Figure 1

than linear as they expected.

From the data on percent sorbed in their Table I, one can compute K_p values for the three isomers using

$$K_p = \frac{1}{100/F - 1}\frac{1}{\rho} \tag{3}$$

The correlation coefficient of these computed K_p values with organic carbon is 0.98 for each isomer, and the K_{oc} values (averaged over the 12 sediments) are 1900, 2100, and 1900 for the α, β, and γ isomers, respectively; the correlation coefficients are considerably higher than those for F vs. oc reported by Wahid and Sethunathan (0.78, 0.76, and 0.79). How well their data conform to this analysis can be shown by reconstructing their Figure 1 of F (averaged over the three isomers) vs. oc, with a computed line drawn from eq 2 (above), using a K_{oc} of 2000.

In addition to the "single point" partitioning data for the 12 soils, Wahid and Sethunathan presented sorption isotherms for 5 additional soils. At low HCH concentrations, the adsorption isotherms should approximate linearity, which is evidenced in their Figure 3. By inspection one can see that the slopes for linear fitting compare well in all cases with the K_p values computed above. In their second figure, however, the isotherms were log–log fitted to the nonlinear Freundlich equation, a step that can introduce unnecessary complexity in this instance. The K values derived from nonlinear fitting depend on the particular choice of concentration units for HCH; in comparing K values for different soils, the absolute as well as relative values are unit dependent. In this particular instance, the use of a more complex isotherm form may serve to reduce the conformity to expected trends in sorption behavior.

In a previous publication, these same authors (Wahid and Sethunathan, 1978) described parathion sorption on these same soils. Again, they correlated percentage sorbed F, with organic carbon ($\gamma_c = 0.84$) and developed a log–log regression equation relating F and oc. In this instance, just as with the HCH isomers, computed K_p values for parathion (derived from their reported values of F) correlate better with oc ($\gamma = 0.96$) and give an average K_{oc} of 2100. This is consistent with a K_{oc} estimate of 2600, derived from a published K_{ow} of 6400 (Chiou et al., 1977).

In both papers, important information on sorption is presented. The data are consistent with other published data and with estimates derived from related physical properties. Also, the sorption behavior conforms to that expected for hydrophobic sorption. Unfortunately, the analyses presented by the authors, involving bilinear or log–log equations relating F to oc, propagate a complex picture of sorption and create perplexity for those in search of congruity in the published sorption literature.

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Sir: The main criticism by Karickhoff (1981) is with regard to the bilinear or log–log approach of relating percent soil sorption (F) of parathion (Wahid and Sethunathan, 1978) and α, β, and γ isomers of hexachlorocyclohexane (HCH) (Wahid and Sethunathan, 1979) to soil organic matter content (om). Furthermore, Karickhoff in his correspondence describes the relationship between the sorption partition coefficient (K_p) and organic carbon (oc) as a simpler and less misleading approach to understand sorption behavior of such hydrophobic organic compounds.

According to our earlier study [Figure 1 of Wahid and Sethunathan (1977)], equilibrium concentration ratios (or K_p) for parathion designated as

$$\theta = \frac{\mu g \text{ of pesticide sorbed/g of soil}}{\mu g \text{ of pesticide/mL of solution}}$$

were linearly related to om, as noticed by Karickhoff. Nevertheless, on close scrutiny, we do find some values deviating from linear correspondence. These deviations may be attributed to the differences in the active fraction of soil om (designated as ω) involved in sorption (Lambert, 1968). Likewise, K_{oc} values for γ-HCH either reported by Farmer (1976) or computed from our data by Karickhoff showed variations from 1000 to 2000. These variations, albeit significant in the two independent analyses, were ignored by Karickhoff as reflected in his statement that K_{oc} is highly independent of the soil or sediment, seldom varying more than a factor of 2 for nonpolar organics. This, we feel, is an underestimate of the role of soil constituents other than om or oc in pesticide sorption.

Certainly om or oc is the most important single, but not the only, factor affecting the sorption of parathion (Wahid and Sethunathan, 1978) and HCH isomers (Wahid and Sethunathan, 1979) in soil. The relationship $K_p/\text{oc} = K_{oc}$, used by Karickhoff, is based on the asumptions that oc is *solely* responsible for the soil sorption of these organic molecules and that, when oc is zero, K_p is also zero which, indeed, is not valid.

Besides oc or om, inorganic soil constituents also contribute to the sorption of the pesticides in the soil, especially when the organic matter content is low. This was

demonstrated both for parathion (Wahid and Sethunathan, 1978) and HCH isomers (Wahid and Sethunathan, 1979) by using H_2O_2-oxidized soils. Also, from the bilinear plot relating F to om, the theoretical value for HCH sorption at zero organic matter content [Y intercept of the first linear portion in Figure 1 of Wahid and Sethunathan (1979)] was 36.58% which was close to the value of 28% for H_2O_2-oxidized soils. According to Karickhoff's Figure 1, the F value for HCH isomers was ~20% when no organic carbon was present in the soil. Therefore, the assumptions implicit in the relationship $K_p/oc = K_{oc}$ are not valid.

Thus, bilinear analysis helped in demonstrating the role of inorganic soil constituents in the sorption of parathion and isomers of HCH, especially at organic matter levels of <2–3%. If the sorption values were treated as suggested by Karickhoff by the equation $K_p/oc = K_{oc}$, this information would not have been obtained, because the straight line plot of oc (X axis) vs. K_p (Y axis) should invariably pass through zero without a Y intercept, leading to an erroneous conclusion. Thus, K_{oc} values derived from the K_p/oc relationship can be misleading since K_p of an organic molecule is not strictly the sorption partition coefficient from the soil organic carbon–water system but rather an "effective" partition coefficient from a heterogeneous solid (involving both organic and inorganic constituents)–water system. We, therefore, feel that bilinear or log–log analysis is more useful in systems such as in soil where the sorption of organic molecules is governed by both organic and inorganic surfaces.

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CORRECTIONS

[13]C NUCLEAR MAGNETIC RESONANCE OF GRASS LIGNINS, by David S. Himmelsbach* and Franklin E. Barton II, *J. Agric. Food Chem.* **1980**, *28*, 1203.

Table I, on p 1206, contains two errors. Data for signal no. 29 were omitted and should be as follows: for CBG δ (int), 115.5 (855); for Ky-31 δ (int), 115.8 (312). Also, the assignment for signal no. 28–30 should read as follows: C-5 in coniferyl, C-3/5 in p-coumaryl with α,β unsaturated, and C-β in cinnamic acids.