FIELD EVALUATION OF A MATHEMATICAL MODEL OF SOIL-TO-CARROT TRANSFER OF PCBs

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Introduction. Soil-to-root crop transfer of SOCs such as PCBs and PCDD/Fs is widely assumed to be governed by two consecutive equilibrium partitioning processes. These are: (i) between soil organic carbon (or organic matter) and soil pore water; and (ii) between soil pore water and root crop lipid. This basic conceptual framework has been incorporated into mathematical models:

$$C_{rc} = C_{pw} * RCF \text{ (equation 1)}$$

Where C_{rc} = contaminant concentration in root crop (ng kg^{-1} dw); C_{pw} = contaminant concentration in soil pore water (ng dm^{-3}); and RCF = root concentration factor (1).

Given the practical difficulties in monitoring contaminant concentrations in soil pore water, it is common practice to estimate such concentrations from measured concentrations in soil:

$$C_{PW} = \frac{C_S}{K_{ds}} \text{ (equation 2)}$$

$$K_{ds} = f_{oc} x K_{oc} \qquad \text{(equation 3)}$$

$$K_{OC} = 0.411\, K_{OW} \text{ (equation 4 - taken from Karickhoff (2))}$$

where C_S is the concentration in soil (ng kg^{-1} fw); Kd_s the soil-water partition coefficient (dm^3 kg^{-1}); f_{OC} the fraction of organic carbon in the soil; K_{OC} the organic carbon/water partition coefficient and K_{OW} the octanol/water partition coefficient.

RCF values are widely derived from Briggs *et al* (3), who reported a positive linear relationship between the RCF and log K_{ow} from a study of the transfer of O-methylcarbamoyloximes and substituted phenylureas from artificially contaminated nutrient solution into barley roots. This relationship stated that for these chemicals:

$$\log(RCF - 0.82) = 0.77 \log K_{OW} - 1.52 \text{ (equation 5)}$$

Based on the above, an equation to predict soil-to-root crop transfer has been suggested by various authors (4,5).
the barley roots used by Briggs *et al*. (3) and bulky roots such as carrots (as suggested by

$$C_{rc} = \frac{C_S * RCF * VG_{BG}}{Kd_s} \qquad \text{(equation 6)}$$

where VG_{BG} is an empirical correction factor, introduced to take into account the differences between *inter alia* (6)). These data suggest that the whole barley root concentrations would be similar to the concentrations near the peel of the vegetable and *not* the whole root. VG_{BG} is derived thus:

$$VG_{BG} = \frac{Mass_{skin}}{Mass_{vegetable}} \qquad \text{(equation 7)}$$

where $Mass_{skin}$ is the mass of the peel and $Mass_{vegetable}$ is the mass of the entire vegetable. Suggested VG_{BG} values range from 0.001 to 1. This study examined the transfer of PCBs from soil to carrots. Its aims were to evaluate the validity of equations 3-6 for carrots grown in unamended soils with background PCB concentrations, and to assess the validity of extrapolating data obtained from experiments using artificially enriched ("spiked") soils to field conditions.

Experimental Approach

Six experiments were conducted: Experiments 1 and 2 used unamended agricultural soils for which f_{oc} = 0.0213 and 0.0171 respectively. Concentrations of individual congeners in these soils ranged from 2-130 ng kg^{-1} dry weight. Experiments 3-6 used the same soil as Experiment 2, but "spiked" with congeners 28, 52, 101, 138, and 180 at known concentrations of each congener of *ca* 3, 5, 8, and 20 □g kg^{-1} dry weight respectively. In all experiments, carrots (*Daucus Carota*, cv. Autumn King) were sown 4/97 and harvested 10/97. All carrots from individual experiments were washed (but not peeled) and pooled prior to freeze-drying and PCB analysis, conducted using GC/MS procedures reported elsewhere (7). Concentrations in soils and carrots were recorded for the 45 congeners (35 chromatographic peaks) detected in at least one carrot sample.

Results and Discussion

How effective are equations 3-6? Table 1 gives observed/predicted ratios of carrot concentrations of individual congeners in each experiment. Predicted values were derived from equations 3-6 using source term data of C_s, assuming a VG_{BG} value of 1, and taking K_{ow} data from Hawker and Connell (8). Clearly, this modelling approach underestimates PCB concentrations in carrots in Experiments 1 and 2 (observed/predicted ratios>1), but overestimates in Experiments 3-6. The following sections discuss possible reasons for these discrepancies.

What are the principal sources of error in equations 3-6? As discussed above, the modelling approach followed by equations 3-6 assumes that equilibrium is attained between soil organic carbon and soil pore water, and between pore water and carrot lipid. To evaluate whether this fundamental assumption applied to our experiments, observed Log (C_{rc}/C_s) values for individual congeners were plotted versus Log K_{ow} (8) for Experiments 1 and 2 separately; those for Experiments 3-6 were combined to derive a single plot, in order to obtain a statistically relevant number of data points. For Experiments 1 and 2, highly significant (>99.9% level) negative linear correlations were obtained. For Experiments 3-6, a significant correlation was not observed. However, removal of two outlying data points - *viz* those for congener 28 in Experiments 3 and 4, where carrot uptake was significantly lower than (i) other congeners in these experiments, and (ii) of congener 28 in Experiments 5 and 6 - reveals a highly significant (>99.9% level) negative linear correlation for these experiments also. These negative correlations confirm that the theoretical framework underpinning equations 3-6 - namely the consecutive equilibrium partitioning approach - is appropriate to describe soil-to-carrot transfer in each of our experiments.

Having established that the assumption of equilibrium was correct, we considered other possible explanations for the fact that equations 3-6 underestimated uptake in Experiments 1 and 2. Firstly, it is clear that the maximum value of 1 for VG_{BG} is the most appropriate - using lower values would exacerbate the underestimation. This has potentially important implications, as it suggests that PCB uptake was not limited to the peel. The other possible explanations are that: (a) equations 3 and 4 underestimate the magnitude of Kd_s; and (b) equation 5 underestimates the magnitude of RCF. Either or both of these explanations could account for the overall underestimation. In the absence of direct measurements of C_{pw} - which would permit experimental measurement of both Kd_s and RCF - it is impossible to draw definite conclusions. However, we consider (a) to be the most significant factor. This is because of the marked differences in uptake observed in Experiments 1 and 2. In these experiments, the only difference was the soil type. If Kd_s was correctly predicted for both soils, then - as uptake from pore water by the same species under identical climatic conditions would be expected to be identical - the degree of underestimation of soil-to-root transfer would be the same for both experiments.

Can data from "spiking" experiments be extrapolated to "field" conditions? Clearly, on the evidence presented here, the answer to this question is no. Observed PCB uptake by carrots from the same soil was significantly less from the "spiking" Experiments 3-6 than from the unamended soil - Experiment 2. The use of "spiking" experiments to evaluate soil-to-root crop transfer of PCBs appears to systematically underestimate the extent to which it occurs in unamended agricultural soils.

Why is uptake lower from "spiked" soils? We considered two possible explanations for the reduced uptake of PCBs by carrots grown in "spiked" compared with unamended soil. Firstly, O'Connor *et al.* (9) suggested that at elevated PCB concentrations in soil, uptake would be limited by the fixed amount available of peel. If this applied to our data, then carrot contamination would increase proportionally at low soil concentrations before approaching a constant value at high soil concentrations as the peel reaches saturation. There was no evidence of such behaviour in our experiments, which were in any case conducted at concentrations lower than those for which such a "plateau" effect was detected (9). Secondly, if the rate-determining step in soil-to-root transfer is the partitioning between the soil organic matter and the pore water (10) then it is possible that, for "spiked" soils, insufficient time could elapse during the growing season for this process to reach equilibrium. However, as mentioned above, equilibrium appeared to be reached in all experiments, and at present, we are unable to offer a satisfactory explanation for the reduced uptake from "spiked" soils.

References

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Table 1: Observed:Predicted Ratios for PCB Concentrations in Carrots

	Observed:Predicted Ratio in Experiment Number					
Congener	**1**	**2**	**3**	**4**	**5**	**6**
18	5.84	3.53				
32/16	10.83	3.91				
31/28	na	1.65	0.09	0.15	0.54	0.36
33	24.02	na				
22	17.07	na				
45	23.01	na				
52	na	3.80				
49	6.18	2.10	0.37	0.86	na	na
47	6.46	na				
44	4.01	1.26				
41/64	na	1.57				
74	5.40	3.91				
70/76	3.71	2.17				
66	6.96	4.17				
95	3.34	1.05				
91	3.12	2.36				
84/92	na	1.36				
90/101	na	1.86	0.64	0.54	0.90	0.53
99/113	1.77	1.43				
97	2.63	2.56				
87	2.83	1.81				
111	2.45	2.57				
110	2.59	1.59				
118	3.71	1.85				
105	6.05	0.92				
148	na	2.46				
151	na	1.73				
135/144	na	2.27				
149	2.26	1.68				
153	3.17	2.40				
132	na	1.39				
138/164	na	1.73	0.47	0.59	0.55	0.34
179	na	2.57				
187/182	1.00	0.65				
180	na	0.91	0.36	0.39	0.42	0.36

na = not available