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OFFICE OF CHEMICAL SAFETY
AND POLLUTION PREVENTION

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MEMORANDUM

SUBJECT: Dimethyl 2,3,5,6-Tetrachloroterephthalate **(DCPA):** Response to Registrant's Waiver Requests of Environmental Fate Data for DCPA and Its Degradate Tetrachlorophthalic Acid (TPA).

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In support of Registration Review, the Environmental Fate and Effects Division (EFED) has evaluated the following waiver requests for environmental fate studies of dimethyl 2,3,5,6-Tetrachloroterephthalate (also known as Dacthal® and DCPA) and its degradate tetrachlorophthalic acid (TPA) by AMVAC Chemical Corporation:

- MRID 51398101. Freedlander, D. (2020) Dacthal (DCPA) Field Dissipation Waiver Request. Project Number: 100-REV-047. Report prepared by AMVAC Chemical Corporation. 19p.

- MRID 51398102. Freedlander, D. (2020) Tetrachlorophthalic Acid (TPA) Anaerobic Terrestrial and Aquatic Metabolism Waiver Request. Project Number: 100-REV-048. Report prepared by AMVAC Chemical Corporation. 14p.

CONCLUSIONS/ RECOMMENDATIONS

EFED recommends that Pesticide Re-evaluation Division (PRD) grant AMVAC's waiver request (MRID 51398101) for a terrestrial field dissipation study (OCSPP Guideline # 835.6100) of dimethyl 2,3,5,6-Tetrachloroterephthalate (DCPA) and its metabolite tetrachlorophthalic acid (TPA). However, EFED recommends that PRD not grant AMVAC's waiver requests (MRID 51398102) for an anaerobic soil metabolism study of TPA (OCSPP Guideline # 835.4200), and an anaerobic aquatic metabolism study of TPA (OCSPP Guideline # 835.4400). EFED's recommendations regarding these waiver requests are summarized in **Table 1.**

The lack of anaerobic soil and aquatic metabolism data for TPA is important because, based on available fate data and the assumption of stability for other routes of exposure for TPA, there are few or no known pathways for degradation of this chemical. In the absence of the anaerobic soil and aquatic metabolism studies for TPA, EFED will assume stability (*i.e.* no degradation) of TPA through these potential degradation pathways. These conservative assumptions may overestimate the actual persistence of TPA. EFED's modeled aquatic exposures show increased TPA concentrations over time with repeated use of DCPA and potentially exceed levels of concern in receiving surface water systems. Therefore, these data gaps reduce confidence in both the drinking water and ecological risk assessment conclusions.

Table 1. EFED's Recommendations on Waiver Requests for Environmental Fate Studies of DCPA and TPA.

MRID	OCSPP Study Type (Guideline Number)	Chemical	EFED Recommendation
51398101	Terrestrial Field Dissipation (835.6100)	DCPA TPA	Waive
51398102	Anaerobic Soil Metabolism (835.4200)	TPA	Do Not Waive
	Anaerobic Aquatic Metabolism (835.4400)	TPA	Do Not Waive

BACKGROUND

In 2002 and support of human health dietary risk assessments of DCPA, the Health Effects Division (HED) reaffirmed that the parent DCPA, transient intermediate degradate monomethyl tetrachloroterephthalic acid (MTP), and terminal degradate TPA will be the residues of concern (RoCs) for drinking water assessments (USEPA, 2002; DP Barcode D282838). Similarly in the 2011 DCPA Problem Formulation for Registration Review, the parent DCPA and its major and terminal degradate TPA will be the RoCs for ecological risk assessments (USEPA, 2011; DP Barcode D388337).

TPA forms as a major degradate (*i.e.*, > 10%) and has up to a 100% conversion rate in aerobic and anaerobic metabolism studies of DCPA. EFED identified the need for a number of environmental fate data studies, some using both DCPA and TPA as test substances and some using TPA only, in the Problem Formulation (USEPA, 2011; DP Barcode D388337).

In January 2013, EPA issued the Generic Data Call-in (GDCI) Notice (GDCI-078701-1140) that required registrants of pesticide products containing DCPA to submit certain data to the U.S. Environmental Protection Agency (USEPA, 2013). Based on the recommendations of the Problem Formulation, these data requirements included aerobic and anaerobic soil metabolism studies (TPA only), an anaerobic aquatic metabolism study (TPA only), an aerobic aquatic metabolism study (DCPA and TPA), and terrestrial dissipation studies (DCPA and TPA). Subsequent to and in response to issuance of the GDCI, AMVAC submitted data for several required environmental fate studies, which include adsorption/desorption study of TPA (OCSPP Guideline # 835.1230), aerobic soil metabolism study of TPA (OCSPP Guideline # 835.4100), and aerobic aquatic metabolism study of DCPA (OCSPP Guideline # 835.4300) (USEPA, 2017; DP Barcodes 413733+). EFED classified these three data submissions as supplemental no additional data are needed at this time. The status of the environmental fate studies required via the GDCI is summarized in **Appendix B**.

AMVAC requested waivers for several of the other environmental fate data requirements. In 2014, EFED recommended that PRD deny a waiver request from AMVAC for a terrestrial field dissipation study of DCPA and TPA, and for aerobic and anaerobic aquatic metabolism studies of TPA. EFED continues to recommend that the TPA aerobic aquatic metabolism study (OCSPP Guideline # 835.4300) should not be waived because it is needed to reduce uncertainties in the exposure assessment (USEPA, 2014; DP Barcode 413324+). Also in 2014, EFED recommended that PRD grant a waiver request for a TPA soil column leaching study (OCSPP Guideline # 835.1240; USEPA, 2014; DP Barcode 413324+). In 2017, EFED recommended that PRD waive the hydrolysis study for TPA (OCSPP Guideline # 835.2120), and again recommended that PRD deny a waiver request for the anaerobic soil metabolism study of TPA (OCSPP Guideline # 835.4200; USEPA, 2017; DP Barcodes 413733+).

DISCUSSION OF CURRENT WAIVER REQUESTS

835.4200: Anaerobic Soil Metabolism Study of TPA

AMVAC waiver request: AMVAC requested a waiver for the anaerobic soil metabolism data requirement for TPA based on the following rationale (from MRID 51398102):

> *The anaerobic metabolism of the primary dacthal (DCPA) degradate tetrachlorophthalic acid (TPA) has not been observed in studies of the compound. Also, such metabolism has not been evident under aerobic conditions. For this reason, TPA appears persistent and can migrate to lower depths in the soil and ultimately in the groundwater.*
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> *TPA has been shown to be impervious to metabolism in three different sediment systems for a 60-day anaerobic period. This finding is consistent with the fact that polych[l]orobenzoates are resistant to anaerobic degradation and that there is a considerable lag period before metabolism becomes evident. The fate of TPA in the environment is easily understood based on its propensity to leach through the soil profile. However, the chemical has been shown to be relatively innocuous to mammalian and aquatic life and would not pose an undue burden in the environment. Although the chemical may buildup in certain compartments, it has also*

been demonstrated that over time, anaerobic and aerobic processes are capable of degrading compounds such as TPA fully producing both chloride and carbon dioxide.

. . . .

The general scientific literature provides evidence that microbial processes can degrade simple chloro-aromatic acids and chloro-phthalic acids under anaerobic conditions; but this process is limited and entails a lag period in order for suitable microbial populations to develop. Once an amenable microbial population is established, the polychlorinated aromatic substrate may serve as an electron donor or acceptor and with subsequent addition of oxygen the chemical can be fully mineralized to chloride and carbon dioxide. Degradation mediated by specially adapted microbes that can operate under anaerobic conditions would likely occur through the primary mechanisms of reductive halogenation or decarboxylation.

However, the dissipation of TPA is not governed by these reactions because of the considerable lag period between chemical introduction and microbial degradation.

EFED Response: As an initial point, EFED notes the following statement in AMVAC's waiver request (emphasis added):

Although the chemical may buildup in certain compartments, it has also been demonstrated that ***over time****, anaerobic and aerobic processes are capable of degrading compounds such as TPA fully producing both chloride and carbon dioxide.*

AMVAC proposed to rely on a previously submitted anaerobic soil metabolism study with DCPA to fulfill the anaerobic soil metabolism requirement for TPA. In 2017, EFED recommended against that approach because the DCPA studies to which AMVAC referred (MRIDs 00114651 and 41648802) were classified as supplemental due to an insufficient number of data points (USEPA, 2017; DP Barcodes 413733+).

EFED agrees, as presented in AMVAC's 2020 waiver request that, over time, TPA could be a suitable substrate for some microbial community, which could then act upon it through both anaerobic and aerobic processes to degrade the chemical. For example, with a study duration of 120 days, degradation of TPA was demonstrated in an aerobic soil metabolism study of three separate soils. Half-live values of 101, 208, and 1,603 days (MRID 49307516) were calculated from this study from the three different soils. An anaerobic soil metabolism study could similarly demonstrate the degradation of TPA. Since AMVAC contends that aerobic and anaerobic metabolism of TPA will occur over time, a longer-than-standard study duration might be needed to quantify the potential anaerobic metabolism of TPA. For example, EFED has routinely received metabolism studies with one year study durations.

Although data from anaerobic soil metabolism studies are not used for aquatic exposure modeling, this study may provide an important additional line of evidence for anaerobic aquatic metabolism pathways (see below in discussion of anaerobic aquatic metabolism).

EFED recommends that the data requirement **not be waived**, and that the anaerobic soil metabolism study be of sufficient duration to reliably derive a half-life for TPA. In the absence of a suitable anaerobic soil metabolism study, EFED will continue to assume stability of TPA in this environment. This conservative assumption may overestimate TPA's actual persistence and reduce confidence in the risk assessment conclusions.

835.4400 Anaerobic Aquatic Metabolism of TPA

AMVAC waiver request: Similar to the anaerobic soil metabolism data waiver request, AMVAC seeks a waiver for the anaerobic aquatic metabolism data for TPA, and asserts, as above (in MRID 51398102):

> *The anaerobic metabolism of the primary dacthal (DCPA) degradate tetrachlorophthalic acid (TPA) has not been observed in studies of the compound. Also, such metabolism has not been evident under aerobic conditions. For this reason, TPA appears persistent and can migrate to lower depths in the soil and ultimately in the groundwater.*
>
> *TPA has been shown to be impervious to metabolism in three different sediment systems for a 60-day anaerobic period. This finding is consistent with the fact that polych[l]orobenzoates are resistant to anaerobic degradation and that there is a considerable lag period before metabolism becomes evident. The fate of TPA in the environment is easily understood based on its propensity to leach through the soil profile. However, the chemical has been shown to be relatively innocuous to mammalian and aquatic life and would not pose an undue burden in the environment.*

EFED Response: As an initial point, EFED again notes the following sentence in AMVAC's waiver request (emphasis added):

> *Although the chemical may buildup in certain compartments, it has also been demonstrated that* ***over time****, anaerobic and aerobic processes are capable of degrading compounds such as TPA fully producing both chloride and carbon dioxide.*

EFED evaluated the effect of the assumed stability of TPA in aquatic systems by conducting aquatic exposure modeling using standard surface water scenarios in Pesticide Water Calculator (PWC) Ver. 2.001. Preliminary model results of the FLturfSTD use site scenario are presented in **Appendix A**. For this modeling, TPA was characterized as stable to hydrolysis[1] and aerobic aquatic metabolism.[2] TPA was also characterized as stable to aqueous photolysis and anaerobic aquatic metabolism, due to the lack of supporting data. Under these circumstances, and as expected, the modeling results indicate that TPA does not degrade in the aquatic environment. Furthermore, as illustrated in **Figure 1** of **Appendix A**, aquatic exposure modeling reveals a linearly increasing accumulation pattern **over time** for TPA (in this case, over the course of 30 years), in both the water column and benthic region of receiving water bodies. Although submitted ecotoxicity data generally suggest that TPA is not as toxic as DCPA, this increase of TPA in aquatic environments could result in concentrations that exceed chronic aquatic toxicity

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[1] Derived from the DCPA hydrolysis study MRID 00114648.

[2] Using formation/ decline, the TPA stable half-life was derived from data in an aerobic aquatic metabolism study for DCPA (MRID 49307515).

endpoints. As stated in the Problem Formulation (USEPA, 2011; DP Barcode D388337) and more recent responses to ecotoxicological data waiver requests (USEPA, 2022, DP Barcode 437397 and 461052), EFED will use chronic DCPA aquatic toxicity endpoints in the absence of chronic TPA aquatic toxicity endpoints, which may overestimate potential risks.

Because of the uncertainty around aquatic exposure, EFED continues to recommend that the requirement for an anaerobic aquatic metabolism study for TPA **not be waived**. A longer-than-standard study duration may be needed to quantify the potential anaerobic metabolism of TPA. EFED recommends that the anaerobic aquatic metabolism study be conducted for sufficient duration (*e.g.,* 365 days) to reliably derive a half-life for TPA. In the absence of these data, EFED will continue to assume TPA is stable to this pathway for both drinking water (surface water systems) and ecological aquatic risk assessments. This conservative assumption may overestimate TPA's actual persistence and further reduce confidence in the risk assessment conclusions.

<u>835.6100: Terrestrial Field Dissipation (TFD) of DCPA and TPA</u>

AMVAC waiver request: AMVAC seeks a waiver of the requirement for TFD data for DCPA and TPA, and asserts (MRID 51398101):

> *…it is evident that DCPA dissipation has been well defined in the field and further attempts to study the dissipation of the chemical would not be useful. It is clear that DCPA degradation patterns vary widely and the underlying mechanisms that give rise to these different dissipation patterns have been discerned. Appropriate concerns raised by the Agency regarding past study utility can now be resolved.*
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> *With the submission of these high tier studies, there is no merit in developing additional field dissipation study data. The more in-depth analysis and connectivity of different data elements, including new information, provides for a satisfactory understanding of the field dissipation of DCPA, including the potential for volatility. This report [MRID 51398101] is therefore being submitted for consideration of fulfilling the study requirement for DCPA under field conditions.*
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> . . . .
>
> *…the main degradate TPA once formed is leached at a sufficient rate that these slower reactions are not measurable.*

AMVAC also asserts that, in soils acclimated to DCPA through previous use, degradation of DCPA can be very rapid, and that conditions in the field (climate, soil texture, etc.) affect the rate of degradation.

EFED Response: EFED has concluded that, under field conditions, DCPA degradation rates vary based on 1) the use site's history of DCPA applications, and 2) environmental conditions (*e.g.,* climate, soil texture, temperature, and moisture). This is evident in the available TFD studies (MRID 41508609 and 41508610), which were initially classified as *Unacceptable* because of the highly variable data that prevented calculation of DCPA dissipation half-lives. EFED subsequently upgraded the TFD studies to *Supplemental* in 2009, in part because they provide useful information on the leaching behavior of DCPA, TPA, and MTP; and on the degradates found in the terrestrial environment after application of DCPA.

To further evaluate the utility of and uncertainties in the TFD studies, EFED also looked at the prospective ground water (PGW) study that was conducted in 1996 (MRID 44082601). Although it serves a different purpose than a TFD study, a PGW study can provide information regarding mobility and environmental fate of DCPA and its soil metabolites under use sites and climatic conditions that are representative of agronomic and turf-use areas. In this case, the PGW study did not provide sufficient insight to explain the uncertainties in the previously submitted TFD studies. However, the PGW study did provide sufficient data to indicate that DCPA degrades to TPA in the upper soil horizons. The PGW study further elucidates TPA's persistence and high mobility that enable it to leach downward through the soil column into groundwater faster than its rate of degradation (USEPA, 1996; DP Barcode D215972).

EFED concurs with the rationale presented in AMVAC's 2020 waiver request, that requiring another TFD study for DCPA and TPA at this time is not likely to provide additional meaningful data beyond what is currently known about the degradation or dissipation rates of these chemicals. However, given the uncertainties identified in the study review, the supplemental studies do not fulfill TFD study guideline requirements (USEPA, 2009a; DP Barcode 361331 and USEPA, 2009b; DP Barcode 361336).

Although the guideline requirement remains unfulfilled because of previously presented rationale (USEPA, 2017; DP Barcode D413733+), EFED has determined that a new study is not needed at this time and recommends that the current requirement for a TFD study of DCPA and TPA be **waived**.

REFERENCES

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APPENDIX A: Preliminary Ecological Aquatic Exposure Modeling Results

Summary of Water Modeling of TPA and the USEPA Standard Pond

Estimated Environmental Concentrations for TPA are presented in Table 1 for the USEPA standard pond with the FLturfSTD field scenario. A graphical presentation of the year-to-year acute values is presented in Figure 1. These values were generated with the Pesticide Water Calculator (PWC), Version 2.001. Critical input values for the model are summarized in Tables 2 and 3.

This model estimates that about 0.21% of TPA produced on the field eventually reaches the water body. The main mechanism of transport from the field to the water body is by runoff (100% of the total transport) followed by erosion (0.04%).

In the water body, pesticide dissipates with an effective water column half-life of 14,949,350,000.0 days. (This value does not include dissipation by transport to the benthic region; it includes only processes that result in removal of pesticide from the complete system.) The main source of dissipation in the water column is volatilization (effective average half-life = 1.494935E+10 days).

In the benthic region, TPA is stable. Most of the pesticide in the benthic region (80%) is sorbed to sediment rather than in the pore water.

Table 1. Estimated Environmental Concentrations (ppb) for TPA.

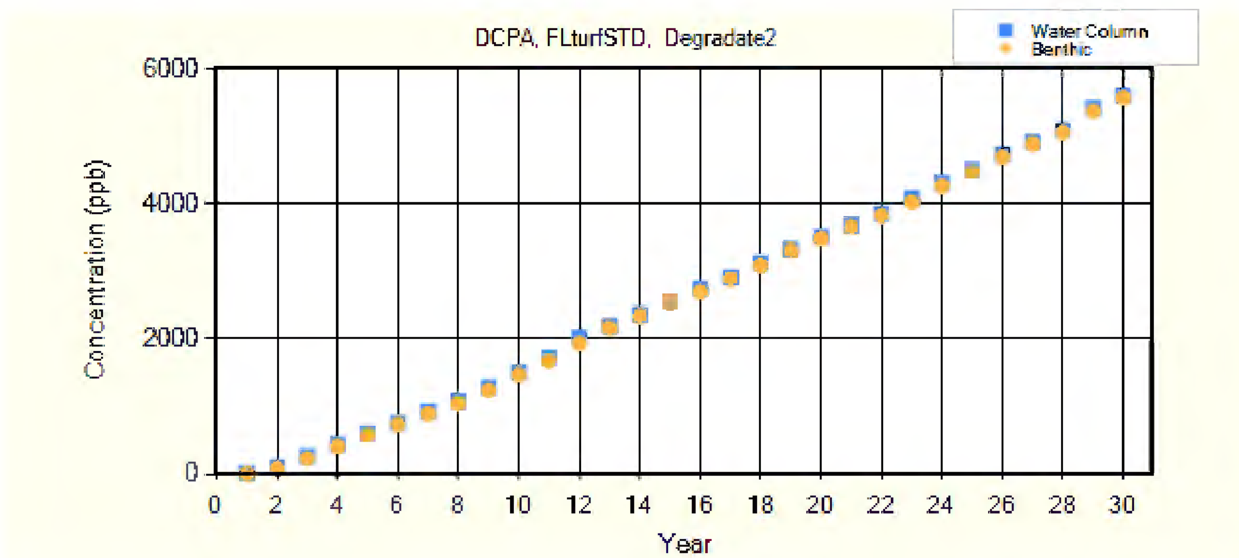
1-day Avg (1-in-10 yr)	5081.
4-day Avg (1-in-10 yr)	5081.
21-day Avg (1-in-10 yr)	5078.
60-day Avg (1-in-10 yr)	5063.
365-day Avg (1-in-10 yr)	4976.
Entire Simulation Mean	2551.

Table 2. Summary of Model Inputs for TPA.

Scenario	FLturfSTD
Cropped Area Fraction	1
Koc (ml/g)	38
Water Half-Life (days) @ 25 °C	0
Benthic Half-Life (days) @ 25 °C	0
Photolysis Half-Life (days) @ 25 °Lat	0
Hydrolysis Half-Life (days)	0
Soil Half-Life (days) @ 30 °C	0

Foliar Half-Life (days)	10e8
Molecular Weight	303.91
Vapor Pressure (torr)	4.89e-8
Solubility (mg/l)	175.4
Molar Conversion: Metabolism	1
Molar Conversion: Soil Degradation	0.89

Figure 1. Yearly Highest 1-day Average Concentrations



Appendix B. Status of Fate Data DCI Requirements for TPA and DCPA

OCSPP Guideline #	Study Title	Study Status
835.1230	Adsorption/desorption (TPA)	Supplemental[1,2]; additional data not needed at this time
835.1240	Leaching (TPA)	Waived[3]
835.2120	Hydrolysis (TPA)	Waived[2]
835.4100	Aerobic soil metabolism (TPA)	Supplemental[2,4]; additional data not needed at this time
835.4200	Anaerobic soil metabolism (TPA)	Waiver request denied: outstanding.[2]
835.4300	Aerobic aquatic metabolism (DCPA)	Supplemental[2,5]; additional data not needed at this time
835.4300	Aerobic aquatic metabolism (TPA)	Waiver request denied; outstanding[3]
835.4400	Anaerobic aquatic metabolism (TPA)	Waiver request denied; outstanding[3]
835.6100	Terrestrial field dissipation (DCPA)	Initial waiver requests denied[3]; EFED now recommends waiving
835.6100	Terrestrial field dissipation (TPA)	

[1] *See* 078701_49307517_DER-Fate_835.1230_01-10-17.pdf
[2] *See* 078701_413733+_RTWVR_DER_Memo_02-07-17.pdf
[3] *See* 078701_413324+_RTWVR_03-21-14.pdf
[4] *See* 078701_49307516_DER-Fate_835.4100_01-13-17.pdf
[5] *See* 078701_49307515_DER-Fate_835.4300_01-19-17.pdf