

Chapter 4: DCPA Mono- and Di-Acid Degradates

A chapter from:

**Regulatory Determinations Support Document for Selected Contaminants
from the Second Drinking Water Contaminant Candidate List (CCL 2)**

EPA Report 815-R-08-012

Executive Summary

Dimethyl tetrachloroterephthalate (DCPA), a synthetic organic compound (SOC) marketed under the trade name “Dacthal,” is a pre-emergent herbicide historically used to control weeds in ornamental turf and plants, strawberries, seeded and transplanted vegetables, cotton, and field beans. As of 1990, more than 80 percent of its use was for turf, including golf courses and home lawns. Available data indicate that DCPA use declined significantly over the course of the 1990s. On July 27, 2005, in response to concerns about groundwater contamination (especially for one of the DCPA degradates), the registrant voluntarily terminated most uses for products containing DCPA. DCPA is currently registered only for use on sweet potatoes, eggplant, kale, and turnips.

DCPA is not particularly mobile or persistent in the environment. Biodegradation and volatilization are the primary dissipation routes. Degradation of DCPA forms two breakdown products, the mono-acid degradate (monomethyl tetrachloroterephthalate or MTP) and the di-acid degradate (tetrachloroterephthalic acid or TPA). The di-acid, which is the major degradate, is mobile and persistent in the field, with a potential to leach into water.

The present toxicity database for MTP and TPA is not sufficient to derive reference doses (RfDs) for these two chemicals. However, since the available data indicate that neither MTP nor TPA is more toxic than their parent compound, DCPA, the Agency believes that the RfD for the DCPA parent would be protective against exposure from the two DCPA metabolites. Both compounds are formed in the body from the DCPA parent, and therefore the toxicity of the degradates is reflected in the observed toxicity of the parent compound. The RfD of 0.01 mg/kg/day for DCPA is based on a chronic rat study with a no-observed-adverse-effect level (NOAEL) of 1.0 mg/kg/day, and incorporates an uncertainty factor of 100. Using the DCPA RfD of 0.01 mg/kg/day and a 20 percent screening relative source contribution (RSC), the Agency calculated a health reference level (HRL) of 0.07 mg/L or 70 µg/L for DCPA and used this HRL for TPA and MTP. No sensitive subpopulations have been identified. Based on the cancer data for DCPA and evidence that neither TPA nor DCPA is mutagenic, the Agency concludes that TPA is unlikely to pose a cancer risk.

EPA evaluated the occurrence of the DCPA degradates in drinking water based on data from the First Unregulated Contaminant Monitoring Regulation (UCMR 1). The results for the two degradates are reported in aggregate. While the UCMR 1 data indicate that the DCPA degradates were the most commonly reported analytes in the monitoring survey (detected at a minimum reporting level or MRL of 1 µg/L in 776 samples from 177 of the 3,876 public water systems or PWSs sampled, in 24 States and 1 Territory), very few systems exceeded thresholds of health concern. Approximately 0.05 percent of the 3,876 PWSs sampled had a detection of the DCPA degradates at levels greater than ½ the DCPA HRL (35 µg/L), affecting approximately 0.33 percent of the population served. Approximately 0.03 percent of the 3,876 PWSs sampled had a detection of the DCPA degradates at levels greater than the DCPA HRL (70 µg/L), affecting less than 0.01 percent of the population served.

EPA evaluated additional data on the occurrence of DCPA and its degradates in ambient and drinking water from several sources. These supplemental sources included: the United States Geological Survey’s (USGS’s) National Ambient Water Quality Assessment (NAWQA)

program, studies performed by the DCPA or dacthal registrant, the Pesticides in Ground Water Database, and the National Pesticide Survey.

The Agency has made a determination not to regulate the DCPA mono-acid degradate and/or the DCPA di-acid degradate with a national primary drinking water regulation (NPDWR). Because these degradates appear to occur infrequently at health levels of concern in PWSs, the Agency believes that an NPDWR does not present a meaningful opportunity for health risk reduction. While the Agency recognizes that these degradates have been detected in the PWSs monitored under the UCMR 1, only 1 PWS detected the degradates at a concentration above the HRL.

The Agency plans to update the Health Advisory for the DCPA parent to include the mono- and di- acid degradates, as well as any recent health information related to these compounds. The updated Health Advisory will provide information to any States with public water systems that may have DCPA degradates at levels above the HRL. If a State finds highly localized occurrence of DCPA degradates at concentrations above the HRL, it should consider whether State-level guidance (or some other type of action) may be appropriate.

The Agency's regulatory determination for these contaminants is presented formally in the *Federal Register*.

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Abbreviations

a.i.	Active Ingredient
AOAC	Association of Analytical Communities
AOP	Advanced Oxidation Process
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
CAS	Chemical Abstracts Service
CCL 2	Second Contaminant Candidate List
CWS	Community Water System
DCPA	Dimethyl tetrachloroterephthalate (Dacthal)
GAC	Granular Activated Carbon
GC/ECD	Gas Chromatography with Electron Capture Detection
GW	Ground Water
HRL	Health Reference Level
MDL	Method Detection Limit
MF	Microfiltration
MRL	Minimum Reporting Level
MTBE	Methyl Tertiary Butyl Ether
MTP	Monomethyl tetrachloroterephthalate
NAWQA	National Water Quality Assessment
NCFAP	National Center for Food and Agricultural Policy
NF	Nanofiltration
NOAEL	No-Observed-Adverse-Effect Level
NPDWR	National Primary Drinking Water Regulation
NPS	National Pesticide Survey
NTNCWS	Non-Transient Non-Community Water System
PGWDB	Pesticides in Ground Water Database
PWS	Public Water System
RED	Reregistration Eligibility Decision
RfD	Reference Dose
RL	Reporting Limit
RO	Reverse Osmosis
RSC	Relative Source Contribution
SOC	Synthetic Organic Compound
SW	Surface Water
TPA	Tetrachloroterephthalic Acid
UCMR 1	First Unregulated Contaminant Monitoring Regulation
UF	Ultrafiltration or Uncertainty Factor
USGS	United States Geological Survey
UV	Ultraviolet

4 DCPA Mono- and Di-Acid Degradates

4.1 Definition

Dimethyl tetrachloroterephthalate (DCPA), a synthetic organic compound (SOC), is a phthalate herbicide. Common names for DCPA include Dacthal, 2,3,5,6-tetrachloro-1,4-benzenedicarboxylic acid dimethyl ester, dimethyl 2,3,5,6-tetrachloroterephthalate, chlorthal dimethyl, and Rid. The Chemical Abstracts Service (CAS) registry number for DCPA is 1861-32-1. In the environment, DCPA is readily metabolized. Tetrachloroterephthalic acid (TPA or di-acid; $C_8H_2Cl_4O_4$; CAS number 2136-79-0) is the only significant DCPA metabolite, with monomethyl tetrachloroterephthalic acid (mono-acid; $C_9H_4Cl_4O_4$; CAS number 887-54-7) as a minor metabolite (USEPA, 1998).

4.1.1 Properties and Sources

DCPA is synthesized for use as a pre-emergent herbicide on annual grasses and broadleaf weed species. As of 1990, more than 80 percent of DCPA use was for turf, including golf courses and home lawns (USEPA, 1990a). Exttoxnet (1996) estimated that roughly 20 percent was used around homes and gardens (Exttoxnet, 1996). DCPA does not occur naturally in the environment. As of 1998, the manufacturing of DCPA was limited to three products registered to ISK Biosciences Corporation (formerly Fermenta ASC Corporation) (USEPA, 1998). In 2005, many uses of DCPA were voluntarily cancelled by the current registrant, AMVAC (70 FR 43408). Technical grade DCPA exists as a colorless or white crystal. DCPA is virtually insoluble in water. It is soluble in the following organic solvents in descending order of solubility: benzene, toluene, xylene, dioxane, acetone, and carbon tetrachloride (USEPA, 1998).

Biodegradation is the primary dissipation process of DCPA, and degradation can occur by several lytic and metabolic pathways (e.g., photolysis, or aerobic and anaerobic metabolism). With the hydrolyzation of one ester bond, DCPA degrades to the mono-acid. When the second ester bond is hydrolyzed, it is degraded to the di-acid. Some physical and chemical properties of DCPA are listed in Exhibit 4-1. No information is available on the physical and chemical properties of the mono- and di-acid degradates.

Exhibit 4-1: Physical and Chemical Properties of DCPA

Identification	
Chemical Abstracts Service (CAS) Number	1861-32-1
Molecular Formula	C ₁₀ H ₆ Cl ₄ O ₄
Physical and Chemical Properties	
Boiling Point	360 - 370 °C ¹
Melting Point	156 °C ²
Molecular Weight	331.99 g/mol ¹
Log K _{oc}	3.81 ³
Log K _{ow}	4.19 ⁴
Water Solubility	0.5 mg/L at 25 °C ⁵
Vapor Pressure	2.5 x 10 ⁻⁶ mm Hg at 25 °C ⁶
Henry's Law Constant	2.18 x 10 ⁻⁶ atm-m ³ /mol ⁷
Freundlich Isotherm Constant (K)	--

¹ Tomlin, 1997 (as cited in HSDB, 2004)

² Budavari, 1989 (as cited in HSDB, 2004)

³ Lyman *et al.*, 1990 (as cited in HSDB, 2004)

⁴ Hansch *et al.*, 1995 (as cited in HSDB, 2004)

⁵ Yalkowsky and Dannenfelser, 1992 (as cited in HSDB, 2004)

⁶ Glotfelty *et al.*, 1984 (as cited in HSDB, 2004)

⁷ HSDB, 2004

4.1.2 Environmental Fate and Behavior

DCPA is neither particularly persistent nor mobile in the environment. Although DCPA is relatively stable to hydrolysis and photolysis, it is susceptible to microbial degradation and volatilization. In laboratory studies, DCPA half-lives ranged between 15 and 30 days (USEPA, 1998). In most soils and ground water, the half-life of DCPA is more variable, ranging from 14 to 100 days (Wauchope *et al.*, 1992 as cited in Exttoxnet, 1996). DCPA's adsorption to clay and organic matter results in minimal soil mobility (HSDB, 2004).

Microbial degradation of DCPA occurs under aerobic and anaerobic soil conditions. The degradation rate increases with temperature and soil moisture (USEPA, 1998). The primary product of both aerobic and anaerobic metabolism is the di-acid degradate, which is mobile, persistent, and will leach in any type of soil. Under anaerobic soil conditions, the estimated half-life of DCPA is 37 to 59 days, with the final product being the di-acid degradate (USEPA, 1998). Under aerobic conditions, the estimated half-life is 18 to 37 days. In a 1993 study by Wettasinghe and Tinsley cited in the Reregistration Eligibility Decision (RED), essentially all of

the DCPA was transformed to di-acid DCPA after 197 days, although minor amounts of mono-acid DCPA were observed (USEPA, 1998). In a 300-day study, the half-life of mono-acid DCPA was about 2.8 days, while di-acid DCPA was persistent and barely degraded at all (Doran, 1990 as cited in USEPA, 1998).

Accumulation of DCPA in water is a major fate process for this contaminant. There is virtually no degradation of DCPA in water ranging from moderately acidic to moderately alkaline (pH 5.0 to pH 9.0). Breakdown is due to the action of sunlight and the half-life is greater than 1 week (Exttoxnet, 1996). Substantial bioaccumulation of DCPA was observed in bluegill sunfish. Bioconcentration factors of 1,984, 777, and 2,574 were measured in whole fish, edible tissue, and viscera, respectively (USEPA, 1998). DCPA metabolism in fish tissues is inconsequential, but demethylation is detectable (Szalkowski *et al.*, 1980; Szalkowski *et al.*, 1981 both as cited in USEPA, 1998).

Volatilization is also a major route of DCPA dissipation from soil. Despite a relatively low Henry's Law Constant (see Exhibit 4-1) and a high log K_{oc} , numerous published studies document the volatility of parent DCPA (USEPA, 1998). Nash and Gish (1989 as cited in USEPA, 1998) suggest that DCPA volatilization may be controlled by adsorption and diffusion; thus vapor pressure would not be a good indicator (USEPA, 1998). Volatilization accounts for 20 to 40 percent of DCPA loss under normal soil conditions, but can be significantly higher with increased field moisture and soil temperature (USEPA, 1998).

In the atmosphere, DCPA exists in both the vapor phase and the particulate phase. In the vapor phase, DCPA degrades through a reaction with photochemically produced hydroxyl radicals and has an estimated half-life of 36 days (HSDB, 2004). Wet and dry deposition can physically remove particulate-phase DCPA from the atmosphere (HSDB, 2004). Atmospheric transport has been implicated in DCPA contamination of crops that were not treated with DCPA (USEPA, 1998).

4.2 Health Effects

Currently, no subchronic or chronic studies are available to assess the toxicological effects of MTP (the mono-acid degradate) and 3 studies in rats (30 and 90-day feeding studies and a one-generation reproductive study) are available for TPA (the di-acid degradate). The effects of exposure were mild (weight loss and diarrhea) and occurred at doses greater than or equal to 2,000 mg/kg/day. No reproductive effects were observed.

The present toxicity database for MTP and TPA is not sufficient to derive reference doses (RfDs) for these two chemicals. However, since the available data indicate that neither MTP nor TPA are more toxic than their parent compound, DCPA, the Agency suggests that the RfD for the DCPA parent would be protective against exposure from these two DCPA metabolites (USEPA, 1998). Both compounds are formed in the body from the DCPA parent and therefore, the toxicity of these degradates is reflected in the toxicity of the parent. The RfD for DCPA is 0.01 mg/kg/day based on a chronic rat study (ISK Biotech Corporation, 1993) with a no-observed-adverse-effect level (NOAEL) of 1.0 mg/kg/day and an uncertainty factor of 100 for rat to human extrapolation and intra-species variability.

No carcinogenicity studies have been performed using either TPA or MTP. Based on the cancer data for the parent and lack of mutagenicity for TPA and DCPA, the Agency (USEPA, 2004) concludes that TPA is unlikely to pose a cancer risk. Klopman *et al.* (1996) evaluated the carcinogenic potential of TPA based on its chemical and biological properties, as well as by a variety of computational tools, and determined that it did not present any substantial carcinogenic risk. There was suggestive evidence that DCPA could be carcinogenic based on an increased incidence of thyroid and liver tumors in rats. The presence of hexachlorobenzene and dioxin as impurities in the material tested could have contributed to the cancer risk.

Using the DCPA RfD of 0.01 mg/kg/day (USEPA, 1994) and a 20 percent screening relative source contribution (RSC), the Agency calculated a health reference level (HRL) of 0.07 mg/L or 70 µg/L for DCPA and used this HRL for TPA and MTP.

EPA also evaluated whether health information is available regarding the potential effects on children and other sensitive populations. There are no data that identify a particular sensitive population for DCPA exposure. Results of a single developmental study indicate that exposure to pregnant dams with doses less than or equal to 2,500 mg/kg/day of TPA via gavage did not have an adverse effect on the fetus. EPA did not identify any data that suggest gender-related differences in toxicity or sensitivity in the elderly.

4.3 Occurrence and Exposure

4.3.1 Use and Environmental Release

DCPA, marketed under the trade name “Dacthal,” was first introduced as a pesticide in 1958. Until recently it was registered for both commercial and residential use, including use as a selective pre-emergence weed control on ornamental turf and plants, strawberries, seeded and transplanted vegetables, cotton, and field beans (USEPA, 1998). On July 27, 2005, in response to concerns about groundwater contamination (especially for one of the DCPA degradates), the registrant voluntarily terminated residential uses of DCPA and many uses on vegetable and nut products (70 FR 43408). The only uses retained were for sweet potatoes, eggplant, kale, and turnip.

To prevent the direct ingestion of DCPA by humans or livestock, DCPA use is subject to certain restrictions. These restrictions prohibit: direct application of DCPA to water or wetlands; effluent discharge containing DCPA to sewage plants without notifying the proper authorities; effluent discharge to rivers, lakes, ponds or other bodies of fresh- or saltwater; feeding clippings or vegetation treated with DCPA to livestock; and grazing livestock in treated areas (USEPA, 1998).

Several studies and reports, described below, provide estimates of recent DCPA use in the United States. However, these estimates should be interpreted with caution, because none of them consider all uses. In 1990, an EPA report suggested that more than 80 percent of DCPA use was on turf, including golf courses and home lawns (USEPA, 1990a). It is not clear how the percentage of turf use may have changed since then, and what percentage of DCPA use (including turf use) is commercial as opposed to residential.

EPA's estimate of commercial DCPA use in the early 1990s, based on proprietary data as well as data from the United States Department of Agriculture, the State of California, and the National Center for Food and Agricultural Policy (NCFAP), is that approximately 1.6 million pounds of active ingredient (a.i.) (range of 1.1 million pounds to 2.1 million pounds) were used annually on about 241,000 to 404,000 acres (USEPA 1998). That estimate includes application on golf courses and sod farms (totaling approximately 225,000 to 450,000 pounds a.i. on 37,000 to 58,000 acres), but does not include residential uses. Separately, EPA has estimated that annual use of DCPA in homes and gardens between 1994 and 1999 has consistently fallen in the range of 1 million to 3 million pounds a.i. (USEPA 1997, 1999, 2002)

NCFAP lists annual DCPA use on 26 crops totaling approximately 1.7 million pounds a.i. on approximately 273,000 acres around the year 1992, and annual DCPA use on 18 crops totaling approximately 0.6 million pounds a.i. on approximately 106,000 acres around the year 1997 (NCFAP, 2003). The NCFAP estimates are based on State-level usage patterns for the periods 1990-1993 and 1995-1998, keyed to State-level crop acreage for 1992 and 1997. Only cropland uses are included in these data; the estimates include sod farms but exclude golf courses and residential uses. For more information on NCFAP pesticide use estimates, see Chapter 2.

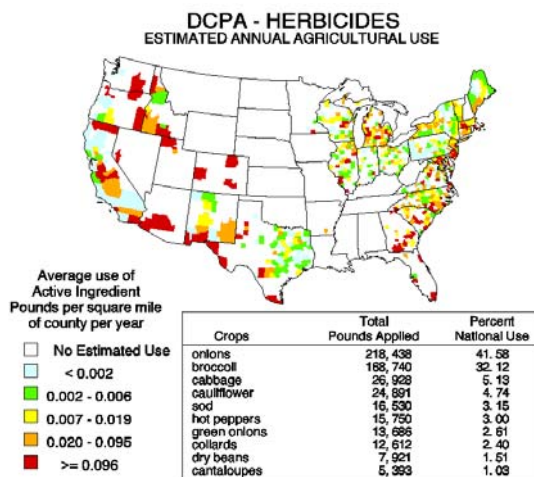
The United States Geological Survey (USGS) has combined State-level NCFAP pesticide usage data with more precise county-level Census of Agriculture acreage data to calculate national pesticide use (Thelin and Gianessi, 2000). Annual DCPA use around 1992 was estimated to be approximately 998,000 pounds a.i. on approximately 185,000 acres. While USGS has not published national estimates for 1997, an estimate of approximately 525,000 pounds a.i. can be inferred from the "total pounds applied" and "percent national use" data in the 1997 geographical distribution map (Exhibit 4-2). USGS estimates, based partly on NCFAP data, also have limitations; the estimates reflect cropland uses, including sod farming, but no other uses.

Total annual DCPA usage in recent years, including agricultural usage, commercial non-agricultural turf usage (e.g., on golf courses), and residential usage, can not be estimated with precision from the data summarized above. The annual total might fall anywhere between 1.5 million and 5 million pounds. No trends are apparent in the EPA estimates of homeowner use, but both the NCFAP data and the USGS estimates suggest a significant decline in agricultural use of DCPA during the 1990s (i.e., from 1.0-1.7 million pounds a.i. per year to 0.5-0.6 million pounds a.i. per year). With the recent termination of many DCPA uses, it is reasonable to expect that DCPA applications will continue to decline.

Exhibit 4-2 shows the estimated geographic distribution and intensity of typical annual DCPA use in the United States in the late 1990s. A breakdown of use by crop is also included. The map indicates that agricultural uses of DCPA are generally concentrated along the entire eastern seaboard, in the Great Lakes States, and in a large, ten-State area of the west, stretching from Washington and Idaho to California, Colorado, and Texas. The map was created by the USGS using NCFAP State-level estimates of pesticide use rates from 1995-1998 and county-level data on harvested crop acreage from the 1997 Census of Agriculture (USGS, 2004). Due to the nature of the data sources, non-agricultural uses are not reflected here and variations in use at the county-level are also not well represented (Thelin and Gianessi, 2000). For more

information on the USGS pesticide use maps, see Chapter 2. As noted above, approximately 80 percent of DCPA use is for weed control on turf, including golf courses, and home lawns; these uses are not represented in the map. The actual geographic distribution of most DCPA use, therefore, is not well known.

Exhibit 4-2: Estimated Annual Agricultural Use of DCPA (c. 1997)



Source: USGS, 2004

The DCPA mono- and di-acid degradates have no known uses, and the application of DCPA is the only known source of the degradates in the environment.

4.3.2 Ambient Water Occurrence

Ambient lakes, rivers, and aquifers are the source of most drinking water. Data on the occurrence of DCPA and its mono-acid degradate in ambient surface and ground water are available from the National Water Quality Assessment (NAWQA) program of the USGS. For details on the NAWQA program, see discussion in Chapter 2. NAWQA data have been analyzed independently by USGS and EPA. In addition, several smaller studies of ambient occurrence were conducted for purposes of pesticide reregistration.

NAWQA National Pesticide Synthesis

Surface Water and Ground Water

Under the NAWQA program, USGS monitored DCPA (listed as “dacthal”) and DCPA mono-acid degradate (listed as “dacthal monoacid”) between 1992 and 2001 in representative watersheds and aquifers across the country. Reporting limits varied but did not exceed 0.003 µg/L for DCPA and 0.070 µg/L for the degradate.

In surface water NAWQA samples (Exhibit 4-3), DCPA was found at frequencies ranging from 6.34% of samples in undeveloped areas to 11.46% of samples in agricultural

settings, 15.4% of samples in mixed land use settings, and 21.78% of samples in urban areas. The higher frequency of occurrence in samples from urban areas may reflect that the majority of DCPA use is on turf (e.g., golf courses and lawns) rather than on agricultural crops. The 95th percentile concentrations were a non-detect in undeveloped settings, 0.003 µg/L in agricultural settings, 0.004 µg/L in mixed land use settings, and 0.007 µg/L in urban land use settings. The highest concentration, estimated at 40 µg/L, was found at an agricultural site (Martin *et al.*, 2003).

Exhibit 4-3: USGS National Synthesis Summary of NAWQA Monitoring of DCPA (Dacthal) in Ambient Surface Water, 1992-2001

Land Use Type	No. of Samples (and No. of Sites)	Detection Frequency	50 th Percentile (Median) Concentration	95 th Percentile Concentration	Maximum Concentration
Agricultural	1,890 (78)	11.46%	<RL	0.003 µg/L	40 µg/L (E)
Mixed	1,020 (47)	15.40%	<RL	0.004 µg/L	0.179 µg/L
Undeveloped	60 (4)	6.34%	<RL	<RL	0.003 µg/L
Urban	902 (33)	21.78%	<RL	0.007 µg/L	0.045 µg/L

Abbreviations:

RL = Reporting limit. Reporting limits for dacthal varied, but did not exceed 0.003 µg/L.

E = Estimated (outside normal calibration limits)

Note: The USGS Pesticide National Synthesis used one year of data, generally the year with the most sampling results, to represent each site in this analysis. The sampling results were time-weighted, to eliminate bias from more frequent sampling at certain times of year. Detection Frequencies and Percentile Concentrations can be interpreted as representing annual occurrence. For instance, the detection frequency can be thought of as the percent of the year in which detections are found at a typical site in this land use category, and the 95th percentile concentration can be thought of as a concentration that is not exceeded for 95% of the year at a typical site in this land use category.

Source: Martin *et al.*, 2003

The DCPA mono-acid degradate was not detected in surface water samples in undeveloped areas, mixed land use settings, or urban areas (Exhibit 4-4). It was detected in 0.18% of surface water samples in agricultural settings. The 95th percentile concentrations were non-detects in all land use settings. The maximum surface water concentration in agricultural settings was 0.430 µg/L (Martin *et al.*, 2003).

Exhibit 4-4: USGS National Synthesis Summary of NAWQA Monitoring of DCPA's Mono-Acid Degradate in Ambient Surface Water, 1992-2001

Land Use Type	No. of Samples (and No. of Sites)	Detection Frequency	50 th Percentile (Median) Concentration	95 th Percentile Concentration	Maximum Concentration
Agricultural	1,233 (48)	0.18%	<RL	<RL	0.430 µg/L
Mixed	561 (25)	0.00%	<RL	<RL	<RL
Undeveloped	19 (1)	0.00%	<RL	<RL	<RL
Urban	503 (18)	0.00%	<RL	<RL	<RL

Abbreviations:

RL = Reporting limit. Reporting limits for dacthal mono-acid varied, but did not exceed 0.070 µg/L.

Note: The USGS Pesticide National Synthesis used one year of data, generally the year with the most sampling results, to represent each site in this analysis. The sampling results were time-weighted to eliminate bias from more frequent sampling at certain times of year. Detection Frequencies and Percentile Concentrations can be interpreted as representing annual occurrence. For instance, the detection frequency can be thought of as the percent of the year in which detections are found at a typical site in this land use category, and the 95th percentile concentration can be thought of as a concentration that is not exceeded for 95% of the year at a typical site in this land use category.

Source: Martin et al., 2003

In ground water (Exhibit 4-5), DCPA detection frequencies ranged from 0% (no detects) in undeveloped settings to 0.44% in mixed land use (major aquifer) settings, 0.96% in urban settings, and 1.18% in agricultural settings. The 95th percentile concentrations were non-detects in all land use settings. The highest ground water concentration, estimated at 10 µg/L, was found at an agricultural site (Kolpin and Martin, 2003).

Exhibit 4-5: USGS National Synthesis Summary of NAWQA Monitoring of DCPA (Dacthal) in Ambient Ground Water, 1992-2001

Land Use Type	No. of Wells	Detection Frequency	50 th Percentile (Median) Concentration	95 th Percentile Concentration	Maximum Concentration
Agricultural	1,443	1.18%	<RL	<RL	10 µg/L (E)
Mixed (Major Aquifer)	2,717	0.44%	<RL	<RL	0.004 µg/L
Undeveloped	67	0.00%	<RL	<RL	<RL
Urban	834	0.96%	<RL	<RL	0.011 µg/L

Abbreviations:

RL = Reporting limit. Reporting limits for dacthal varied, but did not exceed 0.003 µg/L.

E = Estimated (outside normal calibration limits)

Notes: The USGS Pesticide National Synthesis considered each well a distinct site in this analysis. Each well was represented by one sample: normally the first one taken, but possibly a later sample if the first sample was not analyzed for the full range of analytes.

Percentile Concentrations were drawn from the range of detects and non-detects. The method for calculating Percentile Concentrations varied depending on how much of the data was censored at particular levels by the laboratory.

Source: Kolpin and Martin, 2003

The DCPA mono-acid degradate was not detected in ground water samples in undeveloped areas, mixed land use (major aquifer) settings, or urban areas (Exhibit 4-6). It was detected in 0.08% of ground water samples in agricultural settings. The 95th percentile concentrations were non-detects in all land use settings. The maximum ground water concentration in agricultural settings was 1.1 µg/L (Kolpin and Martin, 2003).

Exhibit 4-6: USGS National Synthesis Summary of NAWQA Monitoring of DCPA's Mono-Acid Degradate in Ambient Ground Water, 1992-2001

Land Use Type	No. of Wells	Detection Frequency	50 th Percentile (Median) Concentration	95 th Percentile Concentration	Maximum Concentration
Agricultural	1,217	0.08%	<RL	<RL	1.1 µg/L
Mixed (Major Aquifer)	1,474	0.00%	<RL	<RL	<RL
Undeveloped	46	0.00%	<RL	<RL	<RL
Urban	619	0.00%	<RL	<RL	<RL

Abbreviations:

RL = Reporting limit. Reporting limits for dacthal mono-acid varied, but did not exceed 0.07 µg/L.

Notes: The USGS Pesticide National Synthesis considered each well a distinct site in this analysis. Each well was represented by one sample: normally the first one taken, but possibly a later sample if the first sample was not analyzed for the full range of analytes.

Percentile Concentrations were drawn from the range of detects and non-detects. The method for calculating Percentile Concentrations varied depending on how much of the data was censored at particular levels by the laboratory.

Source: Kolpin and Martin, 2003

Bed Sediments and Biotic Tissue

The NAWQA program also investigated the occurrence of select organochlorine compounds, including DCPA, in bed sediments and biotic tissue. Sampling was conducted at 1,310 sites from 1992 to 2001. Method detection limits were 5 µg/kg dry weight in sediment, and 5 µg/kg wet weight in tissue. Details regarding sampling techniques and analytical methods are described by Nowell (2003). Organochlorines can be present in biotic tissue and in bed sediments of aquatic systems even when they are undetectable in the water column using conventional methods. The occurrence of a toxic compound in stream sediments is pertinent to drinking water concerns because some desorption of the compound from sediments into water, albeit at low rates, may be expected to occur through equilibrium reactions.

Exhibit 4-7 presents the NAWQA occurrence data for DCPA in bed sediment. These data indicate that DCPA occurred in bed sediment at detection frequencies ranging from 0.0% in urban settings to 0.5% in undeveloped settings, 0.6% in mixed land use settings, and 1.8% in agricultural land use settings. The 95th percentile concentrations in all land use settings were non-detects. The highest concentration, 33.7 µg/kg dry weight, was found in a mixed land use setting (Nowell, 2003).

Exhibit 4-7: USGS National Synthesis Summary of NAWQA Monitoring of DCPA in Bed Sediment, 1992-2001

Land Use Type	No. of Sites	Detection Frequency	50 th Percentile (Median) Concentration	95 th Percentile Concentration	Maximum Concentration
Agricultural	282	1.8%	<RL	<RL	25 µg/kg
Mixed	338	0.6%	<RL	<RL	33.7 µg/kg
Undeveloped	224	0.5%	<RL	<RL	5 µg/kg
Urban	166	0.0%	<RL	<RL	<RL

Abbreviations:

RL = Reporting limit. Reporting limits for DCPA varied, but did not exceed 5 µg/kg.

Notes: For bed sediment, all weights are dry weights.

Most sites were sampled only once. In the case of sites sampled multiple times, USGS used a single sample (the earliest sample with complete data for key analytes) to represent each site in this analysis.

Percentile Concentrations were drawn from the range of detects and non-detects. The method for calculating Percentile Concentrations varied depending on how much of the data was censored at particular levels by the laboratory.

Source: Nowell, 2003

In whole fish, DCPA detection frequencies ranged from 1.9% in undeveloped settings to 2.0% in urban settings, 4.5% in mixed settings, and 5.0% in agricultural settings (Exhibit 4-8). The 95th percentile concentrations in all settings were non-detects. The highest concentration, 78 µg/kg wet weight, was found in an agricultural setting (Nowell, 2003).

Exhibit 4-8: USGS National Synthesis Summary of NAWQA Monitoring of DCPA in Whole Fish, 1992-2001

Land Use Type	No. of Sites	Detection Frequency	50th Percentile (Median) Concentration	95th Percentile Concentration	Maximum Concentration
Agricultural	204	5.0%	<RL	<RL	78 µg/kg
Mixed	207	4.5%	<RL	<RL	63 µg/kg
Undeveloped	162	1.9%	<RL	<RL	32 µg/kg
Urban	100	2.0%	<RL	<RL	8.5 µg/kg

Abbreviations:

RL = Reporting limit. Reporting limits for DCPA varied, but did not exceed 5 µg/kg.

Notes:

For whole fish, all weights are wet weights.

Most sites were sampled only once. In the case of sites sampled multiple times, USGS used a single sample (from the first year of sampling, the earliest sample of the variety of fish most often sampled in that Study Unit) to represent each site in this analysis.

Percentile Concentrations were drawn from the range of detects and non-detects. The method for calculating Percentile Concentrations varied depending on how much of the data was censored at particular levels by the laboratory.

Source: Nowell, 2003

EPA Summary Analysis of NAWQA Data

Whereas the NAWQA program often uses the most representative data for a site to calculate summary statistics, EPA, with the cooperation of USGS, has performed a summary analysis of all Cycle 1 water monitoring data from all study units (1991-2001) for many of the Second Contaminant Candidate List (CCL 2) contaminants being considered for regulatory determination, including DCPA and the mono-acid degradate. Detection frequencies were simply computed as the percentage of samples and sites with detections (i.e., with at least one result equal to or greater than the reporting limit). Note that reporting limits were not uniform. Sample detections can be biased by frequent sampling in areas with high (or low) occurrence. Calculating the percentage of sites with detections can reduce this bias. For more details on the data set and the EPA analysis, see Chapter 2.

The results of the EPA analysis are presented in the following two Exhibits. Overall, DCPA was detected in 10.9% of samples and at 6.3% of sites. DCPA was detected more frequently in surface water than in ground water, and the highest concentration (100 µg/L) was found in surface water.

Exhibit 4-9: EPA Summary Analysis of DCPA Data from NAWQA Study Units, 1992-2001

	Detection Frequency (detections are results \geq RL ¹)				Concentration Values (of detections, in $\mu\text{g/L}$)				
	Number of Samples	% Samples with Detections	Number of Sites	% Sites with Detections	Minimum	Median	95 th Percen- tile	99 th Percen- tile	Maximum
surface water	14,872	15.1%	1,907	21.0%	0.000004	0.003	0.078	0.99	100
ground water	6,080	0.8%	5,211	0.8%	0.0006	0.002	0.011	10	10
all sites	20,952	10.9%	7,118	6.3%	0.000004	0.003	0.0756	1	100

¹ RLs (Reporting Limits) for DCPA varied but did not exceed 0.003 $\mu\text{g/L}$. See Chapter 2 for more information.

Note that because this EPA analysis involves more data points than the USGS analyses presented above, a direct comparison is not possible.

The DCPA mono-acid degradate was detected in 0.2% of samples and at 0.3% of sites. The DCPA mono-acid degradate was detected more frequently in surface water than in ground water, and the highest concentration (1.2 $\mu\text{g/L}$) was found in surface water.

Exhibit 4-10: EPA Summary Analysis of DCPA Mono-Acid Degradate Data from NAWQA Study Units, 1992-2001

	Detection Frequency (detections are results \geq RL ¹)				Concentration Values (of detections, in $\mu\text{g/L}$)				
	Number of Samples	% Samples with Detections	Number of Sites	% Sites with Detections	Minimum	Median	95 th Percen- tile	99 th Percen- tile	Maximum
surface water	5,535	0.3%	894	1.1%	0.007	0.11	1.2	1.2	1.2
ground water	4,019	0.05%	3,645	0.1%	0.0395	0.5698	1.1	1.1	1.1
all sites	9,554	0.2%	4,539	0.3%	0.007	0.11	1.2	1.2	1.2

¹ RLs (Reporting Limits) for DCPA mono-acid varied but did not exceed 0.07 $\mu\text{g/L}$. See Chapter 2 for more information.

Note that because this EPA analysis involves more data points than the USGS analyses presented above, a direct comparison is not possible.

Pesticide Reregistration Studies

Several small-scale studies on DCPA occurrence began in 1992 in support of DCPA reregistration. The studies are summarized in EPA's RED for DCPA (USEPA, 1998).

For ground water, two monitoring studies were conducted. In New York State, a total of 29.4 pounds a.i. per acre were applied in three applications to a turf crop. Nine wells were tested over 17 months for detection of DCPA and its two metabolites. In California, a total of 18.2 pounds a.i. per acre were applied in two applications to an onion crop. Eight wells were tested over 22 months for detection of DCPA residues. In both ground water studies, the detection limit was 0.1 µg/L (USEPA, 1998).

Detected concentrations of DCPA and its two degradates were summed together. The New York site had an average sum of 50.36 µg/L for nine wells, and the California site had an average sum of 12.75 µg/L for eight wells (USEPA, 1998).

4.3.3 Drinking Water Occurrence

Nationally representative data on the occurrence of DCPA mono-acid and di-acid degradates in drinking water have been collected by large and small public water systems in accordance with EPA's First Unregulated Contaminant Monitoring Regulation (UCMR 1). For details on the UCMR 1, see Chapter 2 and USEPA (2008). Supplemental data from State and regional studies provide an indication of DCPA occurrence, and the occurrence of its most common degradates, in high-use areas.

UCMR 1

UCMR 1 monitoring was conducted primarily between 2001 and 2003, though some results were not collected and reported until as late as 2006. As List 1 contaminants, DCPA mono- and di-acid degradates were scheduled to be monitored by all large community water systems (CWSs) and non-transient non-community water systems (NTNCWSs) and a statistically representative sample of small CWSs and NTNCWSs. The data presented in this report reflect UCMR 1 analytical samples submitted and quality-checked under the regulation as of March 2006. DCPA degradate data were collected and submitted by 797 (99.6 percent) of the 800 small systems selected for the small system sample and 3,079 (99.3 percent) of the 3,100 large systems defined as eligible for the UCMR 1 large system census.

Because the analytical method approved for UCMR 1 use does not distinguish between the two degradates, they are measured and reported in aggregate. The DCPA degradate data have been analyzed at the level of simple detections (at or above the minimum reporting level, \geq minimum reporting level (MRL), or ≥ 1 µg/L), exceedances of the HRL ($>$ HRL, or > 70 µg/L), and exceedances of one-half the value of the HRL ($> \frac{1}{2}$ HRL, or > 35 µg/L). Results of the analysis are presented in Exhibits 4-11 and 4-12.

Among small systems, DCPA degradate detections (\geq MRL, or ≥ 1 µg/L) were reported by 2.13% of public water systems (PWSs), representing 3.19% of the population served, equivalent to approximately 1.1 million people nationally. All but one of these systems was served by ground water. Only a single small system had a concentration greater than half the Health Reference Level ($> \frac{1}{2}$ HRL, or > 35 µg/L) and the full HRL ($>$ HRL, or > 70 µg/L); this ground water system represented 0.13% of small PWSs and 0.02% of the population served by them, equivalent to 113,000 persons nationally.

Among large systems, 160 systems (5.20%) had detections (\geq MRL, or $\geq 1 \mu\text{g/L}$), affecting approximately 11.3 million people (5.07% of the population served). Most of these were ground water systems. A single large system had a concentration greater than half the Health Reference Level ($> \frac{1}{2}$ HRL, or $> 35 \mu\text{g/L}$); this surface water system represented 0.03% of large PWSs and 0.33% of the population served by them (approximately 738,000 people). No large systems had detections at concentrations greater than the HRL ($>$ HRL, or $> 70 \mu\text{g/L}$).

Exhibit 4-11: Summary UCMR 1 Occurrence Statistics for DCPA Mono- and Di-Acid Degradates in Small Systems (Based on Statistically Representative National Sample of Small Systems)

Frequency Factors	UCMR Data - Small Systems		National System & Population Numbers ¹
Total Number of Samples	3,272		--
Percent of Samples with Detections	1.16%		--
99 th Percentile Concentration (all samples)	1.3 µg/L		--
Health Reference Level (HRL)	70 µg/L		--
Minimum Reporting Level (MRL)	1 µg/L		--
Maximum Concentration of Detections	190 µg/L		--
99 th Percentile Concentration of Detections	190 µg/L		--
Median Concentration of Detections	1.8 µg/L		--
Total Number of PWSs	797		60,414
Number of GW PWSs	590		56,072
Number of SW PWSs	207		4,342
Total Population	2,760,570		45,414,590
Population of GW PWSs	1,939,815		36,224,336
Population of SW PWSs	820,755		9,190,254
Occurrence by System	Number	Percentage	National Extrapolation ²
PWSs with Detections (≥ MRL)	17	2.13%	689
GW PWSs with Detections	16	2.71%	652
SW PWSs with Detections	1	0.48%	37
PWSs > 1/2 HRL	1	0.13%	373
GW PWSs > 1/2 HRL	1	0.17%	373
SW PWSs > 1/2 HRL	0	0.00%	0
PWSs > HRL	1	0.13%	373
GW PWSs > HRL	1	0.17%	373
SW PWSs > HRL	0	0.00%	0
Occurrence by Population Served			
Population Served by PWSs with Detections	87,933	3.19%	1,118,000
Pop. Served by GW PWSs with Detections	86,433	4.46%	1,074,000
Pop. Served by SW PWSs with Detections	1,500	0.18%	44,000
Population Served by PWSs > 1/2 HRL	500	0.02%	113,000
Pop. Served by GW PWSs > 1/2 HRL	500	0.03%	113,000
Pop. Served by SW PWSs > 1/2 HRL	0	0.00%	0
Population Served by PWSs > HRL	500	0.02%	113,000
Pop. Served by GW PWSs > HRL	500	0.03%	113,000
Pop. Served by SW PWSs > HRL	0	0.00%	0

1. Total PWS and population numbers are from EPA September 2004 Drinking Water Baseline Handbook, 4th edition.

2. National extrapolations are generated separately for each population-served size stratum and then added to yield the national estimate of GW PWSs with detections (and population served) and SW PWSs with detections (and population served). For intermediate calculations at the level of individual strata, see EPA's UCMR 1 Occurrence Report, entitled "The Analysis of Occurrence Data from the First Unregulated Contaminant Monitoring Regulation (UCMR 1) in Support of Regulatory Determinations for the Second Drinking Water Contaminant Candidate List."

Abbreviations:

PWS = Public Water Systems; GW = Ground Water; SW = Surface Water; N/A = Not Applicable; Total Number of Samples = the total number of samples on record for the contaminant; 99th Percentile Concentration = the concentration in the 99th percentile sample (out of either all samples or just samples with detections); Median Concentration of Detections = the concentration in the median sample (out of samples with detections); Total Number of PWSs = the total number of PWSs for which sampling results are available; Total Population Served = the total population served by PWSs for which sampling results are available; PWSs with detections, PWSs > 1/2 HRL, or PWSs > HRL = PWSs with at least one sampling result greater than or equal to the MRL, exceeding the 1/2 HRL benchmark, or exceeding the HRL benchmark, respectively; Population Served by PWSs with detections, by PWSs > 1/2 HRL, or by PWSs > HRL = population served by PWSs with at least one sampling result greater than or equal to the MRL, exceeding the 1/2 HRL benchmark, or exceeding the HRL benchmark, respectively.

Notes:

-Small systems are those that serve 10,000 persons or fewer.

-Only results at or above the MRL were reported as detections. Concentrations below the MRL are considered non-detects.

Exhibit 4-12: Summary UCMR 1 Occurrence Statistics for DCPA Mono- and Di-Acid Degradates in Large Systems (Based on the Census of Large Systems)

Frequency Factors	UCMR Data - Large Systems	
Total Number of Samples	30,638	
Percent of Samples with Detections	2.41%	
99 th Percentile Concentration (all samples)	< MRL	
Health Reference Level (HRL)	70 µg/L	
Minimum Reporting Level (MRL)	1 µg/L	
Maximum Concentration of Detections	39.0 µg/L	
99 th Percentile Concentration of Detections	16.0 µg/L	
Median Concentration of Detections	2.0 µg/L	
Total Number of PWSs	3,079	
Number of GW PWSs	1,389	
Number of SW PWSs	1,690	
Total Population	222,266,208	
Population of GW PWSs	53,537,353	
Population of SW PWSs	168,728,855	
Occurrence by System	Number	Percentage
PWSs with Detections (≥ MRL)	160	5.20%
GW PWSs with Detections	109	7.85%
SW PWSs with Detections	51	3.02%
PWSs > 1/2 HRL	1	0.03%
GW PWSs > 1/2 HRL	0	0.00%
SW PWSs > 1/2 HRL	1	0.06%
PWSs > HRL	0	0.00%
GW PWSs > HRL	0	0.00%
SW PWSs > HRL	0	0.00%
Occurrence by Population Served		
Population Served by PWSs with Detections	11,269,436	5.07%
Pop. Served by GW PWSs with Detections	6,082,979	11.36%
Pop. Served by SW PWSs with Detections	5,186,457	3.07%
Population Served by PWSs > 1/2 HRL	738,337	0.33%
Pop. Served by GW PWSs > 1/2 HRL	0	0.00%
Pop. Served by SW PWSs > 1/2 HRL	738,337	0.44%
Population Served by PWSs > HRL	0	0.00%
Pop. Served by GW PWSs > HRL	0	0.00%
Pop. Served by SW PWSs > HRL	0	0.00%

Abbreviations:

PWS = Public Water Systems; GW = Ground Water; SW = Surface Water; N/A = Not Applicable; Total Number of Samples = the total number of samples on record for the contaminant; 99th Percentile Concentration = the concentration in the 99th percentile sample (out of either all samples or just samples with detections); Median Concentration of Detections = the concentration in the median sample (out of samples with detections); Total Number of PWSs = the total number of PWSs for which sampling results are available; Total Population Served = the total population served by PWSs for which sampling results are available; PWSs with detections, PWSs > 1/2 HRL, or PWSs > HRL = PWSs with at least one sampling result greater than or equal to the MRL, exceeding the 1/2 HRL benchmark, or exceeding the HRL benchmark, respectively; Population Served by PWSs with detections, by PWSs > 1/2 HRL, or by PWSs > HRL = population served by PWSs with at least one sampling result greater than or equal to the MRL, exceeding the 1/2 HRL benchmark, or exceeding the HRL benchmark, respectively.

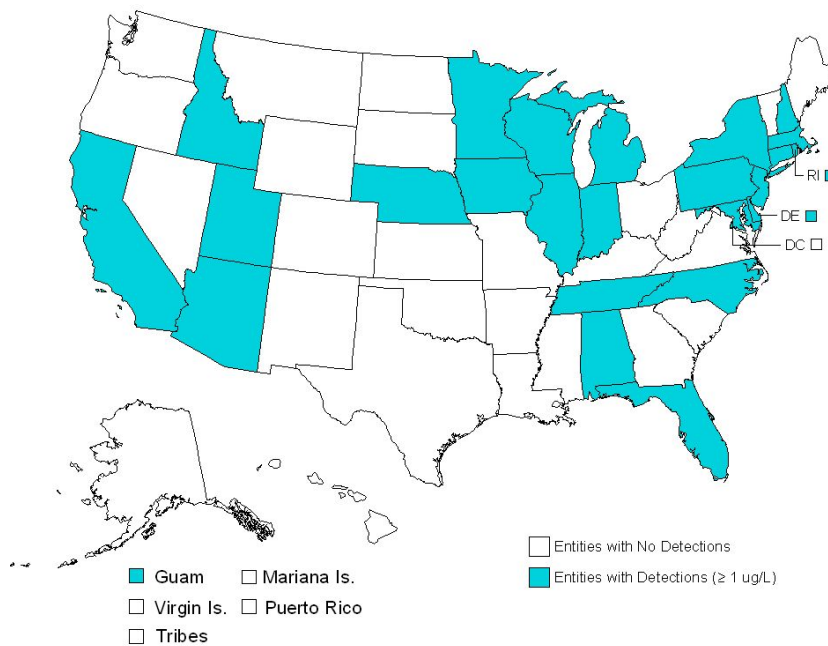
Notes:

-Large systems are those that serve more than 10,000 persons.

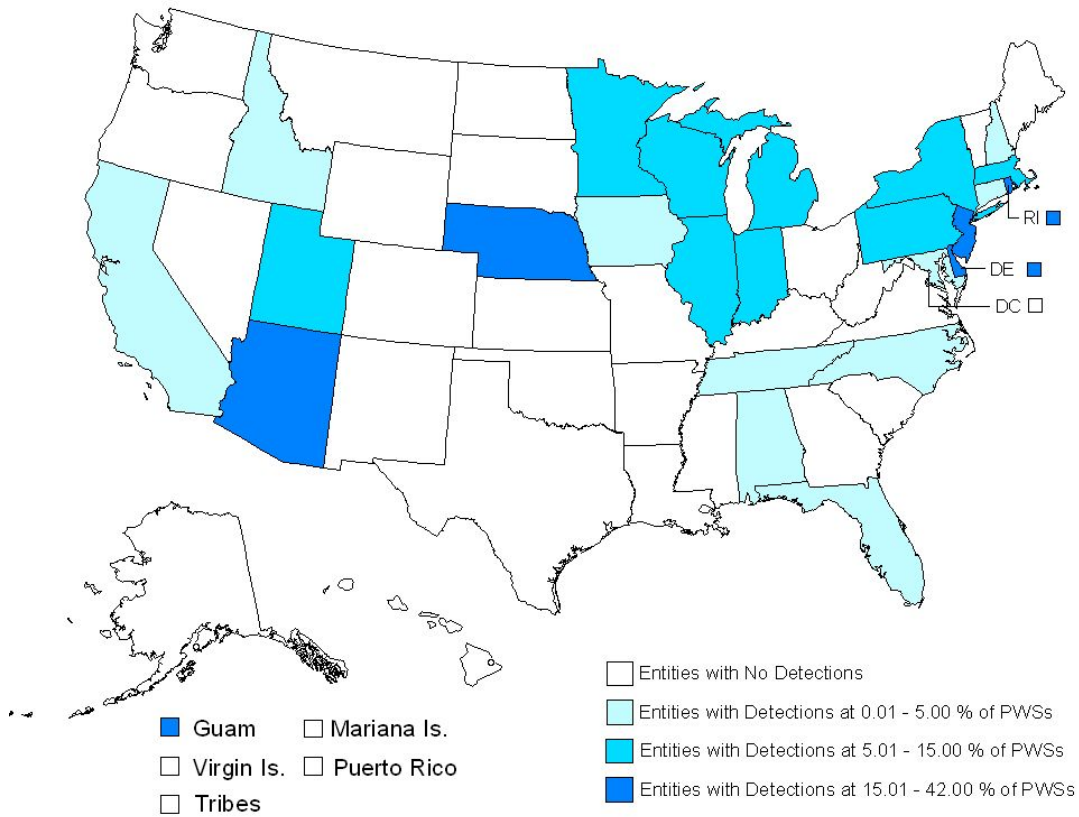
-Only results at or above the MRL were reported as detections. Concentrations below the MRL are considered non-detections.

The following maps, based on UCMR 1 data, give an indication of the geographic distribution of DCPA degradate occurrence in drinking water. Exhibit 4-13 shows the distribution of States with at least one detection. Exhibit 4-14 shows the relative frequency of detection in those States. Exhibit 4-15 shows the distribution of States with HRL exceedances. Although detections of DCPA degradates were relatively widespread, only one State—Michigan—had a concentration in excess of the HRL.

Exhibit 4-13: Geographic Distribution of DCPA Degradates in UCMR 1 Monitoring – States With At Least One Detection At or Above the MRL ($\geq 1 \mu\text{g/L}$)



**Exhibit 4-14: Geographic Distribution of DCPA Degradates in UCMR 1 Monitoring
 - Percentage of PWSs With At Least One Detection At or Above the MRL (≥ 1 $\mu\text{g/L}$), By State**



Note: This map depicts UCMR 1 results from both small systems and large systems. The statistical selection of UCMR 1 small systems was designed to be representative at the national level, but not at the state level. Therefore, this map should only be considered a rough approximation of state-level patterns of contaminant occurrence.

**Exhibit 4-15: Geographic Distribution of DCPA Degradates in UCMR 1 Monitoring
– States With at Least One Detection Above the HRL (> 70 µg/L)**



Exhibit 4-16 shows the location of PWSs with detections even more precisely. At this level of analysis, it is clear that the 177 systems with detections of DCPA degradates are generally restricted to a few areas: California and Arizona, the Salt Lake City region, Nebraska, the Minneapolis-St. Paul metropolitan area, southern Lake Michigan, Philadelphia to New York City, and eastern Massachusetts and Rhode Island. The size of the dot represents the magnitude of the highest concentration detected at the system. The greatest grouping of high-concentration detections is in the Philadelphia to New York City vicinity. It is important to note, however, that all of the concentrations of DCPA degradates detected--with the exception of a single detection in Michigan--are below the HRL of 70 µg/L.

Exhibit 4-16: System-level Geographic Distribution of DCPA Degradates in UCMR 1 Monitoring – Maximum Concentration at Each System with Detections



For further analysis of UCMR 1 results for DCPA, see USEPA (2008).

Summary Analysis of Combined Large and Small System UCMR 1 Data

While the UCMR 1 data indicate that the DCPA degradates were the most commonly reported analytes in the monitoring survey (detected at an MRL of 1 µg/L in 776 samples from 177 of the 3,876 PWSs sampled), very few systems exceeded the health level of concern. PWSs with detections were found in 24 States and 1 Territory. The UCMR 1 data indicate that approximately 0.05 percent (or 2) of the 3,876 PWSs sampled had a detection of the DCPA degradates at levels greater than 35 µg/L, affecting approximately 0.33 percent of the population served (or 739,000 people from 225 million). Approximately 0.03 percent (or 1) of the 3,876 PWSs sampled have a detection of the DCPA degradates at levels greater than 70 µg/L, affecting less than 0.01 percent of the population served (or 500 people from 225 million). The average DCPA degradate concentration among detections was 3.04 µg/L and the median concentration was 2.00 µg/L.

Pesticides in Ground Water Database (PGWDB)

The Pesticides in Ground Water Database (PGWDB) is a compilation of data from ground water studies conducted by federal, State, and local governments, the pesticide industry, and other institutions between 1971 and 1991 (USEPA, 1992). Most of the data are from drinking water wells. Since PGWDB data come from multiple sources, they should be interpreted with caution. Results might be biased high, because areas with suspected contamination are likely to have been sampled more frequently than pristine areas. For more information on PGWDB and the National Pesticide Survey (below), see Chapter 2.

According to the data compiled in the PGWDB, DCPA acid metabolites were detected in 59 of 118 wells (50.0 percent). Detections were found in all three states where the metabolites were investigated. Concentrations ranged from 0.223 to 0.308 µg/L in California, from 0.21 to 1.07 µg/L in Massachusetts, and from 1.0 to 431 µg/L in Oregon. The parent compound DCPA was detected in 5 of 2,033 wells sampled (0.25 percent). The parent compound was found in 3 out of 11 States where it was investigated. Concentrations ranged from 0.70 to 300 µg/L in California, and from 0.010 to 0.030 µg/L in Iowa; one Georgia well had a concentration of 99.0 µg/L. The HRL of 70 µg/L was exceeded in one State by degradates (Oregon) and in two States by the parent compound (California and Georgia) (USEPA, 1992).

In addition, the State of Washington sampled 81 wells for “DCPA and/or acid metabolites.” Seven (8.64 percent) of the wells had detections. Concentrations ranged from 0.2 to 1.08 µg/L (USEPA, 1992).

National Pesticide Survey (NPS)

EPA collected samples from approximately 1,300 CWS wells and rural drinking water wells between 1988 and 1990 for the NPS. The survey was designed to provide a statistically reliable estimate of pesticide occurrence in the nation’s drinking water wells. For details about NPS, see Chapter 2.

Of 126 pesticides and pesticide degradates monitored in the NPS, DCPA acid metabolites were the most commonly detected analyte. The survey projected that approximately 6.4 percent of CWSs and 2.5 percent of rural domestic wells nationwide were contaminated with DCPA acid metabolites at the level of the study’s minimum reporting limit (0.10 µg/L) (USEPA, 1990b, 1990c). A correlation was found between the rate of DCPA application by urban applicators and on golf courses and detections of DCPA acid metabolites (USEPA, 1991a).

With a minimum reporting limit of 0.060 µg/L, the parent compound was not detected in the survey (USEPA, 1990d).

4.4 Technology Assessment

4.4.1 Analytical Methods

EPA evaluated the availability of analytical methods for all unregulated contaminants considered for UCMR 1 (64 FR 50556). Sources for these methods include publications by EPA

and by voluntary consensus standard organizations such as the American Society for Testing and Materials (ASTM), the Association of Analytical Communities (AOAC), and the American Public Health Association (APHA).

Mono- and di-acid DCPA degradates are UCMR 1 List 1 contaminants which can be detected in drinking water by EPA Methods 515.1, 515.2, 515.3, and 515.4. The first two methods were approved for the monitoring of mono- and di-acid DCPA degradates in 1999 (64 FR 50556). The latter two were approved in a subsequent action (66 FR 2273). Methods 515.1, 515.2, and 515.4 do not distinguish between the two degradates, and give the total degradate concentration. Method 515.3 gives the total concentration of DCPA plus the two degradates. No EPA-approved method is currently available that distinguishes the mono-acid degradate from the di-acid degradate. The four EPA methods are generally similar, and involve hydrolyzation, extraction, derivatization, and cleanup steps before detection by gas chromatography with electron capture detection (GC/ECD). A full description of EPA Method 515.1 can be found in EPA's *Method for the Determination of Organic Compounds in Water* (USEPA, 1991b). Method 515.2 can be found in EPA's *Methods for the Determination of Organic Compounds in Drinking Water, Supplement 3* (USEPA, 1995a), and EPA Method 515.3 can be found in EPA's *Methods for the Determination of Organic and Inorganic Compounds in Drinking Water, Volume 1* (USEPA, 2000a). EPA Method 515.4 is available on EPA's Web site at: http://www.epa.gov/safewater/methods/met515_4.pdf (USEPA, 2000b). Additional methods approved for mono- and di-acid DCPA degradates include the ASTM Method D5317-93 (ASTM, 1996; 1998) and AOAC International 992.32 (AOAC, 1998).

The method detection limit (MDL) and the average recovery for each analytical method that can be used for the analysis of DCPA degradates in water are included in the method descriptions below.¹

EPA Method 515.1

In EPA Method 515.1 (Revision 4.0), "*Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector*," a sample is adjusted to pH 12 with 6 N sodium hydroxide. The sample is then mixed for one hour to hydrolyze the derivatives. A solvent wash removes foreign organic material as well as the DCPA parent compound. Next, the sample is acidified, and the chlorinated acids are extracted with ethyl ether by shaking in a separatory funnel. Conversion of the extracted acids to methyl esters is achieved by utilizing diazomethane as the derivatizing agent. Extra derivatizing reagent is expelled, and the esters are separated and identified by GC/ECD (USEPA, 1991b).

¹ The Method Detection Limit (MDL) is a statistical estimate of the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero, *i.e.*, greater than the background signal. The calculation of the MDL is based upon the precision of a series of replicate measurements of the analyte at low concentrations. The MDL incorporates estimates of the accuracy of the determination. The MDL is not a concentration that can typically be measured by the method on a routine basis. Detection limits may vary between analysts and laboratories under various laboratory conditions.

The average recovery is the fraction or percent concentration of a target analyte determined relative to the true or expected concentration from a sample containing a known amount of the target analyte. (This can result in apparent recovery values greater than 100 percent.)

The MDL for total mono- and di-acid DCPA degradates is 0.067 µg/L and the average recovery ranges from 74 to 81 percent depending on the method option used (USEPA, 1991b).

EPA Method 515.2

In EPA Method 515.2 (Revision 1.1), “*Determination of Chlorinated Acids in Water Using Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector,*” a sample is adjusted to pH 12 with 6 N sodium hydroxide. The sample is then mixed for one hour to hydrolyze the derivatives. A solvent wash removes foreign organic material as well as the DCPA parent compound. Next, the sample is acidified and the chlorinated acids are extracted with a 47 mm resin based extraction disk. The acids are eluted from the disk with 10 percent methanol in methyl tertiary butyl ether (MTBE). Conversion of the extracted acids to methyl esters is accomplished by utilizing diazomethane as the derivatizing agent. Extra derivatizing reagent is expelled, and the esters are separated and detected by GC/ECD (USEPA, 1995b).

The MDL demonstrated for the total mono- and di-acid degradates in Method 515.2 is 0.13 µg/L. The percent recovery ranges from 60 to 118 percent depending on the method option used (USEPA, 1995b).

EPA Method 515.3

In EPA Method 515.3 (Revision 1.0), “*Determination of Chlorinated Acids in Drinking Water By Liquid-Liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection,*” a sample is adjusted to pH 12 with 4 N sodium hydroxide to hydrolyze the derivatives. Next, the aqueous sample is acidified and extracted with MTBE. The chlorinated acids, which have been separated into the organic phase, are then transformed to their methyl esters by one of two derivatization techniques. The first technique uses diazomethane as the methylating agent; the latter is a base-promoted esterification procedure and entails the addition of tetramethylammonium hydroxide and subsequent addition of methyl iodide. The target esters are then separated and identified by capillary column GC/ECD. Analytes are quantitated using procedural standard calibration (USEPA, 1996). Because there is no solvent wash step after the hydrolysis in this method, the parent compound DCPA will also be present in the sample extract, if it was present in the sample. Thus, this method does not distinguish between the mono- acid degradate, di-acid degradate, and parent compound, and the quantitative result from Method 515.3 represents the total of all of these forms. Data on the acid degradates collected for the UCMR 1 with Method 515.3 were required to be reanalyzed by Method 515.1, 515.2, or 515.4 if the initial result was greater than the MRL since Method 515.3 measures the total concentration of the parent and the two degradation products instead of only the degradation products.

The MDL for total DCPA and degradates using Method 515.3 is reported to range from 0.38 to 0.63 µg/L depending on the derivatization method used (USEPA, 1996). The recovery is reported to range from 88 to 123 percent depending on the derivatization method and the type of water used (USEPA, 1996).

EPA Method 515.4

In EPA Method 515.4, “*Determination of Chlorinated Acids in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Fast Gas Chromatography with Electron Capture Detection*,” a sample is adjusted to $\text{pH} \geq 12$ with 4 N sodium hydroxide to hydrolyze the derivatives. Next, the sample is washed using a hexane and MTBE mixture for sample cleanup and to remove DCPA. Then the aqueous sample is acidified with sulfuric acid to a pH of less than 1 and extracted with MTBE. The chlorinated acids are then transformed to their methyl esters by derivatization with diazomethane. The target esters are then separated and identified by GC/ECD. Analytes are quantitated using the procedural standard calibration technique with an internal standard (USEPA, 2000b).

The primary column detection limit is 0.113 $\mu\text{g/L}$ and the secondary column detection limit is 0.105 $\mu\text{g/L}$ in reagent water (USEPA, 2000b). The average recovery ranges from 92 to 100 percent depending on the method option used (USEPA, 2000b).

4.4.2 Treatment Technologies

Treatment technology status does not influence the determination of whether or not a contaminant should be regulated. However, treatment technologies must be readily available before a contaminant can be regulated with a national primary drinking water regulation (NPDWR). There is no evidence that DCPA and its mono- and di-acid degradates are substantially removed by conventional treatments, such as coagulation/flocculation, sedimentation, and inert media filtration. Potential treatment technologies include membrane processes, activated carbon, and advanced oxidation.

Membranes are used in both low-pressure and high-pressure treatment processes. Low-pressure systems, which include microfiltration (MF) and ultrafiltration (UF), are most effective in removing particles and large molecules. High-pressure technologies, including nanofiltration (NF) and reverse osmosis (RO), are capable of removing dissolved organic contaminants. Both NF and RO are expected to be effective in removing DCPA and its degradates.

Granular activated carbon (GAC) treatment removes contaminants via the physical and chemical process of sorption: the contaminants attach to the carbon surface as water passes through the carbon bed. Activated carbon has a large sorption capacity for many water impurities, including synthetic organic chemicals, taste- and odor-causing compounds, and some species of mercury.

Adsorption capacity is typically represented by the Freundlich isotherm constant, with higher Freundlich (K) values indicating greater sorption potential. However, the Freundlich (K) values for DCPA and its mono- and di-acid degradates are not available. In general, contaminants containing halogen groups and contaminants with double bonds, as DCPA does, have a high affinity for carbon. In addition, compounds exhibiting low water solubility are expected to have high binding affinity for activated carbon. DCPA's degradates tend to be more soluble than the parent compound and therefore are expected to be less amenable to activated carbon treatment.

Advanced oxidation processes (AOPs) produce free hydroxyl radicals that have a high potential for oxidizing organic or inorganic contaminants in water. AOPs often employ combinations of oxidants, such as ultraviolet (UV) light, hydrogen peroxide, and ozone, for treatment that is more effective than one oxidant alone. AOPs are capable of treating many contaminants, including synthetic organic chemicals, taste- and odor-causing compounds, and inorganic contaminants such as sulfide, iron, and manganese (Najm and Trussell, 1999).

The susceptibility of a pesticide to oxidation may be inferred from aerobic soil metabolism data. Compounds with short aerobic metabolism half-lives are expected to be more amenable to treatment using AOPs. USEPA (1998) reports that the half-life of DCPA is between 18 to 37 days, while the half-life of the mono-acid degradate is shorter (2.8 days) and that of the di-acid degradate is longer (virtually no degradation in 300 days). These findings suggest that AOPs may be effective for the mono-acid degradate, less effective for the parent compound, and not effective for the di-acid degradate.

4.5 Regulatory Determination

The Agency has made a determination not to regulate the DCPA mono-acid degradate and/or the DCPA di-acid degradate with a national primary drinking water regulation (NPDWR).

Because these degradates appear to occur infrequently at health levels of concern in PWSs, the Agency believes that an NPDWR does not present a meaningful opportunity for health risk reduction. While the Agency recognizes that these degradates have been detected in the PWSs monitored under the UCMR 1, only 1 PWS detected the degradates at a concentration above the HRL.

The Agency plans to update the Health Advisory for the DCPA parent to include the mono- and di- acid degradates, as well as any recent health information related to these compounds. The updated Health Advisory will provide information to any States with public water systems that may have DCPA degradates at levels above the HRL. If a State finds highly localized occurrence of DCPA degradates at concentrations above the HRL, it should consider whether State-level guidance (or some other type of action) may be appropriate.

The Agency's regulatory determination for these contaminants is presented formally in the *Federal Register*.

4.6 References

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