RESPONDENT'S EXHIBIT 17

Adsorption and desorption of TPA, a transformation product of DCPA, in one soil.

Report: MRID 49307517. Swales, S. 2014. (14C)-TPA, A Metabolite of DCPA: Adsorption/Desorption in Soil (Revised per PRN 11-03 and 86-5). Unpublished study performed, sponsored and submitted by AMVAC Chemical Company, Newport Beach, CA. AMVAC ID: 100-MET-012a. Experimental initiation June 10, 2003 and completion August 22, 2003 (p. 14). Study completion date October 16, 2003. Revised study completed January 29, 2014.

Document No.: MRID 49307517

Guideline: OCSPP 835.1230

Statements: The study was conducted in accordance with OECD GLP and UK GLP (p. 5). Signed and dated Data Confidentiality, GLP, Quality Assurance, and Certification of Authenticity statements were provided (pp. 2-3, 5-7).

Classification: This study is supplemental. The definitive study was conducted using only one type of soil rather than across five soil types. It was unclear whether the foreign test soil was representative of use sites. Limits of Quantification (LOQ) were not reported.

PC Code: 078701 (for DCPA)

Reviewer:

James Lin, Environmental Engineer
U.S. EPA

Signature:
Date: January 10, 2017

Executive Summary

In a batch equilibrium study, one European soil (pH 4.1) was used to measure sorption coefficients of [^{14}C]TPA in darkness at 20 ± 2°C. The determined Freundlich Adsorption Coefficient (K_F) value was 1.68 L/kg; the respective K_{FOC} value was 4.[1] The Freundlich Desorption Coefficient ($K_{F\text{-}des}$) value was 1.97; the respective K_{FOC} value was 4. Percent adsorption ranged from 28.6-32.9% of the applied. Percent desorption, as percent of the adsorbed, ranged from -1.9 to 6.9% of the applied. The Freundlich exponent corresponding to the K_F value was 0.96 following the adsorption phase and 0.96 following the desorption phase.

Table 3 summarizes the adsorption coefficients measured in the study. **Table 4** summarizes the desorption coefficients measured in the study.

Overall recoveries ranged from 96.0-100.7% of the applied for the Saddleworth Moor clay loam. The definitive samples were not analyzed for the parent compound. The stability of the parent compound was confirmed by HPLC analysis during preliminary testing.

Coefficients of variation (CV) could not be determined.

[1] Sorption is a generic term that applies to absorption, adsorption, and desorption processes. Adsorption refers to sorption onto a two-dimensional surface; absorption refers to sorption into a three dimensional matrix. Both types of sorption occur in soils and sediments. Desorption refers to a sorbate becoming desorbed from a sorbent. Desorption distribution coefficients are measured by removing solution from a sorption experiment and adding fresh solution, so that all material measured in solution will be the desorbed material. The guideline uses the term adsorption in place of sorption and refers to the initial measurement of sorption.

Results Synopsis:

Table 1. Summary of Adsorption/Desorption Results[A]

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											
Saddleworth Moor Clay loam (47.5% OC, pH 4.1)	1.60 ± 0.0	0.999	9.1E-17	1.54-1.94	3 ± 0.0	1.68 ± 1.0	0.999	2.2E-09	0.96 ± 0.0	4 ± 0.0	0.0335-3.634
Desorption											
Saddleworth Moor Clay loam (47.5% OC, pH 4.1)	1.92 ± 0.0	0.999	1.1E-15	1.83-2.29	4 ± 0.0	1.97 ± 1.0	0.999	3.9E-11	0.96 ± 0.0	4 ± 2.1	0.027-2.947

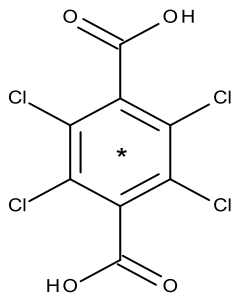
Abbreviations: SE = standard error of regression.

[A] Reviewer-calculated values using data obtained from Table 6, p. 33 of the study report. See Attachment 2 for equations used for calculations.

I. Material and Methods

A. Materials

1. Test Material: [^{14}C]Tetrachloroterephthalic acid (TPA, Chlorthal; p. 15; Appendix 1, p. 46)
Batch/Lot number: 03BLY009
Specific radioactivity: 1.2 MBq/mg
Radiochemical purity: 99.94% (HPLC; Appendix 1, p. 47)
Purity: Not reported
Solubility in water: 5 µg/L (p. 27)



2. Reference Compounds: TPA (p. 16)
Batch/Lot number: 021101
Purity: 99.94%

3. Soils/Sediment: The study was conducted using four European test soils (p. 17). Each soil was collected from *ca*. 0-8 inch layer that had not been treated with pesticides for more than 5 years (Appendix 3, pp. 49-52). Prior to use in the study, the soils were passed through a 2-mm sieve and the sieved soils were air-dried and stored in the dark at room temperature. A summary of the physical and chemical properties of the soils using USDA Soil Taxonomy is provided in **Table 2**. It was unclear whether the test soils were representative of use sites.

Table 2. Description of Soil/Sediment

Soil Name	PT103	SK920191	SK15556090	Saddleworth Moor
Origin	Baylham, Ipswich	South Witham Quarry, South Witham, Lincolnshire	Hartington Upper Quarter, Derbyshire	Saddleworth Moor, Huddersfield, West Yorkshire
USDA Textural Class	Sandy loam	Clay	Silty clay loam	Clay loam
% Sand	75	38	20	44.57
% Silt	12	26	61	24.76
% Clay	13	36	19	30.67
%OC	1.2	2.1	4.2	47.5
CEC (meq/100 g)	6.1	23.0	20.2	74.5
pH in water	5.3	8.0	7.0	4.1
% moisture (1/3 bar)	9.9	34.4	32.9	Not reported
Water holding capacity (g/100 g)	36.2	78.6	93.5	421.1
Soil Taxonomy	Not reported	Not reported	Not reported	Not reported
$CaCO_3$ (%)	Not reported	Not reported	Not reported	Not reported

Data were obtained from Appendix 3, pp. 49-52 of the study report.

B. Study design

1. **Experimental conditions:** Preliminary tests were conducted to determine the solubility of the test substance in 0.01M $CaCl_2$ solution, the adsorption of the test substance to test containers, the appropriate soil:solution ratio and equilibration times to be used in the definitive study, and the stability of TPA in 0.01M $CaCl_2$ solution (pp. 19-21). The solubility of TPA in 0.01M $CaCl_2$ solution was determined to be 5 µg/mL (p. 27). No adsorption of TPA to polypropylene co-polymer (PPCO) and Teflon centrifuge tubes was observed. PPCO centrifuge tubes were selected for the remainder of the study. Little to no adsorption was observed in the initial three soils (PT103 sandy loam, SK920191 clay, and SK15556090 silty clay loam) at soil:solution ratios of 1:1, 1:5, and 1:25 (w:v). Therefore, a fourth soil (Saddleworth Moor clay loam) was assessed at soil:solution ratios of 1:3.5 and 1:25 (w:v). A soil:solution ratio of 1:4 (w:v) was selected for use in the definitive test. In addition, the equilibrium time test and isotherms test were performed using the Saddleworth Moor clay loam soil since no further information could be obtained using the initial three soils. It was determined that 24 hours was a suitable equilibration time for the definitive test (pp. 20-21). HPLC and TLC analyses confirmed the stability of TPA in 0.01M $CaCl_2$ solution for 48 hours.

   For the definitive study, sorption kinetics were determined by pre-equilibrating duplicate aliquots of test soil in 0.01M $CaCl_2$ solution at a soil:solution ratio of 1:4 (w:v; pp. 17-18, 21). The samples were dosed with [^{14}C]TPA at a nominal concentration range of 0.05 to 5.05 µg/mL and shaken in the dark at 20 ± 2°C for 24 hours (p. 22). Following centrifugation, aliquots of the supernatants were removed for analysis. For desorption, an equivalent volume of fresh 0.01M aqueous $CaCl_2$ solution was added to each test vessel and the samples were equilibrated by shaking for 24 hours. Following centrifugation, aliquots of the supernatants were removed for to analysis.

2. **Analytical procedures:** Radioactivity in the aqueous supernatants was determined by

Liquid Scintillation Counting (LSC; pp. 22-23). Following desorption, the soils were shaken with acetonitrile and analyzed using LSC. Non-extractable residues were measured by combustion and LSC.

The Limit of Detection (LOD) for LSC analysis was 1.5 times the background radioactivity (p. 23).

II. Results and Discussion

A. Mass Balance: Overall recoveries ranged from 96.0-100.7% of the applied for the Saddleworth Moor clay loam soil (p. 28; Table 10, p. 35).

B. Transformation of Parent Compound: The definitive samples were not analyzed for the parent compound. The stability of the parent compound was confirmed during preliminary testing.

C. Findings: Reported values were calculated using linear regression (Excel) and the equations and methods discussed in the calculations section.

Following the adsorption phase, equilibration concentrations in water were appropriate, ranging from 0.0335 to 3.6340 µg/mL (Table 6, p. 33). Following the desorption phase, equilibration concentrations in water were appropriate, ranging from 0.0270 to 2.9470 µg/mL.

Percent adsorption ranged from 28.6-32.9% of the applied. Percent desorption, as percent of the adsorbed, ranged from -1.9 to 6.9% of the applied (Table 7, p. 34).

Coefficients of variation (CV) could not be determined.

Table 3. Description of Adsorption Coefficients[A]

Soil	K_d (L/kg)	K_{oc}	K_F (L/kg)	K_{Foc}
Saddleworth Moor Clay loam	1.60	3	1.68	4

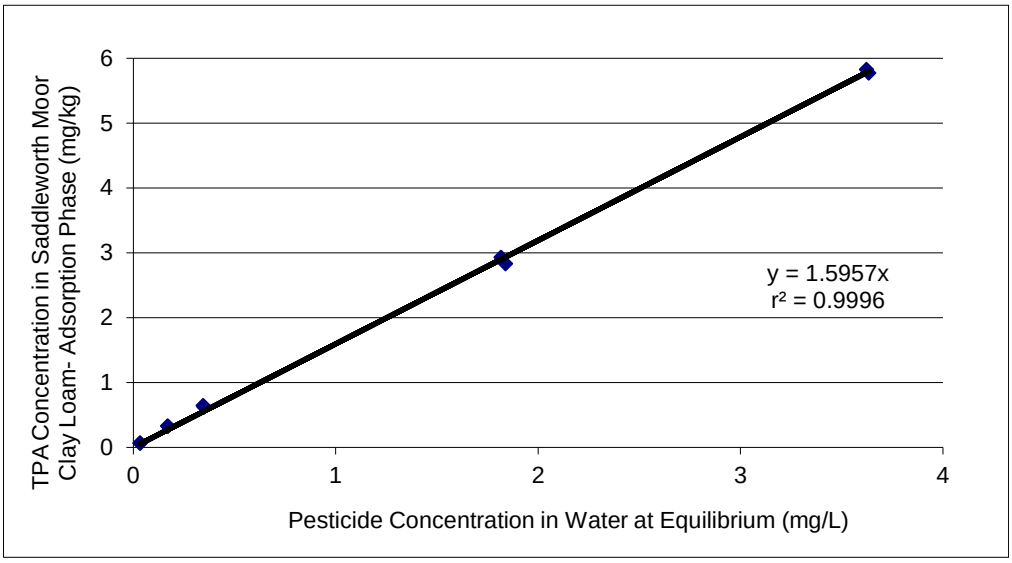
[A] Reviewer-calculated values using data obtained from Table 6, p. 33 of the study report.

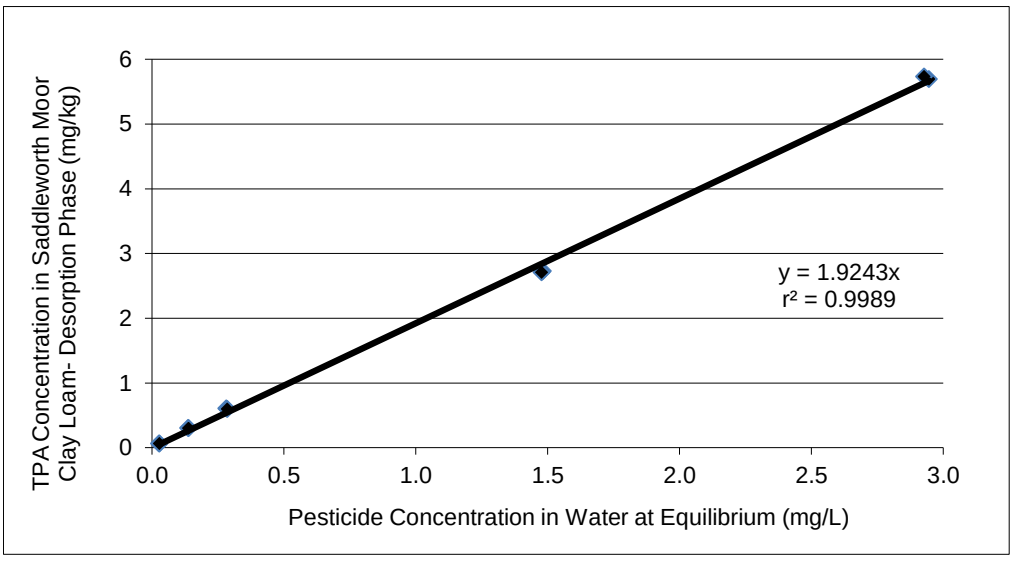
Table 4. Description of Desorption Coefficients[A]

Soil	K_{des} (L/kg)	$K_{oc\text{-}des}$	K_{Fdes} (L/kg)	$K_{Foc\text{-}des}$
Saddleworth Moor Clay loam	1.92	4	1.97	4

[A] Reviewer-calculated values using data obtained from Table 6, p. 33 of the study report.

Reviewer-calculated Freundlich sorption coefficients were in agreement with those reported by the study author (Tables 8-9, pp. 34-35).





Regression of K_d by percent organic carbon, percent clay, and CEC could not be determined.

Table 5. Summary of Regressed Kd vs %OC, %Clay, and CEC

Parameter	r^2	p-value
Kd vs. % organic carbon	Not determined	Not determined
Kd vs. % clay	Not determined	Not determined
Kd vs. CEC	Not determined	Not determined

III. Study Deficiencies and Reviewer's Comments

1. The following deviations were noted:

    a. The definitive study was conducted using only one type of soil rather than across five soil types. The guidelines state that the study should be conducted using different soil types with a varying range of organic carbon content, clay content and soil texture, and pH.

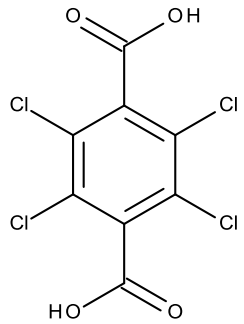
b. It is unclear whether the foreign test soil was representative of use sites.
c. Limits of Quantification (LOQ) were not reported.

2. In a separate study to investigate the rate of degradation of (^{14}C)-TPA in the soils originally selected for this study (PT103, SK920191 and SK15556090), aged sorption coefficients were determined. Aged sorption coefficients (K_{oc}) were 19.9, 14.5 and 11.9 for PT103, SK920191 and SK15556090, respectively, indicating that adsorption of TPA to soils may also be influenced by time (i.e. soil aging; p. 29).

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. TPA and Its Environmental Transformation Products. [A]

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)
PARENT						
TPA (Chlorthal, Dacthal diacid, SDS-954)	**IUPAC:** 2,3,5,6-Tetrachloroterephthalic acid **CAS #:** 2136-79-0 **Formula:** $C_8H_2Cl_4O_4$ **MW:** 303.9 g/mol **SMILES:** c1(c(c(c(c(c1Cl)Cl)C(=O)O)Cl)Cl)C(=O)O		835.1230 Batch equilibrium	49307517	PRT	PRT
MAJOR (>10%) TRANSFORMATION PRODUCTS						
No major transformation products were identified.						
MINOR (<10%) TRANSFORMATION PRODUCTS						
No minor transformation products were identified.						
REFERENCE COMPOUNDS NOT IDENTIFIED						
All compounds used as reference compounds were identified.						

[A] AR means “applied radioactivity”. MW means “molecular weight”. PRT means "parent".

Attachment 2: 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-$_{DES}$ = 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)