Chapter 9:
Fonofos

A chapter from:

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

EPA Report 815-D-06-007

Executive Summary

Fonofos, an organophosphate, is a soil insecticide used until recently to control pests such as corn rootworms, cutworms, symphylans (i.e., garden centipedes), and wireworms. Primarily used on corn crops, fonofos was also used on other crops such as asparagus, beans, beets, corn, onions, peppers, tomatoes, cole crops, sweet potatoes, peanuts, peas, peppermint, plantains, sorghum, soybeans, spearmint, strawberries, sugarcane, sugar beets, white (Irish) potatoes, and tobacco.

Fonofos was scheduled for a reregistration decision in 1999. However, before the review was completed, the registrant requested voluntary cancellation. The cancellation was announced in the *Federal Register* on May 6, 1998 (63 FR 25033), with an effective date of November 2, 1998, plus a one-year grace period to permit the exhaustion of existing stocks.

Fonofos is moderately persistent in soil and its persistence depends on soil type, organic matter, rainfall, and sunlight. Since fonofos adsorbs moderately well to soil, it is not readily leached or transported to ground water but it can be transported to surface waters in runoff. Fonofos is rapidly degraded by soil microorganisms. Fonofos tends to volatilize from wet soil and water surfaces, but the process is slowed by adsorption to organic material in soil, suspended solids, and sediment.

Fonofos (like many organophosphates) is toxic to humans and animals. Case reports and acute oral toxicity studies in animals indicate that oral exposure to fonofos induces clinical signs of toxicity that are typical of cholinesterase inhibitors. Chronic exposure studies also indicated that oral administration of fonofos inhibits cholinesterase. Cholinesterase inhibition is one of the critical effects associated with the reference dose (RfD), which was verified by EPA at 0.002 mg/kg/day. EPA derived the RfD using an no-observed-adverse-effect level (NOAEL) of 0.2 mg/kg/day and a 100-fold uncertainty factor to account for inter- and intraspecies differences.

Fonofos is classified as an unlikely human carcinogen (Group E) because available long-term feeding studies in rats and mice show no evidence of carcinogenicity. Fonofos does not appear to be mutagenic.

The Agency believes that the current RfD is adequately protective of children. The current fonofos RfD of 0.002 mg/kg/day is 1000-fold lower than the NOAEL observed in rat developmental studies. Using the RfD of 0.002 mg/kg/day for fonofos and a 20 percent screening relative source contribution, the Agency derived a health reference level (HRL) of 0.014 mg/L and rounded to 0.01 mg/L (or 10 µg/L).

National Center for Food and Agricultural Policy (NCFAP) data indicate that fonofos use declined significantly during the 1990s. According to NCFAP, approximately 3.2 million pounds of fonofos were applied annually around 1992 and approximately 0.4 million pounds were applied annually around 1997. Fonofos use was cancelled in 1998.

Data on the ambient occurrence of fonofos are available from the first monitoring cycle (1992-2001) of the United States Geological Survey's (USGS's) National Ambient Water

Quality Assessment (NAWQA) program. While the USGS detected fonofos in both surface and ground waters, in no land use setting did the 95th percentile concentration of fonofos exceed 0.003 µg/L (the reporting limit). The maximum surface water concentration, 1.20 µg/L (from an agricultural setting), and the maximum ground water concentration, 0.009 µg/L (also from an agricultural setting), are both less than the fonofos HRL and ½ the HRL.

To estimate fonofos occurrence in drinking water, EPA included it as an analyte in the first Unregulated Contaminant Monitoring Regulation (UCMR 1) List 2 Screening Survey. None of the 2,306 samples from the 295 public water systems (PWSs) sampled (serving a total population of 41 million) had fonofos detections at or above the minimum reporting level (MRL) of 0.5 µg/L. These results suggest that no occurrence and exposure is expected at levels greater than the HRL (10 µg/L) or even ½ the HRL (5 µg/L).

The Agency has made a preliminary determination not to regulate fonofos with a national primary drinking water regulation (NPDWR). Because fonofos does not appear to occur at health levels of concern in PWSs, the Agency believes that an NPDWR does not present a meaningful opportunity for health risk reduction.

The Agency's preliminary regulatory determination for this contaminant is presented formally in the *Federal Register*.

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Abbreviations

a.i.	Active Ingredient
AOAC	Association of Official Analytical Chemists
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
CAS	Chemical Abstracts Service
CCL 2	Second Contaminant Candidate List
GAC	Granular Activated Carbon
GC/MS	Gas Chromatography with Mass Spectrometry
HRL	Health Reference Level
MDL	Method Detection Limit
MRL	Minimum Reporting Level
NAWQA	National Water Quality Assessment
NCFAP	National Center for Food and Agricultural Policy
NOAEL	No Observed Adverse Effect Level
NPDWR	National Primary Drinking Water Regulation
PGWDB	Pesticides in Ground Water Database
PWS	Public Water System
RfD	Reference Dose
RL	Reporting Limit
RO	Reverse Osmosis
SDVB	Polystyrenedivinylbenzene
SPE	Solid Phase Extraction
UCMR 1	First Unregulated Contaminant Monitoring Regulation
USGS	United States Geological Survey

9 Fonofos

9.1 Definition

Fonofos is a highly toxic organophosphate insecticide. The Chemical Abstracts Service (CAS) chemical name for fonofos is O-ethyl S-phenyl ethylphosphonodithioate, and its registry number is 944-22-9. Trade name synonyms include Difonate, Dyfonate, Dyphonate, Capfos, Cudgel, and Stauffer N 2790 (Extoxnet, 1993). Two chiral forms of fonofos exist, of which the (R)-isomer is more toxic to mice and insects than the (S)-isomer (Tomlin, 2002 as cited in HSDB, 2004).

9.1.1 Properties and Sources

At room temperature, fonofos is a clear-to-yellow liquid with a distinct mercaptan (sulfur) odor. As a synthetic compound, it is not found naturally in the environment. Fonofos is applied to soil to control insects around crops (predominantly corn). It is relatively insoluble in water, but miscible in most common organic solvents. Fonofos is available in a variety of formulations, including granular, microgranular, emusifiable concentrate, and suspension concentrate forms (Extoxnet, 1993). Some additional physical and chemical properties of fonofos are listed in Exhibit 9-1.

Exhibit 9-1: Physical and Chemical Properties of Fonofos

Identification	
CAS number	944-22-9
Molecular Formula	$C_{10}H_{15}OPS_2$
Physical and Chemical Properties	
Boiling Point	130 °C at 0.1 mm Hg [1]
Melting Point	< 25 ° C [1]
Molecular Weight	246.32 g/mol [1]
Log K_{oc}	870 [2]
Log K_{ow}	3.94 [3]
Water Solubility	15.7 mg/L at 20 °C [4]
Vapor Pressure	0.000338 mm Hg at 25 ° C [5]
Henry's Law Constant	7.0×10^{-6} atm-m^3/mole [6] 2.1×10^{-4} (dimensionless), predicted [7] 2.6×10^{-4} (dimensionless), from literature [7]
Freundlich Isotherm Constant (K)	251,000 (µg/g)(L/µg)$^{1/n}$ [7]

[1] *Windholz et al., 1983*

[2] *Wauchope at al., 1992 (as cited in Extoxnet, 1993)*

[3] *Hansch et al., 1995 (as cited in HSDB, 2004)*

[4] *Yalkowsky & He, 2003 (as cited in HSDB, 2004)*

[5] *USDA, 2003 (as cited in HSDB, 2004)*

[6] *HSDB, 2004*

[7] *Speth et al., 2001*

9.1.2 Environmental Fate and Behavior

Fonofos is moderately persistent in soil and its persistence depends on soil type, organic matter, rainfall, and sunlight. Since fonofos adsorbs moderately well to soil, it is not readily leached or transported to ground water but it can be transported to surface waters in runoff. Fonofos is rapidly degraded by soil microorganisms (Extoxnet, 1993). Fonofos tends to volatilize from wet soil and water surfaces, but the process is slowed by adsorption to organic material in soil, suspended solids, and sediment (HSDB, 2004).

According to a model of gas/particle partitioning of semivolatile organic compounds in the atmosphere, fonofos will exist in both the vapor and particulate phases in the ambient atmosphere (Bidleman, 1988 as cited in HSDB, 2004). In a laboratory volatility study, approximately 35 percent of the fonofos that was applied to soil volatilized after 24 hours (USEPA, 1999).

9.2 Health Effects

Fonofos (like many organophosphates) is toxic to humans and animals. Case reports and acute oral toxicity studies in animals indicate that oral exposure to fonofos induces clinical signs of toxicity that are typical of cholinesterase inhibitors. In humans, accidental exposures produced symptoms of acute intoxication, nausea, vomiting, salivation, sweating, muscle twitches, decreased blood pressure and pulse rate, pinpoint pupils, profuse salivary and bronchial secretions, cardiorespiratory arrest, and even death in one exposed individual (Hayes, 1982 as cited in USEPA 1988; Pena Gonzalez *et al.*, 1996).

In animals, clinical signs of exposure included tremors, salivation, diarrhea, and labored breathing (USEPA, 1996). Chronic exposure studies also indicated that oral administration of fonofos inhibits cholinesterase (Banerjee *et al.*, 1968; Cockrell *et al.*, 1966; both as cited in USEPA, 1988; Hodge, 1995; Horner, 1993; Pavkov and Taylor, 1988; Woodard *et al.*, 1969 both as cited in USEPA, 1996; Miller, 1987 as cited in USEPA 1996; Miller *et al.*, 1979). Cholinesterase inhibition is one of the critical effects associated with the reference dose (RfD), which was verified by EPA (1991) at 0.002 mg/kg/day. EPA derived the RfD value of 0.002 mg/kg/day using a no-observed-adverse-effect level (NOAEL) of 0.2 mg/kg/day (Hodge, 1995 as cited in USEPA, 1996) and a 100-fold uncertainty factor to account for inter- and intraspecies differences.

Fonofos is classified as an unlikely human carcinogen (Group E) because there is no evidence of carcinogenic potential in the available long-term feeding studies in rats and mice (Banerjee *et al.* 1968 as cited in USEPA, 1988; Pavkov and Taylor, 1988, Sprague and Zwicker, 1987 both as cited in USEPA, 1996). In addition, fonofos does not appear to be mutagenic (USEPA, 1996).

EPA evaluated whether health information is available regarding the potential effects on children and other sensitive populations. In the available developmental studies with rabbits (Sauerhoff, 1987 as cited in USEPA, 1996) and mice (Minor *et al.*, 1982 as cited in USEPA, 1988; Pulsford, 1991 as cited in USEPA, 1996), no developmental effects were observed at oral doses as high as 1.5 mg/kg/day in the rabbit (highest dose tested) nor in mice at doses as high as 2.0 mg/kg/day (Minor *et al.*, 1982 as cited in USEPA, 1988; Pulsford, 1991 as cited in USEPA, 1996). However, in mice, effects were noted at higher dose levels. These effects include an increase in the incidence of variant sternebrae ossifications (at 6 mg/kg/day or greater) and a slight dilation of the fourth brain ventricle in offspring (at 4 mg/kg/day or greater). No developmental neurotoxicity study with fonofos is available for further assessment of this endpoint. In a three-generation reproduction study in rats (Woodard *et al.*, 1968 as cited in USEPA, 1996), no treatment-related adverse effects were observed at the two dose levels used in this study, 0.5 and 1.58 mg/kg/day.

The Agency believes that the current RfD is adequately protective of children. The current fonofos RfD of 0.002 mg/kg/day is 1000-fold lower than the NOAEL observed in the Woodard *et al.* (1968 as cited in USEPA, 1996) developmental studies.

Using the RfD of 0.002 mg/kg/day for fonofos and a 20 percent screening relative source contribution, the Agency derived a health reference level (HRL) of 0.014 mg/L and rounded to 0.01 mg/L (or 10 µg/L).

9.3 Occurrence and Exposure

9.3.1 Use and Environmental Release

Fonofos, a highly toxic liquid organophosphate insecticide, was initially marketed in 1967 by Stauffer Chemical Company, and most recently licensed to Zeneca Ag Products. Fonofos was used primarily on corn crops, but was also applied to others, including asparagus, beans, beets, corn, onions, peppers, tomatoes, cole crops, sweet potatoes, peanuts, peas, peppermint, plantains, sorghum, soybeans, spearmint, strawberries, sugarcane, sugar beets, white (Irish) potatoes, and tobacco. Applied at rates between 1 and 4 pounds per acre, fonofos was used to control insects such as corn rootworms, cutworms, symphylans (garden centipedes), and wireworms (USEPA, 1999).

In March 1984, EPA issued a Registration Standard for fonofos. Although fonofos was scheduled for a reregistration decision in 1999, the registrants requested voluntary cancellation before the review. Cancellation of the pesticide was announced in the Federal Register on May 8, 1998 (63 FR 25033), with an effective date of November 2, 1998, plus a one-year grace period to permit the exhaustion of existing stocks (USEPA, 1999).

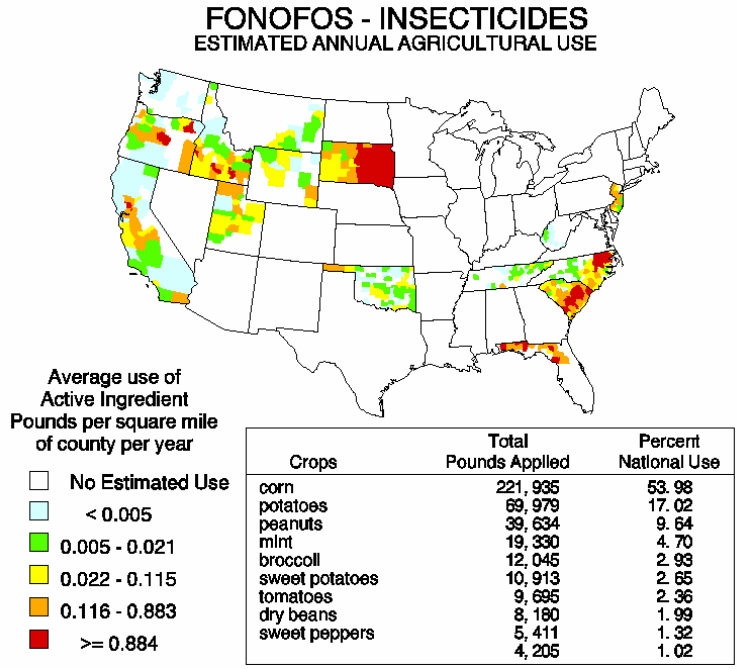
The National Center for Food and Agricultural Policy (NCFAP) estimates of national fonofos use indicate a significant decline during the 1990s (NCFAP, 2004). According to NCFAP, approximately 3.2 million pounds of active ingredient (a.i.) were applied annually to 24 types of crops on 2.6 million acres around 1992, and approximately 0.4 million pounds a.i. were applied annually to 19 types of crops on 0.3 million acres around 1997. NCFAP estimates are based on State-level commercial agriculture usage patterns for the periods 1990-1993 and 1995-1998, and State-level crop acreage for 1992 and 1997. For more information on NCFAP pesticide use estimates, see Chapter 2.

The United States Geological Survey (USGS) combined data collected by NCFAP with data from the Census of Agriculture to estimate that 2.7 million pounds of fonofos a.i. per year were used on approximately 2.4 million agricultural acres in the early 1990s (Thelin and Gianessi, 2000). While USGS has not published national estimates for 1997, an estimate of approximately 0.4 million pounds a.i. can be inferred from the "total pounds applied" and "percent national use" data in the 1997 geographical distribution map (Exhibit 9-2).

Exhibit 9-2 shows the estimated geographic distribution and intensity of typical annual fonofos use in the United States in the late 1990s. A breakdown of use by crop is also included. The map was created by USGS using State-level data sets on pesticide use rates from 1995-1998 compiled by NCFAP, combined with county-level data on harvested crop acreage obtained from the 1997 Census of Agriculture (USGS, 2004). Due to the nature of the data sources, non-agricultural uses are not reflected on the map and variations in use at the county-level are also not well represented (Thelin and Gianessi, 2000). For background on the USGS pesticide use

maps, see Chapter 2. The map suggests that around 1997, fonofos was used in a geographically dispersed minority of States, most intensely in South Dakota.

Exhibit 9-2: Estimated Annual Agricultural Use of Fonofos, c. 1997



Crops	Total Pounds Applied	Percent National Use
corn	221, 935	53. 98
potatoes	69, 979	17. 02
peanuts	39, 634	9. 64
mint	19, 330	4. 70
broccoli	12, 045	2. 93
sweet potatoes	10, 913	2. 65
tomatoes	9, 695	2. 36
dry beans	8, 180	1. 99
sweet peppers	5, 411	1. 32
	4, 205	1. 02

Source: USGS, 2004

9.3.2 Ambient Water Occurrence

Ambient lakes, rivers, and aquifers are the source of most drinking water. Data on the occurrence of fonofos in ambient surface and ground water are available from the National Water Quality Assessment (NAWQA) program of the USGS. For details on this program, see the discussion in Chapter 2. NAWQA data have been analyzed independently by USGS and EPA.

NAWQA National Pesticide Synthesis

Under the NAWQA program, USGS monitored fonofos between 1992 and 2001 in representative watersheds and aquifers across the country. Reporting limits varied but did not exceed 0.003 µg/L.

In surface water (Exhibit 9-3), fonofos was detected at frequencies ranging from 0.0% of samples in undeveloped land settings to 0.92% in urban land use settings, 1.20% in mixed land use settings, and 3.05% in agricultural land use settings. The 95th percentile concentrations in all land use settings were below the reporting limit. The highest concentration, 1.20 µg/L, occurred in an agricultural land use setting (Martin *et al.*, 2003).

Exhibit 9-3: USGS National Synthesis Summary of NAWQA Monitoring of Fonofos in Ambient Surface Water, 1992-2001

Land Use Type	No. of Samples (and No. of Sites)	Detection Frequency	50th Percentile (Median) Concentration	95th Percentile Concentration	Maximum Concentration
Agricultural	1,889 (78)	3.05%	<RL	<RL	1.20 µg/L
Mixed	1,020 (47)	1.20%	<RL	<RL	0.014 µg/L
Undeveloped	60 (4)	0.00%	<RL	<RL	<RL
Urban	900 (33)	0.92%	<RL	<RL	0.084 µg/L

Notes:

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

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, fonofos detection frequencies ranged from 0.0% of samples in urban and undeveloped settings to 0.07% in agricultural and mixed land use (major aquifer) settings (Exhibit 9-4). The 95th percentile concentrations were less than the reporting limit in all settings. The highest concentration, 0.009 µg/L, occurred in an agricultural setting (Kolpin and Martin, 2003).

Exhibit 9-4: USGS National Synthesis Summary of NAWQA Monitoring of Fonofos in Ambient Ground Water, 1992-2001

Land Use Type	No. of Wells	Detection Frequency	50th Percentile (Median) Concentration	95th Percentile Concentration	Maximum Concentration
Agricultural	1,443	0.07%	<RL	<RL	0.009 µg/L
Mixed (Major Aquifer)	2,717	0.07%	<RL	<RL	0.003 µg/L
Undeveloped	67	0.0%	<RL	<RL	<RL
Urban	835	0.0%	<RL	<RL	<RL

Notes:

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

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

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 fonofos. 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 Exhibit 9-5. Overall, fonofos was detected in 2.20% of samples and at 1.34% of sites. Fonofos was detected more frequently and at higher concentrations (maximum of 1.2 µg/L) in surface water.

Exhibit 9-5: EPA Summary Analysis of Fonofos Data from NAWQA Study Units, 1992-2001

	Detection Frequency (detections are results ≥ RL[1])				Concentration Values (of detections, in µg/L)				
	Number of Samples	% Samples with Detections	Number of Sites	% Sites with Detections	Minimum	Median	95th Percen-tile	99th Percen-tile	Maximum
surface water	14,880	3.08%	1,907	4.82%	0.0005	0.007	0.073	0.21	1.2
ground water	6,078	0.05%	5,209	0.06%	0.002	0.003	0.009	0.009	0.009
all sites	20,958	2.20%	7,116	1.34%	0.0005	0.007	0.07	0.21	1.2

[1]RLs (reporting limits) for fonofos varied but did not exceed 0.003 µg/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.

9.3.3 Drinking Water Occurrence

Nationally representative data on fonofos occurrence 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 a detailed description of UCMR 1, see Chapter 2 and USEPA (2006).

UCMR 1

UCMR 1 monitoring was conducted primarily between 2001 and 2003. As a List 2 contaminant, fonofos was scheduled to be monitored by 300 public water systems, including both large and small systems. The data presented in this report reflect UCMR 1 analytical samples submitted and quality-checked under the regulation as of July 2005. Fonofos data were collected and submitted by 178 (98.9 percent) of the 180 small systems selected for the small system sample and 117 (97.5 percent) of the 120 large systems selected for the large system sample. These included two systems in South Dakota, twelve systems in North Carolina, and four systems in South Carolina (States where fonofos use is particularly intensive). The data have been analyzed at the level of simple detections (at or above the minimum reporting level, ≥ MRL, or ≥ 0.5 µg/L), exceedances of the health reference level (> HRL, or > 10 µg/L), and exceedances of one-half the value of the HRL (> ½ HRL, or > 5 µg/L).

Results of the analysis are presented in Exhibits 9-6 and 9-7. No detections of fonofos were found in any samples, and thus there were also no exceedances of the HRL or one-half the HRL.

Exhibit 9-6: Summary UCMR 1 Occurrence Statistics for Fonofos in Small Systems

Frequency Factors	UCMR Data - Small Systems		National System & Population Numbers[1]
Total Number of Samples	643		--
Percent of Samples with Detections	0.00%		--
99th Percentile Concentration (all samples)	< MRL		--
Health Reference Level (HRL)	10 µg/L		--
Minimum Reporting Level (MRL)	0.5 µg/L		--
Maximum Concentration of Detections	< MRL		--
99th Percentile Concentration of Detections	< MRL		--
Median Concentration of Detections	< MRL		--
Total Number of PWSs Number of GW PWSs Number of SW PWSs	178 114 64		60,414 56,072 4,342
Total Population Population of GW PWSs Population of SW PWSs	508,136 275,185 232,951		45,414,590 36,224,336 9,190,254
Occurrence by System	**Number**	**Percentage**	**National Extrapolation[2]**
PWSs (GW & SW) with Detections (≥ MRL)	0	0.00%	0
PWSs (GW & SW) > 1/2 HRL	0	0.00%	0
PWSs (GW & SW) > HRL	0	0.00%	0
Occurrence by Population Served			
Population Served by PWSs with Detections	0	0.00%	0
Population Served by PWSs > 1/2 HRL	0	0.00%	0
Population Served by 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 > ½ HRL, or PWSs > HRL = PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, or exceeding the HRL benchmark, respectively; Population Served by PWSs with detections, by PWSs > ½ HRL, or by PWSs > HRL = population served by PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ 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.
-The HRL used in this analysis is a draft value for working review only.

Exhibit 9-7: Summary UCMR 1 Occurrence Statistics for Fonofos in Large Systems

Frequency Factors	UCMR Data - Large Systems	
Total Number of Samples	1,663	
Percent of Samples with Detections	0.00%	
99th Percentile Concentration (all samples)	< MRL	
Health Reference Level (HRL)	10 µg/L	
Minimum Reporting Level (MRL)	0.5 µg/L	
Maximum Concentration of Detections	< MRL	
99th Percentile Concentration of Detections	< MRL	
Median Concentration of Detections	< MRL	
Total Number of PWSs Number of GW PWSs Number of SW PWSs	117 50 67	
Total Population Population of GW PWSs Population of SW PWSs	40,259,344 8,000,122 32,259,222	
Occurrence by System	**Number**	**Percentage**
PWSs (GW & SW) with Detections (≥ MRL)	0	0.00%
PWSs (GW & SW) > 1/2 HRL	0	0.00%
PWSs (GW & SW) > HRL	0	0.00%
Occurrence by Population Served		
Population Served by PWSs with Detections	0	0.00%
Population Served by PWSs > 1/2 HRL	0	0.00%
Population Served by 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 > ½ HRL, or PWSs > HRL = PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ HRL benchmark, or exceeding the HRL benchmark, respectively; Population Served by PWSs with detections, by PWSs > ½ HRL, or by PWSs > HRL = population served by PWSs with at least one sampling result greater than or equal to the MRL, exceeding the ½ 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-detects.
-The HRL used in this analysis is a draft value for working review only.

Summary Analysis of Combined Large and Small System UCMR 1 Data

None of the 2,306 samples from the 295 public water systems (PWSs) sampled (serving a population of 41 million) contained detects for fonofos at the MRL of 0.5 µg/L. Hence, these data indicate that no occurrence and exposure is expected at levels greater than 5 µg/L (½ the HRL) and greater than 10 µg/L (the HRL).

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 the PGWDB, see Chapter 2.

According to the data compiled in the PGWDB, fonofos was detected in 18 (0.4 percent) of 4,446 wells sampled. The detections were found in 5 out of 13 States where fonofos was investigated. Concentrations ranged from 0.11 to 0.90 µg/L in Iowa, from 0.007 to 0.05 µg/L in Oregon, and from 0.007 to 0.06 µg/L in South Dakota; one Montana well had a concentration of 0.43 µg/L and one Maine well had a concentration of 0.05 µg/L. These detections were all well below the HRL of 10 µg/L (USEPA, 1992).

9.4 Technology Assessment

9.4.1 Analytical Methods

EPA evaluated the availability of analytical methods for all of the unregulated contaminants considered for UCMR 1 (64 FR 50556; September 17, 1999). Sources for these methods include publications by EPA and voluntary consensus standard organizations, such as the American Society for Testing and Materials (ASTM), the Association of Official Analytical Chemists (AOAC), and the American Public Health Association (APHA).

Fonofos is a UCMR 1 List 2 contaminant that can be detected in drinking water using EPA Method 526. This method was approved in the UCMR 1 List 2 Rule (66 FR 2273; January 11, 2001) for monitoring fonofos. EPA Method 526 relies on solid phase extraction (SPE) followed by capillary column gas chromatography coupled with mass spectrometry (GC/MS). A full description of EPA Method 526 can be found in EPA's *Methods for the Determination of Organic and Inorganic Compounds in Drinking Water, Volume 1* (USEPA, 2000a). A brief summary of the method is provided below.

EPA Method 526

For EPA Method 526 (Revision 1.0), *"Determination of Selected Semivolatile Organic Compounds in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS),"* target analytes are extracted from a water sample by passing the water through a SPE disk or cartridge containing polystyrenedivinylbenzene (SDVB). The extract is then dried, concentrated and diluted by the addition of internal standards. An aliquot of the extract is injected into a gas chromatograph with a high resolution fused silica capillary column to separate the components. The analytes are transferred from the capillary column to the mass spectrometer and subsequently identified. Mass spectrometry is advantageous as a detection method since it reports few false positive results compared to conventional detection methods (USEPA, 2000b).

The MDL for fonofos demonstrated by Method 526 ranges from 0.022 to 0.06 µg/L depending upon the extraction media used (USEPA, 2000b). The average recovery for fonofos using Method 526 ranges from 89 to 109 percent, depending on the method option used (USEPA, 2000b).[1]

9.4.2 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 fonofos is substantially removed by conventional treatments, such as coagulation/flocculation, sedimentation, and inert media filtration. Potential treatment technologies include activated carbon, reverse osmosis, and advanced oxidation.

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. Activated carbon is considered to be cost-effective for removing a particular contaminant if the Freundlich (K) value

[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.)

of the contaminant is above 200 µg/g $(L/\mu g)^{1/n}$ (Speth *et al.*, 2001). Speth *et al.* (2001) report that the Freundlich (K) value for fonofos is 251,000 µg/g $(L/\mu g)^{1/n}$, which indicates that GAC is a promising treatment option.

Reverse osmosis (RO) is similar to other membrane processes, such as ultrafiltration and nanofiltration, in that water passes through a semi-permeable membrane. However, in the case of RO, the membrane is non-porous. RO involves the use of applied hydraulic pressure to oppose the osmotic pressure across the membrane, forcing the water from the concentrated-solution side to the dilute-solution side. The water dissolves into the membrane, diffuses across, then dissolves out into the permeate. Most inorganic and many organic contaminants are rejected by the membrane and will be retained in the concentrate.

USEPA (2000c) report that the organophosphate class of pesticides can be removed with 97.8 to 99 percent efficiency using a cellulose acetate membrane and 98.5 to 100 percent efficiency using a thin-film composite membrane. These results indicate that RO is a promising option for removal of fonofos in drinking water.

9.5 Regulatory Determination

The Agency has made a preliminary determination not to regulate fonofos with a national primary drinking water regulation (NPDWR). Because fonofos does not appear to occur at health levels of concern in PWSs, the Agency believes that an NPDWR does not present a meaningful opportunity for health risk reduction. While fonofos has been found in ambient waters, it was detected only at levels less than the HRL (as well as ½ the HRL) and it was not found in UCMR 1 Screening Survey of public water supplies. Fonofos was voluntarily cancelled in 1998 and the Agency expects any remaining stocks and releases into the environment to decline. In addition, since fonofos tends to bind strongly to soil, any releases to the environment are not likely to contaminant source waters.

The Agency's preliminary regulatory determination for this contaminant is presented formally in the *Federal Register*.

9.6 References

Banerjee, B.M., D. Howard, and M.W. Woodard. 1968. *Dyfonate (N-2790) safety evaluation by dietary administration to rats for 105 weeks.* (As cited in USEPA, 1988).

Bidleman, T.F. 1988. Atmospheric processes. *Environmental Science and Technology*. 22:361-367. (As cited in HSDB, 2004).

Cockrell, K.O., M.W. Woodard, and G. Woodard. 1966. *N-2790 Safety evaluation by repeated oral administration to dogs for 14 weeks and to rats for 13 weeks.* (As cited in USEPA, 1988).

Extoxnet. 1993. "Extension Toxicology Network Pesticide Information Profiles–Fonofos." Available on the Internet at: http://pmep.cce.cornell.edu/profiles/extoxnet/dienochlor-glyphosate/fonofos-ext.html. Accessed March 10, 2006.

Hansch, C., A.J. Leo, and D. Hoekman. 1995. *Exploring QSAR – Hydrophobic, Electronic, and Steric Constants*. Washington, DC: American Chemical Society. (As cited in HSDB, 2004).

Hayes, W.J. 1982. Pesticides Studied in Man. Baltimore, MD: Williams and Wilkins. P. 413. (As cited in USEPA, 1988).

Hazardous Substances Data Bank (HSDB). 2004. Search for Fonofos. Available on the Internet through TOXNET, sponsored by the National Institute of Health's National Library of Medicine. Available on the Internet at: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB. Accessed November 1, 2004.

Hodge, M. 1995. *Fonofos: 1-Year Old Toxicity Study in Dogs*. Report Number CTL/P/4499, Study Number PDO944. Zeneca Central Toxicology Lab. (As cited in USEPA, 1996).

Horner, J. 1993. *Fonofos: Subchronic Neurotoxicity Study in Rats*. Lab Project Number: CTL/P/3879, PRO889. Zeneca Central Toxicology Lab. (As cited in USEPA, 1996).

Kolpin, D.W. and J.D. Martin. 2003. "Pesticides in Ground Water: Summary Statistics; Preliminary Results from Cycle I of the National Water Quality Assessment Program (NAWQA), 1992-2001." Available on the Internet at: http://ca.water.usgs.gov/pnsp/pestgw/Pest-GW_2001_Text.html. Accessed August 24, 2004.

Martin, J.D., C.G. Crawford, and S.J. Larson. 2003. "Pesticides in Streams: Summary Statistics; Preliminary Results from Cycle I of the National Water Quality Assessment Program (NAWQA), 1992-2001." Available on the Internet at: http://ca.water.usgs.gov/pnsp/pestsw/Pest-SW_2001_Text.html. Accessed August 24, 2004.

Miller, J.L., L. Sandvik, G.L. Sprague, A.A. Bickford, and T.R. Castles. 1979. Evaluation of delayed neurotoxic potential of chronically administered Dyfonate in adult hens. Abstract presented in *Toxicology and Applied Pharmacology*. 48(Part 2):A197.

Miller, J. 1987. *Neurotoxicity of 90-Day Oral Administration of Technical Dyfonate to Adult Hens*. T-6237: Final Report. Stauffer Chemical Co. p. 59. (As cited in USEPA, 1996).

Minor, J., J. Downs, G. Zwicker, *et al.* 1982. *A teratology study in CD-1 mice with Dyfonate technical.* T-10192. Final report. Stauffer Chemical Company. (As cited in USEPA, 1988).

National Center for Food and Agricultural Policy (NCFAP). 2004. National Pesticide Use Database. Available on the Internet at: http://www.ncfap.org/database/national/default.asp. Accessed August 24, 2004.

Pavkov, K. and D. Taylor. 1988. *Rat Chronic Toxicity and Oncogenicity Study with Dyfonate. Laboratory Project ID T-11997.* (Unpublished study, as cited in USEPA, 1996).

Pena Gonzalez, P., J. Perez-Rendon Gonzalez, E. Dominguez Alberdi, M. Gomez Labat, and J. Bajo Arenas. 1996. Epidemic outbreak of acute food poisoning caused by pesticides [Article in Spanish]. *Atencion Primaria*. 17(7):467-70.

Pulsford, A. 1991. *First Amendment to a Teratology Study in CD-1 Mice with Dyfonate Technical (MRID No. 118423), Lab Project No. T-10192, T-10192C*. MRID No. 42057601. (Unpublished study as cited in USEPA, 1996).

Sauerhoff, M. 1987. *A Teratology Study in Rabbits with Dyfonate Technical*. T-l2630:Volume 1: Final Report: Laboratory Project ID: WIL 27027. (As cited in USEPA, 1996).

Speth, T.F., M.L. Magnuson, C.A. Kelty, and C.J. Parrett. 2001. Treatment Studies of CCL Contaminants. In: *Proceedings, AWWA Water Quality Technology Conference*. Nashville, TN. November 11-15, 2001.

Sprague, G. and G. Zwicker. 1987. *18-Month Dietary Oncogenicity Study with Dyfonate Technical in Mice*. Final Report: T-11995. (As cited in USEPA, 1996).

Thelin, G.P. and L.P. Gianessi. 2000. *Method for Estimating Pesticide Use for County Areas of the Conterminous United States.* U.S. Geological Survey Open-File Report 00-250, 62 p. Available on the Internet at: http://ca.water.usgs.gov/pnsp/rep/ofr00250/ofr00250.pdf.

Tomlin, C.D.S. (ed). 2002. Fonofos (944-2-9). In: The e-Pesticide Manual, Version 2.2. Surrey, UK, British Crop Protection Council. (As cited in HSDB, 2004).

United States Department of Agriculture (USDA). 2003. ARS Pesticide Properties Database: Fonofos. (As cited in HSDB, 2004).

USEPA. 1988. *Fonofos Health Advisory*. EPA Report 820-K-88-003. August, 1988.

USEPA. 1991. Integrated Risk Information System (IRIS), Fonofos. March 1991. Available on the Internet at: http://www.epa.gov/iris/subst/0158.htm. Accessed February 2, 2005.

USEPA. 1992. *Pesticides in Ground Water Database: A Compilation of Monitoring Studies, 1971-1991. National Summary.* Office of Prevention, Pesticides and Toxic Substances. EPA Report 734-12-92-001. Available on the Internet at: http://nepis.epa.gov/pubtitleOPPTS.htm. [Search for document number 7341292001.]

USEPA. 1996. *Memorandum – 041701. Fonofos (Dyfonate®). Draft Toxicology Chapter for Reregistration Eligibility.* Health Effects Division. September 11, 1996.

USEPA. 1999. Reregistration Eligibility Decision (RED) Facts--O-Ethyl S-phenyl ethylphosphonodithiolate (Fonofos). EPA Report 738-F-99-019. Washington, DC: Office of Prevention, Pesticides and Toxic Substances. November 1999. Available on the Internet at: http://www.epa.gov/oppsrrd1/REDs/factsheets/0105fact.pdf.

USEPA. 2000a. *Methods for the Determination of Organic and Inorganic Compounds in Drinking Water, Volume 1*. EPA Report 815-R-00-014.

USEPA. 2000b. Method 526 - Determination of Selected Semivolatile Organic Compounds in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS). Revision 1.0. In: *Methods for the Determination of Organic and Inorganic Compounds in Drinking Water, Volume I*. EPA Report 815-R-00-014.

USEPA. 2000c. *Summary of Pesticide Removal/Transformation Efficiencies from Various Drinking Water Treatment Processes*. Report prepared for the Committee to Advise on Reassessment And Transition (CARAT). Available on the Internet at: http://www.epa.gov/oppfead1/carat/2000/oct/dw4.pdf.

USEPA. 2006. *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*. EPA Report 815-D-06-008. Draft. December 2006.

United States Geological Survey (USGS). 2004. 1997 Pesticide Use Maps. Available on the Internet at: http://ca.water.usgs.gov/pnsp/pesticide_use_maps_1997/. Accessed August 17, 2004. Last updated August 14, 2003.

Wauchope, R.D., T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers, and J.P. Burt. 1992. The SCS/ARS/CES Pesticide Properties Database for Environmental Decision-Making. *Reviews of Environment Contamination and Toxicology*. 123:1-157. (As cited in Extoxnet, 1993).

Windholz, M., S. Budavari, R.F. Blumetti, and E.S. Otterbein (eds.) 1983. *The Merck Index - Encyclopedia of Chemicals, Drugs and Biologicals*. 10th ed. Rahway, NJ: Merck and Co., Inc.

Woodard, M.W., C.L. Leigh, and G. Woodard. 1968. *Dyfonate (N-2790) Three-Generation Reproduction Study in Rats*. (Unpublished study, as cited in USEPA, 1996).

Woodard, M.W., C.I. Donoso, and J.P. Gray, et al. 1969. *Dyfonate (N-2790) Safety Evaluation by Dietary Administration to Dogs for 106 Weeks*. (Unpublished study, as cited in USEPA, 1988 and USEPA, 1996).

Yalkowsky, S.H. and Y. He. (eds.) 2003. *Handbook of aqueous solubility data*. Boca Raton, FL: CRC Press. (As cited in HSDB, 2004).