

An improved analytical approach to estimate *in situ* biodegradation rates

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Abstract Biodegradation is a major process in reducing most organic contaminants in aquifers. Estimation of *in situ* biodegradation rates is significant for studying the natural attenuation of contaminants in the field. Buscheck & Alcantar (1995) have developed a method based on field data to estimate biodegradation rates for 1-dimensional (1-D) steady-state plumes. However, in simplifying a field plume, which is usually 2- or 3-D, into a 1-D case, a certain degree of error will occur. In this paper, case studies are performed to assess the errors caused by such simplification. Moreover, an improved analytical method is suggested in steps. Application of the newly developed analytical approach to a field site gives quite good agreement.

Key words biodegradation rate; groundwater contaminant

INTRODUCTION

It is well known that a major factor responsible for natural attenuation and mass reduction of fuel hydrocarbons and other common organic contaminants in groundwater plumes is biodegradation by microorganisms in aquifer materials. First-order decay is usually used to describe the biodegradation process with the parameter–biodegradation rate. Moreover, many theoretical solutions have already been discussed in past decades (Bear, 1979; Domenico, 1987), making the estimation of biodegradation rate a key step to assessing the contribution of biodegradation to attenuation in different sites.

The general range of attenuation rates of some familiar organic chemicals were collected and published by Howard *et al.* (1991). However, the attenuation rates are quite different, not only for different chemicals, but also for the specified situations of the aquifers.

Lots of research has been carried out to estimate the biodegradation rate for a specified site over the last few decades, including laboratory approaches (Rubin *et al.*, 1982; Klecka *et al.*, 1990), field tests (MacIntyre *et al.*, 1993), and a combination of laboratory and field approaches (Chapelle *et al.*, 1996). Such methods have their own pros and cons: laboratory approaches could easily be controlled, but have difficulties in reproducing the *in situ* conditions; results of field tests are always unsatisfactory because of the intricate situations of sites, and it is also hard to distinguish the contribution of biodegradation to attenuation of concentrations from that of dispersion, adsorption, and volatilization. A combination of laboratory and field approaches sounds more reasonable at first glance, however, considering the inherent uncertainties of both approaches, such a combination would hardly represent a unique value of biodegradation rate.

Buscheck & Alcantar (1995) introduced a field-data-based method to estimate biodegradation rates for steady-state plumes, via regression techniques and analytical solutions. This technique is routinely used to estimate biodegradation rates of contaminants in groundwater (McNab & Doohar, 1998). Assuming a first-order decay coefficient as an approximation for the *in situ* biodegradation of the contaminant, Buscheck & Alcantar (1995) showed, for a 1-D idealization, that the degradation rate may be given by:

$$\lambda = \left(\frac{v_c}{4\alpha_x} \right) [(1 - 2\alpha_x m)^2 - 1] \quad (1)$$

where m reflects the slope of a regression line fit to the log of contaminant concentration data *versus* the distance along the plume centreline. In fact, $m = k/v_x$, where k is the overall attenuation rate (T^{-1}), v_x is the groundwater linear velocity; v_c is the contaminant velocity along the

longitudinal direction (adjusted for retardation, $v_c = v_x/r_f$, r_f is the retardation coefficient); α_x is the longitudinal dispersivity (L), which represents the contribution of dispersion; λ is the biodegradation rate (T^{-1}), which is the main concern in this paper). When biodegradation only occurs in the aqueous phase, v_c is replaced by v_x in equation (1).

Since the information on v_c and α_x for a special site could be achieved through field or laboratory experiments, and slope of the fit line m could be gained through concentration data fitting, then the biodegradation rate λ can be calculated using equation (1).

Though this technique is routinely used to estimate *in situ* degradation rates, its application to field sites is limited by the assumption of the 1-D condition. Since there are usually two or even three dimensions for a real field plume caused by the fuel hydrocarbons or other organic compounds, there is a potential error in estimating *in situ* biodegradation rate when misusing this technique. The objective of this paper is to assess the degree of the errors caused by using the method of Buscheck & Alcantar (1995) in 2-D cases, and to develop an improved analytical approach to estimate biodegradation rates for 2-D plumes.

ASSESSMENT OF THE ERRORS

Concentration distribution along the centreline in a steady-state 3-D site was given by Domenico (1987) as:

$$C(x,0,0) = C_0 \exp\left\{\frac{x}{2\alpha_x}\left[1 - \sqrt{1 + \frac{4\lambda\alpha_x}{v_c}}\right]\right\} \bullet \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y x}}\right] \bullet \operatorname{erf}\left[\frac{Z}{4\sqrt{\alpha_z x}}\right] \quad (2)$$

where Y , Z represent the source dimensions; and α_y , α_z are the dispersivities in the transverse and the vertical directions, respectively.

Compared to equation (1), the difference between the 3-D and 1-D cases is the factor $\operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y x}}\right] \bullet \operatorname{erf}\left[\frac{Z}{4\sqrt{\alpha_z x}}\right]$ at the right side of equation (2), which indicates that the error from simplification is related to the four parameters – the source width, the source thickness, the transverse dispersivity and the vertical dispersivity.

In order to get some quantitative understanding of the error resulting from misusing Buscheck and Alcantar's analytical solutions to estimate biodegradation rates for 2-D, case studies were performed to study the concentration distribution along the centreline for a 2-D plume. The same value of the related parameters provided in the case of Buscheck & Alcantar's paper (1995) were used: $v_x = 0.06 \text{ m day}^{-1}$, $r_f = 2$, $v_c = 0.03 \text{ m day}^{-1}$, $\alpha_x = 7.5 \text{ m}$, $C_0 = 3660 \text{ } \mu\text{g L}^{-1}$, assuming the actual biodegradation rate to be $\lambda = 0.003 \text{ day}^{-1}$.

For 2-D situations, equation (2) can be simplified as:

$$C(x,0) = C_0 \exp\left\{\frac{x}{2\alpha_x}\left[1 - \sqrt{1 + \frac{4\lambda\alpha_x}{v_c}}\right]\right\} \bullet \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y x}}\right] \quad (3)$$

So the inaccurate estimation of biodegradation rate is related to the two new parameters – the source width Y and transverse dispersivity α_y , in equation (3).

Effect of the source width on the error

To research the effect of the source width on the estimation error, several typical cases were studied.

Although it is practically very difficult to accurately estimate the width of the contaminant source on the field, the width of the contaminant source ranges from several metres to tens of metres in the field in general. For this research, Y is assumed to be 1 m, 5 m and 10 m. Concentration distributions along the centreline of the three cases were calculated separately. In addition, the transverse dispersivity is calculated as a factor of the longitudinal dispersivity, which

is known to be 7.5 m.

$$\alpha_y = 0.1 \bullet \alpha_x \quad (\text{Gelhar } et \text{ al.}, 1992) \tag{4}$$

Then the contaminant concentration distribution along the centreline in a 2-D plume can be calculated via equation (3), whose results are shown in Fig. 1. It is obvious that for a 2-D plume, the relationship between the centreline concentration and distance from the source is nonlinear in the semi-logarithmic coordinate. However, it is interesting to notice that when the distance from the source is far enough, the curve becomes similar to a linear line, and visually it is almost parallel to the line of the 1-D situation. This phenomenon suggests that using the monitoring data, which are relatively far from the source, to estimate the slope m may give a result close to the 1-D case. Regression techniques were applied to estimate the slope m of the almost linear part in Fig. 1, and equation (1) was used to calculate the biodegradation rate, which includes a certain degree of error. The errors for different values of Y are given in Table 1.

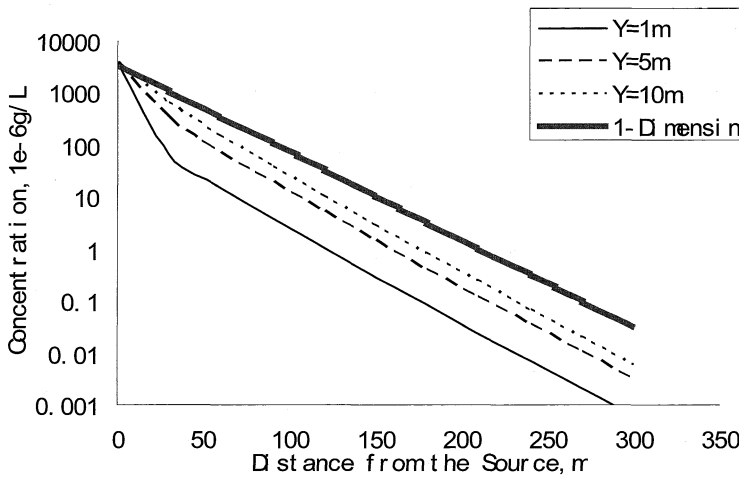


Fig.1 Effect of source width on concentration distribution along centreline.

Table 1 Assessment on the errors for different source widths.

Y (m)	m (m^{-1})	Calculated λ ($year^{-1}$)	Actual λ ($year^{-1}$)	Error (%)
1	-0.04104	1.17527	1.095	7.3%
5	-0.04102	1.17476	1.095	7.3%
10	-0.04098	1.17318	1.095	7.1%

Y : Source width; m : the slope of regression line; λ : biodegradation rate.

The results show that estimating the slope m using the almost linear part of the curves gives a very similar estimation of the biodegradation rates for three different source widths. In other words, estimation of m is not sensitive to the source width, and neither is the further estimation of the biodegradation rate for a 2-D case. However, for a 2-D problem, the biodegradation rate estimated using the method of Buscheck & Alcantar includes an error of about 7%.

Effect of α_y on the error

Following the same considerations, the impact of transverse dispersivity α_y on the estimation error is discussed below.

For this case, assume the source width Y to be a constant at 5 m. Equations (4) and (5) are used to express the ratio of α_y to α_x :

$$\alpha_y = 0.33 \bullet \alpha_x \quad (\text{EPA, 2000}) \quad (5)$$

Doing the same calculation and drawing the concentration distribution along the centreline in a semi-logarithmic coordinate, gives the results in Fig. 2 and Table 2. In Fig. 2, very similar phenomena can be observed to Fig. 1. Close to the contamination source, there is a quick decline of the concentration along the centreline. However, when the distance of the monitoring well is far enough from the source, the curves turn almost parallel to the line in the 1-D case. The slopes of the latter part of these curves were calculated based on the data far from the source, and biodegradation rates were calculated using equation (1). The results illustrating the transverse dispersivity's influence on the biodegradation rates are almost the same as the influence caused by the source width. The results show that estimating the slope m using the almost linear part of the curves gives very similar estimation of the biodegradation rates for two different transverse dispersivities. Estimation of m is not sensitive to the transverse dispersivity. However, for a 2-D problem, the Buscheck & Alcantar method (1995) will cause an error of about 7%.

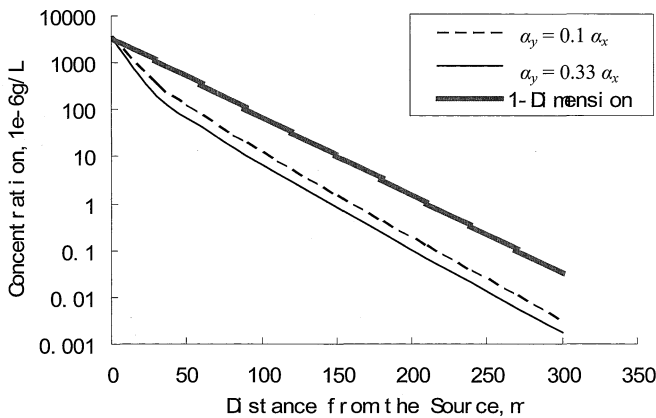


Fig. 2 Effect of transverse dispersivity on concentration distribution along the centreline.

Table 2 Assessment on the errors for different ratio of α_y to α_x .

α_y/α_x	m (m^{-1})	Calculated λ (year^{-1})	Actual λ (year^{-1})	Error (%)
0.1	-0.04102	1.17476	1.095	7.3%
0.33	-0.04103	1.17513	1.095	7.3%

IMPROVED ANALYTICAL METHOD

As discussed above, for a 2-D plume, using the almost linear part of the monitoring data to estimate the slope m , the results will not be very sensitive to the source width and the transverse dispersivity, so an assumption of constant source width and transverse dispersivity can be made when field data are not available, such as $Y = 10$ m and $\alpha_y = 0.1 \bullet \alpha_x$. Under this assumption, an improved analytical approach to estimate the biodegradation rate is developed.

Equation (3) can be changed into the following equation:

$$C(x,0)/\text{erf}\left[\frac{Y}{4\sqrt{\alpha_y x}}\right] = C_0 \bullet \exp\left\{\frac{x}{2\alpha_x}\left[1 - \sqrt{1 + \frac{4\lambda\alpha_x}{v_c}}\right]\right\} \quad (6)$$

The left side of equation (6) can be expressed as a modified concentration $\tilde{C}(x,0)$:

$$\tilde{C}(x,0) = C(x,0) / \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y x}}\right] \quad (7)$$

Then equation (6) is given as:

$$\tilde{C}(x,0) = C_0 \bullet \exp\left\{\frac{x}{2\alpha_x} \left[1 - \sqrt{1 + \frac{4\lambda\alpha_x}{v_c}}\right]\right\} \quad (8)$$

When biodegradation only occurs in the aqueous phase, v_c should be replaced by v_x .

Obviously, the modified concentration $\tilde{C}(x,0)$ is an exponential function of the distance from the source, and equation (8) can be expressed as:

$$\tilde{C}(x,0) = C_0 \bullet \exp(mx) \quad (9)$$

This is very similar to the method of Buscheck and Alcantar. Substituting the modified concentration $\tilde{C}(x,0)$ for the contaminant concentration $C(x,0)$ in the method of Buscheck and Alcantar, an almost linear line can be plotted with the modified concentration *versus* distance in a semi-logarithmic coordinate, and the slope of the line in such a figure can be obtained. Then the slope m can be used to calculate the biodegradation rate λ .

Comparing equations (8) and (9), λ can be obtained as the same as equation (1):

$$\lambda = \left(\frac{v_c}{4\alpha_x}\right) \left[(1 - 2\alpha_x m)^2 - 1 \right] \quad (10)$$

So with the modified concentration, using the concept developed by Buscheck & Alcantar (1995), it is possible to extend the technique from 1-D situations to 2-D situations. This new analytical approach gives more accurate results for *in situ* biodegradation rates than the method of Buscheck and Alcantar.

APPLYING THE IMPROVED ANALYTICAL APPROACH TO A 2-D FIELD SITE

The improved analytical approach is used to estimate the biodegradation rate of a field site. The site was an industrial plant, which used perchloroethylene (PCE) as the organic solvent and PCE was released to the aquifer about 14 years before the field investigation. At the groundwater flow downgradient of the plant, PCE concentration decrease with the distance from the PCE source was monitored from seven monitoring wells along the centreline (as shown in Fig. 3). The aquifer of the site is mainly composed of sand and gravels, and the thickness of the contaminated aquifer in the site is about 20 m.

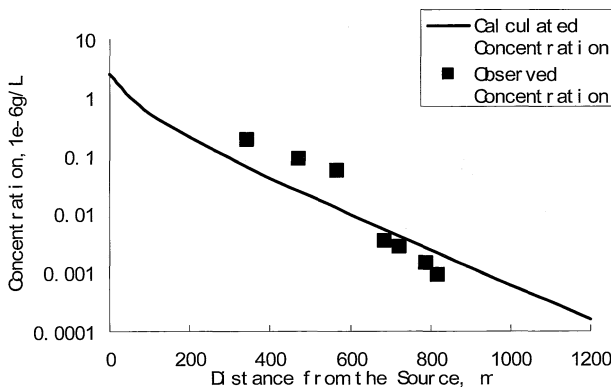


Fig. 3 Comparison of calculated concentration with observed PCE concentration.

Groundwater levels in the site were measured several times in different seasons over two investigation years. Despite a 1-m groundwater level fluctuation, the groundwater gradients were quite stable at 1×10^{-3} . The hydraulic conductivity of the aquifer was obtained from the pumping test result and the data was $3.13 \times 10^{-4} \text{ m s}^{-1}$.

According to the current PCE plume in the aquifer and historical use of PCE in the plant, it is reasonable to simplify the PCE plume as a 2-D plume created by the steady-state groundwater flow from a constant concentration source in the aquifer. Several significant parameters, including effective porosity of the aquifer formation, size of the constant concentration source, and concentration of the source, were obtained through investigation at the field site, as shown in Table 3. Investigation of the field site also illustrated that biodegradation in this site only occurred in the aqueous phase.

Table 3 Parameters of the field site.

Source width, S_w (m)	30	Hydraulic conductivity, K (m s^{-1})	3.13×10^{-4}
Source length, S_L (m)	30	Hydraulic gradient, i (-)	1×10^{-3}
Source thickness, S_T (m)	20	Effective porosity, θ_e (-)	0.2
Source concentration, C_0 (mg L^{-1})	2.5	Retardation coefficient, R (-)	1.737
Longitudinal dispersivity, α_x (m)	40	Transverse dispersivity, α_y (m)	$0.1 \times \alpha_x$

Application of the improved approach could be separated into three steps:

- Calculating the modified concentration $\tilde{C}(x,0)$ using equation (7).
- Plotting the modified concentration $\tilde{C}(x,0)$ versus the distance in a semi-logarithmic coordinate, and using regression to estimate the slope m of the fitting line.
- Calculating the biodegradation rate λ using equation (1). (Substitute v_x for v_e in equation (1), because investigation showed that biodegradation only occurred in the aqueous phase.)

For the field site, λ is estimated to be 0.389 year^{-1} , namely a half-life of 1.8 years. This result is in accordance with the typical PCE biodegradation half-life range in groundwater – 12 months to 2 years (Howard, 1991). It can be seen from Fig. 3 that the calculated results fit the field data quite well.

CONCLUSIONS

Although the method of Buscheck & Alcantar (1995) is routinely used to estimate *in situ* biodegradation rates, it would lead to some degree of error for any multi-dimensional contamination site, because of the 1-D assumption. For a 2-D plume, two new parameters – the source width and the transverse dispersivity – need to be introduced into the analytical solution. Calculations for several typical cases show that close to the source, there is a quick decline of the contaminant concentration along the centreline. However, when the monitoring data is far from the source, the concentration decline curve almost turns into a straight line, then the line can be used to estimate the biodegradation rate following the method of Buscheck & Alcantar (1995). Research has shown that the estimation of the biodegradation rate is not sensitive to the source width or the transverse dispersivity. For the 2-D situations discussed in this paper, the method of Buscheck & Alcantar (1995) gave an error of about 7%.

An improved analytical approach was developed to estimate the *in situ* biodegradation rate based on the field monitoring data. When the main parameters of the plume have been investigated from field or laboratory experiments, the calculations and regression could be easily performed to get the biodegradation rate. However, there are still some factors needing to be considered: (1) quantities and locations of monitoring wells to represent the concentration decline along the centreline; (2) the rationality of assuming steady-state conditions; (3) reasonable investigation of

dispersivity and other main parameters for a field site; (4) if the monitoring wells are off the centreline or the field problem is a 3-D one, more intricate equations should be used instead of equation (3) (more details of such equations can be found in Domenico (1987)); (5) for a heterogeneous problem, the simplified analytical equations are not likely to function, and complex numerical simulations would be needed; and (6) for sites where the source location is difficult to identify, the improved analytical solution could not be performed.

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