

V.2

Modeling bioavailability of PAH in soil

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V.2.1. Introduction

Soils contaminated with organic pollutants such as polycyclic aromatic hydrocarbons (PAH) may cause serious risks for ecosystems and humans. To reduce these risks, a lot of research into remediation processes has been carried out over the last 20 years. Initially, the remediation was focused on the cleanup of excavated soil by means of thermal treatment or wet classification/extraction. The aim was to reduce the concentration of pollutants in the soil below a so-called target value. Below this target value the soil can be considered non-polluted. In a later stage, biological treatment techniques and *in situ* treatment were developed and applied (Wilson and Jones, 1993; Mueller et al., 1996). During the last 5–10 years, the approach to solve the problem of contaminated soil has changed strongly. The assessment of risks of polluted soil for ecosystems and humans, and ways to reduce these risks, have become central issues. In this approach, the decision whether a site has to be remediated or not, and if it has to be remediated, in which way, is dependent on the risks of this site for humans and ecosystems.

Regarding the actual cleanup of soil contaminated with organic pollutants such as PAH, the attention is shifting more and more to extensive bioremediation systems such as natural attenuation, *in situ* bioremediation or a combination of these methods. In bioremediation, pollutants are biodegraded by micro-organisms such as bacteria and fungi. For this biodegradation process, favorable environmental conditions with respect to pH, redox potential, presence of nutrients, temperature and moisture content are required, as well as the presence of appropriate micro-organisms and the absence of components which may inhibit the biodegradation process (Sims and Overcash, 1983; Wilson and Jones, 1993). Besides, the organic pollutants have to be available for conversion by the micro-organisms (Bosma et al., 1997; Alexander, 2000). In general, the rate and extent at which micro-organisms biodegrade organic pollutants depends on three factors:

- the presence of the appropriate micro-organisms and the environmental conditions;
- the rate of uptake and metabolism of the pollutants by the micro-organisms;
- the rate of transfer of the pollutants to the micro-organisms.

In bioremediation research, a lot of effort has been put into the stimulation of the activity of micro-organisms by optimization of the environmental conditions for bioconversion and by augmentation (Mueller et al., 1996). However, very often this did not lead to improved bioremediation rates, especially when the bioremediation of soil polluted with PAH was considered. It has become evident that the reason for this phenomenon has to be found in the limitation of mass transfer of the pollutant to the soil micro-organisms (Chung et al., 1993; Bosma et al., 1997). This limitation of mass transfer primarily involves the limited transport rate in soil micro-regions. The slow release of PAH from the soil constituents in the soil micro-regions to the aqueous phase (moisture phase) around the soil particles, where the micro-organisms are present, is proven to be limiting for the overall biodegradation rate in many cases (Mulder, 1999; Bonten, 2001). Low mass-transfer rates caused by the low solubility of PAH in water, strong sorptive interactions of PAH with soil organic matter and diffusion limitations are responsible for the low bioavailability of PAH in soil. In general, mass transfer of pollutants to the micro-organisms is controlled by various physical/chemical transport processes, such as dissolution, diffusion, desorption, adsorption, redesorption. Also, chemical incorporation and conversion in the natural organic soil matrix may occur for PAH (Richnow et al., 1999).

In view of the previous discussion, bioavailability can be defined as the extent to which pollutants may become available for uptake by micro-organisms, soil animals and plants, leading to biodegradation, bioaccumulation and/or toxicity (Cuypers, 2001). For pollutants such as PAH, which have a low solubility in water and a strong binding to the soil matrix, bioavailability is directly related to the mass transfer rate in the soil micro-regions. A limited bioavailability is in that case defined as a limitation by mass transfer in the soil micro-region.

Insight in and understanding of the phenomenon of the limited bioavailability of pollutants is currently very poor. Better understanding of the bioavailability of pollutants not only by modeling but also by empirically quantifying bioavailability is of crucial importance for:

- assessment of the toxicological risks of a polluted site;
- evaluation of the expected decrease in risks as a result of remediation of a polluted site;
- evaluation of the potential applicability of bioremediation as cleanup method for a contaminated site;
- optimization and steering of a bioremediation process.

For a proper risk assessment, focused on the long-term prediction of anthropogenic and geogenic contaminant pathways of pollutants, quantitative insight is necessary into transport processes of the pollutants and the way these pollutants may affect soil organisms. This is also necessary for a proper assessment of potential remediation methods, and if a specific method is chosen, for an optimal control and steering of this method. Basically this quantitative insight can be obtained by the development of mechanistic transport models in which a description is given of the basic processes responsible for the transport of pollutants and the intrinsic parameters that govern this transport process. However, especially regarding transport processes of pollutants in the

soil matrices, there is a lack of quantitative insight (Luthy et al., 1997; Mulder et al., 2000, 2001). The main reason is of course the extremely complex structure of the polluted soil on the micro-scale level. Approaches mentioned in literature mainly use simplified or complex equilibrium models, which relate the concentration of organic pollutants (such as PAH) in the soil matrix and the equilibrium concentration in a surrounding water phase, although some authors also consider diffusion aspects of pollutants in soil matrices more qualitatively. These approaches may lead to incorrect calculations of transport and bioremediation processes. Another way to quantify the bioavailability of pollutants is the use of analytical tools to measure the overall bioavailability. For PAH, various methods can be mentioned:

- extraction with a water phase containing solid adsorbents, such as Tenax (Cornelissen et al., 1998);
- extraction with an aqueous solution of cyclodextrins (Reid et al., 2000; Cuypers et al., 2001);
- supercritical extraction with carbon dioxide (Hawthorne and Grabanski, 2000);
- superheated water extraction (Johnson and Weber, 2001);
- extraction with organic solvents or aqueous solutions of organic solvents (Alexander, 2000);
- oxidation with persulfate (Cuypers et al., 2000).

These methods give only limited insight into the mechanisms of the limitations of the bioavailability. They give no detailed insight into the transport processes, which take place on micro-scale in the various soil micro-domains. However, they are very often useful for an estimation of the bioremediation potential of a polluted site or a first estimation of the ecotoxicological risks of a polluted site.

This chapter primarily focuses on mechanistic models and not on empirical methods for quantifying bioavailability. The main aim of the chapter is to discuss an improved, more realistic, mechanistic transport model of PAH as an example of a group of organic pollutants, which have a low solubility in water, are omnipresent constituents of many solid waste originated from human activities, are often strongly bound to the soil matrix and can be present in various physical states in soil matrices, and to show the effect of some major intrinsic mass-transfer parameters on the environmental (bio)availability of these pollutants.

The mechanistic models will be limited to the transport of pollutants in the various types of micro-domains in the soil matrix. Additional hydraulic transport and/or micro-biological conversion processes are not discussed here. These processes are in general not limiting for the bioremediation rate and can, if necessary, e.g. in case of risk assessments, easily be integrated in these models.

In the following, first a short overview of some relevant physical/chemical properties of PAH is presented. Thereupon the physical state, the PAH pollutants may be present in soil will be discussed. Based on the various physical states, mechanistic models of the transport of PAH to a surrounding liquid phase or wet phase, where the micro-organisms are supposed to be present, are derived and results obtained with these models are considered. Finally the impact and practical applicability, as well as the limitations of these models with respect to the assessments of risks and remediation techniques are discussed. In this discussion also,

the state of the art and the present role of the empirical methods to measure the bioavailability of PAH pollutants are briefly included.

V.2.2. Properties of the pure PAH pollutants

In the evaluation of the cleanup possibilities of a soil contaminated with PAH, usually the PAH of the so-called EPA priority pollutant list are considered. Some relevant physical properties of the PAH mentioned in this list are given in Table V.2.1.

It is observed from this table that the solubility of PAH in water is extremely low, with the exception of naphthalene. The table further shows a tendency that the solubility decreases with increasing number of aromatic rings. In general, this means that the hydrophobicity of the PAH also increases with increasing molecular weight. This is also in agreement with the octanol/water partition coefficient. This coefficient in general increases with increasing molecular weight and corresponds with the phenomenon that high molecular PAH are strongly adsorbed onto organic soil substances. Strongly adsorbed PAH have of course a much lower equilibrium solubility in water and equilibrium vapour pressure than pure PAH.

A lot of research has been carried out into the biodegradability of the PAH (Mueller et al., 1996; Volkering, 1996). These studies were dealing with single PAH and mixtures of PAH. Biodegradation was studied in water, soil slurries and soil. The biodegradation process was studied with pure cultures or mixed cultures. The character of these studies

Table V.2.1. Physical and chemical properties of the most frequently occurring PAH (after Sims and Overcash, 1983).

PAH	Molecular weight	Aqueous solubility at 30°C (mg/l)	Vapour pressure (N/m ² at 20°C)	Log octanol/water partition coefficient
Naphthalene	128	31.7	6.56	3.37
Acenaphthylene	152	3.93	3.87	4.07
Acenaphthene	154	3.47	2.67	4.33
Fluorene	166	1.98	1.73	4.18
Phenanthrene	178	1.29	9.07×10^{-2}	4.46
Anthracene	178	7.3×10^{-2}	2.61×10^{-2}	4.45
Pyrene	202	1.35×10^{-1}	8.00×10^{-4}	5.32
Fluoranthene	202	2.60×10^{-1}	9.11×10^{-5}	5.33
Benz[<i>a</i>]anthracene	228	4.0×10^{-2}	6.67×10^{-7}	5.61
Chrysene	228	2.0×10^{-3}	8.40×10^{-5}	5.61
Benz[<i>a</i>]pyrene	252	4.0×10^{-3}	6.67×10^{-5}	6.04
Benzo[<i>k</i>]fluoranthene	252	1.2×10^{-3}	6.67×10^{-5}	6.57
Benzo[<i>b</i>]fluoranthene	252	5.5×10^{-4}	6.67×10^{-5}	6.84
Indeno[123- <i>cd</i>]pyrene	276	6.2×10^{-2}	1.33×10^{-8}	7.66
Benzo[<i>ghi</i>]perylene	276	2.6×10^{-4}	1.33×10^{-8}	7.23
Dibenz[<i>ah</i>]anthracene	278	5.0×10^{-4}	1.33×10^{-8}	5.97

varied from strongly fundamentally oriented to practically applicable. The observed biodegradation rates and also the final PAH concentrations that could be achieved varied strongly especially in experiments with soil. From the results it can be concluded that all PAH with three or less benzene rings, mentioned in Table V.2.1, are biodegradable (Kastner, 2000). As far as PAH with more than three rings are concerned, biodegradation is in general more difficult.

As already mentioned the rate of biodegradation of PAH in soil varies strongly. High molecular weight PAH is more recalcitrant to biodegradation than the low molecular PAH. Biodegradation is a real option for practical application, provided the conditions for biodegradation are optimal and mass transfer limitations, which often are the cause of the low bioavailability, are eliminated.

V.2.3. General concept of PAH polluted soil

Polluted soil has a very heterogeneous structure. The soil itself contains various types of soil substances in the form of particles of different size and composition, mostly aggregated to larger particles or domains. According to recent conceptual models presented in the literature, three major types of sorption domains in the soil can be distinguished, each with its specific affinity for PAH pollutants (Pignatello and Xing, 1996; Luthy et al., 1997; Cornelissen et al., 1998; Cuypers et al., 2000). These three major types are:

1. *Amorphous (natural) organic matter.* This type of organic material may also be referred to as expanded, rubbery or soft organic matter. It is likely to consist of polar structures of complex organic macromolecules integrated with a variety of low molecular weight organic compounds. The polar organic matter has relatively high oxygen content, low carbon content and low acidity. In sorption processes, the amorphous organic matter behaves like a homogeneous, gel-like partition phase, also called dissolution phase. The partitioning/dissolution phase is composed of thermally dynamic sites, which are constantly disappearing and reforming as a result of thermal motion of the humic backbone. Flexibility of the humic backbone is a result of weak cohesive forces and causes the sorption energies to average out as in a liquid phase. Sorption of hydrophobic organic contaminants to amorphous organic matter is characterized by isotherms that are linear over a wide solute concentration range. Moreover, sorption is reversible (non-hysteretic) and non-competitive. The sorption process is fast, with low activation energy and low heat of sorption. Transport is by diffusion, characterized with a high diffusivity.

2. *Condensed (natural) organic matter.* This type of organic material may also be referred to as glassy or hard organic matter. It is likely to consist of apolar structures of complex organic macromolecules that have a relatively high carbon/oxygen atomic ratio. These structures are formed by aliphatic and aromatic moieties in the organic macromolecule.

Sorption to condensed organic matter is a combination of partitioning/dissolution and specific sorption, which occurs at sorption sites provided by flexible (deformable) micropores. As a result of specific sorption, isotherms are non-linear, non-linearity being most expressed at relatively low aqueous solute concentrations. Non-linearity increases with increasing contact time. In general, sorption to the condensed organic matter domain

is more or less irreversible (hysteretic) and competitive, and characterized by slow sorption kinetics, high activation energy and a moderate to high heat of sorption. Transport is by diffusion, characterized by a low diffusivity.

A special kind of condensed organic matter is represented by highly aromatic coal or soot particles, which have an extremely high affinity for hydrophobic organic contaminants. Sorption sites in these particles are provided by rigid (non-flexible) pores.

3. *Micropores of mineral material.* This sorption domain is of particular importance in relatively dry material with little organic matter. In general, sorption in micropores is slow, hysteretic and competitive. In accordance, sorption isotherms are non-linear. In the pores, steric effects may occur due to strongly constricted regions. The sorption process is characterized by high activation energy and a moderate to high heat of sorption.

Besides absorption or adsorption of PAH in the above-mentioned soil domains, dependent on the anthropogenic activities which caused the pollution of the soil, PAH may also be present as (Rulkens and Bruning, 1995):

4. *particulate pollutants of pure PAH.*

5. *pure PAH pollutant in soil pores.*

6. *PAH dissolved in the water phase of water-filled pores in the soil.*

7. *PAH adsorbed to the pore walls of water-filled pores in the soil.*

8. *PAH present in a pure organic liquid phase, e.g. a mineral oil phase.*

It should also be noted that this overall picture of a polluted soil, schematically shown in Figure V.2.1, is beyond reality, which is much more complex. However, also from simplified models quantitative information regarding the environmental availability of pollutants, characteristic to the actual situation, can be derived. Because transport and release of pollutants, such as PAH, always take place via a surrounding water phase or wet phase, we will limit our further discussion to the situation that the soil particles are surrounded by a water phase. It is further assumed that the PAH concentration in this water phase is almost zero. In that case, the desorption and dissolving rates are maximal.

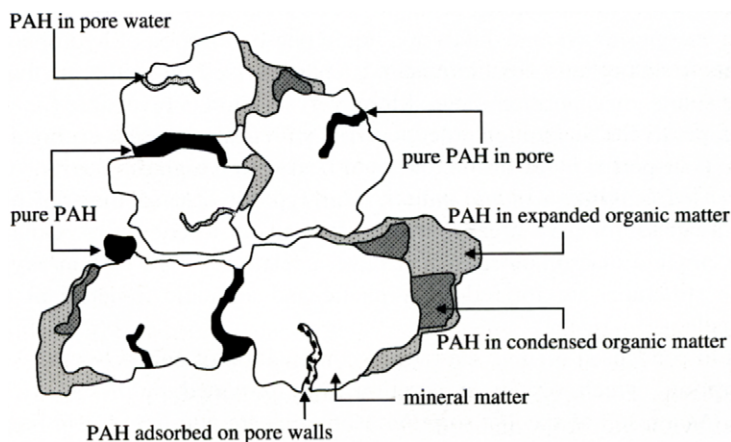


Figure V.2.1. Schematic representation of a PAH polluted soil.

The subsequent transport of the pollutants released from the soil micro-region via the water phase is not discussed here because there are already numerous models for this type of transport. We will consider now in detail the following four strongly simplified cases.

- (a) Dissolving spherical particles consisting of pure PAH into a water phase in dependence of the solubility of PAH in pure water, C_s and the radius R_0 of the particle. It is assumed in the model that the mass transfer coefficient in the water phase outside the particle, k , can be calculated from $Sh = 2kR_0/D_1 = 2$, where Sh is the Sherwood number and D_1 the diffusivity of PAH in the water phase.
- (b) Dissolving pure PAH out of pores (length L) of a soil matrix. Initially these pores are completely filled with PAH. Dissolving the PAH causes a retreat of the PAH–water interface in the pores. It is assumed that no resistance for mass transfer exists outside the particle.
- (c) Diffusion of PAH out of a homogeneous spherical organic soil matrix consisting of either an amorphous expanded organic phase or a condensed organic phase. Transport is governed by the diffusivity D_s . It is assumed that no resistance for mass transfer exists outside the particle.
- (d) Diffusion of PAH, adsorbed to the inner pore walls of a porous spherical soil particle in which the pores are homogeneously distributed. The transport process of pollutants in such a particle is mathematically analogous to the transport in a homogeneous particle. The diffusion process has to be now described by means of an effective pore diffusivity D_{por} , which is defined as $D_{por} = D_1/(1 + ma_s/\varepsilon)f_t$, where m is the ratio between the surface concentration of PAH at the pore walls and the equilibrium concentration of PAH in the water phase in the pore, a_s the specific surface area of the pore walls, ε the porosity of the particle and f_t the tortuosity of the pores.

The other cases which have been identified as being possible will not be discussed here because they can be described in a more or less similar way as will be given for the selected cases.

V.2.4. Mathematical models

V.2.4.1. The dissolving of a pure particulate pollutant

Figure V.2.2 shows the diagram of a single, solid spherical particle with initial radius R_0 and consisting of a pure pollutant that is more or less soluble in the surrounding liquid water phase. The mass flux N of this pollutant at the solid/liquid interface is expressed by the following equation

$$N = k(C_s - C_{bulk}) \quad (V.2.1)$$

where k is the mass transfer coefficient and C_s the concentration of the pollutant in the liquid phase at the interface (which is equal to the solubility of the pollutant). The mass transfer coefficient k depends on the flow conditions around the particle, which are characterised by the Reynolds number (Re)

$$Re = 2\rho v_p R / \eta \quad (V.2.2)$$

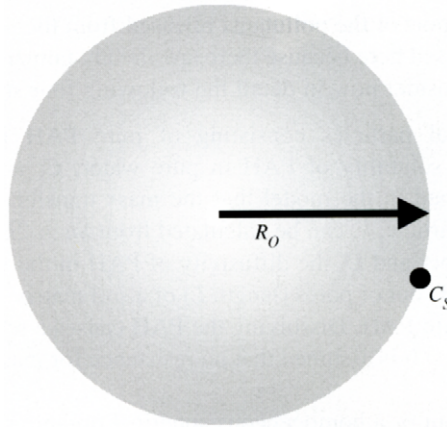


Figure V.2.2. Particle pollutant.

where ρ is the density of the liquid, v_p the relative velocity between the particle and liquid phase, R the radius of the particle and η the dynamic viscosity of the liquid. The value of k can be calculated from the following semi-empirical relationship:

$$Sh = 2 + 0.6Re^{1/2}Sc^{1/2} \quad (V.2.3)$$

In this equation, Sh represents the Sherwood number, which is defined by

$$Sh = 2kR/D_1 \quad (V.2.4)$$

where D_1 is the molecular diffusivity of the pollutant in the liquid phase. Sc represents the Schmidt number, which is given by

$$Sc = \eta/\rho D_1 \quad (V.2.5)$$

If $Re \ll 1$, which is the case for small particles and for large particles if the relative velocity is small, then Equation (V.2.3) can be simplified by

$$Sh = 2kR/D_1 = 2 \quad (V.2.6)$$

If it is assumed that $C_{bulk} = 0$, then it follows from Equations (V.2.1) and (V.2.6) that

$$N = D_1 C_s / R \quad (V.2.7)$$

Radius R is not constant but will decrease over time t during the dissolving process. This process may be considered quasi-stationary and expressed as follows:

$$-\rho_s \frac{dR}{dt} = N \quad (V.2.8)$$

where ρ_s is the density of the solid particle. Substitution of Equation (V.2.7) in Equation (V.2.8) and integration of the resultant differential equation under the initial condition:

$$R = R_0 \quad t = 0 \quad (V.2.9)$$

results in the following relationship between t and R :

$$R^2 = R_0^2 - 2D_1C_s t / \rho_s \tag{V.2.10}$$

The total time τ_{sol} required for complete dissolving of the particle can be calculated from Equation (V.2.10) and is given by

$$\tau_{sol} = \frac{\rho_s R_0^2}{2D_1 C_s} \tag{V.2.11}$$

In practice, there are no great variations in the diffusivity D_1 of a pollutant in an aqueous liquid phase. However, this does not apply to its particle radius R_0 and solubility C_s . The effect of R_0 and C_s on τ_{sol} is given in Figure V.2.3, assuming that $D_1 = 10^{-5} \text{ cm}^2/\text{s}$ and $\rho_s = 1 \text{ g/cm}^3$. The figure shows that for particles with a radius of $1000 \text{ }\mu\text{m}$, τ_{sol} will decrease approximately from 10^6 to 10 days if the solubility increases from 0.005 to 500 mg/l . If the same range of solubility values is assumed for particles with $R_0 = 100 \text{ }\mu\text{m}$, then the value of τ_{sol} will vary approximately between 10^{-1} and 10^4 days. For particles with $R_0 = 10 \text{ }\mu\text{m}$, the value of τ_{sol} is always lower than 100 days.

It should be noted that Figure V.2.3 gives a simplified picture of the reality. In practice, C_s may be influenced by additives (e.g. surfactants) or natural complexing agents. This will result in lower dissolving times.

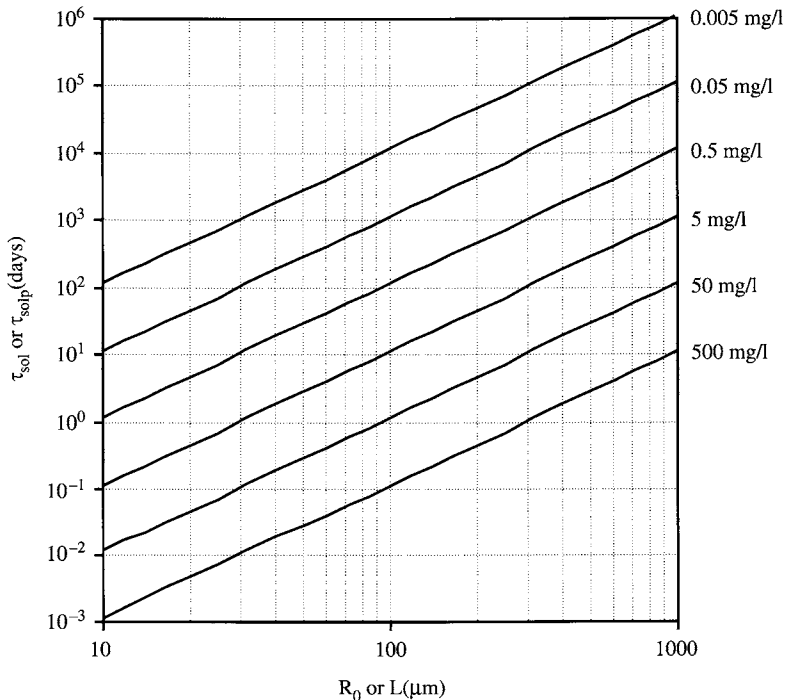


Figure V.2.3. Dissolving time of a particle pollutant with radius R_0 (τ_{sol}). Desorption time of a pollutant from a pore with length L (τ_{solp}). Parameter is the solubility (C_s).

V.2.4.2. The diffusion of pollutants from a soil particle

V.2.4.2.1. The diffusion of a solid pollutant out of a soil pore

Figure V.2.4 is a diagram of a pore in a spherical soil particle. Initially, the pore is filled with pure pollutant in the solid state. When it comes into contact with water, the pollutant will dissolve in the liquid phase. As a result, the pollutant–water interface will move inwards and the water will penetrate into the pore. At the interface, the concentration of the pollutant in the water is equal to its solubility. Because the pore diameter is relatively small, the transport of the pollutant through the liquid phase in the pore occurs by molecular diffusion. The velocity at which the liquid/pollutant interface moves inwards is relatively low, and this means that the diffusive transport through the liquid phase present in the pores may be considered quasi-stationary. Under this assumption, the concentration profile of the pollutant in the liquid phase in the pore may be considered linear. The mass flux N of the pollutant in the pore can then be expressed as follows:

$$N = D_1(C_s - C_{R_0})/l \quad (\text{V.2.12})$$

where C_{R_0} is the concentration of the pollutant in the liquid phase at the particle surface. The mass flux of the pollutants at the particle surface is represented by

$$N = k(C_{R_0} - C_{\text{bulk}}) \quad (\text{V.2.13})$$

If it is assumed that $C_{\text{bulk}} = 0$, then it follows from Equations (V.2.12) and (V.2.13) that

$$N = \frac{D_1 k}{D_1 + kl} C_s \quad (\text{V.2.14})$$

The change in length l of the section of the pore that is filled with water is given by

$$\rho_s \frac{dl}{dt} = N \quad (\text{V.2.15})$$

Substitution of Equation (V.2.14) in Equation (V.2.15) and integration of the differential equation, under the condition that initially $l = 0$ at $t = 0$, results in the

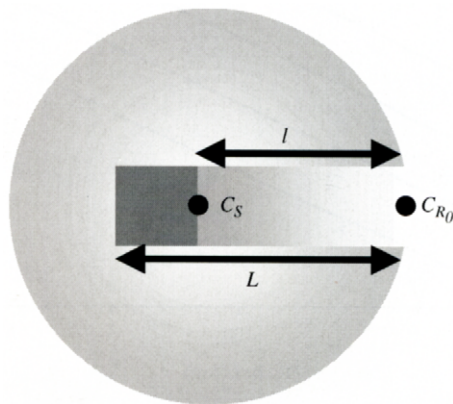


Figure V.2.4. Diffusion of a solid pollutant from a pore.

following relationship between l and t :

$$\frac{l^2}{2D_1} + \frac{l}{k} = \frac{C_s}{\rho_s} t \tag{V.2.16}$$

From Equation (V.2.16), it is possible to calculate the total time τ_{solp} required for the complete desorption of the pollutant from the pore

$$\tau_{\text{solp}} = \frac{\rho_s L^2}{2D_1 C_s} \left(1 + \frac{D_1}{Lk} \right) \tag{V.2.17}$$

where L is the total length of the pore. The mass transfer coefficient k is given by Equation (V.2.3). From Equations (V.2.3) and (V.2.4), it is clear that for relatively large particles and pore lengths in the order of R_0 the value of k satisfies the relationship $k \gg D_1/L$. Equation (V.2.17) can then be simplified to

$$\tau_{\text{solp}} = \frac{\rho_s L^2}{2D_1 C_s} \tag{V.2.18}$$

For small particles ($Re \ll 1$) and/or pores with a length L considerably smaller than R_0 , the value of τ_{solp} is higher than according to Equation (V.2.18). In Figure V.2.3, the value of τ_{solp} is given as a function of L with the solubility C_s as parameter. The equations for τ_{sol} and τ_{solp} are, in fact, similar. This means that the conclusions drawn for a spherical particle are also relevant to the transport of a solid pollutant from a pore.

V.2.4.2.2. *The diffusion of pollutants from a homogeneous soil particle*

Figure V.2.5 shows a homogeneously polluted, spherical soil particle. When it comes into contact with water phase, the pollutant will be transported by diffusion. The general diffusion equation for the transport of this pollutant in the spherical particle is given by

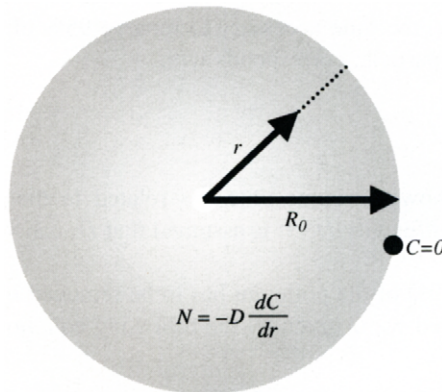


Figure V.2.5. Diffusion of pollutant from a homogeneous soil particle.

the following equation:

$$\frac{\partial C}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial C}{\partial r} \quad (\text{V.2.19})$$

where D_s is the molecular diffusivity of the pollutant in the soil particle and r the coordinate in the direction of transport. Because generally D_s will be much smaller than D_1 , it may be assumed that there is hardly any resistance to mass transfer on the outside of the particle. Assuming that the bulk concentration of the pollutant in the water phase is zero, the initial and boundary conditions of Equation (V.2.19) are

$$C = C_0 \quad t = 0 \quad 0 \leq r \leq R_0 \quad (\text{V.2.20})$$

$$C = 0 \quad t > 0 \quad r = R_0 \quad (\text{V.2.21})$$

$$-D_s \frac{\partial C}{\partial r} = 0 \quad t > 0 \quad r = 0 \quad (\text{V.2.22})$$

From the solution of Equations (V.2.19)–(V.2.22), it follows that the ratio between the mean pollutant concentration in the sphere (\bar{C}) and the initial concentration (C_0) is a function of only the Fourier number (Fo), which is defined as

$$Fo = \frac{D_s t}{R_0^2} \quad (\text{V.2.23})$$

If $Fo > 0.02$, then the relation between \bar{C} and C_0 can be given by the following equation (Crank, 1964):

$$\frac{\bar{C}}{C_0} = \frac{6}{\pi^2} e^{-\pi^2 Fo} \quad (\text{V.2.24})$$

In practice, the relative quantity of a pollutant that must be removed in order to satisfy clean-soil standards varies from less than 90% to more than 99%. From Equation (V.2.24), it can be derived that τ_{95} , the time necessary to remove 95% of the amount of pollutant originally present in the particle, corresponds with

$$Fo = \frac{D_s \tau_{95}}{R_0^2} = 0.25 \quad (\text{V.2.25})$$

Figure V.2.7 shows how the value of τ_{95} is related to the particle radius R_0 . The parameter is molecular diffusivity D_s . It is assumed that D_s can vary between 2.5×10^{-6} and 2.5×10^{-12} cm²/s.

If it is assumed that 99% of the pollutant has to be removed in order to obtain a clean soil, then the time required τ_{99} is given by the following equation:

$$Fo = \frac{D_s \tau_{99}}{R_0^2} = 0.42 \quad (\text{V.2.26})$$



Figure V.2.6. Diffusion of soluble and adsorbed pollutant Left: porous particle. Right: pore in porous particle.

V.2.4.3. The diffusion of soluble and adsorbed pollutants from the pores of a porous particle

Figure V.2.6 shows a porous, spherical soil particle where the pollutant is present in the water phase in the soil pores. The pollutant is partly adsorbed onto the pore walls and partly dissolved in the liquid phase in the pores. It is assumed that there is a proportional relationship between the equilibrium concentration of the pollutant in the pores (C) and the adsorbed concentration of the pollutant at the pore wall (C_{ad}):

$$C = C_{ad}/m \tag{V.2.27}$$

where m is a constant. It is also assumed that the concentration gradient of the pollutant in the radial direction in the pores is always negligible compared to the concentration gradient in the longitudinal direction. If a homogeneous distribution of pores in the porous particle is assumed, the diffusion equation for the transport of the pollutant in the porous sphere is given by

$$\varepsilon \frac{\partial C}{\partial t} + a_s \frac{\partial C_{ad}}{\partial t} = \varepsilon \frac{D_1}{r^2 f_t} \frac{\partial}{\partial r} r^2 \frac{\partial C}{\partial r} \tag{V.2.28}$$

where ε is the porosity of the soil particle, a_s the specific surface area of the pore walls and f_t the tortuosity of the pores. Substitution of Equation (V.2.27) in Equation (V.2.28) results in

$$\frac{\partial C}{\partial t} = \frac{D_{por}}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial C}{\partial r} \tag{V.2.29}$$

where

$$D_{por} = \frac{D_1}{(1 + ma_s/\varepsilon)f_t} \tag{V.2.30}$$

Assuming that the concentration of the pollutant in the surrounding liquid phase is zero and that there is no mass transfer limitation outside the particle, the initial and boundary

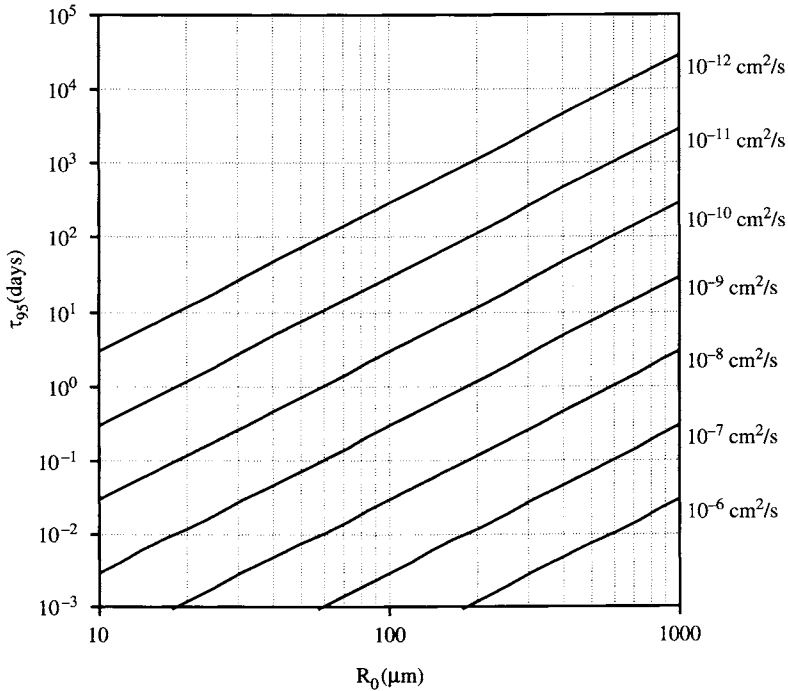


Figure V.2.7. Diffusion time necessary to remove 95% of the amount of pollutant (τ_{95}) as a function of particle radius R_0 . Parameter is the diffusivity D_s or D_{por} .

conditions of Equation (V.1.2.29) can be given by

$$C = C_0 \quad t = 0 \quad 0 \leq r \leq R_0 \quad (\text{V.2.31})$$

$$C = 0 \quad t > 0 \quad r = R_0 \quad (\text{V.2.32})$$

$$-D_{por} \frac{\partial C}{\partial r} = 0 \quad t > 0 \quad r = 0 \quad (\text{V.2.33})$$

The solution of Equation (V.2.29) is identical to that of Equation (V.2.19). The time τ_{95} necessary to remove 95% of the amount of pollutant originally present in the particle is given in Figure V.2.7 as a function of R_0 and with parameter D_{por} . It will be clear from Equation (V.2.30) that in the case of strong adsorption (corresponding with a high value of m) and a high specific adsorption area a_s , the value of D_{por} will be considerably lower than that of D_l . Consequently, in practice, long residence times are necessary in order to attain the almost complete desorption of a pollutant from the soil particle.

V.2.5. Discussion

In the foregoing paragraph, mechanistic models for the mass transport rate of PAH pollutants from specific separate micro-regions have been derived. The mass transfer rate

strongly depends on the physical state of the PAH pollutants, the characteristic dimensions of the micro-domains, the diffusivity in these micro-domains, the adsorption coefficient and the water solubility of these pollutants. The mechanistic models have been derived for well defined micro-domains. The reality is of course more complicated than these model micro-domains suggest. In reality, a large number of different PAH hydrocarbons will be present simultaneously with strong varying relative concentrations. The release of these PAH to the water phase or wet phase is much more complex than the mechanistic models suggest. It can be expected that initially especially the low molecular PAH will release from the matrix and that later on this occurs for the high molecular PAH. Due to differences not only in solubility, but also in diffusivity of the different PAH, the relative concentration of the different PAH in the water phase can strongly deviate from the relative concentrations of PAH in the soil matrix. Not only the relative concentrations, but also the absolute concentrations, will change with time due to microbial and chemical conversion or further transport of PAH in the water phase. The phenomenon ageing is also strongly influencing this process.

The micro-domains have seldom the well-defined simple structure as assumed in the mechanistic models. A micro-domain can be encapsulated by other micro-domains, so that the transport pathways for the pollutants are longer than the characteristic size of one micro-domain. Micropores inside several micro-domains can be connected with each other. Besides it has to be noticed that the microporous structure (and this also holds for the macroporous structure) of the polluted soil is not a fixed property but changes continuously with time. This not only holds for the size of the various micro-domains but also for the physical properties of these micro-domains, the size and length of the micro- and mesopores in these domains and the degree of aggregation and encapsulation of these micro-domains.

It is evident that not only the concentration of PAH but also the distribution of PAH over the various micro-domains will change with time. This change concerns three ways. It can be expected that the amount of PAH present as pure particulate PAH and also the size of these particles will decrease in time. Besides PAH will diffuse more deeply into condensed or expanded soil organic matter. Part of the PAH will also be incorporated into the natural organic matter of the soil. All these processes cause a decrease in the bioavailability of the PAH pollutants in soils in course of time. The phenomenon of decreased availability in course of time is also clearly observed in practise and is indicated as ageing or weathering. The final conclusion from this picture is that the (bio)availability should be handled as a dynamic process.

The practical value of the mechanistic models, as derived in the previous paragraphs, is that these models give at least a semi-quantitative indication of the bioavailability of the pollutant at a certain moment. A prerequisite to be able to use these models for practical purposes is that some relevant data regarding the micro-domains and the PAH in these micro-domains are available. These data are the size of the micro-domains, the diffusivity of the PAH in these domains, the distribution of PAH over these domains and the solubility of PAH in the water phase surrounding these domains. To obtain sufficiently accurate data it will be clear that advanced analytical techniques and tools are necessary. Experience in this respect is however still very limited. A long way still has to be gone. The assessment of ecotoxicological risks and also of bioremediation methods require information about possible changes of the porous structure in course of time.

In case of risk assessment, periods of several years up to more than 100 years have to be considered. However, as is pointed out in the foregoing paragraph, it can be expected that the bioavailability of PAH pollutants, assessed for the micro-domains, will decrease in course of time. This means that the risk assessments can safely be based on the actual bioavailability. In case of bioremediation, the time scale varies from one year or less to 10 years or more. Strong intrinsic changes of the structure of the micro-domains cannot be expected for that period. However, a change in the structure of the micro-domains may be possible due to the application of external processes which are applied to the soil during the bioremediation process such as heating, soil flushing, ultrasonic treatment and so on.

Due to the lack on advanced analytical techniques and tools or practical experience with existing tools, the mechanistic models have at present a limited significance. However, as already mentioned in the introduction, there are some tools to quantify the overall (bio)availability. The first technique is to carry out biodegradation experiments on lab scale. A drawback of this method is that a long experimental period is required to obtain reliable data. Other methods mentioned are solid phase extraction with water or an aqueous solution of cyclodextrin, extraction with an organic solvent or a mixture of water and an organic solvent and extraction with supercritical CO₂. The first method is also quite laborious and requires long-term experiments while the other methods are still in the laboratory stage. A very promising method is the use of a rapid oxidation method, using persulfate. With this oxidation method the PAH bound to expanded organic matter and probably also the PAH present as pure PAH can be easily determined. All methods have the drawback that they can insufficiently distinguish between the various physical states, PAH are present in the micro-domains of the soil. The practical applicability of these methods for risk assessment studies is less than those for assessment of the bioremediation potential and the steering of the bioremediation process.

V.2.6. Concluding remark

The main conclusion from the foregoing is that modeling and quantifying the bioavailability of PAH (and other organic pollutants) is very complex, mainly due to the heterogeneous structure of the soil and the lack of experience with advanced analytical techniques and tools. Nevertheless the mechanistic models derived here provide a basis for a first estimation of bioavailability of PAH pollutants in soil. Further developments are necessary to get a sufficiently accurate picture of bioavailability. Also, knowledge regarding changes in bioavailability in course of time is necessary. Analytical tools to measure the (macroscopic) overall bioavailability of PAH may support further developments of these mechanistic models to practical application.

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