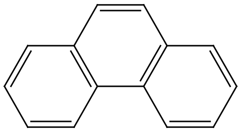
# Homework Problem Set 5. Advanced Sorption

## Problem 1. Group H.

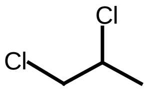
A column leaching test with a contaminated soil is performed. Phenanthrene is the main contaminant. During the initial stages of the experiment, equilibrium conditions prevail. From analysis of the material it is known, that the concentration of phenanthrene in the soil is 1 mg/kg. The fraction of organic carbon content in the soil is 0.005 (foc [-]). The Koc of phenanthrene is 20.000 L/kg. What is the expected phenanthrene concentration in the column effluent?



Phenanthrene

## Problem 2. Group G.

A group of investigators from the USGS recently discovered a large plume of the soil fumigant 1,2-dichloropropane (DCP) in the groundwater flowing away from an air field. The aquifer through which the DCP plume is passing has been found to have a porosity of 0.3. The aquifer solids consist of 95% quartz (density 2.65 g/mL; surface area 0.1 $m^2$/g), 4% kaolinite (density 2.6 g/mL; surface area 10 $m^2$/g), 1% iron oxides (density 3.5 g/mL; surface area 50 $m^2$/g), and organic carbon content of 0.2%. What retardation factor $R_{fi}$ ( $f_{iw}^{-1}$) do you expect at minimum (assumption that only POM is responsible for sorption) for DCP transport in the plume assuming that sorptive exchanges are always at equilibrium? First estimate $K_{oc}$ from a LFER with $K_{ow}$ using a = 0.42 and b = 0.93.



1,2-dichloropropane
(log $K_{iow}$=2.28; Montgomery, 1997)

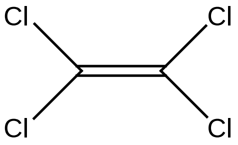
## Problem 3. Group F.

For the adsorption of DDT onto activated carbon, the following Langmuir isotherm constants were found: $K_{ads}$ = 303 L/mg and $C_{s,max}$ = 41.3 mg/g. Find the aqueous equilibrium concentration of DDT if 100 mg of activated carbon and 1 µg of DDT are combined in 1 L of water.

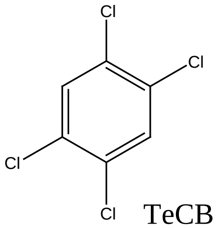
**Problem 4. Group E.**

Because of a leak in a waste container, traces of tetrachloroethylene (PER) and 1,2,4,5-tetrachlorobenzene (TeCB) escape in a groundwater. Provide an estimate of how long it takes to find a conservative tracer and these pollutants at a receptor 25 m downgradient. The flow velocity is 2 m $day^{-1}$. The following characteristics of the aquifer are available:

| | |
|---|---|
| Bulk density: 2.0 kg $L^{-1}$ | |
| Porosity: 0.2 | |
| Fraction of organic carbon: 0.0015 | |
| $K_{OC}$ PER: | 130 L $kg^{-1}$ |
| $K_{OC}$ TeCB: | 3900 L $kg^{-1}$ |



PER



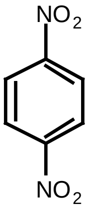
TeCB

**Problem 5. Group D.**

A common way to determine $K_d$ values is to measure sorption isotherms in batch experiments. To this end, the equilibrium concentrations of a given compound in the solid phase ($C_s$) and in the aqueous phase ($C_w$) are determined at various compound concentrations and /or solid-water ratios. Consider now the sorption of 1,4-dinitrobenzene (1,4-DNB) to the homoionic clay mineral, K+-illite, at pH 7.0 and 20 °C. 1,4-DNB forms electron donor-acceptor (EDA) complexes with clay minerals. In a series of batch experiments, Haderlein et al. (1996) measured the data given in the margin. Using these data, estimate the Kd-values for 1,4-DNB in a K+-illite-water suspension (pH 7.0 at 20 °C) for equilibrium concentrations of 1,4-DNB in the aqueous phase of

a) 0.20 µM and
b) 15 µM.

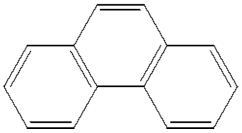
| $C_W$ ($\mu mol \cdot L^{-1}$) | $C_S$ ($\mu mol \cdot kg^{-1}$) |
|---|---|
| 0.06 | 97 |
| 0.17 | 241 |
| 0.24 | 363 |
| 0.34 | 483 |
| 0.51 | 633 |
| 0.85 | 915 |
| 1.8 | 1640 |
| 2.8 | 2160 |
| 3.6 | 2850 |
| 7.6 | 4240 |
| 19.5 | 6100 |
| 26.5 | 7060 |



1,4-dinitrobenzene

### Problem 6. Group C & B.

Sorption of phenanthrene to “dark sand” in a groundwater system needs to be evaluated in order to estimate its transport time from a point source contamination.
An experiment on sorption of phenanthrene to the “dark sand” was done to estimate the effect of DOM on the transport of the compound through the porous medium. The “dark sand” has a bulk density of 1.8 kg $L^{-1}$, a porosity of 0.36, and an organic carbon concentration of 0.15%. In the solution phase, the DOM concentration is 50 mg $L^{-1}$ and the DOM itself does not sorb to the “dark sand”.



$K_{OW} = 10^{+4.57}$

Which fraction f of phenanthrene is “mobile” (i.e. dissolved in the water phase) in the absence of DOM? What is the retardation factor R for phenanthrene? Estimate $K_{OC}$ from LFER with $K_{OW}$ using a = 0.98 and b = -0.32 and use $K_{OC}$ to calculate $K_d$.

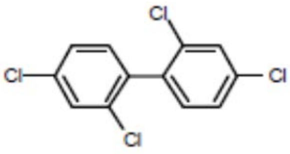
a) **Group C.** Which fraction f of phenanthrene is “mobile” (i.e. dissolved in the water phase) in the absence of DOM? What is the retardation factor R for phenanthrene? Estimate $K_{OC}$ from LFER with $K_{OW}$ using a = 0.98 and b = -0.32 and use $K_{OC}$ to calculate $K_d$.

**b)** **Group B.** Which fraction f of phenanthrene is “mobile” in the presence of DOM (i.e. truly dissolved and DOM-bound)? What is the retardation factor R for phenanthrene in the presence of DOM? Assume that phenanthrene binds to the DOM just as it does to the soil organic matter (i.e. same partition coefficient for DOM and organic matter in the “dark sand”).

### Problem 7. Group B.

*Assessing the speciation of a PCB-Congener in a Sediment–Pore Water System*

Consider a surface sediment exhibiting a porosity $\phi = 0.8$, solids with average density $\rho s = 2.0$ $kg \cdot L^{-1}$ solid, a particulate organic carbon content of 5%, and a DOC concentration in the pore water of 20 mg $DOC \cdot L^{-1}$. Estimate the fractions of the total 2,2',4,4'-tetrachlorobiphenyl (PCB47) present in truly dissolved form in the porewater and associated with the pore water DOM. Assume that absorption into the organic material is the major sorption mechanism and that $K\mathrm{DOC} \cong 1/3\ K\mathrm{ioc}$. Estimate $K\mathrm{oc}$ from a LFER with $K_{\mathrm{ow}}$ using a = 0.74 and b = 0.15 with the $K\mathrm{ow}$ value of PCB47 (log $K_{\mathrm{ow}} = 6.29$)



2,2',4,4'-tetrachlorobiphenyl
(PCB47)

**Problem 8. Group A.**

Why does the sorption of organic vapours to polar inorganic surfaces generally decrease with increasing humidity? Why does the relative humidity have a negligible influence on sorption of organic vapours to apolar surfaces?

**Problem 9. Group A.**

*Evaluating the Concentration Dependence of Equilibrium Sorption of (TeCB) to an Aquitard Material*

Xia and Ball (1999) measured sorption isotherms for a series of chlorinated benzenes and PAHs for an aquitard material ($f_{oc}$=0.015 kg OC/kg solid) from a formation believed to date to the middle to late Miocene. Hence, compared to soils or recent sediment POM, the organic matter present in this aquitard material can be assumed to be fairly mature and/or contain char particles from prehistoric fires. A nonlinear isotherm was found for 1,2,4,5-Tetrachlorobenzene (TeCB) and the following Freundlich parameters were reported: $K_{TeCB\ F}$=128 (mg/g)(mg/mL)$^{-nTeCB}$ and $n_{TeCB}$=0.80. For partitioning of TeCB to this material (linear part of the isotherm at higher concentrations), the authors found a $K_{iOC}$ value of $4.2 \times 10^4$ L/kg OC.

Calculate the apparent $K_{iOC}$ values of TeCB for the aquitard material for aqueous TeCB concentrations of $C_{iW}$=1, 10, and 100 µg/L using the Freundlich isotherm given above. Compare these values to the $Ki_{OC}$ values given above for POM-water partitioning. Comment on the result.