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Comment on "Partition Coefficients of Organic Contaminants with Carbohydrates"

Hung et al. (1) measured carbohydrate–water partition coefficients (K_{ch}) for cellulose (microcrystalline powder from cotton linears) and starch (amylopectin from unmodified waxy corn) for 59 organic compounds. These coefficients are highly relevant as sorption to carbohydrates influences the translocation of organic contaminants in vegetated areas. Hung et al. (1) note that available K_{ch} data are highly variable, with measured values for PAHs by Zhang and Zhu (2) and Jonker (3) being 3–66 times higher than Hung et al.'s (1) values. Three explanations are possible: (1) heterogeneity of carbohydrates present (e.g., mixed carbohydrate extract in (2)), (2) residual impurities (e.g., lignin or lipids), and (3) variable crystallinity. Hung et al. (1) mainly discuss the second explanation. However, we hypothesize the third explanation may also be partly responsible. Crystalline subdomains are unavailable or show low capacity for sorption and their alignment can influence availability of amorphous domains. Carbohydrate biopolymers come in a wide range of crystallinities, for example <47–100% for cellulose (4). Little attention has been given to modeling the availability of amorphous domains of semicrystalline biopolymers. We address this here in two independent manners by (i) deriving a poly parameter linear free energy relationship (PP-LFER) and (ii) estimating K_{ch} for a completely amorphous carbohydrate phase (via the SPARC online calculator (<http://ibmlc2.chem.uga.edu/sparc/>, accessed October 2010)).

The PP-LFER considered describes partitioning of a nonionic solute (i) between water (w) and another condensed phase (j) (5), according to the generic equation:

$$\log K = e_{jw}E_i + s_{jw}S_i + a_{jw}A_i + b_{jw}B_i + v_{jw}V_i + c_{jw} \quad (1)$$

The molecular interactions that govern the partitioning process are represented by e_{jw} , s_{jw} , a_{jw} , b_{jw} , and v_{jw} . The value c_{jw} is a fitting parameter. Using the data from Hung et al. (1) and available molecular descriptors, a PP-LFER was obtained as $\log K_{ch} = 0.36E_i - 0.26S_i + 0.44A_i - 2.22B_i + 2.25V_i - 1.55$ ($n = 51$) (Figure 1a). We do not recommend this PP-LFER for predictive purposes as polar compounds with a limited range of A_i values were used in its calibration. Of note is the c_{jw} value, which is very negative (-1.55 ± 0.09 log units). The constant is offset from the observed experimental values of -0.4 to $+0.4$ for amorphous solvents (5). This indicates a reduced free volume and sorption capacity from c. $10^{-1.55}/10^{-0.4}$ to $10^{-1.55}/10^{0.4}$ in other words, only 1–7% of the bulk volume of cellulose could be available for sorption.

In the second estimation method, SPARC was used to estimate K_{ch} , using the CAS number of starch 9005258 and the formula $(C_6H_{10}O_5)_n$ as input. The resulting comparison with Hung et al.'s (1) values is shown in Figure 1b. SPARC overpredicts measured partition coefficients, presumably accountable to the underlying assumption that the sorbing phase is amorphous. Consistent with the PP-LFER, the average deviation of experimental and SPARC predicted log K_{starch} values is -1.38 ± 0.44 . Using this deviation (i.e. c_{jw}) as

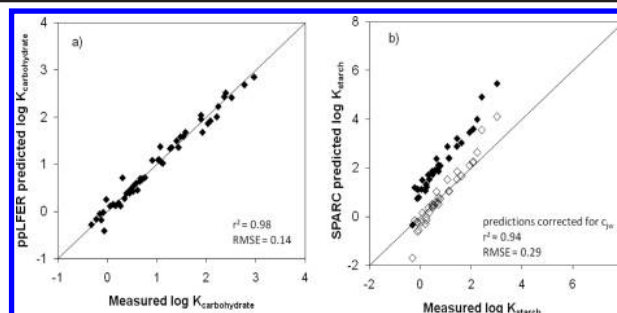


FIGURE 1. Comparison of measured (a) log $K_{carbohydrate}$ values with fitted PP-LFER predicted values and (b) log K_{starch} with nonfitted SPARC predicted values where closed symbols are uncorrected values and open symbols are corrected by the SPARC c_{jw} . The reported values for diethyl phthalate and dibutyl phthalate were considered to be unreliable and were therefore discluded from the regression (based on an internal consistency check of the influence of alkyl C on K_{ch}).

an offset value, a good correlation between measured and predicted values results (Figure 1b).

Thus we conclude that crystallinity could influence the partitioning of organic compounds to carbohydrates and can be an additional cause for the substantial discrepancy of measured K_{ch} values across studies, as well as partitioning data for other semicrystalline (bio)polymers.

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