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Comments on “Analytical modelling of fringe and core biodegradation in groundwater plumes.” by Gutierrez-Neri et al. in J. Contam. Hydrol. 107: 1–9

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A B S T R A C T

In this comment, we revisit equations concerning the analytical solutions presented by Gutierrez-Neri and co-workers for reactive transport for a pollutant undergoing core and fringe degradations. We state that a correction needs to be made in Eq. (9) of the work of Gutierrez-Neri et al. in order that the equation follows closely previous work published by J. Bear (in 1-D) and P.A. Domenico (in 3-D). Furthermore we derive alternative solutions for Eqs. (13)–(16) which separate more clearly the first-order reaction and the instantaneous reaction. It is shown that the corrected solution agrees better with the results from the numerical model than the previous solution. An improvement is also made by giving a solution which avoids negative concentrations. Furthermore, the corresponding solution for the electron acceptor reacting with the pollutant is given.

1. Introduction

Recently, Gutierrez-Neri et al. (2009) presented an analytical approach to modelling groundwater plumes of organic pollutants with biological degradation in the core and the fringe of the plume. Both, core degradation and fringe degradation, are well known concepts in contaminant hydrology (Wiedemeier et al., 1999). The manuscript in question states that the solution developed in this work is the first for combining core and fringe degradations. Using a well known solution for three-dimensional solute transport from a planar source, approximate solutions for non-reactive transport and reactive transport were derived (Gutierrez-Neri et al., 2009). We re-examine here only the part concerning reactive contaminant transport (Section 3.2).

2. Examination

In Gutierrez-Neri et al. (2009), the analytical solution derived for reactive transport is discussed in two extreme cases: Section 3.2.1 — core degradation model, and Section 3.2.2 — fringe degradation model.

The core degradation model (Eq. (G-N 9) from Gutierrez-Neri et al. (2009), restricted to the x–y space), reads:

$$C_{ED}^{C}(x,y,t) = C_{ED}^{T}\cdot K(x,\lambda) = \frac{C_{ED}^{0}}{4}\cdot F_1(x,t)\cdot F_2(x,y)\cdot K(x,\lambda) \quad (1)$$

where $C_{ED}^{C}(x,y,t)$ is the spatio-temporal distribution of the electron donor, C_{ED}^{T} is the total concentration of electron donor invariant to degradation (taken from Eq. (G-N 4)), and

$$K(x,\lambda) = exp\left[\left(\frac{x}{2\alpha_x}\right)\left(1-\sqrt{1+\frac{4\lambda\alpha_x}{v}}\right)\right]$$

C_{ED}^{0} is the constant concentration of the electron donor in the source, and F_1 and F_2 are

$$F_1(x,t) = erfc\left(\frac{x-vt}{2\sqrt{\alpha_x vt}}\right)$$

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$$F_2(x,y) = \left[erf\left(\frac{y+\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right) - erf\left(\frac{y-\frac{Y}{2}}{2\sqrt{\alpha_y x}}\right)\right]$$

Furthermore, λ is the first-order degradation rate constant, Y is the width of the source, v is the groundwater flow velocity, α_x and α_y are the dispersivities in the x and y direction, and t is time.

Gutierrez-Neri and co-workers use the $F_1(x, t)$ published by Domenico and Robbins (1985) for non-reactive contaminant transport. For reactive transport, Domenico (1987) published later an extended version of F_1 which depends also on the degradation rate λ and reads:

$$F_1(x,\lambda,t) = erfc\left(\frac{x - vt\sqrt{1+4\lambda\alpha_x/v}}{2\sqrt{\alpha_x vt}}\right)$$

This function was first published by Bear (1979) in the 1-D space. We argue that the correct version of Eq. (G-N 9) of Gutierrez-Neri et al. (2009) should include $F_1(x, \lambda, t)$ instead of $F_1(x, t)$. The correct version of Eq. (G-N 9) should thus read (in x–y space, Eq. (2)):

$$C_{ED}^{C}(x,y,t) = C_{ED}^{T}\cdot K(x,\lambda)\frac{F_1(x,\lambda,t)}{F_1(x,t)} \quad (2a)$$

with

$$C_{ED}^{T} = \frac{C_{ED}^{0}}{4}\cdot F_1(x,t)\cdot F_2(x,y) \quad (2b)$$

The model for fringe degradation is obtained by superposition (Fig. 1) i.e. by subtracting the concentration distribution of the electron acceptor from the concentration distribution of the electron donor taking into account the stoichiometric factors. The concentration distribution of the electron donor is given by Eq. (2b), while the concentration of the electron acceptor can be expressed as:

$$C_{EA} = \frac{C_{EA}^{0}}{4}\cdot(4 - F_1(x,t)\cdot F_2(x,y)) \quad (3)$$

As can be seen in Fig. 1a, the electron acceptor distribution corresponds to the complementary of the concentration distribution of the non-degrading electron donor (assuming stoichiometric factors of 1).

Hence the fringe degradation model is given by:

$$\begin{aligned} C_{ED}^{F}(x,y,t) &= C_{ED}^{T} - C_{EA} \\ &= \frac{C_{ED}^{0}}{4}\cdot F_1(x,t)\cdot F_2(x,y) - \frac{C_{EA}^{0}}{4}\cdot(4 - F_1(x,t)\cdot F_2(x,y)) \\ &= C_{ED}^{T}\cdot\left(1+\frac{C_{EA}^{0}}{C_{ED}^{0}}\right) - C_{EA}^{0} \end{aligned} \quad (4)$$

which corresponds to Eq. (G-N 12). Note that here it is correct that the F_1-term inherent in C_{ED}^{T} does not depend on λ. As discussed by Cirpka and Valocchi (2007), C_{ED}^{T} can be viewed as the mixing ratio, i.e. the concentration which a conservative tracer would have in the x–y space.

Gutierrez-Neri et al. presented thereafter in Section 3.2.3 a combined core and fringe degradation model (Eq. (G-N 13)) by inserting Eq. (2b) into Eq. (3) without any justification.

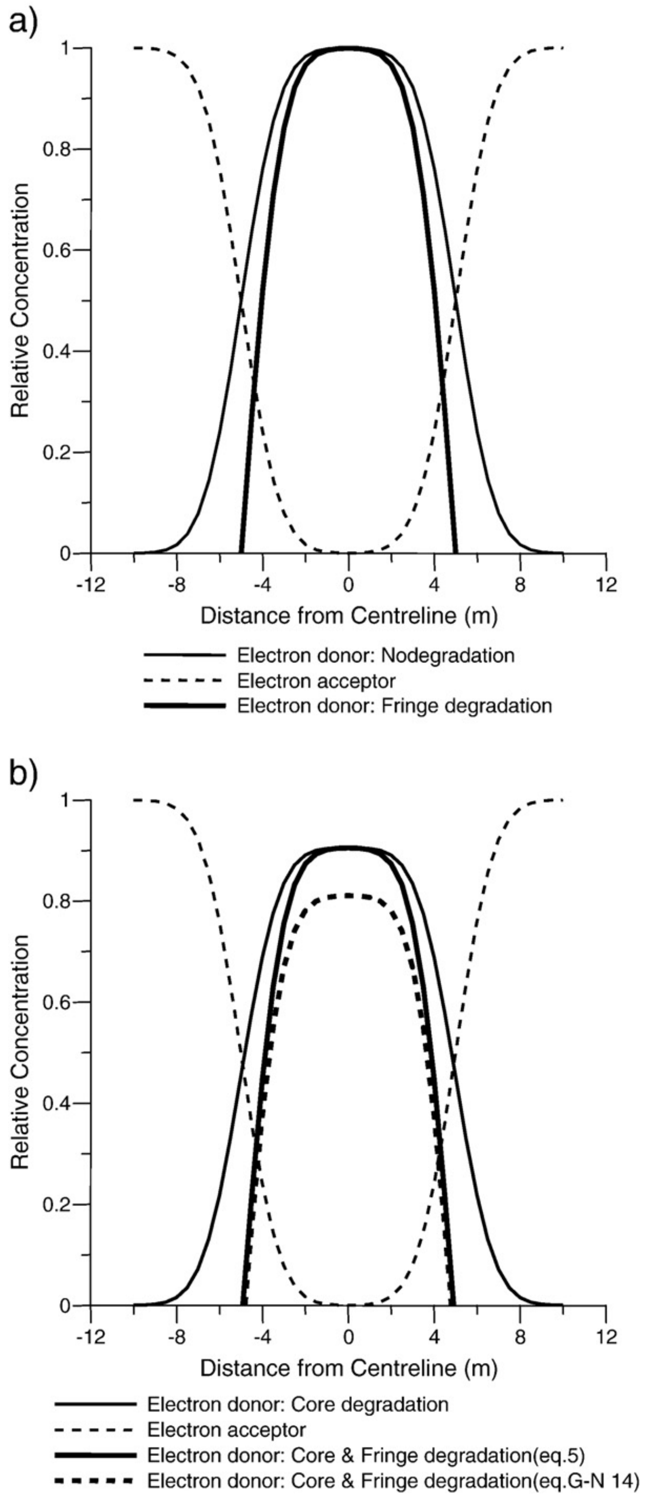

Fig. 1. Superposition model for fringe degradation (a), and comparison of superposition model and Gutierrez-Neri equation for combined core and fringe degradations (b). The calculations were carried out for groundwater flow velocity of 1 m/d, $\alpha_x = 1$ m, $\alpha_y = 0.1$ m, width of the source $Y = 10$ m, distance from the source $x = 10$ m, time = 10 years corresponding to a steady state plume, degradation rate constant 0.01 d^{-1}. All stoichiometric factors are set to 1.

Furthermore, in their equation F_1 does not depend on λ although for the core model, this should be the case. We propose to derive a combined degradation model by using again the superposition principle analogous as for fringe degradation only. The combined model is obtained by subtracting the electron acceptor distribution (Eq. (3)) from the distribution of the electron donor subject to core degradation (Eq. (2a)) as illustrated in Fig. 1b:

$$\begin{aligned} C_{ED}^{C\&F}(x,y,t) &= C_{ED}^{C} - C_{EA} = C_{ED}^{T}\cdot K(x,\lambda)\frac{F_1(x,\lambda,t)}{F_1(x,t)} \\ &\quad - \frac{C_{EA}^{0}}{4}\cdot\left(4 - F_1(x,t)\cdot F_2(x,y)\right) \\ &= C_{ED}^{T}\cdot\left(K(x,\lambda)\cdot\frac{F_1(x,\lambda,t)}{F_1(x,t)} + \frac{C_{EA}^{0}}{C_{ED}^{0}}\right) - C_{EA}^{0} \end{aligned} \tag{5}$$

The analytical solution presented by Gutierrez-Neri et al. (2009) for the *x*–*y* space reads:

$$C_{ED}^{C\&F}(x,y,t) = C_{ED}^{T}\cdot K(x,\lambda)\cdot\left(1 + \frac{C_{EA}^{0}}{C_{ED}^{0}}\right) - C_{EA}^{0} \tag{G – N14}$$

When comparing the two solutions, one finds that there are two major differences between the equations. The first concerns the F_1-terms. Eq. (5) converges to Eq. (2a) and (2b) in the absence of electron acceptor (when $C_{EA}^0 = 0$), and to Eq. (3) in the absence of core degradation (when $\lambda = 0$). Eq. (G-N 14) fails to converge to Eq. (2a) and (2b) in the absence of electron acceptor. Furthermore, in Eq. (5), the concentration of the electron acceptor is not multiplied with a term containing the first-order degradation rate λ. In other words, the core degradation does not affect the electron acceptor. In the solution of Gutierrez-Neri et al. (2009), the concentration of the electron acceptor is multiplied by the degradation term *K*. Differences between the two equations mainly occur in the centre of the plume as illustrated in Fig. 1b. In the illustrated profile, it is expected that in the plume centre only core degradation occurs since electron acceptors are absent (Fig. 1b). This expected degradation pattern is indeed well reproduced by our equation: In the centre of the plume, the electron donor concentration corresponds to the concentration pattern for the case with core degradation only. In contrast, Eq. (G-N 13) provides lower electron donor concentrations than core degradation only in the plume centre, which is not plausible given the absence of electron acceptors. Hence, Eq. (G-N 13) introduces fringe degradation even in zones where no electron acceptor is present. At the plume fringes, the two models agree better.

The two models provide also very notable differences for concentration profiles in groundwater flow direction (Fig. 2). The Gutierrez-Neri equation leads to substantially shorter plumes than Eq. (5) because it artificially creates fringe degradation in the core of the plume.

Gutierrez-Neri et al. applied their solution (Eq. (G-N 14)) and compared the results to those obtained from a numerical model. The comparison (Fig. 2 in Gutierrez-Neri et al.) revealed that the analytical solution yielded somewhat lower concentrations along a plume centreline than the numerical model, especially from 10 to 30 m distance from the source. We evaluated both, Eqs. (5) and (G-N 14), using the parameters given in the text and in Table 2 in the manuscript (Gutierrez-Neri et al., 2009). We used a concentration of 4 mmol L^{-1} for the electron donor, as stated in the text. The results of our comparison are shown in Fig. 3.

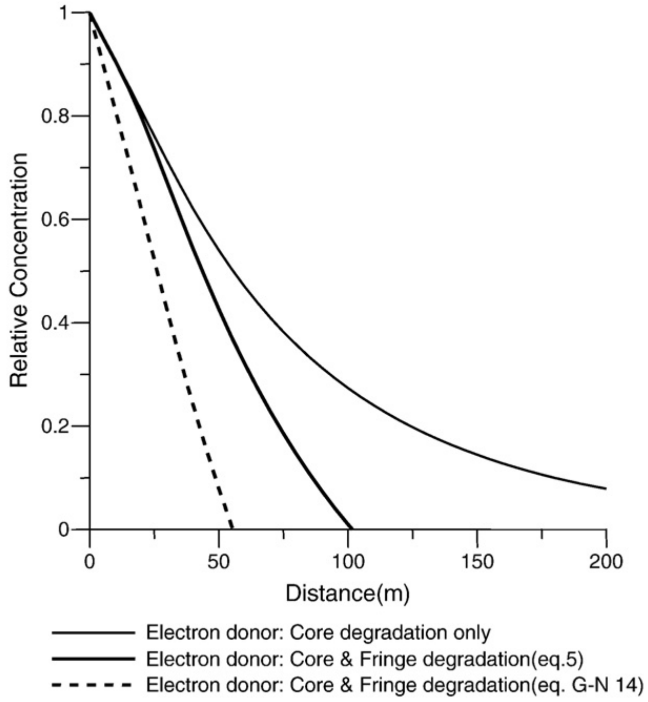

Fig. 2. Electron donor concentration along plume centre for different models using the same parameters as in Fig. 1.

Interestingly, our solution (Eq. (5)) suggests somewhat higher concentrations along the plume centreline than Eq. (G-N 14), especially after 10 m from the source, and would thus match better the results from the numerical model reported in Gutierrez-Neri et al. (2009). Both curves start with 4 mmol L^{-1} of electron donor at the source, unlike the data presented in Fig. 2 of Gutierrez-Neri et al. (2009) which start at 3 mmol L^{-1}. It might be that the curves were calculated actually with $C_{ED}^0 = 3$ mmol L^{-1} in the source, although the text states 4 mmol L^{-1}. A similar inconsistency is furthermore observed in Fig. 7 of Gutierrez-Neri et al. (2009) where the curves start at

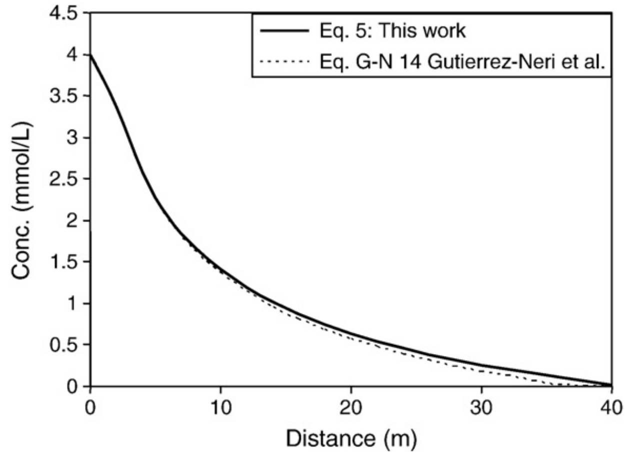

Fig. 3. Comparison of the two analytical equations under discussion when evaluated for the 2-dimensional test case given in Gutierrez-Neri et al. (2009) for $t = 80$ days.

concentrations of 10.5 mmol L^{-1} of the electron donor, whereas the table 3 states 10 mmol L^{-1}.

There is still a problem with Eq. (5). In the mathematical language in which it is formulated, negative concentrations are possible. For example, along a plume centreline, the concentrations $C(x,y,t)$ will go from positive to negative values when the borderline is crossed where more equivalents of the electron acceptor are available than equivalents of the electron donor having undergone first-order degradation. Gutierrez-Neri and co-workers do not really discuss this issue. However, a strict solution which avoids negative concentrations is available. We follow here the way how Cirpka and Valocchi (2007) treated this issue.

The domain in which positive concentrations are possible can be defined in space. The borderline around this space is given by all points where the concentrations $C(x,y,t)$ of the electron donor fall to zero. Thus the borderline of the space in which positive concentrations are found is defined by setting the left hand side of Eq. (5) to zero and transforming (Eq. (6)):

$$C_{ED}^{T}\cdot\ \ K(x,\lambda)\cdot\frac{F_1(x,\lambda,t)}{F_1(x,t)}+\frac{C_{EA}^{0}}{C_{ED}^{0}}\Bigg)=C_{EA}^{0} \tag{6}$$

This leads to a better formulation of Eq. (5):

$$C_{ED(x,y,t)}=\begin{Bmatrix} 0\ \text{for\_}C_{ED}^{T}\cdot\ \ K(x,\lambda)\cdot\frac{F_1(x,\lambda,t)}{F_1(x,t)}+\frac{C_{EA}^{0}}{C_{ED}^{0}}\Bigg)\leq C_{EA}^{0} \\ C_{ED}^{T}\cdot\ \ K(x,\lambda)\cdot\frac{F_1(x,\lambda,t)}{F_1(x,t)}+\frac{C_{EA}^{0}}{C_{ED}^{0}}\Bigg)-C_{EA}^{0}\text{\_elsewhere} \end{Bmatrix} \tag{7}$$

A comparison of Eqs. 7 to (G-N 14) is shown in Fig. 4 for a trans-section across the plume 10 m from the source. The plume is modelled with the same parameters as used already for Fig. 3. The transversal distributions of concentrations are given for two times, 15 and 80 days after the start of migration.

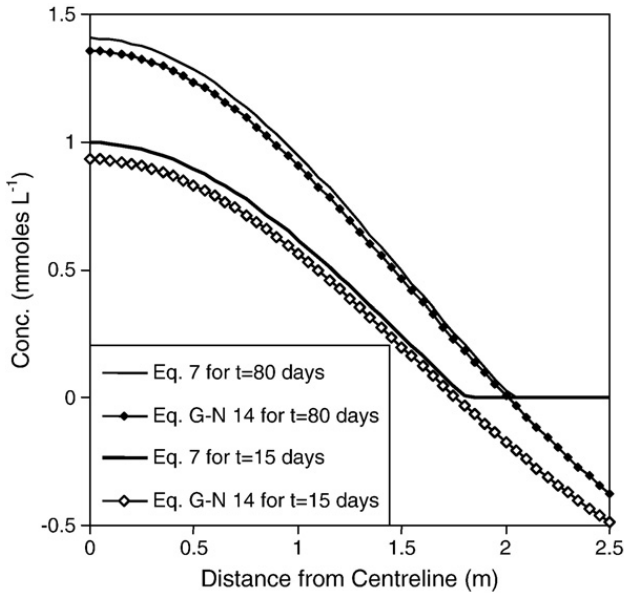

Fig. 4. Comparison of concentrations modelled on a trans-section at $x=10$ m for two times, 15 and 80 days.

The differences between the original solution (Eq. (G-N 14)) and our modified solution (Eq. (7)) are largest on the plume centreline and become smaller towards the lateral fringes of the plume. The relative differences in concentrations are larger after 15 days than after 80 days. The profiles do not change substantially after 80 days.

One can furthermore develop the equation of the spatio-temporal distribution of the electron acceptor, $C_{EA}(x,y,t)$, which is (Eq. (8)):

$$C_{EA(x,y,t)}=\begin{Bmatrix} 0\ \text{for\_}C_{ED}^{T}\cdot\ \ K(x,\lambda)\cdot\frac{F_1(x,\lambda,t)}{F_1(x,t)}+\frac{C_{EA}^{0}}{C_{ED}^{0}}\Bigg)\geq C_{EA}^{0} \\ C_{EA}^{0}+C_{ED}^{K}\cdot(1-F_1(x,t)F_2(x,y)/4)-C_{ED}^{K}\text{\_elsewhere} \end{Bmatrix} \tag{8}$$

$$\text{where\_}C_{ED}^{K}=C_{ED}^{0}\cdot(K(x,\lambda)\cdot\frac{F_1(x,\lambda,t)}{F_1(x,t)}$$

Fig. 5 illustrates Eq. (7) for the electron donor (left) and Eq. (8) for the electron acceptor (right) for the test case described in Gutierrez-Neri et al. (2009) and modelled in Fig. 3.

Eqs. (7) and (8) can be extended to the three-dimensional space as outlined in Gutierrez-Neri et al. by introducing the vertical term $F_3(\alpha_z, z)$

$$F_3(x,z)=\left[erf\ \ \frac{z+\frac{Z}{2}}{2\sqrt{\alpha_z x}}\Bigg)-erf\ \ \frac{z-\frac{Z}{2}}{2\sqrt{\alpha_z x}}\Bigg)\right]$$

and by changing the denominator in C_{ED}^{T} from 1/4 to 1/8. The extension to alternative source regimes is also possible. However, the additional term given in Gutierrez-Neri et al. (2009) for a decaying term in their Eq. (G-N 15) reading $S^{decay}=S*\exp^{(-\varepsilon t)}$ is wrong. The correct term is given in Newell et al. (1997) on P. 9 of the revisions of version 1.4 of the model BIOSCREEN and reads:

$$S^{decay}=S\,exp^{\left(-\varepsilon\left(t-\frac{x}{v}\right)\right)} \tag{9}$$

where ε is the first-order source decay constant, and v the unretarded flow velocity of the groundwater in x direction. Eq. (G-N 16) in Gutierrez-Neri et al. (2009) should consequently be corrected into (Eq. (10)):

$$C_{ED}^{T}(x,y,z,t)=\left(S\,exp^{\left(-\varepsilon\left(t-\frac{x}{v}\right)\right)}\right)\cdot F_1(x,t)\cdot F_2(x,y)\cdot F_3(x,z) \tag{10}$$

A few final remarks should be given in addition. To start with, the solution of Domenico which underlies this work is only an approximate solution, while a rigorous solution exists (Sagar, 1982), which unfortunately needs more CPU time due to a lateral integration of the plume. Further work should investigate whether the rigorous solution instead of the approximate solution of Domenico can be used for further modelling, since the latter shows some deviations at lateral plume extensions and near the source for early times (Guyonnet and Neville, 2004).

It is worth to mention also that Newell and co-workers (1996) published a similar solution like the one by Gutierrez-Neri et al. (2009) in 1996 in the manual version 1.3 of the software BIOSCREEN model (See Appendix A). Furthermore,

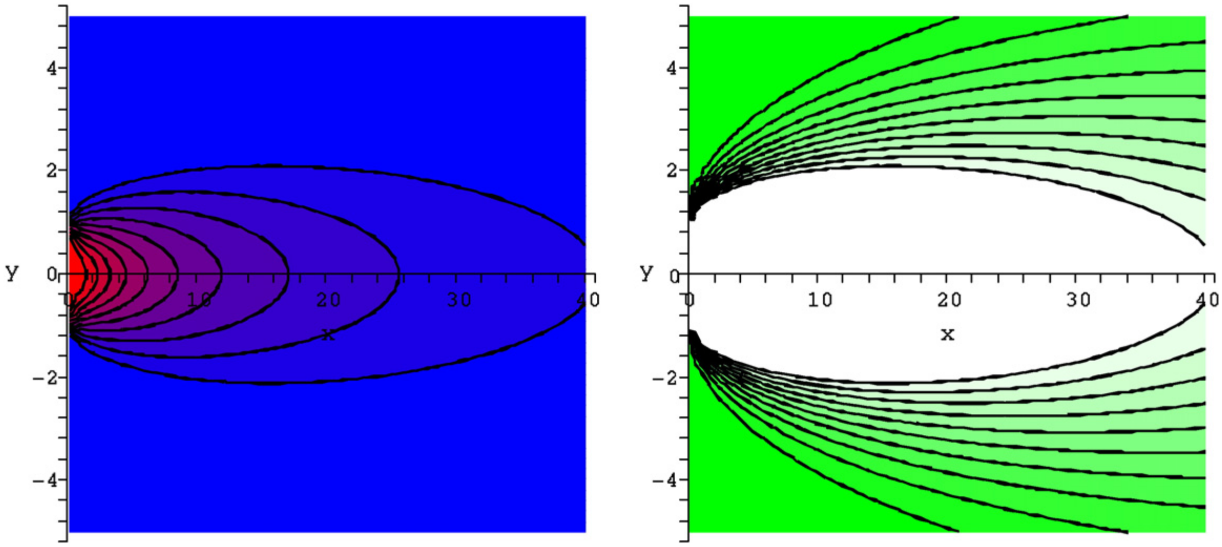

Fig. 5. Illustration of the spatial distribution of the electron donor (left) and the electron acceptor (right) given by Eqs. (7) and (8) for the test case described in Gutierrez-Neri et al. (2009) for $t = 80$ days. The increments between contour lines are 1/10 C_0.

the analysis of the maximum plume length using the analytical equations derived in this work should be compared to the maximum plume length analysis by Atteia and Guillot (2007) which was also derived based on an analytical approach, although it differed from the work by Gutierrez-Neri et al. (2009) in some details.

Finally, the work of Gutierrez-Neri et al. (2009) is still a valuable contribution, since it goes one step further compared to previous works by combining core and fringe degradations. This has not been sufficiently addressed so far in analytical models. Correct analytical solutions are tools to verify numerical models and thus valuable gifts for hydrogeologists and environmental scientists.

Appendix A

1. Basic assumptions

For the equations developed here, the following assumptions are made:

- Biodegradation is occurring by two processes: instantaneous reaction of the pollutant with a strong oxidant (e.g. O_2) at the fringes of the plume, and first-order degradation independent of the oxidant in the core (e.g. by anaerobic degradation).
- All groundwater that has passed through the source zone is devoid of dissolved strong oxidant because it is “instantaneously” consumed when coming in contact with dissolved contaminants. The dissolved oxidant is only present laterally of the plume and in front of the plume in zones that have not been reached yet by groundwater that has crossed the source zone.
- The contaminant concentration at the source is constant (or exponentially decaying) and not affected by the oxidant. The contaminant is subject to first-order plume core degradation throughout the plume. The core degradation does not have any effect on the concentration of dissolved oxidant.
- For simplicity it is assumed that contaminant (electron donor) and oxidant react at a 1:1 stoichiometry.

2. Solution of Newell et al., 1996

In the version 1.3 of the manual of the software BIOSCREEN (Newell et al., 1996), an analytical solution was published that was somewhat alike the solution of Gutierrez-Neri et al. We give here the equation in the notation that was published in the original publication (Eq. (A1)):

$$\frac{C(x,y,z,0,t)}{(C_0+BC)} = \frac{1}{8} exp\left[\frac{x}{\alpha_x 2}\left(1-(1+4\lambda\alpha_x/v)^{1/2}\right)\right] \quad \text{(A1)}$$

$$erfc\left[\frac{\left(x-vt(1+4\lambda\alpha_x/v)^{1/2}\right)}{2(\alpha_x vt)^{1/2}}\right]$$

$$\left\{erf\left[\frac{(y+Y/2)}{2\left(\alpha_y x\right)^{1/2}}\right]-erf\left[\frac{(y+Y/2)}{2\left(\alpha_y x\right)^{1/2}}\right]\right\}$$

$$\left\{erf\left[\frac{(Z)}{2(\alpha_s x)^{1/2}}\right]-erf\left[\frac{(-Z)}{2(\alpha_z x)^{1/2}}\right]\right\}-BC$$

$$\text{where :} \quad v = \frac{K\cdot i}{\theta_\varepsilon R} \quad BC = \Sigma\frac{C(ea)_n}{UF_n}$$

This equation would be similar to Eq. (G-N-9), if not a serious typesetting error had occurred: the bracket (C_0+BC) on the left hand side of the equation should stand above the 8 on the right hand side of the equation and not under $C(x, y,0,t)$, in order to maintain consistent units on both sides of the equations. If we would move (C_0+BC) to the correct place, the equation would almost equal Eq. (G-N 9), except that the term F1 was extended correctly by Newell et al. while it was simplified by Gutierrez-Neri et al. One can conclude thus that ideas for a combined core-and-fringe model were developed as early as in 1996, but not promoted furthermore. In a later version 1.4 of the manual (Newell et al., 1997), the equation was not given anymore and was replaced by other equations, which gave solutions for either core or fringe degradation, but not accounting for simultaneous core-and-fringe degradation. Our work here documents that Eq. (A1), even typesetted correctly, does as Eq. (G-N 9) not correctly represent the core-and-fringe degradation model.

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