ANALYTICAL MODELLING AS A BASIS FOR MONITORED NATURAL ATTENUATION STUDIES

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Abstract

In this paper, an analytical approach to modelling coupled fringe and core degradation of a contaminant plume is presented. Explicit steady-state solutions are derived in three dimensions using a well-known analytical solution for a continuous planar source problem. These solutions provide rapid methods to evaluate the risk of subsurface pollution by contaminated groundwater plumes at field sites, particulary in terms of maximum potential plume length. The resulting fringe-core degradation model suggests the controlling parameters of natural attenuation are (i) the size of the contaminant source, (ii) electron acceptor to electron donor ratio, (iii) transverse dispersivities and (iv) a term (λ/ν). The latter term provides a simple check on the relative weights of transport to core degradation and can be used to estimate the importance of core degradation in the overall plume attenuation. The developed method is applied to data from a well-known field site to demonstrate its applicability in MNA studies where both fringe and core degradation occur. Results demonstrate that only through the consideration of both of these degradation processes, can the maximum length of the steady-state plume be better approximated.

1. INTRODUCTION

Monitored natural attenuation (MNA) can be an acceptable remediation method for managing subsurface contamination, particularly, for organic pollutants [Suarez and Rifai, 2002]. Increasingly, MNA employs mathematical modelling techniques in the analysis of environmental systems and, in particular, in the quantification of natural attenuation processes [Prommer *et al.*, 2002].

One method of analysis is through the use of analytical models derived from the governing flow and transport equations. By making simplifying assumptions about environmental systems, closed-form expressions can be obtained to quantify the migration of contaminants from a source zone [Hunt, 1978, Domenico and Robbins, 1985]. Since MNA is a 'risk-based' engineering strategy, the question most frequently posed is: *To what extent will a contaminant plume develop before it reaches a steady-state?* Therefore, the preliminary assessment of field-scale MNA scenarios typically focuses on steady-state plume behavior (e.g. in terms of plume lengths, concentration profiles). Indeed, in field cases where subsurface conditions can be considered relatively homogeneous, analytical solutions may even provide sufficient results in order to decide if MNA is a suitable option for aquifer remediation.

In terms of aquifer remediation, the most important process is biodegradation. Degradation processes can be divided into two categories depending on the location at which it occurs within the plume: degradation occurring at the plume fringes, and degradation occurring in the interior (core) of the plume [Lerner *et al.*, 2005]. A number of analytical solutions exist that consider degradation using first-order kinetics, e.g., [Hunt, 1978, Domenico, 1987]. In these models, degradation processes are represented using an uniform first-order decay over the whole plume volume. We refer to this as the core-style degradation model. Other models consider degradation as a process limited by electron acceptor mixing. These include, most recently, [Ham *et al.*, 2004, Chu *et al.*, 2005]. In these models, degradation is assumed to occur as an instantaneous reaction between the electron donor and the electron acceptor. We shall refer to this as the fringe-style degradation model.

Given that existing analytical solutions assume that biodegradation follows either a fringe- or core-style degradation model, in this work an approach is presented which represents a combination of both fringe and core degradation. This approach utilizes the analytical solution from [Domenico and Robbins, 1985]. The resulting model is then applied to a the well-known field-scale problem described by [Essaid *et al.*, 1995].

2. PROBLEM DESCRIPTION

In typical cases of NA, the contaminant (a non-sorbing organic compound) acts as the electron donor (ED). At time $t = 0$, the three-dimensional domain Ω, contains only electron acceptor species (EA), which has a constant concentration ${C_{EA}}^0$ throughout the domain. Species ED with a constant concentration ${C_{ED}}^0$, is continuously injected into the flow domain. The flow field in Ω is considered steady and uniform. As the plume develops, aerobic degradation can occur at the fringes as a result of mixing with pristine groundwater containing the dissolved EA species [Borden and Bedient, 1986]. Experimental evidence suggests that degradation at the plume edges progresses rapidly and as a mixing-limited process [Huang *et al.*, 2003]. Therefore, in this paper an instantaneous reaction between ED and EA is considered to occur at the plume fringe. In contrast, inside the plume, where dissolved species, e.g. oxygen and nitrate are usually absent, anaerobic degradation can occur as a result of interactions with metal oxides (e.g. manganese and iron), or as a result of methane fermentation [Christensen *et al.*, 2000a]. A common approach to represent anaerobic core degradation is to simplify these biotransformations to first-order reactions [Essaid *et al.*, 1995]. The same approach is followed here. Figure 1 is a schematic representation of the problem description.

3. ANALYTICAL APPROACH

3.1. **Non-reactive transport.** The three-dimensional transport equation of a non-sorbing, conservative species, under the assumption that molecular diffusion is negligible compared to mechanical dispersion, is given by

$$\frac{\partial C(k)}{\partial t} = \alpha_x \nu \frac{\partial^2 C(k)}{\partial x^2} + \alpha_y \nu \frac{\partial^2 C(k)}{\partial y^2} + \alpha_z \nu \frac{\partial^2 C(k)}{\partial z^2} - \nu \frac{\partial C(k)}{\partial x}, \tag{1}$$

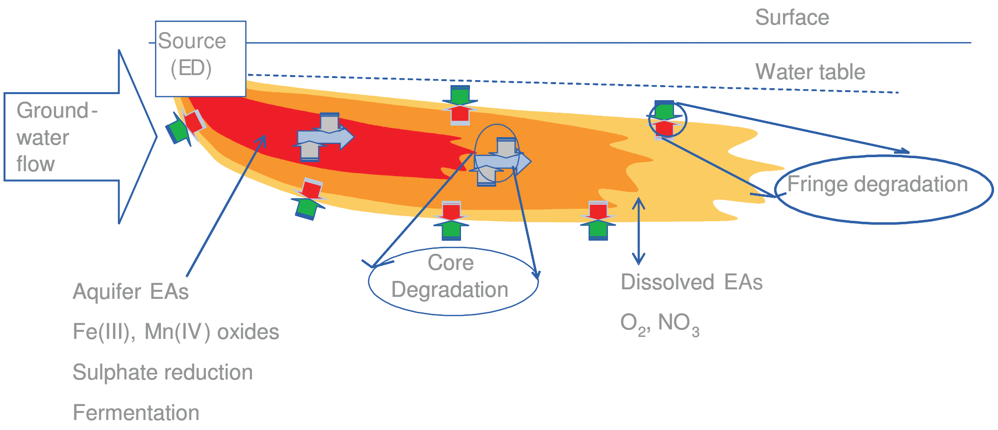

FIGURE 1. Schematic representation of fringe and core processes occurring in a contaminant plume emitted from a continuous source, adapted from [Lerner *et al.*, 2005]

where C denotes the concentration of species k, t is the time, ν is the effective velocity, α_x, α_y and α_z are the longitudinal, transversal horizontal and transversal vertical dispersivities respectively. Closed-form solutions techniques have been employed to solve equation (1). In some cases these solutions can be written as the product of three one-dimensional solutions [Hunt, 1978, Domenico and Robbins, 1985]

$$C_{ED}{}^{T}(x,y,z,t) = S \ \cdot F_1(x,\alpha_x,t) \ \cdot F_2(\alpha_y,y) \ \cdot F_3(\alpha_z,z), \tag{2}$$

where $C_{ED}{}^{T}$ denotes the total aqueous concentration of species ED in domain Ω, i.e. a conservative species [Ham *et al.*, 2004]. S denotes the source term, F_1 is the function in the x-direction that accounts for advection and longitudinal dispersion, F_2 and F_3 are the solution functions in y- and z-directions that account for the transverse dispersion effects. Then, using the analytical solution by [Domenico and Robbins, 1985] for steady-state 3D conservative transport, equation (2) takes the form

$$\begin{aligned} S &= \frac{C_0}{4}, \\ F_2 &= \left[\operatorname{erf}\left(\frac{y+Y/2}{2\sqrt{\alpha_y x}}\right) - \operatorname{erf}\left(\frac{y-Y/2}{2\sqrt{\alpha_y x}}\right)\right], \\ F_3 &= \left[\operatorname{erf}\left(\frac{z+Z/2}{2\sqrt{\alpha_z x}}\right) - \operatorname{erf}\left(\frac{z-Z/2}{2\sqrt{\alpha_z x}}\right)\right], \end{aligned} \tag{3}$$

where C_0 is the initial concentration, Y is the source width and Z is the source height.

3.2. **Reactive transport.** In the case of simultaneous transport and biodegradation of a species, the addition of a reaction term to the governing equation (1) yields

$$\frac{\partial C(k)}{\partial t} = \alpha_x \nu \frac{\partial^2 C(k)}{\partial x^2} + \alpha_y \nu \frac{\partial^2 C(k)}{\partial y^2} + \alpha_z \nu \frac{\partial^2 C(k)}{\partial z^2} - \nu \frac{\partial C(k)}{\partial x} - r^{C(k)}, \tag{4}$$

where r is the reaction rate.

3.3. **Core Degradation Model.** If biodegradation is assumed to follow a first-order kinetic law (i.e. decay), r is defined by

$$r = \lambda\, C(k), \tag{5}$$

where the decay constant λ is defined as

$$\lambda = \frac{\ln(2)}{t^{1/2}}, \tag{6}$$

and ($t^{1/2}$) is the half-life of the biodegradable species. Analytical solutions to the advection-dispersion equation, including species decay, may be generalized in the form

$$C_{ED} = {C_{ED}}^{T} \cdot K(\lambda), \tag{7}$$

where C_{ED} denotes the concentration of the ED species, K is a function that accounts for first-order decay. The analytical solution provided by [Domenico, 1987] defines K as

$$K(\lambda) \;=\; \exp\left[\left(\frac{x}{2\alpha_x}\right)\left(1 - \sqrt{1 + \frac{4\lambda\alpha_x}{\nu}}\right)\right]. \tag{8}$$

Other analytical solutions to transport and decay include work by [Hunt, 1978]. We refer to equation (7) as the core degradation model.

3.4. **Fringe Degradation Model.** It follows from [Ham *et al.*, 2004] that the general solution for the transport of species undergoing an instantaneous bimolecular reaction of the form $EA + ED = P$ is given by

$$C_{ED} \;=\; {C_{ED}}^{T} - {C_{EA}}^{0}. \tag{9}$$

We refer to equation (9) as the fringe degradation model.

3.5. **Combined Degradation Model.** Here, a solution to equation (4), where the reaction term accounts for both first-order kinetics and the instantaneous reaction, is obtained through the combination of the two independent solutions for core degradation and fringe degradation. The combined degradation model can be mathematically represented as

$$C_{ED} = {C_{ED}}^{T} \cdot \;\; K(\lambda) - {C_{EA}}^{0}. \tag{10}$$

The procedure proposed in equation (10) implies that the degradation of the electron donor is two-fold, first occurring throughout the entire plume following a first-order decay law, and subsequently as a instantaneous reaction with species EA in the resident groundwater on the plume fringe.

It follows from equation (10) that if $\lambda = 0$, equation (10) reduces to solutions for fringe degradation, i.e., equation (9). If ${C_{EA}}^{0}$ is small, solutions are reduced to core degradation, i.e., equation (7). In addition, if $\lambda = 0$ and ${C_{EA}}^{0}$ is small, solutions reduce to equation 2 for non-reactive transport, e.g., as given by equation (3).

Implementing the combined degradation model in equation (3), the analytical solution takes the form

$$C_{ED}(x, y, z) \;=\; S \;\cdot F_2(\alpha_y, y) \;\cdot F_3(\alpha_z, z) \;\cdot K(\lambda) - {C_{EA}}^{0}, \tag{11}$$

with the rest of the terms being as previously defined.

3.6. **Plume Length.** Plume length is defined as the distance measured along the centreline to where all of the electron donor species are completely exhausted, i.e., $C_{ED} = 0$. It follows that the maximum plume length L, in three dimensions, is given by the solution to

$$\frac{{C_{EA}}^0}{{C_{ED}}^0} = \operatorname{erf}\left(\frac{Y}{4\sqrt{\alpha_y L}}\right)\operatorname{erf}\left(\frac{Z}{4\sqrt{\alpha_Z L}}\right)\exp\left[\frac{L}{2\alpha_x}\left(1-\sqrt{1+\frac{4\lambda\alpha_x}{\nu}}\right)\right]. \tag{12}$$

An iterative numerical method has to be used to solve for the exact value of L. Equation (12) implicitly suggests that controlling parameters on plume length are (i) size of contaminant source, (ii) ratio of EA to ED, (iii) longitudinal and transversal dispersivities, and (iv) the dimensionless group $(\alpha_x\lambda/\nu)$ contained within the exponential term.

The latter term is a form of Damkohler number and is defined as the (bio)degradation rate relative to the advective transport

$$Da = \frac{\lambda\alpha_x}{\nu}, \tag{13}$$

with the longitudinal dispersion length, α_x, as the characteristic length.

The exponential term can be recast as

$$\exp\left[\frac{L}{2\alpha_x}\left(1-\sqrt{1+4Da}\right)\right]. \tag{14}$$

Figure 2 is a plot of plume length L obtained from the exact solution, equation (12) for different values of Da. It can be seen that for values of $Da >> 0.1$, the length of the steady state plume is independent of Da.

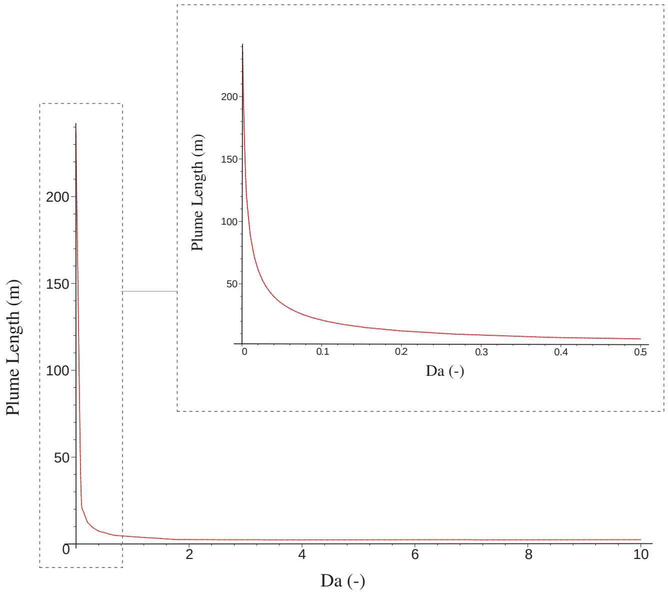

FIGURE 2. Variation of plume length with value of Da. Parameter values used: Y= 5 m, Z= 2 m, $\alpha_x = 1\ m$, $\alpha_y = 0.1\ m$, $\alpha_z = 0.01\ m$, ${C_{ED}}^0 = 10\ meq/L$, ${C_{EA}}^0 = 1\ meq/L$.

Parameter	**Measurement**
Y	2.5m
ν	0.06 m day^{-1}
α_x	1 m
α_z	0.036 m
λ	0.00065 day^{-1}
α_z	0.036 m
${C_{ED}}^0$	10 meq/L
${C_{EA}}^0$	0.5meq/L

Table 1. Predicted Parameter values and plume characteristics, obtained from [Essaid *et al.*, 1995, Essaid *et al.*, 2003]

Therefore, if $Da \ll 1$, the exponential term then yields

$$\exp\left(\frac{-L\,\lambda}{\nu}\right), \tag{15}$$

thus equation (12) reduces to

$$\frac{{C_{EA}}^0}{{C_{ED}}^0} = \operatorname{erf}\left(\frac{Y}{4\sqrt{\alpha_y L}}\right)\operatorname{erf}\left(\frac{Z}{4\sqrt{\alpha_Z L}}\right)\exp\left(\frac{-L\,\lambda}{\nu}\right). \tag{16}$$

Note that this approximation implies that plume length L is a function only of the transversal dispersivities α_y and α_z, i.e., independent of longitudinal dispersivity α_x. This condition has also been previously demonstrated mathematically in a study by [Ham *et al.*, 2004].

An explicit expression for the plume length L can be obtained if only the first term of the right-hand side of the series expansion is considered (see [Beyer, 1987]) . A first approximation for the plume length L yields

$$L \approx \frac{Y\;Z}{4\pi\sqrt{\alpha_y\;\alpha_z}\,\frac{{C_A}^0}{{C_B}^0}\;+\;Y\;Z\;\frac{\lambda}{\nu}}. \tag{17}$$

From equation (17) it can be seen that the main controlling variables for the steady state plume length are (i) size of contaminant source, (ii) ratio of EA to ED, (iii) transversal dispersivities, and (iv) the term λ/ν.

4. APPLICATION TO FIELD-SCALE NATURAL ATTENUATION STUDY

In this section the combined fringe-core model is applied to a suitable field-case. Moreover, the combined model is compared to the fringe and core models to demonstrate the difference between the values predicted. The field-case, discussed in detail in [Essaid *et al.*, 1995, Essaid *et al.*, 2003], relates to the attenuation of a plume of petroleum hydrocarbons. This BTEX plume has been investigated significantly, and two-dimensional contour plots constructed from data analysis are available. [Essaid *et al.*, 1995] indicates that it is necessary to consider both fringe and core processes in order to accurately quantify the fate of the hydrocarbon plume. The parameters values used are listed in Table 1.

4.1. **Analysis.** In order to be able to compare with available data, the modelling exercise considers the combined, core, and fringe models in their two-dimensional form. In Figure 3, centerline profiles are shown for the three models which allows the determination of the plume length, i.e. at ED concentration = 0. Previous field estimates and numerical modelling efforts indicate the length of the plume to be approximately 180m. [Essaid *et al.*, 1995, Essaid *et al.*, 2003].

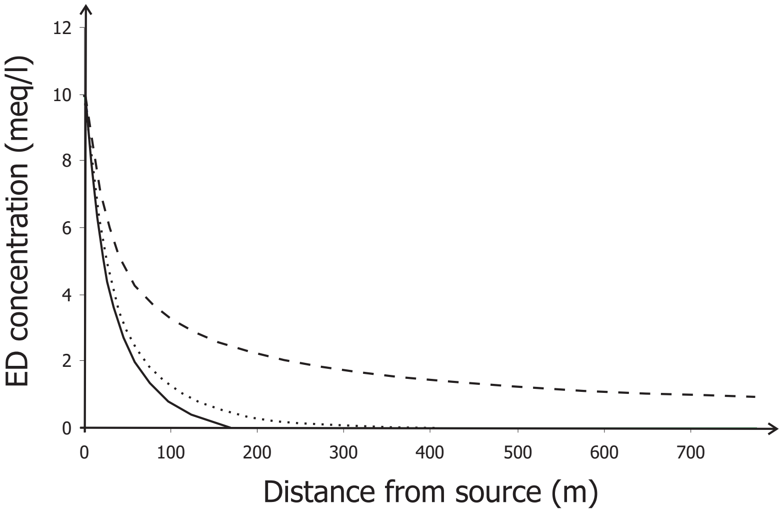

FIGURE 3. BTEX plume centreline concentration as predicted by the three models. The long-dash line denotes the fringe degradation model, the doted line denotes the core degradation model, the solid line denotes the combined model.

It should be noted that for this case, the maximum plume length is given by benzene, which in this particular case was the less attenuated compound. As illustrated in Figure 3, in order to better match the reported plume length, consideration of both fringe and core processes is indeed necessary. If only fringe degradation, i.e., aerobic degradation, is considered, the plume length is estimated to be approx 4km (not shown in plot). Furthermore, consideration of core degradation alone is not enough to account for the plume attenuation reported.

5. SUMMARY AND CONCLUSION

An analytical approach to model coupled fringe and core degradation was proposed using a combination of instantaneous and first-order reactions. A well-known analytical solution was used to provide a closed-form expression to evaluate plume behaviour, in particular steady-state length of a hydrocarbon plume emitted from a continuous source. This steady-state solution provides a rapid method to evaluate risk at a particular site, in terms of the potential maximum plume length, in cases where both fringe and core degradation processes are important. This was demonstrated through a comparison of the analytical model to field data obtained from a field-scale natural attenuation study. In that case, excellent agreement between modelled and predicted (from data) plume lengths was found. In contrast, both the fringe model and the core model failed to accurately predict the plume length.

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