CoronaScreen

A Spreadsheet Tool for the Prediction of Contaminant Plume Length in Groundwater

Version 1.0

Electron Balance Model

User Guide

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Contents

1. Concept and model development

1.1 Introduction

This section describes the conceptual basis for the Electron Balance Model (EBM), its set-up and physical dimensions. The development of the model and its adaptation to calculate plume lengths is presented.

The biodegradation of organic compounds in a contaminant plume can be represented by two cases, which describe the general distribution of degradation processes occurring in the plume. These cases are based on the Corona concept defining the contribution of degradation processes in plume development and include:

1. Plumes where degradation occurs predominantly at the fringe of the plume and is controlled by dispersion of electron acceptors into and electron donors out of the plume;
2. Plumes where degradation occurs predominantly in the anaerobic core and is normally diffusion-controlled and depends on availability of sediment-bound electron donors in the aquifer matrix.

In general, the first case describes the development of plumes containing organic or inorganic compounds which are transformed by oxidation processes, that occur when the contaminant (electron donor) is oxidised by an oxidant (electron acceptor) provided through mixing (via dispersion) of the contaminant plume and uncontaminated groundwater at the plume fringe. Examples include the oxidation of many aromatic hydrocarbon compounds (e.g. BTEX and phenols) and ammonium (NH_4^+) in landfill leachate plumes. It is known (and acknowledged in this analysis) that oxidation processes may occur in the anaerobic core of the plume as well as at the plume fringe. However, studies show that where oxidation is the primary pathway for transformation of a contaminant, oxidation processes occurring at the plume fringe are primarily responsible for most degradation in a plume (Thornton et. al., 1998; 2001a,b).

The second case describes the development of plumes containing organic or inorganic compounds which are transformed by reduction processes, rather than oxidation. In this case, the contaminant functions as an electron acceptor and is reduced by an electron donor present in the plume. The electron donors required for this transformation may be a co-contaminant, degradation product, naturally occurring organic compound or inorganic compound in the aquifer. Examples include the reduction of halogenated hydrocarbons (e.g. TeCE, TeCA, TCE and TCA, amongst others).

The EBM presented here focuses on **the first type of plume only** (typically organic contaminants degraded by oxidation processes). Transformation of contaminants by reduction processes in the anaerobic core of the plume is not considered in the model. However, in addition to fringe-processes, oxidation of contaminants by sediment-bound electron-acceptors inside the plume is also taken into account in the EBM. The conceptual framework underpinning the application of the EBM for the performance assessment of attenuation in oxidising plumes is described below.

1.2 Governing assumptions and reactions

The model is based on the assumption that an oxidisable (typically organic) contaminant will be biodegraded, depending on availability of electron acceptors needed for degradation. Under the assumption that biodegradation occurs instantaneously and thus taking into account only the concentrations of electron donors (the contaminant) and electron acceptors (oxidants), the degradation processes in a plume can be represented as series of simple redox reactions. These are presented in terms of the number of electrons donated or gained, according to the stoichiometry of each half reaction (see below). This approach allows an electron balance to be completed for the plume, based on all redox reactions included in the calculation. The number and type of redox half reaction included in the electron balance are determined from the range of electron donors (contaminants) and electron acceptors (oxidants). The magnitude of the electron donor and electron acceptor inputs in the electron balance is defined by the concentration of both contaminants and oxidants, based on groundwater quality data for the uncontaminated aquifer and plume (see below). In principle, the amount of electron donors degraded in a plume should be balanced by the amount of electron acceptors consumed by the various degradation processes. On this basis, the difference between the electron donor and electron acceptor inputs in the overall plume-scale electron balance is used to evaluate the status (e.g. expanding, steady-state condition or shrinking) and expected behaviour of a contaminant plume.

Redox half reactions for a typical range of electron acceptors and electron donors (using phenol compounds and total organic carbon, TOC, as an example) that may be included in a plume-scale electron balance are shown in Table 1. The number of electrons transferred in each half reaction is illustrated for each electron donor (e.g. 28 donated by phenol) and electron acceptor (e.g. 4 accepted by dissolved oxygen).

Table 1. Example redox half reactions used to calculate a plume-scale electron balance

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Electron donating reactions: *Oxidation of organic fractions*

Phenol: $C_6H_6O + 11H_2O \rightarrow 6CO_2 + 28e^- + 28H^+$

Cresols: $C_7H_8O + 13H_2O \rightarrow 7CO_2 + 34e^- + 34H^+$

Xylenols: $C_8H_{10}O + 15H_2O \rightarrow 8CO_2 + 40e^- + 40H^+$

TOC: $CH_2O + H_2O \rightarrow CO_2 + 4e^- + 4H^+$

Electron accepting reactions: *Reduction of aqueous and mineral oxidants*

Dissolved oxygen: $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

Dissolved nitrate (denitrification): $NO_3^- + 5e^- + 6H^+ \rightarrow 1/2\,N_2 + 3H_2O$

Dissolved sulphate: $SO_4^{2-} + 8e^- + 8H^+ \rightarrow S^{2-} + 4H_2O$

Dissolved carbon dioxide (methanogenesis): $CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$

Solid phase manganese oxide: $MnO_2 + 2e^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O$

Solid phase iron oxide: $FeOOH + e^- + 3H^+ \rightarrow Fe^{2+} + 2H_2O$

The range of electron acceptors chosen comprises dissolved and mineral oxidants in the aquifer, which may participate in the oxidation of contaminants. A range of typical electron donors has been included in the model database and these can be increased by the addition of specific contaminants during the creation of input files. Inorganic compounds can be included in the source-term of the model as well, provided these compounds are assumed to be oxidised during degradation. The reactions for inorganic compounds have to be formulated as the complete oxidation half reaction expected for the given site and redox-conditions. The half reactions are written with CO_2 as the end product for oxidised organic carbon. The dissolved CO_2 will be speciated into other forms of inorganic carbon in groundwater, according to the groundwater chemistry and pH (Appelo and Postma, 1993). This is taken into account in the model by using total dissolved inorganic carbon (DIC) as an input for contaminant mass degraded, since DIC includes all forms of CO_2. The key assumptions underlying the calculation of the plume-scale electron balance using the redox half reactions are listed below:

- Degradation is instantaneous and not rate-limited by inhibition effects in the plume or mass transport processes in the aquifer;
- All degradation is assumed to occur by biological processes and abiotic reactions (e.g. formation of FeS phases via direct reduction of Fe oxides by S^{2-}) are not explicitly considered (although this can be estimated indirectly with the model);
- No pathway or sequence is assumed for the redox half reactions, that is a total budget of electron acceptor and electron donor consumption is calculated for the plume, rather than, for example, consumption of dissolved oxygen by oxidation of specific electron donors;
- Constant concentrations of electron donor and electron acceptor inputs, as determined from the background and plume groundwater chemistry, are assumed over the time-scale of the analysis;

- Methane produced in the plume is assumed to have originated from reduction of dissolved CO_2, as opposed to fermentation of organic acids (Chapelle, 1993);
- The aquifer is assumed to be homogeneous, with respect to the values of properties and groundwater chemistry used to calculate inputs for the EBM, that is spatial heterogeneity in these parameters is not considered.

The redox half reactions listed in Table 1 can be coupled to generate a complete reaction involving the oxidation of an electron donor by an electron acceptor, which describes the appropriate degradation process. A summary of full reactions for these electron donors and electron acceptors is given in Table 2, using phenol as the model compound.

Table 2. Summary of degradation processes for phenol

Aerobic oxidation: $C_6H_6O + 7O_2 \rightarrow 6CO_2 + 3H_2O$

Reduction of nitrate: $C_6H_6O + 14NO_3^- \rightarrow 6CO_2 + 14NO_2^- + 3H_2O$

Denitrification: $C_6H_6O + 28/5\,NO_3^- + 28/5\,H^+ \rightarrow 6CO_2 + 14/5\,N_2 + 29/5\,H_2O$

Reduction of sulphate: $C_6H_6O + 7/2\,SO_4^{2-} \rightarrow 6CO_2 + 7/2\,S^{2-} + 3H_2O$

Reduction of solid phase Mn-oxide: $C_6H_6O + 14MnO_2 + 28H^+ \rightarrow 6CO_2 + 14Mn^{2+} + 17H_2O$

Reduction of solid phase Fe-oxide: $C_6H_6O + 28FeOOH + 56H^+ \rightarrow 6CO_2 + 28Fe^{2+} + 45H_2O$

Methanogenesis (fermentation): $C_6H_6O + 4H_2O \rightarrow 5/2\,CO_2 + 7/2\,CH_4$

1.3 Conceptual box model for the plume

The reactions described above are combined with physical mass transport processes to produce a box model for a given aquifer, which enables electron and carbon mass balances to be calculated for contaminant plumes. The box model used in CoronaScreen is based on the quantitative framework developed by Thornton et. al., (2001a) and is shown schematically in Figure 1.

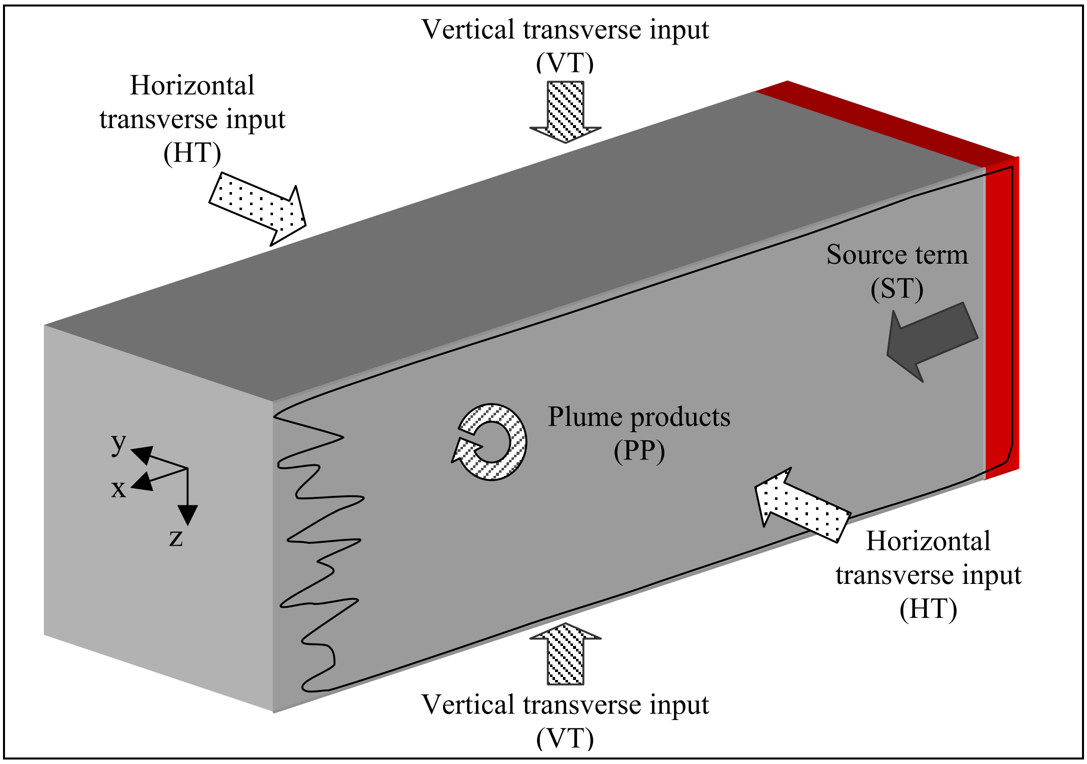

Figure 1. Schematic of box model showing inputs for electron acceptors (EA, textured arrows) and electron donors (ED, grey arrow)

The box model includes four input terms, which represent components from the contaminant source term (ST), transverse dispersion (HT, VT), and plume product fractions (PP). These terms are explained in Table 3. Inputs from dispersion arise from mixing of contaminated and uncontaminated background groundwater at the plume fringe. This input includes two horizontal and two vertical components across a fringe which is conceptualised as a planar surface (Figure 1). Plume product fractions (PP) include products of degradation processes (e.g. CO_2 and CH_4) and inorganic dissolved species (e.g. Mn^{2+} and Fe^{2+}), which can be used to estimate consumption of mineral-based electron acceptors (e.g. MnO_2 and FeOOH) in the plume. Electron acceptor inputs enter the plume through dispersion (VT & HT), as well as originating from the plume products (PP). Conversely, electron donors are introduced into the plume solely by advection through the source term (ST).

Table 3. Nomenclature of input terms for plume box model

Input notation	Input term	Parameter	Comment
Source term (ST)	n_e x vel x A_{yz} x C_{source}	n_e	Aquifer effective porosity
		vel	Horizontal linear velocity
		A_{yz}	Rear cross sectional area of plume
		C_{source}	Concentration of contaminant in source area
Horizontal transverse (HT)	2 x n_e x vel x α_y x A_{xz} x $\delta C_{EA}/\delta y$	A_{xz}	Transverse sectional area of plume
		α_y	Horizontal transverse dispersivity
		$\delta C_{EA}/\delta y$	Electron acceptor concentration gradient at horizontal plume fringe
Vertical transverse (VT)	2 x n_e x vel x α_z x A_{xy} x $\delta C_{EA}/\delta z$	A_{xy}	Plan cross sectional area of plume
		α_z	Vertical transverse dispersivity
		$\delta C_{EA}/\delta z$	Electron acceptor concentration gradient at vertical plume fringe
Plume products (PP)	n_e x vel x A_{yz} x $C_{product}$	$C_{product}$	Concentration of species produce *in situ*

To estimate the electron balance for the plume, concentrations of electron donors and acceptors (in for example mg/l) are converted to concentrations in moles (mol/l) and then multiplied by the number of electrons donated or accepted per mole of compound (as illustrated in Table 1). This conversion provides the equivalent concentration of electrons (in mol e^-/l) for every compound, which is in turn converted into a flux of electrons (mol e^-/day), using the groundwater flow velocity and the relevant cross-sectional area over which the flux takes place (see Chapter 4). The flux of electron equivalents is summed for electron donors and acceptors separately and balanced to arrive at a plume-scale electron balance for the system. Chapter 4 discusses details of the different inputs for electron acceptors and donors in the EBM.

1.4 Relationship between electron balance and model outputs

For a given set of input parameters (e.g. groundwater chemistry and aquifer properties) the EBM will provide estimates of the following outputs:

☐ Overall electron balance

☐ TOC flux at a given plume length

☐ Predicted plume length

☐ Degradation rate constant for contaminants

☐ Time to reach steady-state plume length

☐ Carbon mass balance

The interpretation of these outputs is explained in detail in Chapter 5 and the main points are summarised here.

The overall electron balance provides an indication of the net balance of electron donors or electron acceptors in the plume. This can be used to deduce the plume status (e.g. expanding, stable or shrinking) for the specific input data used in the simulation. All electron donor inputs entering the plume are converted to electron equivalents and presented by the model as an equivalent flux of total organic carbon (TOC) passing through the plume at a given distance from the source area. This carbon flux can be compared with water quality or remediation targets at various distances from the site, or converted to an equivalent concentration of a specific contaminant, for analysis of a worst case scenario. The EBM will estimate the steady-state plume length, with the condition that the flux of electron donors into the plume must equal the flux of electron acceptors into the plume at steady state. The source term input will not be affected by plume-length; however, the dispersive influx and flux of residual electron acceptors depend on the length of the plume. This is not a linear relationship, and therefore, an iterative process is needed to estimate the plume length. Refer to Chapter 5 for details of the calculation. A first order degradation rate constant is estimated for the plume, based on the consumption of electron acceptors needed to balance the electron donor input. This rate constant applies to the total electron donor input entering the plume, rather than specific contaminants. Since many "plumes" comprise a mixture of contaminants, individual contaminant plumes within the mixture will reach a steady-state length over different time-scales determined by the sorption properties of each contaminant and the aquifer. The time-scale to reach steady-state length is calculated by the model for each contaminant that is specified by the user and included in the database. A carbon mass balance is also calculated for the plume. This is achieved by comparing the equivalent TOC degraded, as estimated from the production of total dissolved inorganic carbon (DIC), with the total consumption of electron acceptors, which is estimated independently from the inputs described in Figure 1. This comparison provides a check on the degradation of electron donors in the plume estimated by the different methods. It is used to review the quality of data inputs and conceptual model used in the EBM simulation; guidance is provided in Chapter 5 to assist the interpretation of this output.

2. Application and scenario modelled

2.1 Introduction

This section presents the field scenario to which the EBM can be applied. Data requirements and the design of monitoring wells to provide groundwater chemistry data for the EBM simulation are described.

2.2 Monitoring well network for scenario modelled

The EBM requires a minimum set of input data for simulations of contaminant plume evolution, as described in the previous chapter. This data and the anticipated analytical methods required to obtain it include:

- ☐ Aquifer physical and hydrogeological properties (e.g. hydraulic conductivity, hydraulic gradient, groundwater flow velocity, effective porosity and bulk density) determined using relevant techniques (e.g. field-scale hydraulic tests and analysis of core samples from the aquifer, or appropriate literature values, where this is justified);

- ☐ Aquifer geochemical properties (e.g. fraction of organic carbon and solute distribution coefficient for contaminants) determined using relevant techniques (e.g. analysis of core samples from the aquifer, batch sorption tests or appropriate literature values, where this is justified);

- ☐ Composition of background and plume groundwater chemistry, to provide concentrations of dissolved electron donors, electron acceptors, products of degradation processes and estimate solute concentration gradients across the plume fringe, using monitoring wells installed in uncontaminated locations, the plume source area and instrumented across the plume fringe.

This section focuses on the design of the monitoring well network to obtain the groundwater quality data required as input parameters for the EBM simulations. The input parameters needed define the design and location of monitoring wells that must be installed at sites for the assessment using the EBM. A monitoring network that fulfils these requirements is crucial for the model to correlate with the actual site under consideration. Figure 2 illustrates the typical location and instrumentation of monitoring wells for the ideal scenario that is assessed with the EBM.

The instrumentation of the individual monitoring wells required in this ideal or "standard" scenario is as follows:

- ☐ Upstream monitoring well
  This monitoring well is required to provide concentration data for **all** dissolved species (O_2, NO_3, SO_4, Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants) present in the background groundwater from the uncontaminated aquifer. These species are also measured in monitoring wells located in the plume (see below). A single screen monitoring well covering a section of the aquifer which samples a representative volume of uncontaminated groundwater is sufficient to provide this data (see section 3.4). If more than one single screened well exists, or if data from different depths at one or several locations from multilevel samplers are available, an averaged concentration can be used; see section 2.4 for a general discussion of this issue. Refer to section 3.4 for details of input parameters derived from this monitoring well. It is assumed in the model that the background concentrations of electron acceptors and other species in groundwater upstream of the plume source area are the same or very similar to concentrations found downstream above the plume (see below). Note that concentrations of TOC and contaminants should be measured in groundwater from this upstream monitoring well. In most aquifers and applications of the model the concentrations of TOC and contaminants found in the plume will be zero or close to zero in the background groundwater upstream of the site. However, there may be cases or aquifer settings where TOC is of interest or needs to be taken into account in the plume prediction, and a background TOC and/or contaminant concentration will be required for this (see section 3.4).

- ☐ Source area monitoring well
  This monitoring well is required to provide concentration data for **all** dissolved species (O_2, NO_3, SO_4, Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants) present in contaminated groundwater from the plume source area. In most cases the dissolved concentration of O_2, NO_3 and SO_4 will be zero, but dissolved

concentrations of contaminants and Mn^{2+}, Fe^{2+}, CH_4, TOC and DIC will be elevated compared with the background groundwater composition sampled in the upstream monitoring well located in the uncontaminated aquifer. The groundwater composition in the source area monitoring well provides the input for estimating fluxes of electron donors, plume products and the carbon mass balance in model simulations. If electron acceptors are part of the plume source term, they can be included, but must be given **negative** concentrations in the input file. The model uses a vertically averaged inflow of electron donors and other species across the vertical plane (A_{yz}) perpendicular to flow to estimate this input, and so a single screen monitoring well which samples a representative depth of the source area is adequate (see section 2.4 for discussion of integrating/using ranges of concentration). Refer to section 3.6 for details of input parameters derived using data from this monitoring well.

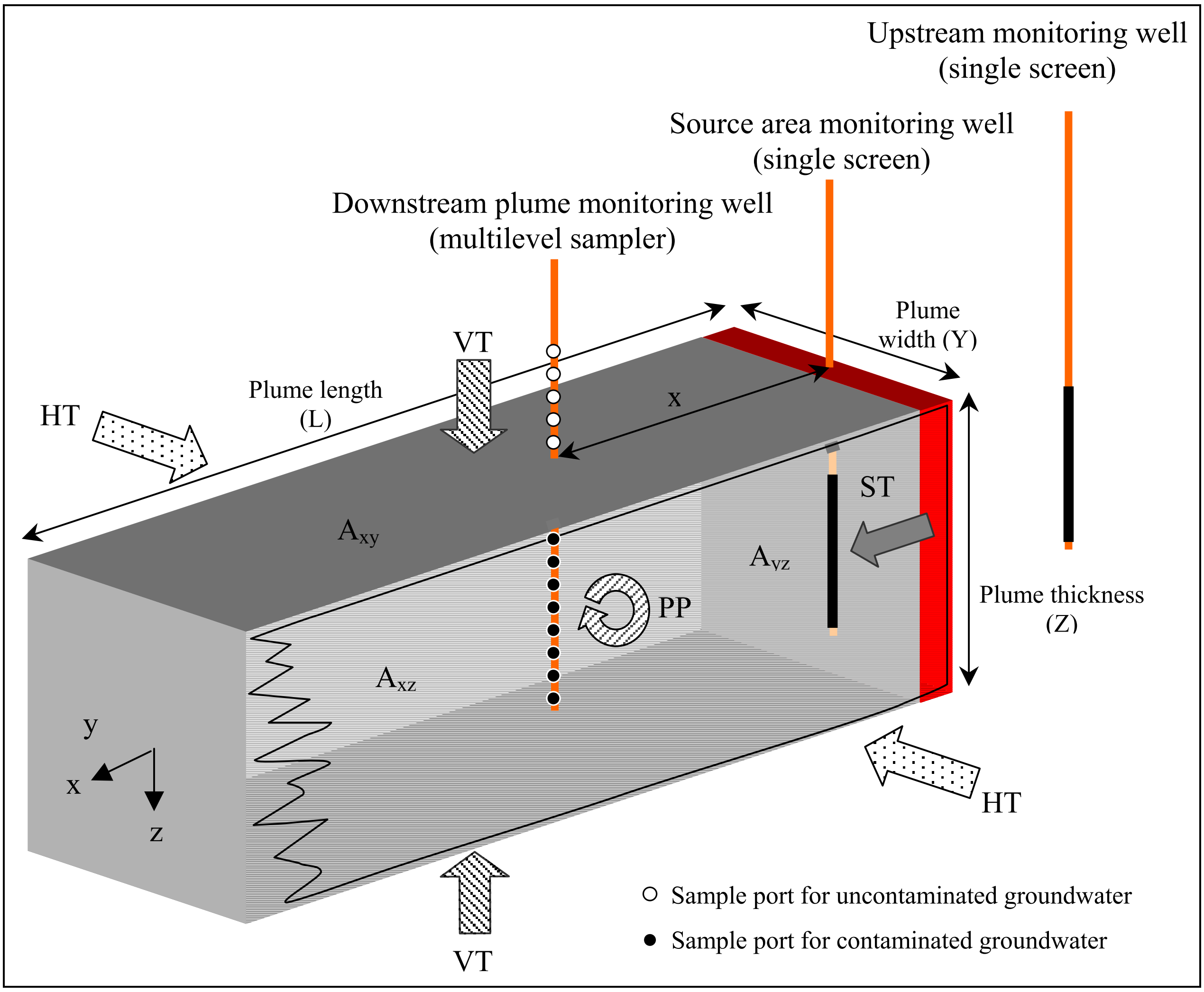

Figure 2. Schematic of monitoring well network for analysis of plume development using EBM

- <u>Downstream plume monitoring well</u>
  This monitoring well is located downstream of the plume source area and is instrumented to sample uncontaminated and contaminated groundwater across the plume fringe. This monitoring well is required to provide concentration data for **all** dissolved species (O_2, NO_3, SO_4, Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants) present in these samples. These data are used to determine the solute concentration gradients across the plume fringe to estimate electron acceptors fluxes into the plume by dispersion. This monitoring well also provides data on the "background groundwater chemistry" and "plume source term composition" when the *alternative* monitoring well scenario is used to provide these inputs for the model (see section 2.3).

In many cases the dissolved concentration of O_2, NO_3, SO_4, Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants sampled in the uncontaminated groundwater above the plume fringe may be similar to those measured in uncontaminated groundwater sampled in the monitoring well located upstream of the source area. Also, the dissolved concentrations of Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants sampled in contaminated groundwater below the plume fringe may be similar to those measured in contaminated groundwater sampled in the plume source area monitoring well. Field observations suggest that there will be a gradient in the concentration of O_2, NO_3, SO_4, Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants across the plume fringe. In some cases, there may be a residual concentration of unconsumed dissolved electron acceptors within the plume (termed "plume residuals" in the EBM input file), which are present at lower concentration than outside the plume (see section 3.3.1). This solute concentration gradient must be sampled in detail to adequately estimate electron acceptor fluxes across the plume fringe with the EBM. For this reason, it is important that this monitoring well is instrumented as a **multilevel sampler** (MLS) with sufficient spatial resolution of sampling ports to characterise the vertical gradient of dissolved electron acceptors across the plume fringe and identify the "thickness" of the plume fringe mixing zone. Furthermore, concentrations of contaminants and other species for the "plume source term composition" and "plume residuals and products" inputs are obtained from sections of this MLS located inside the plume, when the plume "source area" groundwater compositions are determined using the *alternative* monitoring well scenario (see section 2.3). Refer to sections 3.4 and 3.7 for details of input parameters derived from this monitoring well. It is assumed in the model that concentrations of dissolved electron acceptors measured in sample ports above the plume fringe are the same or very similar to those measured in the upstream monitoring well (see above).

On many sites, monitoring wells instrumented with a MLS capable of obtaining the necessary data for using the EBM may not exist. In the planning stage of instrumenting a site to fulfill the data input requirements for the model, some depth-related solute concentration measurement is necessary to determine the approximate location of the plume fringe for placement of the downstream plume monitoring well. If existing monitoring wells do not indicate the location of the plume fringe, but exhibit contaminant concentrations which are representative of the plume, it is possible to instrument the MLS from the water table down to the depth indicated by the single screen plume monitoring wells. Obviously, the more defined the plume fringe zone is from previous groundwater quality monitoring, the more resources can be saved because the MLS can be installed to sample specific depths across the plume fringe mixing zone. For placement of the upstream and the source area monitoring well, some estimate of the upstream edge of the plume is necessary from previous investigations.

The "plume length" calculated by the EBM for this monitoring well scenario equals the distance from the source area monitoring well to the downstream end of the plume. If the source area monitoring well is located a distance "s" downstream of the true plume source area, then this distance ("s") is automatically added to the "plume length" predicted by the model to give a true plume length from the source area, given in the "Results" output section of the model.

2.3 Monitoring well network for alternative scenario

As a very stripped-down version, the ideal scenario described in the previous section can be modified to accommodate data from a very reduced "non-standard" monitoring network, using one MLS monitoring well only. In this *alternative scenario*, the downstream plume MLS monitoring well (as discussed in the previous section and shown in Figure 2) is also treated as the "source area" monitoring well by using the average contaminant concentrations measured inside the plume. These contaminant concentrations are obtained by sampling monitoring ports on the MLS which are located below the plume fringe. Concentrations of Mn^{2+}, Fe^{2+}, CH_4, TOC and DIC used to estimate inputs for "plume residuals and products" in the EBM can also be obtained with these sample ports for this scenario. Furthermore, "background groundwater" concentrations of dissolved chemical species (measured in the upstream monitoring well) are assumed to be equal to the concentration above the plume measured in this MLS (this will generally be acceptable for most sites, but should be supported by relevant data).

The "plume length" calculated by the EBM for this monitoring well scenario equals the distance from the MLS monitoring well to the downstream end of the plume. This is the reference distance for the analysis, since the position of the MLS along the plume flow path is assumed to represent the location of the plume "source area" in this scenario. The distance along the plume flow path from the MLS to the true plume source area ("x" in Figure 2) is identical to the distance "s" from the source area to the source area monitoring well that is used in the standard monitoring well scenario. This distance is entered by the user and automatically added to the plume length calculated in this scenario, to yield an overall true plume length given in the "Results" output section of the model.

It should be noted that this alternative scenario does not account for any spatial variability in groundwater chemistry other than that which occurs across the plume fringe in the vertical direction. It therefore does not allow for averaging of concentrations and reconfirmation of values by measurements of groundwater chemistry at different locations across the site under consideration. Keeping in mind the heterogeneous nature of subsurface environments in general, the determination of inputs for the EBM using this alternative monitoring well scenario has to be treated very carefully. The use of single data values to represent the whole site may increase the uncertainty in the results produced by the model.

2.4 Network of monitoring wells

The monitoring network introduced in section 2.2 includes the minimum number of monitoring wells to generate sufficient input data for the ideal monitoring well scenario. If additional monitoring wells in the same location of the plume (e.g. source area or downstream plume) exist or are planned, an average value can and should be used to reconfirm measurements for the dissolved concentrations of chemical species included in the EBM. Also, sets of different parameter combinations within the range of measured values that occur across the site can be used to evaluate a variety of predicted plume lengths and contaminant spill scenarios (Thornton et. al., 2001a). Reliable estimates of plume width and depth need to be obtained for the EBM. This may be achieved by the installation of additional monitoring wells at the upstream border of the source area, to delineate the plume depth and deduce the plume width in the transverse direction.

2.5 Summary of design options and data requirements for monitoring well networks

A summary of the data requirements and monitoring well design for the typical and alternative monitoring well scenarios is given below.

Monitoring Well Scenario	Monitoring Well Location	Monitoring Well Design	Parameters Measured	Comments
Typical (ideal) case	Upstream	Single screen	O_2, NO_3, SO_4, Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants	☐ Background concentrations of species in uncontaminated aquifer
	Plume source area	Single screen	O_2, NO_3, SO_4, Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants	☐ Concentrations of species in contaminated aquifer
	Downstream plume	High-resolution MLS	O_2, NO_3, SO_4, Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants	☐ Profiles of solute concentrations are used to estimate electron acceptor fluxes across plume fringe
Alternative case	Upstream Plume source area Downstream plume	High-resolution MLS	O_2, NO_3, SO_4, Mn^{2+}, Fe^{2+}, CH_4, TOC, DIC and contaminants	☐ "Background" concentrations of species are measured in uncontaminated groundwater above plume fringe ☐ "Source area" concentrations of species are measured in contaminated groundwater below plume fringe ☐ Profiles of solute concentrations are used to estimate electron acceptor fluxes across plume fringe

3. Model parameters and data inputs

3.1 Introduction

The input parameters for the electron balance model are entered in the spreadsheet marked “DataInput”. Data are included in this spreadsheet under different categories of information, which provide the input terms for the equations used in the electron balance model for the plume. These categories of information include parameter values related to the following inputs:

- ☐ Plume source term
- ☐ Plume chemistry: residuals and products
- ☐ Background ground water chemistry
- ☐ Aquifer properties and hydrogeology
- ☐ Plume dimensions
- ☐ Plume fringe parameters

These inputs and the relevant parameters required for the calculation of each input in model simulations are explained below.

3.2 Plume source term composition

This data block includes concentrations (mg/l) of all species present in the source area, which function as an electron donor and create an electron acceptor demand in the aquifer. These include dissolved organic and inorganic contaminants and other compounds which define the chemical composition of the plume source term. It should be noted that plume source term can include organic and inorganic compounds, according to the specific situation being modelled. This data is used to calculate electron donor fluxes into the plume from the source area. The origin and use by the model of input values included in this data block are described below.

3.2.1 Organic compounds

The organic compounds included in the input data block for the plume source term are those commonly found as relatively mobile constituents in plumes of petroleum hydrocarbons, phenols and other organic chemicals. Acetate is often present in plumes as a degradation product of petroleum hydrocarbons and phenols. TOC is included for situations in which contaminant concentrations are represented by this parameter, or where the migration of this species is of primary interest in defining the plume length and status (e.g. landfill leachate plumes).

3.2.2 Inorganic compounds

Ammonium is included as an inorganic electron donor in the input data block for the plume source term. This species is commonly found as a contaminant in leachate plumes from landfills and plumes from coal carbonisation, gasworks or other similar facilities.

The model uses *dissolved* concentrations of electron donors to define the source term. Non-aqueous phase liquids (NAPLs) are not considered. Concentrations of dissolved electron donors representing the plume source term should be obtained from a monitoring well located below or immediately downgradient of the source area. It should be the same monitoring well that is used to define the plume depth or thickness.

3.2.3 Including electron acceptors in the source term

Electron acceptors, such as sulphate or nitrate, can be included in the source term input if the groundwater chemistry data from the source area monitoring well suggests that these species are components of the contaminant matrix (e.g. Thornton et. al., 2001a,b). This can be achieved by adding the new compound to the database and the list of contaminants included in the calculation (consult the user manual for a description of these actions). Since these (electron acceptor) compounds are part of the contaminant input block, they then need to be assigned a **negative** concentration to account for the fact that they are electron acceptors and not electron donors. This means it is assumed in the model that electron acceptors and electron donors react upon entrance into the plume, so that the source term input of electron donors entering the plume is decreased.

3.3 Plume chemistry: residuals and products

This data block includes input values of all species which are used to estimate the degradation of contaminants in the plume from either consumption of dissolved and mineral-based electron acceptors or production of carbon-based end-products. The origin and use by the model of input values included in this data block are described below.

3.3.1 Plume residuals

A value of the plume residual electron acceptor concentration (mg/l) is required to estimate the consumption of dissolved oxidants within the plume. Evidence from several studies (e.g. Thornton et al, 2001b) shows that SO_4 may not be completely consumed by degradation of organic contaminants in aquifers, so that a residual SO_4 concentration may be measured in plumes. This is not usually the case for O_2 or NO_3 but they have also been included as an input for this data block. The residual plume SO_4 concentration can also be used to estimate the amount of Fe^{2+} that has been removed from the plume by precipitation of iron sulphide compounds during degradation by SO_4-reduction. This value can be used to correct estimates of Fe-oxide consumption by degradation in the plume electron acceptor budget. This is explained in more detail in subsequent sections. The user should enter the concentration of the residual electron acceptors measured in the plume or enter “0” if these are below detection limit.

The concentration of dissolved O_2, NO_3 or SO_4 present as a residual electron acceptor in the plume should be obtained from a monitoring well located vertically below or immediately downgradient of the plume source area. **It should be the same monitoring well that is used to define the plume depth or thickness and plume source term concentrations of electron donors.**

3.3.2 Plume products

A value of the dissolved Mn^{2+} and Fe^{2+} concentration (mg/l) in the plume is required to estimate the consumption by degradation of mineral-based electron acceptors (Mn-oxide and Fe-oxide) in the plume. These estimates are obtained from measured concentrations of dissolved Mn^{2+} and Fe^{2+} in the plume, which are corrected for background concentrations of these species. This correction is necessary to estimate the net consumption of Mn-oxide and Fe-oxide by degradation in the plume.

The concentration of dissolved Mn^{2+} and Fe^{2+} in the plume should be obtained from a monitoring well located vertically below or immediately downgradient of the plume source area. **It should be the same monitoring well that is used to define the plume depth or thickness and plume source term concentrations of electron donors.**

A value of the dissolved inorganic carbon (DIC[1]) and methane (CH_4) concentration (mg/l) in the plume is required to estimate the mass of contaminants that have been degraded to these carbon-based end-products in the plume. This estimate is compared with the mass of contaminant carbon that has been degraded by consumption of electron acceptors in the plume, to provide a carbon mass balance for the system. Degradation of contaminants to DIC and CH_4 in the aquifer is estimated from the concentration of these end-products in groundwater in the plume. A value of the DIC and CH_4 concentration in the plume is compared with the concentration of these species in the background groundwater (section 3.4.3) to determine the net DIC and CH_4 arising from degradation of contaminants in the plume.

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[1] DIC represents the total amount of inorganic carbon in solution, given by the sum of inorganic carbon present in the following carbonate species: H_2CO_3, HCO_3^- and CO_3^{2-}, i.e. **DIC** = $H_2\mathbf{C}O_3 + H\mathbf{C}O_3^- + \mathbf{C}O_3^{2-}$. DIC is often referred to as total inorganic carbon (TIC) in water quality analyses and all these forms of dissolved inorganic carbon are conventionally determined from an analysis of the groundwater TIC concentration. In the majority of cases, $HCO_3^- + CO_3^{2-}$ contribute most to the DIC measured in groundwater samples. Alkalinity, expressed as either mg/l HCO_3^- or mg/l $CaCO_3$ is NOT equivalent to DIC. If either measured concentrations of alkalinity or HCO_3^- are used to represent DIC, the latter input will be overestimated and users of CoronaScreen should instead provide a measured value of TIC for this input, taken from groundwater sampling at the site.

The concentration of dissolved DIC and CH_4 in the plume should be obtained from a monitoring well located vertically below or immediately downgradient of the plume source area. **It should be the same monitoring well that is used to define the plume depth or thickness and plume source term concentrations of electron donors.**

3.4 Background groundwater chemistry

This data block includes input values which provide the chemistry of the background groundwater upgradient of the plume. This data is used to calculate the consumption of electron acceptors in the plume core, based on the concentration of products found in the plume core which arise from this electron acceptor consumption. The origin and use by the model of input values included in this data block are described below.

3.4.1 Background dissolved oxygen, nitrate and sulphate

A value of the dissolved O_2, NO_3 and SO_4 concentration (mg/l) in background groundwater is required to estimate transverse electron acceptor flux into the plume by dispersion at the plume fringe. It is assumed that these concentrations will be the same as the maximum values in background groundwater upstream from the source. The concentration of dissolved O_2, NO_3 and SO_4 in the background groundwater can be obtained from a monitoring well located upgradient of the plume source area or those sampling ports of a multilevel sampler which are located above the plume fringe. **User-specified concentrations of dissolved O_2, NO_3 and SO_4 entered into this data block should be higher than those entered in the "plume residuals" data block (see above), so that fluxes of dissolved electron acceptors entering the plume by dispersion can be calculated by the model.** A "pop-up" window is automatically activated to remind the user of this condition, should background values of dissolved O_2, NO_3 and SO_4 be less than the plume residual value.

3.4.2 Background dissolved manganese and iron

A value of the dissolved manganese (Mn^{2+}) and iron (Fe^{2+}) concentration (mg/l) in background groundwater is required to estimate the consumption by degradation of mineral-based electron acceptors in the plume. The mineral-based electron acceptors include Mn-oxides (e.g. MnO_2) and Fe-oxides (e.g. FeOOH, $Fe(OH)_3$), which are present as solid phases on the aquifer sediment. The consumption of Mn-oxide and Fe-oxide in the aquifer by degradation is estimated from the concentration of the respective inorganic products, Mn^{2+} and Fe^{2+}, in groundwater in the plume. Background concentrations of Mn^{2+} and Fe^{2+} are required to correct the respective concentrations of these species in the plume, to estimate the amount of Mn-oxide and Fe-oxide that has been consumed by degradation in the plume. The concentration of dissolved Mn^{2+} and Fe^{2+} in the background groundwater can be obtained from a monitoring well located upgradient of the plume source area.

3.4.3 Background dissolved inorganic carbon and methane

A value of the dissolved inorganic carbon (DIC) and methane (CH_4) concentration (mg/l) in background groundwater is required to estimate the mass of contaminants that have been degraded to these carbon-based end-products in the plume. This estimate is compared with the mass of contaminant carbon that has been degraded by consumption of electron acceptors in the plume, to provide a carbon mass balance for the system. Degradation of contaminants to DIC and CH_4 in the aquifer is estimated from the concentration of these end-products in groundwater in the plume. Background concentrations of DIC and CH_4 are required to correct the respective concentrations of these species in the plume, to estimate the amount of contaminants degraded to DIC and CH_4 in the plume. The concentration of dissolved DIC and CH_4 in the background groundwater can be obtained from a monitoring well located upgradient of the plume source area.

3.4.4 Background dissolved total organic carbon

A value of the dissolved total organic carbon (TOC) concentration (mg/l) in background groundwater is required to estimate the flux of TOC entering the plume from the source area. This is necessary when contaminant concentrations are measured or expressed in terms of TOC, rather than individual compounds or species. Conceptually, a TOC plume is the same as a plume of individual contaminants, with respect to consumption of electron acceptors during degradation reactions, and is treated as such in the model. In some cases, for example landfill leachate plumes, the migration of the TOC plume will control the attenuation of organic micropollutants which may be present in the leachate plume (Christensen et. al., 1994). Alternatively, there may be cases where the assessment of plume behaviour is required in a naturally anaerobic aquifer containing a high (or significant) background TOC concentration. The TOC arising from the plume source area must be corrected for this background TOC input from the aquifer in the model simulation.

3.4.5 Background contaminant concentration

In most cases, contaminants present in the plume will not be present in the background groundwater sampled in the upstream monitoring well. However, in cases where the target contaminants are also present in the upstream monitoring well (e.g. due to natural conditions or an unrelated contamination event), the concentration of these should be subtracted from the concentration measured in the source area monitoring well, and a net contaminant concentration entered in the input section for the plume source term composition.

3.5 Aquifer properties and hydrogeology

This data block includes input values for basic physico-chemical properties and hydrogeological parameters of the aquifer. This data is used in the calculation of many outputs for the electron balance model. The origin and use by the model of input values included in this data block are described below.

3.5.1 Groundwater velocity

A value of groundwater velocity, v (m/day), is input into the model in either of two ways. Groundwater velocity can be estimated from Darcy's Law using values of mean aquifer hydraulic conductivity (K), effective porosity (n_e) and hydraulic gradient (i), according to the following relationship:

$$v = \frac{K \cdot i}{n_e} \tag{1}$$

An estimate of groundwater velocity determined in this way requires separate estimation of aquifer hydraulic conductivity, effective porosity and hydraulic gradient from the site investigation undertaken for the plume analysis. Alternatively, an estimate of groundwater velocity can be input directly into the data block, if this is known from the site investigation, or if the other input terms (K, i, n_e) are unknown. The user has the option of selecting which method is used to input a value for groundwater velocity, by clicking the button marked "Restore velocity-equation". If this button is selected, groundwater velocity will be calculated by Darcy's Law using the appropriate input values, which will then be required in this data block.

3.5.2 Hydraulic conductivity

A value of hydraulic conductivity, K (m/day), is required to estimate groundwater velocity using Darcy's Law, when this method of input is selected. A site-specific value of K should be used for this input, as determined by appropriate hydraulic testing or other method of estimation.

3.5.3 Hydraulic gradient

A value of hydraulic conductivity, i (m/m), is required to estimate groundwater velocity using Darcy's Law, when this method of input is selected. A site-specific value of i should be used for this input, as determined by appropriate methods, such as measurement of groundwater elevation in monitoring wells. The plume ideally should be included in the network of monitoring wells used for this purpose.

3.5.4 Effective porosity

Effective porosity is defined as that proportion of saturated pore space in a unit volume of aquifer that contributes to fluid flow, which will be less than the total porosity. A value of effective porosity, n_e (dimensionless), is required to estimate groundwater velocity using Darcy's Law, when this method of input is selected. Effective porosity is also used in the calculation of other outputs from the model, including plume residuals and products. A site-specific value of n_e should be used for this input, as determined by appropriate methods, such as analysis of aquifer sediment or rock cores.

3.5.5 Bulk density

A value of aquifer bulk density, ρ_d (g/cm^3) is required to estimate contaminant sorption to the aquifer sediment (see below). Site-specific estimates of bulk density should be used in this data block. These can be obtained from analysis of aquifer sediment or rock cores.

3.5.6 Fraction of organic carbon

The fraction of organic carbon, f_{oc} (dimensionless) is the proportion of native particulate organic carbon attached to the aquifer sediment, which contributes to sorption of organic chemicals in the plume. Sorption of organic chemicals in the plume by the aquifer sediment is estimated with a solute distribution coefficient using the following relationship:

$$K_d = K_{oc} \cdot f_{oc} \qquad (2)$$

where K_d is the solute distribution coefficient for the organic chemical (ml/g sediment), K_{oc} is the organic carbon-referenced distribution coefficient for the organic chemical (ml/g sediment) and f_{oc} is the fraction of organic carbon in the aquifer sediment. A site-specific value of f_{oc} should be determined from appropriate chemical analysis of aquifer sediment or rock cores and used as input in this data block. Values of K_d estimated in this way are then used to determine the retarded solute velocity of each organic chemical in the plume (see below).

3.5.7 Ammonium distribution coefficient

Sorption of ammonium by the aquifer sediment may be estimated using a distribution coefficient for ammonium, NH_4-K_d (ml/g sediment), if this input is available. A user-specified value of NH_4-K_d must be input for this purpose. Values of NH_4-K_d may be determined on a site-specific basis, using aquifer sediment and groundwater with appropriate methods (e.g. representative batch sorption tests), or estimated from the literature, subject to justification for the aquifer setting and contaminant scenario being assessed in the EBM. Values of NH_4-K_d estimated in this way are then used to determine the retarded solute velocity of ammonium in the plume (see below).

3.6 Plume source dimensions

This data block includes input values describing the geometry of the plume and location of the monitoring well used to provide the chemical composition of the plume source term (“source area monitoring well”). This data is used in the calculation of electron acceptor fluxes into the plume by dispersion for the model and to estimate the true plume length. The origin and use by the model of input values included in this data block are described below.

3.6.1 Plume width

A value of the plume width (m) is used to estimate the:

- ☐ Cross-sectional area of the plume normal to the flow path (A_{yz});
- ☐ Cross-sectional area of the plume in plan view along the flow path (A_{xy});
- ☐ Contaminant flux from the source area into the plume;
- ☐ Vertical transverse flux of dissolved electron acceptors in background groundwater by dispersion at the plume fringe;
- ☐ Flux of electron acceptors consumed within the interior of the plume (as opposed to the fringe), which are represented by the respective products of this electron acceptor consumption (see section 4.6).

The plume width can be represented by the known or assumed width of the source area. Alternatively, plume width may be estimated using groundwater quality data from a transect of monitoring wells located across the groundwater flow direction, immediately downgradient of the source area.

3.6.2 Plume thickness

A value of the plume depth or thickness (m) is used to estimate the:

- ☐ Cross-sectional area of the plume normal to the flow path (A_{yz});

- ☐ Cross-sectional area of the plume in section view along the flow path(A_{xz});
- ☐ Contaminant flux from the source area into the plume;
- ☐ Horizontal transverse flux of dissolved electron acceptors in background groundwater by dispersion at the plume fringe;
- ☐ Flux of electron acceptors consumed within the interior of the plume (as opposed to the fringe), which are represented by the respective products of this electron acceptor consumption (see section 4.5 and 4.6).

The plume thickness can be represented by the known or assumed depth of the source area below the water table. For the scenario included in the model, this thickness should be taken as the maximum thickness of dissolved contaminants identified in a monitoring well located below or immediately downgradient of the plume source area.

3.6.3 Distance: source to "source well"

The distance, "s" (m), from the plume source area to the downgradient location of the monitoring well used to provide the plume source term chemical composition ("source area monitoring well" in Figure 2) is required in this input. If the source area monitoring well is located within the true plume source area, this distance will be zero and should be entered by the user as "0" in this cell. This is the case for the ideal monitoring well scenario shown in Figure 2. However, there may be practical reasons (e.g. access limitations) when the monitoring well used to determine the plume source term composition must be located some distance downstream of the source area (e.g underground storage tank). Since the plume length calculated by the EBM is determined as the distance from the source area monitoring well, any offset distance of this monitoring well downstream of the true source area must be added to the plume length to give a "true" plume length from the "true" source area. The value of "s" entered by the user in this cell is automatically added to the plume length calculated from the location of the source area monitoring well to give a true plume length, as described.

When the *alternative monitoring well* scenario (see section 2.3) is used, the distance, s, entered by the user will be the distance from the true plume source area of the downstream MLS used to provide the composition of the plume source term. This distance will also equal the distance, x, entered for this MLS in the "Plume fringe parameters" input section (see section 3.7.1), when this monitoring scenario is used (see also Figure 2).

3.7 Plume fringe parameters

This input block includes values that determine the dispersive flux of solutes across the plume fringe. Due to the significance of the plume fringe with respect to overall degradation in the plume, the input parameters in this block are particularly important for the results of the EBM.

It is not possible to enter more than one MLS at a time. If data from several MLS is available, these must be entered separately, and the results for every scenario compared, in order to identify the most realistic values for the site under consideration.

3.7.1 Distance: source to MLS well

The distance between the plume source area and downstream plume monitoring well ("x" in Figure 2) is used to calculate the vertical transverse dispersivity from the vertical fringe thickness (or vice versa). The plume fringe thickness, as defined by measurements from a MLS, will increase with distance from the plume source; thus, when calculating the dispersivity from the plume fringe thickness, the distance has to be taken into account. This is just as valid for the reverse calculation, when a dispersivity value is known for the site under consideration and the plume fringe thickness is calculated. **A value of "x" greater than one must always be entered in this box to avoid "goal-seek error" or "#DIV/0!" messages occurring when the model is run.**

When the *alternative monitoring well* scenario (see section 2.3) is used, the distance, x, entered by the user in this input section will also be the same distance, s, entered for the distance from the source area to the source area monitoring well in the "Plume source dimensions" input section (section 3.6.3). This is because for this alternative monitoring scenario, a single MLS borehole, located downgradient of the plume source area, is simultaneously used to provide data on the background groundwater chemistry, plume fringe thickness and plume source term composition (see section 2.3).

3.7.2 Vertical fringe thickness

A value of the vertical thickness (m) of the "mixing zone" at the plume fringe is required to estimate the vertical transverse flux of dissolved electron acceptors in background groundwater into the plume by dispersion at the plume fringe. The "mixing zone" refers to the interval across the plume fringe where significant gradients in the spatial distribution of dissolved electron acceptors and electron donors exist, due to mixing by dispersion, of uncontaminated groundwater with contaminated groundwater in the plume. An estimate of the plume fringe thickness can be obtained from a profile of dissolved O_2, NO_3 and SO_4 versus depth, using a MLS instrumented across the plume fringe. The fringe thickness will be given by the vertical distance between the maximum and minimum concentration of these electron acceptors in the background groundwater and plume, respectively, as measured in the MLS profile instrumented across the plume fringe (see above). An alternative possibility is to calculate the vertical thickness of the plume fringe from an estimate of alpha z (see below) by clicking the button "Calc. dz from alpha_z". The fringe thickness is used with the concentration difference in O_2, NO_3 and SO_4 across the fringe to determine the O_2, NO_3 and SO_4 concentration gradient across the plume fringe.

3.7.3 Vertical transverse dispersivity

Vertical transverse dispersivity, alpha z (m), is used in the estimation of vertical transverse inputs of dissolved electron acceptors from background groundwater into the plume by dispersion at the plume fringe. Alpha z can be either entered directly in the relevant cell of this input block (click the button "Calc. dz from alpha_z" in the right column if the cell is locked), or calculated from vertical fringe thickness (click the button "Calc. alpha_z from dz" to calculate). When entering values directly, an estimate of alpha z (more commonly denoted α_z) may be obtained from the literature, where caution is advised in the selection of specific values, to ensure these are appropriate for the aquifer setting and properties assessed in the EBM. **It is strongly recommended that alpha z is estimated for individual sites using a measurement of the plume fringe thickness obtained from a MLS installed across the plume fringe and the "Calc. alpha_z from dz" option in the model. Entering separate values of alpha z and/or the plume fringe thickness by decoupling the relationship which predicts these parameters (completed by accessing the "Dispersivity" tab in the "Calculation settings" section of the model) should only be undertaken by experienced modellers, using realistic values of these parameters for the scenario being evaluated with CoronaScreen.**

The link between user-defined inputs and the value of vertical dispersivity (alpha z, α_z) or plume fringe mixing zone thickness (dz) estimated in the CoronaScreen model is shown in Table 4.

Table 4. Data inputs and model outputs for coupled and uncoupled link between vertical dispersivity and plume fringe mixing zone

Option Coupled	**Required data inputs**	**Model outputs[1]**	**Comments**
"Calc alpha z from dz"	☐ Distance: source to MLS well, "x" ☐ Vertical fringe thickness, "dz"	☐ Vertical dispersivity, "α_z"	☐ A value of "dz" is obtained from vertical profiles of electron acceptor concentrations across the plume fringe, using an MLS ☐ If "x" is changed for a fixed user-defined value of "dz", then "α_z" will change ☐ If "dz" is changed for a fixed user-defined value of "x", then "α_z" will change
"Calc dz from alpha z"	☐ Distance: source to MLS well, "x" ☐ Vertical dispersivity, "α_z"	☐ Vertical fringe thickness, "dz"	☐ A value of "α_z" is obtained from the literature[2] ☐ If "x" is changed for a fixed user-defined value of "α_z", then "dz" will change ☐ If "α_z" is changed for a fixed user-defined value of "x", then "dz" will change
Option Decoupled	☐ Vertical fringe thickness, "dz" ☐ Vertical dispersivity, "α_z"	☐ As entered by the user	☐ The distance from the source to the MLS has no effect on these model outputs ☐ Values of "dz" or "α_z" are not predicted by the model as the relationship between these is decoupled by the user

1. Model outputs in this case are either vertical dispersivity, "α_z", or vertical fringe thickness, "dz"
2. Values of "α_z" selected from the literature should be representative of the aquifer setting and scenario modelled

The table shows the data inputs that are required and the model outputs which are estimated when the relationship between alpha z and dz is either coupled or decoupled, as described above.

3.7.4 Horizontal transverse dispersivity

Horizontal transverse dispersivity, alpha y (m), is used in the estimation of horizontal transverse inputs of dissolved electron acceptors from background groundwater into the plume by dispersion at the plume fringe. This value cannot be entered directly, but is linked to alpha z by the following relation:

$$\alpha_y = \frac{\alpha_z}{DR_{z/y}} \tag{3}$$

where $DR_{z/y}$ denotes the ratio of alpha z over alpha y. The value of this ratio is set to 0.1 (i.e. α_z = one tenth of α_y) by default, as this value has been found in the literature to be typical for many field sites. However, if needed the user can change this ratio by clicking the button “Calculation settings…” and entering a new value on the “Dispersivity”-tab in the dialog shown.

Since the horizontal transverse dispersivity is assumed to be different to the vertical transverse dispersivity – by default, one order of magnitude – the horizontal plume fringe thickness is assumed to be different. Thus, a different plume fringe thickness is derived from the horizontal dispersivity. This is automatically calculated in the spreadsheet and used for the calculation of horizontal dispersive input of electron acceptors.

4. Model formulation and outputs

4.1 Introduction

This section describes the mathematical equations that are used to derive outputs for prediction of plume behaviour by the EBM. The outputs are described under headings which correspond directly with respective blocks of input data on the "Data Input" spreadsheet, or are marked with the same colour to indicate relevant input data used to derive the outputs.

Outputs of electron donors and electron acceptors used in the electron balance by the model are presented as flux of "electron equivalents" per day (e/day). Values of "electron equivalents" are obtained by converting mass/day of electron donors or electron acceptors using the following expression:

$$\text{Electron equivalents of electron donor or electron acceptor} = \frac{\text{Flux}_{\text{ED,EA}}}{\text{MW}_{\text{ED,EA}}} \times \text{E}^{-}\text{transferred}_{\text{ED,EA}} \qquad (4)$$

Where $\text{Flux}_{\text{ED,EA}}$ is the mass flux of the electron donor or electron acceptor (grams/day), $\text{MW}_{\text{ED,EA}}$ is the molecular weight of the electron donor or electron acceptor(grams/mole) and E^{-} $\text{transferred}_{\text{ED,EA}}$ is the number of electrons transferred per mole in the redox half reaction for oxidation of the electron donor or reduction of the electron acceptor (e/mole). Expression of mass in this way converts all inputs into a common input term for the EBM, and allows outputs to be expressed as equivalent electron acceptor or electron donor species, as desired.

The calculation of the different outputs for the EBM is described in the sections below. The outputs of the calculations in the spreadsheet are denoted as "inputs" to the model for the electron balance.

4.2 Plume source input

The mass flux of electron donors into the plume from the source area is treated as an advective flux of dissolved components occurring in a vertical plane, which extends the full width and thickness of the plume. The plume width and thickness is defined by data from monitoring wells located in the plume source area (see previous chapter). Concentrations of electron donors are assumed to be equal over this vertical plane. The mass flux of electron donors from the source area is then estimated using the following expression:

$$\text{Flux}_{\text{ED}\cdot\text{source}} = \text{C}_{\text{ED}\cdot\text{source}} \times v \times \text{n}_{\text{e}} \times \text{A}_{\text{yz}} \qquad (5)$$

where $\text{Flux}_{\text{ED source}}$ is the mass flux of electron donors (grams/day), $\text{C}_{\text{ED source}}$ is the concentration of the electron donor in the source area monitoring well (mg/l), v is the groundwater velocity (m/day), n_e is the effective porosity (fraction) and A_{yz} is the area of the plume, normal to the plume flow path (m^2).

An estimate of the solute velocity, v_s, is obtained from the following relationships:

$$v_s = \frac{v}{R_f} \qquad (6)$$

$$R_f = 1 + \frac{K_d \cdot \rho_b}{n_e} \qquad (7)$$

where v_s is the velocity of the electron donor accounting for sorption to the aquifer sediment (m/day), R_f is the solute retardation factor and other terms have been previously explained. An estimate of K_d for organic electron donors is obtained using Eq. 2, whereas a user-specified value for K_d is used to estimate R_f for ammonium. The individual electron donor inputs from the source area are then summed to provide a total mass flux of electron donors into the plume.

4.3 Plume EA vertical dispersive input

The mass flux of dissolved electron acceptors supplied to the plume by vertical dispersion of uncontaminated groundwater at the plume fringe is estimated using the following expression:

$$\mathrm{Flux}_{\mathrm{EA\cdot vert\cdot trans\cdot disp}} = 2 \times \frac{\delta C_{\mathrm{EA\cdot fringe}}}{\delta z} \times v \times n_e \times A_{xy} \times \alpha_z \tag{8}$$

where Flux $_{\mathrm{EAvert\ trans\ disp}}$ is the mass flux of dissolved O_2, NO_3 and SO_4 supplied to the plume by vertical dispersion (grams/day), $\delta C_{\mathrm{EAfringe}}$ is the difference in concentration of O_2, NO_3 and SO_4 measured over the plume fringe (mg/l), δz is the thickness of the "mixing zone" at the plume fringe (m), A_{xy} is the cross-sectional area of the plume in plan view (m^2) and α_z is the vertical transverse dispersivity of the aquifer (m).

The difference in concentration of dissolved O_2, NO_3 and SO_4 across the plume fringe and the thickness of the plume fringe mixing zone are obtained by analysis of vertical concentration profiles of these species in groundwater. This data is obtained using a MLS instrumented across the plume fringe. In most cases, the maximum concentration of O_2, NO_3 and SO_4 used to determine $\delta C_{\mathrm{EAfringe}}$ will be the same as the background concentration measured upstream from the source. A multiplier of two is used to account for the dispersive flux into the upper and lower plan area of the plume. The individual electron acceptor inputs are then summed to provide a total mass flux of electron acceptors entering the plume by vertical transverse dispersion of background groundwater. The vertical dispersive flux determined with these inputs is scaled over the full size of the plume.

4.4 Plume EA horizontal dispersive input

The mass flux of dissolved electron acceptors supplied to the plume by horizontal dispersion of uncontaminated groundwater at the plume fringe is estimated using the following expression:

$$\mathrm{Flux}_{\mathrm{EA\cdot horiz\cdot trans\cdot disp}} = 2 \times \frac{\delta C_{\mathrm{EA\cdot fringe}}}{\delta y} \times v \times n_e \times A_{xz} \times \alpha_y \tag{9}$$

where Flux $_{\mathrm{EAhoriz\ trans\ disp}}$ is the mass flux of dissolved O_2, NO_3 and SO_4 supplied to the plume by horizontal dispersion (grams/day), δy is the thickness of the mixing zone at the plume fringe in the horizontal direction (m), A_{xz} is the cross-sectional area of the plume in section view (m^2), α_y is the horizontal transverse dispersivity of the aquifer (m) and the other terms have been previously explained.

The difference in concentration of dissolved O_2, NO_3 and SO_4 across the plume fringe are obtained by analysis of vertical concentration profiles of these species in groundwater, i.e., it is assumed that the difference between the maximum and minimum concentrations inside and outside the plume is the same in the vertical and horizontal direction. The thickness of the plume fringe in the horizontal direction is different from the thickness of the plume fringe in the vertical direction. The value for δy is calculated from the horizontal transverse dispersivity, α_y. The user has the option of setting the ratio between vertical and horizontal transverse dispersivity, α_z/α_y, when clicking "Calculation settings…" on the "Dispersivity"-tab. A multiplier of two is used to account for the dispersive flux into the "left" and "right" hand sides of the plume. The individual electron acceptor inputs are then summed to provide a total mass flux of electron acceptors entering the plume by horizontal transverse dispersion of background groundwater. The electron acceptor inputs from vertical and horizontal transverse dispersion are summed to provide a total mass flux of electron acceptors entering the plume by dispersion of background groundwater (Total $\mathrm{EA}_{\mathrm{dispersion}}$). The vertical dispersive flux determined with these inputs is scaled over the full size of the plume.

4.5 Plume EA products input

This data block estimates the degradation of contaminants in the plume from either consumption of mineral-based electron acceptors or production of carbon-based end-products. These outputs are based on the production of dissolved Mn^{2+}, Fe^{2+} and CH_4 measured in the plume. The output is presented in terms of the mass flux of each species, expressed as e/day for consistency with the other model outputs in the electron balance.

The assumption made in the calculation of these outputs is that dissolved concentrations of $Mn^{2+}$and Fe^{2+} in the plume originate from consumption of Mn-oxide and Fe-oxide on the aquifer sediment during contaminant degradation, whereas CH_4 originates from contaminant degradation by methanogenesis. This implies that these products are conserved in the plume and that observed concentrations of Mn^{2+}, Fe^{2+} and CH_4 reflect the total amount of degradation that has occurred by each degradation pathway.

This is an acceptable generalisation for Mn^{2+}, which may by removed primarily by cation-exchange reactions under anaerobic conditions in plumes. However, the extent of cation-exchange involving Mn^{2+} is likely to be low in most aquifers and this effect can be ignored, so that estimates of degradation based on Mn^{2+} production will be conservative.

Dissolved Fe^{2+} may be lost from solution under anaerobic conditions by cation-exchange reactions with the aquifer sediment and precipitation of iron sulphide minerals (e.g. FeS). In most cases Fe^{2+} loss by cation exchange will be small in anaerobic aquifers and, similar to Mn^{2+}, can be reasonably ignored in the model. However, loss of dissolved Fe^{2+} by precipitation of iron sulphides can be important under anaerobic conditions. This process will occur where Fe-oxide reduction occurs concurrently with SO_4-reduction. In this case, estimates of degradation based on measured Fe^{2+} (and attributed to Fe-oxide reduction) will be underestimated by the amount of Fe^{2+} that has been lost from solution by precipitation of iron sulphide. In the model, the amount of Fe^{2+} potentially lost via precipitation of FeS is estimated from the loss of SO_4 in the plume by SO_4-reduction. This additional fraction is used to correct the estimate of degradation by Fe-oxide consumption that is obtained from the measured Fe^{2+} concentration in the plume.

Dissolved CH_4 produced by methanogenesis in the plume is conservative under anaerobic conditions. Methanotrophic oxidation of CH_4 to CO_2 may occur at the plume fringe in response to the mixing of O_2 into the plume dispersion. If this reaction occurs, it will lead to the underestimation of degradation by methanogenesis. However, this is taken into account in the overall electron balance for the plume, which is based on global inputs of electron donors and acceptors, without specifying specific pathways for possible redox reactions.

The mass flux of dissolved Mn^{2+}, $Fe^{2+}$and CH_4 into the plume, from respectively the reduction of solid phase Mn-oxide and Fe-oxide, and methanogenesis, is estimated using the following expressions:

$$\mathrm{Flux}_{\mathrm{EA\cdot Mn^{2+}\,produced}} = \mathrm{C}_{\mathrm{Mn^{2+}\,produced}} \times v \times \mathrm{n_e} \times \mathrm{A_{yz}} \tag{10}$$

$$\mathrm{Flux}_{\mathrm{EA\cdot Fe^{2+}\,produced}} = \mathrm{C}_{\mathrm{Fe^{2+}\,produced}} \times v \times \mathrm{n_e} \times \mathrm{A_{yz}} \tag{11}$$

$$\mathrm{Flux}_{\mathrm{EA\cdot CH_4\,produced}} = \mathrm{C}_{\mathrm{CH_4\,produced}} \times v \times \mathrm{n_e} \times \mathrm{A_{yz}} \tag{12}$$

where $\mathrm{Flux}_{\mathrm{EA\ Mn^{2+}\ produced}}$, $\mathrm{Flux}_{\mathrm{EA\ Fe^{2+}\ produced}}$ and $\mathrm{Flux}_{\mathrm{EA\ CH4\ produced}}$ is the mass flux or dissolved Mn^{2+}, Fe^{2+} and CH_4 entering the plume (grams/day) from the source area, $C_{\mathrm{Mn^{2+}\ produced}}$, $C_{\mathrm{Fe^{2+}\ produced}}$ and $C_{\mathrm{CH4\ produced}}$ is the concentration of dissolved Mn^{2+}, Fe^{2+} and CH_4 measured in the source area monitoring well (mg/l) and the other terms have been previously explained. Values (in mg/l) of $C_{\mathrm{Mn^{2+}\ produced}}$, $C_{\mathrm{Fe^{2+}\ produced}}$ and $C_{\mathrm{CH4\ produced}}$ are provided in the "Plume products (residual minus background)" output data block, where measured plume concentrations of Mn^{2+}, Fe^{2+} and CH_4 are corrected for background concentrations in the upstream monitoring well.

In these calculations (Eq. 10-12) it is assumed that the concentrations of Mn^{2+}, Fe^{2+} and CH_4 measured in the source area monitoring well reflect the degradation potential in the plume for these processes and that this activity is propagated through the entire plume by advection as the plume grows. In this way contaminant degradation by these processes is estimated at the same rate of plume growth, based on dissolved concentrations of these species in the source area monitoring well. It then implicitly assumes that the concentrations of these species are the same in the source area and elsewhere in the plume. This will provide a maximum input for degradation by these processes over the plume history for the electron balance. If this assumption is not acceptable or justified, based on groundwater quality data from the plume monitoring wells, the Mn, Fe and CH_4 contributions to the electron balance can be excluded to provide a conservative estimate of plume development. This is done by setting the background chemistry and plume Mn, Fe and CH_4 concentrations to zero in the input data block.

The correction made to estimates of degradation by Fe-oxide reduction to account for additional Fe^{2+} that has been lost from solution by precipitation of iron sulphide during SO_4-reduction, is based on the following redox half reactions:

SO_4-reduction : $$SO_4^{2-} + 8e^- + 8H^+ \rightarrow S^{2-} + 4H_2O \qquad (13)$$

Fe-reduction : $$FeOOH + e^- + 3H^+ \rightarrow Fe^{2+} + 2H_2O \qquad (14)$$

FeS precipitation : $$Fe^{2+} + S^{2-} \rightarrow FeS \qquad (15)$$

The residual SO_4 concentration in the plume will define the amount of SO_4-reduction that has occurred according to Eq. 13, taking account of all other SO_4 inputs from advection and transverse dispersion. This assumption is justified because in most cases S^{2-} will be highly insoluble under anaerobic conditions in the presence of dissolved Fe^{2+}, so that S^{2-} concentrations in the plume will be negligible. This means no correction is required in the SO_4 budget to account for residual S^{2-} concentrations and SO_4 consumption by Eq. 13 can be based on the residual SO_4 concentration and mass balance with other SO_4 inputs.

According to Eq. 13, 1 mole S^{2-} is produced by the reduction of 1 mole of SO_4. Similarly, 1 mole of Fe^{2+} is produced by the reduction of 1 mole FeOOH using Eq. 14. Because equimolar quantities of Fe^{2+} and S^{2-} are lost by precipitation of FeS using Eq. 15, the depletion of SO_4 in the plume provides an estimate of the additional Fe^{2+} tied up with FeS that is not accounted for by the residual dissolved Fe^{2+} concentration in the plume.

The mass flux of residual dissolved SO_4 into the plume is estimated using the following expression:

$$\mathrm{Flux}_{\mathrm{EA\cdot residual\cdot SO_4}} = \mathrm{C}_{\mathrm{residual\cdot SO_4}} \times v \times \mathrm{n}_{\mathrm{e}} \times \mathrm{A}_{\mathrm{yz}} \qquad (16)$$

where $\mathrm{Flux}_{\mathrm{EA\ residual\ SO4}}$ is the mass flux of dissolved SO_4 entering the plume (grams/day) from the source area, $\mathrm{C}_{\mathrm{residualSO4}}$ is the concentration of dissolved SO_4 measured in the source area monitoring well (mg/l) and the other terms have been previously explained. In this way, the mass flux of residual SO_4 in the plume is determined by the dissolved SO_4 concentration in the source area and the advective groundwater flux. This is consistent with the method of estimating the flux of contaminants and electron acceptor consumption via production of Mn^{2+}, Fe^{2+} and CH_4 from the plume source area. The amount of Fe^{2+} attributable to Fe-oxide reduction but lost from solution via precipitation of FeS, is then estimated using the following relationship:

$$\mathrm{Flux}_{\mathrm{EA\ produced\ equivalent\ Fe^{2+}}}$$

$$= \mathrm{Flux}_{\mathrm{EA\ vert\ trans\ disp\ SO4}} + \mathrm{Flux}_{\mathrm{EA\ horiz\ trans\ disp\ SO4}}) - \mathrm{Flux}_{\mathrm{EA\ residual\ SO4}} \qquad (17)$$

where $\mathrm{Flux}_{\mathrm{EA\ produced\ equivalent\ Fe^{2+}}}$ is the equivalent flux of Fe^{2+} attributable to Fe-oxide reduction, but lost via precipitation of FeS in the plume, and the other terms have been previously explained. This additional contribution from Fe-oxide reduction in the plume is then included in the electron acceptor budget for the "plume EA products input" in the electron balance. The additional Fe^{2+} contribution which is attributed to FeS precipitation will then provide a maximum estimate of the contribution of Fe-oxide reduction in the electron acceptor budget for the plume. No correction is made in this budget for either dissolved Mn^{2+} or Fe^{2+} that are lost by cation-exchange to the aquifer sediment. The individual electron acceptor inputs in this data block are then summed to provide a total mass flux of electron acceptors entering the plume based on the products of Mn-oxide reduction, Fe-oxide reduction and methanogenesis (Total $\mathrm{EA}_{\mathrm{products}}$).

4.6 Plume DIC and CH_4 products input

The mass of carbon-based end-products of contaminant degradation processes in the plume are estimated in this data block. These end-products include total dissolved inorganic carbon (DIC) and methane (CH_4). Carbon dioxide is produced as an end-product of most degradation processes involving the oxidation of organic compounds and will increase the DIC concentration in the plume. Methane is a product of degradation by methanogenesis in the plume. Analyses of DIC and CH_4 in groundwater can therefore provide an estimate of the total organic contaminant carbon that has been degraded and converted to these end-products. This is an alternative method of estimating the degradation of electron donors to that used in the electron donor / electron acceptor balance. The outputs from this data block are calculated in a different way to that used to estimate the $\text{Flux}_{\text{EA CH4 produced}}$ input for the electron balance and are **not** used in the latter. However, both methods use the same input data in the model and this enables a mass balance to be undertaken for contaminant degradation in the plume using results obtained by each method. This mass balance comparison is described below.

The mass of dissolved inorganic carbon produced in the plume by degradation is estimated for the volume of the plume defined by the plume width, depth and predicted length. A correction is made for the concentration of DIC in background groundwater upstream of the source area and the mass of DIC in the plume is estimated using the following expression:

$$\text{Mass}_{\text{DIC produced}} = \text{C}_{\text{DIC produced}} \times v \times \text{n}_{\text{e}} \times \text{A}_{\text{yz}} \times \text{L} \qquad (18)$$

where $\text{Mass}_{\text{DICproduced}}$ is the mass of DIC produced in the plume (moles), $\text{C}_{\text{DICproduced}}$ is the concentration of DIC in the plume corrected for DIC concentration in background groundwater (mg/l), L is the steady-state length (m) of the mixed plume (see section 5.2) and the other terms have been previously explained. The mass of CH_4 produced by methanogenesis in the plume is similarly estimated from the following expression:

$$\text{Mass}_{\text{CH4 produced}} = \text{C}_{\text{CH4 produced}} \times v \times \text{n}_{\text{e}} \times \text{A}_{\text{yz}} \times \text{L} \qquad (19)$$

where $\text{Mass}_{\text{CH4produced}}$ is the mass of CH_4 produced in the plume (moles), $\text{C}_{\text{CH4produced}}$ is the concentration of CH_4 in the plume corrected for CH_4 concentration in background groundwater (mg/l) and the other terms have been previously explained.

For consistency in the mass balance, the carbon in CH_4 is converted to a mass of CH_4-equivalent DIC produced in the plume ($\text{Mass}_{\text{CH4-equivalent DICproduced}}$) using the following reaction stoichiometry:

$$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O \qquad (20)$$

This conversion assumes that the DIC measured in groundwater represents all the CO_2 produced by degradation in the plume, that there are no other reactions removing or adding CO_2 to the plume and that CH_4 is produced entirely by reduction of CO_2. According to this reaction, 1 mole of CH_4 is produced from 1 mole of CO_2, so that the mass of total DIC produced in the plume ($\text{Mass}_{\text{Total DIC produced}}$) will be given by the following expression:

$$\text{Mass}_{\text{Total DIC produced}} = \text{Mass}_{\text{DIC produced}} + \text{Mass}_{\text{CH4-equivalent DICproduced}} \qquad (21)$$

where $\text{Mass}_{\text{Total DIC produced}}$ is in moles. To compare the inorganic carbon produced by degradation in the plume with the electron acceptor consumption resulting from degradation, both terms must be converted to a common unit. This is achieved by representing these inputs in terms of equivalent TOC consumed. The mass in moles of equivalent TOC degraded based on the total DIC produced in the plume ($\text{Mass}_{\text{Equivalent TOC / Total DIC produced}}$), is obtained using the following reaction stoichiometry:

$$CH_2O + H_2O \rightarrow CO_2 + 4e^- + 4H^+ \qquad (22)$$

where 1 mole of CO_2 is produced for 1 mole of TOC degraded. The mass in moles of equivalent TOC degraded (Mass $_{\text{Equivalent TOC / Total EA groundwater}}$), based on the total consumption of electron acceptors in the plume (Total EA $_{\text{groundwater}}$), is obtained using the following expression:

$$\text{Mass}_{\text{Equivalent TOC / Total EA groundwater}} = \text{Total}_{\text{EAgroundwater}} \times \frac{L}{v} \times \frac{1\text{mole}CH_2O}{4e^-} \qquad (23)$$

where Total EA $_{\text{groundwater}}$ is in e/day, L is the mixed plume steady-state length (m) and v is the plume velocity (m/day). The consumption of electron donors in this calculation is estimated over the complete timescale of the plume, and this timescale (in days) is obtained by the term L/v in Eq. 23. The last term in Eq. 23 converts the electron equivalents of TOC to moles of TOC, based on the stoichiometry of Eq. 22. The net mass balance between equivalent TOC degradation obtained by these two methods is then compared, using the expression:

$$\text{Mass}_{\text{Equivalent TOC plume balance}} = \text{Mass}_{\text{Equivalent TOC / Total DIC produced}} - \text{Mass}_{\text{Equivalent TOC / Total EA groundwater}} \qquad (24)$$

5. Interpretation of model outputs

5.1 Introduction

This section explains how the different outputs from the electron balance model can be interpreted in the context of plume development and quality of data used in the analysis. The outputs described in this section include predictions of plume ED-EA balance, plume length, contaminant degradation rates, contaminant transport times, TOC flux at a given plume length and carbon mass balance. These outputs are shown in the "Results" and Plume balance" data blocks for the electron balance model.

5.2 Plume predictions

5.2.1 Overall electron balance

The model calculates the net electron balance (e/day) from the plume-scale electron acceptor and electron donor inputs previously described. The plume EA-ED balance is given by the following expression:

$$\text{Net plume electron balance} = \text{Total EA}_{\text{groundwater}} - \text{Total ED}_{\text{source}} \qquad (25)$$

where Total $\text{EA}_{\text{groundwater}}$ is the total flux (e/day) of electron acceptor inputs into the plume from transverse dispersion (Total $\text{EA}_{\text{dispersion}}$) and the products of Mn-oxide reduction, Fe-oxide reduction and methanogenesis (Total $\text{EA}_{\text{products}}$). Total $\text{ED}_{\text{source}}$ is the total flux (e/day) of all electron donors entering the plume from the source area.

In principal a negative electron balance means that the electron donor flux from the source exceeds the electron acceptor flux into the plume. This implies that the plume will grow in size. A positive electron balance means that the electron acceptor flux into the plume exceeds the electron donor flux from the source area. This implies that the plume will not grow in size and that there is an excess of electron acceptor inputs in the aquifer to meet the electron donor demand from the plume source area. An electron balance of zero means that the electron donor flux from the source area is balanced by the electron acceptor input into the plume. This implies that the plume has reached a "steady-state"condition and will not grow under the present conditions. The model calculates the plume length necessary to achieve an electron balance of "0" using the input parameters for the simulation. By definition, this condition represents the steady-state plume length.

5.2.2 TOC flux at a given plume length

In some applications of the EBM it is desirable to know the net concentration or flux of organic contaminants passing a particular distance from the plume source area. An example is where the model shows that there will be a net flux of electron donors at a distance from the source area, which represents a compliance point or borehole location (monitoring well or abstraction well).

Because all electron donors entering the plume from the source are converted to electron equivalents, it is not possible to determine the concentration of individual contaminants at a given distance. Instead, the model converts the net electron donor flux (e/day) at a given distance into an equivalent flux (mg/day) of total organic carbon (TOC). This parameter will provide an estimate of the total carbon flux passing through the plume at a given distance, $d_{\text{TOC flux}}$, for comparison with relevant water quality standards or remediation targets. Separately, the user may convert this TOC flux into an equivalent flux of a specific contaminant, assuming a worst case scenario is being evaluated. It should be noted that the flux of TOC at a given plume length is estimated for the cross-sectional area (A_{yz}) of the plume, normal to the plume flow path. When the plume has reached a steady-state length or there is a net excess of electron acceptor inputs into the plume, the net flux of TOC will be zero. When this occurs, "zero" is displayed in the output box. To obtain an estimate of the equivalent TOC flux at a given distance from the source, the user must enter a value for the distance of interest, $d_{\text{TOC flux}}$,in the cell located in the "Plume balance" data block on the "EB Output" worksheet. It should be noted that the equivalent TOC flux estimated by the model is calculated with the distance from the monitoring well used to represent the plume source term composition. If this monitoring well is located in the plume downgradient of the true source area, as would be the case when the *alternative* monitoring scenario is used for the monitoring well locations, then the equivalent TOC flux will be estimated from the location of this monitoring well, rather than the true source area at the site.

5.2.3 Predicted plume length

The overall plume electron balance is used to estimate the plume length. In most cases, the plume will consist of several electron donors and so this plume length represents that of the "mixed" plume of all electron donors. By definition, the plume has reached a steady-state condition with respect to the electron donor and electron acceptor inputs when these are balanced. By clicking the button marked "Calculate plume length(s)" the model calculates the plume length necessary to achieve this electron balance ("steady-state") condition, based on the user-specified input parameters previously described. At this plume length, the net TOC flux should be zero. The plume length given in the "Results" section is the true plume length from the site source area, taking into account the downgradient distance from the site of the monitoring well used to provide the plume source term composition for the different monitoring scenarios (see section 3.6 and 3.7).

5.2.4 Degradation rate constant

The model estimates a *plume-scale* degradation rate for the total electron donor input, assuming contaminant degradation follows first-order degradation kinetics. This is achieved by determining the net electron donor / electron acceptor balance for different time steps in the model. For this calculation, the "predicted plume length" defined by the overall electron balance (section 5.2.3) is divided into an equal number of "length steps", ΔL (m). A default number of 10 length steps is included in the model, which provides satisfactory detail in most applications. Each time step, ΔT (days), is then defined by the following expression:

$$\Delta T = \frac{\Delta L}{v} \qquad (26)$$

where v is the groundwater velocity (m/day). The electron donor flux from the plume source area is considered to be constant for each time step. The model then calculates the electron acceptor input and net electron balance for each time step up to the plume length. A first-order degradation rate constant (day^{-1}) for the plume is calculated from the slope of a regression of the electron balance at each time step against time (days).

5.3 Time to reach steady-state condition

A mixed plume of contaminants is composed from the sum of each contaminant plume in the mixture. Different plumes in the mixture will reach their steady-state length at different times, according to the sorption properties of the contaminants and aquifer. The model calculates the time for each contaminant to reach steady-state plume length, based on the predicted length of the entire (mixed contaminant) plume (determined by the electron balance) and the velocity of each contaminant, using the following expression:

$$\text{Time to reach steady state} = \frac{L}{v_s} \qquad (27)$$

where L is the predicted length of the mixed plume (m) and v_s is the velocity (m/day) of the contaminant estimated by Eq. 6. The output from this data block is given as the time (days) for each electron donor plume in the mixed plume to reach the steady-state length determined for the mixed plume (see section 5.2.3).

5.4 Carbon mass balance

The carbon mass balance for the plume compares the mass of equivalent TOC degraded, based on the production of inorganic carbon, with the mass of equivalent TOC degraded, based on the total electron acceptor consumption. This analysis provides an independent check on the estimated degradation of electron donors in the plume by the different methods. Ideally there should be good agreement between the estimate obtained by each method and the net TOC mass balance ("Plume TOC balance") should be close to zero. A TOC mass balance which is significantly different from zero may result from the following:

- ☐ Missing data or inaccurate analyses for concentrations of dissolved inorganic carbon (DIC) and methane (CH_4) in groundwater samples used to compute the electron balance for the plume. This will result in the underestimation or overestimation of equivalent TOC degraded (based on the production of biogenic inorganic carbon) depending on the source of error in the data for DIC and CH_4.
- ☐ An additional source of inorganic carbon in the aquifer which contributes DIC to the plume. In calcareous aquifers dissolution of $CaCO_3$ by CO_2 derived from degradation processes will increase the measured DIC concentration in groundwater and overestimate the TOC attributed to production of biogenic DIC.
- ☐ Sampling errors which result in the loss of DIC from groundwater. Below pH 7, a significant quantity of DIC from degradation will be present as dissolved CO_2 in groundwater. Volatilisation and exsolution of dissolved CO_2 from samples may then occur if the groundwater is not sampled using appropriate methods to conserve the CO_2 concentration for DIC analysis. A similar problem can occur for dissolved CH_4. This will underestimate the TOC attributed to production of biogenic DIC.
- ☐ Sampling or monitoring errors which result in the inaccurate determination of electron acceptor concentrations in groundwater. These errors include oxidation of reduced chemical species (e.g. Mn^{2+}, Fe^{2+}) prior to analysis, the inappropriate location of monitoring wells which characterise the background groundwater composition and inadequate delineation of the electron acceptor distribution across the plume fringe. These errors will affect the estimation of many inputs in the electron acceptor budget for the plume.

The carbon mass balance should be used as a guide to the quality of data and assumptions underpinning the analysis of this output from the model. Significant differences in the carbon balance should prompt the user to evaluate possible sources of error in the input data or application of the model, with respect to the scenario and conceptual model for the plume being assessed.

6. References

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