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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
Office of Prevention, Pesticides, and Toxic Substances  
Washington, DC 20460

December 18, 1998

**MEMORANDUM****SUBJECT:** Revised EFED Environmental Risk Assessment For Profenofos**TO:** Carmelita White, CRM  
Betty Shackelford, Acting Branch Chief  
Reregistration Branch III, SRRD (7508C)**FROM:** ERB 4 Profenofos RED Task Team  
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Environmental Risk Branch 4, EFED (7507C)*Nelson Thurman***THROUGH:** Mah Shamim, Branch Chief  
Environmental Risk Branch 4, EFED (7507C)*Mah Shamim*

The revised EFED Environmental Risk Assessment for Profenofos is attached. EFED based the revised assessment on the following documents, which are also attached for your referral:

- (1) The 6/14/96 EFED chapter for the Profenofos RED (with minor revisions 10/25/98)
- (2) Refined surface water modeling (PRZM/EXAMS) report from Ron Parker, EFED, dated 9/25/96 [this document detailed the tier 2 surface water modeling for ecological risk assessments; it may not have been forwarded to SRRD earlier]
- (3) The EFED response to comments from the registrant and the public on the draft profenofos RED, 12/1/98

The most significant change in the risk assessment is the addition of incident data relating to fish kills from profenofos. These reports, not included in the 1996 risk assessment, provided a greater degree of certainty regarding EFED's assessment of the impact of profenofos on aquatic organisms.

**Data Gaps**

The environmental fate database has significant gaps regarding the persistence of profenofos under the acidic soil and water conditions that characterize its major use areas. However, EFED



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is not asking for additional data at this time because fish kill incident reports provide evidence that profenofos will indeed persist for sufficient time at concentrations that will result in fish mortality within the use area. Any additional studies on soil and water characteristic of the major use area would only confirm quantitatively what we already know qualitatively.

While the fish kill incident reports confirm EFED's assessment of acute effects (mortality) from exposure to profenofos, EFED does not have sufficient information to assess chronic effects to fish from exposure to profenofos. Water levels measured at the time of the fish kills (exceeding 10% of the NOAEC in the fish early life stage test) and reproductive impairment in other animals (birds and small mammals) trigger the data requirement for a full life cycle study. **Therefore the fish life cycle study (72-5) for freshwater fish is needed to complete the chronic risk assessment of profenofos.**

### **Risk Reduction Considerations**

Consideration of any measures to reduce the risk of profenofos to fish should take into account the following points:

- (1) The original risk quotients, based on refined modeling, exceeded levels of concern for fish and aquatic invertebrates. However, our assessment of the risk to fish is based on the reported incidents which show that, under actual use conditions, profenofos does indeed reach surface waters in concentrations sufficient to cause fish kills.
- (2) The risk quotients for aquatic invertebrates is greater than that for fish. Because of the small size of such organisms, such kills are not easily observable and we do not receive incident reports for invertebrates. The impact of large aquatic invertebrate kills may be more subtle, resulting in the loss of a food source for fish and subsequent die-off in the fish population.
- (3) The fate assessment which suggests that profenofos is not highly persistent (with a half-life of several days in alkaline soils) is likely to underestimate profenofos persistence in its major use areas, where the soil and water are likely to be acidic (conditions that would favor a slower breakdown of profenofos).
- (4) The fish kill incidents were clustered in 3 counties in northeast Louisiana and 3 in west-central Mississippi where profenofos use is high and where the soil and water tend to be acidic. Whether these factors alone, or in combination with other site-specific factors, led to the fish kills cannot be determined from the incident reports. It is also possible the incidents are clustered because of better reporting in these areas.
- (5) The incidents show that the existing label language is not adequate to prevent fish kills under actual use conditions. Any serious attempts to reduce the risk to fish from the use of profenofos on cotton will have to go beyond these existing measures.

With these points in mind, EFED recommends that consideration of risk reduction measures for aquatic organisms include the following:

- (1) Expand all spray drift and runoff buffer recommendations on the label to all water bodies (or aquatic habitats). Right now, the buffers pertain to impounded waters. The definition of "impounded" water may be subject to interpretation. A lake created by a dam is impounded (and thus subject to buffers) while a natural lake may not be so protected. The reported incidents occurred in a number of water bodies that are not impounded.
- (2) Consider adding a vegetated buffer strip as a means of protecting water bodies from runoff. The adsorption/desorption characteristics of profenofos suggest that vegetated buffers should be effective for this chemical. The actual width of the buffers should be based on reported runoff concentrations (if available, under acidic soil conditions that represent the major use area) and an evaluation of the amount of buffer that would be needed to reduce these concentrations below a potentially lethal concentration.
- (3) Consider a more thorough evaluation of the specific incident areas to determine what, if any, site factors may have contributed to the fish kills. This information would be useful in determining the need for additional risk reduction measures (or use restrictions based on site factors).
- (4) Tie an assessment of the need for additional mitigation measures (beyond those already mentioned) to a continuing assessment of fish kill incidents. Although the registrant claims their stewardship program and declining use of profenofos have reduced the frequency of fish kill incidents, EFED has no reliable data to assess this. A thorough evaluation of such risk reduction measures would require studies which evaluated the measures against controls (in other words, anecdotal evidence is not sufficient to determine whether risk reduction measures are working).
- (5) If fish kill incidents continue, consider geographic or soil/site-related restrictions which would be based on an evaluation of the conditions which led to the fish kills.



## ENVIRONMENTAL ASSESSMENT FOR PROFENOFOS

### 1. Use Characterization in Relation to Exposure

Profenofos is a broad-spectrum acaricide and insecticide registered for use on cotton. The end-use product, Curacron 8E, is applied as an emulsifiable concentrate in aerial or ground spray at a maximum single application rate of 1 lb a.i./A and a maximum dose of 6 lb a.i./A/year.

Cotton is grown in four major areas in the US (information is from the Cotton Council, International, <http://www.cotton.org/cci/bcotprod.htm>):

**Southeast:** Alabama, Florida, Georgia, North Carolina, South Carolina and Virginia produce 21 percent of the total U.S. crop. Planting is from early April to early June; harvesting is from late September to early December. About 20 percent of the crop is irrigated.

**Mid-South:** Arkansas, Louisiana, Mississippi, Missouri and Tennessee produce 33 percent of the total crop. Planting is from mid-April to early June; harvesting is from late September to early December. About 35 percent of the region is irrigated.

**Southwest:** Kansas, Oklahoma and Texas produce 26 percent of the total crop. Planting in South Texas begins in late February with harvesting running from late July until mid-September. In the rest of the region, planting starts in mid-April. Harvesting begins in mid-October and lasts through December. Approximately 30 percent of the crop is irrigated.

**West:** Arizona, California and New Mexico produce 20 percent of the total crop. Planting begins from late September to early December. Virtually all of the cotton grown in this region is irrigated.

Profenofos is used in all of the regions, although usage is concentrated in the mid-south area. BEAD data (Quantitative Usage Analysis, 1998) show 81% of the total pounds of active ingredient are used in Mississippi, Louisiana, Texas, Arizona, and Georgia.

### 2. Environmental Fate Assessment

The available environmental fate database is relatively complete but contains substantial gaps related to profenofos degradates. While the guideline requirements have been met, our understanding of the fate of profenofos is confined primarily to neutral to alkaline environments (which are more prevalent in the Southwest and West cotton-growing regions). The fate of profenofos under acidic conditions (common to the Southeast and Mid South regions) is not well understood.

Available environmental fate studies show that pH-dependent hydrolysis is the major route of dissipation for profenofos while aerobic and anaerobic metabolism become important after the

initial hydrolysis. Profenofos dissipates in neutral to alkaline soils with a half-life of several days. Little data exists for acid soils, although it can be inferred that profenofos will dissipate at a slower rate. One of the major degradates, 4-bromo-2-chlorophenol, is persistent in the environment while the fate of another degrade, O-ethyl-S-propyl phosphorothioate, is not well known. Profenofos is not highly mobile and, although the field dissipation studies did not allow for an assessment of the leaching potential, is not expected to leach to ground water under normal use. The mobility and leaching potential of the degradates is unknown. The chemical can reach surface waters through spray drift or runoff.

**Table 1: Summary of Environmental Fate Parameters For Profenofos (See Text for Discussion)**

Fate Parameter	Value	Reference/Comments
<i>Persistence</i>		
Hydrolysis pH 5 pH 7 pH 9	$t_{1/2}$ = 104-108 days $t_{1/2}$ = 24-62 days $t_{1/2}$ = 0.33 days	MRIDs 416273-09, 419390-01
Photolysis in water on soil	stable stable	MRID 418799-01, 419390-02 MRID 416273-10
Aerobic soil metabolism	$t_{1/2}$ = 2 days @ pH 7.8	MRID 423343-02
Anaerobic soil metabolism	$t_{1/2}$ = 3 days @ pH 7.8	MRID 423343-03
Anaerobic aquatic metabolism	$t_{1/2}$ = 3 days @ pH 7.3 (water), 5.1 (sediment)	MRID 422181-01
<i>Mobility/Adsorption-Desorption</i>		
Batch Equilibrium (4 soils)	$K_d$ = 4.6 - 89.3 $K_{oc}$ = 869 - 3162	MRID 416273-11
Lab Volatility	$6.13 \times 10^{-3}$ ug/cm <sup>2</sup> /hr	MRID 419050-01
<i>Field Dissipation</i>		
Terr. Dissipation in CA bare and cotton plots, TX bare and cotton plots	$t_{1/2}$ of several days; actual $t_{1/2}$ uncertain due to degradation in storage	MRIDs 428513-01, 429009-01
<i>Bioaccumulation</i>		
Accumulation in Fish	BCF 29x body, 45x head, 682x viscera; depurates rapidly	MRID 00085952, 921480-59

**a. Persistence**

Hydrolysis is the primary route of dissipation. Profenofos hydrolyzes in neutral and alkaline solutions, with half-lives of 104-108 days at pH 5, 24-62 days at pH 7, and 7-8 hours at

pH 9 (416273-09, 419390-01). The major degradates are 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate. Photolysis is not a major pathway in the degradation of profenofos (418799-01, 419390-02, 416273-10, 420304-01). The UV spectrum of profenofos overlaps slightly with the visible spectrum around 290-295 nm (420304-01). However, the overlap is minimal and extensive photolysis is not expected.

Profenofos metabolizes rapidly in alkaline aerobic and anaerobic conditions. In an alkaline (pH 7.8) soil, profenofos degraded with a half-life of 2 days under aerobic conditions (423343-02) and 3 days under anaerobic conditions (423343-03). The rate of metabolism was influenced by hydrolysis and aerobic and anaerobic metabolism in neutral and acid soils is likely to be slower. The major degradates are 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate. 4-Bromo-2-chlorophenol concentrations in both soil metabolism studies did not decline until 60 to 120 days after application. Additional metabolites form slowly. In anaerobic aquatic conditions, profenofos degraded with a half-life of 3 days in a pH 5.1 sediment flooded with pH 7.3 water (422181-01). The major degradates are 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate. Additional metabolites -- 4-bromo-2-chlorophenyl ethyl ether (BCPEE), cyclohexadienyl sulfate, and phenol complex increased in concentration after 180 days.

#### **b. Mobility**

Profenofos is expected to be somewhat mobile, with Freundlich  $K_{ads}$  values of 4.6 for sand, 7.5 for sandy loam, 17.0 for loam, and 89.3 for clay soil samples. Desorption values ranged from 6.2 (sand) to 128.1 (clay). Adsorption generally increased with increasing soil organic matter content, clay content, and CEC.  $K_{oc}$  values ranged from 869 to 3162 (416273-11). Additional data is needed on the mobility of the major degradates/metabolites of profenofos, in particular 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate.

Laboratory studies show that some profenofos may be released to the atmosphere through volatilization. Over 30 days, volatility averaged  $6.13 \times 10^{-3}$  ug/cm<sup>2</sup>/hr and the vapor pressure averaged  $3.46 \times 10^{-6}$  mm Hg (419050-01). 4-bromo-2-chlorophenol was the major volatile residue.

#### **c. Field Dissipation**

The submitted field studies provide adequate information for a qualitative assessment of profenofos dissipation in the field. Dissipation rate evaluations are complicated because profenofos degrades during storage, probably due to hydrolysis. Both profenofos and its degradate 4-bromo-2-chlorophenol dissipate from the surface 6 inches of cotton and bareground plots in California and Texas with a half-life of several days (428513-01, 429009-01). Neither profenofos or 4-bromo-2-chlorophenol were detected below 12 inches in either study. However, because the studies were conducted in soil and weather conditions that resulted in a moisture deficit, with little or no excess water available for downward movement through the soil, the leaching potential could not be reliably assessed in the studies.



#### **d. Accumulation**

Profenofos residues accumulate preferentially in the viscera of bluegill sunfish. The maximum bioconcentration factors were 29x in the bodies, 45x in the heads, and 682x in the viscera (000859-52, 921480-59). Profenofos residues depurated rapidly, with concentrations decreasing to 1 ppb in the bodies, 2 ppb in the heads, and 7 ppb in the viscera after 8 days. The dominant chemical identified in the viscera was 4-bromo-2-chlorophenol (33-48% of the recovered radioactivity).

### **3. Water Resource Assessment**

Based on available information, the Agency does not expect profenofos to be a ground-water concern. Profenofos may contaminate surface water via spray drift and to a lesser degree by runoff. While profenofos is not expected to persist in alkaline waters, it may be more persistent under acidic to neutral conditions. Fish kill incidents reported in Louisiana, Mississippi, and Alabama suggest profenofos is persistent for a long enough period of time in sufficient quantities to result in fish kills under certain conditions (see section 5).

#### **a. Ground Water**

Laboratory mobility data suggest profenofos is not likely to leach to ground water under normal use. The potential for profenofos to move to ground water is further reduced under alkaline conditions because it appears to hydrolyze rapidly. Without data on the persistence in acidic soil and water, a definitive assessment cannot be made for these conditions. The mobility and leaching potential of the degradates is unknown. In EPA's National Pesticides in Ground Water Database, profenofos was not detected in any of the 188 wells sampled in a Texas study (1987-88). No other study included in the database analyzed for profenofos.

Ground Water Modeling: An estimate of the concentration of profenofos that might be present in ground water under highly-vulnerable conditions (permeable sandy soils with a shallow depth to ground water) was made with SCI-GROW. The model simulated 6 applications of 1 lb a.i./acre each, using a median  $K_{oc}$  (2465) and an aerobic soil metabolism half life of 6 days (3 times the value of the single study submitted on a pH 7.8 soil). This resulted in a screening-level concentration of 0.03 ug/L.

#### **b. Surface Water**

Profenofos may contaminate surface water by spray drift during application or runoff. The intermediate soil/water partitioning of profenofos suggests that little of the chemical will leach into the subsurface. The majority of the applied chemical will remain at the surface, where it will be susceptible to runoff. In alkaline soils, substantial fractions of applied profenofos should be available for runoff for only a few days after application due to rapid dissipation. Profenofos is likely to persist longer in acidic soils and, thus, be available to runoff in higher quantities for a longer time. However, because of the uncertainty in the fate of profenofos under acidic conditions, the extent to which profenofos is available cannot be quantified. Profenofos will likely

be transported in runoff both dissolved in water and sorbed to sediment.

The persistence of profenofos in receiving waters will vary depending on the pH, microbiological population, and hydrologic residence time of the water body. Profenofos will not persist in alkaline waters due to its susceptibility to hydrolysis. It may not persist in waters with a substantial microbiological population. However, it will be somewhat more persistent in neutral to acidic waters with low microbiological activities and long hydrologic residence times. The soil/water partitioning coefficient suggests profenofos will occur both sorbed to suspended and bottom sediment and dissolved in the water.

Except for O-ethyl-S-propyl phosphorothioate, for which no direct fate data exists, the major degradates [4-bromo-2-chlorophenol, 4-bromo-2-chlorophenyl ethyl ether (BCPEE), and cyclohexadienyl sulfate) appear to be more persistent than profenofos. Consequently, substantial amounts of those degradates should remain available for runoff for longer periods than for profenofos. The presence of hydrolyzable groups on the O-ethyl-S-propyl phosphorothioate indicate it may be less persistent than some of the other major degradates, but its actual persistence was not determined.

Although no direct soil/water partitioning data are available for the major degradates, a greater partitioning of both 4-bromo-2-chlorophenol and cyclohexadienyl sulfate into water than profenofos in the aquatic anaerobic metabolism study suggests they may exhibit substantially lower soil/water partitioning than profenofos. If so, runoff of those degradates may occur primarily by dissolution in runoff water as opposed to adsorption to eroding soil, and most of their mass in receiving waters may be dissolved in the water column as opposed to adsorbed to suspended and bottom sediment.

Monitoring studies have, for the most part, not included profenofos as an analyte. Subsequently, EFED does not have any data on the concentrations of profenofos in surface water. The STORET database included no entries for profenofos in surface water. Profenofos is not included in the USGS National Water Quality Assessment (NAWQA) program.

Surface Water Modeling. In the absence of monitoring data, the Agency estimated profenofos concentrations in surface water resulting from use on cotton using the models PRZM2.3 and EXAMS 2.94. Details of the model, including parameter selection, assumptions, and limitations, can be found in Parker (1996). The model used a cotton site in Yazoo County, MS, which was vulnerable to runoff. A 10- hectare cotton field drained into a 1-hectare, 2-m deep body of water at the edge of the field. The site was modeled over a 36-year period using actual weather data collected from a NOAA station in Brownsville, MS.

The following inputs were used in the model (details can be found in Parker, 1996):

- 6 single aerial applications of 1.0 lb ai/acre each at 6-day intervals
- 5 percent spray drift from the field to the water body was assumed
- Aerobic soil metabolism half-life of 6 days (3X the single 2 day value from 1 study)
- Hydrolysis half-life at pH 7 of 62 days



- Photolysis half-life of 75 days
- Combined pond half-life of 61.6 days
- Partition coefficient ( $K_d$ ) of 9.7 cm<sup>3</sup>/g

Table 2 summarizes the resulting estimated environmental concentrations (EECs) generated by the PRZM/EXAMS model.

**Table 2: EECs for Aquatic Environments Adjacent to Cotton, PRZM2.3/EXAMS 2.94**

Time Period	36-Year Maximum Event	1-in-10-Year Event
Peak	41.7 ug/l	5.9 ug/l
Maximum 4-day average	15.1 ug/l	2.6 ug/l
Maximum 21-day average	4.0 ug/l	1.2 ug/l
Maximum 60-day average	2.1 ug/l	0.8 ug/l
Maximum 90-day average	1.4 ug/l	0.5 ug/l

Several factors contribute to the uncertainty of the Tier 2 analysis including, the selection of the high-exposure scenarios, the quality of the input data, the ability of the models to represent the real world, and the number of years modeled. Parker (1996) discusses these limitations and uncertainties in detail. While the selection of a scenario which is vulnerable to runoff would tend to provide conservative estimates of the EEC, the uncertainty in the extent to which profenofos is more persistent in acidic soil and water contributes to uncertainty in these estimates. In the mid-south and southeast cotton-growing regions, the soils are predominantly acidic (based on a preliminary search of STATSGO, the USDA Natural Resource Conservation Service State Soil Geographic Data Base, 1995). In these areas, the optimal pH for cotton is acidic, 6.2 to 6.5 (Hodges, 1998). Thus, EECs generated using environmental fate data biased toward more rapid degradation under alkaline conditions may underestimate concentrations in some instances. Fish kill incidents reported in Section 5 occurred in Louisiana and Mississippi, where both the soils and the water bodies in question tend toward acidic pH values. These incidents suggest that profenofos can persist in sufficient concentrations to result in fish kills under certain conditions.

#### **4. Ecological Toxicity Assessment**

The Agency has adequate data needed to assess the hazard of profenofos to nontarget terrestrial organisms. Profenofos is moderately to highly toxic to birds, moderately toxic to small mammals, highly toxic to bees, and highly to very highly toxic to fish and aquatic invertebrates.

Results of the toxicity studies do not represent all species of bird, mammal, or aquatic organisms. Only one or two surrogate species for both freshwater fish and birds are used to represent all freshwater fish (2000+) and bird (680+) species in the United States. For mammals, acute studies are usually limited to a Norway rat or house mouse. Estuarine/marine testing is usually limited to a crustacean, a mollusk, and a fish. Neither reptiles nor amphibians are tested. The assessment of risk or hazard makes the assumption that avian and reptilian toxicity are

similar. The same assumption is used for fish and amphibians.

**a. Toxicity to Nontarget Terrestrial Animals**

**(1) Birds**

Profenofos appears to be more toxic to bobwhite quail than to mallard ducks in available studies. The technical product (89.4% a.i.) was moderately toxic to mallard duck ( $LD_{50}$  of 55.0 mg/kg) in an avian single-dose acute oral toxicity study (MRID 416273-01). In subacute dietary studies, profenofos was highly toxic ( $LC_{50}$  of 57 ppm) to northern bobwhite quail (431073-01) and slightly toxic ( $LC_{50}$  of 1,646 ppm) to mallard ducks (431073-02).

Avian reproduction studies indicate that profenofos (90.6% a.i.) affects egg production. The No Observed Adverse Effect Concentration (NOAEC) was 10 ppm for northern bobwhite quail and 30 ppm for mallard ducks; the Lowest Observed Adverse Effect Concentration (LOAEC) was 30 ppm for quail and 100 mg/kg for mallards (92148004, 92148006).

**(2) Mammals**

For small mammals, toxicity studies reported by HED suggest profenofos is moderately toxic on an acute basis, using the EFED system for categorizing toxicity. An  $LD_{50}$  of 300 mg/kg, based on  $LD_{50}$  values of 298 mg/kg for mice (00104226) and 300 mg/kg for rabbits (00105228), was used for the assessment of hazard and risk to nontarget small mammals.

**(3) Insects**

Profenofos was highly toxic to honey bees in an acute contact study, with an  $LD_{50}$  of 0.095  $\mu$ g a.i./bee (416273-08).

**(4) Terrestrial Field Testing for Birds and Mammals**

A simulated field study in which Curacron was applied in 6 treatments of 1 lb a.i./acre to broadleaf field crops did not detect biological effects attributable to profenofos exposure in bobwhite quail, mallard ducks and rabbits. However, the study was not used in the assessment of dietary risk because the test diets were supplemented with untreated food (92148007).

**b. Toxicity to Aquatic Animals**

Profenofos is highly toxic to freshwater fish and aquatic invertebrates, on both an acute and chronic basis. It is very highly toxic to estuarine and marine organisms on an acute basis.

**(1) Freshwater Fish**

Profenofos was highly toxic to fish in 96-hour acute toxicity studies, with  $LC_{50}$  values of 25  $\mu$ g/L for rainbow trout (92148009) and 41  $\mu$ g/L for bluegill sunfish (92148008). In an early

life-stage study on fathead minnow, profenofos affected survival, with a NOAEC of 2.0 ug/L and a LOAEC of 4.4 ug/L (92148014).

A fish full life-cycle test is required because profenofos can be transported to water via runoff or spray drift, the EEC is equal to or greater than one-tenth of the NOAEC in the fish early life-stage, and studies of other organisms (birds and small mammals) indicate the reproductive physiology of fish may be affected. Water levels measured at the time of reported fish kills (see section 5) ranged from less than 1 ppb to greater than 30 ug/L, with most in the range of 0.6 to 1.5 ug/L. These residue levels exceed 0.1 of the NOAEC in the fish early life stage test. Therefore the fish life cycle study (72-5) for freshwater fish is needed to complete the chronic risk assessment of profenofos. This requirement remains outstanding.

## **(2) Freshwater Invertebrates**

In a freshwater invertebrate toxicity test on *Daphnia magna*, profenofos (90.4% a.i.) was very highly toxic to aquatic invertebrates, with an EC<sub>50</sub> of 0.93 ug/L (41627304). In an early life cycle test conducted on the invertebrate *Daphnia magna*, profenofos affected survival, with a NOAEC of 0.2 ug/L and a LOAEC of 0.26 ug/L (92148013).

## **(3) Estuarine and Marine Animals**

Because profenofos use on cotton may result in exposure to organisms in marine/estuarine environments via runoff, acute toxicity testing on selected estuarine organisms is required. These studies suggest profenofos is highly toxic to estuarine fish (96-hour LC<sub>50</sub> of 7.7 ug/L for pinfish), invertebrates (96-hour LC<sub>50</sub> of 2.4 ug/L for *Mysid*), and shellfish (96-hour shell deposition LC<sub>50</sub> of 263 ug/L for eastern oysters) (92148010, 92148012, and 92148011, respectively).

An early life cycle test conducted on the estuarine invertebrate *Mysid* indicate profenofos affects the number of offspring per hatch, with a NOAEC of 0.22 ug/L and a LOAEC of 0.35 ug/L (Acc 246216). Because profenofos has the potential to move from cotton fields to estuarine waters (by runoff or drift) and it has a high acute toxicity to estuarine fish, EFED requests an estuarine fish early life stage study, preferably on silverside, to complete its assessment of profenofos on estuarine/marine organisms.

## **c. Toxicity to Plants**

Although the assessment of toxicity to terrestrial or aquatic plants is not required for profenofos, studies have been submitted and reviewed for soybeans, lettuce, carrot, tomato, cucumber, cabbage, corn oat, ryegrass and onion. Cucumber was the most sensitive species and the only one that demonstrated a dose response relationship permitting quantification of toxicity. The results indicate that profenofos affects seedling emergence at 0.13 lbs ai/A (41627305). Vegetative vigor was not affected for any species tested.



## 5. Incident Data

The EFED Ecological Incident Information System (EIIS) lists 13 fish kills between 1994 and 1996 (the only years currently listed in the database) attributable to profenofos use in Louisiana (10 incidents) and Mississippi (3 incidents) (ERB 4 Memo to Kylie Rothwell, 5/14/98). Only those incidents in which profenofos was considered to be the probable or highly probable cause of death are included. Thousands of fish (up to 150,000) were killed in each of 7 reported incidents while more than 100 fish died in each of the other events (Table 3). Aquatic habitats included lakes (7 incidents), rivers/creeks (5 incidents), and bayous (1 incident). The kills were generally attributed to runoff of profenofos, although spray drift during application also caused several hundred fish to die in one incident.

In the majority of the incidents, water samples were taken and analyzed for profenofos. While measured concentrations were below the fish  $LC_{50}$ , initial profenofos concentrations were likely higher prior to dilution in the water bodies and dissipation prior to sampling (post incident). Profenofos was detected in fish tissue in the four incidents in which it was analyzed. Profenofos was the only pesticide detected in 3 incidents. Of the remaining 10 incidents, the other pesticides found were considered unlikely contributors in 6 of the fish kills because of toxicity, concentration, or lack of detection in fish tissues. Methyl parathion was believed to be a co-contributor in 2 incidents; atrazine and/or cyanazine were contributing factors in two incidents.

The reliability of the reports is considered excellent because most incidents were investigated by a state agency and analyzed by a state university. In addition to water and sediment samples, fish tissue samples were sometimes analyzed. Records indicate the Curacron 8E product used at the time of these incidents had the label statement prohibiting aerial application "within 300 feet upwind of impounded water" and that label directions and precautions were followed by certified applicators. None of the reported incidents were attributed to misuse.

The incidents indicate that, even when used according to label directions under normal agricultural practices, profenofos can reach fish-bearing waters in sufficient concentrations to result in large fish kills. Fish-kill incidents occurred since the product labels were last revised, indicating that existing label recommendations are inadequate to protect aquatic organisms.

**Table 3: Fish Kill Incidents Involving Profenofos Reported in the EFED Ecological Incident Information System (EIIIS) From 1994 to 1996.**

<i>Case No/ Incident No.</i>	<i>Date</i>	<i>State/ County/ Water Body</i>	<i>Species</i>	<i>Reported Kill</i>	<i>Chemical Analysis (1)</i>	<i>Pesticide(s) Involved [Probability] (2)</i>
94-57 I001849-009	7/25/94	LA Crews Lake, Little Lake Lafourche, Lake Lafourche	shad, bowfin, buffalo, gar, drum, catfish	2,395	w, s, f	Profenofos [HP] Methyl parathion [HP]
96-74 I004668-010 I004875-010	8/8/96	LA/Madison Joe's Bayou	shad	200	w (4 da)	Profenofos: 0.23-1.19 ppb Atrazine: 0.59-0.79 ppb Cyanazine: 2.93-3.66 ppb
96-69 I004668-007 I004875-007	8/6/96	LA/Morehouse Little Lake Lafourche	shad, buffalo, bowfin	6,000	w	Profenofos: 0.75-1.5 ppb [HP] Atrazine: 0.43-2.35 ppb [UL] Cyanazine: 0.20-0.28 ppb [UL] Norflurazone: 0.20-0.77 ppb [UL]
94-54 I001849-007	7/20/94	LA/Richland Big Creek	fish	400	f	Profenofos [HP]
96-64 I004875-004 I004021-001 I004668-004	8/2/96	LA/Richland Boeuf River	shad, buffalo, gar	150,000	w, s, Liver	Profenofos: >0.28 ppm, liver [HP] Azinphos-methyl [UL] several pesticides in water, sediment [UL]
96-66 I004608-005 I004021-003 I004875-005	8/5/96	LA/Richard Big Creek	shad, buffalo, drum, gar	300	w	Profenofos: 1.1 ppb (bluegill LC50 0.019-0.3 ppb) [P -HP] Methyl parathion: 0.2 ppb (bluegill LC50 18 ppb) [P] Atrazine, prometryn, cyanazine, norflurazon, metolachlor [UL]
96-68 I004021-004 I004668-006 I004875-006	8/6/96	LA/Richard Crew Lake	shad, carp, buffalo, bowfin	1200 - "extensive"	w, sm, sl	Profenofos: 0.62-1.08 ppb (w); 78.2- 363 ppb (sm); 100-1181 ppb (sl) [P] Methyl parathion: 0.21ppb (w) [UL] Atrazine, prometryn, cyanazine, norflurazon, metolachlor [UL]

**Table 3: Fish Kill Incidents Involving Profenofos Reported in the EFED Ecological Incident Information System (EIS) From 1994 to 1996.**

Case No/ Incident No.	Date	State/ County/ Water Body	Species	Reported Kill	Chemical Analysis (1)	Pesticide(s) Involved [Probability] (2)
96-69 I004021-005	8/6/96	LA/Richard La Fourche Lake	shad, buffalo	thousands	w	Profenofos: 0.7-1.05 ppb (w) [P] Atrazine, prometryn, cyanazine, norflurazon, metolachlor, clomazone [UL]
96-71 I004668-009 I004875-009	8/6/96	LA/Richard Cedar Lake in Delhi	shad, bowfin, bluegill	500	w	Profenofos: 0.16-0.68 ppb Cyanazine: 0.05-0.11 ppb Low dissolved oxygen
96-70 I004668-008 I004875-008	8/6/96	LA/Richard Boeuf River	shad, buffalo	200	w	Profenofos: 0.08-3.58 ppb [P] Atrazine: 1.18 ppb [UL] Cyanazine: 0.43-0.58 ppb [UL]
I002211-003	7/28/94	MS/Humphreys Four Mile Lake	channel catfish, buffalo, bowfin, carp, gar	600	w	Profenofos: 0.71-0.38 ppb (w) only chemical detected
I002211-001	8/7/94	MS/Rankin Cane Creek	shad, catfish	3,000	w	Profenofos: 0.6-36.4 ppb (w) (8/12); 0.07-0.56 ppb (8/19) [P] Azinphos-methyl [UL]
I002211-002	8/14/94	MS/Warren Eagle Lake	buffalo, shad, bluegill, carp	650		Profenofos: [P] from drift

- (1) Chemical Analysis: w = Water; t = Tissue; s = Sediment; f = Fish; sm= Shad muscle; sl=Shad Liver  
(2) Probability of Causing Incident: HP = Highly Probable; P = Possible; UL = Unlikely



## 6. Ecological Risk Assessment

To evaluate the potential risk to nontarget organisms from the use of profenofos products, risk quotients (RQs) are calculated from the ratio of estimated environmental concentrations (EECs) to ecotoxicity values. RQs are then compared to levels of concern (LOCs) used by OPP to indicate potential risk to nontarget organisms and the need to consider regulatory action.

### a. Nontarget Terrestrial Animals

The assessment of risk to nontarget terrestrial animals from exposure to profenofos is based on a single application of Curacron 8E applied at a rate of 1 lb active ingredient per acre. The estimated environmental concentration (EEC) values are derived from the Kenega nomograph, as modified by Fletcher et al. (1994), based on a large set of actual field residue data. The upper limit values from the nomograph represent the 95th percentile of residue values from actual field measurements (Hoerger and Kenega, 1972). The Fletcher et al. (1994) modifications to the Kenega nomograph are based on measured field residues from 249 published research papers, including information on 118 species of plants, 121 pesticides, and 17 chemical classes. These modifications represent the 95th percentile of the expanded data set. Risk quotients (Table 4) are based on the most sensitive  $LC_{50}$  and NOAEC for birds (in this instance, bobwhite quail) and  $LD_{50}$  for mammals.

**Table 4: Risk Quotients (RQs) and Level of Concern (LOC) Exceedances for Non-target Terrestrial Animals Exposed to a Single Profenofos Application of 1 lb ai/acre.**

Non-Target Organism Toxicity Endpoints	Representative Food Items (EEC, mg/kg) <sup>1</sup>	Acute RQ <sup>2</sup>	Chronic RQ <sup>3</sup>
Birds	Short range grasses (240)	4.21 ***	24.0 *
$LC_{50}$ = 57 ppm (bobwhite quail, acute)	Fruit/vegetable leaves (125)	2.19 ***	12.5 *
	Forage legumes/insects (58)	1.02 ***	5.8 *
NOEC = 10 ppm (bobwhite quail, chronic)	Seeds/fruit (12)	0.21 **	1.2 *
Mammals (15-35g wt)	Short range grasses (240)	0.53-0.76 ***	
$LD_{50}$ = 300 mg/kg (mouse, rabbit)	Forage/small insects (58)	0.13-0.18 *	
	Large insects (15)	0.03-0.05	
Mammals (1000g wt)	Short range grasses (240)	0.12 *	
$LD_{50}$ = 300 mg/kg (mouse, rabbit)	Forage/small insects (58)	0.03	
	Large insects (15)	0.01	

<sup>1</sup> EECs are based on Hoerger and Kenega (1972), modified by Fletcher et al (1994).

<sup>2</sup> Acute RQ =  $EEC/LC_{50}$  for birds and  $EEC/(LD_{50}/BWC)$ , where BWC is the mass food consumed per day as a fraction of body mass (0.95 for 10-g mammals, 0.66 for 35-g mammals, and 0.15 for 1000-g mammals).

<sup>3</sup> Chronic RQ =  $EEC/NOAEC$  for birds

**Table 4: Risk Quotients (RQs) and Level of Concern (LOC) Exceedances for Non-target Terrestrial Animals Exposed to a Single Profenofos Application of 1 lb ai/acre.**

Non-Target Organism Toxicity Endpoints	Representative Food Items (EEC, mg/kg) <sup>1</sup>	Acute RQ <sup>2</sup>	Chronic RQ <sup>3</sup>
<b>Level of Concern (LOC) Criteria</b>			
High acute risk		≥ 0.5 ***	
Acute risk may be mitigated through restricted use		≥ 0.2 **	
Endangered species may be affected acutely		≥ 0.1 *	
Chronic risk; endangered species may be affected chronically			≥ 1 *

Exposure from a single application of 1 lb profenofos ai/acre exceeded acute and chronic levels of concern for birds on all modeled food sources. Table 4 indicates high acute risk for birds may occur from exposure to a single application at maximum label rates on all but seed/fruit food sources. Small mammals (10-35 g size) feeding primarily on a short-range grass type of food are also at high acute risk. Endangered species levels of concern are triggered for nontarget birds and small mammals from a single application of profenofos.

Profenofos can be applied up to 6 times at a rate of 1 lb ai/acre at 6-day intervals. When terrestrial EECs are modeled for 6 applications, accounting for first-order degradation (for model purposes, a half-life of 6 days was used, based on the aerobic soil metabolism rate used for PRZM EXAMS modeling), the resulting peak EECs are roughly two-fold greater than the peak EECs from a single application. Consequently, RQs based on 6 applications would be roughly two-fold greater. It is important to note that RQs are a risk index and not absolute risk values. Therefore, it is improper to conclude that the risk from 6 applications of profenofos is twice that from a single application. It does suggest that the certainty of risk is greater for 6 applications.

#### **b. Nontarget Aquatic Animals**

Profenofos displays high toxicity to most aquatic organisms tested to date. The pesticide may reach aquatic habitats via spray drift during application and runoff after application. The assessment of risk to nontarget aquatic animals from exposure to profenofos is based on runoff and spray drift from 6 applications of Curacron 8E applied at a rate of 1 lb a.i./acre at 6-day intervals. The estimated environmental concentration (EEC) values are derived from Tier 2 modeling using PRZM 2.3 and EXAMS 2.75 (see section 3.b.). Acute RQs compare the 1-in-10-year peak EECs with the most sensitive LC<sub>50</sub>/EC<sub>50</sub> from representative species; chronic RQs compare the 1-in-10 year 21-day average EECs with the most sensitive NOAEC for representative species (Table 5).

**Table 5: Risk Quotients (RQs) and Level of Concern (LOC) Exceedances for Non-Target Aquatic Animals Exposed to Profenofos Applied to Cotton at 1 lb ai/acre 6 times at 6-day Intervals.**

Non-target Organism / Toxicity Endpoints	Acute RQ <sup>1</sup>	Chronic RQ <sup>2</sup>
Freshwater fish LC <sub>50</sub> = 25 ug/L (rainbow trout) NOAEC = 2.0 ug/L (fathead minnow)	0.24 **	0.58
Freshwater invertebrates EC <sub>50</sub> = 0.9 ug/L ( <i>Daphnia magna</i> ) NOAEC = 0.2 ug/L ( <i>Daphnia magna</i> )	6.4 ***	5.8 *
Estuarine/marine fish LC <sub>50</sub> = 7.7 ug/L (Pinfish)	0.77 ***	
Estuarine/marine invertebrates LC <sub>50</sub> = 2.4 ug/L (Mysid) NOAEC = 0.2 ug/L (Mysid)	2.5 ***	5.2 *
Estuarine/marine shellfish LC <sub>50</sub> = 263 ug/L	0.02	

<sup>1</sup> Acute RQ = Peak EEC / LC<sub>50</sub> or EC<sub>50</sub>, where the 1-in-10 year peak EEC is 5.9 ug/L.

<sup>2</sup> Chronic RQ = 21-da EEC / NOAEC, where the 1-in-10 year 21-day average EEC is 1.2 ug/L.

#### Level of Concern (LOC) Criteria

High acute risk	≥ 0.5 ***	
Acute risk may be mitigated through restricted use	≥ 0.1 **	
Endangered species may be affected acutely	≥ 0.05 *	
Chronic risk, endangered species may be affected chronically		≥ 1 *

Acute risk LOCs for both freshwater and marine/estuarine fish and invertebrates are exceeded for profenofos use on cotton at maximum label rates. Chronic risk LOCs are exceeded for aquatic invertebrates, but not for fish. The EECs used for the RQs are derived from data which reflect the fate of profenofos under alkaline to neutral conditions. As noted earlier, this data is biased toward rapid degradation due to hydrolysis. Because profenofos is expected to persist longer under acidic conditions, the EECs will potentially be greater under these conditions. Thus, the EECs generated may reflect a high-end (1-in-10-year) concentration at a high-runoff site at which the soil and water are neutral to alkaline.

No chronic toxicity are available for estuarine/marine fish. A comparison of risks identified for freshwater fish and estuarine invertebrates suggests estuarine fish may be at high chronic risk. Presumption of high acute and chronic risk to endangered and non-endangered species is indicated for this chemical.



### c. Nontarget Plants

Non-target terrestrial and semi-aquatic (plants that inhabit low-lying wet areas which may or may not be dry in certain times of the year) plants may be exposed to profenofos from runoff or drift. Exposure by runoff may occur via sheet flow (modeled as one acre running into an adjacent acre) or as channelized flow (such as drainage ditches, modeled as 10 acres running into one acre). For screening purposes, EFED assumes 5% of the applied pesticide moves from the field via runoff (this is within the range of 0-10% runoff estimated by GENECC) and 5% of the pesticide applied aerially will drift onto an adjacent field (the same assumption used for aquatic exposure assessments). Table 6 compares the modeled EECs for each route of exposure to the EC<sub>25</sub> value for the most sensitive species in the seedling emergence study (0.13 lb ai/acre for cucumber seedling emergence). The assessment is made on a single application of 1 lb ai/acre.

**Table 6: Risk Quotients for Nontarget Plants Exposed By Runoff or Drift to Profenofos Applied to Cotton at 1 lb ai/acre.**

Source of Exposure	EEC (lbs a.i./A)	Risk Quotient
sheet runoff	0.05	0.38
channel runoff	0.50	3.85 *
drift + runoff	0.10	0.77
spray drift	0.05	0.38
Level of Concern		≥ 1 *

The LOC is not exceeded for terrestrial and semi-aquatic plant species, except for channel runoff at a maximum application rate of 1.0 lb ai/A of profenofos.

### d. Exposure and Risk to Endangered Species

Endangered species levels of concern are exceeded for birds and small mammals from the use of a single application of Curacron 8E at a rate of 1 lb profenofos per acre on cotton. Endangered species levels of concern are also exceeded for freshwater fish and invertebrates and estuarine/marine fish and invertebrates when profenofos is applied at maximum label rates.

The Agency has developed a program (the "Endangered Species Protection Program") to identify pesticides whose use may cause adverse impacts on endangered and threatened species, and to implement mitigation measures that will eliminate the adverse impacts. At present, the program is being implemented on an interim basis as described in a Federal Register notice (54 FR 27984-28008, July 3, 1989), and is providing information to pesticide users to help them protect these species on a voluntary basis. As currently planned, the final program will call for label modifications referring to required limitations on pesticide uses, typically as depicted in county-specific bulletins or by other site-specific mechanisms as specified by state partners. A final program, which may be altered from the interim program, will be described in a future Federal

Register notice. The Agency is not imposing label modifications at this time through the RED. Rather, any requirements for product use modifications will occur in the future under the Endangered Species Protection Program.

## **7. Risk Characterization**

Because the environmental fate data were conducted in neutral to alkaline soil and water media which favor more rapid degradation than would likely occur under acidic conditions, the environmental fate assessment may be more reflective of profenofos use on cotton in the southwest and western U.S. than in the southeast and mid-south. Even so, risk quotients exceeded most levels of concern for terrestrial and aquatic nontarget organisms from profenofos use. Fish kill incidents in Louisiana and Mississippi indicate that existing label precautions are not adequate to protect aquatic organisms in the mid-south to southeastern U.S.

### **a. Certainties and Uncertainties in the Environmental Fate Assessment**

The environmental risk assessment for profenofos is based on fate data generated primarily under neutral to alkaline conditions which tend to favor more rapid degradation by hydrolysis. Such data suggest that profenofos is not very persistent, with half-lives of several days in soil. However, little data exists on the persistence of profenofos in acidic soils, where hydrolysis proceeds slowly (a half-life of 108 days at pH 5 vs. 7 hours at pH 9). While it can be inferred that profenofos dissipates at a *slower rate in acidic soils*, the degree to which profenofos would be more persistent cannot be quantified based on existing data.

While the guideline requirements have been met, our understanding of the fate of profenofos is confined primarily to neutral to alkaline environments (which are more prevalent in the Southwest and West cotton-growing regions). The fate of profenofos under acidic conditions (common to the Southeast and Mid South regions) is not well understood. Thus, this risk assessment may be appropriate for profenofos use in the southwest and west, but may underestimate risk in the major use areas of the southeast and mid-south cotton regions.

Because of the extent to which it adsorbs to soil, profenofos is not expected to leach to ground water under normal use. Profenofos may reach surface waters through spray drift or runoff. The amount of profenofos reaching surface water will depend on factors such as the rate of application, the timing and intensity of the rainfall after application, the proximity of the water body from the treated field, and the pH condition of the soil and water (with profenofos likely dissipating rapidly in alkaline conditions but persisting for an unspecified time in acidic soils and water bodies). While profenofos has not been included in available water monitoring studies, reported fish kill incidents attributed to profenofos have detected the pesticide in water and fish tissue samples. Therefore, under certain conditions, profenofos can reach water at concentrations sufficient to result in fish mortality.

The available environmental fate database contains substantial gaps related to profenofos degradates. One of the major degradates, 4-bromo-2-chlorophenol (BCP), is persistent in the environment while the fate of another degrade, O-ethyl-S-propyl phosphorothioate, is not well

known. The Agency thinks it is likely that both degradates have fate and toxicity properties significantly different from those of parent profenofos. Additional metabolites apparently result from reactions involving BCP and O-ethyl-S-propyl phosphorothioate.

#### **b. Certainties and Uncertainties in the Ecological Risk Assessment**

Profenofos is highly to moderately toxic to birds on an acute oral and subacute dietary basis and highly toxic on a chronic basis, affecting reproduction. It is also moderately toxic to small mammals on an acute oral basis and highly toxic to insects (honeybees). Among aquatic species, profenofos is highly toxic to freshwater fish and invertebrate and very highly toxic to estuarine and marine organisms on an acute basis. Because limited information is available to assess the chronic effects of profenofos on fish, and because the EEC exceeds the early life stage NOEC by over seven fold (suggesting a potential for long-term effects), an estuarine fish early life stage study is needed to further define a fish chronic level of concern.

Risk quotients triggered levels of concern for nontarget terrestrial species from the use of a single application rate of 1 lb of profenofos per acre. Multiple applications of profenofos (label rates allow for up to 6 applications of 1 lb a.i./acre at 6-day intervals) will only increase the concentration of profenofos in the terrestrial environment, leading to higher risk quotients and even greater exceedances of the levels of concern.

Risk quotients based on the maximum of 6 applications of profenofos at 1 lb ai/acre at 6-day intervals also exceed levels of concern for freshwater and marine fish and invertebrates. These exceedances indicate high acute risk to fish species and high acute and chronic risks to aquatic invertebrates.

The risk quotients for aquatic organisms may be more reflective of risks posed from profenofos use on neutral to alkaline soils and in neutral to alkaline water bodies (both of which are more likely to occur where profenofos is used in the southwest and west than in the southeast and mid-south cotton regions). The estimated environmental concentrations (EECs) used in the assessment more appropriately reflect profenofos levels under alkaline rather than acidic conditions. Although insufficient data exists to estimate EECs under such conditions, profenofos is expected to persist longer in acidic soils and water. This results in a greater potential for risk because (1) more profenofos will be available to runoff for longer periods of time in acidic soils, and (2) the profenofos that reaches aquatic habitats will not degrade as rapidly in acidic waters. Both acute (peak) and chronic (longer-term average) concentrations will be greater, resulting in greater risk to nontarget organisms under acidic environments than is predicted from the available fate data.

Fish kill incidents found in the EFED Ecological Incident Information System (EIIIS) provide reliable evidence (actual water and/or fish tissue analyses) that profenofos was the probable to highly probable cause of hundreds to thousands of fish (up to 150,000) in 13 separate incidents. These kills occurred in lakes, rivers/creeks, and bayous. Records indicate the profenofos product used at the time had the label statement prohibiting aerial application "within 300 feet upwind of impounded water" and that label directions and precautions were followed by



certified applicators. None of the reported incidents were attributed to misuse. The incident reports do not provide any indication whether maximum or typical application rates were used. The incidents provide further evidence that risk to aquatic organisms is likely to be even greater than predicted using EECs derived from biased fate data. They also suggest large fish kills can result even when using existing label precautions.

Ten of the incidents occurred in 7 waterbodies in 3 adjacent counties (Madison, Morehouse, and Richland) in northeast Louisiana; the remaining incidents occurred in 3 west central counties in Mississippi. The soils and water bodies in these areas tend to be acidic. Without further investigation, it is uncertain whether these incidents are clustered because of other site-specific factors, high profenofos use, or more thorough reporting in those areas. Because later incidents have not yet been entered into the incident database, EFED is unable to determine whether the trend in incidents is increasing, decreasing, or remaining the same.

**c. Certainties and Uncertainties in the Water Resource Assessment for Human Health Exposure**

Concentrations of profenofos in surface water sources of drinking water better reflect neutral to alkaline sources of water. Estimated profenofos concentrations under acidic conditions are likely to be greater than those estimated here. However, as already discussed, the data is not sufficient to provide estimates under the conditions that are likely to occur in the southeastern and midsouth cotton-growing regions where profenofos is used. Profenofos is likely to be more persistent under the acidic soil and water conditions that exist in this region than is predicted by existing fate data. However, no estimates can be made for this region and monitoring data does not exist to make an assessment.

# EFED ENVIRONMENTAL FATE ASSESSMENT FOR PROFENOFOS

Original Chapter Draft 6/14/96

Minor Revisions 10/25/98

## C. ENVIRONMENTAL ASSESSMENT

### 1. Ecological Toxicity Data

The Agency has adequate data needed to assess the hazard of profenofos to nontarget terrestrial organisms.

#### a. Toxicity to Terrestrial Animals

##### (1) Birds, Acute and Subacute

In order to establish the toxicity of profenofos to birds, the following tests are required using the technical grade material: one avian single-dose oral ( $LD_{50}$ ) study on one species (preferably mallard or bobwhite quail); two subacute dietary studies ( $LC_{50}$ ) on one species of waterfowl (preferably the mallard duck) and one species of upland game bird (preferably bobwhite quail).

Avian Acute Oral Toxicity Findings					
Species	% A.I.	$LD_{50}$ mg/kg	MRID No. Author/Year	Toxicity Category	Study Classification
Mallard Duck	89.4	55.0	41627301 Pedersen, 1990	Moderately Toxic	Core

Avian Subacute Dietary Toxicity Findings					
Species	% A.I.	$LC_{50}$ ppm	MRID No. Author/Year	Toxicity Category	Study Classification
Northern Bobwhite Quail	89.4	57	43107301 Brewer, and Taliaferro, 1994	Highly Toxic	Core
Mallard Duck	89.4	1646	43107302 Brewer and Taliaferro, 1994	Slightly Toxic	Core

These results indicate that profenofos is highly to moderately toxic to avian species on an acute oral and subacute dietary basis. The guideline requirements are fulfilled (MRID 43107301, 43107302)

##### (2) Birds, Chronic

Avian reproduction studies are required when birds may be exposed repeatedly or continuously through persistence, bioaccumulation, or multiple applications, or if mammalian

reproduction tests indicate reproductive hazard. Due to multiple applications of profenofos, avian reproduction studies are required.

Avian Reproduction Findings						
Species	% A.I.	NOEC ppm	LOEC ppm	Endpoints affected	MRID No. Author/Year	Study Classification
Northern Bobwhite	90.6	10	30	egg production	92148004 Fink, 1978	Core
Mallard Duck	90.6	30	100	egg production	92148006 Fink, 1978	Core

The avian reproductive studies indicate that profenofos is highly toxic to birds and significantly affects reproduction. The guideline requirements are fulfilled (MRID 92148004, 92148006).

### (3) Mammals

Wild mammal testing is required on a case-by-case basis, depending on the results of the lower tier studies such as acute and subacute testing, intended use pattern, and pertinent environmental fate characteristics. In most cases, however, findings for small mammals are based on an acute oral LD<sub>50</sub> determined by the Agency's Office of Pesticide Programs, Health Effects Division.

Based on the review of mammalian toxicity measurements, the LD<sub>50</sub> value used to assess hazard and risk to nontarget small mammals is 300 mg/kg (mouse LD<sub>50</sub> of 298 mg/kg [00105226]; rabbit LD<sub>50</sub> of 300 mg/kg [00105228]). Profenofos is characterized as moderately toxic according to the Agency classification for hazard assessment for wild small mammals.

### (4) Insects

A honey bee acute contact LD<sub>50</sub> study is required if the proposed use will result in honey bee exposure.

Nontarget Insect Acute Contact Toxicity Findings					
Species	% AI	LD <sub>50</sub> µg a.i./bee	MRID No. Author/Year	Toxicity Category	Study Classification
Honey Bee	90.4	0.0953	41627308 Winter, 1990	Highly toxic	Core

There is sufficient information to characterize profenofos as highly toxic to bees. The guideline requirement is fulfilled (MRID 41627308).



## (5) Terrestrial Field Testing for Birds and Mammals

A simulated field study with Curacron was conducted to assess hazard to bobwhite quail, mallard ducks and rabbits (Fink, 1978). Curacron was applied in 6 treatments of 1 lb per acre to broadleaf field crops. During the period of the study, biological effects were not observed that could be attributed to profenofos exposure. The study was not used in assessment of dietary risk because diets were supplemented with untreated food (MRID 92148007).

### b. Toxicity to Aquatic Animals

#### (1) Freshwater Fish

In order to establish the toxicity of a pesticide to freshwater fish, the minimum data required on the technical grade of the active ingredient are two freshwater fish toxicity studies. One study should use a coldwater species (preferably the rainbow trout), and the other should use a warmwater species (preferably the bluegill sunfish).

Freshwater Fish Acute Toxicity Findings					
Species	% A.I.	LC <sub>50</sub> ppb a.i.	MRID No.	Toxicity Category	Study Classification
Rainbow trout	90.6	25	92148009 Buccafusco, 1979	Highly Toxic	Core
Bluegill sunfish	90.6	41	92148008 Buccafusco, 1978	Highly Toxic	Core

The results of the 96-hour acute toxicity studies indicate that profenofos is highly toxic to fish. The guideline requirements are fulfilled (MRID 92148008, 92148009). Data from fish early life-stage tests are required if the product is applied directly to water or expected to be transported to water from the intended use site and if the pesticide is intended for use such that its presence in water is likely to be continuous or recurrent regardless of toxicity; or if any acute LC<sub>50</sub> or EC<sub>50</sub> is less than 1 mg/L; or if the EEC in water is equal to or greater than 0.01 of any acute EC<sub>50</sub> or LC<sub>50</sub> value; or if the actual or estimated environmental concentration in water resulting from use is less than 0.01 of any acute EC<sub>50</sub> or LC<sub>50</sub> value and any of the following conditions exist: studies of other organisms indicate the reproductive physiology of fish and/or invertebrates may be affected; or physicochemical properties indicate cumulative effects; or the pesticide is persistent in water (e.g. half-life greater than 4 days). Each of these criteria is met for profenofos. A study has been submitted and found to be acceptable. Results are shown in the following table.

Fish Early Life-Stage Toxicity Findings							
Species	% A.I.	NOEC (ug/L)	LOEC (ug/L)	MATC (ug/L)	MRID No. Author/Year	Endpoints Affected	Study Classification
Fathead minnow	90.6	2.0	4.4	3.0	92148014 Hoberg & Dean 1979	Survival	Core

These results indicate that profenofos is very highly toxic on a chronic basis. The guideline requirement is fulfilled (MRID 92148014).

The fish life-cycle test is required when an end-use product is intended to be applied directly to water or is expected to transport to water from the intended use site, when any of the following conditions apply: the EEC is equal to or greater than one-tenth of the NOEC in the fish early life-stage or invertebrate life-cycle test; or if studies of other organisms indicate the reproductive physiology of fish may be affected. Each of these criteria is met for profenofos but no fish life-cycle test has been submitted.

## (2) Freshwater Invertebrates

The minimum testing required to assess the hazard of a pesticide to freshwater invertebrates is a freshwater aquatic invertebrate toxicity test, preferably using the first instar *Daphnia magna* or early instar amphipods, stoneflies, mayflies, or midges.

Freshwater Invertebrate Toxicity Findings				
Species	% A.I.	EC <sub>50</sub> (ppb)	MRID NO. Author/Year	Study Classification
<i>Daphnia magna</i>	90.4	0.93	41627304 Bellantoni, 1990	Core

There is sufficient information to characterize profenofos as highly toxic to aquatic invertebrates. The guideline requirement is fulfilled (MRID 41627304).

The criteria for requiring an invertebrate life cycle test are similar to those for requiring a fish early life stage test. These criteria are met for profenofos. An invertebrate life cycle test has been submitted for profenofos and found to be acceptable. The results are summarized in the following table.

Aquatic Invertebrate Life-Cycle Toxicity Findings							
Species	% A.I.	NOEC (ug/L)	LOEC (ug/L)	MATC (ug/L)	MRID No. Author	Endpoints Affected	Study Classification
<i>Daphnia magna</i>	90.6	0.2	0.33	0.26	92148013 Surprenant 1980	Survival	Core

The results indicate that profenofos is highly toxic to invertebrate early life stages. The guideline requirement is fulfilled (MRID 92148013).

### (3) Estuarine and Marine Animals

Acute toxicity testing with estuarine and marine organisms is required when an end-use product is intended for direct application to the marine/estuarine environment or is expected to reach this environment in significant concentrations. The terrestrial non-food use of profenofos may result in exposure to the estuarine environment.

The requirements under this category include a 96-hour  $LC_{50}$  for an estuarine fish, a 96-hour  $LC_{50}$  for shrimp, and either a 48-hour embryo-larvae study or a 96-hour shell deposition study with oysters.

Estuarine/Marine Acute Toxicity Findings					
Species	% A.I.	$LC_{50}/EC_{50}$ (ppb)	MRID No. Author/Year	Toxicity Category	Study Classification
Eastern oyster shell deposition	90.6	263	92148011 Heitmuller, 1980	Highly Toxic	Core
Pink Shrimp	90.6	4.6	92148012 Heitmuller, 1980	Highly Toxic	Core
Pinfish	90.6	7.7	92148010 Heitmuller, 1980	Highly Toxic	Core
Mysid	90.6	2.4	Acc. 24621	Highly Toxic	Core

There is sufficient information to characterize profenofos as very highly toxic to estuarine/marine organisms. The guideline requirement is fulfilled (MRID 92148010, 92148011, 92148012).

Chronic estuarine/marine organism testing is required for the same reasons as cited for freshwater organisms. The required tests are a fish (preferably silverside) early life stage and a mysid life cycle. Life cycle tests conducted on *Mysid* indicate profenofos is highly toxic to early life stages of estuarine invertebrates, with a NOEC of 0.22 ug/L and a LOEC of 0.35 ug/L. The affected endpoint was the number of offspring per hatch (Acc 246216). There are no data available for chronic toxicity of profenofos to estuarine and marine fish.

#### c. Toxicity to Plants

Tests of toxicity to terrestrial or aquatic plants are not required for profenofos. Testing may be required on a case-by-case basis if there are indications that a pesticide may be phytotoxic. Studies have been submitted and reviewed for soybeans, lettuce, carrot, tomato, cucumber, cabbage, corn oat, ryegrass and onion. Cucumber was apparently the most sensitive species, and



the only species that demonstrated a dose response relationship permitting quantification of toxicity. Toxicity data on the technical/TEP material for cucumber is displayed below:

Nontarget Terrestrial Plant Toxicity Findings			
Species	% A.I.	Seedling emergence EC <sub>25</sub> lbs ai/A	Vegetative vigor EC <sub>25</sub>
Cucumber (seedling emergence)	90.4	0.13	[Not affected]

The results indicate that profenofos affects seedling emergence at 0.13 lbs ai/A. Vegetative vigor was not affected for any species tested. The guideline requirements are fulfilled (MRID 41627305).

## 2. Environmental Fate

### a. Environmental Fate Assessment

Available acceptable and supplemental environmental fate studies show that profenofos is not persistent, particularly in neutral and alkaline soils. Hydrolysis is the major route of dissipation. Photolysis is not a major pathway while biotic processes -- aerobic and anaerobic metabolism -- become important after the initial hydrolysis. Profenofos dissipates in neutral to alkaline soils with a half-life of several days. Little data exists for acid soils, although it can be inferred that profenofos dissipates at a slower rate. One of the major degradates, 4-bromo-2-chlorophenol, is persistent in the environment while the fate of another degrade, O-ethyl-S-propyl phosphorothioate, is not well known. Profenofos is not highly mobile and, although the field dissipation studies did not allow for an assessment of the leaching potential, is not expected to leach to ground water under normal use. The mobility and leaching potential of the degradates is unknown. The chemical may reach surface waters through spray drift or runoff.

**Persistence.** Hydrolysis is the primary route of dissipation. Profenofos hydrolyzes in neutral and alkaline solutions, with half-lives of 104-108 days at pH 5, 24-62 days at pH 7, and 7-8 hours at pH 9 (416273-09, 419390-01). The major degradates are 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate. Photolysis is not a major pathway in the degradation of profenofos in water, soil, or air (418799-01, 419390-02, 416273-10, 420304-01). The UV spectrum of profenofos overlaps slightly with the visible spectrum around 290-295 nm (420304-01). However, the overlap is minimal and extensive photolysis is not expected.

Profenofos metabolizes rapidly in aerobic and anaerobic conditions. In an alkaline (pH 7.8) soil, profenofos degraded with a half-life of 2 days under aerobic conditions (423343-02) and 3 days under anaerobic conditions (423343-03). The rate of metabolism was influenced by hydrolysis and aerobic and anaerobic metabolism in neutral and acid soils is likely to be slower. The major degradates are 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate. 4-Bromo-2-chlorophenol concentrations in both soil metabolism studies did not decline until 60 to

120 days after application. Additional metabolites form slowly. In anaerobic aquatic conditions, profenofos degraded with a half-life of 3 days in an acid (pH 5.1) sediment flooded with neutral (pH 7.3) water (422181-01). The major degradates are 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate. Additional metabolites -- 4-bromo-2-chlorophenyl ethyl ether (BCPEE), cyclohexadienyl sulfate, and phenol complex increased in concentration after 180 days.

**Mobility.** Profenofos is mobile to somewhat mobile, with Freundlich  $K_{ads}$  values of 4.60 for sand, 7.46 for sandy loam, 16.96 for loam, and 89.28 for clay soil samples. Desorption values ranged from 6.24 (sand) to 128.1 (clay). Adsorption generally increased with increasing soil organic matter content, clay content, and CEC.  $K_{oc}$  values ranged from 869 to 3162 (416273-11). Additional data is needed on the mobility of the major degradates/metabolites of profenofos, in particular 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate.

Laboratory studies show that some profenofos may be released to the atmosphere through volatilization. Over 30 days, volatility averaged  $6.13 \times 10^{-3}$  ug/cm<sup>2</sup>/hr and the vapor pressure averaged  $3.46 \times 10^{-6}$  mm Hg (419050-01). 4-bromo-2-chlorophenol was the major volatile residue.

**Field Dissipation.** The submitted field studies do not provide adequate information for more than a rough qualitative assessment of profenofos dissipation in the field. Dissipation rate evaluations are complicated because profenofos degrades during storage, probably due to hydrolysis. Both profenofos and its degradate 4-bromo-2-chlorophenol dissipate from the surface 6 inches of cotton and bareground plots in California and Texas with a half-life of several days (428513-01, 429009-01). Neither profenofos or 4-bromo-2-chlorophenol were detected below 12 inches in either study. However, because the studies were conducted in soil and weather conditions that resulted in a moisture deficit, with little or no excess water available for downward movement through the soil, the leaching potential could not be reliably assessed in the studies.

**Accumulation.** The bioaccumulation potential of profenofos is relatively low in fish. Profenofos residues accumulate preferentially in the viscera of bluegill sunfish, but the residues depurate rapidly after exposure is terminated.

In the studies submitted to the Agency, profenofos residues accumulated preferentially in the viscera of bluegill sunfish. The maximum bioconcentration factors were 29x in the bodies, 45x in the heads, and 682x in the viscera (000859-52, 921480-59). Profenofos residues depurated rapidly, with concentrations decreasing to 1 ppb in the bodies, 2 ppb in the heads, and 7 ppb in the viscera after 8 days. The dominant chemical identified in the viscera was 4-bromo-2-chlorophenol (33-48% of the recovered radioactivity).

**Information Needs.** While the existing data base is essentially complete for profenofos, data gaps exist for the major degradates. Information is needed on the mobility of 4-bromo-2-chlorophenol and on the persistence, mobility and dissipation pathways of O-ethyl-S-propyl phosphorothioate. Because of the missing information on the degradates, the *overall*

environmental fate assessment must be considered incomplete.

**b. Detailed Information on Supporting Environmental Fate Studies**

**(1) Degradation**

**161-1 Hydrolysis**

In a study submitted, profenofos degraded in sterile aqueous buffered solutions with half-lives of 108 days at pH 5, 62 days at pH 7, and 7.2 hours at pH 9. The solutions were incubated in the dark at 25°C. At pH 5, profenofos declined from 95% of the applied radioactivity to 77% after 30 days; 4-bromo-2-chlorophenol increased to 5% after 30 days. At pH 7, profenofos declined from 96% to 67% after 30 days; 4-bromo-2-chlorophenol increased to 23% after 30 days. At pH 9, profenofos declined to 10% of the applied after 24 hours; 4-bromo-2-chlorophenol increased rapidly to a maximum of 80% after 24 hours (MRID 416273-09).

In a second study, profenofos degraded in sterile buffered aqueous solutions with calculated half-lives of 104 days at pH 5, 24 days at pH 7, and 8 hours at pH 9. At pH 5, profenofos declined from 98% of the recovered radioactivity at 0 days to 79% after 30 days. O-(2-chloro-4-bromophenyl)-S-n-propyl thiophosphate increased to a maximum of 8% after 30 days. At pH 7, profenofos declined from 97% to 55% after 21 days and 40% after 30 days. 4-bromo-2-chlorophenol increased from 1% to 40% after 21 days and 52% after 30 days. At pH 9, profenofos decreased from 97% to 44% after 8 hours and 13% after 24 hours. 4-bromo-2-chlorophenol continued to increase, from 10% after 1 hour to 54% after 8 hours and 84% after 24 hours (MRID 419390-01).

While not tracked in either study, O-ethyl-S-propyl phosphorothioate is expected to form in equimolar proportions with 4-bromo-2-chlorophenol. The proposed pathway suggests that this degradate will further hydrolyze into O-ethyl phosphate and 1-propanethiol, although no data is provided in support of this.

**161-2 Photodegradation in Water**

In a study submitted, profenofos applied at 10 ppm to a pH 5 buffer solution and irradiated continuously with a xenon arc lamp at 25°C for 360 hours, degraded with a half-life of 51 days (adjusted to 12-hour photoperiods), compared to 60 days for dark controls. The rates of degradation between irradiated and dark control solutions were not statistically different. Profenofos declined from 92% of the recovered radioactivity to 60% in the irradiated samples, and from 92% to 63% in the dark controls. O-(2-chloro-4-bromophenyl)-S-n-propyl thiophosphate, the degradate found in the pH 5 hydrolysis study, was detected in both the irradiated and dark control solutions at 19-20% of the recovered radioactivity after 360 hours (MRID 418799-01).



In a second study, profenofos applied at 11.6 ppm to a pH 5 buffer solution and irradiated on 12-hour light:dark cycles with a xenon arc lamp at 25°C for 30 days, degraded with a half-life of 75 days (adjusted to 12-hour photoperiods), compared to 104 days in the dark control. Profenofos declined from 98% of the recovered radioactivity to 89% at 14 days and 74% after 30 days. In the dark controls, profenofos declined to 79% after 30 days. Two hydrolysis degradates -- O-(2-chloro-4-bromophenyl)-S-n-propyl thiophosphate and 4-bromo-2-chlorophenol -- comprised less than 9% of the recovered after 30 days in both the irradiated and dark control solutions (MRID 419390-02).

### **161-3 Photodegradation on Soil**

In a marginally acceptable study, profenofos degraded more rapidly in the dark control samples (half-life of 7 days) than on a pH 7.5 sandy loam soil irradiated on 12 hour light:dark cycles with a xenon arc lamp (half-life of 28 days). Problems with the experimental design or analytical procedures may have led to these atypical results. However, the results do indicate photolysis on soil is not an important route of dissipation and are in line with the results of aqueous and air photodegradation studies (MRID 416273-10).

### **161-4 Photodegradation in Air**

While this supplemental study was not designed to adequately distinguish between photolysis in the air and in the condensate, EPA recognizes the difficulties inherent in this procedure (EPA, 1993). Since no photolysis was evident in the combined samples, an additional study is not required. The UV spectrum of profenofos overlaps slightly with the visible spectrum around 290-295 nm. The overlap is minimal and extensive photolysis would not be expected (MRID 420304-01).

## **(2) Metabolism**

### **162-1 Aerobic Soil Metabolism**

In a study submitted, profenofos applied at 10.9 ppm to a pH 7.8 sandy loam soil, degraded with a half-life of 1.9 days. Profenofos concentrations declined to 56% of the applied radioactivity at 2 days, 36% at 3 days, and 9% at 9 days. The major metabolites were: (1) 4-bromo-2-chlorophenol, increasing from 11% at 1 day to a maximum concentration of 79% at 120 days before declining to 32% at 270-360 days; (2) BCPEE [4-bromo-2-chlorophenol ethyl ether], increasing from 2% at 5 days to 13% at 90 days and 42% at 270-360 days; and (3) THPME [2-thioethylenecarboxy-4-hydroxyphenyl methyl ether], reaching a maximum of 10% at 180-270 days. Although not tracked in this study, O-ethyl-S-propyl phosphorothioate is expected to form in equimolar proportions with 4-bromo-2-chlorophenol. Volatilized profenofos residues totaled over 50% of the applied by 30 days posttreatment.

The concentrations of profenofos and 4-bromo-2-chlorophenol at 2 days were similar in

the non-sterile and sterile samples, suggesting that processes other than metabolism may be at work. The major degradates are the same as in the hydrolysis studies, which could be expected since profenofos hydrolyzes rapidly under alkaline conditions and the soil used in the study was alkaline. At the end of the study (360 days), 4-bromo-2-chlorophenol comprised 94% of the applied radioactivity in the sterile soils, compared to 32% in the non-sterile samples. Aerobic metabolism may be important in the formation of subsequent 4-bromo-2-chlorophenol metabolites (MRID 423343-02).

#### **162-2 Anaerobic Soil Metabolism**

In a study submitted, profenofos degraded with a half-life of 3 days when incubated anaerobically in a pH 7.8 sandy loam soil for 60 days following 2 days of aerobic incubation. Profenofos declined to 58% of the applied radioactivity after 2 days of aerobic conditions. Under anaerobic conditions, it declined to 20% after 3 days, 10% after 7 days, and 1.5% after 60 days. The major degradate, 4-bromo-2-chlorophenol, increased from 35% at the start of anaerobic conditions to 82.5% at 60 days. O-ethyl-S-propyl phosphorothioate will be formed in equimolar proportions with 4-bromo-2-chlorophenol. Other degradates were 4-bromo-2-chlorophenol ethyl ether (BCPEE), cyclohexadienyl sulfate, and phenol and/or its conjugate.

The major degradates are the same as in the hydrolysis studies, which could be expected since profenofos hydrolyzes rapidly under alkaline conditions and the soil used in the study was alkaline (MRID 423343-03).

#### **162-3 Anaerobic Aquatic Metabolism**

In a study submitted, profenofos degraded with a half-life of 3.2 days in an anaerobic sandy loam soil (pH 5.1) flooded with creek water (pH 7.3). Profenofos concentrations declined from 98% of the applied at 0 days to 66% at 3 days, 23% at 6 days, and <0.1% after 60 days. The major degradate, 4-bromo-2-chlorophenol, increased from 29% at 3 days to a plateau of 68 to 81% between 6 and 180 days before declining to 3% at 360 days. After 180 days, additional degradates increased in concentration: 4-bromo-2-chlorophenol ethyl ether (BCPEE) from 7% to 20%, cyclohexadienyl sulfate from 5% to 47%, and phenol complex from 4% to 28% (270 days).

Profenofos and CGA-55960 were detected in both the soil and water fractions. While greater concentrations of profenofos occurred in the soil fraction, CGA-55960 was found in greater concentrations in the water. BCPEE was detected in the soil and volatile fractions. Cyclohexadienyl sulfate and the phenol complex were associated primarily with the water fraction (MRID 422181-01).

#### **162-4 Aerobic Aquatic Metabolism**

These data are not required for terrestrial uses.

### (3) Mobility

#### 163-1 Leaching and Adsorption/Desorption

In a study submitted, profenofos was somewhat mobile to mobile, with Freundlich  $K_{ads}$  values of 4.60 ( $n = 0.965$ ) for sand (2% clay; 0.5% organic C), 7.46 ( $n = 1.509$ ) for sandy loam (6% clay; 0.3% organic C), 16.96 ( $n = 1.012$ ) for loam (11% clay; 0.7% organic C), and 89.28 ( $n = 1.097$ ) for clay (42% clay; 2.8% organic C) soil samples. Freundlich  $K_{des}$  values ranged from 6.24 (sand) to 128.1 (clay). Adsorption generally increased with increasing soil organic matter content, clay content, and CEC.  $K_{oc}$  values calculated by the registrant ranged from 869 to 3162.

This study provides information on the mobility of profenofos in soils. Additional data is needed on the mobility of the major degradates/metabolites of profenofos, in particular 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate (MRID 416273-11).

#### 163-2 Volatility -- Laboratory

The results of a supplemental study show that some profenofos may be released to the atmosphere as a result of volatility. The average rate of volatilization for profenofos decreased with time from an average  $10.62 \times 10^{-3}$  ug/cm<sup>2</sup>/hr after 1 day to  $2.93 \times 10^{-3}$  ug/cm<sup>2</sup>/hr after 30 days. For the entire study, volatility averaged  $6.13 \times 10^{-3}$  ug/cm<sup>2</sup>/hr and the vapor pressure averaged  $3.46 \times 10^{-6}$  mm Hg. After 30 days, over 90% of the volatilized [<sup>14</sup>C]residues were 4-bromo-2-chlorophenol, which forms as a result of hydrolysis. 4-bromo-2-chlorophenol was also the major degradate identified in the soil extracts. Because of the high degree of variability in duplicate samples, "mean" results are of questionable value and should be interpreted with caution (MRID 419050-01).

### (4) Field Dissipation

#### 164-1 Terrestrial Field Dissipation

Two studies submitted provide supplemental information about the terrestrial field dissipation of profenofos. Neither meet Subdivision N guidelines because profenofos appears to have degraded during storage and because the site conditions were not conducive to assessing the potential of profenofos and its degradates/metabolites to leach. However, both provide a qualitative assessment of the dissipation of profenofos and 4-bromo-2-chlorophenol. Because of potential storage stability problems, the half-life values should be interpreted with care. While actual dissipation rates may be longer, they should be within the same order of magnitude. The leaching potential could not be reliably assessed in the studies.

Profenofos was applied as Curacron 8E to the cotton plots in 6 applications of 1 lb ai/A each in 4-7 day intervals and to the bareground plots at 6 lb ai/A. Profenofos dissipated rapidly on bareground and cotton test plots situated on a sandy soil (a slightly acid pH and low organic



matter content) located near Madera, California (428513-01). The registrant-calculated half-life for the upper 6 inches of soil was 2 days on the cotton plot and 3 days on the bareground plot. In Terry, Texas, profenofos also dissipated rapidly on bareground and cotton test plots situated on an alkaline (pH 7.6) soil (429009-01). The registrant-calculated half-life for the upper 6 inches of soil was approximately 2 days for both test plots. Neither profenofos or 4-bromo-2-chlorophenol were detected below 12 inches in either study (MRID 428513-01, 429009-01).

## **164-2 Aquatic Field Dissipation**

These data are not required for terrestrial uses.

### **(5) Accumulation**

#### **165-4 Accumulation in Fish**

A study submitted partially fulfills environmental fate data requirements by providing information on the bioaccumulation and depuration of profenofos residues in bluegill sunfish. Profenofos residues accumulated preferentially in the viscera of bluegill exposed to profenofos at 1 ppb for 28 days in a flow-through aquarium. The maximum bioconcentration factors were 29x (25 ppb) in the bodies, 45x (38 ppb) in the heads, and 682x (580 ppb) in the viscera. Chemicals identified in the viscera tissue included profenofos (1-4% of the recovered radioactivity), 4-bromo-2-chlorophenol (33-48%), 4-bromo-2-chlorophenol sulfate (6%) and two aqueous-soluble unknowns (10 and 29%). Profenofos residues depurated rapidly, with concentrations decreasing to 1 ppb in the bodies, 2 ppb in the heads, and 7 ppb in the viscera after 8 days. Two degradates comprising 10 to 29% of the recovered radioactivity were not identified. Degradate identification could have been facilitated by analyzing whole-fish tissues rather than just viscera and by using a larger dose rate (1 ppb was 3% of the LC50 of 30 ppb, concentrations up to 10% of the LC50 could have been used) (MRID 000859-52, 921480-59).

### **c. Water Resources**

#### **(1) Ground Water**

While laboratory mobility data suggest that profenofos is not likely to leach to ground water under normal use, a terrestrial field dissipation study conducted under potential leaching conditions is needed to confirm this. The mobility and leaching potential of the degradates is unknown. In EPA's National Pesticides in Ground Water Database, profenofos was not detected in any of the 188 well sampled in a Texas study (1987-88). No other study included in the database analyzed for profenofos.

#### **(2) Surface Water**

Profenofos can contaminate surface water at application via spray drift. However,

substantial fractions of applied profenofos should be available for runoff for only a few days post-application because of its relatively rapid dissipation in soil (aerobic soil metabolism half-life of 1.9 days; terrestrial field dissipation half-lives of 2, 2.2, 3.1, and 1.8 days). The somewhat intermediate soil/water partitioning of profenofos ( $K_{oc}$ s of 869, 2540, 2400, and 3160;  $K_{ads}$ s of 4.6, 7.5, 20, and 89;  $K_{des}$ s of 6.2, 7.6, 23, and 128) suggests that substantial portions of runoff will occur via both dissolution in runoff water and adsorption to eroding soil. Although soil/water partition coefficients greater than 1 indicate that concentrations in soil will be greater than concentrations in runoff water, the normally much greater mass of runoff water than eroding soil should ensure that both pathways generally contribute significantly to runoff.

The persistence of profenofos in the water column may vary substantially depending upon the pH, the microbiological activity and the hydrologic residence time of the water body. The rapid hydrolysis of profenofos in alkaline waters (hydrolysis half-life of 8.2 hours at pH 9) and its apparent susceptibility to biodegradation indicate that it will not persist in alkaline waters or in waters with much lower pHs that have substantial microbiological activity. However, the substantial increase in its hydrolysis half-life with decreasing pH (23.8 days at pH 7 and 104 days at pH 5) coupled with a low susceptibility to direct photolysis (irradiated half-life of 75 days) and relatively low potential for volatilization from water (Henry's Law constant of  $3.34 \times 10^{-7}$  atm·m<sup>3</sup>/mol) indicate it will be somewhat more persistent in neutral to acidic waters with low microbiological activities and long hydrologic residence times. An anaerobic soil metabolism half-life of 2.9 days and an anaerobic aquatic metabolism half-life of 3.2 days indicate that it will probably not persist in normally anaerobic sediments.

The intermediate soil/water partitioning of profenofos indicates that significant portions of profenofos in surface water will be dissolved in the water column and adsorbed to suspended and bottom sediment. Although soil/water partition coefficients greater than 1 indicate that concentrations adsorbed to suspended and bottom sediment will probably be greater than concentrations dissolved in the water column, the mass of water in the water column will generally be much greater than the suspended and bottom sediment available for binding profenofos. Reported BCFs for the bluegill sunfish of 45X, 682X, and 29X for head, viscera, and the whole fish, respectively indicate that the bioaccumulation potential of profenofos is relatively low.

The major primary degradates of profenofos under both aerobic and anaerobic conditions in soil are also its major hydrolysis degradates: 4-bromo-2-chlorophenol and O-ethyl-S-propyl phosphorothioate. A major secondary degradate under both aerobic and anaerobic conditions is 4-bromo-2-chlorophenyl ethyl ether (BCPEE). A major tertiary degradate under anaerobic conditions is cyclohexadienyl sulfate.

Except for O-ethyl-S-propyl phosphorothioate for which there is no direct fate data, the major degradates listed above all appear to be substantially more persistent than profenofos. Consequently, substantial amounts of those degradates in terms of fractions of applied should remain available for runoff for longer periods than for profenofos. The presence of hydrolyzable

groups on the O-ethyl-S-propyl phosphorothioate indicate that it may be less persistent than some of the other major degradates, but its actual persistence was not determined.

Although no direct soil/water partitioning data are available for the major degradates, a greater partitioning of both 4-bromo-2-chlorophenol and cyclohexadienyl sulfate into water than profenofos in the aquatic anaerobic metabolism study suggests they may exhibit substantially lower soil/water partitioning than profenofos. If so, runoff of those degradates may occur primarily by dissolution in runoff water as opposed to adsorption to eroding soil, and most of their mass in receiving waters may be dissolved in the water column as opposed to adsorbed to suspended and bottom sediment.

EFGWB does not have any data on the concentrations of profenofos in surface water. Also, no entries for profenofos in surface water were found in the STORET database.

Surface Water Modeling. The Agency has modeled contamination of surface water resulting from profenofos use on cotton, using the models PRZM2 and EXAM II. The site modeled was a hydrologic Group C silt loam soil in Yazoo County, Mississippi. It was assumed that a 10 hectare cotton field drains into a body of water at the edge of the field with 1 hectare surface and depth 2 meters. The Agency believes that these assumptions represent a reasonable high-runoff and high-erosion scenario.

The site was modeled over 36 years. One in 10 year peak, maximum 96-hour average, maximum 21-day average, maximum 60-day average, and maximum 90 day average estimated environmental concentrations in the pond were 5.9 ug/L, 2.6 ug/L, 1.1 ug/L, 0.75 ug/L, and 0.50 ug/L, respectively. These results are used in Section C.3 above as estimates of exposure to nontarget aquatic organisms.

For the profenofos loaded into the body of water, 84% was transported as spray drift and 16% in runoff water (15% dissolved and 1% adsorbed to particles).

### **3. Exposure and Risk Characterization**

#### **a. Ecological Exposure and Risk Characterization**

Explanation of the Risk Quotient (RQ) and the Level of Concern (LOC): The Levels of Concern are criteria used to indicate potential risk to nontarget organisms. The criteria indicate that a chemical, when used as directed, has the potential to cause undesirable effects on nontarget organisms. There are two general categories of LOC (acute and chronic) for each of the four nontarget faunal groups and one category (acute) for each of two nontarget floral groups. In order to determine if an LOC has been exceeded, a risk quotient must be derived and compared to the LOC's. A risk quotient is calculated by dividing an appropriate exposure estimate, e.g., the estimated environmental concentration, (EEC) by an appropriate toxicity test effect level, e.g., the LC<sub>50</sub>. The acute effect levels typically are:

- EC<sub>25</sub> (terrestrial plants),
- EC<sub>50</sub> (aquatic plants and invertebrates),
- LC<sub>50</sub> (fish and birds), and
- LD<sub>50</sub> (birds and mammals)

The chronic test results are the:

- NOEL (sometimes referred to as the NOEC) for avian and mammal reproduction studies, and either the NOEL for chronic aquatic studies, or the Maximum Allowable Toxicant Concentration (MATC), the geometric mean of the NOEL and the LOEL (sometimes referred to as the LOEC) for chronic aquatic studies.

When the risk quotient exceeds the LOC for a particular category, risk to that particular category is presumed to exist. Risk presumptions are presented along with the corresponding LOC's.

<b>Levels of Concern (LOC) and Associated Risk Presumptions</b>	
<b>Mammals and Birds</b>	
<b>Criterion</b>	<b>Presumption when Criterion Met</b>
Acute RQ $\geq$ 0.5	High acute risk.
Acute RQ $\geq$ 0.2	Risk that may be mitigated through restricted use.
Acute RQ $\geq$ 0.1	Endangered species may be affected acutely.
Chronic RQ $\geq$ 1	Chronic risk, endangered species may be affected chronically.



<b>Fish and Aquatic Invertebrates</b>	
Acute RQ $\geq 0.5$	High acute risk.
Acute RQ $\geq 0.1$	Risk that may be mitigated through restricted use.
Acute RQ $\geq 0.05$	Endangered species may be affected acutely.
Chronic RQ $\geq 1$	Chronic risk, endangered species may be affected chronically.
<b>Plants</b>	
RQ $\geq 1$	High risk.
RQ $\geq 1$	Endangered plants may be affected.
For plants, there are not separate criteria for restricted use or chronic effects.	

Risk to nontarget organisms has been assessed based on the assumption that the product Curacron 8E is applied at a rate of 1 lb active ingredient per acre. The maximum application rate per season is 3 qts Curacron per acre. Curacron 8E contains 8 lbs active ingredient per gallon.

#### **(1) Exposure and Risk to Nontarget Terrestrial Animals**

##### **(a) Birds**

Estimation of the potential for adverse effects to wild birds upon the Agency's draft 1995 Standard Evaluation Procedure for risk assessments and methods used by Hoerger and Kenaga (1973) as modified by Fletcher et al. (1994) for terrestrial EEC determinations.

Residues found on dietary food items following one application may be compared to  $LC_{50}$  values to predict hazard. The maximum concentration of residues of profenofos which may be expected to occur on selected avian or mammalian dietary food items following a single application rate is provided in the table below, where the EEC is the Estimated Environmental Concentration, RQ equals  $EEC/LC_{50}$  for acute risk and  $EEC/NOEC$  for chronic risk;  $LC_{50}$  equals 57 ppm (for bobwhite quail) and  $NOEC$  equals 10 ppm (for northern bobwhite quail).