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7. Subjects were students at the University of Tennessee who volunteered to participate; they were not enrolled in a design curriculum.
8. Typical activities listed by subjects included waiting for someone, relaxing, and a casual conversation. The only restriction placed on the activity simulated was that the subject not place hands or arms in the model during the experiment, which would have constituted a kinesthetic mixing of scales. Subjects were comfortably seated and viewed the scale figure throughout the experiment. It is important to inform subjects they are not being tested with respect to their accuracy of temporal estimation.
9. The cross-checking index ratio derived between 1/6 and 1/12 and between 1/6 and 1/24 scales in experiment 2 are 1.67 ± 0.145 and 3.15 ± 0.353, respectively ($N = 27$). Correlations based on linear regressions between 1/6 and 1/12 and between 1/6 and 1/24 scales are .588 ($P < .01$) and .307 (not significant), respectively (as in Table 2, the larger scale T's are the independent variables and the cross-checking index ratios the dependent variables).
10. R. R. Ward, *The Living Clocks* (Mentor, New York, 1972).
11. Preliminary studies relating scale reduction to neurological functioning indicate clear shifts in electroencephalographic (EEG) activity. Neurological activity was measured through EEG power (absolute and relative) spectral analysis [A. J. De Long and J. Lubar, *Soc. Neurosci. Abstr.* **5**, 203 (1979)].
12. Partially funded by the School of Graduate Studies and the School of Architecture, University of Tennessee, and National Institutes of Health biomedical support grant RR-07088 to the University of Tennessee. Special thanks to J. E. Seiber, M. Robin, and O. Leslie for assistance and to an anonymous reviewer for cogent criticism of earlier drafts.

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Soil-Water Equilibria for Nonionic Organic Compounds

Chiou *et al.* (*1*) suggest that solubility in the soil organic matter, rather than physical adsorption, is the appropriate mechanism to explain the soil-water distribution behavior they observed. They eliminated adsorption on the basis of (i) the linearity of isotherms, (ii) heat effects, and (iii) their correlation of distribution coefficients. However, an alternative mechanism involving adsorption may be more appropriate.

The linearity of all the species over the entire composition range is not convincingly established, nor do Chiou *et al.* present an argument, either empirical or theoretical, that prohibits linear isotherms for adsorption. Their discussion of heat effects is apparently based on the assumption that the enthalpy change accompanying adsorption from solution can be determined from the temperature dependence of isotherms, as is possible for the adsorption of pure gases. In the case of pure gases, the state of the adsorbed phase is determined only by the adsorbent loading and the temperature and thermodynamic analysis leads to a Clapeyron-type equation involving the heat of adsorption. When more than one component is adsorbed, however, an additional composition variable is required to determine the state of the adsorbed phase, and the expression involving the heat of adsorption is more complex.

Chiou *et al.* do not show how their proposed mechanism would lead to their correlation of distribution coefficients, or how such a correlation would preclude other mechanisms such as adsorption. Further, a solubility mechanism apparently cannot explain the results of Yaron and Saltzman (*2*), who found that parathion sorption from hexane solution decreased as the water content of soil increased. If parathion were merely dissolving in the soil organic matter, the existence of small quantities of water, which should be immiscible with the oily constituents of the organic matter, would not affect the distribution. Yaron and Saltzman's explanation in terms of competition between water and parathion for adsorption sites seems more plausible; Spencer *et al.* (*3*) reported similar results for lindane and dieldrin.

A simple adsorption model suggests the distribution coefficient correlation found by Chiou *et al.* Manes and Hofer (*4*) adapted Polanyi's theory of adsorption from solution and express the adsorption potential of a solute, ε_s, as

$$\varepsilon_s = RT \ell n \frac{C_s}{C_e} + \frac{\varepsilon_\ell V_s}{V_\ell} \qquad (1)$$

where C_s and C_e are saturation and adsorption equilibrium concentrations, V_s and V_ℓ are characteristic volumes of solute and solvent, ε_ℓ is the adsorption potential of the solvent, R is the gas constant, and T is absolute temperature. A characteristic curve for the adsorption of a solute on a given adsorbent is constructed by plotting ε_s as a function of the volume adsorbed, ϕ, with

$$\phi = \mu V_s \qquad (2)$$

where μ is the molar solute uptake. Following Dubinin (*5*), characteristic curves of various solutes on the same adsorbent are assumed to have the same shape and can be superimposed with the use of an appropriate scale factor for each solute. The solute characteristic volume is commonly used and is expected to lead to a universal characteristic curve, where the scaled adsorption potential, α

$$\alpha = \frac{\varepsilon_s}{V_s} = \frac{1}{V_s}\left(RT \ell n \frac{C_s}{C_e} + \frac{\varepsilon_\ell V_s}{V_\ell}\right) \qquad (3)$$

should be identical for each solute at equal values of ϕ. The systems under study span a wide range of composition, but the solute concentration is low, and it is reasonable to assign a constant adsorption potential to the solvent. The scaled adsorption potentials for any two solutes will be equal when

$$\frac{RT}{V_{s_1}} \ell n \left(\frac{C_s}{C_e}\right)_1 = \frac{RT}{V_{s_2}} \ell n \left(\frac{C_s}{C_e}\right)_2 \qquad (4)$$

In the region where isotherms are linear, the isotherm equation is

$$\mu = G C_s \left(\frac{C_e}{C_s}\right) \qquad (5)$$

where G is the distribution coefficient of Chiou *et al.* The condition of equal ϕ for any two solutes is now

$$V_{s_1} G_1 C_{s_1} \left(\frac{C_e}{C_s}\right)_1 = V_{s_2} G_2 C_{s_2} \left(\frac{C_e}{C_s}\right)_2 \qquad (6)$$

Thus, Eqs. 4 and 6 are the conditions of equivalency. If the crude approximation of equal characteristic volumes for all solutes is made (*6*), these equations reduce to

$$G_1 C_{s_1} = G_2 C_{s_2} = K \qquad (7)$$

where K is a constant.

Equation 7 predicts that a plot of log G versus log C_s should be linear with slope −1. Although the slope of Chiou *et al.*'s correlation is −0.557, the model at least predicts the functionality. Thus, an adsorption mechanism offers a possible explanation for the results of Yaron and Saltzman and of Spencer *et al.* and suggests the correlation found by Chiou *et al.*; the solubility mechanism appears unable to do either.

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6. This approximation may be justified by the fact that the liquid molar volumes of compounds studied by Chiou *et al.* lie in a fairly narrow range.

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We limited our discussion to sorption of neutral compounds from water (*1*). Based on the observed soil-water equilibrium data, we suggested that these compounds are taken up primarily by soil organic matter through partitioning. The soil inorganic fraction does not make a significant contribution in aqueous systems, presumably because of its strong dipole interaction with water, which precludes active association of these compounds with this portion of the soil. In nonaqueous systems, the contribution of soil minerals can be important even for neutral (especially polar) compounds.

Our discussion of the heat effect in soil-water systems was based on the temperature dependence of the equilibrium constants (that is, the slopes of the isotherms). Calculations of the enthalpy change $\Delta\bar{H}$ from a Clapeyron-type equation involve no restrictions on the number of components in the systems. The $\Delta\bar{H}$ for a partition process must, in principle, be equal to the difference in heats of solution in the two equilibrating phases. For adsorption, $\Delta\bar{H}$ is always more exothermic than the heat of condensation in water.

Our hypothesis does not rule out the possibility of adsorption from an organic solvent or from the gas phase on dry and partially hydrated soils (*2*). A dehydrated soil might show significant uptake of a neutral solute from some nonpolar solvents by adsorption through dipole interactions or London forces on high-surface-area inorganic minerals (*3*), although partitioning of the solute to the organic matter may be weak because of its high solubility in the solvents (*4*). Thus, while uptake by the soil mineral fraction is unimportant in comparison with that by soil organic matter in aqueous solutions, the reverse may be true in nonpolar organic solvents such as hexane.

For parathion in dry soil–hexane systems, for example, we would expect that adsorption on the soil inorganic fraction would be largely responsible for the soil uptake and that such adsorption would be suppressed by the soil water (*3*), which can compete more effectively than less polar parathion for polar inorganic minerals. This analysis leads to the expectation that sorption of a neutral solute, such as parathion, on soil from polar organic solvents (for example, methanol, acetone, and dioxane) will be insignificant (*3*), because these solvents would wet the inorganic minerals effectively and their high solvating capability would reduce solute partitioning to the organic matter. The adsorption model suggested by Kyle cannot explain the results in aqueous and nonaqueous systems.

Our reasoning, moreover, accounts for the anomalous temperature effect for the uptake of parathion in moist soil-hexane systems (*3*). The enhanced sorption at higher temperatures is apparently caused by the gradual weakening of dipole interactions between water and soil minerals, assisting parathion in competing for this portion of the soil. This analysis also explains to a large extent the finding of Spencer and Cliath (*5*) that the vapor density of lindane applied to a hydrated soil has a smaller temperature coefficient than that of pure lindane. The ability of the soil mineral fraction to adsorb lindane would be lost due to the presence of water, restricting lindane to partition to the soil organic phase. Thus, the vapor density would be much higher in the hydrated soil than in the dehydrated soil. Hance's observations (*6*) of the sorption of a pesticide (diuron) from aqueous and petroleum solutions are also consistent with this analysis.

Kyle's view of the Polanyi theory appears to be incomplete. First, the isotherm assumed by his Eq. 1 is nonlinear, since solute condensation is implied (*7*). Second, the scaled adsorption potential curves (ϕ versus ϵ/V) are the same only for chemically similar compounds that have nearly identical polarizability per unit (molar) volume, or refractivity per unit volume (*8*). The difference in the values of ϵ/V for different compounds at fixed loadings may be related to their refractivities per unit volume or refractive indices (*9*). We were unable to apply the Polanyi model because it could not be reconciled with the high degree of linearity of the soil-water isotherms. Nonlinearity is normal in Polanyi isotherms, whereas linearity is limited to very low relative concentrations (C_e/C_S). Similarly, a Langmuir isotherm is indistinguishable from a linear partition isotherm only in the limit of low relative concentrations. Our high-concentration data and observed heat effects cannot be reconciled with a Langmuir equation.

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2. More data have been obtained in our laboratory to address this problem. The results are now in preparation for publication.
3. B. Yaron and S. Saltzman, *Soil Sci. Soc. Am. Proc.* **36**, 583 (1972).
4. Parathion is miscible with acetone, chloroform, dioxane, methanol, ethanol, ethyl acetate, and benzene [E. F. Williams, *Ind. Eng. Chem.* **43**, 950 (1951)] and has a solubility of 5.74×10^4 mg/liter in hexane at 20°C (unpublished data). The G values [see (*1*)] of parathion in the selected organic solvents (*3*) would be about 10 or less. With a soil to solvent ratio of 1 to 20 and low percentages of the soil organic matter (*3*), parathion partitioned to soil organic matter would be negligible.
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7. Note also that Eq. 1 appears to be misquoted; if E_s refers to the adsorption potential of a solute from solution, the second term on the right of Eq. 1 should be deleted. Check with (*8*) and (*9*) for clarity.
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An Upper Bound to the Lightning Flash Rate in Jupiter's Atmosphere

Lewis (*1*) discussed Voyager optical measurements and low-frequency radio-wave observations related to lightning discharges in the atmosphere of Jupiter. He used a specific set of assumptions together with whistler measurements from the plasma-wave system to arrive at estimates of the average planetary lightning stroke rate r ranging between 10^{-4} and 4×10^{-2} flashes per square kilometer per year. Here we show that when the same Voyager whistler data are combined with different physical assumptions about the source area, the whistler paths, and the whistler amplitude distributions over the paths, a planetary lightning rate as high as several tens of flashes per square kilometer per year cannot be ruled out.

The Voyager 1 wave instrument detected lightning whistlers only when the spacecraft was at a Jovicentric distance of about 5.5 to 6.0 Jupiter radii (R_J) near the equatorial plane. The Voyager event rate was about 0.12 whistlers per second (*2*), and the ray-tracing analysis by Menietti and Gurnett (*3*) confirmed that these whistlers originate at high latitudes ($\approx 66°$) near the feet of the field lines passing through the Io torus. The geometric situation is indicated in the upper part of Fig. 1, which shows Jupiter, some