CoronaScreen models applicable?

All three models described above are only intended for use in evaluating the natural attenuation of oxidising contaminants, which includes fuel range hydrocarbons, phenolics, PAHs, phenoxyacid pesticides, and ammonium. To assess the NA potential of contaminants that undergo reduction (i.e. chlorinated solvents), the choices are limited to BioChlor or perhaps a more complex numerical package. Figure 11 shows some of the conceptual scenarios for which the CoronaScreen models are appropriate.

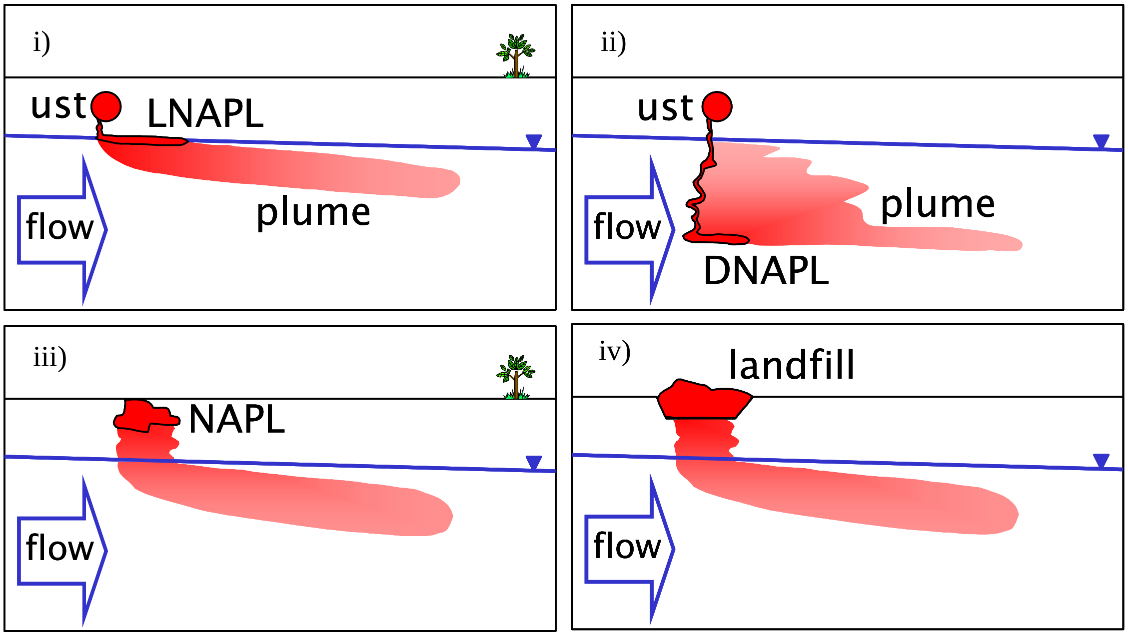

Figure 11. Conceptual scenarios for which CoronaScreen models are applicable. i) LNAPL (e.g. petrol) spill from an underground storage tank. Thin plume close to the water table. ii) DNAPL (e.g. coal tar) spill from an underground storage tank. Thick plume distributed to depth. iii) NAPL trapped in vadose zone. Dissolved phase washed down by recharge. Thin plume near water table. iv) Dissolved, solid or NAPL source in landfill. Transported to water table as a component of leachate. Thin plume near water table.

As described in Section 2.3.1, oxidised contaminants may degrade under aerobic or nitrate, iron, sulphate or carbon dioxide reducing conditions. Aerobic or nitrate reducing conditions are generally confined to the plume fringe, where mixing with background dissolved oxygen and nitrate occurs. Reactions supported by iron and sulphate reduction and methanogenesis will occur primarily toward the plume core. The Analytical and Travelling 1-D models only account for fringe reactions, while the Electron Balance model can account for both fringe and core reactions (it also implicitly accounts for fermentation reactions). Thus, if it were believed that both core and fringe reactions are equally important, the Electron Balance model is recommended.

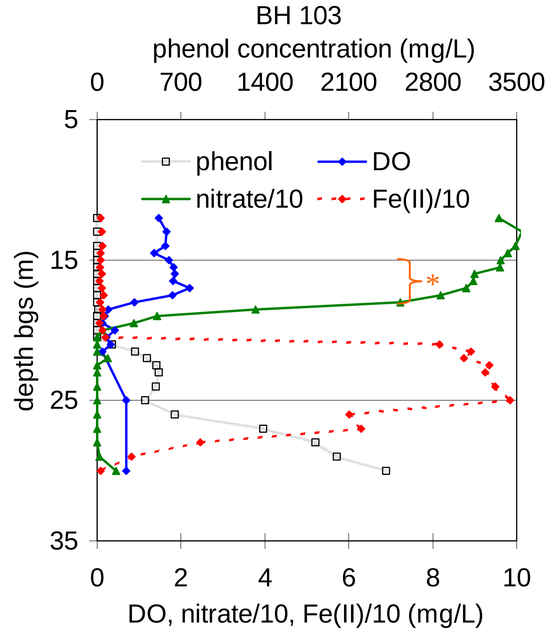

Figure 12. Reactive fringe thickness (denoted by *) from field data derived from a high-resolution multilevel sampler installed at one of the CORONA project sites.

The availability of input parameters may define which CoronaScreen model can be used for a given site, especially if the user is not willing to make certain parameter estimates because of the sensitivity of the model to that parameter. The Travelling 1-D model has the fewest parameter input requirements (Table 3). However, due to convergence and practical run time issues related to PHREEQC, it is limited to sites where dispersive mixing is at the scale of diffusion. The Electron Balance model uses all the input required by the analytical models, but also requires an estimate of the plume reactive fringe thickness (Figure 12), porosity, bulk media density and the fraction of organic carbon. Theoretically, reactive fringe mixing zone thickness is related to transverse vertical dispersivity – the smaller the dispersivity, the thinner the mixing zone. A relationship between mixing zone thickness and dispersivity is given by the equation presented in Section .5.2.2. Using this simple relationship, appropriate values for one can be estimated from measured values of the other. This is powerful because it is easier to measure mixing zone thickness (from high resolution multilevel well data) than dispersivity.

6. Using CoronaScreen model results

Meaningful interpretation and incorporation of CoronaScreen results into site management decisions requires an understanding of output uncertainty. As mentioned previously, the CoronaScreen models are a simplification of complex flow and reactive transport principles, and as such cannot be expected to be as comprehensive or accurate as fully deterministic numerical models. Nevertheless, for relatively simple plumes such as that derived from petroleum hydrocarbons, screening models are accurate to within a factor of 2-5, which is sufficient to be of value at the early stage of site NA assessment.

6.1 Uncertainty of results

The effects of varying different input parameters on estimated plume length for the Eden Hill case were presented in Figures 6 (analytical model) and 8 (electron balance model). If a plume length accuracy tolerance is chosen, it is possible to evaluate how precisely input parameters need to be quantified. For example, if calculated plume length must be within 80% of the actual length (known in the Eden Hill case), then vertical dispersivity, source geometry and source strength input for the Analytical model must all be measured within ±14-16% of their true value. It should in general be possible to measure source thickness and maximum source area concentrations to that degree of accuracy using standard sampling techniques and theoretical considerations of the spill scenario. It is much more difficult to measure source width without investing a great deal in spatial characterisation. Measuring vertical dispersivity to that degree of accuracy may prove to be very difficult – high-resolution (50 to 25 cm spacing) multilevels offer some promise. The Electron Balance model is less sensitive to input parameter accuracy. Source concentration must be within 13%, but vertical dispersivity can be off by as much as 50% and source width off by 33%. Therefore, for the same set of input parameters, the Electron Balance model is more likely to be closer to the real plume length than the Analytical model. Whether any of the models is accurate depends on whether any of the model assumptions are significantly violated. For example, the reactive fringe of a very long plume will vary greatly, which will affect the Electron Balance model more than the other two.

6.2 What if model results don't compare?

Since each of the three CoronaScreen models is based on different principles of NA assessment, it should not be surprising to find that results for the same plume are not comparable. There are a number of reasons for this. If certain parameters have been estimated, different results may be due to the variable sensitivity each model has to that parameter. As an example, the sensitivity of plume length to vertical dispersivity in the Analytical model is markedly different than that in the Electron Balance model (compare Figures 6 and 8). Alternatively, a key model assumption may be violated, or an important process is not accounted for, in which case the site conceptual model should be reviewed and updated. In some cases the plume may simply be too complex to model with these simplified tools – a more sophisticated numerical model may be necessary. Input data should be critically considered and re-measured if possible. Non-representative data can be the result of analytical problems, data handling errors, or even temporal or spatial plume variability.

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Appendix I. Performance model verification

Verification procedure

The performance of the CoronaScreen models in predicting plume development were tested on two plume case studies where required inputs and plume length were independently known with some precision, from site investigation and monitoring well networks at each site. The first case, a BTEX plume migrating in a sandy aquifer in Eden Hill, Australia, was studied and reported by Davis et al., 1999. The assistance of Prof. Davis and his colleagues is gratefully acknowledged. The second case was drawn from the archives of the EU Nicole MNA project, studying the feasibility of natural attenuation of a range of plumes in different European countries. Site H was a fuel storage and distribution depot, and as such is contaminated solely with associated fuel hydrocarbons. We are indebted to Anja Sinke for making the Site H data available for this study. For both plumes, the point defining maximum length was that where contaminant concentrations were reduced to zero.

BTEX plume, Eden Hill, Australia

The Eden Hill site is located close to the west coast near Perth, Western Australia. The host aquifer consists of relatively homogeneous unconsolidated beach sand deposits typified by cross, trough and laminar bedding features. The relevant CoronaScreen inputs from the Eden Hill plume are:

Plume Source Term:

benzene	36 mg/L	toluene	75 mg/L
ethylbenzene	8.2 mg/L	m/p-xylene	38.7 mg/L
o-xylene	15.6 mg/L		

Plume Residual Chemistry:

dissolved oxygen	0.16 mg/L	nitrate	0.22 mg/L
sulphate	15.2 mg/L	ferrous iron	1.6 mg/L

Background Groundwater Chemistry:

dissolved oxygen	0.56 mg/L	nitrate	0.8 mg/L
sulphate	82.5 mg/L	ferrous iron	1.4 mg/L

Aquifer Properties:

g.w. velocity	0.41 m/day	porosity	0.27
bulk density	2 g/cm3		

Plume Dimensions:

source width	20 m	source thickness	1.35 m

Plume Fringe Parameters:

distance: well to plume source	0 m
vertical transverse dispersivity	0.0123 m

Contaminant concentrations were measured in multilevel wells near source, and electron acceptor concentrations were measured in an upgradient background monitoring well.

Sediment parameters were determined from core samples, source geometry was estimated from a number of site investigation phases, and reactive fringe thickness estimated from reported multilevel well data. Vertical transverse dispersivity was derived from field tracer test data. Vertical transverse dispersivity, α_{tv}, at the site was estimated by conventional methods to range between 0.025 to 0.0025. The value used here was obtained using site multilevel data and the α_{tv} estimation tool in CoronaScreen.

From these inputs the following model results were obtained:

Analytical model	518 m	Electron Balance model	456 m
Travelling 1-D model	----- m	BioScreen model	764 m

The approximate plume length observed in the field was between 420-480 m. The BioScreen length was estimated from output centreline profile. The Travelling 1-D model did not converge properly because the product of velocity and transverse dispersivity (0.01 m^2/day) exceeds the allowable limit of 8.6E-04 m^2/day.

BTEX plume, Site H

The Site H plume emanates from a fuel hydrocarbon source LNAPL that was released from an underground tank located at a large storage/distribution depot. A clay/sandy clay unit overlies an unconfined sand/clayey sand aquifer on the order of 40 m thick. The relevant CoronaScreen inputs from the Site H plume are:

Plume Source Term:

benzene	14.2 mg/L	toluene	46.8 mg/L
ethylbenzene	2.98 mg/L	total xylenes	10.8 mg/L

Background Groundwater Chemistry:

dissolved oxygen	9 mg/L	nitrate	90 mg/L (avg)
sulphate	<1 mg/L		

Aquifer Properties:

g.w. velocity	0.068 m/day	porosity	0.3 (assumed)
bulk density	1.7 g/cm3 (assumed)		

Plume Dimensions:

source width	15 m	source thickness	1 m

Plume Fringe Parameters:

reactive fringe thickness	1 m
vertical transverse dispersivity	not reported - assumed 0.01 m

Groundwater samples were collected from standard long screened monitoring wells. Source term concentrations were from a well located within the suspected LNAPL source area, and background electron acceptor concentrations were measured in an upgradient monitoring well. Source geometry was estimated from the documented size of the underground tank bunker as well as evidence from monitoring wells installed transverse to the plume axis. Since there were no multilevel wells installed, no estimates of reactive fringe thickness were available (likely a common situation at many sites). The EB model requires fringe thickness as input, so a value of 1m (within the bounds observed at many BTEX sites) was used. Also, no estimate for vertical transverse dispersivity was reported: a value was assumed consistent with other aquifers with similar grain size reported in the literature.

From these inputs the following model results were obtained:

Analytical model	119 m	Electron Balance model	144 m
Travelling 1-D model	122 m	BioScreen model	245 m

The actual measured plume length was ~130 m. The BioScreen model prediction is roughly double the three CoronaScreen estimates, presumably due to differences in the conceptual approach to data collection and use in the models.

Appendix II. Worked example using CoronaScreen models

Simple synthetic benzene plume

Consider a simple benzene plume that is migrating through a mildly aerobic aquifer at 10 cm/day. Source geometry, source concentrations, electron acceptor (oxygen only) concentrations and dispersivity are as shown in Table 4. The plume emanates from a vertical plane oriented transverse to groundwater flow, roughly approximating a distribution of petrol NAPL in a smear zone just below the water table. The reactive plume fringe thickness was estimated from data collected in a multilevel well located 20 m downgradient of the source.

Table 4. Parameters used in worked example

Parameter	Value
Benzene conc.	13 mg/L
Dissolved oxygen conc.	8 mg/L
Source width	1 m
Source thickness	1 m
Reactive fringe thickness	0.49 m
Distance: source to MLS	20 m
porosity	0.27
Aquifer bulk density	2 g/cm^3
Groundwater velocity	0.1 m/day

After opening the CoronaScreen spreadsheet, click on the “go to data input” button. Enter “13” in the benzene box in the “Plume source term composition” section. If benzene is not present, click the “add/delete contaminants” button in the upper right corner of the spreadsheet. Highlight benzene in the left hand column and transfer it to the right hand column by clicking the “add>” button and then “OK”. Back on the input sheet, enter “8” in the “O_2” box in the “Background groundwater chemistry” section. In the “Aquifer properties and hydrogeology” section, enter “0.1” in the “Groundwater flow velocity” box (make sure units are consistent), “0.27” in the “Effective porosity” box, and “2” in the “Bulk density” box. Groundwater flow velocity and effective porosity are used by the Electron Balance model to calculate dispersive fluxes of electron acceptors into the plume. Enter “1” in both the “Plume width” and “Plume thickness” boxes in the “Plume source dimensions” section. In the left hand margin, find and click the box “calc. alpha z from dz. The vertical fringe thickness box should now be available in the “Plume fringe parameter” section: enter “0.49”. Also enter “20” in the “Distance: source to MLS” box. Now return to the top of the spreadsheet. Just to the right of the “Results” section, click the “Calculation settings” box. For each of the tabs, ensure each model is enabled, including options if desired. On the “Travelling 1D” tab, ensure the “Run PHREEQC” button is selected and tick both dialog options. Under the “Dispersivity” tab, ensure that dz and alpha z are coupled.

The model is now ready to calculate plume lengths. Click the red “Calculate plume lengths” button. Results for the Analytical and Electron Balance model will be reported almost immediately. A File Save window will pop up - this is for the Travelling 1D model - click OK. Another window appears asking for a name for the PHREEQC output file. If it is not already visible, enter “fringe.sel” (must be this name) and then click OK. The spreadsheet will save (this may take a few moments) and PHREEQC will then be called. For this problem, it should only take a minute for PHREEQC to finish. The following results should appear in the relevant boxes: 53 m for the Electron Balance, 23 m for the Analytical, and 360 m for the T1D model (poor match for the T1D model may be due to boundary conditions defined for

PHREEQC: additional model development is on-going at the time CoronaScreen was released). If you click on the “go to Analytical Model” button in the right margin, you can see additional results: time to steady state, plume centreline profile and vertical electron acceptor and donor profile plots (both user adjustable). By increasing the vertical profile distance along centreline, it can be seen that the reactive plume fringe does indeed increase with travel distance. Go back to the input sheet and then go to the Travelling 1D model sheet. Click on the “See Raw Output” button, where a plot of reactive fringe distance from the plume centre is plotted against plume length. The plot should show an arc starting away from the plume centre and then converging back.

Appendix III. Monitoring strategy and techniques

The various NA assessment protocols all advocate a similar basic monitoring strategy: centreline wells sampled at least 4 times/year. Early site investigations are usually designed to delineate plumes and source zones, and result in wells scattered around a site in no particular pattern. A new metric rapidly gaining favour is transects of wells to allow mass flux estimates (considered superior to concentration-based assessments). The CORONA approach relies on accurate estimation of vertical transverse dispersivity, which requires the installation of high-resolution multilevel wells. Depending on the source/plume scenario and expected aquifer heterogeneity, sample points may have to be as close as 25 cm apart vertically to provide the required resolution.

Well types

The most common well type found at sites are medium to long screen large bore wells. These are inexpensive to install, simple and quick to sample, and provide depth-averaged concentration data. Occasionally, coarse vertical resolution may be provided by nested short screen wells.

Less common are multilevel samplers. These have been available for roughly 20 years, but have not gained wide acceptance outside research circles due in part to their material and installation costs, but mostly due to the analytical cost burden. This disadvantage must be weighed against the benefits of more accurate characterisation of a plume and better resolution of key transport parameters, principally vertical dispersivity. One may argue that the cost of installing and monitoring one or two high-resolution multilevel samplers may easily be offset by the cost benefit of demonstrating that MNA is a viable plume management option.

Multilevels focussing on fringe processes

The purpose of high-resolution multilevel wells is to allow refined characterisation of the plume fringe. Therefore, the ML must be installed across the fringe, which requires a priori knowledge of that depth. Such information can be drawn from initial site characterisation data, but to ensure the ML is installed to provide the best data, a special investigation should be conducted near the proposed ML location to pinpoint the upper (and lower if desired) plume fringe. Figure 12 is an example of data from a ML installed across the upper fringe of a phenolics plume. Sampler spacing was 0.5 m, providing 3 or 4 data points within each of the electron acceptor fringes.

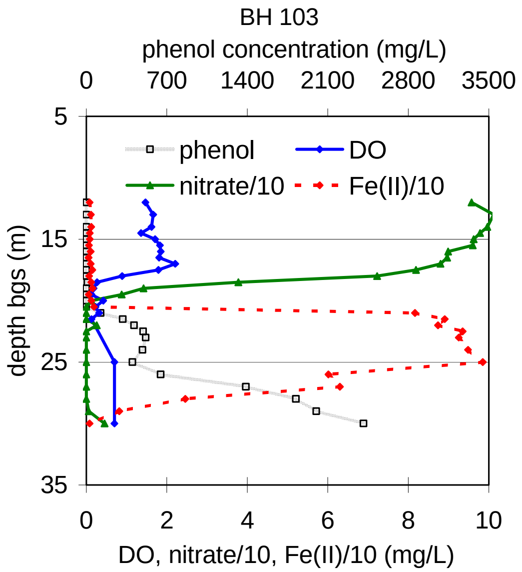

Figure 12. Example of data from a high-resolution ML sampler that can be used to estimate reactive fringe thickness. Such data can be used to estimate vertical dispersivity with reasonable precision.

Multilevel construction and installation.

There are a number of methods to construct a multilevel well. Installation methods are determined by the nature of the aquifer material. For shallow installations in unconsolidated sands, a direct-push method can be used where a hollow drill pipe is pushed into the ground with a drive tip on the end to prevent sediment from invading the pipe. Once at the desired depth, the pre-constructed multilevel is inserted into the open pipe, which is then extracted leaving the ML in place. Sediment collapses around the ML, forming natural seals around each ML sampling point. In rock aquifers or deep installations in unconsolidated material, a rotary drill rig will need to be used. A borehole is formed either with a cutting bit (rock) or hollow stem auger (unconsolidated), extending temporary casing as needed. Once at depth, a pre-constructed ML is lowered into the borehole and the annulus filled with sand of a similar grain size as the native material. This is to encourage horizontal flow through the borehole, rather than vertical. Finally, temporary casing is removed and the well completed in the required manner.

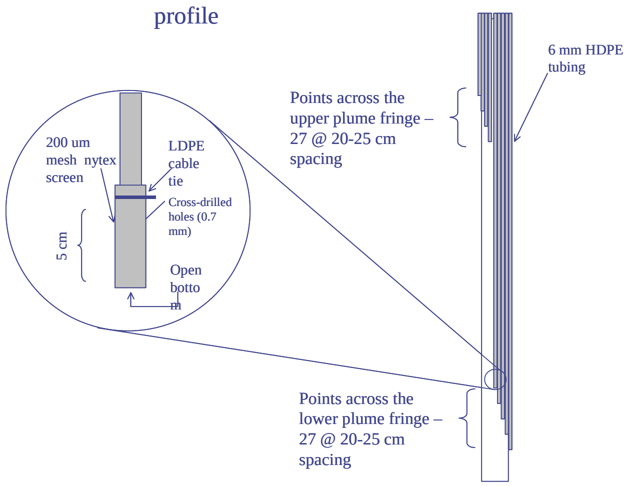

Figure 13. Sketch of a ML installed in a rock aquifer to monitor a phenolics plume. Materials are HDPE, and the annulus was filled with fine sand.

Multilevel samplers for groundwater monitoring are constructed in a number of different ways, but the basic idea is a central supporting pipe with smaller diameter sample tubes strapped in some fashion to the outside of the pipe. The sample tubes terminate at different depths and all run to the surface, where they can be connected to a sampling device (peristaltic pump, gas-push system, etc). Figure 13 shows a sketch of a ML installed in a sandstone aquifer at one of the CORONA project sites.

Areal well distribution - implications of spatial variability

Following the CORONA approach, at least 1 multilevel should be installed near the source zone: estimates of plume length will be enhanced if another ML is installed some distance downgradient. A monitoring well should also be installed upgradient of the source to establish background electron acceptor geochemistry. Samples should be collected at least 4 times/year to establish any temporal trends in concentration. In highly spatially variable aquifers, it may be desirable to use mass flux as a complimentary NA assessment tool. A row of monitoring wells can be installed in transect across the plume, at least one of which being a high-resolution ML to characterise the upper and lower plume fringes.