



# Role of natural attenuation in modeling the leaching of contaminants in the risk analysis framework

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## ABSTRACT

Natural attenuation (NA) processes occurring in the subsurface can significantly affect the impact on groundwater from contamination sources located in the vadose zone, especially when mobile and readily biodegradable compounds, such as BTEX, are present. Besides, in the last decades several studies have shown natural attenuation to take place also for more persistent compounds, such as Polycyclic Aromatic Hydrocarbons (PAHs). Nevertheless, common risk analysis frameworks, based on the ASTM RBCA (Risk Based Corrective Action) approach, do not include NA pathways in the fate and transport models, thus possibly leading to an overestimation of the calculated risk. The aim of this study was to provide an insight on the relevance of the different key natural attenuation processes usually taking place in the subsurface and to highlight for which contamination scenarios their inclusion in the risk-analysis framework could provide a more realistic risk assessment. To this end, an analytical model accounting for source depletion and biodegradation, dispersion and diffusion during leaching was developed and applied to several contamination scenarios. These scenarios included contamination by BTEX, characterized by relatively high mobility and biodegradation rate, and PAHs, i.e. a more persistent class of compounds. The obtained results showed that BTEX are likely to be attenuated in the source zone due to their mobility and ready biodegradation (assuming biodegradation constant rates in the order of  $0.01-1 \text{ d}^{-1}$ ). Instead, attenuation along transport through the vadose zone was found to be less important, as the residence time of the contaminant in the unsaturated zone is often too low with respect to the time required to get a relevant biodegradation of BTEX. On the other hand, heavier compounds such as PAHs, were found to be attenuated during leaching since the residence time in the vadose zone can reach values up to thousands of years. In these cases, even with the relatively slow biodegradation rate of PAHs, in the order of  $0.0001-0.001 \text{ d}^{-1}$ , attenuation can result significant. These conclusions were also confirmed by comparing the model results with experimental data collected at an hydrocarbon-contaminated site. The proposed model, that neglects the transport of NAPLs, could be easily included in the risk-analysis framework, allowing to get a more realistic assessment of risks, while keeping the intrinsic simplicity of the ASTM-RBCA approach.

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## 1. Introduction

Contamination of soils by petroleum products due to leaking underground storage tanks, accidental spills or improper surface applications is a widespread environmental problem (Karapanagioti et al., 2003). When the volume of spilled product is small, the hydrocarbon may be retained in an immobile condition in the unsaturated zone by capillary forces (Andre et al., 2009). In this case,

source zones generating a dissolved-phase, may lead to a long term risk to groundwater since plume in the vadose zone can gradually leach by infiltrating water. Whereas a significant volume spill of Nonaqueous Phase Liquids (DNAPL or LNAPL) may take hours to days to reach a water table, a dissolved plume leached from a shallow source may require years to decades and leached plumes may never reach groundwater, or else be substantially delayed with reduced concentrations (Rivett et al., 2011). As a matter of fact, in the last decades several studies have demonstrated the occurrence of natural attenuation by studying the attenuation in the unsaturated zone (Lundegard and Johnson, 2006; Johnson et al., 2006; Lahvis et al., 1999; Kastanek et al., 1999; Lee et al., 2001), the evolution of the plume length (Shih et al., 2004; Newell and Connor, 1998;

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Prommer et al., 2002; Kao and Prosser, 2001), the mass reduction (Christensen et al., 2000), the geochemical processes (Cozzarelli et al., 2001; Molins et al., 2010) and the vertical vapors profiles (Hers et al., 2000; Roggemans et al., 2001; Hohener et al., 2003; Verginelli and Baciocchi, 2011). Hence, accounting for these processes is a crucial issue in order to properly assess the risk for groundwater contamination from point sources (Trolborg et al., 2009; Mulligan and Yong, 2004). However, in most screening tools for risk assessment, the description of transport through the unsaturated zone is very simplified. For instance, the leachate ASTM model (ASTM, 2000) accounts just for dissolution of contaminants into infiltrating water and dilution within the underlying groundwater, whereas no attenuation pathways are considered. The simplicity of this approach has led to a wide application of this model for the calculation of risk-based remediation standards. In fact, the risk analysis procedure is usually performed using simple analytical fate and transport models (i.e. RBCA Tier 2 application), that represent a reasonable compromise between the need for a detailed site assessment and the advantage of handling a rather simple and easy-to-use management tool (Baciocchi et al., 2010). In addition, the site-specific data required for the application of these simple models are quite limited and are generally associated to the geometric descriptions of the source and to the identification of the physical properties of the environmental media through which migration is occurring.

Despite the application of the Tier 2 ASTM approach has clear advantages, the experience gained over the years has shown that the leachate ASTM model can lead in some cases to an overestimation of the concentrations expected in the underlying aquifer up to several orders of magnitude. This may lead to unreasonably low clean-up goals, that can make the whole remediation economically unsustainable.

In this view, in order to evaluate the expected significance of the different attenuation pathways, in this work an analytical model accounting for the transport and attenuation by multiple mechanisms in the unsaturated zone and in the source was developed. The model is made of three terms, accounting for attenuation during transport in the vadose zone, source depletion and dilution of the contaminant in groundwater, respectively. The analytical solutions of each term were individually developed and coupled to get an expression suitable for being easily included in the Tier 2 risk-analysis framework; this enables to get a more realistic assessment of risks while keeping the intrinsic simplicity of the ASTM-RBCA approach. Besides, the model allows to highlight the dependence and the expected relevance of natural attenuation and depletion timeframes on soil conditions, site geometry and compounds properties. To this end, after a brief description of the model, several simulations related to typical contamination scenarios are reported and discussed in order to highlight in which cases the ASTM model is expected to lead to an overestimation of the risk for the downstream receptor. These scenarios include contamination by compounds characterized by different biodegradability and mobility: namely, BTEX were chosen as a class of compounds characterized by relatively high mobility and biodegradation rate, whereas PAHs as a more persistent class of compounds.

## 2. Modeling

### 2.1. Fate and transport models

Fate and transport models in the risk analysis procedure can be applied in a forward-calculation mode where constituent concentration at point of exposure ( $C_{poe}$ ) is predicted based on source area concentration ( $C_{source}$ ):

$$C_{poe} = C_{source} \cdot FT \quad (1)$$

where FT is the transport factor that accounts for the attenuation of the compound along the migration pathway.

Analytical models can also be applied in a back-calculation mode to determine the source-area constituent concentration corresponding to an acceptable concentration at the point of interest (ASTM, 2000).

The transport factor focused in this work is the Leaching Factor, LF, representing the ratio between total soil concentration and groundwater. LF accounts for the contaminant's attenuation during the transport from the source, located in the vadose zone, to the groundwater table.

The conceptual model of the leaching process of chemicals to ground water is reported in Fig. 1.

### 2.2. ASTM model

The leachate model proposed by the ASTM standard is based on the following assumptions: (i) constant chemical concentration in soil, (ii) linear equilibrium partitioning between the different phases, (iii) steady-state leaching from the vadose zone to ground water resulting from the constant leaching rate and (iv) well-mixed dispersion of the leachate within the groundwater "mixing zone". Under these conditions the leaching factor, LF, is calculated as follows:

$$LF_{ASTM} = \frac{1}{K_{sw} \cdot LDF} \quad (2)$$

$K_{sw}$  is the soil – water partition coefficient:

$$K_{sw} = \frac{\theta_w + H \cdot \theta_a + \rho_s \cdot K_d}{\rho_s} \quad (3)$$

where  $\theta_w$  is the water-filled porosity of the soil,  $H$  the dimensionless Henry's law constant,  $\theta_a$  the air-filled porosity,  $\rho_s$  the bulk soil density and  $K_d$  the soil sorbed – water partition coefficient.

LDF is the Leachate Dilution Factor, which accounts for the dilution of the concentration occurring when the contaminant is transferred from the leachate to groundwater:

$$LDF = 1 + \frac{v_{gw} \cdot \delta_{gw}}{I_{ef} \cdot W} \quad (4)$$

Where  $\delta_{gw}$  is the groundwater mixing zone height,  $v_{gw}$  the groundwater Darcy velocity,  $W$  the width of source-zone area longitudinal to the groundwater flow and  $I_{ef}$  the water infiltration rate.

Hence the ASTM model accounts just for the soil-water partitioning and the dilution occurring in groundwater, whereas no contaminant attenuation (e.g. biodegradation) or source depletion are considered. In the next section a model accounting for the different attenuation processes is reported.

### 2.3. Natural attenuation model

#### 2.3.1. Attenuation during transport

The steady state 1-D transport and reaction of leached contaminants in the vadose zone can be described by the usual diffusion-advection differential equation with reaction term:

$$D \frac{d^2 C_w}{dz^2} - v_{leach} \cdot \frac{dC_w}{dz} - \lambda \cdot \theta_w \cdot C_w = 0 \quad (5)$$

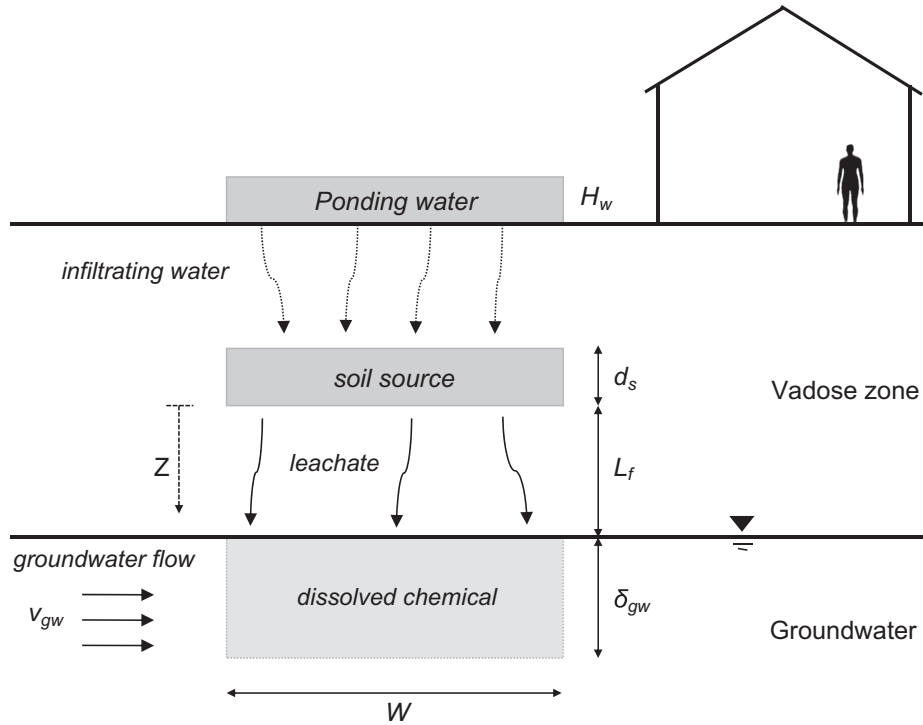


Fig. 1. Conceptual model. The symbol  $z$  represents the spatial variable and is positive with increasing depth. The origin of  $z$  is placed at the bottom of the soil source.

where  $C_w$  is the solute concentration in the water phase,  $\lambda$  the first-order degradation rate,  $v_{leach}$  the seepage velocity and  $D$  the dispersion–diffusion coefficient:

$$D = \alpha_z \cdot v_{leach} + D^{eff} \tag{6}$$

With  $\alpha_z$  representing the contaminant dispersivity and  $D^{eff}$  the effective porous medium diffusion coefficient:

$$D^{eff} = D_w \cdot \frac{\theta_w^{10/3}}{\theta_e^2} \tag{7}$$

Where  $D_w$  is the diffusion coefficient in water,  $\theta_w$  the water-filled porosity of the soil and  $\theta_e$  the effective soil porosity.

The time required for infiltrating water to reach the underlying water table ( $t_w$ ) can be calculated by applying the Green and Ampt (1911) equation:

$$t_w = R \cdot \frac{\theta_a}{K_{sat}} \cdot \left[ L_f - (H_w - h_{cr}) \cdot \ln \left( \frac{H_w + L_f - h_{cr}}{H_w - h_{cr}} \right) \right] \tag{8}$$

where  $\theta_a$  is the air-filled porosity of the soil,  $K_{sat}$  the saturated hydraulic conductivity of the wetted zone,  $H_w$  the ponding depth of water at the surface,  $h_{cr}$  the wetting front suction head and  $L_f$  the water table depth.

Hence the time required for the contaminant of concern to reach the water table ( $t_{leach}$ ) can be estimated as a function of the retardation coefficient specific of the contaminant,  $R$ :

$$t_{leach} = R \cdot t_w \tag{9}$$

Assuming a linear equilibrium partitioning, the retardation coefficient can be determined as follows:

$$R = 1 + \frac{\rho_s \cdot K_{sw}}{\theta_e} \tag{10}$$

where  $\theta_e$  is the effective soil porosity,  $\rho_s$  the soil bulk density and  $K_{sw}$  the soil–water partition coefficient.

**Analytical solution.** An analytical solution of Eq. (5) was obtained by assuming the following boundary conditions:  $C = C_0$  at  $z = 0$  and  $D \frac{d^2C}{dz^2} = 0$  at  $z = L_f$ . Under these assumptions, the attenuation factor occurring during leaching,  $\alpha_{leach}$ , can be calculated as follows:

$$\alpha_{leach} = \frac{C(L_f)}{C_0} = \frac{\sigma \cdot \exp(k \cdot L_f)}{k \cdot \sinh(\sigma \cdot L_f) + \sigma \cdot \cosh(\sigma \cdot L_f)} \tag{11}$$

with:

$$k = \frac{L_f}{2 \cdot D \cdot t_{leach}} \tag{12}$$

$$\sigma = \sqrt{k^2 + \frac{\lambda \cdot \theta_w}{D}} \tag{13}$$

Where  $\lambda$  is the first-order degradation rate and  $D$  the dispersion–diffusion coefficient described in Eq. (6).

A similar expressions of Eq. (11) was obtained by Troldborg et al. (2009).

### 2.3.2. Depleting source

The change of the mass source ( $m_s$ ) over time ( $t$ ), due to infiltrating water and biodegradation, can be described by the following mass balance:

$$-\frac{dm_s}{dt} = \mu_{inf} + \mu_{bio} \tag{14}$$

where  $\mu_{inf}$  and  $\mu_{bio}$  are the mass lost per unit time by leaching (Eq. (15)) and by biodegradation (Eq. (16)) respectively, which can be calculated as follows:

$$\mu_{inf} = \frac{I_{ef}}{R} A \cdot C_w(t) \tag{15}$$

$$\mu_{\text{bio}} = \lambda_{\text{source}} \cdot \theta_w \cdot A \cdot d_s \cdot C_w(t) \tag{16}$$

$C_w$  is the source concentration in the water phase,  $\lambda_{\text{source}}$  is the first-order kinetic rate constant,  $A$  the source area,  $d_s$  the source thickness and  $I_{\text{ef}}$  the water infiltration rate

The mass source,  $m_s$ , can be expressed in terms of the total source concentration  $C_{\text{tot}}$ :

$$m_s = \rho_s \cdot A \cdot d_s \cdot C_{\text{tot}}(t) \tag{17}$$

The total concentration  $C_{\text{tot}}$ , assuming linear equilibrium partitioning, is given by the sum of the concentrations in the different phases of the soil:

$$C_{\text{tot}} = \frac{1}{\rho_s} (\theta_w + H \cdot \theta_a + \rho_s \cdot K_d) \cdot C_w + C_{\text{free}} \tag{18}$$

$C_{\text{free}}$  is the concentration of the contaminant as free phase and is present only when the total concentration,  $C_{\text{tot}}$ , exceeds the saturation concentration  $C_{\text{sat}}$ :

$$C_{\text{sat}} = K_{\text{sw}} \cdot S \tag{19}$$

with  $S$  representing the solubility of the contaminant and  $K_{\text{sw}}$  the soil–water partition coefficient reported in Eq. (3).

Hence the source depletion can be described by substituting Eqs. (15)–(17) in Eq. (14):

$$-\rho_s \cdot A \cdot d_s \cdot \int_{C_0}^{C(t)} \frac{1}{\left(\frac{I_{\text{eff}}}{R} \cdot A + \lambda_{\text{source}} \cdot \theta_w \cdot A \cdot d_s\right) \cdot \frac{C_{\text{tot}}}{K_{\text{sw}}}} \cdot \frac{dC_{\text{tot}}}{C_{\text{tot}}} = \int_0^t dt \tag{20}$$

Eq. (20) was solved by dividing the problem into different domains corresponding to the condition of initial source concentration above or below the saturation limit,  $C_{\text{sat}}$ :

$$C_{\text{tot}}(t) = \begin{cases} C_{\text{tot}}(0) - C_{\text{sat}} \cdot \mu \cdot t & \text{for } C_{\text{tot}}(0) > C_{\text{sat}} \\ C_{\text{tot}}(0) \cdot \exp[-\mu \cdot (t - t^*)] & \text{for } C_{\text{tot}}(0) \leq C_{\text{sat}} \end{cases} \tag{21}$$

with:

$$\mu = \frac{I_{\text{eff}}}{R \cdot d_s \cdot \rho_s \cdot K_{\text{sw}}} + \frac{\lambda_{\text{source}} \cdot \theta_w}{\rho_s \cdot K_{\text{sw}}} \tag{22}$$

It is worth noting that Eq. (21) is valid above the saturation concentration as long as the total concentration is lower than the residual concentration ( $C_{\text{res}}$ ) which represents the upper limit above which the free phase (i.e. mobile NAPL) is expected to leach directly without the infiltrating water. In fact, as described by ASTM (2000), free phase may be present in unsaturated soil, but immobile due to capillary, viscous, and gravity forces acting on the bulk free phase.

$t^*$  reported in Eq. (21) is the time at which the initial source concentration reaches the saturation conditions (i.e.  $C_{\text{tot}}(t) = C_{\text{sat}}$ )

$$t^* = \frac{C_{\text{tot}}(0) - C_{\text{sat}}}{C_{\text{sat}} \cdot \mu} \tag{23}$$

Namely when the initial source concentration is higher than the saturation concentration ( $C_{\text{sat}}$ ), assuming that the dissolution of the free product is faster or comparable to the attenuation processes which lead to a decrease of the concentration in the water phase, the source depletion can be described as a linear decrease of the

concentration in the free phase, i.e. the concentrations of the other phases are assumed constant and equal to the saturated conditions. On the contrary, when the source concentration reaches the saturation conditions (i.e.  $C_{\text{free}} = 0$ ) the depletion law becomes exponential, since infiltrating water and biodegradation processes reduce the concentration in water phase and consequently, assuming a linear equilibrium partitioning, also in the sorbed and vapor phase.

Thus the change of the solute concentration over time,  $C_w(t)$ , in the case of initial source concentration below the saturation limit,  $C_{\text{sat}}$  (i.e.  $t^* < 0$ ), will be equal to:

$$C_w(t) = C_w(0) \cdot \exp(-\mu \cdot t) \quad \text{if } t^* \leq 0 \tag{24}$$

In the case of  $t^* > 0$  (i.e.  $C_{\text{tot}} > C_{\text{sat}}$ ) the change of the solute concentration over time  $C_w(t)$ , can be calculated as follows:

$$C_w(t) = \begin{cases} S & \text{if } t \leq t^* \\ S \cdot \exp[-\mu \cdot (t - t^*)] & \text{if } t > t^* \end{cases} \tag{25}$$

Hence the modified leaching factor,  $LF_{\text{bio}}$ , may be calculated by combining Eq. (2) with Eq. (11) and Eqs. (24)–(25) as follows:

$$LF_{\text{bio}}(t) = \frac{\alpha_{\text{leach}} \cdot \alpha_{\text{dep}}(t)}{K_{\text{sw}} \cdot \text{LDF}} \tag{26}$$

where:

$$\alpha_{\text{DEP}}(t) = \begin{cases} \exp[-\mu \cdot t] & \text{for } t^* \leq 0 \\ \exp[-\mu \cdot (t - t^*)] & \text{for } t > t^* \\ 1 & \text{for } t \leq t^* \end{cases} \tag{27}$$

#### 2.4. Risk calculation

The overall risk can be calculated by dividing the whole exposure period (e.g. 25 years) in a given number of exposure intervals. For each interval the average concentration at point of exposure ( $C_{\text{poe}}$ ) can be calculated using Eq. (1) and Eq. (26). Thus the total risk,  $R_T$ , can be calculated as the sum of the incremental risk values associated to each exposure interval:

$$R_T = \sum_{i=1}^n R_i \tag{28}$$

where  $R_i$  is the risk calculated to a generic  $i$ -th time interval, with ED equal to the duration of the time interval itself (Baciocchi et al., 2010):

$$R_i = \text{SF} \cdot \frac{\text{CR} \cdot \text{EF}}{\text{BW} \cdot \text{AT}} \cdot C_{\text{poe},i} \cdot \text{ED}_i \tag{29}$$

Where SF is the slope factor, CR is the ingestion rate, EF the Exposure Frequency, ED the Exposure Duration, BW the Body Weight, and AT the Averaging Time.

The same equation can be used for the calculation of the hazard index (HI) substituting the slope factor, SF, with the reference dose,  $\text{RfD}$ :

$$\text{HI}_i = \frac{1}{\text{RfD}} \cdot \frac{\text{CR} \cdot \text{EF}}{\text{BW} \cdot \text{AT}} \cdot \sum C_{\text{poe},i} \cdot \text{ED}_i \tag{30}$$

### 3. Results and discussion

The model described above, was solved analytically and used to assess under which site conditions natural attenuation is expected to play a significant role. To this end, solutions have been calculated, using representative parameter ranges and values (Table 1 and Table S1).

Namely these elaborations are aimed to evaluate the different leaching behavior as a function of the site-specific characteristics and chemical properties of the contaminants. In this view, in order to evaluate the relevance of the natural attenuation depending on the chemical properties, the model described in this work is applied to BTEX and PAHs which are characterized by completely different behaviors. In fact, as known, BTEX are quite soluble and characterized by relatively high biodegradation constant rates. Evidence for vadose zone biodegradation of BTEX has been seen at several field studies reporting typical average values of biodegradation constant rates in the order of 0.01 and  $10 \text{ d}^{-1}$  (e.g. see Davis et al., 2009; DeVauil et al., 1997; Hers et al., 2000; Hoener et al., 2003). On the contrary, PAHs are largely sorbed to the soil and are slowly biodegradable. Typical biodegradation rate constants values available in literature for these compounds are in the range of  $0.0001\text{--}0.01 \text{ d}^{-1}$  (e.g. see Brauner et al., 2002; Blum et al., 2009; Bockelmann et al., 2001).

In addition, in order to highlight the processes controlling the vadose zone transport and the attenuation of plumes leached from source zone, the results hereby presented, separately discuss the influence of natural attenuation occurring during the transport and in the source zone.

#### 3.1. Attenuation during leaching

Fig. 2 reports the leachate attenuation factor ( $\alpha_{\text{leach}}$ ), calculated with the model described in this work, as a function of the time required for the contaminant to reach the water table. The simulations were performed assuming different water depths and different biodegradation constant rates. The obtained results, reported in the figure, show that the increase of the time required for the contaminant to reach the water table leads to a corresponding significant decrease of the calculated attenuation factor. Namely, for leaching time higher than 10 days, the attenuation due to biodegradation and dispersion is expected to lead to a relevant attenuation of the solute concentration up to several order of magnitude. This is more evident for deeper groundwater (e.g.  $L_f = 10 \text{ m}$ , Fig. 2d) and for high biodegradation rate constants (see e.g.  $\lambda = 1 \text{ d}^{-1}$ ). On the contrary, for time

frames below 1 day the attenuation factor during the transport is negligible even in the case of very high biodegradation constant rates (i.e.  $\lambda = 1 \text{ d}^{-1}$ ).

To assess more specifically this behavior, Fig. 3 reports the time required for BTEX and some PAHs to reach the water table calculated with Eq. (8) assuming the same scenarios reported in Fig. 2. This figure shows that BTEX are generally characterized by leaching times in the range of 0.1–10 days whereas the PAHs, for the same scenario, are expected to reach the water table after 10–100 years (i.e.  $10^4\text{--}10^5$  days). In fact as discussed above, the time required to reach the water tables depends on the site specific conditions (e.g. soil texture) but especially on the contaminant properties. In fact, soluble contaminants move quickly in the subsurface with infiltration rates approaching the infiltration water. On the contrary, heavier contaminants are largely sorbed to the soil with traveling time retarded up to thousands times with respect to infiltrating water.

Hence, by evaluating these results with the ones reported in Fig. 2, it can be noticed that even assuming relatively slow biodegradation rates (e.g.  $\lambda \leq 0.01 \text{ d}^{-1}$ ), PAHs are expected to be significantly attenuated during the leaching process (e.g. Fig. 2c shows that for  $\lambda = 0.001 \text{ d}^{-1}$  the attenuation factor for a leaching time of  $10^5$  days is equal to  $\alpha_{\text{leach}} = 10^{-3}$ ). Fig. 2 also shows that for BTEX the different simulations approach each other, as long as relatively low biodegradation rate constants are considered (below  $\lambda = 0.1 \text{ d}^{-1}$  for leaching time of 1 days). On the contrary, a slight attenuation is observed for higher biodegradation rate constant values and deep aquifers (e.g. see Fig. 2d for a leaching time of 10 days and for  $\lambda > 1 \text{ d}^{-1}$ ).

Fig. 4 reports the concentration profiles in the vadose zone obtained during an investigation of a contaminated site located in a petrochemical complex of north Italy. Specifically, the figure shows the concentrations of some PAHs and BTEX measured in three surveys at different depths. For reference the profiles obtained with the model described in this work are also reported. With reference to this figure it can be noticed that, especially for the PAHs, concentrations are significantly reduced with increasing depth, indicative of a non-negligible attenuation during transport. In addition the figure shows that the concentration profiles, simulated with the model, fits quite well trends observed in the field, confirming that neglecting the attenuation in the unsaturated zone can lead to an overestimation of the effective concentration in the subsurface (other concentration profiles for further 6 PAHs are reported in Figure S1). Finally it is worth noting that the first-order degradation rates used in the model to best fit the field data are achieved assuming values that are in line with those reported in the literature (e.g. Davis et al., 2009; DeVauil et al., 1997; Brauner et al., 2002; Blum et al., 2009; Bockelmann et al., 2001). Namely, as discussed before, typical average median values of biodegradation constant rates for BTEX are in the order of 0.01 and  $10 \text{ d}^{-1}$  whereas for PAHs are in the range of  $0.0001\text{--}0.01 \text{ d}^{-1}$ .

#### 3.2. Attenuation in the source

Fig. 5 reports the source attenuation factor ( $\alpha_{\text{dep}}$ ) calculated with the developed model as a function of time. The results were obtained assuming different soil – water partition coefficients ( $K_{\text{sw}}$ ) and different contamination scenarios assuming that the initial source concentration is lower than the saturation concentration,  $C_{\text{sat}}$  (i.e.  $C_{\text{free}} = 0$ ). With reference to these figures it can be noticed, that the contaminant source attenuation is relevant only for soluble compounds characterized by partition coefficient below 10 L/kg. This suggest that the BTEX, that are characterized by  $K_{\text{sw}}$  in the range of 0.1–10 L/kg (see Table S1),

**Table 1**  
Model input parameters (unless otherwise noted in figures).

Parameter	Symbol	Unit	Value	
			Sand	Clay
Water table depth	$L_f$	m	0.5; 1; 2; 10	
Source thickness	$d_s$	m	1; 5	
Length of source-zone area	$W$	m	45	
Dispersivity factor <sup>(a)</sup>	$A$	cm	$0.33 \times L_f^{0.62}$	
Ponding depth	$H_w$	m	0.3	
Soil bulk density	$\rho_s$	$\text{g/cm}^3$	1.7	
Water-filled porosity	$\theta_w$	–	0.2	
Groundwater gradient	$I$	m/m	0.01	
Organic fraction	$f_{\text{oc}}$	–	0.001	0.01
Effective infiltration	$I_{\text{ef}}$	cm/year	10	1
Effective soil porosity	$\theta_e$	–	0.38	0.31
Suction head	$h_{\text{cr}}$	cm	–4	–111.7
Hydraulic conductivity	$K_{\text{sat}}$	m/s	8.3E – 05	5.6E – 07

<sup>a</sup> Vanderborght and Vereecken, 2007.



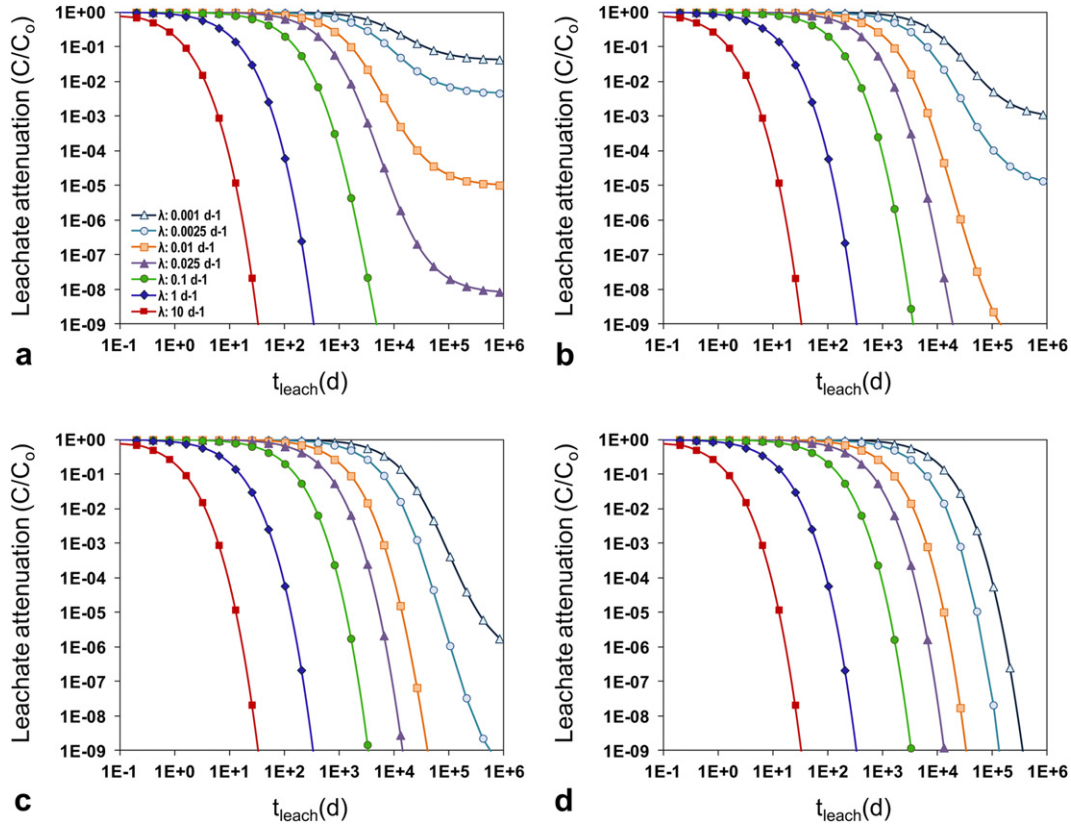


Fig. 2. Leachate attenuation factor ( $\alpha_{leach}$ ) calculated as a function of the time required for the contaminant to reach the underlying aquifer ( $t_{leach}$ ). The results are reported assuming different biodegradation constant rates,  $\theta_e = 0.35$ ,  $D_w = 10^{-5} \text{ cm}^2/\text{s}$  and the following aquifer depths: (a)  $L_f = 0.5 \text{ m}$ ; (b)  $L_f = 1 \text{ m}$ ; (c)  $L_f = 2 \text{ m}$ , (d)  $L_f = 10 \text{ m}$ .

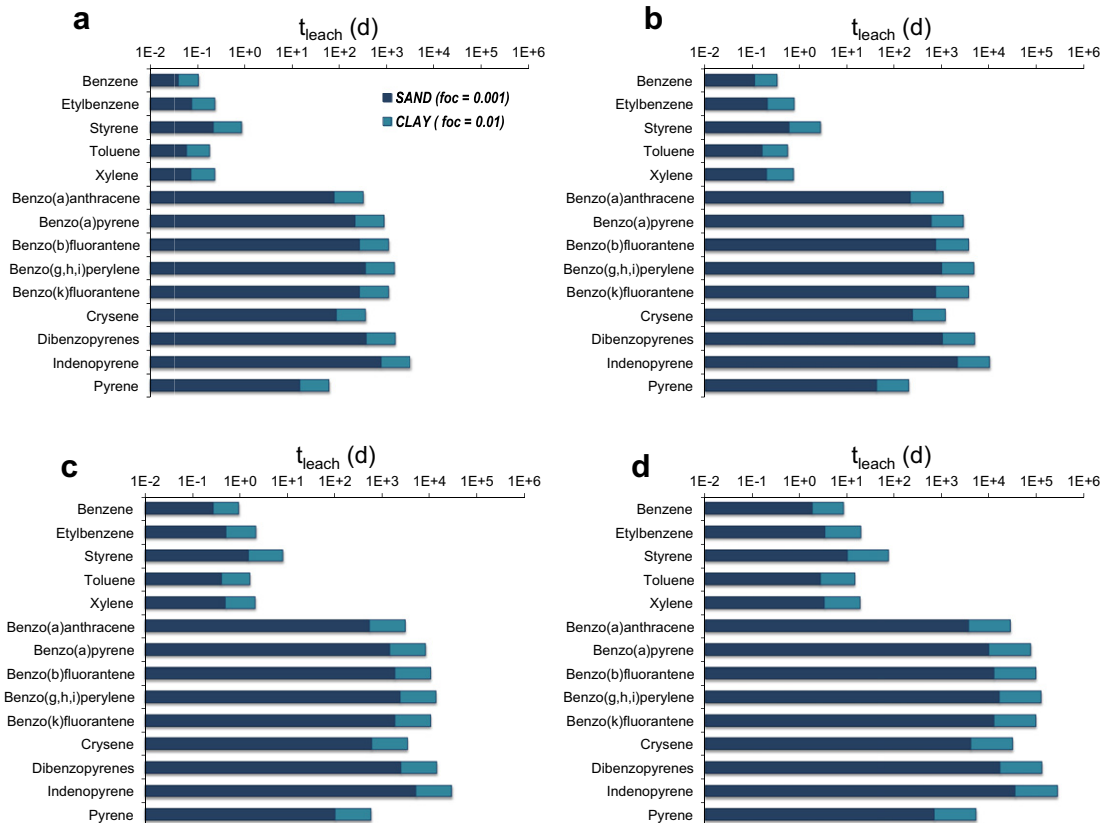
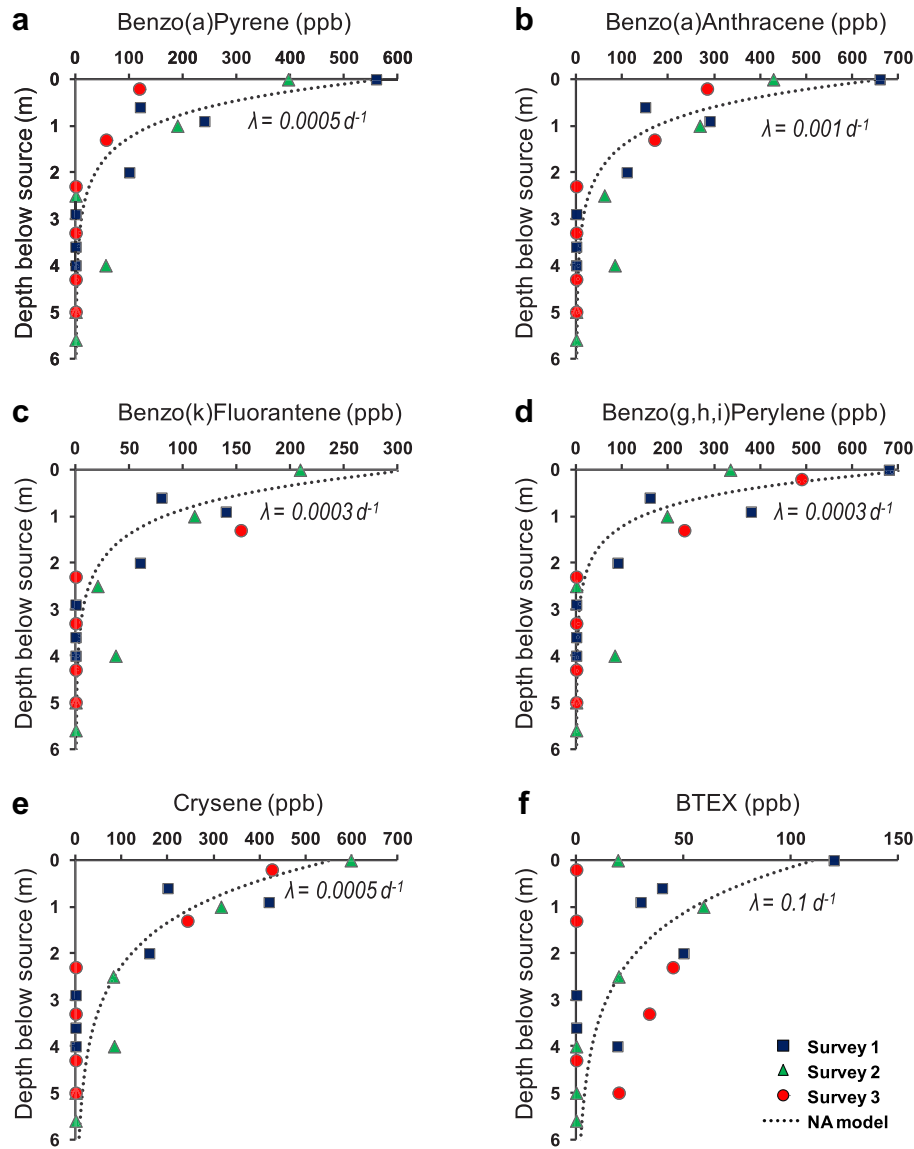


Fig. 3. Time required to reach the water table ( $t_{leach}$ ) calculated with the Green and Ampt equation (Eq. (8)) for different aquifer depths: (a)  $L_f = 0.5 \text{ m}$ ; (b)  $L_f = 1 \text{ m}$ ; (c)  $L_f = 2 \text{ m}$ , (d)  $L_f = 10 \text{ m}$ .



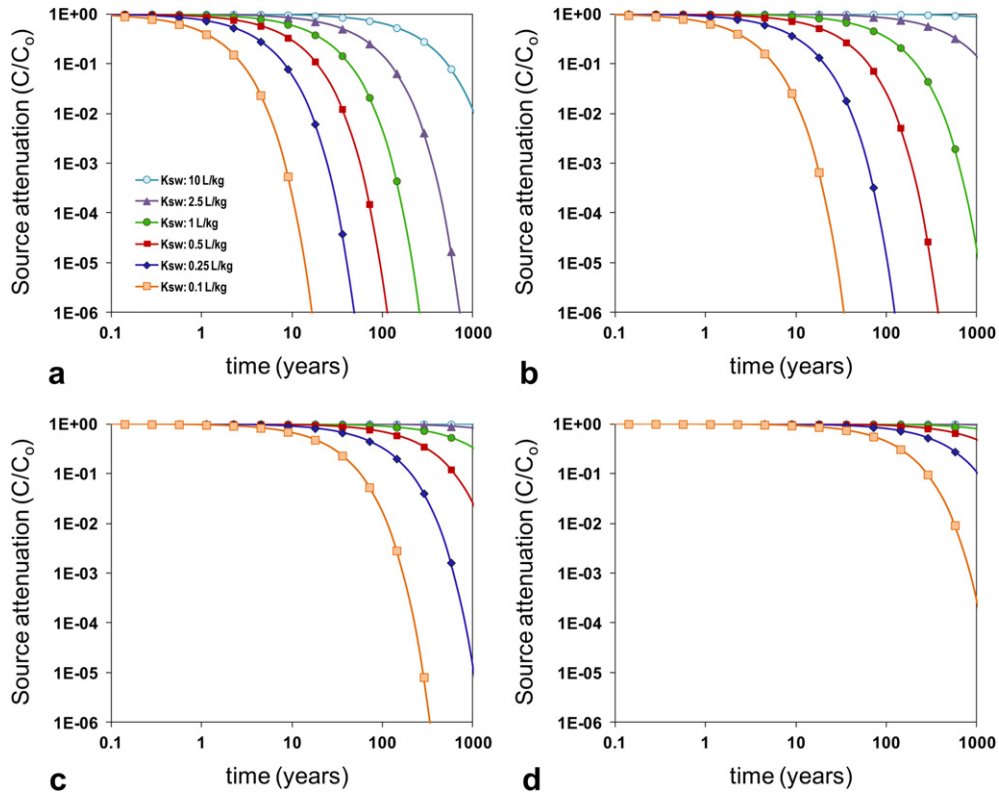
**Fig. 4.** Concentration profiles of some PAHs and for BTEX measured in 3 surveys. For reference the profiles obtained with the model described in this work (NA model) are also reported. Soil: Silt Loam,  $f_{oc}$ : 0.001.

could be significant reduced over time (e.g. 10–100 years) and thus the ASTM model which assumes a constant time source concentration for the entire period of exposure can lead to a significant overestimation of the effective impact on the groundwater. On the contrary heavier compounds such as PAHs (characterized by  $K_{sw}$  ranging from  $10^3$ – $10^5$  L/kg) are very persistent and the source depletion mechanism could be neglected. Fig. 5 also shows that the source attenuation rate strongly depends on the site-specific conditions influencing the contaminant depletion such as the infiltration rate ( $I_{ef}$ ), the occurrence of biodegradation in the source ( $\lambda_{source}$ ) and the thickness of the source ( $d_s$ ).

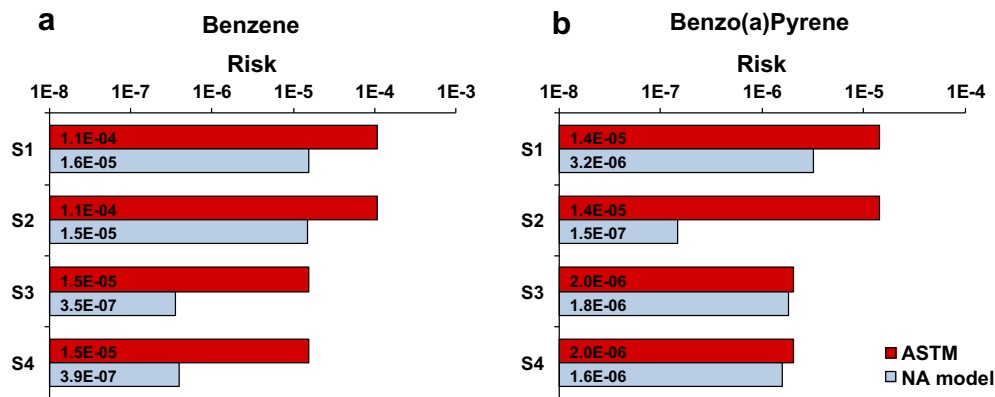
In the case of initial source concentration higher than the saturation concentration,  $C_{sat}$ , Fig. 5 can still be used but in this case the time for depletion should also account for the time  $t^*$  required to reach the  $C_{sat}$ , below which the solute concentration in the source begins to decrease (see Fig. S2 in the Supplementary Material).

### 3.3. Risk calculation

In this section the risk values obtained for different contaminant scenarios by applying the different modeling approaches described in this work are reported in Fig. 6. Namely the carcinogenic risk associated to ingestion of benzene contaminated and benzo(a) pyrene contaminated groundwater was calculated using Eq. (29), assuming a solute source concentration of 1 and 0.001 mg/L, respectively. The comparison shows that the ASTM-RBCA approach provides more conservative carcinogenic risk values up to two orders of magnitude higher than those obtained applying the model accounting for the different natural attenuation processes. The magnitude of this overestimation depends strongly on the contaminant scenario and on the characteristics of the contaminant. In fact, for the more soluble contaminants, such as benzene, for which the attenuation mainly occurs in the source, this overestimation is more important for sandy soils or reduced contamination thicknesses (see e.g. S3 and S4 in Fig. 6). On the contrary for



**Fig. 5.** Source attenuation factor ( $\alpha_{dep}$ ) calculated as a function of time for different soil-water partition coefficient values ( $K_{sw}$ ) for different contaminant scenarios: (a)  $\lambda_{source} = 0.001 \text{ d}^{-1}$ ,  $I_{ef} = 10 \text{ cm/year}$ ,  $d_s = 1 \text{ m}$ ; (b)  $\lambda_{source} = 0$ ,  $I_{ef} = 10 \text{ cm/year}$ ,  $d_s = 1 \text{ m}$ ; (c)  $\lambda_{source} = 0$ ,  $I_{ef} = 1 \text{ cm/year}$ ,  $d_s = 1 \text{ m}$ ; (d)  $\lambda_{source} = 0$ ,  $I_{ef} = 1 \text{ cm/year}$ ,  $d_s = 5 \text{ m}$ . These results are obtained assuming a non-NAPL source.



**Fig. 6.** Carcinogenic risk associated to ingestion of contaminated groundwater for benzene (a) and benzo(a)pyrene for different contaminant scenarios: (S1) clay,  $foc = 0.01$ ,  $d = 1 \text{ m}$ ,  $L_f = 2 \text{ m}$ ; (S2) clay,  $foc = 0.01$ ,  $d = 5 \text{ m}$ ,  $L_f = 5 \text{ m}$ ; (S3) Sand,  $foc = 0.001$ ,  $d = 1 \text{ m}$ ,  $L_f = 10 \text{ m}$ ; (S4) Sand,  $foc = 0.001$ ,  $d = 5 \text{ m}$ ,  $L_f = 25 \text{ m}$ . The slope factor, SF, used for the calculation are 0.055 and 7.3 (mg/kg/d)<sup>-1</sup> for benzene and benzo(a)pyrene, respectively.

heavier compounds such as PAHs, the ASTM model tends to overestimate the overall risk for clay soils or deep groundwater, i.e. for scenarios leading to residence times of contaminants in the subsurface high enough to make the attenuation occurring during transport significant (see e.g. S1 and S2 in Fig. 6).

**4. Conclusions**

This work was aimed to assess the relevance of the different attenuation processes occurring during the transport in the unsaturated zone of dissolved organic compounds plumes leached contamination source zones.

To this end, an analytical model accounting for source depletion and biodegradation, dispersion and diffusion during leaching was developed and applied to different contamination scenarios. The obtained results showed that BTEX are likely to be attenuated in the source zone due to their mobility and ready biodegradation (assuming biodegradation constant rates in the order of 0.01–1 d<sup>-1</sup>). Instead, attenuation along transport through the vadose zone was found to be less important, as the residence time of the contaminant in the unsaturated zone is often too low with respect to the time required to get a relevant biodegradation of BTEX. On the other hand, heavier compounds such as PAHs, were found to be attenuated during leaching since the residence time in the vadose



zone can reach values up to thousands of years. In these cases, even with the relatively slow biodegradation rate of PAHs, in the order of  $0.0001\text{--}0.001\text{ d}^{-1}$ , attenuation can result significant. These conclusions were also confirmed by comparing the model results with experimental data collected at an hydrocarbon-contaminated site. The proposed model, that neglects the transport of NAPLs, could be easily included in the risk-analysis framework, allowing to get a more realistic assessment of risks, while keeping the intrinsic simplicity of the ASTM-RBCA approach.

## Nomenclature

$A$	Source area $\text{m}^2$
$C_{\text{free}}$	Free phase concentration $\text{mg/kg}$
$C_{\text{poe}}$	Concentration at the point of exposure $\text{mg/L}$
$C_{\text{sat}}$	Saturation concentration in the soil $\text{mg/kg}$
$C_{\text{source}}$	Source concentration $\text{mg/kg}$
$C_{\text{tot}}$	Total source concentration $\text{mg/kg}$
$C_w$	Solute concentration $\text{mg/L}$
$d_s$	Source thickness $\text{m}$
$D_w$	Diffusion coefficient in water $\text{m}^2/\text{s}$
$f_{\text{oc}}$	Organic carbon fraction $g_{\text{oc}}/g_{\text{soil}}$
$H$	Dimensionless Henry's constant –
$h_{\text{cr}}$	Wetting front suction head $\text{m}$
$H_w$	Ponding depth $\text{m}$
$I$	Groundwater Gradient –
$I_{\text{ef}}$	Effective infiltration $\text{m/s}$
$K_d$	Soil sorbed – water partition coefficient $(\text{mg/kg})/(\text{mg/L})$
$K_{\text{sat}}$	Hydraulic conductivity $\text{m/s}$
$K_{\text{sw}}$	Total soil – water partition coefficient $(\text{mg/kg})/(\text{mg/L})$
LDF	Leachate Dilution Factor –
$L_f$	Depth of the water table from the bottom of the source $\text{m}$
$R$	Retardation coefficient –
RfD	Reference dose $\text{mg}/(\text{kg} \times \text{d})$
$S$	Solubility $\text{mg/l}$
SF	Slope factor $[\text{mg}/(\text{kg} \times \text{d})]^{-1}$
$v_{\text{gw}}$	Darcy velocity $\text{m/s}$
$v_{\text{leach}}$	Leaching velocity $\text{m/s}$
$W$	Width of source area $\text{m}$
$\alpha_z$	Dispersivity $\text{m}$
$\delta_{\text{gw}}$	Mixing zone depth $\text{m}$
$\theta_a$	Vapor-filled soil porosity –
$\theta_e$	Soil porosity –
$\theta_w$	Water-filled soil porosity –
$\lambda$	Biodegradation first-order rate constant $\text{d}^{-1}$
$\lambda_{\text{source}}$	Biodegradation first-order rate constant in the source $\text{d}^{-1}$
$\rho_s$	Soil bulk density $\text{g}/\text{m}^3$

## Appendix A. Supplementary material

Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.jenvman.2012.10.035>.

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