

A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds

Abstract. Soil-water equilibrium data suggest that the transfer of nonionic chemicals from water to soil may be described in terms of a hypothesis of solute partitioning in the soil organic matter. This concept allows estimation of soil-water distribution coefficients either from solvent-water partition coefficients or aqueous solubilities.

Earlier studies of the uptake by soil of nonionic organic compounds from water have indicated that soil organic matter is the principal adsorbent (1-3), and it has been speculated that the high surface area of this organic matter is an important factor (4). We here present data for the hypothesis that sorption by soil organic matter is essentially a partitioning process. The supporting data consist of (i) our own determination of the isotherms of seven organic compounds that show no indication of curvature even at concentrations approaching saturation and (ii) extensive data (those of ours and others) over seven orders of magnitude of solubilities and with various soils, in which the partition coefficients are well correlated by solubilities and the organic contents of the soils.

Figure 1 shows the 20°C equilibrium isotherms of 1,2-dichloroethane, 1,2-dichloropropane, 1,2-dibromoethane, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, tetrachloroethene, and 1,2-dichlorobenzene from water, at pH 6.8, onto a Willamette silt loam (1.6 percent organic matter, 26 percent clay, 3.3 percent sand, and 69 percent silt). Isotherms plotted in micrograms of organic per gram of soil versus C_e [in parts per million (ppm)] are essentially linear; moreover, the highest C_e is about 0.30 to 0.50 of the aqueous solubility (S) for the first five compounds and 0.75 to 0.95 S for the last two compounds.

In addition to the fact that the isotherms show no indication of curvature even at high relative concentrations, the soil-water distribution coefficients (as determined from the slopes of the isotherms) appear to be inversely proportional to the corresponding solubilities (Fig. 2). The isotherm data for polychlorinated biphenyl (PCB) isomers show similar results (5). These findings, together with the lack of isotherm curvature, are consistent with the idea that the uptake of neutral organic chemicals by soil is essentially a process of partitioning (dissolution) rather than physical adsorption (6).

Since the distribution coefficient of an organic chemical is known to depend largely on the content of organic matter

(3), the above reasoning leads to the further postulate that the uptake of neutral organics by soil is due mainly to partitioning in the soil organic matter as suggested by Swoboda and Thomas (7) for parathion in soil. Hartley (8) speculated that a solvent action of the oily constituents of the organic matter might be responsible for soil uptake. If we assume a partition concept, the reported correlation of soil organics-water distribution

coefficients (G) with octanol-water partition coefficients (K) for nonionic chemicals (9) is presumably a result of similar equilibrium processes.

The partitioning hypothesis, moreover, is consistent with the observed enthalpies. Adsorption of a trace component, as on activated carbon (10), requires a relatively high exothermic $\Delta\bar{H}$ to balance the resultant decrease in entropy. By contrast, partitioning of a solute may not be exothermic and would have a nearly constant $\Delta\bar{H}$ since

$$\Delta\bar{H} = \Delta\bar{H}_o - \Delta\bar{H}_w \quad (1)$$

where $\Delta\bar{H}_o$ and $\Delta\bar{H}_w$ are the molar heats of solution in the organic phase (in this case, soil organics) and in water, respectively. Low water solubilities of organic compounds are usually associated with

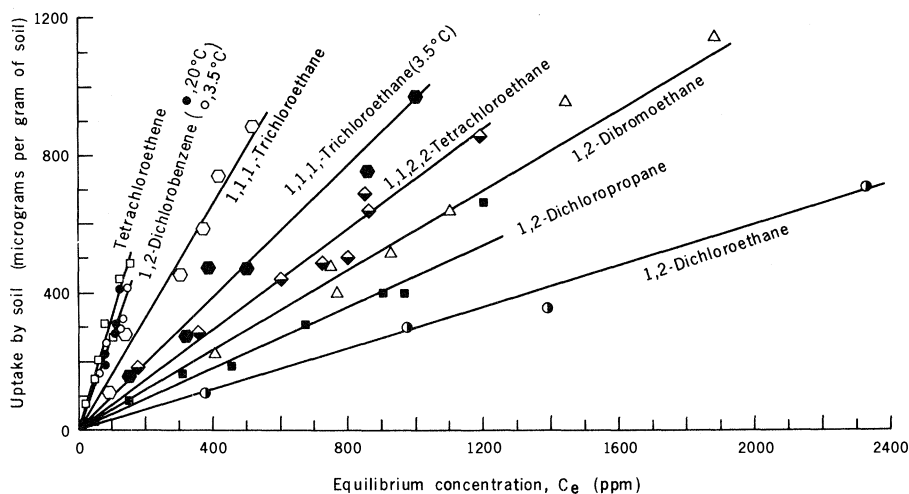


Fig. 1. Soil-water equilibrium isotherms at 20°C.

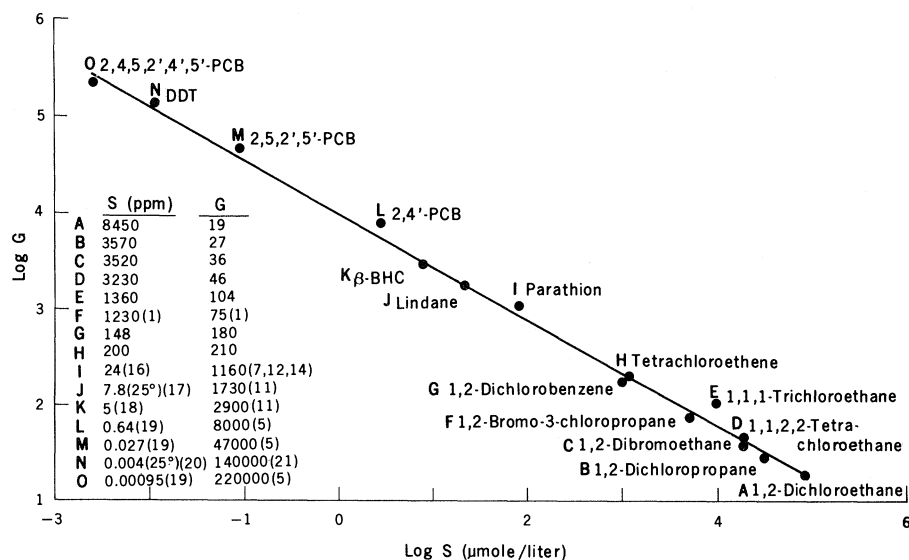


Fig. 2. Soil organics-water distribution coefficients (G) plotted as a function of the aqueous solubilities (S) of selected nonionic compounds. Reference numbers are given in parentheses after the S and G values.

large (positive) $\Delta\bar{H}_w$. The corresponding $\Delta\bar{H}_o$ terms should be much smaller, reflecting the improved compatibility in an organic phase. For compounds of low water solubility, $\Delta\bar{H}$ would be somewhat less negative (exothermic) than $-\Delta\bar{H}_w$. This readily accounts for the $\Delta\bar{H}$ values for β - and γ -BHC (benzene hexachloride) (11) and parathion (12) in soil-water equilibria; $\Delta\bar{H}$ will be small for compounds with low $\Delta\bar{H}_w$ and may even be positive if $\Delta\bar{H}_w$ is negative. In our data, $\Delta\bar{H}$ for 1,2-dichlorobenzene is practically zero as a result of the low $\Delta\bar{H}_w$ ($S = 133$ ppm at 3.5°C; 148 ppm at 20°C), and $\Delta\bar{H}$ for 1,1,1-trichloroethane is positive ($> -\Delta\bar{H}_w$) because of the negative $\Delta\bar{H}_w$ value for this compound ($S = 1790$ ppm at 3.5°C; 1360 ppm at 20°C). These results are not compatible with an adsorption model.

Consider now the relation between G and S . Since S is a good estimator of the organic-water partition coefficients for slightly soluble organic compounds (13), we may expect to find a correlation between $\log G$ and $\log S$, similar to that between $\log G$ and $\log K$. The G values calculated on the basis of the individual soil organic matter contents for the seven compounds from this work and other nonionic compounds from the literature are shown in Fig. 2. The regression equation is

$$\log G = 4.040 (\pm 0.038) - 0.557 (\pm 0.012) \log S \quad (2)$$

with $r^2 = 0.988$ and $n = 15$ (where G is dimensionless and S is in micromoles per liter) and covers more than seven orders of magnitude in S and four orders of magnitude in G .

The close fit suggests that the makeup of organic matter in soil is not critical in determining $\log G$ values for neutral chemicals (14). Moreover, it implies that, although the uptake by other soil constituents may involve other mechanisms, their contribution will be relatively small. For instance, the uptake by clays is considerably lower than that of organic materials (11, 15).

Since a chemical's partition value depends on its relative solubilities in the two phases, the solution pH may be expected to have a strong effect on the partition coefficients of organic acids and bases. At high pH , the dissociated anion of an organic acid should be poorly distributed in soil organics because of its high water solubility and possibly the repulsion by the surface negative charge of the organic matter. At low pH , certain cationic species (for example, paraquat)

may show substantial adsorption through ion-exchange even though partitioning is not favored by their high water solubilities. Surface binding (for example, hydrogen bonding) may potentially be a factor for highly polar compounds. The contribution of these effects needs to be considered separately.

It thus appears that the uptake of neutral chemicals by soils is consistent with the hypothesis of solute partitioning to the organic content of the soil. The resulting relationship between $\log G$ and $\log S$ provides a means for estimating the soil-water distribution.

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Widmanstaetten Patterns in Josephinite, a Metal-Bearing Terrestrial Rock

Abstract. *Widmanstaetten patterns have been found in several specimens of josephinite, a complex, metamorphosed, metal-bearing rock from placers on serpentinized peridotite in southwest Oregon. The patterns, in interior less-altered regions of the specimens, are typical of exsolution textures produced during slow cooling of a homogeneous metal. The bulk composition of the metal phases indicates that the homogeneous metal must have existed at temperatures above 500°C. Josephinite Widmanstaetten patterns are the first known in terrestrial rock. We interpret them as further evidence that josephinite was derived from the mantle.*

Josephinite, which is variable in composition, contains alloys of Ni, Fe, and Co. Other phases include garnet, sulfides, and arsenides; alteration phases include magnetite and serpentine. Josephinite is found in placers of streams which originate on and traverse the Josephine Peridotite, which is the depleted mantle of an obducted ophiolite complex (1). The josephinite specimen described in this report consists primarily of Fe, Ni, and Co. The specimen, 3 cm long and 2 cm wide, has been sectioned and polished for this study.

X-ray diffractometer analyses of polished surfaces show that there are face-centered cubic (γ) and body-centered cubic (α) metal phases present. Observa-

tions of polished surfaces made with optical and scanning electron microscopes reveal that the α and γ phases are intergrown in a pattern similar to Widmanstaetten patterns found in some meteorites. Figures 1 and 2 are scanning electron microscope images of the Widmanstaetten pattern from an unetched surface. The γ lamellae are arranged with a symmetry similar to that found in a (111) section of an octahedrite meteorite. This is a Widmanstaetten pattern in the metallurgical sense. However, it differs from the Widmanstaetten patterns found in meteorites in two significant ways. The lamellae in the josephinite specimen have the γ structure, whereas lamellae in meteorites consist of