

Table II. Correlation Coefficients between Total Nitrogen and Nonprotein Nitrogen in Ninety-eight Germ Plasm Accessions of Chickpea

component	range	mean	correlation coefficient of % total N
total N as % of meal	2.43-4.85	3.58	
NPN as % of meal	0.16-0.73	0.36	0.802 <sup>a</sup>
NPN as % of total N	5.84-16.48	9.84	0.468 <sup>a</sup>

<sup>a</sup> Significant at the 1% level.

10.5% of total nitrogen of the meal was found in the supernatant. A positive reaction is obtained with the biuret reagent even with small peptides. Therefore, small peptides may be present as such in mature chickpea seeds. As a negligible amount of protein (peptides) was dissolved by 10%  $\text{Cl}_3\text{AcOH}$ , it can be concluded that the values obtained by direct extraction using 10%  $\text{Cl}_3\text{AcOH}$  represent the NPN of the meal.

On the basis of the results of this investigation, a  $\text{Cl}_3\text{AcOH}$  concentration of 10% (w/v), at which nitrogen solubility was observed to be minimal, was employed for the extraction of NPN in germ plasm samples. The means and ranges of total meal nitrogen and NPN in 98 germ plasm lines of chickpea are presented in Table II. Total meal nitrogen in these lines varied between 2.43 and 4.85%, whereas NPN as percentage of the meal varied between 0.16 and 0.73. A positive and highly significant correlation [ $r = 0.802$  (significant at the 1% level)] was obtained between percentage of the total meal nitrogen and percentage of the NPN of the meal. On the other hand, when expressed as percentage of the meal nitrogen,

NPN varied between 5.84 and 16.48 and showed a lower but appreciable correlation [ $r = 0.468$  (significant at the 1% level)] with the percentage of the total nitrogen in the meal. Therefore, whether expressed either as percentage of the meal or as percentage of the total nitrogen, NPN increased when the total nitrogen of the meal increased.

It is evident from these results that all nitrogen present in chickpea is not associated with seed protein, suggesting that NPN has to be taken into account if total protein content is to be measured accurately.

#### ACKNOWLEDGMENT

We are grateful to P.V Rao for technical assistance and Dr. L. J. G. van der Maesen for the supply of seed material.

#### LITERATURE CITED

- Association of Official Analytical Chemists "Official Methods of Analysis", 11th ed.; AOAC: Washington, DC, 1970.  
 Bell, P. M. *J. Sci. Food Agric.* **1963**, *14*, 133.  
 Bhaty, R. S. *Cereal Chem.* **1972**, *49*, 729.  
 Bhaty, R. S.; Finalayson, A. J. *Cereal Chem.* **1973**, *50*, 329.  
 Boulter, D.; Davis O. J. *New Phytol.* **1968**, *67*, 935.  
 Millerd, A., paper presented at a seminar held in the Division of Plant Industry, CSIRO, Canberra, March 1972, p 52.

Umaid Singh\*  
 Ramamurthi Jambunathan

International Crops Research Institute for the  
 Semi-Arid Tropics  
 Patancheru P.O.  
 Andhra Pradesh 502 324, India

Received for review August 29, 1980. Accepted January 9, 1981.  
 Submitted as Journal Article No. 128 by the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT).

## CORRESPONDENCE

### On the Sorption of Neutral Organic Solutes in Soils

Sir: Recently, Wahid and Sethunathan (1979) presented excellent data describing the sorption of the  $\alpha$ ,  $\beta$ , and  $\gamma$  isomers of hexachlorocyclohexane (HCH) on a wide variety of soils. They found organic carbon to be the single most important soil property affecting HCH sorption. In the study, the expected linear dependence of sorption on organic carbon was factored into two linear branches with the "breakpoint" at 1.98% organic carbon. These data are amenable, however, to a simpler description and perhaps less misleading analysis.

The relative importance of organic carbon in the sorption of hydrophobic organic compounds is well established [see Kenega and Goring (1978) for a complete documentation]. The sorption partition coefficient,  $K_p$ , or Freundlich  $K$ , when referenced to organic carbon (i.e.,  $K_p/\text{oc} \equiv K_{oc}$ ) is highly independent of the soil or sediment, seldom varying more than a factor of 2 for nonpolar organics. (The fractional mass of organic carbon in the soil/sediment is denoted by oc.) Numerous  $K_{oc}$  values for  $\gamma$ -HCH can be derived from the literature [see Farmer (1976) for a summary of the literature data], and vary from 1000 to 2000 on soils and sediments ranging in organic carbon from 0.38 to 18%. Also, for these types of organic

compounds, Karickhoff et al. (1979) showed that excellent estimates of  $K_{oc}$  can be derived from octanol/water distribution coefficients,  $K_{ow}$ . For unfractionated soils and sediments

$$\log K_{oc} \approx \log K_{ow} - 0.39 \quad (1)$$

Kurihara et al. (1972) published  $K_{ow}$  values for the  $\alpha$ ,  $\beta$ , and  $\gamma$  isomers of 6440, 6250, and 5200, respectively, from which  $K_{oc}$  estimates of 2600, 2500, and 2100 can be derived.

Thus, in Wahid and Sethunathan's work, one would expect  $K_p$  to be proportional to organic carbon, with a proportionality constant,  $K_{oc}$ , between  $1 \times 10^3$  and  $2.5 \times 10^3$ . Unfortunately, these authors investigated the dependence of percent HCH sorbed,  $F$ , on organic carbon.  $F$  is related to the partition coefficient by

$$\frac{F}{100} = \frac{\rho K_p}{1 + \rho K_p} \quad (2)$$

where  $\rho$  is the soil/water ratio, which in this case was 0.1. If  $K_p$  varies linearly with organic carbon, a plot of  $F$  vs. oc should be hyperbolic, as observed in Figure 1, rather

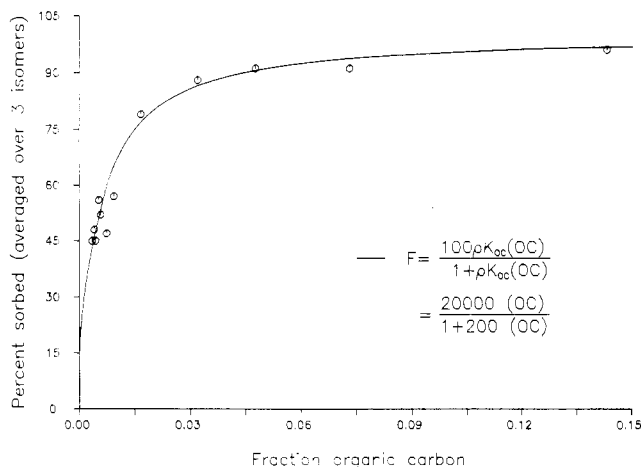


Figure 1

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

$$K_p = \frac{1}{100/F - 1} \frac{1}{\rho} \quad (3)$$

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  $\alpha$ ,  $\beta$ , and  $\gamma$  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 par-

*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  $\alpha$ ,  $\beta$ , and  $\gamma$  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

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

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

ticular 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.

#### Literature Cited

- Chiou, C. T.; Freed, V. H.; Schmedding, D. W.; Kohnert, R. L. *Environ. Sci. Technol.* 1977, 11 (5), 475.  
 Farmer, W. J. "A Literature Survey of Benchmark Pesticides"; George Washington University Medical Center: Washington, DC, 1976; p 222.  
 Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* 1979, 13, 241.  
 Kenega, E. E.; Goring, C. A. I. "Proceedings of the Third Aquatic Toxicology Symposium"; American Chemical Society: Washington, DC, 1978.  
 Kurihara, N.; Uchida, M.; Fujita, T.; Nakajima, M. *Pestic. Biochem. Physiol.* 1972, 2, 383-390.  
 Wahid, P. A.; Sethunathan, N. *J. Agric. Food Chem.* 1978, 26 (1), 101.  
 Wahid, P. A.; Sethunathan, N. *J. Agric. Food Chem.* 1979, 27 (5), 1050.

Samuel W. Karickhoff

U.S. Environmental Protection  
 Agency  
 Environmental Research  
 Laboratory  
 Athens, Georgia 30613

of soil  $om$  (designated as  $\omega$ ) involved in sorption (Lambert, 1968). Likewise,  $K_{oc}$  values for  $\gamma$ -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  $K_p/oc = K_{oc}$ , used by Karickhoff, is based on the assumptions 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