NONLINEAR SORPTION

"A model is a mathematical construct describing real world phenomena. Its justification is only based on the hope that it works" (John von Neumann).

1. SORPTION MODELS

For description of sorption concentrations in solids are typically plotted to the corresponding concentrations of solutes in water under equilibrium conditions. These plots are called sorption isotherms because they are typically temperature dependent and sorption data have to be collected at constant temperature. A number of mathematical models exist to describe sorption isotherms some of which are introduced in this chapter. Chap. 2 discusses two mechanistic models explaining sorption phenomena. Fig. 1.3 compare some of these models and since for nonlinear sorption the distribution of a solute between water and solids is nonlinear Fig. 1.4 shows concentration dependent distribution coefficients.

1.1 LINEAR SORPTION MODELS

The sorptive uptake of a solute by soils or sediment solids from a aqueous solution or vapor phase is commonly described by sorption isotherms, which relates the aqueous to the sorbed concentration at a constant temperature. In the simplest case, the sorbed concentration in the solid (C_s) is directly proportional to the equilibrium solute concentration in aqueous (C_w) or vapor phase (C_g). Here C_{eq} is used to represent both C_w and C_g:

$$C_s = K_d \, C_{eq} \tag{1.1}$$

The distribution coefficient K_d [L³M], used in this text, is simply the ratio between the solute concentrations in water (C_w) and solids (C_s). If sorption is linear, like in partitioning, K_d represents the slope of the sorption isotherm and is often called the partition coefficient (K_p). If sorption isotherms are nonlinear, then the K_d values depend on the solute concentration (C_s, C_{eq}).

1.2 FREUNDLICH-MODEL

For nonlinear sorption isotherms in soils the Freundlich model (Freundlich, 1909) is most commonly used:

$$C_s = K_{Fr} C_{eq}^{1/n} \tag{1.2}$$

K_{Fr} denotes the Freundlich sorption coefficient [mg kg^{-1} (mg l^{-1})$^{-1/n}$] and $1/n$ is an empirical exponent. For $1/n$ = 1, the Freundlich model equals Eq. 1.1. Note that the value of K_{Fr} depends on the units of C_s, and C_{eq}, respectively. Care should be taken if the values of different studies are being compared (see end of this chapter: this can be avoided by solubility normalized concentrations). With the Freundlich model, the dependence of the distribution coefficient on the concentration is obtained by the combination of Eqs. 1.1 and 2.2:

$$K_d = K_{Fr} C_{eq}^{1/n-1} \tag{1.3}$$

For C_{eq} = 1 and for $1/n$ =1, K_d equals K_{Fr}. Fig. 1.1 shows examples for sorption isotherms, some of which are slightly nonlinear.

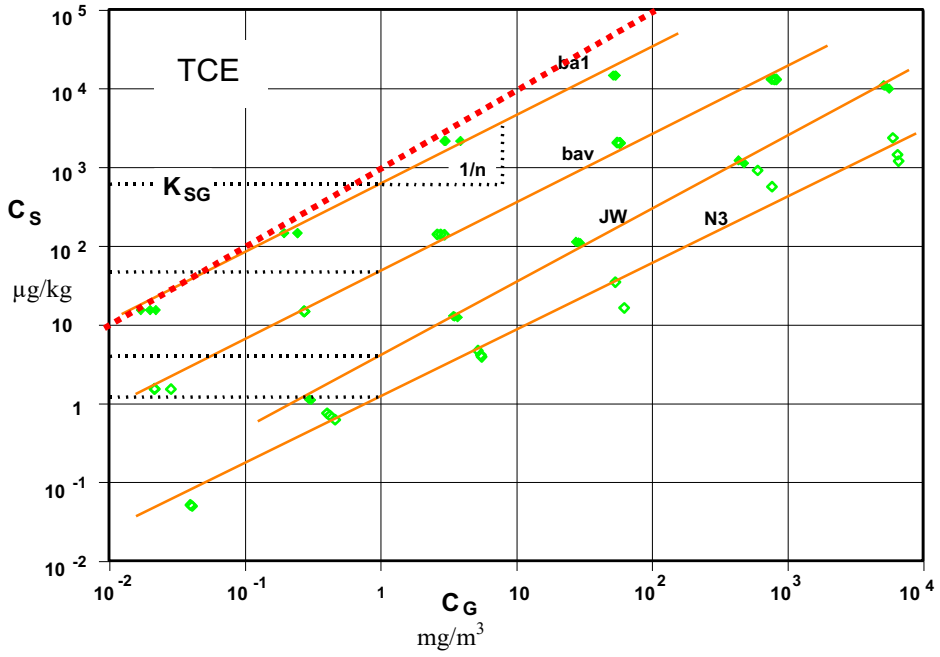


Fig. 1.1: Examples for Freundlich sorption isotherms. C_g is the equilibrium concentration in vapor phase; K_{SG} is the soil air distribution coefficient (= K_d/H); 1/n is the exponent in the Freundlich equation (ba1: Opalinuston (unweathered); bav: Opalinuston (weathered) JW: cambisol; N3: Loess; K_{SG}: distribution coefficient soil/air - all data at 10°C); the bold dashed line denotes a linear relationship (1/n = 1).

1.3 LANGMUIR-MODEL

The Freundlich sorption isotherm can be derived from the Langmuir sorption isotherm for the case of a logarithmic decrease of the adsorption enthalpy with increasing sorption (loading of a surface). The Langmuir model describes adsorption onto a surface where the monolayer coverage represents the maximum (plateau) sorbate concentration ($C_{s,max}$):

$$C_s = \frac{K_L C_{s,max} C_{eq}}{1 + K_L C_{eq}} \tag{1.4}$$

K_L is the Langmuir sorption coefficient. For very low concentrations and $K_L\ C_{eq} << 1$, Eq. 1.4 is linear and equals Eq. 1.1 ($K_L \cdot C_{s,max} = K_d$). At the upper limit if $K_L\ C_{eq} > 1$, C_s approaches $C_{s,max}$, the maximum or plateau concentration in the solids.

As Fig. 1.2 shows, Freundlich isotherms may be constructed by a superposition of Langmuir isotherms (multi-site Langmuir). The exponent $1/n$ in the Freundlich model then is supposed to reflect the heterogeneous energy distribution of sorption sites.

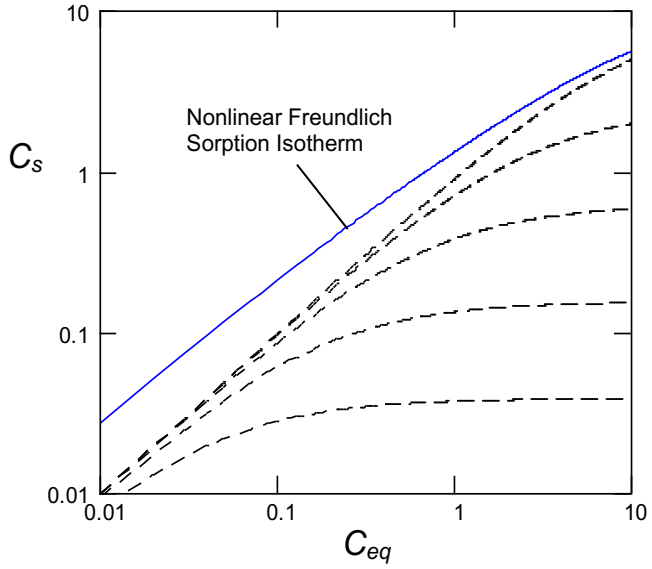


Fig. 1.2: Superimposed Langmuir sorption isotherms (dashed lines) results in a non-linear Freundlich type isotherm (solid line; *1/n* ca. 0.8).

1.4 THE BET-MODEL

The BET model was developed by Brunauer et al. (1938) initially for the adsorption of gases onto solid surfaces in multimolecular layers (as an extension of the Langmuir model):

$$C_s = \frac{K C_{s,max} C_{eq}}{(C_{sat} - C_{eq})[1 + (K-1)C_{eq}/C_{sat}]} \tag{1.5}$$

C_{sat} denotes the saturation concentration in vapor (or the water solubility in aqueous systems). With increasing concentration, the BET isotherm describes the condensation of the adsorbate on the covered substrate surface (in porous media, capillary condensation of the solute occurs in mesopores of 2 nm - 50 nm diameter). The adsorption enthalpy of the second and higher layers equals the enthalpy of condensation of the compound. If $C_{eq} << C_{sat}$, a linear relationship between aqueous and sorbed concentration is obtained again. If C_{eq} approaches C_{sat}, C_s becomes infinitely large (representing capillary condensation of vapors in porous media, precipitation, or clustering of solutes from aqueous solution). The BET adsorption isotherm, e.g. of N_2 is commonly used to determine the surface area of different materials. Fig. 1.3 shows examples of the sorption isotherms discussed above.

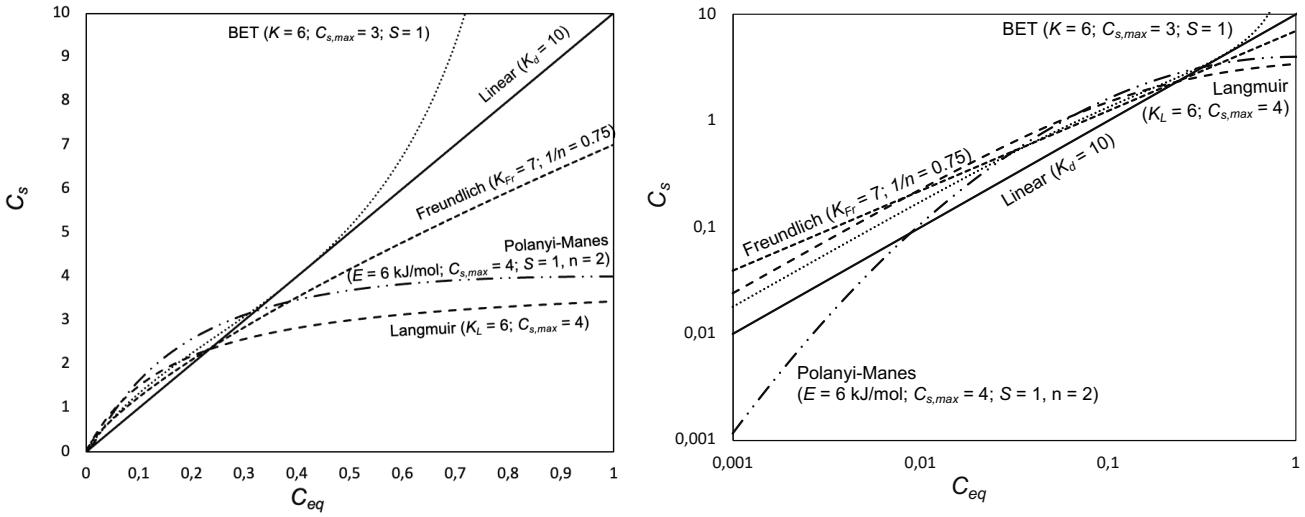


Fig. 1.3: Different models of sorption isotherms (left: linear plot, right: log-log) – note the overlap of the different models in the concentration range of 0.01 – 0.3 (for the Polanyi-Manes model, see chap. 2.2).

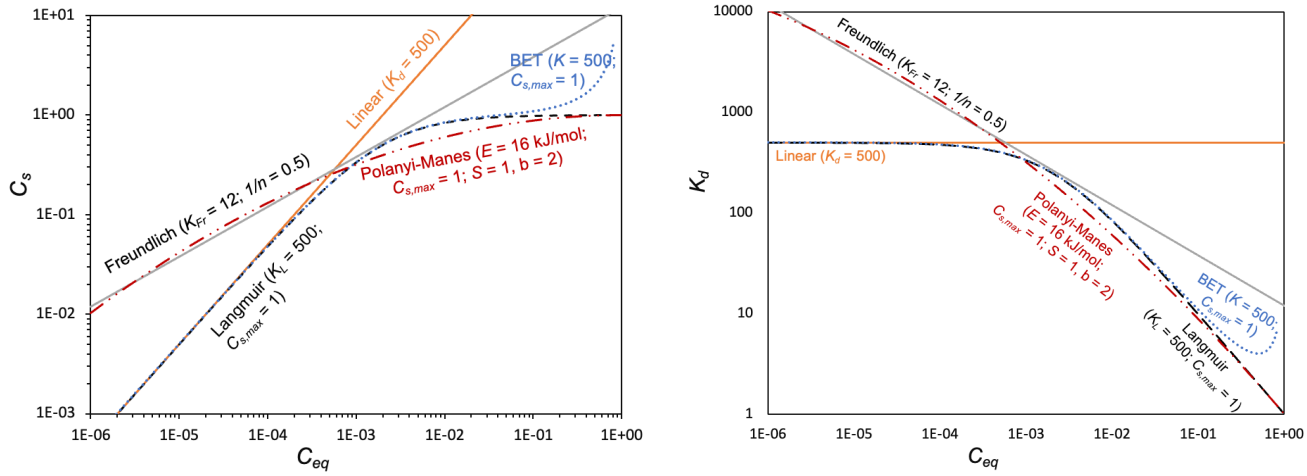
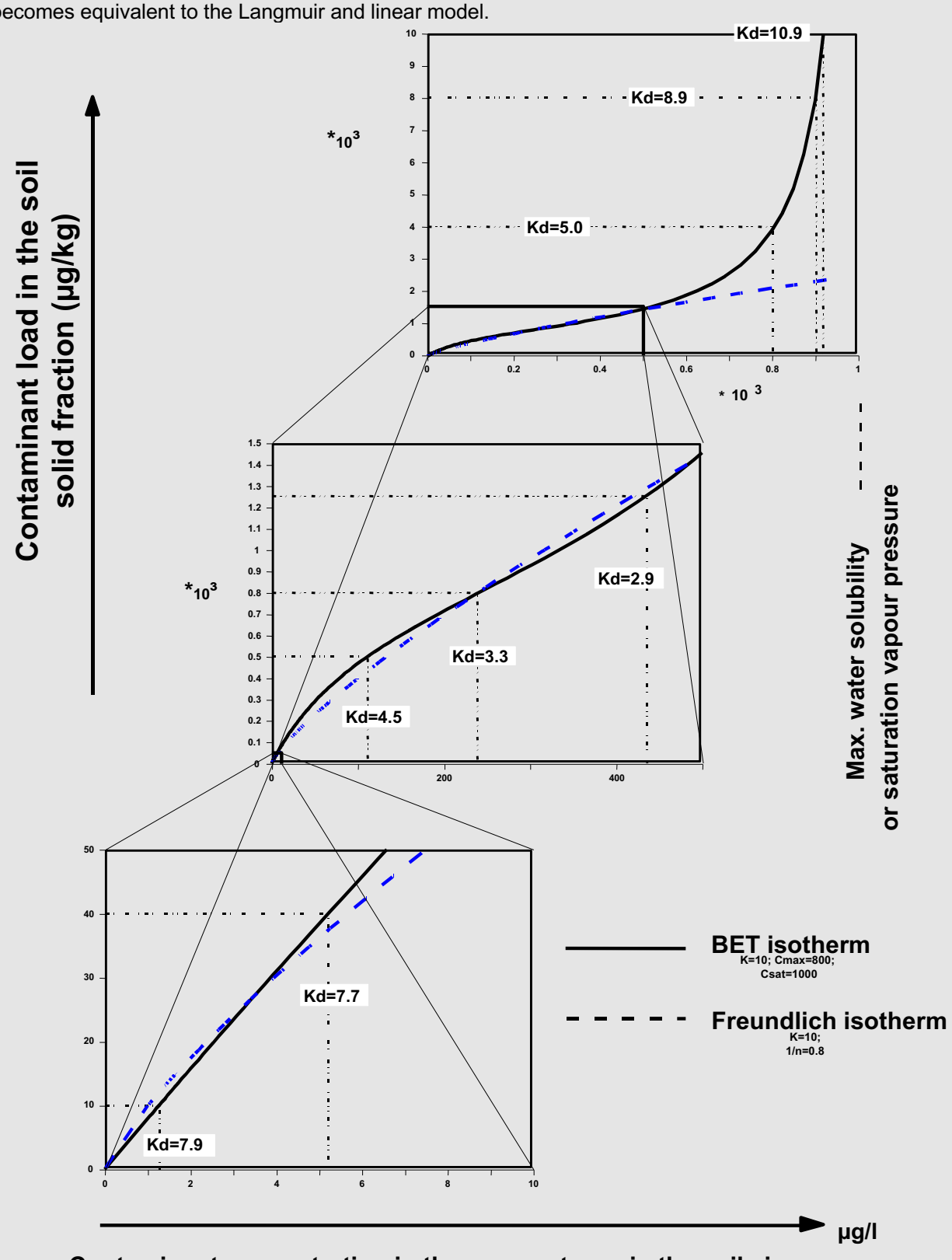


Fig. 1.4: Sorption isotherms (left) and distribution coefficients (right) vs. aqueous concentration for the different models of sorption isotherms (Fig. 1.3).

Box 1. Non-uniqueness of sorption models.

Different mathematical descriptions of sorptive - sorbate relationships may do the job equally well and thus the sorption mechanism cannot directly be determined from the model fit of batch isotherm data. The example below shows that the Freundlich and the BET models fit each very well until high concentrations are reached. At very low concentrations (less than 1% of the solubility), the BET becomes equivalent to the Langmuir and linear model.



2. MECHANISTIC MODELS

Many of the sorption isotherms (models) presented earlier remain largely empirical (i.e., are used in soils more as mathematical models and lack a thoroughly thermodynamic explanation). Partitioning (linear sorption) certainly does not explain all observations in the sorption of hydrophobic compounds in organic matter. Very often, especially if concentration ranges span more than several orders of magnitude, nonlinear sorption isotherms are observed. The organic matter normalized sorption ("partitioning") coefficients - especially in the environmentally relevant low concentration ranges (which are usually much lower than the aqueous solubility limit) are also much higher than partitioning coefficients discussed earlier (see Box 2).

2.1 PARTITIONING (LINEAR SORPTION)

As shown in the previous sections, "partition" coefficients are derived from Raoult's law describing the solution of an organic compound in a mixture with an organic phase (or organic matter). The linear partitioning sorption isotherm is given by:

$$C_s = K_p C_w = \frac{1}{\gamma_o V_o}\frac{C_w}{S} \tag{2.1}$$

C_s denotes the concentration in the partitioning medium (e.g., the organic mixture/matter). K_p is the partitioning coefficient. V_o is the molar volume of the organic liquid. For partitioning, theoretically, an upper limit can be derived, which corresponds to the partition of a compound between its liquid phase and water (activity coefficient = 1). An example is given in Box 2.

2.2 PORE-FILLING (POLANYI POTENTIAL THEORY)

Adsorption of vapors in micro- and mesopores. Depending on the pore size, pore shape, and pore size distribution, characteristic sorption isotherms have been characterized in well defined porous media (adsorption of gases onto solids; for further details, see Gregg and Sing, 1982). Adsorption in micropores according to Polanyi, Dubinin, and Radushkevich etc., is due to a pore-filling mechanism. Conversely, based on sorption isotherms, pore size distributions can be calculated. After an initial mono and multilayer adsorption at the pore walls, adsorption in mesopores continues to capillary condensation (Kelvin equation). Capillary condensation occurs if the equilibrium vapor pressure over a concave meniscus of liquid is less than the saturation vapor pressure, which implied that a vapor will condense to a liquid in the pores even when its relative pressure is less than unity. In micropores, the potential fields from neighboring walls overlap, and the interaction energy (of the solid with the adsorbate) will be enhanced (see Fig. 1.2). This will result in increased adsorption (complete filling of the pores), especially at low relative pressures. The definition of pore sizes here follows the IUPAC (International Union of Pure and Applied Chemistry) pore classification (Sing et al., 1985):

micropores:	pore width < 2 nm
mesopores:	pore width 2 nm - 50 nm
macropores:	pore width > 50 nm

In pore-filling, a maximum sorption capacity $C_{s,max}$ [cm^3 g^{-1}] is reached (which is controlled by the pore volume of the adsorbent), resulting in a highly nonlinear sorption behavior. Pore-filling can be described based on Polanyi's theory of a variable adsorption potential, where the free energy of adsorption is related to the degree of pore filling (Dubinin-Polanyi, Dubinin-Radushkevich or Dubinin-Astakhov isotherms):

$$C_s = C_{s,max} \exp\left[-K\left(-RT\ln\frac{P}{P^o}\right)^2\right] \tag{2.2}$$

where K is in the order of 3 x 10^{-9} mol^2 J^{-2} (Sontheimer et al., 1988). The Polanyi potential theory defines the adsorption potential ε = - R T ln (P/P_o) [kJ mol^{-1}] as the free energy or work to remove the solute from a potential surface. A more general form of Eq. 2.2 is given by (Dubinin-Astakhov):

$$C_s = \frac{V_{micro}}{V_m} \exp\left[-\left(\frac{-RT\ln\frac{P}{P^o}}{\beta E_o}\right)^b\right] \tag{2.3}$$

where b often is 2 (Dubinin-Radushkevich) but for particularly uniform fine micropores can be 3 (or even higher); for b = 1 the Freundlich sorption isotherm is obtained (see Box 4). V_{micro} and V_m are the micropore volume of the adsorbent [cm^3 g^{-1}] and the molar volume of the sorbate [cm^3 mol^{-1}] (C_s has then the units of mol g^{-1}). β is a similarity coefficient (usually for benzene as a standard substance), which can be approximated by the ratio of molar volumes (V_m/V_s) of or parachors (P/P_s) of an adsorbate to a standard adsorbate, regardless of the adsorbent (Urano et al., 1982; Dubinin, 1966). E_o is the characteristic adsorption energy for a standard vapor (ca. 22 kJ mol^{-1}; note for n = 2 in Eq. 2.3 β has to be ≈ 0.8 in order to match K in Eq. 2.2: 22000^{-2} = 2x10^{-9} mol^2 J^{-2}).

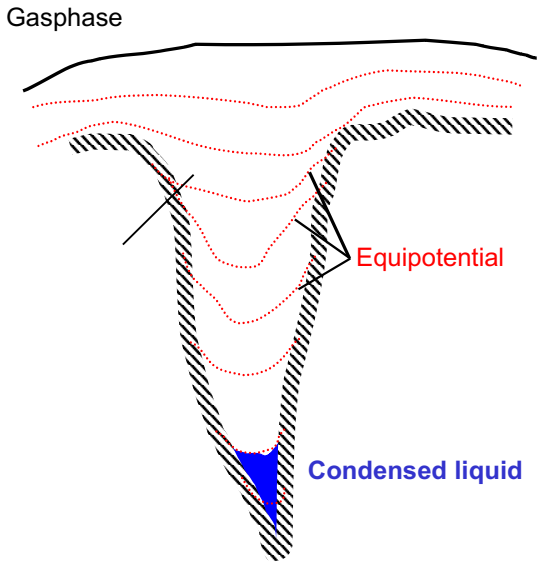


Fig. 2.1: Schematic model for a pore showing the equipotential surfaces corresponding to successively lower values of the adsorption potential with increasing pore size (see also Pan and Zhang, 2014).

Adsorption potential: ε

Vapor-phase

$\varepsilon = RT\ln(P_o/P)$

Aqueous phase

$\varepsilon_{sw} = RT\ln(S/C)$

Box 2. How large can K_p / the pollutant partitioning into organic matter become theoretically?

Sorption to soil organic matter (e.g., in top soils, humus, peat, etc.) can be described by a partitioning process analogous to the solution of a hydrophobic compound in an organic solvent. In such a case, the concentration in the organic phase (C_o) increases linearly with the equilibrium aqueous concentration (C_w) of the compound. The accumulation in the organic phase is given by a simple partitioning coefficient K_p (organic phase/water partition coefficient):

$$C_o = K_p C_w$$

$K_{o/w}$ can be derived from Raoult's law (following Schwarzenbach et al., 1993):

$$K_p = \frac{1}{\gamma_o \, S \, V_o}$$

where γ_o, S and V_o are the activity coefficient [-] of the solute in the organic phase, the aqueous solubility (or subcooled liquid solubility for solid compounds) of the solute [mol L^{-1}], and the molar volume [L mol $^{-1}$] of the organic phase. V_o [L kg^{-1}] can be approximated by the ratio of molecular weight (M_o) and the density of the organic phase (ρ_o [kg L^{-1}]). Ideally γ_o equals 1, and the properties of the solute are matched by the properties of the organic phase (this would yield a maximum K_p). If the molecular weights of solute and organic phase are the same, then K_p in such an ideal partitioning medium would equal simply ρ_o/S with S expressed in kg L^{-1} (S [mol L^{-1}] times the molecular weight of the solute (M [kg mol^{-1}]) yields S in the units kg L^{-1}):

$$K_p = \frac{\rho_o}{S[\text{mol L}^{-1}] \, M[\text{g mol}^{-1}]} = \frac{\rho_o \, [\text{g l}^{-1}]}{S \, [\text{g l}^{-1}]}$$

In such an ideal partitioning medium C_o would theoretically equal ρ_o if C_w approaches S (yielding the maximum pollutant accumulation: $C_{o,max} = \rho_o$), representing partitioning of a compound between itself and water (e.g., the partition coefficient of pure toluene into water is given by the concentration of pure toluene which is its density and its water solubility). If C_o is plotted vs. the normalized aqueous concentrations (C_w/S) of different compounds, all data would be on the same line. The slope is then given by the density of the organic phase (which is for solvents and organic matter reasonably close to 1). Since C_o in soil is commonly expressed on a mass basis [e.g., in kg kg^{-1}] the theoretical, maximum loading in the organic phase (= sorbent) is 1 kg/kg; the slope of such a C_w/S normalized, unique sorption isotherm is one [kg/kg: kg/L] and K_p (= K_{om}) equals simply $1/S$ if S is expressed in kg L^{-1}).

Example: The ideal (= maximum) partition coefficient for benzene (S = 0.0018 kg l^{-1}) and for phenanthrene (S_{scl} = 6.18 x 10^{-6} kg L^{-1}) is $K_{o/w} = 10^{2.74}$ [L kg^{-1}] and $K_{o/w} = 10^{5.2}$ [L kg^{-1}], respectively. For comparison, the octanol-water partitioning coefficients are log K_{ow} = 2.13 (benzene) and log K_{ow} = 4.57 (phenanthrene). K_{ow} is still relatively high - if C_w approaches the solubility limit, the "sorptive" uptake in octanol would be around 30%. K_{ow} is lower than the ideal partition coefficient because of two reasons: 1) it's molar volume and molecular weight are different from the solute, and 2) because the activity coefficient can be higher than one (because of the relatively polar character of the octanol and the presence of water in octanol).

Box 3. Pore-filling extended to capillary condensation

Sontheimer et al. (1988) suggested that the Polanyi potential theory can be related to the Kelvin equation:

$$\frac{P}{P^o} = \exp\left(\frac{-2\sigma V_m \cos\theta}{RTr_c}\right) \Rightarrow -RT\ln\frac{P}{P^o} = \frac{2\,\sigma\,V_m\cos\theta}{r_c}$$

where σ, θ, V_m and r_c denote interfacial tension, contact angle, the molar volume of condensing fluid, and the capillary radius (at P/P_o = 0.1 pore filling of the mesopores with a typical organic solvent such as benzene as a wetting fluid would start, micropores would be already filled), respectively. Combining Kelvin and Dubinin-Radushkevich yields:

$$C_s = C_{s,max}\exp\left[-K\left(\frac{2\,\sigma\,V_m\cos\theta}{r_c}\right)^2\right]$$

Here, the sorbate needs to be the wetting fluid and this is limited to meso- or larger pores, where capillary condensation could occur.

Pore-filling in aqueous systems. Meanwhile it is evident that microporous organic particles occur in soils, sediments, and sedimentary rocks (Allen-King et al., 2002 or Goldberg, 1985). Such particles can adsorb organic compounds by a pore-filling mechanism. Eq. 2.2 has then to be extended to aqueous systems by applying the Polanyi-Manes Theory, which defines the adsorption potential $\varepsilon_{sw} = RT\ln(S/C_w)$ with units in Joule/mol. In Eqs. 2.2 and 2.3 -ln (P/P^o) is replaced by -ln (C_w/S). The difference between vapor phase sorption and aqueous phase sorption is that in an aqueous system, the sorbate has to replace an equal volume of water (see Xia and Ball, 1999).

$$C_s = \frac{V_{micro}}{V_m} exp\left[-\left(\frac{-RT\ln\frac{C_w}{S}}{\beta E_o}\right)^b\right] \tag{2.4}$$

Fig. 2.2 shows that thermally altered organic matter such as coke and activated carbon, which exhibit extremely nonlinear sorption isotherms, contain a significant fraction of micropores corroborating the hypothesis of a pore-filling mechanism leading to highly nonlinear sorption isotherms and extremely high sorption capacities at low solute concentrations.

According to Eqs. 2.2 - 2.4, the loading onto a porous adsorbent depends on the relative concentration with respect to water solubility or vapor pressure of the specific compound. This results in equal loading at equal relative concentrations and, therefore, a unity sorption isotherm is expected if the volume adsorbed (C_s [cm^3 g^{-1}] is plotted vs. C_w/S (see examples in chap. 3.1). Distribution coefficients calculated at a specific relative concentration (e.g., 10% of the water solubility of a compound) are inverse proportional to the water solubility of the compound, as shown by the granular activated carbon data in Fig. 2.3.

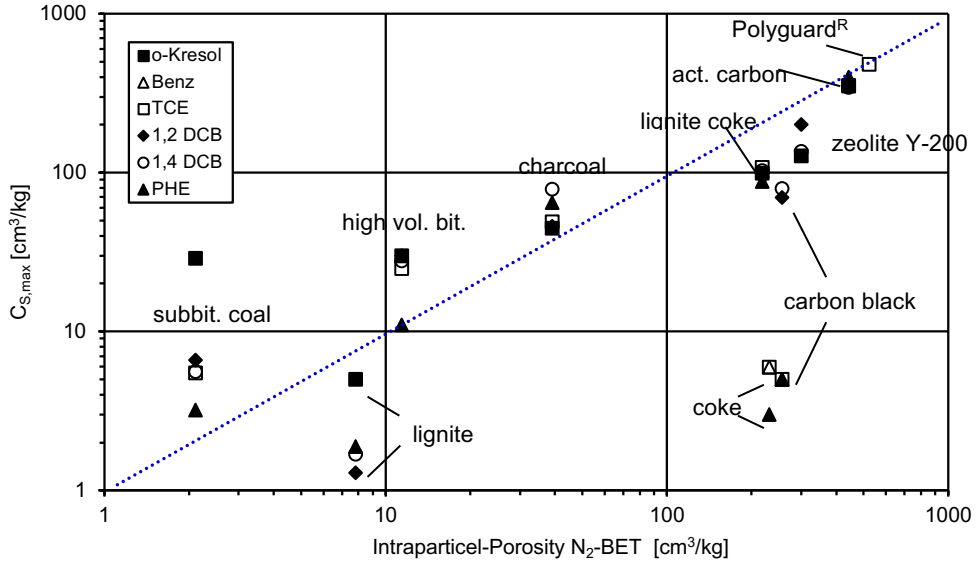


Fig. 2.2: Volume of solute adsorbed ($C_{s,max}$) from the aqueous phase at 20°C vs. the micro- and mesopore volume as determined by N_2 adsorption (BET-method) at -196°C. Note the good agreement for the thermally treated carbons (and hydrophobic zeolites).

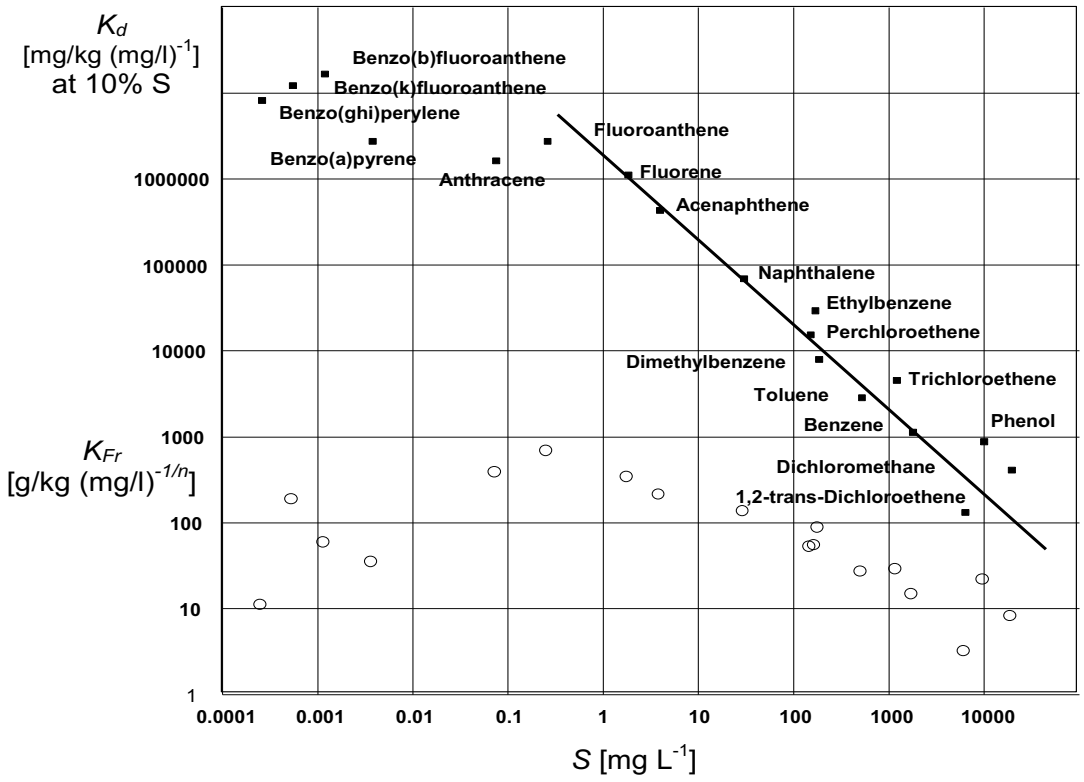


Fig. 2.3: Linear inverse correlation of K_d to the water solubility (S) of organic compounds calculated at 10% of S from Freundlich sorption isotherms for activated carbon (F300) from literature. The loading on the carbon (at 10% of S) is the same for all compounds and is given by K_d 0.1 $S \approx 0.2$ kg kg^{-1} = 20%.

Box 4. Relation of pore filling (Polanyi-Dubinin-Manes) and Freundlich sorption isotherms

Based on the Dubinin-Astakhov equation sorption due to pore filling e.g. for activated carbons in aqueous systems may be described as:

$$\frac{C_s}{C_{s,max}} = \exp\left[-\left(\frac{-RT\ln\frac{C_w}{S}}{E}\right)^b\right]$$

For an exponent b = 1 (and smaller but larger 0) a logarithmic (linear) form is obtained:

$$\ln\frac{C_s}{C_{s,max}} = \frac{RT}{E}\ln\frac{C_w}{S}$$

which corresponds to the solubility normalized Freundlich isotherm:

$$C_s = C_{s,max}\left(\frac{C_w}{S}\right)^{\frac{RT}{E}} = {K_{Fr}}^*\left(\frac{C_w}{S}\right)^{1/n}$$

Where $C_{s,max}$ corresponds to the unit-equivalent Freundlich coefficient (${K_{Fr}}^*$) and RT/E to the Freundlich exponent ($1/n$). If E is bigger than RT (= 8.144 × 298 = 2479 Joule/mol), the exponent is less than one and the sorption isotherm is nonlinear; the linear case is obtained if E equals RT (the energy of an ideal gas).

3. COMBINED MODELS FOR HETEROGENEOUS SYSTEMS

3.1 NONLINEAR SORPTION: ADSORPTION AND PARTITIONING COMBINED

Nonlinear sorption is wide spread in natural solids. In general, non-linearity increases with increasing sorption capacity (K_{Fr}) as shown in Fig. 3.1.

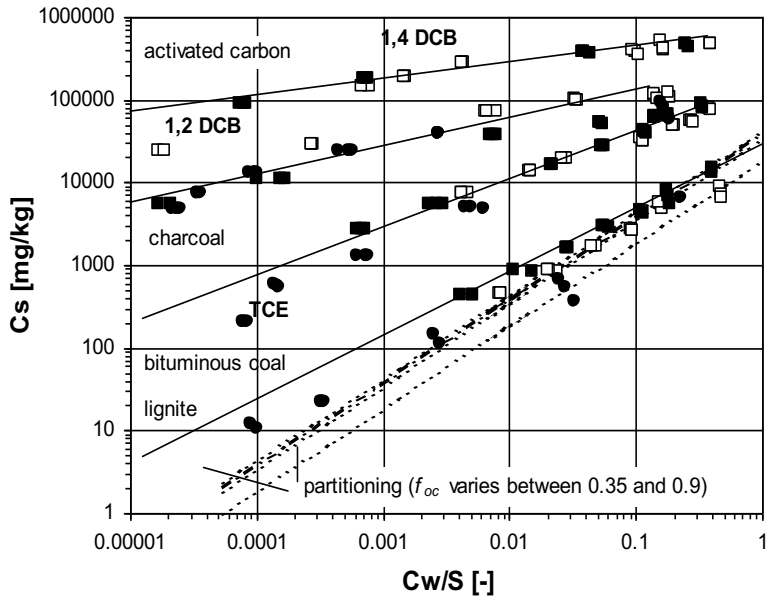


Fig. 3.1: Freundlich sorption isotherms (solid lines) for different geosorbents and TCE (circles), 1,2 DCB (filled squares), and 1,4 DCB (open squares). The results show that sorption capacities C_w /S are reasonably close for the different organic compounds within a given geosorbent. The sorption isotherms are in all cases nonlinear and show higher sorption capacities than expected from an empirical correlation for SOM partitioning (dashed lines).

There have been several attempts to describe nonlinear sorption isotherms (and competitive sorption) by a dual-mode isotherm, which accounts for partitioning and adsorption. Weber and co-

workers termed it “distributed reactivity model,” while Pignatello and co-workers described it as “dual-mode model.” Later, Xia and Ball (1999) used the pore-filling mechanism for the adsorbed part. In general form adsorption and partitioning can be described by:

$$q_e = q_{ads} + K_p C_e \tag{3.1}$$

In micro- mesoporous organic particles (such as activated carbon) with a porosity of 50% and a bulk density of 0.5 g/cm^3 one could expect up to a maximum C_s ($C_{s,max}$) of approx. 0.25 cm^3 of the organic solute filling the pores per g of adsorbent. If the liquid density of the solute is 1 kg L^{-1} then the loading would be around 0.25 kg/kg (which is the same as in an ideal partitioning medium at 25% of S_{scl}). The primary and significant difference compared to the ideal partitioning medium is that the high loadings in pore-filling are reached at concentrations much lower than the solubility limit. Combining the partitioning and pore-filling mechanism (superposition of both) results again in a Freundlich type isotherm. At low concentrations, the pore-filling mechanism dominates, whereas, at concentrations close to the solubility limit, partitioning takes over, as shown in Fig. 3.2.

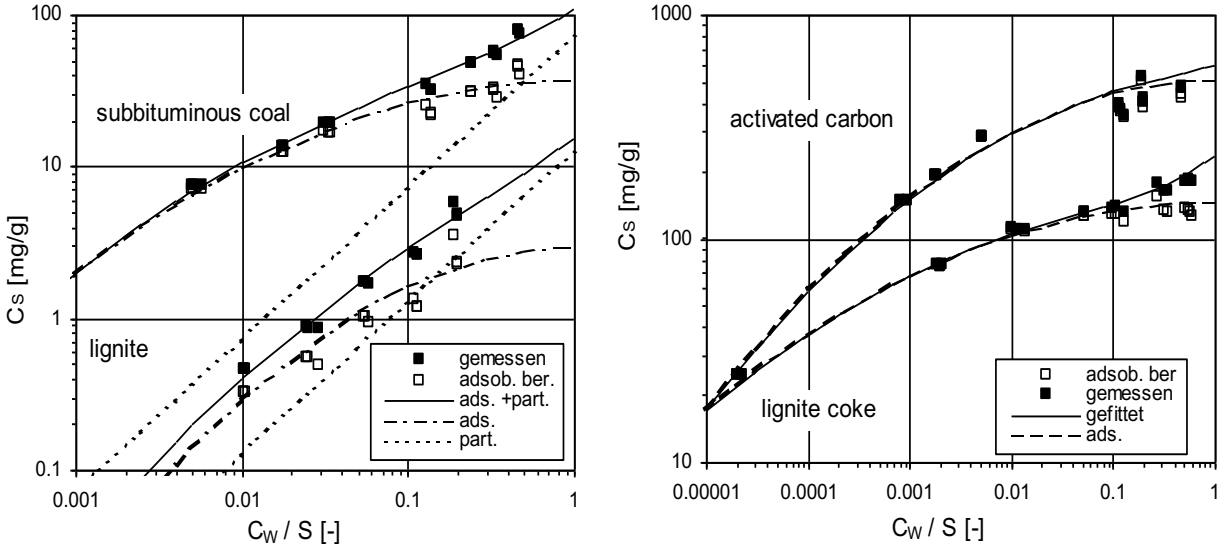


Fig. 3.2: Nonlinear sorption isotherms with separation and combination of pore-filling and partitioning parts for four different sorbents and 1,2 DCB. The dotted lines were calculated by the Polanyi-Manes equation. The fraction of partitioning contributes significantly to the overall sorption only at relatively high concentrations in less sorbing materials such as the lignite sample. Pore-filling seems to dominate in all other samples (bituminous coal, charcoal, and activated carbon). Values for E_0 are similar between the different compounds but increase from lignite (7.5-9 kJ/mol), bituminous coal (10-11.7 kJ/mol) to charcoal, coke (17-19.5 kJ/mol) and activated carbon (12-18 kJ/mol).

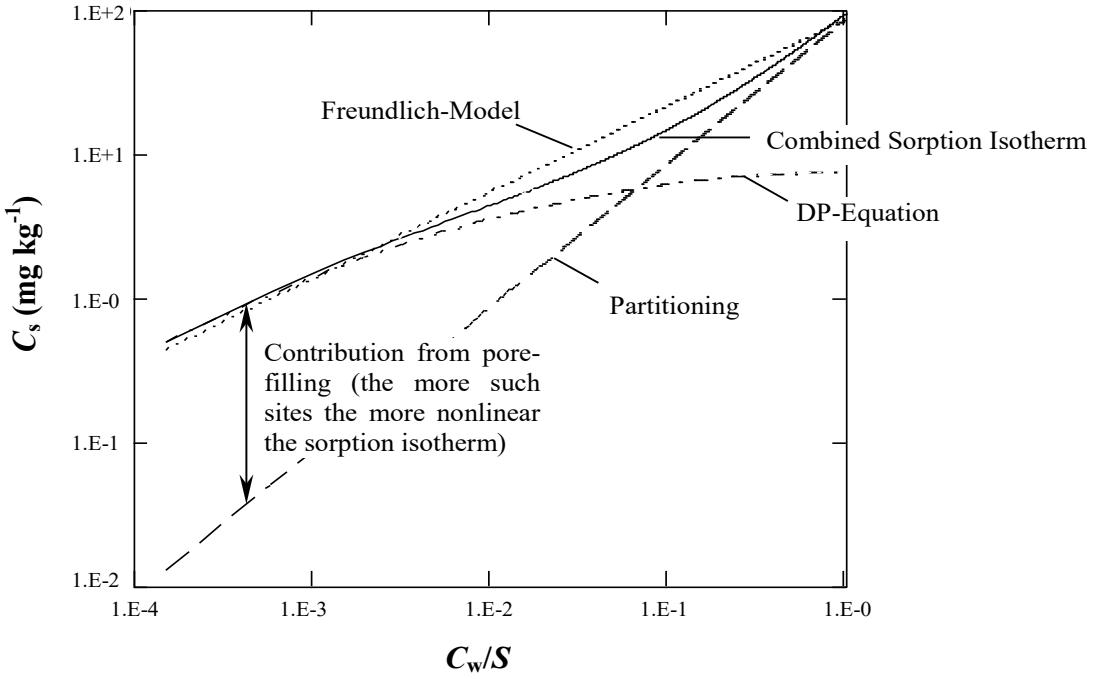


Fig. 3.3: Example for the combination of pore-filling and partitioning. The pore-filling medium approaches at approx. C_w/S = 0.1 a maximum capacity (dash-dot), the partitioning medium dominates sorption at high concentrations above C_w/S = 0.1. The superposition of both (solid line) agrees reasonably well with the empirical Freundlich sorption model (dotted line).

4. S-NORMALIZED FREUNDLICH SORPTION ISOTHERMS

As shown above, total sorption is found to be approximately the same for a given compound "activity" (= C_w/S), and this is an expected effect with both of the two proposed mechanisms (partitioning and pore-filling). Therefore, a solubility-normalized Freundlich sorption isotherm can be used to compare sorption for a range of compounds:

$$C_s = K_{Fr}{}^* \left(\frac{C_w}{S}\right)^{1/n} \tag{4.1}$$

$K_{Fr}{}^*$ is the Freundlich coefficient, which has the units of C_s and which is related to the usual Freundlich model by $K_{Fr}{}^* = K_{Fr} \,/\, S^{1/n}$. Fig. 4.1 shows how this normalization works for 4 different compounds and 2 soil samples. Normalized Freundlich sorption isotherms are easy to handle in terms units and allow comparison of different compounds.

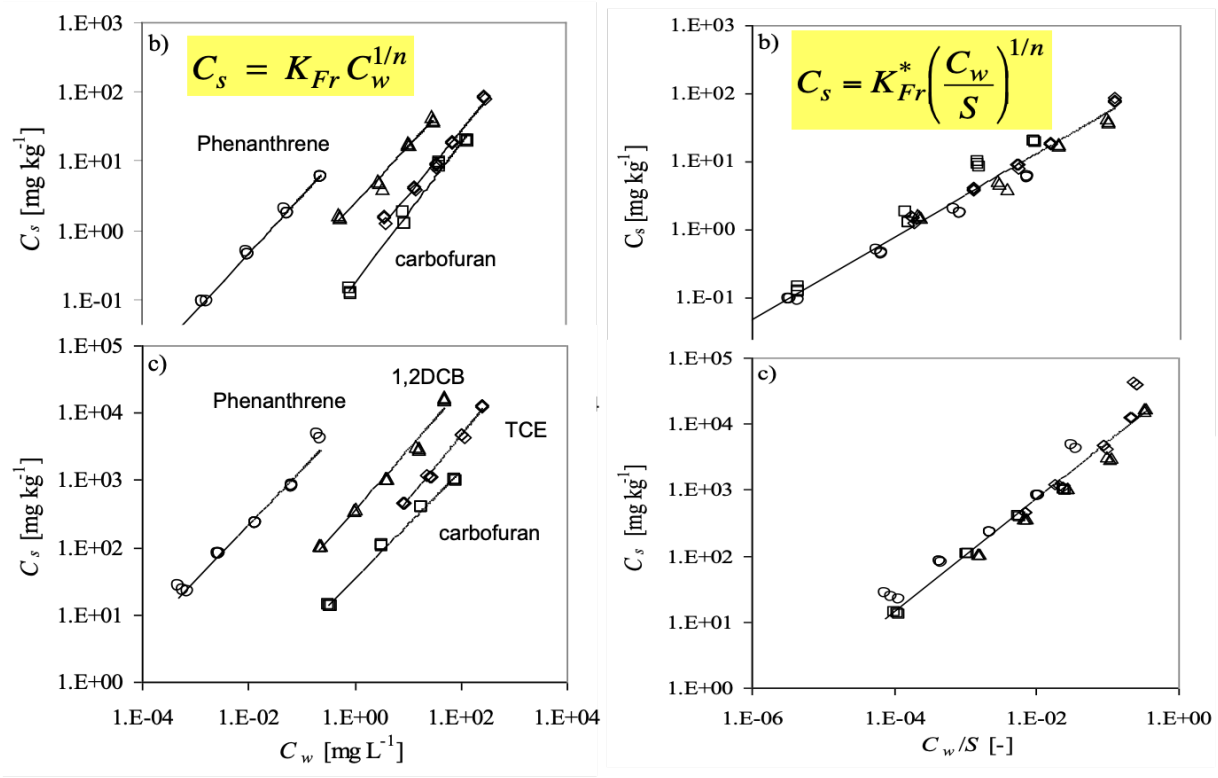


Fig. 4.1: Example for "collapsing" sorption isotherms (left) after the normalization to *S*. Lines denote Freundlich sorption isotherms.

As a consequence of the above, we expect that K_d values show an inverse linear relationship with S as shown in Fig 4.2. Since the slope is close to -1, the product of K_d (at a given C_w/S) times is constant for a given sorbent (independent on the mechanism) and different compounds. If, furthermore, sorption can be normalized by organic matter, then sorption data involving different geosorbents "collapse" (Fig. 4.3), implying that a unique S-normalized K_{oc} might exist (see also Allen-King et al., 2002).

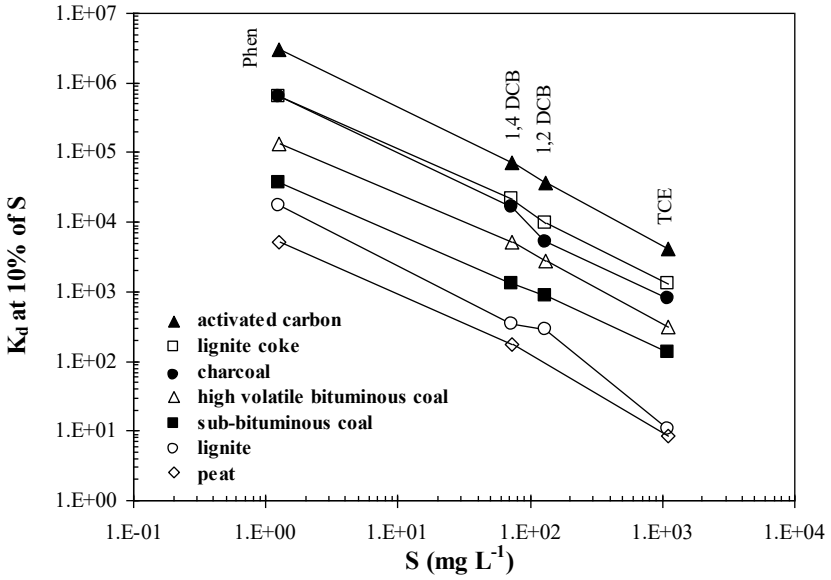


Fig. 4.2: Inverse relationship between K_d and water solubility for very different geosorbents and hydrophobic organic compounds (grey symbols denote sub-cooled liquid solubilities).

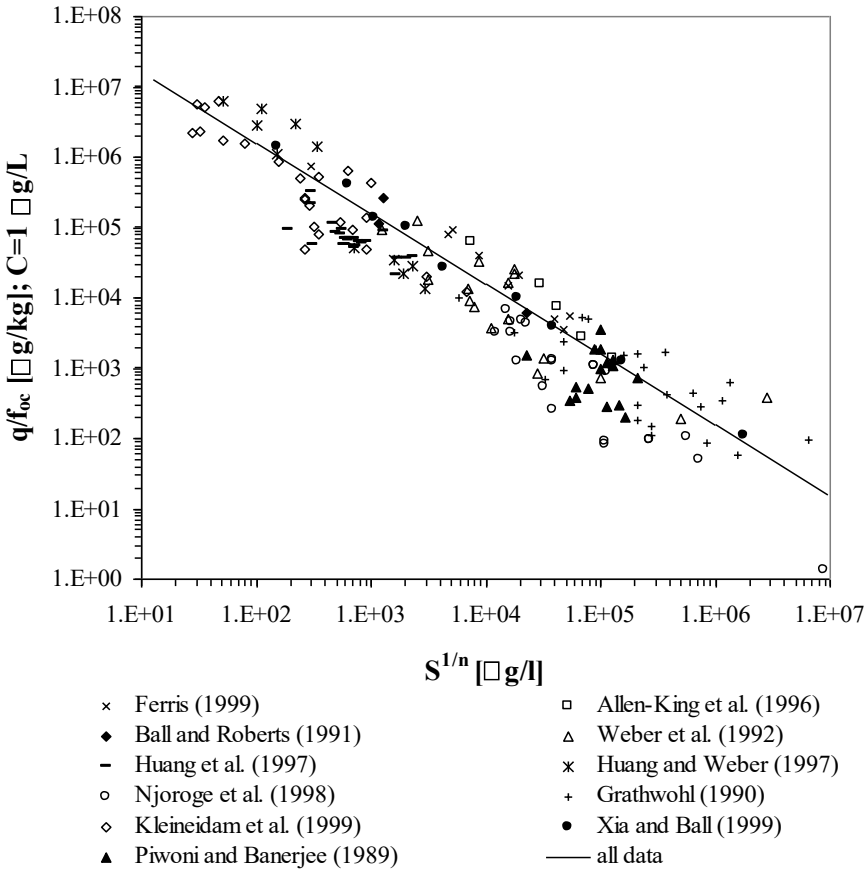


Fig. 4.3: Inverse relationship between the organic carbon-normalized loading (q/f_{oc}) at a given aqueous concentration for many different soil samples and many different hydrophobic organic compounds.

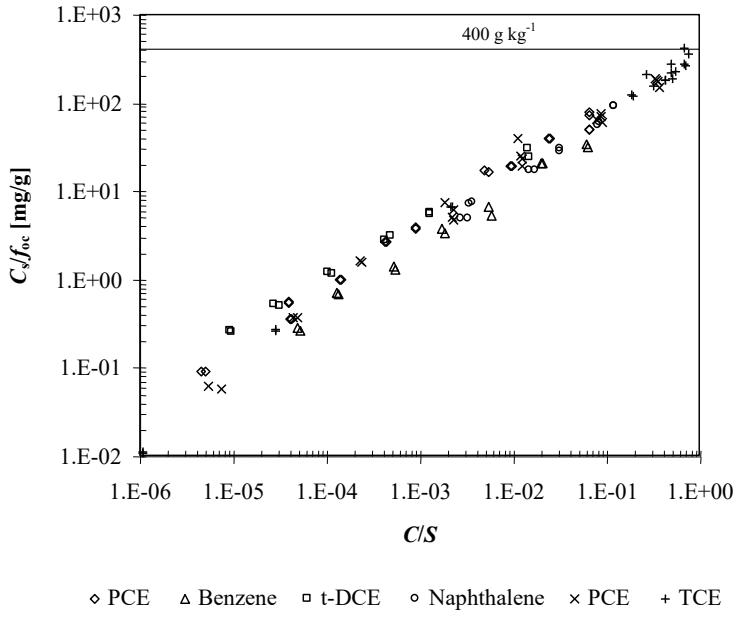


Fig. 4.4: Normalized sorption isotherms. Increase of the organic carbon-normalized loading (q/f_{oc}) with increasing normalized concentration for a shale sample and a range of hydrophobic organic compounds. Note that the intercept for all compounds at C/S is approximately the same.

5. LINEARIZED FREUNDLICH SORPTION ISOTHERMS

Often, e.g. in analytical solutions in transport modelling linear approximations of nonlinear sorption isotherms is needed. K_d values valid for a certain concentration range (here C_w) may be simply calculated from its definition and a Freundlich sorption isotherm:

$$K_d = C_s/C_w = \frac{K_{Fr}(C_w)^{1/n}}{C_w} = K_{Fr}(C_w)^{(1/n-1)} \quad (5.1)$$

For a concentration of one, K_d corresponds to K_{Fr} (see Fig. 5.1). The Freundlich exponent $1/n$ typically is smaller than 1, meaning that K_d increases with decreasing concentration, e.g. for $1/n$ = 0.5, C_w in the denominator decreases by 2 orders of magnitude while the numerator (C_s) decreases just by a factor of 10 and thus K_d will become 10 times higher compared to the original concentration. This illustrates, that K_d values have to be calculated for a representative concentration (range) and if this is considered nonlinear sorption has only minor impact on mass transfer kinetics or transport (Liu et al., 2022, 2021). Fig. 5.1 illustrates how normalization works and shows that for a stepwise change of C_w (from zero to equilibrium), the K_d at the equilibrium concentration is sufficient to describe the data.

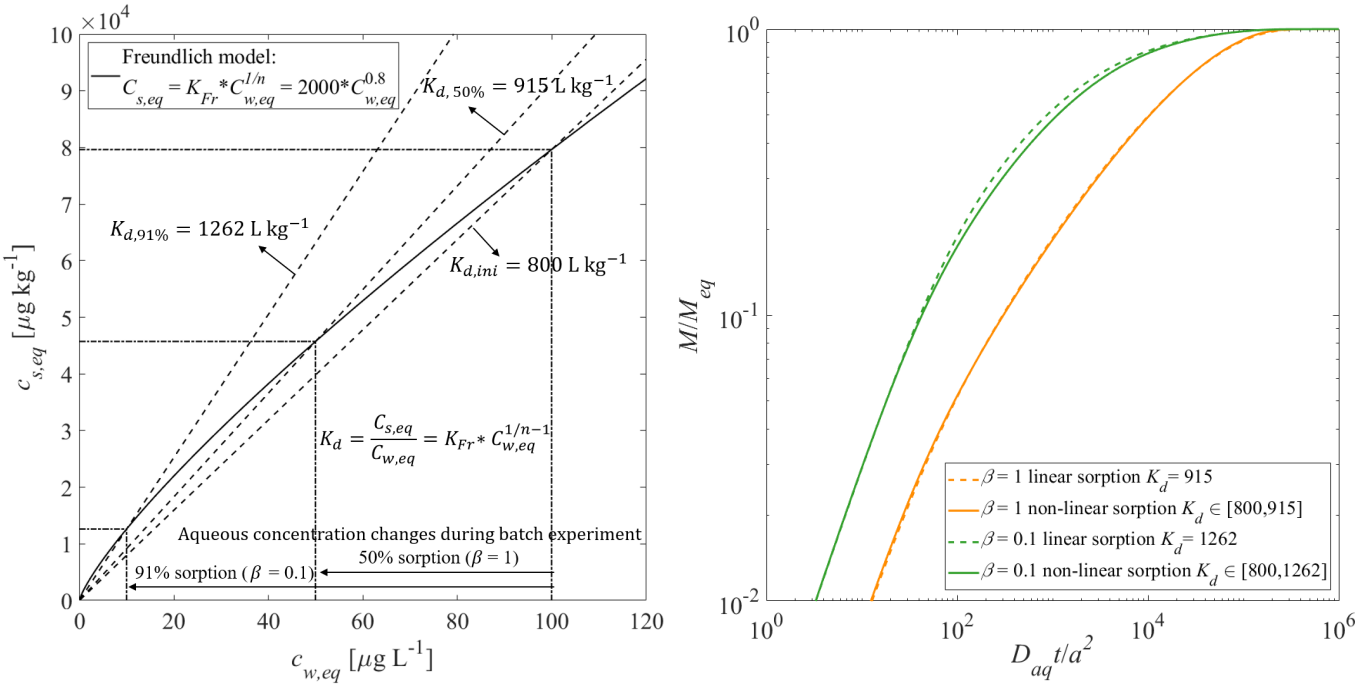


Fig. 5.1 (from Liu et al., 2022): Illustration of linearization of a Freundlich sorption isotherms (K_{Fr} = 2000, $1/n$ = 0.8) for a sorption kinetic batch experiment of 50% (initial concentration drop) and 91% final sorptive uptake; β denotes the solute mass in water relative to the mass in solid phase under equilibrium conditions; K_d values change from 800 l kg^{-1} at the initial concentration (= 100) to 915 l kg^{-1} and 1295 l kg^{-1} for β = 0.5 and 0.1 (they increase because the C_w decreases if $1/n$ > 1). The lower plot compares a numerical model (solid lines) for sorptive uptake (M/M_{eq} would correspond here to the relative change of the concentration in the solids) with the analytical solution with a linear K_d (= $K_{Fr}(C_w)^{(1/n-1)}$ calculated at the final equilibrium concentration $C_{w,eq}$ (dashed lines).

For small concentration changes (e.g. from C_1 to C_2), K_d may be represented by the slope of a secant (chord) going through C_1 and C_2.:

$$K_d = C_s/C_w = \frac{K_{Fr}\ {C_{w1}}^{1/n} - K_{Fr}\ {C_{w2}}^{1/n}}{C_{w1} - C_{w2}} = K_{Fr}\frac{{C_{w1}}^{1/n} - {C_{w2}}^{1/n}}{C_{w1} - C_{w2}} \tag{5.2}$$

For $1/n < 1$ and concentrations smaller than 1, the numerator is larger than the denominator and K_d will be larger than K_{Fr} (opposite if concentrations are larger than 1). If C_1 is much smaller than C_2 then we get eq. 5.1 (for $C_2 = 0$ the chord goes through zero and C_w with slope K_d). If the difference C_1 - C_2 goes to zero, we get the derivative with respect to C_w:

$$K_d = \frac{K_{Fr}\ (C_w)^{1/n}}{\mathrm{d}C_w} = 1/n\ K_{Fr}(C_w)^{(1/n-1)} \tag{5.3}$$

K_d represents now the slope of the tangent going through C_w as shown in Fig. 5.2. We now have two ways for linearization of Freundlich sorption isotherms, which would lead to two different K_d values and thus retardation factors. Retardation factors can be simply derived based on mass balance considerations. For example, breakthrough of a solute in column is expected after all sorption sites are occupied (after by feeding a high inlet concentration, $C_{w,in}$, over a water volume, $V_{w,BTC}$, which leads to breakthrough):

$$\begin{aligned} C_{w,in}\ V_{w,BTC} &= C_{w,in}\ V_w + C_s\ m_d = C_{w,in}\ V_w + K_{Fr}\ \left(C_{w,in}\right)^{1/n} m_d \\ V_{w,BTC} &= V_w + m_d\ K_{Fr}\ \left(C_{w,in}\right)^{1/n-1} \\ R_d &= \frac{V_{w,BTC}}{V_w} = 1 + \frac{m_d}{V_w}\ K_{Fr}\ \left(C_{w,in}\right)^{1/n-1} \end{aligned} \tag{5.4}$$

$V_{w,BTC}/V_w$ denotes the number of pore volumes (= PV) which need to displaced until breakthrough occurs (this is the retardation factor: R_d = total capacity of the system/mobile fraction). In principle, this also holds for leaching (desorption) of a solute from a column after initially equilibrium was achieved. However, with non-linear sorption the concentration profiles look very different for breakthrough and leaching. In the first case a self-sharpening front is observed (compressive wave), because high concentrations want to travel faster than low concentrations (but can't overtake them – here a shock wave develops) and thus counteract dispersion; in this case the retardation factor follows eq. 5.4). In leaching (desorption) extended tailing (i.e. spreading front or dispersive wave) will develop (low concentrations arriving late are much slower than the initial high concentration); the retardation factor for the leading edge is now smaller than before: $1 + 1/n\ K_{Fr}(C_w)^{(1/n-1)}$ (from eq. 5.3). R_d as defined in eq. 5.4 describes now a low concentration (typically less than 0.5 of the initial concentration (C_o)) and may be seen as average retardation or retention time of the front for the compressive and dispersive case (Nicoud, 2015). See Fig. 5.3 for illustration of breakthrough and leaching curves.

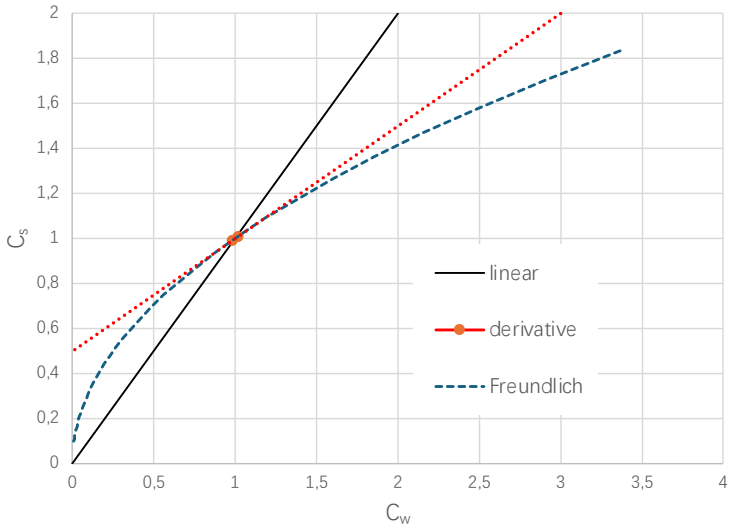


Fig. 5.2: Two ways to linearize Freundlich sorption isotherms (K_{Fr} = 1, $1/n$ = 0.5); linear for transport approximations with step concentration changes: $K_d = K_{Fr}(C_w)^{(1/n-1)}$ (chord between 0 and C); derivative for small concentration changes: $K_d = 1/n\ K_{Fr}(C_w)^{(1/n-1)}$; the intercept of the tangent line is: $K_{Fr}{C_w}^{1/n}(1-1/n)$

Fig. 5.3 illustrates breakthrough curves (loading)) and leaching curves in a column after different time with nonlinear sorption. During breakthrough a self-sharpening front is observed for $1/n < 1$ which counteracts dispersion while during leaching extended tailing occurs.

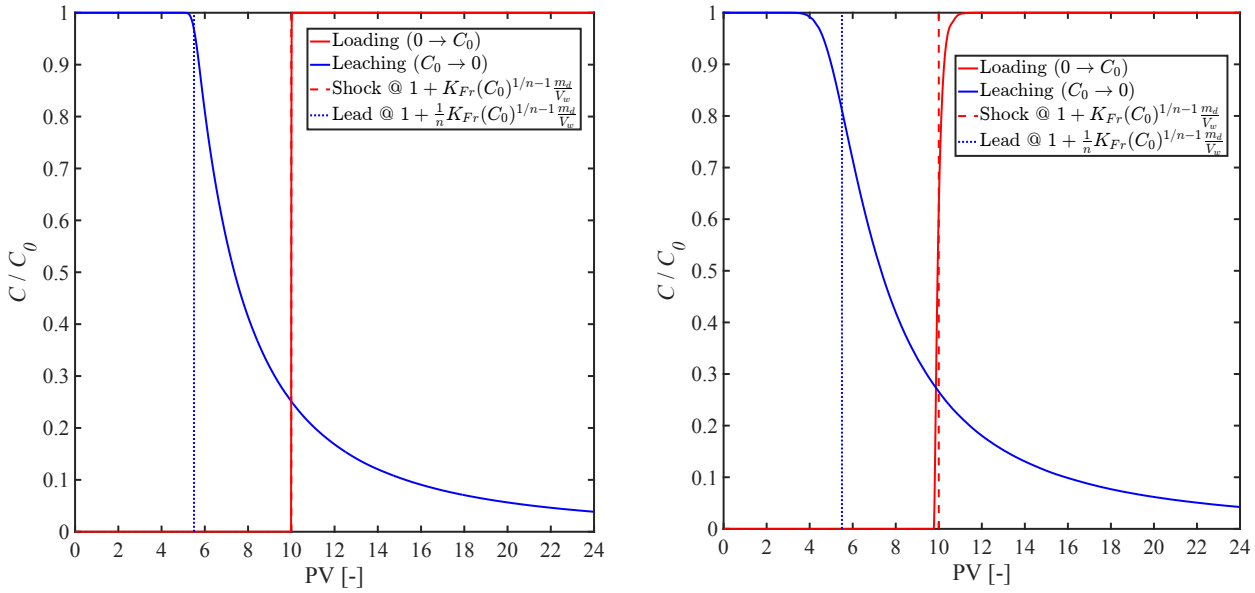


Fig. 5.3: Impact of non-linear sorption on breakthrough and leaching curves (left: no dispersion; right with dispersion). (PV: number of displaced pore volumes = "time"; Freundlich exponent = 0.5); the self-sharpening front ("shock wave": red) moves with a retardation factor of $1 + K_{Fr}\ \frac{m_d}{V_w}\left(C_{w,in}\right)^{1/n-1}$, while the leading edge (blue) of the leaching curve moves with $1 + K_{Fr}\frac{1}{n}\left(C_{w,in}\right)^{1/n-1}\ \frac{m_d}{V_w}$; here 1+9 $1^{-0.5}$ = 10 and here 1+0.5 9 $1^{-0.5}$ = 5.5 (the concentration in the tailing (trailing edge) drops with $(0.5\ 9)^2/(\text{PV-1})^2$, e.g. at PV=10: $(4.5/9)^2$ = 0.25); the centers of mass move with $1 + K_{Fr}\ \frac{m_d}{V_w}\left(C_{w,in}\right)^{1/n-1}$ (the areas above and under the curves are the same: mass conservation).

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