

Organic Pollutant Transport in Unsaturated Porous Media by Atmospheric Breathing Processes(I) - Partition Coefficient -

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ABSTRACT

This paper reports the experimental results for the determination of the overall partition coefficient of VOCs in unsaturated soil.

A chromatographic method was used for the determination of gaseous partition coefficients to natural soil under various water content conditions. The equilibrium vapor pressure of water over saturated salt solution was used to fix the relative humidity of the air and control the water content of the soil systems.

The transport behavior was studied for dichloromethane, trichloroethane and dichlorobenzene pollutants, with log octanol-water partition coefficients($\log K_{ow}$) which range from 1.25 to 3.39, or water to soil partitioning which varies by 135 times; water solubility constants which vary by 3 times; and vapor pressures which range from 1 to 362 torr. Water content of the soil had a pronounced effect on the effective partition coefficient(between gas and soil + water stationary phase) as well as on the effective dispersion coefficient.

1. INTRODUCTION

Having measured the air permeability of the soil, one can determine the soil gas advection in the atmospheric breathing process. To model chemical transport, one needs information about the partitioning between gas and soil. Individual pollutant gases will have a lower advective velocity than the bulk gas and lower dispersive transport than an inert tracer gas as a result of partitioning with the soil and immobile water phases.

Throughout the analysis, the concept of an independent linear adsorption or a single value of the partition coefficient for each pollutants was not considered to be applicable. The reasons are as follows.

1. The chromatograms produced by the soil air chromatography showed a strong tendency to the Gaussian type.
2. No appreciable change in the peak elution times could be distinguished between the injection of a mixture of the pollutants of form those for the corresponding single pollutant injections.
3. Since the peak height point the Gaussian type chromatogram was used for the estimation of the partition coefficient the magnitude of the adsorption phenomena was evaluated

without dispersive interferences.

4. The calculation of a linear adsorption coefficient allowed a direct comparison with published data for the partition coefficient.
5. A simple model was considered to be more useful for the study of the natural environment as long as the simplification was a reasonable approximation.

2. Measurement and analysis

Two different soils, the three different relative humidities and different carrier value of the measured solute detention time with the background detention time the background detention times for each pollutant were measured by by-passing the flow of the GC carrier gas around the soil column. Thus the inlet plus outlet transit time was determined and subtracted from the measured residence time of a species in the soil gas chromatography system.

Following equations were used for the analysis of the data. As the sorption was approximated by the linear isotherm all isochores had the same solute velocity and the peak detention time in the chromatogram was used as the best measure of the mean residence time. The retarded seepage velocity, U_R , for a pollutant gas was the retarded value of the mobile fluid seepage velocity as follows:

$$U_R = U/R_p \quad (1)$$

For non-linear partitioning, R_p and thus U_R would be functions of the pollutant concentration. For linear partitioning, R_p is the retardation factor, or a constant for a given liquid water content, as follows

$$R_p = \{1 + \{ \varphi / (n - \varphi) \} K_H + \{ (1-n) / (n - \varphi) \} K_H K_P \} \quad (2)$$

Where,

R_p = retardation factor as a result of partitioning [dimensionless]

n = porosity [m^3 void volume/ m^3 total volume]

φ = volumetric water or liquid water content (volume of water to total volume)

K_H = the gas-liquid equilibrium constant [$mole/L^3/atm$]

K_P = partition coefficient [($mole/m^3$ of solid)/($mole/m^3$ of liquid)]

The dimensionless partition coefficient (K) is defined such that

$$R_p = 1 + K \quad (3)$$

Since the chromatogram was produced in a time scale, E.Q.(1) was modified as follows.

$$t = L/U \quad (4)$$

$$t_R = L/U_R \quad (5)$$

Thus, the retardation factor becomes

$$R_{p,exp} = t'R/t \quad (6)$$

Where,

$R_{p,exp}$ = the experimentally determined retardation factor.

t = mobile phase detention time in soil GC column.

$t'R$ = solute detention time in soil media, and

L = length of the soil column

From the consideration of the background detention time, and of the definition of t , the following equation can be obtained:

$$R_{p,exp} = \{(t'R)_{exp} - (t'R)_{BKGD}\} / (V_g/Q) \quad (7)$$

Where,

$(t'R)_{exp}$ = the experimental solute residence time between injection port and detector for the soil column GC system

$(t'R)_{BKGD}$ = the background solute residence time between injection port and detector for the GC system without the soil column

V_g = volume of gas in the soil column, as calculated from the mobile phase porosity \times total volume of soil column, and

Q = volumetric flow rate of the phase.

Thus, from measurements of the peak height detention time($t'R$) and flow rate(Q) together with the data of soil compaction the retardation factor was experimentally determined. The experimentally determined dimensionless partition coefficient was determined as follows:

$$K_{exp} = R_{p,exp} - 1 \quad (8)$$

Where,

K_{exp} = the experimentally determined dimensionless partition coefficient

$R_{p,exp}$ = the experimentally determined retardation factor.

3. Results and Discussions

The results of the partition study are measured dimensionless partition coefficient(K_{exp}) of each pollutant is presented as for each relative humidity equilibrated with the soils.

The measured values of the pollutant-vapor to immobile phase(soil+water) partition coefficient(K_{exp}) are much higher than the theoretical values of the dimensionless partition coefficient. For Freon^k the measured values of K are 117 to 440 \times greater than the theoretical

values. Similarly, the experimental values range from 1.7 to $28\times$, 1.6 to $58\times$, and 0.66 to $75\times$ the theoretical value for dichloromethane, trichloromethane and dichlorobenzene, respectively. Only one experimental value of the partition coefficient was less than that predicted by eq.(4)

The effects of the water content of the soil on the theoretically predicted and experimentally determined partition coefficients are presented. From the equilibrium model, a small increase in the dimensionless partition coefficient (K) should result from the small increase in liquid water content. As the water content increase, the mobile gas stationary phase ratio increased. Thus, there was more immobile phase into which the pollutant vapor could partition and the predicted dimensionless partition coefficient(K by eq 4) increased as φ increased.

Instead, a large decrease in the experimentally determined partition coefficient(K_{exp}) values was observed as the liquid water content(φ) increased. This trend was also noticed in the atmospheric breathing experiments. Two aspects are noteworthy.

First, K and K_{exp} asymptotically approach the same value as the liquid water content increases. This indicates better agreement between the theoretical model and the experimental results as φ increases. Except for Freon^{kc} the experimental results for the tests using sand equilibrated with 100% R.H. air agree with the theory within the uncertainty of the equilibrium constants(K_H and K_p) using in the model

Second, K_{exp} is greater than K . If the sorption kinetics in the air-soil chromatograph were slower than the transport, equilibrium would not be attained and the measured retardation factor would be less than that estimated by the theoretical model. Thus if the kinetics are slow, K_{exp} should be less than K . Since K_{exp} is greater than K , the values of the theoretical equilibrium constants, K_H and $K_H K_p$, used to model the partitioning between air and water and air and soil phases, respectively, should be re-evaluated.

One interpretation is that the effective partition coefficient between air and water phases, is a function of φ , since there are two types of surface(dry solid and water covered solid surface) and thus two types of equilibria. $K_H K_p$ describes the equilibrium partitioning for gas to a water-solid interface. Thus, $K_H K_p$ is appropriate only for the fraction of the soil surface which is wetted. At low liquid water content, the surface of the soil particles is not completely covered by water and another equilibrium expression is needed to describe the partitioning of a chemical species between gas and dry solid surface phases. As φ increases, more of the solid surface is covered by water and $K_H K_p$ describes the gas-solid equilibrium partitioning.

There are also notable difference between the tracer species Freon^{kc} and pollutant gases DCM, TCE, and DCB. The three pollutants show an initial large drop does not. Above 70% R.H., the partition coefficients for the pollutants change little. By contrast, Freon^{kc} was chosen originally as a tracer due to its representativeness of the pollutants. Its properties are similar to the pollutants(Table 3.2) except for the low value of the surface tension(which is about 1/2 to 1/3 times as large) the higher values of K_H (which is about 350 to 1000 times as large). Due to the higher wettability of Freon^{kc} than the other pollutants(noticed by the small value in surface tension), it might be able to resist against the strong wetting phase of the water vapor at high water contents.