**DIFFUSION IN NATURAL
POROUS MEDIA:
Contaminant Transport,
Sorption/Desorption and
Dissolution Kinetics**

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**DIFFUSION IN NATURAL
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by

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For Marianne and Max

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FOREWORD

The book is intended for geologists, hydrogeologists, and environmental engineers, who need to quantify transport phenomena in the field involving the molecular diffusion of organic contaminants in natural porous media such as soils, sediments, rocks, waste liner materials, etc. Since sorption/desorption kinetics as well as dissolution rates of organic contaminants are limited by slow molecular diffusion, emphasis is placed on the discussion of these processes. The book compiles methods for calculation of diffusion coefficients of organic compounds in aqueous solutions and vapor phase, as well as in natural porous media. Modeling of diffusive transport for various initial and boundary conditions is treated extensively based on analytical solutions of Fick's 2nd law and some simple numerical models (which may be solved using spreadsheets). Data are supplied on sorption/desorption rates of organic compounds in various soils and aquifer materials as well as on the dissolution kinetics of nonaqueous phase liquids (trapped residual phase and pools) in aquifers. Finally, the widespread difficulties in soil and groundwater decontamination which are due to slow diffusion processes are discussed, together with implications for groundwater risk assessment.

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Notation

The abbreviations shown in brackets represent the dimensionality of the variable being used: M = mass; L = length; L³ = volume, t = time.

a = grain or particle radius [L]
 A_o = specific surface area, e.g. interfacial area per m³ porous medium [L² L⁻³]
 A/V = surface to volume ratio of a particle [-]
 b, c, d = edges of slabs, parallelepipeds, cubes [L]
 C = solute concentration in aqueous or vapor phase [M L⁻³]
 C_{eq} = equilibrium solute concentration in aqueous or vapor phase [M L⁻³]
 C_g = solute concentration in vapor phase [M L⁻³]
 C_{oc} = equilibrium solute concentration normalized to organic carbon [M L⁻³]
 C_{om} = equilibrium solute concentration normalized to organic matter [M L⁻³]
 S = saturation concentration of solute in aqueous or vapor phase [M L⁻³]
 C_w = solute concentration in water [M L⁻³]
 $C_{i,w}$ = aqueous concentration of component i from a complex mixture [M L⁻³]
 d = thickness of a layer or slab [L]
 d_s = solid density [M L⁻³]
 D = diffusion coefficient [L² t⁻¹]; D' = normalized diffusion coefficient [-]
 D_a = apparent diffusion coefficient [L² t⁻¹]
 D_a/a^2 = diffusion rate constant [t⁻¹]
 D_{air} = diffusion coefficient in air [L² t⁻¹]
 D_{aq} = diffusion coefficient in aqueous phase [L² t⁻¹]
 D_g = diffusion coefficient in gas phase [L² t⁻¹]
 D_e = effective diffusion coefficient [L² t⁻¹]
 D_{eg} = effective (gas) diffusion coefficient [L² t⁻¹]
 D_p = pore diffusion coefficient [L² t⁻¹]
 D_{poly} = polymer diffusion coefficient [L² t⁻¹]
 $D_{s,e}$ = effective surface diffusion coefficient [L² t⁻¹]
 f = fractional uptake at equilibrium [-]
 f_{oc} = fraction of organic carbon [-]
 F = diffusive flux [M L⁻² t⁻¹]
 F' = normalized diffusive flux [-]
 F_f = formation factor [-]
 F_{stat} = steady state diffusive flux [M L⁻² t⁻¹]
 h = thickness of an aquifer [L]
 H = Henry's law constant [-]
 i = hydraulic gradient [-]
 k_f = hydraulic conductivity [L t⁻¹]
 K = BET sorption coefficient [L³ M⁻¹]
 K_d = distribution coefficient, sorption coefficient [L³ M⁻¹]
 $K_{d,a}$ = nonequilibrium, apparent sorption coefficient [L³ M⁻¹]
 K_{Fr} = Freundlich sorption coefficient [L³ M⁻¹]
 K_L, K_T = Langmuir, Toth sorption coefficient [L³ M⁻¹]

K_{oc} = organic carbon based distribution coefficient, sorption coefficient [$L^3 M^{-1}$]
 K_{om} = organic matter partition coefficient [$L^3 M^{-1}$]
 K_{ow} = octanol/water partition coefficient [-]
 L_c = length of contaminated zone [L]
 l = (shortest) distance in porous media [L]
 l_e = effective path length in porous media [L]
 m = Archie's law exponent [-]
 m_d = solid mass [M]
 $m_{air}, m_g, m_{sol}, m_s$ = molecular weight of air, gas, solvent and solute, resp. [$g\ mol^{-1}$]
 M = mass of solute which has diffused into / out of a particle or porous medium [M]
 M_{eq} = mass of solute in a particle under equilibrium conditions [M]
 M_s = mass of solute in a particle at a given time [M]
 M_{te} = mass of solute in a particle after a certain exposition time t_e [M]
 n = intergranular porosity [-]
 n_e = (flow) effective porosity [-]
 n_g = air filled porosity [-]
 q = sorbed concentration, sorbate concentration in a solid [$M\ M^{-1}$]
 q_{max} = maximum sorbate concentration in a solid [$M\ M^{-1}$]
 r = radial distance [L]
 r_h = hydraulic radius [L]
 oc = organic carbon content [$mg\ kg^{-1}$]
 P = pressure [atm]
 P_x = probability
 Re = Reynolds number [-]
 R_d = Retardation factor [-]
 R_p = pore retardation factor [-]
 S = water solubility [$M\ L^{-3}$]
 Sc, Sh = Schmidt number and Sherwood number [-]
 S^o = saturation degree, water and NAPL [-]
 T = temperature [K, $^{\circ}C$]
 t = time [t]
 t_c = mean residence time; contact time[t]
 t_e = exposure (equilibration) time [t]
 t_{lag} = lag-time [t], time to reach about 1/3 of steady state conditions
 t_{90}, t_{99} = time to desorb 90% 99% of a contaminant [t]
 v_a = groundwater flow velocity [$L\ t^{-1}$]
 V_{air}, V_g = molar volume of air and gas [$L\ mol^{-1}$]
 V_{om} = molar volume of organic matter [$L\ mol^{-1}$]
 V_w = volume of water, i.e. in a batch system [L^3]
 V' = LeBas molar volume [$cm^3\ mol^{-1}$]
 w, w_{ad} = water content based on dry weight of solids, weight fraction of water adsorbed onto solids (e.g. at a relative humidity of 98.8 % [-]
 x = distance [L]
 X_i = fraction of solute in component i under equilibrium conditions;
 and fraction of instantaneous sorption [-]

X_S = length of mass transfer zone; saturation distance [L]

Z_o = thickness of contaminated zone [L]

Z_S = equivalent saturation height in pool dissolution [L]

$\bar{z}$ = mean square displacement (vertical)

$1/n$ = Freundlich exponent [-]

Greek symbols

α = capacity factor ($\varepsilon + K_d \rho$) [-]

α_t = transverse, vertical dispersivity [$L^2 s^{-1}$]

β = ratio of solute mass dissolved to mass in the solid phase in a batch system [-]

δ = constrictivity factor (<1) [-]

ε = porosity of porous media, intraparticle porosity [-]

ε_t = transport-through porosity [-]

γ = proportionality factor (first order and diffusion kinetics) [-]

$\gamma_{i,w}$, $\gamma_{i,o}$ = activity coefficient in water or organic mixture [-]

γ_{om} = activity coefficient in organic matter [-]

η = dynamic viscosity [$N s m^{-2}$; Pa s; $J s m^{-3}$]

λ = first order rate coefficient [$L t^{-1}$]

λ_p = ratio of molecular solute diameter to pore diameter [-]

θ = liquid to solid ratio in a batch sorption system; NAPL filled porosity [-]

ρ = bulk density of porous media [$M L^{-3}$]

ρ_o , ρ_{om} = density of an organic liquid and organic matter [$M L^{-3}$]

σ = standard deviation [-], cosolvent power

σ_{aq} , σ_{rock} = electrical conductivity of pore water and rock

τ_f = tortuosity factor [-]