Direct vs. Indirect Approaches for Adsorption Coefficient Determination and the Impact on Environmental Risk Assessment of Crop Protection Products

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Summary

According to OECD Guideline 106[1], soil adsorption coefficient is normally derived using "indirect method" based on solution depletion. However, in some cases, the "direct method", where both soil and aqueous phases are analyzed, is recommended to minimize the calculation errors as explained in Annex 3 of the guideline. One of these cases is when the value of K_d*soil/solution ratio is between 0.1-0.3 cm^3g^{-1}. This topic has drawn increasing attentions and was part of an OECD 106 Evaluators Check List developed by EU member state experts to provide guidance for reviewers. In this presentation, adsorption data generated from IN-66036, IN-W6725, and IN-JU122, three of the major soil metabolites of triflusulfuron methyl, on five soils were analyzed to compare the impact of direct vs. indirect calculations on the Freundlich model parameters derived from linear and non-linear fits. Overall, there is no clear indication of superiority of either approach. For IN-66036, the direct approach appears better where the differences in AICc values are striking between the two approaches and the figures are convincing while the reverse is true for IN-W6725. For IN-JU122, the results are mixed among five soils. Taken together, there is very little evidence to suggest the direct approach is more reliable than the indirect approach for compounds with weak adsorptions.

Materials and Methods

Five soils with different properties (Table 1) and three ^{14}C-labeled compounds (Table 2) with weak soil adsorption were used in the batch equilibrium tests using a 1:1 soil/solution ratio. Freundlich linear equation ($Log(C_s) = Log(K_f) + \frac{1}{n}Log(C_w)$) and its non-linear form ($C_s=K_fC_w1/n$) were used to derive the adsorption parameters (K_f, 1/n, and R^2) and to evaluate the model fits using SAS[2]. The expressions of C_s and C_{s_ln} were used for the direct and indirect soil concentrations of a compound at adsorption equilibrium. Four criteria were used to compare the direct vs. indirect methods. (i) The linear models for C_s and C_{s_ln} after a log-transformation were plotted side-by-side, so that a visual assessment of the relative goodness of fit can be made and the estimated values of K_f and 1/n calculated. (ii) The R^2 values were calculated and compared. (iii) The nonlinear models were fitted, the estimated parameters were calculated and compared to each other and to the estimators from the corresponding linear models. (iv) The Aikaiki information criterion, AICc values, adjusted for small sample size, were calculated and compared. Normally, the model with a smaller AICc value is considered the better fitting model. However, this rule is regarded as suggestive here because C_s/Log(C_s), and C_{s_ln}/log(C_{s_ln}) are not the same response. Focus PEARL 4.4.4 was followed for the simulation to estimate PEC_{gw} concentrations. The simulations were performed on winter cereals with 100 g a.s/ha applied in early spring. Geomean DT_{50}, K_f, and average 1/n were used as input parameters for the simulation.

Table 1. Soil Properties

Soil Name	Textural Class (USDA)	% Organic Carbon	pH (0.01M $CaCl_2$)	CEC (meq/100g)
LRA-D1	Sandy Loam	3.1	5.5	10.7
Porterville	Loam	0.47	7.7	12.2
Nambsheim	Sandy Loam	1.7	7.4	10.2
Gross Umstadt	Loam	0.99	6.5	10.0
MCL	Clay Loam	3.0	6.0	22.0

Table 2. MW, estimated[3] Log K_{ow}, water solubility, and vapor pressure

Compound	$Logk_{ow}$	MW	Water Solubility (mg/L, 25°C)	Vapor Pressure (Pa, 25°C)-Modified Grain
A (IN-66036)	3.40	478.40	1.238	$3.05x10^{-11}$
B (IN-W6725)	1.00	197.21	567	$3.83x10^{-5}$
C (IN-JU122)	-0.01	227.19	2870	$2.83x10^{-7}$

Results and Discussions

The Freundlich adsorption and statistical parameters for IN-66036, IN-W6725, and IN-JU122 on selected soils are shown in Tables 3, 4 and 5, respectively. For IN-66036 on all soils, the direct approach is favored over indirect approach because of the smaller AICc values calculated from direct method for both linear and non-linear models as shown in Table 3 and Figure 1. For IN-W6725 on all soils, the opposite was observed as shown in Table 4 and Figure 2. The results from IN-JU122 are mixed with indirect approach is favored on Gross Umstadt, Porterville, and LAR-D1 soils for both linear and non-linear fits (similar to IN-W6725). However, for Nambsheim and MCL soils, AICc values pointed to the opposite directions with linear fit is favored for direct approach while non-linear fit is favored for indirect approach (Table 5 and Figure 3). All R^2 values are not markedly different but agree with AICc except for IN-JU122 on Nambsheim where R^2 values and AICc for the non-linear models pointed to the opposite direction. R^2 is a poor fitting criterion for non-linear models so AICc is a better criterion to compare the model fits.

1/n between 0.7-1.1 and R^2 >0.99 are considered acceptable for a model fit. From our tests, all 1/n values were between 0.7-1.1 except on Nambsheim of indirect approach suggesting that reasonable linearity had been achieved. Overall, approx. 50% of the R^2 values exceeded 0.990 and 90% exceeded 0.90 regardless direct or indirect approach was taken or linear or non-linear models were fitted. These outlier R^2 values are largely due to the variability between the replicates at each sampling time and not related to the calculation methods. These experimental errors have greater impact on the adsorption parameters than the calculation methods or models.

In general, K_f negatively correlated with the PEC_{gw} values where higher K_f resulted in lower PEC_{gw}. PEC_{gw} values could differ more than 10-fold between direct and indirect methods, however, the number of pass/fail scenarios was not significantly impact in all cases with linear fit simulated and thus the conclusions on risk assessment was not impacted by the calculation methods (Table 6).

Table 3. Comparison of parameter estimates for IN-66036 (Nambsheim)

Response	Model	Parameter	Estimate	SSOT	R^2	AICc
C_s	Linear	Kf	0.130	25.199	0.998	-54.0
C_s	Linear	1/n	0.844			
C_{s_ln}	Linear	Kf	0.105	45.236	0.984	-24.1
C_{s_ln}	Linear	1/n	1.123			
C_s	Non-Linear	Kf	0.132	0.073	0.999	-137.9
C_s	Non-Linear	1/n	0.870			
C_{s_ln}	Non-Linear	Kf	0.099	0.037	0.996	-125.7
C_{s_ln}	Non-Linear	1/n	1.173			

Table 4. Comparison of parameter estimates for IN-W6725 (Gross Umstadt)

Response	Model	Parameter	Estimate	SSOT	R^2	AICc
C_s	Linear	Kf	0.056	26.393	0.960	-20.1
C_s	Linear	1/n	0.839			
C_{s_ln}	Linear	Kf	0.095	30.172	0.997	-48.7
C_{s_ln}	Linear	1/n	0.915			
C_s	Non-Linear	Kf	0.055	0.097	0.957	-86.0
C_s	Non-Linear	1/n	0.901			
C_{s_ln}	Non-Linear	Kf	0.100	0.280	0.995	-98.8
C_{s_ln}	Non-Linear	1/n	0.850			

Table 5. Comparison of parameter estimates for IN-JU122 (Nambsheim)

Response	Model	Parameter	Estimate	SSOT	R^2	AICc
C_s	Linear	Kf	0.053	19.424	0.923	-9.7
C_s	Linear	1/n	0.800			
C_{s_ln}	Linear	Kf	0.023	9.455	0.742	-5.3
C_{s_ln}	Linear	1/n	0.500			
C_s	Non-Linear	Kf	0.062	0.058	0.830	-58.5
C_s	Non-Linear	1/n	0.760			
C_{s_ln}	Non-Linear	Kf	0.027	0.009	0.703	-71.0
C_{s_ln}	Non-Linear	1/n	0.519			

C_s, C_{s_ln}-concentration on soil at adsorption equilibrium;
C_w-aqueous concentration at adsorption equilibrium;
K_f Freundlich adsorption coefficient;
1/n-regression constant; SSOT-total sum of square;
R^2-coefficient of determination;
AICc-Aikaiki information criterion adjusted for small sample size

Figure 1. Linear & non-linear models fits favor direct approach for IN-66036 (Nambsheim)

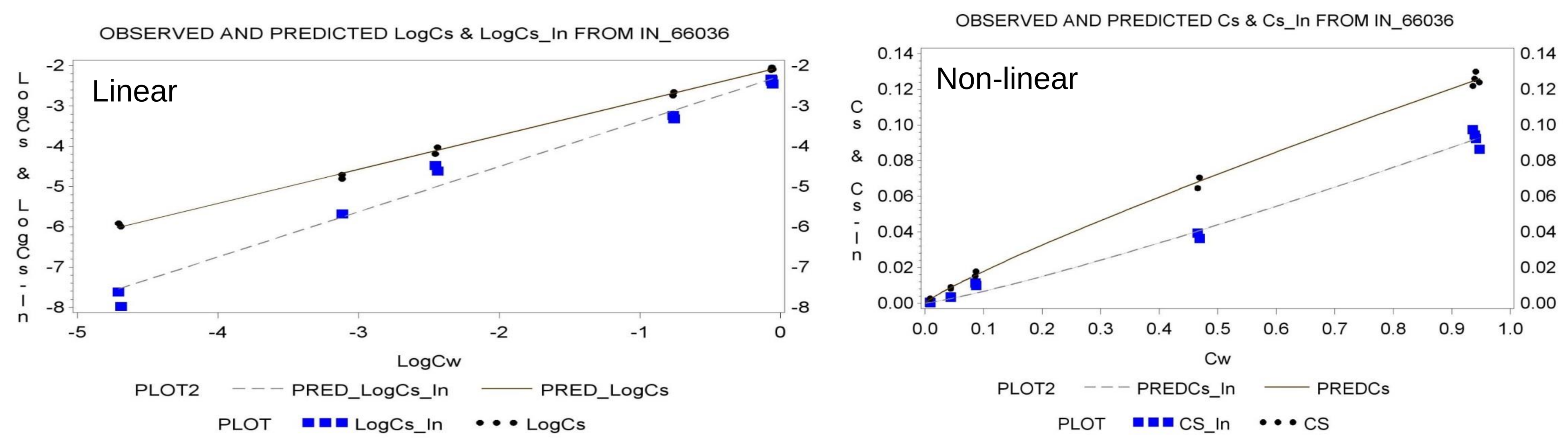

Figure 2. Linear & non-linear models fits favor indirect approach for IN-W6725 (Gross)

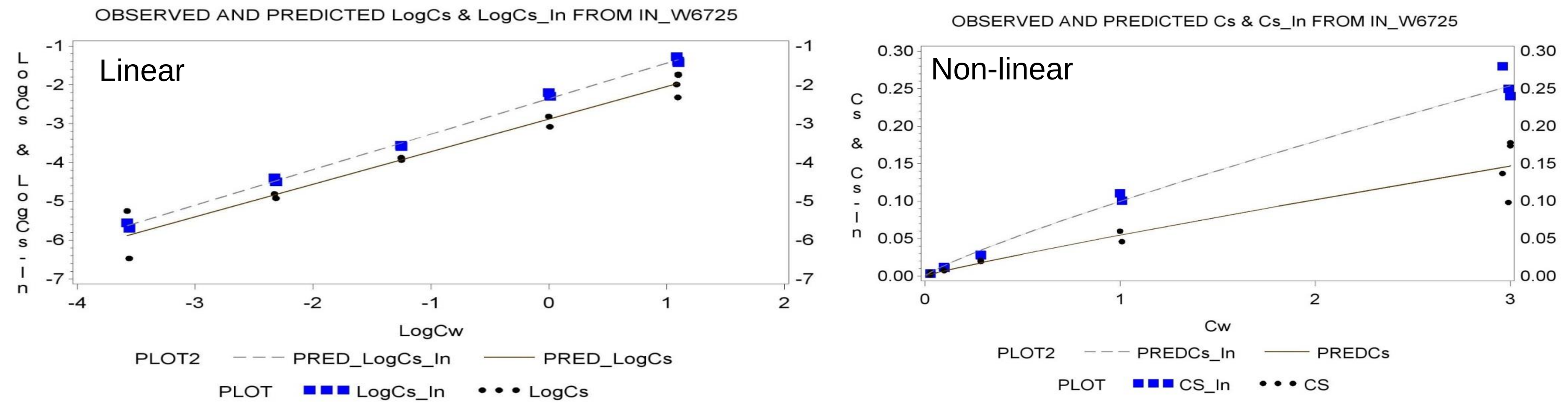

Figure 3. Linear fits favor direct, non-linear fits favor indirect approach for IN-JU122 (Nambsheim)

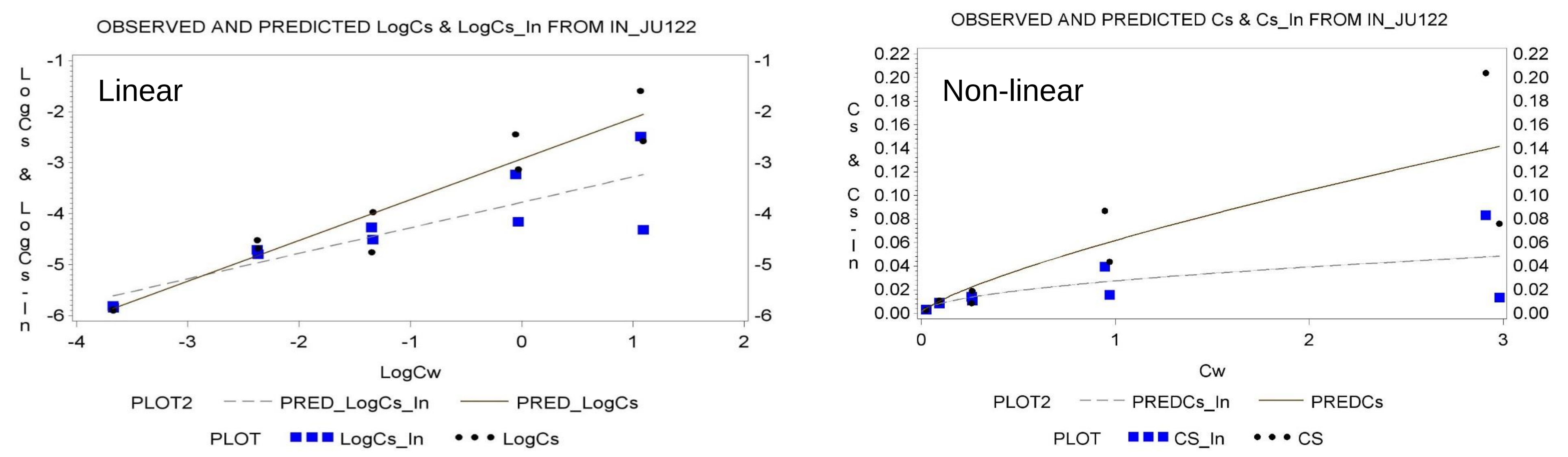

Table 6. PECgw calculations for IN-66036 (Nambsheim)

FOCUS scenario	PECgw based on Direct calculation	PECgw based on non-indirect calculation
Chateaudun	0.000174	0.002024
Hamburg	0.005068	0.054392
Joikioinen	0.004071	0.079750
Kremsmuenster	0.006393	0.049748
Okehampton	0.011100	0.069687
Piacenza	0.005648	0.029984
Porto	0.000306	0.007223
Sevilla	0.000000	0.000001
Thiva	0.000000	0.000002

Conclusions

- Good linearity and fits achieved (R^2>0.99, 1/n between 0.7-1.1), the data from these studies are considered reliable and non-linear fits are unnecessary.
- Based on available data, no clear advantages for direct over indirect approaches for Freundlich model fits
- PEC_{gw} differed between direct and indirect calculations but pass/fail scenarios were not significantly impacted
- Registrants and reviewers could benefit from greater clarity from OECD 106 (soil/solution ratio, consideration of aqueous residue left in soil, apparent adsorption coefficient, etc.)

References:

[1]-OECD Guideline 106: Adsorption-Desorption Using a Batch Equilibrium Method; [2]-SAS9 for Windows. 2002-2012. SAS Institute. Cary, North Carolina; [3]-Estimated using US EPA's EPI Suite 4.1