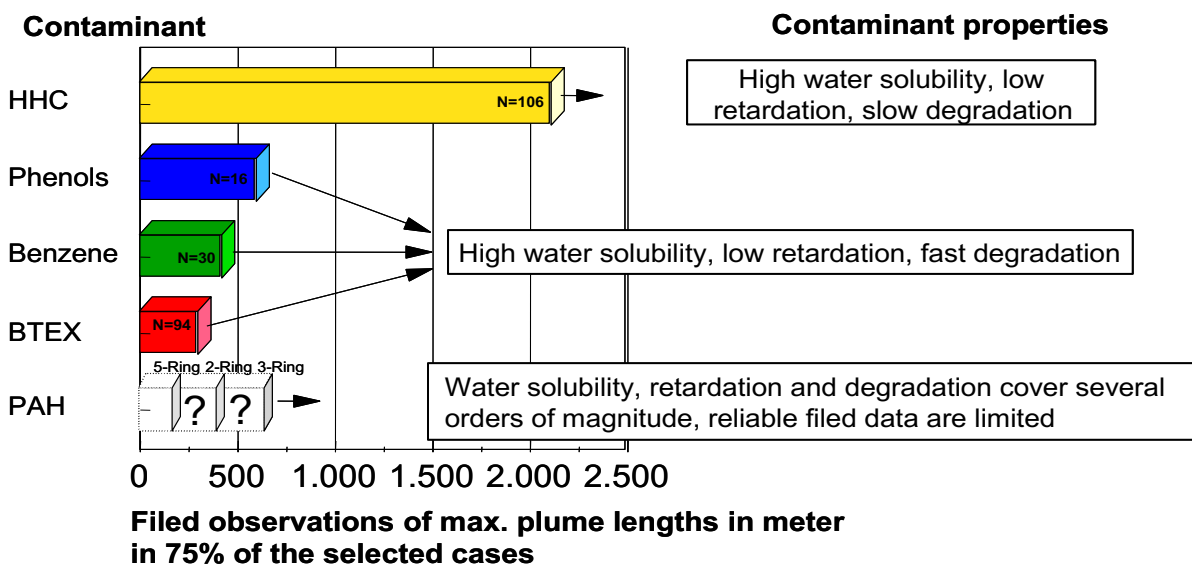


PLUMES – REACTIVE DIFFUSION

1. EVOLUTION OF PLUMES

1.1 NATURAL ATTENUATION

As discussed in former chapters source zones may last for very long time periods especially if NAPLs are concerned. Therefore, plumes have plenty of time to develop and theoretically may grow rapidly especially if retardation of the contaminant is low (e.g., well soluble compounds such as chlorinated solvents or PFAS). However, plumes of biodegradable compounds (e.g., BTEX) may remain quite short, if the emission rate from the source is balanced by the overall degradation rate as shown in Figs. 1.1 and 1.2.



Schiedek et al. 1997

Fig. 1.1: Plumes lengths collected from field studies (N: number of observations)

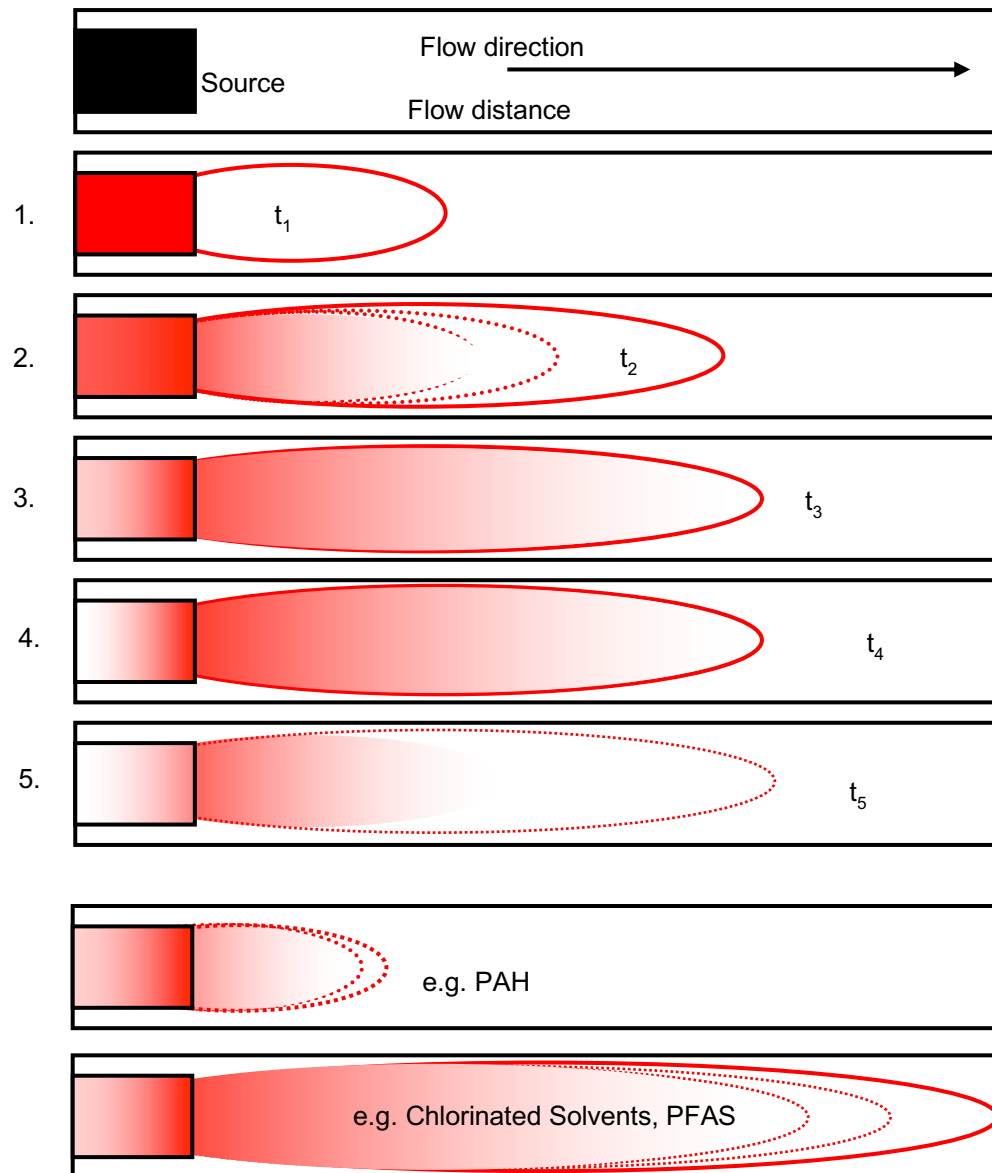


Fig. 1.2: Evolution of plumes during different stages (t_0 - t_5); t_0 : time zero (contaminant spill), dissolution of contaminants with groundwater flow starts in the source area; t_1 : early period (maybe a few months), spreading of contaminants from the source, a plume forms; t_2 : plume grows with time but if biodegradation starts growth slows down (dashed lines); t_3 (a few years): the plume reaches steady state conditions - contaminant emission rates (from the source) are balanced by degradation rates; t_4 (decades): source gets slowly depleted - contaminant emission stays still high and plume is at steady state; t_5 (aging of the source): contaminant emission from the source reduces, the plume shrinks; strongly sorbing compounds such as PAHs form only short plumes while stable and less sorbing compounds such as chlorinated solvents or PFAS grow rapidly to very long plumes.

2. LENGTH OF STEADY STATE PLUMES

2.1 REACTIVE TRANSPORT

If groundwater comes into contact with source zones it gets contaminated and downstream plumes will develop. If source zones are stable, which is the case for contamination with NAPLs, plumes will continue to grow in length unless the contaminants are degraded. If the overall degradation rate is balanced by the contaminant emission rate from the source, a stable steady state plume is formed. Fig. 2.1 summarizes processes relevant for plume growth and degradation. Sorption causes retardation of plume spreading until steady state conditions are reached (storage terms such as sorption do not apply for steady state, $dC/dt = 0$). In many cases biodegradation depends on the supply of electron acceptors (e.g., O_2) across the margins of the plume which react with a suitable electron donor (e.g., hydrocarbons or ammonium) as shown in Fig. 2.1 (and Fig. 2.3).

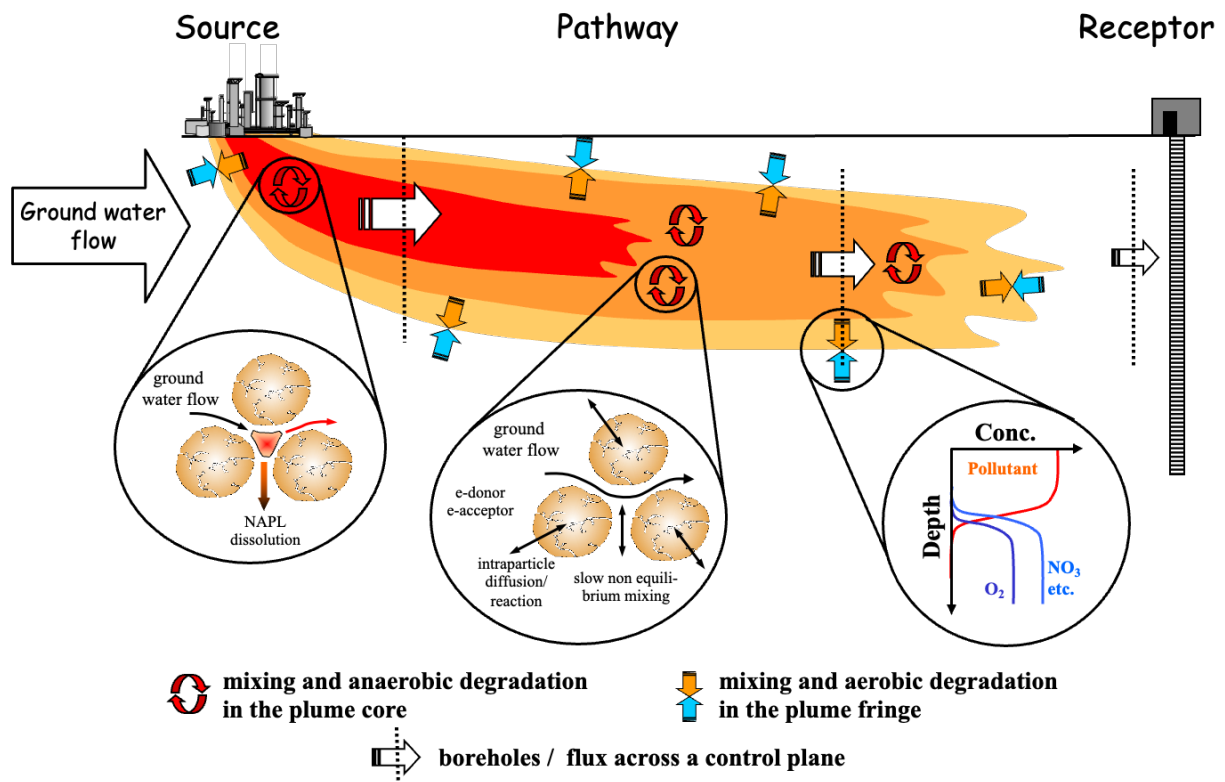


Fig. 2.1: Processes involved in plume growth

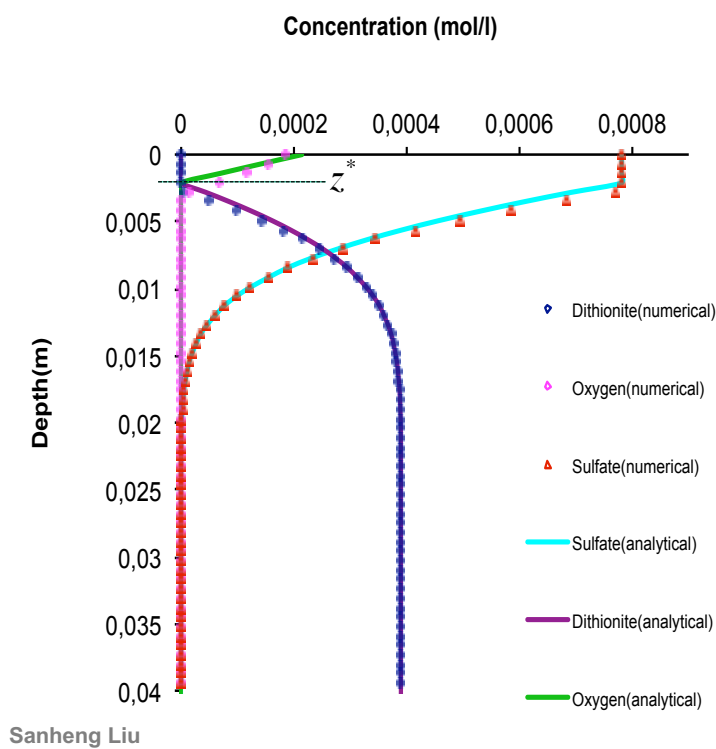
In such a scenario a reaction front moves into the plume as shown in Fig. 2.2 (Liu et al. 2010; Haberer et al., 2011, Haberer et al., 2015) and which is discussed in chap. 3 also for other simple “reaction - diffusion” problems. Theoretically the end of the plume is reached after the reaction front reached the bottom of the aquifer as depicted in Fig. 2.3. Liedl et al. (2005) derived a simple analytical solution to calculate the plume length for the scenario shown in Fig. 2.3:

$$L = \frac{4 M^2 v}{\pi^2 D_t} \ln \left(\frac{4 \gamma C_D + C_A}{\pi C_A} \right) = \frac{4 M^2}{\pi^2 \alpha_t} \ln \left(\frac{4}{\pi} \left(\frac{\gamma C_D}{C_A} + 1 \right) \right) \quad (3.1)$$

M is thickness of a plume which vertically extends over the entire aquifer. γ is a stoichiometric factor which account for how many mols of electron donor (C_D) are needed to consume one mol of electron acceptor (C_A); note, if mass based concentrations are used, then γ will change (see chap. 3 for examples). The right hand term results from replacing the transverse dispersion coefficient (D_t) by the product of the transverse dispersivity and flow velocity ($D_t = \alpha_t v$). Empirical relationships are also available for this scenario (Maier and Grathwohl, 2006):

$$L = 0.5 \frac{M^2}{\alpha_t} \left(\frac{\gamma C_D}{C_A} \right)^{0.3} \tag{3.2}$$

For similar scenarios see Ham et al. (2007) or Cirpka et al. (2006). As obvious from eq. 3.1 and 3.2 the plume length depends on mixing of electron donor and acceptor and thus α_t , which in a porous medium is a function of pore scale processes (Hochstettler et al. 2013) but also influenced by aquifer heterogeneity and structure (Werth et al., 2006; Ye et al., 2015, 2016). For more examples about dispersion dependent reactions in porous media see Haberer et al. (2014), Ye et al. (2014) or Muniruzzaman et al. (2014).



Vertical concentration profile of reactants (O_2 , Na-dithionite) and product (sulfate). The water table is at 0.005 m. Reactants are at steady state whereas sulfate cannot escape to the gas phase and accumulates...

Analytical solution

$$z^* = 2 \sqrt{D \frac{x}{v_a}} \operatorname{erfc}^{-1} \left(\frac{1}{\frac{C_{EA}}{\gamma C_{ED}} + 1} \right)$$

for arguments β between 0.25 and 1,

$\operatorname{erfc}^{-1}(\beta)$ approaches $1 - \beta \Rightarrow$

$$z^* \approx 2 \sqrt{D \frac{x}{v_a}} \left(1 - \frac{1}{\frac{C_{EA}}{\gamma C_{ED}} + 1} \right)$$

$$= 2 \sqrt{D \frac{x}{v_a}} \left(\frac{1}{\frac{\gamma C_{ED}}{C_{EA}} + 1} \right)$$

Fig. 2.2: Movement of a O_2 reaction front into a plume (from the top); from Liu et al. 2012

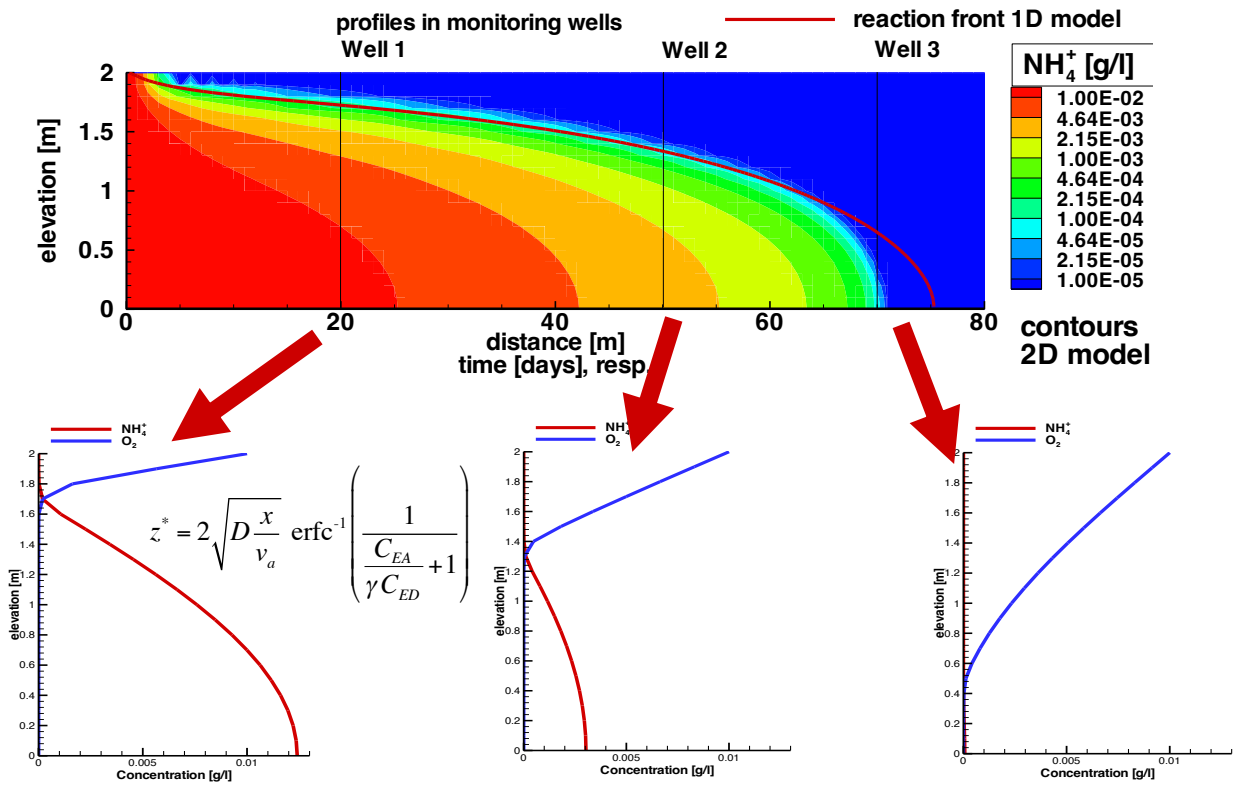


Fig. 2.3: Vertical profiles of electron donor (NH_4^+) and acceptor (O_2) concentrations in a steady state plume

Fig. 2.4 shows an example of the distribution of reactants and biomass for the case of an ammonium plume originating from a landfill which is a frequent scenario (waste filled sand and gravel pits); microbes preferentially settle where both electron donor and acceptor are available (Kappler et al., 2005). From such field investigations real world dispersivities may be calculated by using numerical reactive flow and transport models; some results are summarized in Table 2.1 which shows that in contrast to small scale laboratory investigations dispersivity at the field scale amounts often to several centimeters.

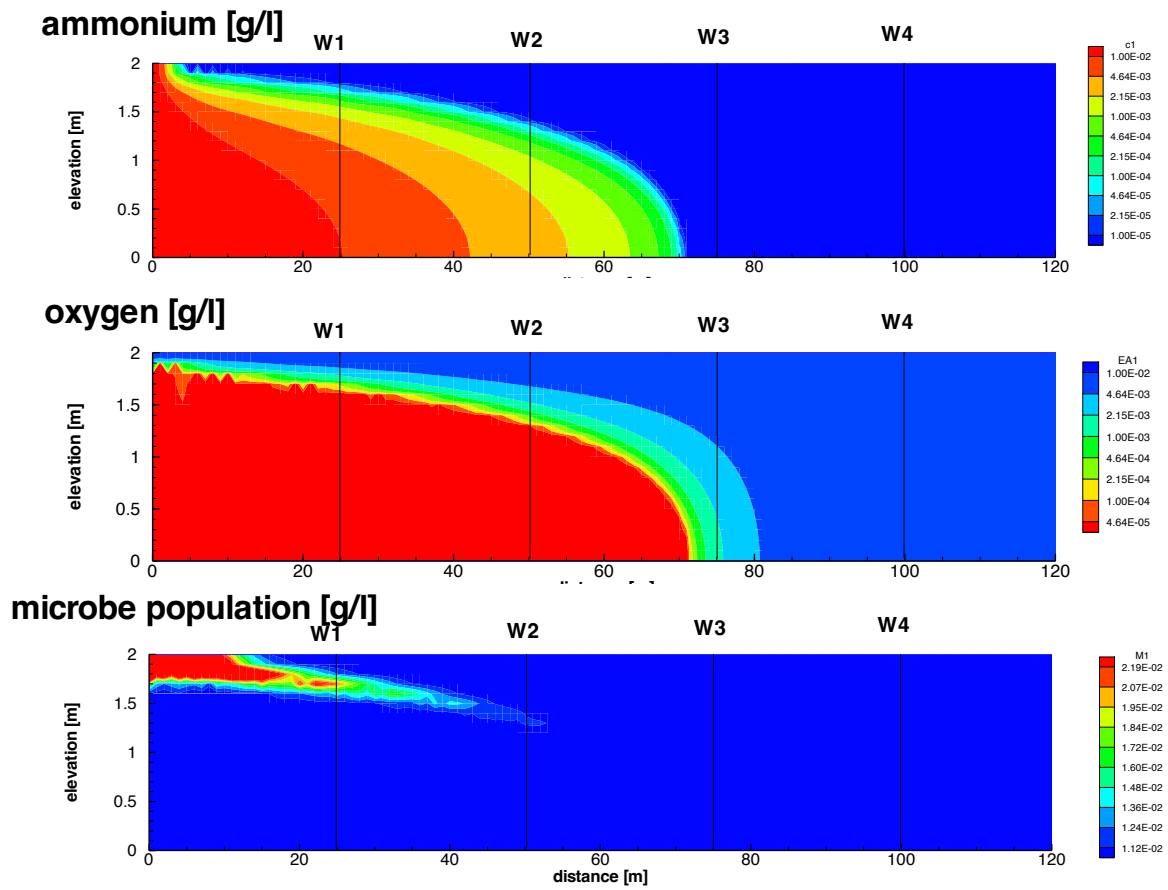


Fig. 2.4: Ammonium plume with O₂ and microbial biomass distribution

Tab. 2.1: Field scale dispersivities obtained from ammonium plumes reacting with O₂ at former landfill sites in quarternary sand and gravel deposits

Site	NH ₄ ⁺ (mg/l)	M _{Cont} (m)	M _{Aqu} (m)	L _{PLUME} (m)	α _T (cm)	Model
Osterhofen 2.7 m/d	15	4.5	4.5	580	3.2	
Röschewasser 2.65 m/d	1.5 1.0 0.3	0-3 3-5 5-12	12	400 - 140	1 - 3	
Seehof 1 m/d	5 17	0-3 3-14	14	5 500 - 1 700	3 - 10	
Cattunlache 0.1 m/d	9 5 0	0-9 9-30 30-70	70	11 000	10	

3. "REACTION - DIFFUSION" EXAMPLES

3.1 VOLATILIZATION

Many NAPL constituents (e.g., in fuels like "gasoline") are volatile and may evaporate from subsurface spills to the atmosphere. Fig. 3.1 illustrates volatilization from residual phase and Fig. 3.2 from NAPL layers floating on the groundwater table additionally affected by biodegradation. The advancement of a volatilization front as shown in Fig. 3.1 may be easily calculated by setting the mass lost to the atmosphere equal to the mass removed from the subsurface as shown in eq. 3.1. As the example shows, this is fairly slow and therefore ventilation systems typically are employed to remove the contamination in such cases. So-called "soil vapor extraction systems" are among the most powerful and efficient remediation technologies for removal of organic compounds from the unsaturated zone.

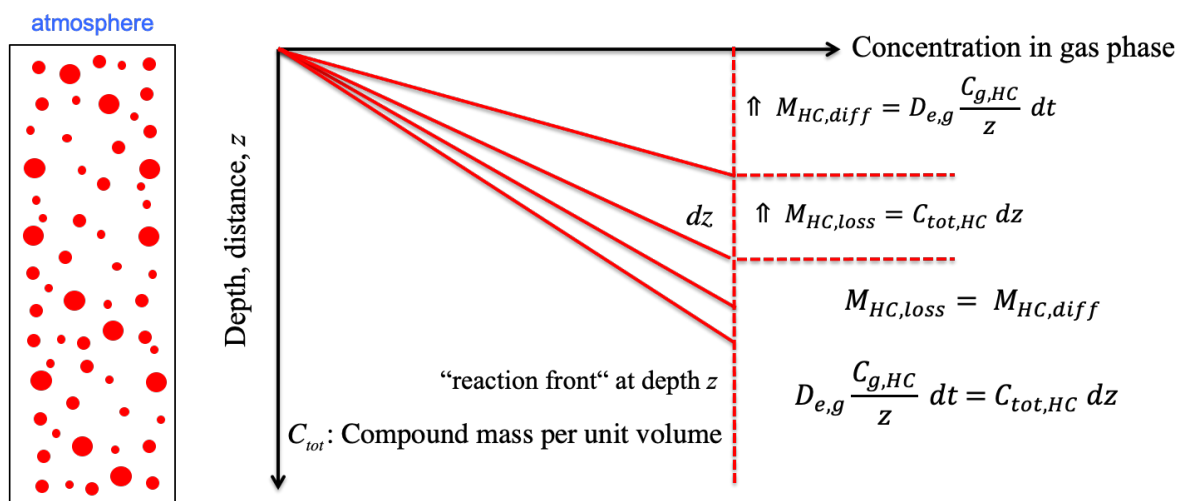


Fig. 3.1: Volatilization of residual hydrocarbons (red blobs) from the unsaturated soil zone and the progress of the volatilization front; $M_{HC,diff}$, $M_{HC,loss}$: mass diffused to the atmosphere and mass lost from the porous medium, $D_{e,g}$, $C_{g,HC}$: effective diffusion coefficient and saturation concentration of hydrocarbon in gas phase; similar approaches may be used to calculate e.g., the advance of a weathering (oxidation) front (see Fig. 3.3).

The depth of the volatilization front may be easily derived based on mass balance considerations (see also Fig. 3.1):

$$\int_0^t D_{e,g} C_{g,HC} dt = \int_0^z C_{tot,HC} z dz$$

$$D_{e,g} C_{g,HC} t = \frac{1}{2} C_{tot,HC} z^2 \quad (3.1)$$

$$z = \sqrt{2 D_{e,g} \frac{C_{g,HC}}{C_{tot,HC}} t} = \sqrt{\frac{2 D_{e,g}}{n_g R_d} t} = \sqrt{\frac{2 D_{p,g}}{R_d} t}$$

The product $n_g R_d$ is the capacity factor (α); $D_{e,g}/\alpha$ is a apparent diffusion coefficient and $D_{p,g}$ is a pore diffusion coefficient in gas phase. The retardation factor (R_d) in that case is (no sorption to soil solids considered):

$$\begin{aligned}
 R_d &= \frac{\text{total concentration}}{\text{mobile concentration}} = \frac{C_{tot,HC}}{C_{g,HC}} = \frac{C_{g,sat} n_g + \frac{C_{g,sat} n_w}{H} + n S_{NAPL}^o \rho_{NAPL}}{C_{g,sat} n_g} \\
 &= 1 + \frac{n_w}{H n_g} + \frac{n S_{NAPL}^o \rho_{NAPL}}{C_{g,sat} n_g} \approx \frac{n S_{Napl}^o \rho_{Napl}}{C_{g,sat}}
 \end{aligned}
 \quad (3.2)$$

For compound mixtures typically encountered in fuels, Raoult's law has to be employed, but since the fraction of a constituent in total mass also has to be considered in calculating the concentration in gas phase it drops out and $C_{g,sat}$ refers to the compound of interest in its pure state. The deeper the volatilization front progresses the lower the diffusion rates become and therefore removal by groundwater recharge may come into play. Fig. 3.2 compares both processes for a hypothetical case and shows that initially diffusion dominates but sooner or later seepage water advection takes over because the former progresses with the square root of time while the later advances linear with time (for retardation of the seepage water dissolution front see Box. 1.2). It should be noted that this feature generally applies: i.e., the movement of diffusion - reaction fronts dominates at early times or short distances and then advection takes over.

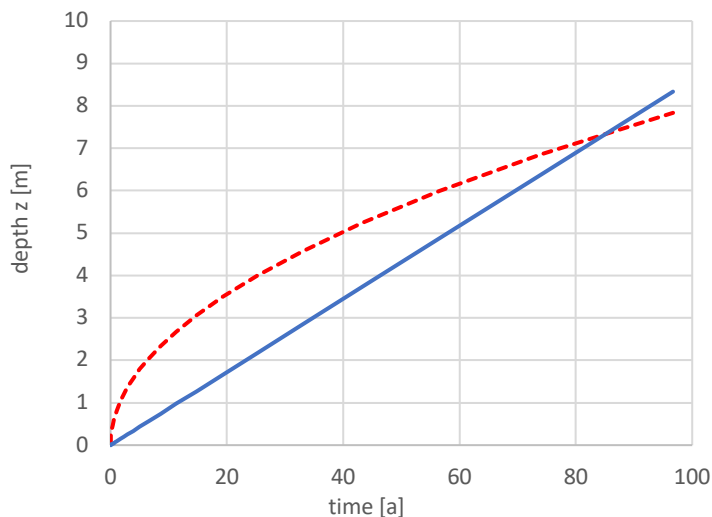


Fig. 3.2: Progress of a volatilization front in the unsaturated soil zone (dashed red) compared to dissolution by seepage water – at a certain point in time and space advection takes over ($C_{sat} = 500 \text{ g m}^{-3}$, $H = 0.2$, $D_g = 6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, $n = 0.4$, $n_w(\theta) = 0.14$, $n_g = 0.24$, $S_{NAPL}^o = 5\%$, $\rho_{NAPL} = 0.85 \text{ kg l}^{-1}$, recharge = 0.6 m a^{-1} , $R_{d,gas \text{ diffusion}} = 146$, $R_{d,recharge} = 44$)

The scenario described above is quite hypothetical and could apply to smear zones with residual NAPL in the capillary fringe. More frequent are LNAPLs floating on the groundwater table. Since many LNAPL constituents (typical non-halogenated hydrocarbons in fuels) are easily aerobically biodegraded, the concentration gradients for volatilization may be steepened. Fig. 3.3 illustrates that for a fuel layer floating on the groundwater table (“pool”). The depth of the reaction zone (z) can be easily calculated setting the flux of the electron donor (hydrocarbon) equal to the flux of the electron donor (oxygen). This scenario is based on an instantaneous reaction (fast biodegradation) which is frequently observed and may be evaluated based on the Damköhler number which is the ratio of the reaction rate to the mass transfer rate. For Damköhler numbers larger than 10 mass transfer is limiting.

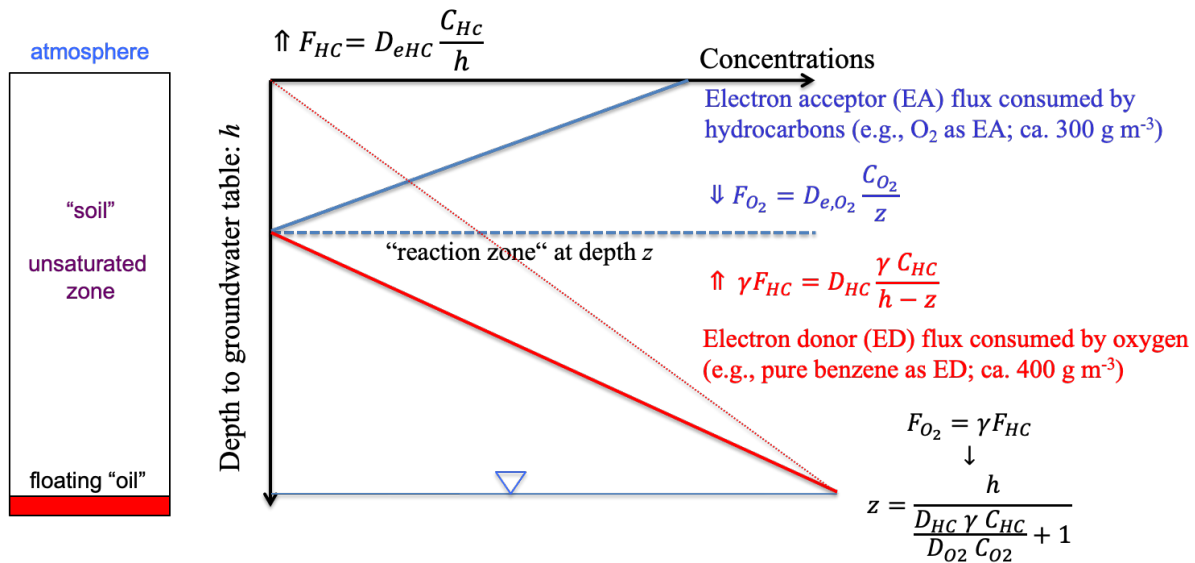


Fig. 3.3: Volatilization of residual hydrocarbons from a floating pool (red) enhanced by biodegradation in the unsaturated soil zone; F_{O_2} , F_{HC} : fluxes of electron donors and acceptors; D_{e,O_2} , D_{HC} : effective diffusion coefficient of oxygen and hydrocarbons in gas phase.

Box 3.1: Example for “reactive” volatilization

The scenario shown in Fig. 3.3 may be illustrated by the volatilization of benzene (or a similar compound). The “oxidation” stoichiometry in this case is: $C_6H_6 + 7.5 O_2 = 6 CO_2 + 3 H_2O$; thus 7.5 moles of O_2 are needed for consumption of 1 mole of C_6H_6 . Therefore, the flux of O_2 has to equal 7.5 times the flux of C_6H_6 ($F_{acceptor} = \gamma F_{donor}$). γ is the stoichiometric ratio (here 7.5 \rightarrow number of moles of O_2 consumed per mole C_6H_6). The depth (z) of the reaction zone relative to the distance to the groundwater table (h) is:

$$z = \frac{h}{\frac{D_{HC} \gamma C_{HC}}{D_{O_2} C_{O_2}} + 1}$$

D_{HC} , D_{O_2} and C_{HC} , C_{O_2} are the effective diffusion coefficients in the unsaturated soil zone and the concentrations of electron donor and acceptor at the boundaries; since this is based on the ratios of fluxes, only ratios of diffusion coefficients and concentrations are relevant. Examples for electron donor and acceptor concentrations are:

$$C_{benzene,air} = 400 \frac{g}{m^3} \approx 5 \frac{mol}{m^3}$$

$$C_{O_2,air} = 0.21 \frac{vol}{vol} \approx 210 \frac{liters}{m^3} = 9.4 \frac{mol}{m^3}$$

(1 mol O_2 = 22.4 liters)

The depth of the reaction front is:

$$z = \frac{h}{\frac{D_{HC} \gamma C_{HC}}{D_{O_2} C_{O_2}} + 1} = \frac{h}{0.4 \cdot 7.5 \frac{5}{9.4} + 1} = \frac{h}{2.6} \rightarrow 3.85 \text{ m (instead of 10 m)}$$

Thus, the volatilization rate of the benzene is accelerated by more than twice by biodegradation.

3.2 WEATHERING OF ORGANIC MATTER

A similar example is the weathering of rocks which involves the oxidation of organic matter or mineral phases such as Fe^{2+} - bearing species (pyrite, siderite, saddle dolomites). Oxygen diffuses from the atmosphere into the porous media and a reaction front develops as shown in Fig. 3.4 (see e.g., Lebedeva et al. 2007).

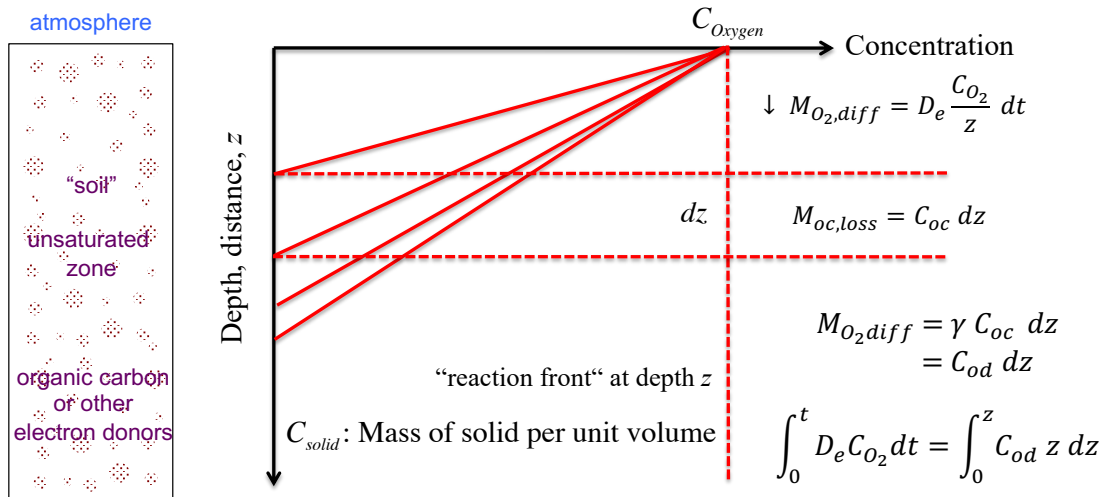


Fig. 3.4: Progress of a weathering front e.g., during oxidation of organic carbon (oc) with a fixed O_2 concentration at the subsurface; $M_{\text{O}_2,diff}$, $M_{oc,loss}$: O_2 (electron acceptor) mass diffused from the atmosphere into the porous media and organic carbon lost (electron donor), D_e , C_{O_2} , C_{oc} : effective diffusion coefficient, concentrations of O_2 and oc, γ is a stoichiometric coefficient and C_{od} denotes the oxygen demand (an analogous approach may be used to calculate the progress of an oxidation front e.g. if Fe^{2+} bearing minerals are present).

The depth of the weathering (oxidation) front (z) may be derived similar to the depth of the volatilization front discussed before based on mass balance considerations (see also Fig. 3.1):

$$\int_0^t D_e C_{\text{O}_2} dt = \int_0^z C_{od} z dz$$

$$D_e C_{\text{O}_2} t = \frac{1}{2} C_{od} z^2 \quad (3.3)$$

$$z = \sqrt{2 D_e \frac{C_{\text{O}_2}}{C_{od}} t} = \sqrt{\frac{2 D_e}{n R} t}$$

C_{od} denotes the oxygen demand as explained in Box 3.2. The product $n R$ is the capacity factor ($\alpha = C_{od}/C_{\text{O}_2}$); D_e/α is an apparent diffusion coefficient and the retardation factor (R) is α/n (or $C_{od}/(C_{\text{O}_2} n)$).

Box 3.2: Example for a “reactive” weathering front

The oxygen demand during oxidation of organic carbon depends on the stoichiometry of the reaction, e.g.: 1 mol carbon needs 1 mol O₂ for oxidation (yielding CO₂), thus 12 grams of carbon consume 32 grams of oxygen or 2.67 g of oxygen are needed to oxidize 1 gram of oc. The stoichiometric coefficient γ here is mass based (= 2.67). C_{od} may be considered as the oxygen consumption capacity (= oxygen demand) per unit volume porous medium (it also including the initially O₂ free pore space: $C_{od} = \gamma_m f_{oc} \rho_{bulk} + C_{oxygen} n$).

Example: In a water saturated porous medium the aqueous oxygen concentration is 10 g/m³ which corresponds to an oxygen content of 3.5 g/m³ per unit volume porous media if the porosity (n) is 0.35 (= $n C_{oxygen}$). For an organic carbon content of 0.1 weight percent the depth of the oxidation front after 1000 years then is:

$$z = \sqrt{2 \frac{D_e C_{oxygen}}{C_{od}} t} = \sqrt{2 \frac{D_p n C_{oxygen}}{\gamma f_{oc} \rho_{bulk} + n C_{oxygen}} t} \left(= \sqrt{2 \frac{D_p}{\frac{\gamma f_{oc} \rho_{bulk}}{n C_{oxygen}} + 1}} t \right)$$

$$= \sqrt{2 \frac{1 \times 10^{-9} \times 0.35}{2.67 \times \frac{0.001 \times 1730 \text{ kg/m}^3}{0.0035 \text{ kg/m}^3} + 1}} \times 1000 \text{ a} = \sqrt{\frac{22}{1320}} = 0.13 \text{ m}$$

Aqueous diffusion coefficients (D_{aq}) are in the order of $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; note, $D_e \approx D_{aq} n^2$; $D_p \approx D_{aq} n$.

The depth of the reaction front is quite low and thus the question comes up how deep it would be if water infiltration (groundwater recharge) is considered. The retardation factor in that case is the same as in the pure diffusion case:

$$R = \frac{C_{od}}{n C_{oxygen}} = \frac{\gamma f_{oc} \rho_{bulk} + n C_{oxygen}}{n C_{oxygen}} = \frac{\gamma f_{oc} \rho_{bulk}}{n C_{oxygen}} + 1 = \frac{2.67 \times 0.001 \times 1730 \text{ kg/m}^3}{0.0035 \text{ kg/m}^3} + 1 = 1320$$

For a groundwater recharge rate (q) of 0.5 mm d⁻¹ (=0.365/2 m a⁻¹) we get:

$$z = \frac{q t}{n R} = \frac{0.365/2}{0.35 \times 1320} \times 1000 = 0.40 \text{ m}$$

Thus, groundwater recharge dominates the progress of weathering front in the long term.

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