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Test Material:	Profenofos
MRID	48612101
Title:	Keenan, D.J. 2011. Profenofos. [^{14}C]-Profenofos - adsorption and desorption properties in soils. Final Report.
EPA PC Code:	111401
OCSPP Guideline:	835.1230

For CDM Smith

Primary Reviewer: Kindra Bozicevic**h** **Signature:** 

Date: 11/25/13

Secondary Reviewer: Joan Harlin **Signature:** 

Date: 11/25/13

QC/QA Manager: Joan Gaidos **Signature:** 

Date: 11/25/13

Adsorption and desorption of Profenofos in five soils.

Report:	MRID 48612101. Keenan, D.J. 2011. Profenofos. [^{14}C]-Profenofos - adsorption and desorption properties in soils. Final Report. Unpublished study performed by Ricerca Biosciences, LLC, Concord, OH; sponsored and submitted by Syngenta Crop Protection, LLC, Greensboro, North Carolina. Report Number: 027138-1. Study Number: 027138. Task Number: TK0053456. Experimental initiation January 5, 2011 and completion July 21, 2011 (p. 11). Study completion date September 23, 2011.
Document No.:	MRID 48612101
Guideline:	OCSPP 835.1230
Statements:	The study was conducted in accordance with USEPA Title 40 Part 160 CFR (p. 3). Signed and dated Data Confidentiality, GLP, Quality Assurance statements were provided (pp. 2-4). A Certification of Authenticity was not provided.
Classification:	This study is supplemental.
PC Code:	111401
Reviewer:	Michelle Colletti, Chemist U.S. EPA **Signature:** Michelle Colletti **Date:** 02/02/2015
Secondary Reviewer:	William Eckel, Ph.D., Senior Advisor U.S. EPA **Signature:** **Date:** 02/02/2015 William P. Eckel

Executive Summary

In a batch equilibrium study, five U.S. soils (pH range 4.7-6.0) were used to measure sorption coefficients of [phenyl-U-^{14}C]-labeled profenofos (CGA015324). Preliminary studies showed that [^{14}C]profenofos was highly unstable in all soil:solution slurries following 24 hours in darkness at 20 ± 2°C using both non-irradiated and gamma irradiated test soils. K_{oc} values were determined using OECD Guideline 121 employing an isocratic HPLC system (cyanopropyl [CN] column). Seven reference standards were injected onto the column along with profenofos, including a similar reference compound sulprofos.

Adsorption K_{oc} values were determined to be 3.922 (log K_{oc} = 3.59) for profenofos and 6.740 (log K_{oc} = 3.83) for sulprofos.

Based on profenofos instability in soils and its HPLC determined adsorption K_{oc}, profenofos has a very low mobility potential. Sulprofos was considered immobile.

Results Synopsis:

Table 1. Summary of Adsorption/Desorption Results

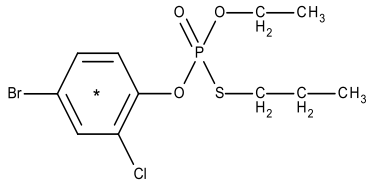
Soil/ Sediment, % OC pH	Regressed K_d (L/kg-soil)			Range of K_d (L/kg-soil)	Regressed K_{OC} (L/kg-OC)	K_F ((L/kg-soil)$^{-1/n}$)			1/n for adsorption	K_{FOC} (L/kg-OC)$^{-1/n}$	Ceq Range (mg/L)
	Value ± SE	r^2	p-value		Value ± SE	Value ± SE	r^2	p-value	Value ± SE	Value ± SE	
Adsorption											
Not determined.											
Desorption											
Not determined.											

Abbreviations: SE = standard error of regression.

I. Material and Methods

A. Materials

1. Test Material: [Phenyl-U-^{14}C]-labeled profenofos (CGA015324; p. 13)
Batch/Lot number: RDR-X-36
Specific radioactivity: 63.9 μCi/mg
Radiochemical purity: ≥95% (Figures 3-4, pp. 31-32)
Chemical purity: Not reported
Solubility in water: 16 mg/L at 20°C (p. 16; Appendix 1, p. 62)
Structure:



2. Reference Compounds: Profenofos (CGA015324; p. 13; Appendix 1, p. 60)
Lot number: AMS137\6
Purity: 98.7%

CGA055960
Lot number: GAN-XI-46
Purity: 99.2%

3. Soils/Sediment: The study was conducted using five U.S. soils (p. 14; Tables 1-2, pp. 21-22). Soils were collected at depths up to 15 cm. There were no pesticides used at the Kansas, Montana, and North Carolina collection sites. Glyphosate was used in the last 5 years at the Arkansas and Ohio collection sites. The soils were air dried and sieved (2 mm), then stored at ambient temperature. A summary of the physical and chemical properties of the soils using USDA Soil Taxonomy is provided in Table 2. The soils were representative of use sites.

Table 2. Description of Soil/Sediment

Soil Name Origin	Jackson Jackson, AR	Crawford Crawford, KS	Butler Butler MO	Lenoir Lenoir, NC	Union Union, OH
USDA Textural Class	Sandy loam	Loam	Loamy sand	Loamy sand	Clay loam
% Sand	53	27	87	85	27
% Silt	42	48	8	12	36
% Clay	5	25	5	3	37
%OC[A]	0.64	2.4	0.48	1.91	2.44
CEC (meq/100 g)	6.2	14.1	5.8	6.5	13.1
pH (1:1 water)	6.3	6.0	6.1	5.4	6.5
pH (1:1 0.01M $CaCl_2$)	6.0	5.3	5.7	4.7	6.0
% moisture (1/3 bar)	13.4	30.6	5.7	12.1	28.3
Soil Taxonomy	NR	NR	NR	NR	NR
$CaCO_3$ equivalence	NR	NR	NR	NR	NR

Data were obtained from Table 1, p. 21 of the study report.
A Determined by the reviewer as % om/1.72.
NR = not reported.

B. Study design

1. **Experimental conditions:** Preliminary tests were conducted to determine the optimal conditions to be used in the definitive study (p. 15; Appendix 1, pp. 62-71). Adsorption to the test containers was examined at nominal concentrations of 0.02, 0.1, 0.3, 1, and 3 µg/mL. No significant adsorption to the test containers was observed. To determine the soil:solution ratio to be used in the definitive test, aliquots of air-dried soils were added to 0.01M $CaCl_2$ solution and treated with [phenyl-U-^{14}C]profenofos at a nominal test concentration of 0.3 µg/mL. The soil:solution ratios tested were 1:1, 1:2, 1:4, 1:10, and 1:20 (w:v). The samples were shaken in the dark at 20 ± 2°C for 24 hours. Following equilibration, the samples were centrifuged and aliquots of the supernatants were analyzed using LSC and HPLC (Phenomenex Synergi 4 µ Hydro RP 80A column, gradient mobile phase of (A) HPLC grade water with 0.1% acetic acid and (B) acetonitrile, with UV (245 nm) and radioactive flow detection; p. 14; Appendix 1, pp. 72-73). It was determined that [^{14}C]profenofos was stable in 0.01M $CaCl_2$ solution without soil, but was unstable in all soil slurries (p. 17; Table 6, p. 26; Figure 5, p. 33). The percent of degradation ranged from *ca*. 29-82%, based on HPLC analysis (Figures 6-10, pp. 34-38).

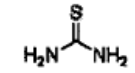
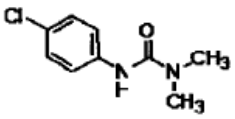
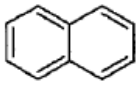
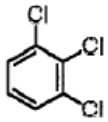
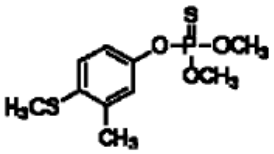
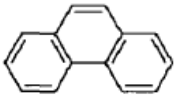
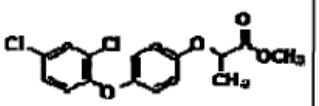
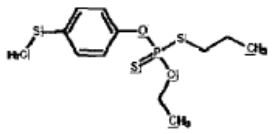
   In an attempt to eliminate any biotic premature degradation, all soils were sterilized by gamma irradiation (523 minutes at 40.6-50.8 kGy) and re-analyzed under the same preliminary test conditions (p. 17; Appendix 1, p. 65). [^{14}C]Profenofos was still unstable in all soil slurries (Table 6, p. 26; Figure 17, p. 45). The percent of degradation ranged from *ca*. 25-66%, based on HPLC analysis (Figures 12-16, pp. 40-44).

   Due to instability of [^{14}C]profenofos in all soil slurries, a cyanopropyl HPLC column (bearing lipophilic and polar moieties) with an isocratic mobile phase was used to generate a calibration curve using seven reference standards with different and known adsorption coefficient K_{oc} values (pp. 15-16; Appendix 1, p. 61; Appendix 1, pp. 74-76). The following reference standards were used:

Table 3. Reference Standards

Reference Standards

Selected Koc Reference Standards Cited by OECD Guideline 121

Compound ID and Description	*Log Koc	Lot/Batch #	Purity % (Supplier)	CAS Number	Structure
Thiourea	**	A0285880	99% (Acros Organics)	62-56-6	
Monuron	1.99	SZE8114X	99.9% (Sigma-Aldrich)	150-68-5	
Linuron	2.59	SZBA013XV	99.9% (Sigma-Aldrich)	330-55-2	
Naphthalene	2.75	MKBF8633	99.9% (Sigma-Aldrich)	91-20-3	
1,2,3-Trichloro-benzene	3.16	12912pfv	99.9% (Sigma-Aldrich)	87-61-6	
Fenthion	3.31	SZBA125XV	98.3% (Sigma-Aldrich)	55-38-9	
Phenanthrene	4.09	MKBF4471V	99.6% (Sigma-Aldrich)	85-01-8	
Diclofop-methyl	4.20	SZBA130XV	99.2% (Sigma-Aldrich)	51338-27-3	
Sulprofos (IUPAC name: O-ethyl o-(4-methylthiophenyl) s-propyl phosphorothioate)	***	457-127A	94.0% (Chem Service)	35400-43-2	

*Log Koc values taken from OECD 121 guidelines. **Thiourea was used to determined the HPLC column 'dead' volume. ***Sulprofos's log Koc was not cited in the OECD 121 guidelines, but determined within this study due to some structure similarities to profenofos.

Individual injections of each reference standard and the test substance, profenofos, were made using HPLC-UV to determine retention times. The reference compounds were injected before and after the test substance to ensure system stability. The adsorption coefficient K_{oc} of profenofos was determined by interpolation from the calibration curve. The K_{oc} value of another insecticide sulprofos, bearing some structure similarities to profenofos, was also determined.

2. **Analytical procedures:** Radioactivity in the aqueous supernatants was determined by Liquid Scintillation Counting (LSC; p. 14). Supernatants were analyzed using HPLC (Phenomenex Luna CN column, isocratic mobile phase of (A) HPLC grade water and (B) acetonitrile, with UV (254 nm) and radioactive flow detection; p. 15; Appendix 1, p. 75). The Limit of Detection (LOD) for LSC analysis was 64 dpm (Appendix 1, p. 73). For the Limit of Quantification (LOQ), it was determined that a peak containing 500 dpm was *ca*. 1% of the applied radioactivity.

II. Results and Discussion

A. Mass Balance: Not applicable.

B. Transformation of Parent Compound: Not applicable.

C. Findings: Adsorption K_{oc} values were determined to be 3890 (log K_{oc} = 3.59) for profenofos and 6760 (log K_{oc} = 3.83) for sulprofos (p. 17; Table 7, p. 27; Figures 28-29, pp. 56-58). Based on McCall et al., profenofos was classified as having a slight mobility potential to leach in soils, while sulprofos was considered immobile.

III. Study Deficiencies and Reviewer's Comments

1. OECD Guidelines for Testing of Chemicals, Guideline 121: Estimation of the Adsorption Coefficient (K_{oc}) on Soil and on Sewage Sludge using High Performance Liquid Chromatography (HPLC) (adopted 22nd January 2001) was used to estimate K_{oc} values for profenofos (p. 11).

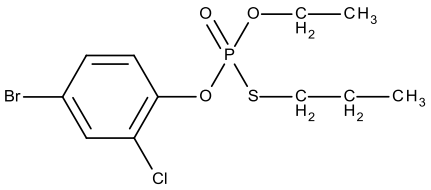
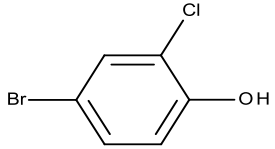
2. The maximum single label application rate for profenofos is 1 lb ai/acre (p. 12).

3. It is unclear why rapid degradation of profenofos occurs in this study and not in similar studies (MRID 41627311).

IV. References

1. U.S. Environmental Protection Agency. 2008. Fate, Transport and Transformation Test Guidelines, OPPTS 835.1230, adsorption/desorption (batch equilibrium). Office of Prevention, Pesticides and Toxic Substances, Washington, DC. EPA 712-C-08-019.

DER ATTACHMENT 1. Profenofos and Its Environmental Transformation Products. [A]

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)
PARENT						
Profenofos (CGA015324)	**IUPAC:** (RS)-(O-4-bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate) **CAS:** O-(4-bromo-2-chlorophenyl) O-ethyl S-propyl phosphorothioate **CAS No.:** 41198-08-7 **Formula:** $C_{11}H_{15}BrClO_3PS$ **MW:** 373.63 g/mol **SMILES:** CCCSP(=O)(OCC)Oc1ccc(Br)cc1Cl		835.1230 Batch equilibrium	48612101	NA	NA
MAJOR (>10%) TRANSFORMATION PRODUCTS						
No major transformation products were identified.						
MINOR (<10%) TRANSFORMATION PRODUCTS						
No minor transformation products were identified.						
REFERENCE COMPOUNDS NOT IDENTIFIED						
CGA055960	**IUPAC:** 4-Bromo-2-chloro-phenol **CAS:** Phenol, 4-Bromo-2-chloro- **CAS No.:** 3964-56-5 **Formula:** C_6H_4BrClO **MW:** 207.45 g/mol **SMILES:** c1cc(c(cc1Br)Cl)O		835.1230 Batch equilibrium	48612101	NA	NA

[A] AR means “applied radioactivity”. MW means “molecular weight”. NA means "not applicable".

Attachment 2: Statistics Spreadsheets and Graphs

Attachment 3: Calculations

Calculations were performed by the reviewer using Excel and the following equations.

Ceq range is the range of test concentrations in water at equilibrium.
Cs is the test concentrations sorbed to soil or sediment at equilibrium.

K_d –Distribution Coefficient for Adsorption = C_s/C_{eq} (eq 1)

- Regressed K_d is calculated using linear regression of Cs versus Ceq with a forced zero intercept over the range of measured Ceq for each soil/sediment.

- Range of K_d reflects the range of each K_d measured at a specific concentration in a soil/sediment

K_{OC} -Organic Carbon Normalized Adsorption Coefficient = regressed K_d *100/% OC (eq 2)

Standard Error (SE) of K_{OC}= K_d SE *100/%OC (eq 3)

K_F -Freundlich Adsorption Coefficient and the Freundlich exponent (1/n) were calculated using nonlinear regression of $C_s = K_F$ x Ceq $^{1/n}$. Cs should be expressed in mg/kg and Ceq should be expressed in mg/L in the regression. (eq 4)

K_{FOC} –Organic Carbon Normalized Adsorption Coefficient = K_F*100/%OC (eq 5)

Standard Error (SE) of K_{FOC}= K_F SE *100/%OC (eq 6)

K_{DES} –Apparent Desorption Coefficient = C_s/C_{eq} where C_s and C_{eq} are measured after an initial sorption measurement and the soil/sediment is placed in a new solution and allowed to equilibrate, so that any material in solution desorbed from the soil/sediment. (eq 7)

- Regressed K_{DES} is calculated using linear regression of Cs versus Ceq over the range of Ceq measured with a forced zero intercept for each soil/sediment.

- Range of K_{DES} reflects the range of each K_{DES} measured at a specific concentration in a soil/sediment

$K_{OC\text{-}DES}$ -Organic Carbon Normalized Apparent Desorption Coefficient = regressed K_{DES} *100/% OC (eq 8)

Standard Error of $Koc\text{-}_{DES}$ = K_{DES} SE* 100/%OC (eq 9)

$K_{F\text{-}DES}$ -Freundlich Desorption Coefficient and the Freundlich Desorption exponent (1/n) were calculated using nonlinear regression of $C_s = K_{F\text{-}DES}$ x Ceq $^{1/n}$ (eq 10)

$K_{FOC\text{-}DES}$ -Organic Carbon Normalized Freundlich Desorption Coefficient= $K_{F\text{-}DES}$*100/%OC (eq 11)

Standard Error of $K_{FOC\text{-}DES}$ = K_F SE *100/%OC (eq 12)