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OFFICE OF  
PREVENTION, PESTICIDES, AND  
TOXIC SUBSTANCES

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**MEMORANDUM:**

**SUBJECT:** METHAMIDOPHOS: Revision of EFED Risk Assessment for the Reregistration Eligibility Decision (RED) Document to Include Registrant's Comments

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and  
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**THRU:**

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**TO:**

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Attached please find a revised EFED Risk Assessment for the Reregistration Eligibility Decision (RED) Document which includes corrections to "errors of omission" identified by the registrant Bayer. The following changes (as listed in the December 8, 1998 letter from Bayer; attached) were made:

- Concerning 2.A. Field Study of Blus et al.:  
On pages 31-32 and page 44, the RED will be revised to reflect the registrant's comments.
- Concerning 2.B. Field study of Perrit et al. (1990):  
On pages 31 and 47-48, the RED will be revised to reflect the registrant's comments.

**These changes will not qualitatively change the results of the EFED risk assessment.**

**Given the short timeframe in which to respond, all other issues raised in the letter will be addressed during the official public docket 60-day comment period.**

#### **Attachments**

# EFED Methamidophos RED Chapter

## Table of Contents

1. Use Characterization .....	1
2. Exposure Characterization .....	2
a. Chemical Profile .....	2
b. Environmental Fate Assessment .....	3
i. Degradation .....	5
ii. Mobility .....	7
iii. Accumulation .....	9
iv. Field Dissipation .....	9
v. Spray Drift .....	9
c. Terrestrial Exposure Assessment .....	10
d. Water Resource Assessment .....	11
i. Ground Water Assessment .....	11
ii. Surface Water Assessment .....	14
iii. Drinking Water Assessment .....	20
3. Ecological Effects Toxicity Assessment .....	21
a. Toxicity to Terrestrial Animals .....	22
i. Birds, Acute and Subacute .....	22
ii. Birds, Chronic .....	23
iii. Mammals, Acute and chronic .....	24
iv. Insects .....	25
b. Toxicity to Freshwater Aquatic Animals .....	25
i. Freshwater Fish, Acute .....	25
ii. Freshwater Fish, Chronic .....	26
iii. Freshwater Invertebrates, Acute .....	26
v. Freshwater Invertebrates, Chronic .....	27
c. Toxicity to Estuarine and Marine Animals .....	27
i. Estuarine and Marine Fish, Acute .....	27
ii. Estuarine and Marine Fish, Chronic .....	28
iii. Estuarine and Marine Invertebrates, Acute .....	28
iv. Estuarine and Marine Invertebrates, Chronic .....	29
d. Toxicity to Plants .....	29
i. Terrestrial .....	29
ii. Aquatic .....	29
e. Field Testing and Literature Findings .....	30
4. Exposure and Risk Characterization .....	34
a. Exposure and Risk to Nontarget Terrestrial Animals .....	36
i. Birds .....	37

ii. Mammals .....	37
iii. Insects .....	40
b. Risk to Nontarget Aquatic Animals .....	40
c. Risk to Nontarget Plants .....	41
5. Endangered Species .....	41
6. Risk Characterization .....	42
7. References .....	51
8. Appendices/Supporting Documentation .....	54
A. PRZM 3.1/2.3 and EXAMS 2.97.5 Chemical-Specific Input Parameters .....	55
B. PRZM Scenario Parameters .....	60
C. EXAMS Scenario Input Parameters .....	65
D. Input File Names .....	68
E. Structure of Methamidophos and Major Degradates .....	69
F. Proposed Degradation Pathways for Methamidophos .....	72

## 1. Use Characterization

Methamidophos is a broad-spectrum non-fumigant systemic/contact organophosphate insecticide registered to control a variety of plant and soil insects in cotton, potato, and tomatoes; it is a restricted use pesticide. The sole registered product (Monitor®) is an emulsifiable concentrate used as foliar treatments during the growing season. The maximum rate per application is 1 lb/A; its pesticidal activity is locally systemic, with a long-lasting biological effect (up to 14 days). Multiple foliar applications are used to control a variety of insect pests, and timing and application rate depend upon which pest is being controlled.

Methamidophos usage on major crops includes potatoes (average of 390,000 pounds up to an estimated maximum of 744,000 pounds applied to an average of 301,000 acres up to an estimated maximum of 389,000 acres; majority of use in WA, ND, OR, CA, ME, and DE), tomatoes (average of 170,000 pounds up to an estimated maximum of 344,000 pounds applied to an average 68,000 acres up to an estimated maximum of 129,000 acres; majority of use in FL), and cotton (average of 54,000 pounds up to an estimated maximum of 106,000 pounds applied to an average of 68,000 acres up to an estimated maximum of 136,000 acres; majority of use in CA, AZ, MS, and LA). Crops with a high percentage of acreage treated are fresh tomatoes (46%) and potatoes (21%). The trend shows increasing cotton acreage treated by methamidophos from a current treated acreage of 1% (BEAD usage data up to 1996) to a projected usage of 10% (registrant-provided information, 1997).

To assess risk, one must know what the exposure of the pesticide would be. The exposure of organisms to pesticide is based on the rate of application, method of application and the use site of the application, in combination with the fate and transport of the chemical in the environment. The maximum allowed label rate per application for methamidophos is 1 lb/A, although the typical amount per application is less than that (registrant info, 1997). According to information provided by the registrant, the use allows up to four applications per season on cotton and potatoes; however, the label for cotton does not specify either a maximum rate per season nor an application interval. According to information provided by the registrant, the maximum number of applications is five per season for tomatoes; however, information provided by LUIS (BEAD, 1998) indicates there can be up to nine applications per growing cycle. All tomato registrations are Special Local Need (SLN) registrations (also referred to as FIFRA 24(c) registrations) granted by states; there are 17 states with SLNs on record (LUIS report, 1998) for the use of methamidophos on tomatoes. These are: Alabama (AL89000800); California (CA78016300, CA79009600); Delaware (91000200, 92000200); Florida (FL80004600, FL89000700, FL89004100, FL90000300, FL92000400); Georgia (86000400, 90000100); Indiana (79000100, 93000300); Louisiana (91000800, 91000600); Maryland (91000900); Michigan (78001600, 93000300); North Carolina (89000700); New Jersey (90000600, 96001000); Ohio (79000800, 79001000); Puerto Rico (92000100); South Carolina (78001600); Tennessee (89000700, 93000300, 96000600); Texas (91001200, 91001600); and Virginia (91000500, 93000200).

Below are the use sites, applications, and assumptions used in this risk assessment and characterization to derive exposure.

Use Site	Application Type	Application Method	Application Rate (lb ai/A)	Number of Applications	Interval Between Application (days)
Tomatoes (Florida)	spray	aerial & ground spray	1.0	9 <sup>1</sup>	5
Tomatoes (other)	spray	aerial & ground spray	1.0	5	7
Potatoes	spray	aerial & ground spray	1.0	4	7
Cotton	spray	aerial & ground spray	1.0	4 <sup>2</sup>	7

<sup>1</sup> The maximum application in a season is 9 lb ai/A (FL SLN). The typical application was assumed to be 5 per season.

<sup>2</sup> The maximum application in a season is 4 lb ai/A (registrant info). Since the maximum application rate permitted for potatoes is 1 lb ai/A, EFED assumes four applications.

## 2. Exposure Characterization

### a. Chemical Profile

Identifying information on methamidophos and its metabolites is presented in the following table.

Chemical	CAS Number	PC Code Number	Chemical names and synonyms
Methamidophos	10265-92-6	101201	O,S-dimethyl phosphoramidothioate; O,S-dimethyl thiophosphoric acid amide; RE-9006
O-Desmethyl methamidophos	17808-29-6	-	S-methyl phosphoramidothioate
DMPT	42576-53-4	-	O,S-dimethyl phosphorothioate; RE18421; desamino-methamidophos; deaminated methamidophos
Methyl mercaptan	-	-	Methyl mercaptan
Dimethyl disulfide	-	-	Dimethyl disulfide
Methyl disulfide	-	-	Methyl disulfide

The physical and chemical properties of methamidophos are presented in the following table:

Physical and chemical properties of methamidophos.		
Property	Value	Data Source
Molecular formula	$C_2H_8NO_2PS$	
Molecular weight	141.14 g/mol	
Physical State	Clear colorless liquid at 23 °C (Technical)	43661003
Odor	Pungent, mercaptan-like (Technical)	43661003
Melting Point	N/A (Technical)	43661003
Boiling Point	Decomposes at temps > 150 °C N/A	43661003
Density (Specific gravity)	1.343 g/mL at 20 °C (Technical)	43661003
Solubility	Technical: > 200 g/L [ $2.0 \times 10^5$ ppm] (Technical); 2-propanol: > 200 g/L; toluene: 2-5 g/L; dichloromethane: > 200 g/L; n-hexane: < 1 g/L; acetone: > 200 g/L; dimethylformamide: > 200 g/L	43661003
Vapor Pressure	$2.3 \times 10^{-5}$ hPa at 20 °C [ $1.725 \times 10^{-5}$ mm Hg]	43661003
Dissociation constant (pKa)	N/A (does not dissociate)	43661003
Octanol/water Partition Coefficient ( $K_{ow}$ )	0.16 at 20 °C; Log $K_{ow}$ : -0.796	43661003

#### b. Environmental Fate Assessment

Although the environmental fate data base for methamidophos is not complete, supplemental information from upgradeable laboratory studies indicate that methamidophos is not persistent in aerobic environments but may be persistent in anaerobic aquatic environments where it will be associated with the aqueous phase. No acceptable data are available on the behavior of methamidophos under field conditions, but information from acceptable terrestrial field dissipation studies for acephate (methamidophos is the major degradate of acephate) indicated that methamidophos was not persistent.

Aerobic soil metabolism is the main degradative process for methamidophos. Methamidophos degraded with a calculated half-life of 14 hours in a sandy loam soil at greater than the currently registered application rate (nominal application rate of 6.5 ppm, compared to the expected 0.5 ppm from the maximum label rate of 1 lb ai/A), producing the intermediate degradate O-desmethyl methamidophos, which is itself rapidly metabolized by soil microorganisms to carbon dioxide and microbial biomass (half-life of < 5 days). Supplemental information also identifies DMPT as a major degradate which is also rapidly degraded in soil (half-life of < 4 days). Methamidophos photodegrades rapidly on soil irradiated with a mercury vapor lamp (dark control-corrected half-life 63 hours); however, in sterile aqueous solutions, methamidophos photodegrades slowly (dark control-corrected half-life > 200 days) and is stable against hydrolysis at acid pHs. Hydrolysis degradates at neutral and alkaline pHs include O-desmethyl methamidophos, DMPT, and the volatile degradate dimethyldisulfide.

Supplemental information showed that methamidophos degraded in anaerobic sandy loam sediment:pond water systems in the laboratory with a  $DT_{50}$  of 41 days. Observed major degradates in the same study were DMPT and O-desmethyl methamidophos, but their persistence could not be determined due to incomplete material balances after 3 months of anaerobic incubation. [ $^{14}C$ ]residues were distributed between the water and sediment fractions with the majority of residues observed in the water phase in a ratio of approximately 10 to 1. There are no acceptable data for the aerobic aquatic metabolism of methamidophos.

Methamidophos is very soluble ( $>200$  g/L;  $2.0 \times 10^5$  ppm) and very mobile ( $K_{oc} = 0.9$ ) in the laboratory. Only one  $K_{oc}$  value is available, because methamidophos was adsorbed in only one of the five soils (a clay loam) used in the batch equilibrium studies. The methamidophos degradate DMPT is also very mobile ( $K_{oc} = 1.6$ ); no data are available for O-desmethyl methamidophos, but it is expected to have similar mobility as its parent compound. Because methamidophos and its degradates are not persistent under aerobic conditions, little methamidophos residue could be expected to leach to groundwater. If any methamidophos residues did reach ground water, they might be expected to persist based on an observed anaerobic aquatic  $DT_{50}$  of 41 days for methamidophos and undetermined persistence for DMPT and O-desmethyl methamidophos. Volatilization from soil or water is not expected to be a major route of dissipation for methamidophos because of its rapid metabolism in soil and its calculated Henry's constant ( $1.6 \times 10^{-11}$  atm mole /m<sup>3</sup>).

No acceptable field studies are available for methamidophos. Information of marginal value comes from a terrestrial field dissipation study in which methamidophos could not be detected at 3 days following a single and the last of 6 applications of methamidophos to potato plants in two sites in California. However, the study was not scientifically valid because methamidophos could not be detected at the first sampling interval after application. In addition, the formation and decline of degradates were not followed.



Laboratory studies showed that bioaccumulation of methamidophos in largemouth bass was insignificant; the maximum bioconcentration factor of 0.09X in whole fish occurred on day 28 and decreased to <0.014 ppm (quantification limit) after one day depuration.

### **i. Degradation**

#### **Abiotic Hydrolysis**

The rate of abiotic hydrolysis of methamidophos is pH dependent. In sterile aqueous buffered solutions at 12 ppm incubated at 25°C in the dark, methamidophos was stable at pH 5 (<10% degraded after 30 days incubation); at pHs 7 and 9, the calculated hydrolysis half-lives were 27 and 3.2 days, respectively. The predominant degradate at pH 7 was dimethyldisulfide; at pH 9, both dimethyldisulfide and O-desmethylmethamidophos were formed. Maximum concentrations of degradates were: dimethyldisulfide (41% of the applied at 30 days at pH 7); O-desmethyl-methamidophos (51% of the applied at 7 days at pH 9); and DMPT (3% at 21 days at pH 5). These degradates were apparently stable to further hydrolysis, since concentrations continued to increase throughout the duration of the study. This study is acceptable and satisfies the data requirement for aqueous hydrolysis of methamidophos at pHs 5, 7, and 9 (GLN 161-1; 00150609).

#### **Photodegradation in Water**

Methamidophos photodegraded slowly in sterile buffer solutions under both artificial and natural light. In pH 5 solutions containing 10 ppm methamidophos, 89% of the initial application remained as methamidophos following 5 days of continuous irradiation under a mercury lamp at 33°C. Degradates found were desmethylmethamidophos (3% of the applied) and DMPT (6% of the applied). In the dark controls, 93% remained unchanged; desmethylmethamidophos (<1% of the applied), DMPT (3% of the applied) and dimethyldisulfide (2% of the applied) were seen.

In pH 5 solutions containing 12 ppm methamidophos, 78% of the applied methamidophos remained following 30 days under natural sunlight in August - September in Kansas (temperature was not controlled and ranged between 9 and 42°C). The registrant calculated a half-life of 90 days for the irradiated samples; the dark-control-corrected photolysis half-life was 200.5 days. Degradates formed were desmethylmethamidophos (7% of the applied), DMPT (13% of the applied). In the dark controls, 87% remained unchanged; desmethylmethamidophos (<1% of the applied), DMPT (6% of the applied), and dimethyldisulfide (6% of the applied) were seen. This study is acceptable and satisfies the data requirement for aqueous photolysis of methamidophos (GLN 161-2; 00150610).

#### **Photolysis on Soil**

Methamidophos was apparently not stable to photodegradation on soil. When surface-applied at 35 ppm to thin soil layers on glass slides and continuously irradiated at 33°C for 87 hours with light from a mercury lamp filtered through borosilicate glass, methamidophos degraded with a dark-control-corrected half-life of 62.6 hours. Degradates included desmethylnmethamidophos (increasing to 24% of the applied by 87 hours) and DMPT (max 6% of the applied; apparently not resistant to photodegradation). Unextracted residues increased during irradiation, and one-third of the applied radioactivity had volatilized following 87 hours of irradiation; volatiles were not characterized. Although this study showed that methamidophos degraded when irradiated using a mercury vapor lamp, it cannot be used to fulfill the data requirement for photolysis of methamidophos on soil because the light spectrum coming from a mercury vapor lamp is not similar to natural sunlight. A new study is required; the data requirement is not fulfilled (GLN 161-3; 00150611).

### **Photodegradation in Air**

Based on the vapor pressure of methamidophos (Pure active:  $1.725 \times 10^5$  mm Hg/Torr [43661003]) and its calculated Henry's constant ( $1.6 \times 10^{-11}$  atm mole /m<sup>3</sup>), it is not expected that methamidophos will volatilize in significant amounts from either soil or water. Therefore it is not expected that there will be sufficient residues of methamidophos in air for photodegradation in air to be a significant route of dissipation for methamidophos.

### **Aerobic Soil Metabolism**

Methamidophos degraded rapidly in aerobic soil. At a nominal application rate of 6.5 ppm, the registrant-calculated half-life was 14 hours in sandy loam soil adjusted to 75% of 0.33 bar moisture content and incubated in darkness at 25 °C for 5 days. Based on TLC analysis of the soil extracts, the parent compound was initially present at 93% (6.04 ppm) of the applied radioactivity at 0 days posttreatment, decreased to 71% (4.65 ppm) by 6 hours and 1% (0.06 ppm) of the applied by 2 day posttreatment, and was less than the limit of quantitation by 5 days posttreatment. The major degradate was radiolabeled <sup>14</sup>CO<sub>2</sub>, which accounted for 49% of the applied radioactivity at 5 days posttreatment. The major non-volatile degradate, O-desmethyl methamidophos, was initially present at 1% (0.06 ppm) of the applied radioactivity at 0 days posttreatment, increased to a maximum concentration of 27% of the applied by 1 day posttreatment, then decreased to 11% (0.72 ppm) by 2 days posttreatment and was not detected at 5 days posttreatment. Volatile organic compounds accounted for a maximum of 6% of the applied radioactivity at 2 days posttreatment; GC/FPD analysis detected methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Nonextractable [<sup>14</sup>C]residues increased to a maximum of 31% of the applied radioactivity at 5 days posttreatment. This study is not acceptable at this time because the sieve screen size used to prepare the test soil was not reported. In order for this study to be upgraded to acceptable, it is necessary that the registrant report the sieve size. The data requirement for the aerobic metabolism of methamidophos in soil is not satisfied (GLN 162-1; 41372201).

### **Anaerobic soil Metabolism**

No acceptable data are available. However, because the Anaerobic Soil Metabolism (162-2) study protocol described in Subdivision N is considered by EPA to be inadequate to determine the patterns of decline of the parent compound and the formation and decline of degradates, the EPA currently recommends that the Anaerobic Aquatic Metabolism (162-3) study protocol be followed when an Anaerobic Soil Metabolism (162-2) data requirement has been triggered (Pesticide Reregistration Rejection Rate Analysis - Environmental Fate, 1993. EPA 738-R-93-010, p. 95). Data from an acceptable Anaerobic Aquatic Metabolism study can be used towards fulfillment of the Anaerobic Soil Metabolism (162-2) data requirement.

### **Anaerobic Aquatic Metabolism**

Information of marginal value indicates that the  $DT_{50}$  for methamidophos in anaerobic pond water:sandy loam sediment systems (calculated using a linear regression on the total methamidophos in water and sediment) is approximately 41 days. [ $^{14}C$ ]residues were distributed between the water and sediment fractions with the majority of residues observed in the water phase (ratio approximately 10:1). The study cannot be used to fulfill data requirements because the material balance was incomplete (below 70%) from 4 months posttreatment onward and was only 32.9% at 12 months posttreatment. Because of the incomplete material balance, this study cannot be upgraded; a new study is required. The data requirement is not satisfied (GLN 162-3; 43541202).

### **Aerobic Aquatic Metabolism**

No acceptable data are available.

## **ii. Mobility**

### **Batch equilibrium studies**

Supplemental information from an upgradeable mobility study is available. Batch equilibrium studies using acephate, methamidophos, and O,S-dimethyl phosphorothioate (DMPT) were conducted using four soils ranging in texture from sand to clay loam. In three of the soils, acephate, methamidophos, and DMPT were not adsorbed in sufficient quantities to permit the calculation of Freundlich adsorption coefficients (Freundlich  $K_{ads}$ ). For the clay loam soil, the reported adsorption values for parent acephate and its degradates are listed in the following table:

Soil	pH	CEC (meq/ 100g)	% clay	% Organic matter	Acephate			Methamidophos			DMPT		
					K	1/n	r <sup>2</sup>	K	1/n	r <sup>2</sup>	K	1/n	r <sup>2</sup>
Clay loam	5.8	20.2	32	3.3	0.090	1.06	0.96	0.029	0.64	0.93	0.030	0.69	0.92

Calculated  $K_{oc}$ s for acephate, methamidophos, and DMPT in this clay loam soil were 2.7, 0.9, and 0.9, respectively. Because of the minimal adsorption of the chemicals in the adsorption phase of the study, it was not possible to determine desorption values in the soils.

Based on the values listed above, it appears that acephate, methamidophos, and DMPT will be very mobile in soils. This study is not acceptable at this time because the soils used in the study were not adequately identified and it could not be determined how the registrant calculated the  $K_{oc}$ s. This study can be upgraded to acceptable when the registrant submits information identifying the soils used in this study by soil series name and specifies what the % organic carbon of the clay loam soil was. The data requirement for mobility of **unaged** and **aged** acephate is not satisfied (GLN 163-1; 40504811).

No data have been provided on the mobility of the methamidophos degradate O-desmethyl methamidophos (methamidophos minus the O-methyl group). However, after consideration of the measured  $K_{ads}$  of DMPT (methamidophos minus the amide group), it is not expected that O-desmethyl methamidophos would be less mobile than its parent. Therefore, no further information will be required on the mobility of **aged** methamidophos.

### Volatility

Methamidophos residues, at an initial application rate of 9 ppm, volatilized from a sand soil over a 10-day test period at an average rate of  $1.8 \times 10^3 \mu\text{g}/\text{cm}^2/\text{hr}$ , with an average air concentration was  $58 \mu\text{g}/\text{m}^3$ . The maximum amount of volatilized methamidophos residues was at day 4 when 1.1% of the applied  $^{14}\text{C}$  was found in the methanol trap. This corresponds to a maximum air concentration at 4 days after soil treatment of  $171 \mu\text{g}/\text{m}^3$ . The rate of loss of  $^{14}\text{C}$  from the soil was calculated to be  $2.8 \times 10^2 \mu\text{g}/\text{cm}^2/\text{hr}$ , with the difference in rates due to metabolism in the soil (calculated half-life in soil of 6 days; volatile degradates included methyl mercaptan and its derivatives and  $\text{CO}_2$ ). This study is acceptable and satisfies the data requirement for laboratory volatility of methamidophos (GLN 163-2; 40985206).

### **iii. Accumulation**

#### **Bioaccumulation in Fish**

Methamidophos residues did not bioaccumulate in largemouth bass (*Micropterus salmoides*) repeatedly exposed to approximately 1 ppm methamidophos (fish were moved every 7 days into static tanks containing an initial concentration of approximately 1 ppm methamidophos). After 4 exposure periods (on Day 28), fish were transferred to an untreated tank for a 21-day depuration period. The maximum bioconcentration factor of 0.09X occurred on day 28 and decreased to <0.014 ppm (quantification limit) after one day depuration. This study is acceptable and satisfies the data requirement for bioaccumulation in fish of methamidophos (GLN 165-4; 00014015).

#### **Accumulation in aquatic non-target organisms**

Supplemental information from studies discussed in the Registration Standard for methamidophos indicates that methamidophos does not bioaccumulate in non-target aquatic organisms [BCFs < 2 in marine diatoms (00014496) and *Daphnia magna* (00015242)]. This is consistent with the low octanol-water partition coefficient ( $K_{ow}$  0.16) and high water solubility (>200g/L) of methamidophos.

### **iv. Field Dissipation**

A study conducted on sandy loam soil at two field sites (Chualar and Fresno) in California is not scientifically valid and cannot be used to establish half-lives of methamidophos. Too few sampling intervals were used at each site to accurately assess dissipation of the parent compound under field conditions. No analyses were conducted to determine the presence of methamidophos metabolites in soil samples collected from the field sites; therefore, the pattern of formation and decline of methamidophos metabolites under field conditions could not be assessed. Additionally, the frozen storage stability data were inadequate because the studies were not conducted using soils obtained from the field test sites.

This study cannot be repaired with the submission of additional data. New field studies are required to be conducted on potatoes and cotton; the rate of dissipation of methamidophos and the rates of formation and decline of its degradates O-desmethyl methamidophos and DMPT must be determined. The study does not satisfy the data requirement for the terrestrial field dissipation of methamidophos (GLN 164-1; 43541201).

### **vi. Spray Drift**

Because there are methamidophos products which are applied by aircraft, droplet size spectrum (201-1) and drift field evaluation (202-1) studies were required due to the concern for potential risk to nontarget aquatic organisms. No methamidophos spray drift-specific studies have been

received. However, the Spray Drift Task Force (SDTF), a consortium of pesticide registrants, has submitted to the Agency a series of studies which are intended to characterize spray droplet drift potential due to various factors, including application methods, application equipment, meteorological conditions, crop geometry, and droplet characteristics. EPA is evaluating these studies, which include ground spray as well as aerial application methods. In the interim for this assessment, the Agency is relying on previously submitted spray drift data and the open literature for off-target drift rates. The amount of drift from ground spray is estimated at 1% of the applied spray volume at 100 feet downwind. After its review of the studies, the Agency will determine whether a reassessment of the potential risks from the application of methamidophos to nontarget organisms is warranted.

### c. Terrestrial Exposure Assessment

#### Nongranular applications:

The Agency used the model of Hoerger and Kenaga (1972), as modified by Fletcher et al. (1994) to estimate pesticide concentrations on selected avian and mammalian food items immediately after application. The predicted 0-day maximum and mean residues of a pesticide that may be expected to occur on selected avian or mammalian food items immediately following a direct single application at 1 lb ai/A are tabulated below.

Estimated Environmental Concentrations on Avian and Mammalian Food Items (ppm) Following a Single Application at 1 lb ai/A)

Food Items	EEC (ppm) Predicted Maximum Residue <sup>1</sup>	EEC (ppm) Predicted Mean Residue <sup>1</sup>
Short grass	240	85
Tall grass	110	36
Broadleaf/forage plants and small insects	135	45
Fruits, pods, seeds, and large insects	15	7

<sup>1</sup> Predicted maximum and mean residues are for a 1 lb ai/a application rate and are based on Hoerger and Kenaga (1972) as modified by Fletcher *et al.* (1994).

Methamidophos is very toxic via other routes of exposure than the traditional oral exposure, i.e. dermal and inhalation. Although the short grass residue exposure may not be present in field or even on the edge of the field, for purposes of this assessment, the amount of residues for short grass is used as an index for inhalation, dermal, drinking water, and other routes of exposure to mammals and birds. Risks still exist from small insects and foliage present in the field.

The Agency estimated peak residues (EEC's) for multiple applications by making assumptions of the application intervals and number of applications based on information provided by the

Registrant, the LUIS report, and SRRD. The peak EEC was the cumulative residue value predicted immediately following the last application. The FATE model, which calculates cumulative residues assuming a first-order dissipation on plant foliage and insects used the aerobic soil metabolism half-life as an estimate of rate of dissipation after application, to estimate these peak residues. The value chosen was the 90% upper bound mean aerobic soil metabolism half-life (1.75 days; see Section 2.d.i.)

For assessing chronic risk to birds and mammals, we used the predicted mean Kenaga values to calculate the risk quotients for multiple applications by using the mean values as an input to the FATE program with the shortest application intervals and the maximum number of applications to calculate the exposure (in ppm) that would be used in generating risk quotients. We also used the predicted mean Kenaga values as an input to the FATE program to estimate the length of time that residues were present at greater than the NOAEC for birds (3 ppm) and the NOAEC for mammals (10 ppm).

#### **Granular applications:**

There are no granular formulations currently registered for methamidophos.

#### **d. Water Resources Assessment**

##### **i. Ground Water Assessment**

Based on the laboratory and field studies conducted, it does not appear that methamidophos will pose a significant threat to ground water resources. Methamidophos has high mobility ( $K_{ads}$  0.029 mL/g); it also is very susceptible to aerobic soil metabolism ( $t_{1/2}$  = 14 hours). No acceptable field dissipation studies are available for methamidophos, but reported data suggest that methamidophos does not persist long enough to exhibit substantial leaching.

Methamidophos was detected in 1986 at up to 10  $\mu$ g/L (the detection limit) in four wells located adjacent to potato fields in Maine which had been treated with methamidophos; however, resampling the same wells the next year detected no residues.

Because methamidophos and its degradates are not persistent under aerobic conditions, little methamidophos residue could be expected to leach to groundwater. No acceptable field studies are available for methamidophos, so it is not possible to confirm that methamidophos or its degradates do not leach under field conditions.

#### **Ground Water EECs**

Groundwater calculations for methamidophos were based on the SCI-GROW model (Screening Concentrations in Ground Water), which is a model for estimating concentrations of pesticides in ground water under conditions of maximum exposure. SCI-GROW provides a screening concentration or an estimate of likely ground water concentration if the pesticide is used at the

maximum allowed label rate in areas with ground water that is exceptionally vulnerable to contamination. In most cases, a majority of the use area will have ground water that is less vulnerable to contamination than the areas used to derive the SCI-GROW estimate.

The SCI-GROW model is based on normalized ground water concentrations from ground water monitoring studies, environmental fate properties (aerobic soil half-lives and organic carbon partitioning coefficients- $K_{oc}$ 's) and application rates. The model is based on permeable (sandy) soils that are vulnerable to leaching and that overlie shallow ground water (10-30 feet).

Methamidophos is used on potatoes, cotton and tomatoes. The maximum application rate for all crops is 1 lb/A; the maximum number of applications is not specified for cotton. There can be up to nine applications for tomatoes (based on one SLN registration in Florida); the most common number of applications is five. The maximum number of applications for potatoes is four per season. The input parameters for SCI-GROW are reported in the following table.

Input parameters used for calculating the ground water EEC for Methamidophos using SCI-GROW2			
Parameter	Value	Source	Quality
Soil half-life	1.75 d	Multiplication of a single value by 3; MRID 41372201 <sup>1</sup>	Fair
Soil $K_{oc}$	0.88	Single value for a clay loam soil; MRID 40504811	Fair
Crop modeled	Tomatoes	Crop with maximum number of applications for methamidophos; information from LUIS	Fair
Number of applications	9 / crop cycle	Maximum number of applications of methamidophos on tomatoes; information from LUIS	Fair
Application rate	1.0 lb/A	Maximum application rate from label	Excellent

<sup>1</sup> Although current SCI-GROW guidance recommends using the simple mean half-life, this value was selected using guidance for GENEEC and PRZM-EXAMS to be more protective.

Using the SCI-GROW model to estimate concentrations of methamidophos in ground water, the calculated EEC resulting from the use with the maximum yearly total application (nine applications at 1.0 lb methamidophos/A/application on tomatoes in Florida) is 0.029  $\mu\text{g/L}$ .

Because methamidophos is not persistent under aerobic conditions, very little methamidophos could be expected to leach to groundwater, as indicated by the SCI-GROW estimate. If any methamidophos did reach ground water, they might be expected to persist (anaerobic aquatic  $\text{DT}_{50}$  of 41 days for methamidophos; undetermined persistence for degradates DMPT and O-desmethyl methamidiphos).



## **Ground Water Monitoring Data**

A small amount of monitoring data on the occurrence of methamidophos between 1984 and 1993 have been collected and reported to the Pesticide in Ground Water Database; four detections of methamidophos in ground water have been reported. The US Geological Survey National Water Quality Assessment program (NAWQA) is not currently analyzing for methamidophos in their samples, and they do not have analytical methods in place. Discussion of the extracted studies follows.

### **Pesticides in Ground Water Database**

The results of sampling conducted in 1984-89 associated with the Well Inventory Database in California were reported. No detections of methamidophos were reported in samples taken from unfiltered and untreated wells in 58 counties scattered throughout the agricultural areas of the state; data were reported for 779 wells, with detection limits ranging from 0.01  $\mu\text{g/L}$  to 360  $\mu\text{g/L}$ . High detection limits were from the analyses performed in 1987; the more recent samples achieved the lower detection limit. Since the bulk of the data (~ 70%) is based on sampling done by Department of Health Services and seven other agencies, detection limits will vary. In a follow-up conversation with CALEPA/DPR, the data from 1990 to 1997 still shows no detections of methamidophos, so one can be fairly confident that the earlier reports of no detections are valid.

In 1986-87, 35 wells in Maine adjacent to fields where pesticides were used were sampled; these included monitoring wells and private household wells. Four wells in the Aroostook County potato growing areas gave positive detections during the growing season in 1986, ranging from trace levels to 10  $\mu\text{g/L}$ ; however, resampling the same wells the following year gave no positives. The limit of detection was 10  $\mu\text{g/L}$ ; the analytical recoveries are unknown.

### **STORET**

A small amount of ground water monitoring data for methamidophos have been collected and reported to the STORET system. There are records of field measurements on samples taken in 1989 through 1991 from 7 springs and 15 wells in Florida; all were reported at either 0.09 or 2  $\mu\text{g/L}$ . There are records of 844 samples taken in 1984-1987 for a statewide survey of municipal water intakes from ambient streams and ambient wells in California; in all samples, the actual value was known to be less than 10  $\mu\text{g/L}$ . There are records of 437 samples taken in 1989-1991 by the Florida Department of the Environment from ambient wells in Florida. In all cases, there were no detections in any of the samples, but it is uncertain what the actual detection limit was and if samples were taken from an area where methamidophos was not in use.

## ii. Surface Water Assessment

Based on modeling, methamidophos will pose a significant threat to surface water resources on an acute basis. Methamidophos is very soluble ( $> 200$  g/L;  $2.0 \times 10^5$  ppm) and has high mobility ( $K_{ads}$  0.029 mL/g); however, it is very susceptible to aerobic soil metabolism ( $t_{1/2}$  = 14 hours). No acceptable data are available on the persistence of methamidophos in aerobic aquatic systems; however, it is somewhat persistent under anaerobic aquatic conditions, degrading with a  $DT_{50}$  of 41 days. The major degradates of methamidophos were DMPT and O-desmethyl methamidophos; they are at least as mobile as methamidophos. However, they are not persistent under aerobic conditions; their persistence under anaerobic conditions could not be determined. Volatilization from surface water is not expected to be a major route of dissipation for methamidophos because of its rapid metabolism in soil and its calculated Henry's constant ( $1.6 \times 10^{-11}$  atm mole /m<sup>3</sup>); methamidophos does not bioconcentrate in aquatic organisms.

Limited monitoring information on methamidophos indicates that there were no detections of methamidophos in surface water.

### Surface Water EECs

Screening-level exposure estimates for surface water sources were generated using GENEEC (Version 1.0, executable dated May 3, 1995) for the use sites and applications described in the Use Characterization (Section 1) for use in the methamidophos ecological risk assessment. GENEEC is a single event model (one runoff event), but can account for spray drift from multiple applications. GENEEC is hardwired to represent a 10 ha field immediately adjacent to a 1 ha pond, 2 m deep with no outlet. The pond receives a spray drift event from each application plus one runoff event, which moves a maximum of 10% of the applied pesticide into the pond. This runoff can be reduced by degradative processes in the field and by the effects of binding to soil in the field. In the GENEEC model, spray drift is equal to 1% of the applied for ground spray application and 5% of the applied for aerial application.

GENEEC assumes that essentially the whole 10 hectares receives a uniform application of the chemical without considering crop area factor. Furthermore, the persistence of the chemical is usually overestimated because there is always at least some flow in a river or turn over in a reservoir or lake. However, the EECs calculated using GENEEC will be appropriate for assessing risk to any aquatic organisms and plants that are directly exposed to undiluted runoff.

Although GENEEC does have these limitations, it can be used in screening calculations and does provide an upper bound on the environmental concentrations of a pesticide. If a risk assessment based on GENEEC does not exceed the level of concern, then the actual risk is not likely to be exceeded. However, since GENEEC can substantially overestimate true environmental concentrations, it will be necessary to refine the GENEEC estimate when the level of concern is exceeded. In those situations where the level of concern is exceeded and

the GENEEC value is a substantial part of the total exposure, EFED can use a variety of methods to refine the exposure estimates.

Methamidophos is registered for use on potatoes, cotton and tomatoes. The maximum rate per application for all crops is 1 lb/A; the maximum number of applications is not specified for cotton. There can be up to nine applications for tomatoes (based on one SLN registration in Florida); the most common number of applications is five. The maximum number of applications for potatoes is four per season. Based on the more complete label information, it was decided to model potatoes. The GENEEC input values used for methamidophos (and the sources for them) are listed in the following table:

Input parameters used for calculating surface water EECs for Methamidophos using GENEEC			
Parameter	Value	Source	Quality
Crop modeled	Potatoes	Crop with known number of applications; information from product label	Good
Number of applications	4 / year	Maximum number of applications for potatoes; information from product label	Excellent
Application rate	1.0 lb/A	Maximum application rate; information from product label	Good
Application interval	7 d	Minimum retreatment interval for potatoes; information from product label	Good
Application method	Aerial/ Ground	Aerial application scenario assumes 5% drift / ground application assumes 1% drift	Good
Soil half-life	1.75 d	Multiplication of a single value by 3; MRID 41372201	Fair
Soil $K_{oc}$	0.88	Single value for a clay loam soil; MRID 40504811	Fair
Solubility	$2.0 \times 10^5$ mg/L	Temperature and pH not specified; MRID 43661003	Fair
Hydrolysis	27 d	At pH 7 and 25 C; MRID 00150609	Good
Aqueous photolysis	90 d	At pH 5; MRID 00150610	Fair
Aerobic aquatic metabolism	Stable	Acceptable data were not available; assumed that the parent was stable	Fair

Because EFED does not have any acceptable aerobic aquatic metabolism data, we assumed that methamidophos was stable in aerobic aquatic systems, which is the most conservative assumption. GENEEC then used the contributions of hydrolysis and aqueous photolysis to estimate persistence in the pond; by 56 days, the EEC's decreased to approximately one-half the peak concentrations (Table P). The registrant may wish to submit the aerobic aquatic

metabolism study (GLN 162-4) for methamidophos to improve our understanding of the dissipation of methamidophos in aquatic environments and to refine our calculation of aquatic EEC's.

Table P. Generic EECs (in ppb) for Methamidophos after four applications of 1.0 lb/A to potatoes				
Application method	PEAK GEEC	AVERAGE 4 DAY GEEC	AVERAGE 21 DAY GEEC	AVERAGE 56 DAY GEEC
Aerial	65	63	51	35
Ground	61	59	48	33

Based on the Tier I estimates of environmental concentrations that were calculated in Section 4.b., ecotoxicity Levels of Concern (LOCs) were exceeded for cotton, potatoes, and tomatoes. The assessment then proceeded to Tier II, in which the EECs are refined using PRZM-EXAMS.

#### **Tier II Surface Water Exposure Assessment - PRZM-EXAMS**

Because ecological LOCs were exceeded during the Tier I screen (GENEEC), a refinement of the EECs was required. Tier II estimated environmental concentrations (EECs) for methamidophos used on cotton in Mississippi and on potatoes in Idaho were determined using PRZM-EXAMS because these were scenarios for which the label information was most complete. The PRZM scenarios were chosen to represent sites that were expected to produce greater mass pesticide runoff than 90% of the sites where the modeled crops may be grown greater than 90% of the time. Tier II analyses were not performed for methamidophos use on tomatoes because in Florida (the state with the greatest use of methamidophos on tomatoes) most tomato production is conducted using black plastic as a mulch. Therefore, it is not appropriate to use the PRZM-EXAMS model to estimate pesticide runoff for this type of horticultural practice.

Tier II upper tenth percentile EECs for the maximum exposure scenarios are listed in Table 1; EECs from methamidophos applied as aerial broadcast applications were higher for cotton than on potatoes.

Table 2. Tier II upper tenth percentile EECs for Methamidophos ( $\mu\text{g/L}$ )*							
Crop	Peak	4-Day	21-Day	60-day	90-day	Over-all Mean	90% CB Mean
Cotton, Mississippi	40	20	6.8	2.9	2.0	1.1	??
Potatoes, Idaho	30	17	8	3.7	2.7	0.8	0.7

\* Upper 90th percent confidence bound on the overall mean concentration.

### Background

A Tier II exposure assessment uses a single site which represents a high exposure scenario for pesticide use at a particular crop or non-crop site. A high scenario is one that is expected to yield a mass loading of pesticide to surface water that is equal to or greater than 90% of the sites where the chemical may be applied. The weather and agricultural practices are simulated at the site over multiple (in this case, 36) years so the probability of an EEC occurring at that site can be estimated. EECs for acephate were calculated for cotton and tobacco because those were the crops that indicated a potential risk to aquatic wildlife during Tier I screening (Section 4).

Tier II EECs generated in this analysis were calculated for cotton using PRZM 3.1 (Executable file dated October 17, 1997) for simulating the agricultural field and EXAMS 2.97.5 (Executable file dated June 19, 1997) for fate and transport in surface water; for potatoes, PRZM 2.3 was used (Executable file dated April 30, 1997). All scenarios used aerial broadcast application of the maximum rates and number of applications provided by the Registrant. In all scenarios, it is assumed that aerial transport to the pond does occur, but runoff is the primary mechanism of transport to the pond.

### Limitations of this Analysis

There are several factors which limit the accuracy and precision of this 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 that were modeled.

Scenarios that are selected for use in Tier II EEC calculations are ones that are likely to produce large concentrations in the aquatic environment. Scenarios should represent a site that actually exists and would be likely to have the pesticide in question applied. Scenarios should be extreme enough to provide conservative estimates of the EEC, but not so extreme that the model cannot properly simulate the fate and transport processes at the site. Currently, sites are chosen by best professional judgement to represent areas which generally produce EECs larger than 90% of all sites planted in that crop. The EECs in this analysis are accurate only to the

extent that a site represents this hypothetical high exposure site. The most limiting part of site selection is the use of a standard pond with no outlet. Obviously, a Georgia pond, even with appropriately modified temperature data is not the most appropriate water body for use in New York. It should be remembered that while the standard pond would be expected to generate higher EECs than most water bodies, some water bodies would likely have higher concentrations. These may include shallow water bodies near agricultural fields that receive most of their water as runoff from agricultural fields that have been substantially treated with acephate.

The quality of the analysis is directly related to the quality of the input parameters. In general, the fate data for acephate is good based on accepted studies. In particular, the lack of aerobic aquatic metabolism data limit the accuracy of this analysis. Aerobic aquatic metabolism data would greatly increase our confidence in an exposure assessment by providing direct measurements of acephate behavior in aquatic environments.

The models themselves represent a limitation on the analysis quality. While the models are some of the best environmental fate estimation tools available, they have significant limitations in their ability to represent some processes. Spray drift is estimated as a straight percentage of the application rate reaching the pond for each application from aircraft, air-blast, or ground application. In actuality, this value should vary with each application from zero to perhaps as high as 25 percent or more. A second major limitation of the models is the lack of validation at the field level for pesticide runoff. While several of the algorithms (volume of runoff water, eroded sediment mass) are well validated and well understood, no adequate validation has yet been made of PRZM 3.1 for the amount of pesticide transported in runoff events. Other limitations of the models used is the inability to handle within site variation (spatial variability), no crop growth algorithms, and an overly simple soil water transport algorithm (the "tipping bucket" method).

A final limitation is associated with the limited years of weather data available for the analysis at all sites. Consequently there is approximately one chance in ten in the years simulated that the true 10% exceedence EECs are larger than the maximum EEC calculated in the analysis. If the number of years of weather data could be increased it would increase the confidence that the estimated value for the 10% exceedence EEC was close to the true value.

### **Pesticide Use**

Details on the use of methamidophos were presented in Section 1. The following info was pertinent for the purposes of this refinement.

There is no master label for methamidophos, but information provided on the Monitor label contains maximum seasonal application rates of up to 4 lbs a.i./acre (on potatoes and cotton). Methamidophos can be applied by broadcast to the foliage postemergence; maximum application rates for these uses are up to 1 lb a.i./acre. Surface water concentrations were

estimated using the method for each crop that generally produces the greatest exposure; in both cases, it was the aerial broadcast application to the foliage without incorporation.

### Application Rates and Timing

Application information for methamidophos for the modeled crops was extracted from the label for Monitor 4<sup>o</sup> (EPA Reg.No. 3125-280) and/or extracted from LUIS and is listed in Table 2.

Table 2. Usage Practices used for modeling Methamidophos on various crops.		
Crop	Location, (Soil), Hydrologic Group, and (MLRA)	Maximum Labeled Rate (lb ai/A), Application Dates, Pre-Harvest Interval (PHI)
Cotton	Yazoo County, MS (Loring silt loam), Group C, (MLRA 134)	1.0 lb acephate (4 x 1.0 lbs ai) at 7 day interval June 19 - July 10; PHI=NA
Potatoes	Bingham County, ID (Eginbench loamy sand), Group D, (MLRA 11)	1.0 lb (4 x 1.0 lbs ai) at 7 day interval June 20 - July 11; PHI=NA

These values were used to generate Tier II EECs for the crops listed. Applications were assumed to have been made by aerial broadcast spray to the foliage, where it was assumed that 95% of the application hit the target site; no incorporation was assumed. Application intervals were chosen based on intervals as the minimum indicated on the labels and abstracted by LUIS. Application dates were chosen based on pest being controlled and appropriate stage of maturity of the crop.

Detailed information on the selection of input parameters for PRZM and EXAMS are included in Appendices A, B, C, and D.

### Surface Water Monitoring Data

A small amount of surface water monitoring data on the occurrence of methamidophos between 1977 and 1996 have been collected and reported to STORET; no detections of acephate in surface water have been reported. The US Geological Survey National Water Quality Assessment program (NAWQA) is not currently analyzing for methamidophos in their samples, and they do not have analytical methods for this chemical in place. Discussion of the extracted studies follows.

#### STORET

STORET contains no records for methamidophos acephate in samples from lakes, ocean, estuary, or reservoir sites.

There are records of eleven sediment samples taken in 1996 from canals and wetlands in St. Lucie county, Florida; the actual value was known to be less than 10 µg/L, but it is uncertain

what the actual detection limit was and if samples were taken from an area where acephate was not in use.

There are records of 85 samples taken by the Army Corps of Engineers in 1990 from streams in Mississippi and two records of samples taken in 1987 from streams in California. The actual value was known to be less than 10  $\mu\text{g/L}$ , but it is uncertain what the actual detection limit was and if samples were taken from an area where acephate was not in use.

There are records of 241 samples taken from canals in Florida by the South Florida Water Management District in 1987-1989. Methamidophos was analyzed for but not detected at 0.2  $\mu\text{g/L}$ ; however, it is uncertain what the actual detection limit was and if samples were taken from areas where methamidophos.

### **iii. Drinking Water Assessment**

#### **Groundwater Concentration Estimates**

The ground water EEC for both acute and chronic was calculated using SCI-GROW as previously described for the methamidophos use with the maximum yearly total application (nine applications at 1.0 lb methamidophos/A/application on tomatoes in Florida). The EEC was 0.029  $\mu\text{g/L}$ .

Because methamidophos is not persistent under aerobic conditions, very little methamidophos could be expected to leach to groundwater, as indicated by the SCI-GROW estimate. If any methamidophos did reach ground water, they might be expected to persist (anaerobic aquatic  $\text{DT}_{50}$  of 41 days for methamidophos; undetermined persistence for degradates DMPT and O-desmethyl methamidiphos).

As previously discussed, a majority of the use areas will have ground water that is less vulnerable to contamination than that in the areas used to derive the SCI-GROW estimate.

#### **Surface Water Concentration Estimates**

Using the PRZM-EXAMS model and available environmental fate data for methamidophos as previously described, EFED calculated the following Tier II upper tenth percentile EEC's for methamidophos in use in determining surface water drinking water exposure estimates from the uses with the maximum yearly total applications (4x aerial applications at 1 lb methamidophos/A/application on cotton and potatoes):



Surface water drinking water exposure estimates for Methamidophos		
Use site	Acute/peak EECs ( $\mu\text{g/L}$ )	Chronic (60-day) EECs ( $\mu\text{g/L}$ )
Cotton in Mississippi	40	2.9
Potatoes in Idaho	30	3.7

It should be remembered in interpreting these results that they represent the upper limit for possible exposure from these use patterns to aquatic environments at a single high exposure site. In actual practice, the true environmental concentrations will probably be less than indicated by this analysis because most sites will produce less loading to aquatic environments than these scenarios. In addition, surface-water-source drinking water tends to come from bodies of water that are substantially larger than a 1 hectare pond. Furthermore, any extrapolation from the EECs generated would be based on the assumption that essentially the whole basin containing the scenario modeled receives an application of the chemical. In virtually all cases, basins large enough to support a drinking water facility will contain a substantial fraction of area which does not receive the chemical. Furthermore, the persistence of the chemical near the drinking water facility is usually overestimated because there is always at least some flow in a river or turn over in a reservoir or lake.

### 3. Ecological Effects Toxicity Assessment

The following methamidophos toxicological endpoints will be used for determining risk quotients in this document:

- Oral acute bird: bobwhite 8 mg/kg
- Dietary bird: bobwhite quail 42 ppm
- Chronic bird: bobwhite 3 ppm (NOAEL due to egg thickness)
- Acute mammals: female rat 13 mg/kg
- Chronic mammals: mouse 10 ppm (2-generation, due to births, pup wt. and survival)
- Acute freshwater fish: trout 25 ppm
- Chronic freshwater fish: none available
- Acute freshwater invertebrates: daphnids 0.026 ppm; prawn 0.000042 ppm
- Chronic freshwater invertebrates: none available
- Acute estuarine fish: sheepshead minnow 5.6 ppm
- Chronic estuarine fish: none available
- Acute estuarine invertebrate: mysid shrimp 1.05 ppm; blue shrimp 0.00016 ppm
- Acute estuarine invertebrate (oyster): oyster 36 ppm
- Chronic estuarine invertebrate: none available

## a. Toxicity to Terrestrial Animals

### i. Birds, Acute and Subacute

An acute oral toxicity study using the technical grade of the active ingredient (TGAI) is required to establish the toxicity of methamidophos to birds. The preferred test species is either mallard duck (a waterfowl) or bobwhite quail (an upland gamebird). Results of this test are tabulated below.

Avian Acute Oral Toxicity

Species	% ai	LD <sub>50</sub> (mg/kg)	Toxicity Category	MRID No. Author/Year	Study Classification (1)
Northern bobwhite quail ( <i>Colinus virginianus</i> )	75	8	very highly toxic	00014094, 00109717 Fletcher, 1971	supplemental
Northern bobwhite quail ( <i>Colinus virginianus</i> )	75	10.1 (male) 11.0 (female)	highly toxic	00041313 Nelson et al, 1979	core
Mallard duck ( <i>Anas platyrhynchos</i> )	75	8.48	very highly toxic	0016000 Hudson et al 1984	core
Mallard duck ( <i>Anas platyrhynchos</i> )	75	29.5	highly toxic	00014095, 00109718 Fletcher, 1971	supplemental
Dark eyed junco ( <i>Junco hyemalis</i> )	73	8	very highly toxic	00093914 Zinkl et al, 1981	supplemental
Common grackle ( <i>Quiscalus quiscula</i> )	55	6.7 (mg ai/kg)	very highly toxic	00144428 Lamb, 1972	supplemental
Starling	75	10 (2)	very highly toxic	00146286 Schafer, 1984	ancillary
Redwing blackbird	75	1.78 (2)	very highly toxic	00146286 Schafer, 1984	ancillary

(1) Core (study satisfies guideline). Supplemental (study is scientifically sound, but does not satisfy guideline)

(2) Dermal LD<sub>50</sub> = 17.8 mg/kg for starling and 31.6 mg/kg for redwing blackbird.

Since the LD<sub>50</sub> falls in the range of 1 to 50 mg ai/kg, methamidophos is categorized as very highly to highly toxic to avian species on an acute oral basis. The guideline (71-1) is fulfilled (MRID 00014094, 00014095, 00041313, 0016000, 00093914, 00109717, 00109718, 00144428).

Two subacute dietary studies using the TGAI are required to establish the toxicity of methamidophos to birds. The preferred test species are mallard duck and bobwhite quail. Results of these tests are tabulated below.

### Avian Subacute Dietary Toxicity

Species	% ai	5-Day LC <sub>50</sub> (ppm)	Toxicity Category	MRID No. Author/Year	Study Classification
Northern bobwhite quail ( <i>Colinus virginianus</i> )	74	42	very highly toxic	00093904 Beavers & Fink, 1979	core
Northern bobwhite quail ( <i>Colinus virginianus</i> )	75	47.04	Very highly toxic	00014304, 00145655 00130823 Lamb & Bunke, 1977	supplemental
Northern bobwhite quail ( <i>Colinus virginianus</i> )	75	57.5	Highly toxic	00014064 Jackson, 1968	supplemental
Northern bobwhite quail ( <i>Colinus virginianus</i> )	75	59	highly toxic	44484404 Thompson-Cowley, 1981	supplemental
Mallard duck ( <i>Anas platyrhynchos</i> )	75	1302	slightly toxic	00041658, Nelson et al 1979	core
Mallard duck ( <i>Anas platyrhynchos</i> )	75	847.7	Moderately toxic	00130823, 00014304 00145655, Lamb & Bunke 1977	supplemental
Mallard duck ( <i>Anas platyrhynchos</i> )	70	1650	slightly toxic	44484403 Shapiro, 1981	supplemental
Japanese Quail	73	92	highly toxic	(1)	supplemental

(1) Smith, G.J., 1987. *Pesticide Use and Toxicology in Relation to Wildlife: Organophorous and Carbamate Compounds*. U.S. Dept. Of Interior, FWS Resource Publication 170. pg. 71.

Since the LC<sub>50</sub> falls in the range of <50 to 5000 ppm, methamidophos is categorized as slight toxic to very highly toxic to avian species on a subacute dietary basis. The guideline (71-2) is fulfilled (MRID 00093904, 00014304, 00014064, 00041658, 00146286).

### ii. Birds, Chronic

Avian reproduction studies using the TGAI are required for Methamidophos because the birds may be subject to repeated exposure to the pesticide, especially preceding or during the breeding season, field data has indicate that the pesticide is persistent in plant and invertebrate food items in potentially toxic amounts, and information derived from mammalian reproduction studies indicates reproduction in terrestrial vertebrates may be adversely affected by the anticipated use of the product. The preferred test species are mallard duck and bobwhite quail.

The above criteria were developed when the test was primarily used to determine effects of organochlorine pesticides and other persistent chemicals and reflect the concern for pesticides with chronic exposure patterns. The criteria would not necessary trigger a test for pesticides that pose risk of adverse reproductive effects from short term exposure. Several pesticides have been shown to reduce egg production within days after initiation of dietary exposure (Bennett and Bennett 1990, Bennett et al. 1991). Effects of eggshell quality (Bennett and

Bennett 1990, Haegele and Tucker 1974) and incubation and brood rearing behavior (Bennett et al. 1991, Brewer et al. 1988, Busby ) have also resulted from short-term pesticide exposures.

Results of these tests are tabulated below.

#### Avian Reproduction

Species/ Study Duration	% ai	NOAEC/LOAEC (ppm)	LOAEC Endpoints	MRID No. Author/Year	Study Classification
Northern bobwhite quail ( <i>Colinus virginianus</i> )	73	3/5	egg thickness	00014114 Beavers & Fink, 1978	core
Mallard duck ( <i>Anas platyrhynchos</i> )	73	>15	no effect	00014113 Fink, 1977	supplemental

Although the mallard study is supplemental, since the quail is a more sensitive species than the mallard, the study need not be repeated. The guideline (71-4) is fulfilled (MRID 00014114, 00014113).

### iii. Mammals, Acute and Chronic

Wild mammal testing is required on a case-by-case basis, depending on the results of lower tier laboratory mammalian studies, intended use pattern and pertinent environmental fate characteristics. In most cases, rat or mouse toxicity values obtained from the Agency's Health Effects Division (HED) substitute for wild mammal testing. These toxicity values are reported below.

#### Mammalian Toxicity

Species/ Study Duration	% ai	Test Type	Toxicity Value	Affected Endpoints	MRID No.
laboratory rat ( <i>Rattus norvegicus</i> )	75	acute oral	LD <sub>50</sub> = 21 mg/kg (m) LD <sub>50</sub> = 18.9 mg/kg (f)	mortality (ChE depression symptoms observed)	00014045
laboratory rat ( <i>Rattus norvegicus</i> )	95	acute oral	LD <sub>50</sub> = 15.6 mg/kg (m) LD <sub>50</sub> = 13.0 mg/kg (f)	mortality and ChE inhibition symptom observed	00014044
New Zealand white rabbit	72-76	primary dermal irritation	tox category I	0.5 ppm exposure for 24 hrs. Results in 66% of animals died within 48 hrs. ChE inhibition symptoms observed	00014222
New Zealand white rabbit	73	primary dermal irritation	tox category I	5/9 animals died within 24 hrs. After exposure to 0.1 ppm of 73% monitor dilution for 24 hrs. ChE symptoms observed shortly after exposure	00014220

## Mammalian Toxicity

Species/ Study Duration	% ai	Test Type	Toxicity Value	Affected Endpoints	MRID No.
New Zealand white rabbit	72-76	primary eye irritation	tox category I	0.1 ppm of technical applied to one eye results in death of one animal within 30 minutes. ChE syptoms observed in animals	00014221
New Zealand white rabbit	75	acute dermal	LD <sub>50</sub> = 118mg/kg (m) tox category I	mortality and ChE inhibition syptoms observed.	00014049
laboratory mouse ( <i>Mus musculus</i> )	95	acute oral	LD <sub>50</sub> = 16.2 mg/kg (f)	mortality (ChE depression syptoms observed)	00014047
laboratory mouse ( <i>Mus musculus</i> )	75	acute oral	LD <sub>50</sub> = 18 mg/kg (f)	mortality	00014048
laboratory mouse ( <i>Mus musculus</i> )	70.5	2-generation reproductive	NOAEL= 10 ppm (1) LOAEL= 33 ppm (1)	births, pup body weight, pup survival	00148455 41234301

(1) The study indicates that 10 ppm = 0.5 mg/kg/day and 33 ppm = 1.65 mg/kg/day.

An analysis of the results indicate that Methamidophos is categorized as highly toxic to small mammals on an acute oral and dermal basis. There does not appear to be a palatability problem in the above studies (personal communication Nancy McCarroll, HED, 2/10/98). The 10 ppm NOAEL of the 2-generation reproductive mouse study is for ecological risk.

## iv. Insects

A honey bee acute contact study using the TGAI is required for Methamidophos because its use (potato) will result in honey bee exposure. Results of this test are tabulated below.

### Nontarget Insect Acute Contact Toxicity

Species	% ai	LD <sub>50</sub> (µg/bee)	Toxicity Category	MRID No. Author/Year	Study Classification
Honey bee ( <i>Apis mellifera</i> )	63	1.37	Highly toxic	00036935 Atkins et al, 1975	core

An analysis of the results indicate that methamidophos is categorized as highly toxic to bees on an acute contact basis. The guideline (141-1) is fulfilled (MRID 00036935).

## b. Toxicity to Freshwater Aquatic Animals

### i. Freshwater Fish, Acute

Two freshwater fish toxicity studies using the TGAI are required to establish the toxicity of methamidophos to fish. The preferred test species are rainbow trout (a coldwater fish) and bluegill sunfish (a warmwater fish). Results of these tests are tabulated below.

### Freshwater Fish Acute Toxicity

Species	% ai	96-hour LC <sub>50</sub> (ppm)	Toxicity Category	MRID No. Author/Year	Study Classification
Rainbow trout (static) ( <i>Oncorhynchus mykiss</i> )	74	25	slightly toxic	00041312 Nelson & Roney, 1979	core
Rainbow trout (static) ( <i>Oncorhynchus mykiss</i> )	71	40 (ai)	slightly toxic	00144429 Hermann, 1980	not reviewed
Rainbow trout (static) ( <i>Oncorhynchus mykiss</i> )	40 (1)	37	slightly toxic	00144432 Lamb, 1972	not reviewed
Rainbow trout (static) ( <i>Oncorhynchus mykiss</i> )	75	51	slightly toxic	00014063 Schoenig, 1968	supplemental
Bluegill sunfish (static) ( <i>Lepomis macrochirus</i> )	74	34	slightly toxic	00041312 Nelson & Roney, 1979	core
Bluegill sunfish (static) ( <i>Lepomis macrochirus</i> )	40 (1)	31	slightly toxic	00144432 Lamb & Roney, 1972	not reviewed
Bluegill sunfish (static) ( <i>Lepomis macrochirus</i> )	75.4	45	slightly toxic	44484402 McCann, 1977	supplemental
Bluegill sunfish (static) ( <i>Lepomis macrochirus</i> )	75	46	slightly toxic	00014063 Schoenig, 1968	supplemental
Carp (static) ( <i>Cyprinus carpio</i> )	90	68 (2)	slightly toxic	05008361 Chin, 1979	supplemental

(1) Formulation of 40% is in propylene glycol. Author concludes that propylene glycol contributes to toxicity of the formulation.

(2) Sublethal doses affect growth rate of carp. Brain and liver AchE activities are depressed at 20 ppm concentrations for 48 hours.

Since the LC<sub>50</sub> falls in the range of 25 to 68 ppm, methamidophos is categorized as slightly toxic to freshwater fish on an acute basis. The guideline (72-1) is fulfilled (MRID 00041312, 00014063, 05008361, 00144429, 00144432).

### ii. Freshwater Fish, Chronic

A freshwater fish early life-stage test using the TGAI is not required for Methamidophos because the EEC in water is less than 0.01 of any acute LC<sub>50</sub> value.

### iii. Freshwater Invertebrates, Acute

A freshwater aquatic invertebrate toxicity test using the TGAI is required to establish the toxicity of methamidophos to aquatic invertebrates. The preferred test species is *Daphnia magna*. Results of this test are tabulated below.

## Freshwater Invertebrate Acute Toxicity

Species	% ai	48-hour LC <sub>50</sub> / EC <sub>50</sub> (ppm)	Toxicity Category	MRID No. Author/Year	Study Classification
Waterflea ( <i>Daphnia magna</i> )	74	0.026	Very highly toxic	00041311 Nelson & Roney 1979	core
waterflea ( <i>Daphnia magna</i> )	72	0.050	Very highly toxic	00014110 Wheeler 1978	core
waterflea ( <i>Daphnia magna</i> )	technical	0.027	Very highly toxic	00014305 Nelson & Roney 1977	supplemental
Freshwater Prawn ( <i>Macrobrachium rosenbergii</i> )	Tamaron 600 (600 g/L)	0.000042 (1) (42 ng/L)	Very highly toxic	(2)	supplemental

(1) This study used a static renewal every 24 hours. Each time the organisms were handled, mortality occurred in test samples and control. The life stage most similar to the *Daphnia magna* species' life stage during guideline testing is the postlarvae stage. Although the 48-hr. LC<sub>50</sub> value for the postlarvae stage is 30 ppt, the reviewer did not use that value for risk assessment because of the low survival rate in the controls after 24-hr. Therefore the 24 hr. LC<sub>50</sub> value (42 ppt) for the postlarvae stage is used. This study tested Zoea I, IV, VII and postlarve stages with LC<sub>50</sub> values for 24, 48 and 96 hr. These LC<sub>50</sub> values ranges from 0.22 ppt for 96 hr. Zoea IV stage up to 42 ppt for the 24 hr. postlarve stage.

(2) Juarez, L.M., J. Sanchez, 1989. Toxicity of the Organophosphorous Insecticide Methamidophos (O,S-Dimethyl Phosphoramidothioate) to Larvae of the Freshwater Prawn, *Macrobrachium rosenbergii* (DeMan) and the Blue Shrimp, *Penaeus stylirostris* Stimpson. Bull. Environ. Contam. Toxicol. (1989) 43:302-309.

Since the EC<sub>50</sub> falls in the range of < 1 ppm, methamidophos is categorized as very highly toxic to aquatic invertebrates on an acute basis. The guideline (72-2) is fulfilled (MRID 00041311, 00014110, 00014305).

### iv. Freshwater Invertebrate, Chronic

A freshwater aquatic invertebrate life-cycle test using the TGAI is required for Methamidophos since the end-use product is expected to be transported to water from the intended use site, and the following conditions have been met: (1) the pesticide is intended for use such that its presence in water is likely to be continuous or recurrent due to several applications, (2) aquatic acute LC<sub>50</sub> for freshwater prawn is less than 1 mg/L, and (3) the EEC in water is equal to or greater than 0.01 of freshwater prawn acute LC<sub>50</sub> value. The preferred test species is *Daphnia magna*.

No data have been submitted for this study. The guideline (72-4) is not fulfilled.

### c. Toxicity to Estuarine and Marine Animals

#### i. Estuarine and Marine Fish, Acute

Acute toxicity testing with estuarine/marine fish using the TGAI is required for Methamidophos because the end-use product is intended for direct application to the marine/estuarine environment or the active ingredient is expected to reach this environment

because of its use in coastal counties. The preferred test species is sheepshead minnow. Results of these tests are tabulated below.

#### Estuarine/Marine Fish Acute Toxicity

Species/Static or Flow-through	% ai	96-hour LC <sub>50</sub> (ppm) (measured/nominal)	Toxicity Category	MRID No. Author/Year	Study Classification
Sheepshead minnow ( <i>Cyprinodon variegatus</i> )	70.1	5.6	Moderately toxic	00144431 Larkin, 1983	core

Since the LC<sub>50</sub> falls in the range of 1-10 ppm, methamidophos is categorized as moderately toxic to estuarine/marine fish on an acute basis. The guideline (72-3a) is fulfilled (MRID 00144431).

#### ii. Estuarine and Marine Fish, Chronic

An estuarine/marine fish early life-stage test using the TGAI is not required for Methamidophos because the lack of persistence and the EEC in water is less than 0.01 of any acute LC<sub>50</sub> value.

#### iii. Estuarine and Marine Invertebrates, Acute

Acute toxicity testing with estuarine/marine invertebrates using the TGAI is required for Methamidophos because the active ingredient is expected to reach this environment because of its use of cotton and tomatoes in coastal counties. The preferred test species are mysid shrimp and eastern oyster. Results of these tests are tabulated below.

#### Estuarine/Marine Invertebrate Acute Toxicity

Species/Static or Flow-through	% ai.	96-hour LC <sub>50</sub> /EC <sub>50</sub> (ppm)	Toxicity Category	MRID No. Author/Year	Study Classification
oyster ( <i>Crassostrea virginica</i> )	72.9	36	slightly toxic	40088601	supplemental
Mysid shrimp ( <i>Americamysis bahia</i> )	technical	1.05	Moderately toxic	00144430 Larkin, 1983	core
Blue shrimp ( <i>Penaeus stylirostris</i> )	Tamaron 600 (600 g/L)	0.00016 (1) (160 ppt)	very highly toxic	(2)	supplemental

(1) This study used a static renewal every 24 hours. Each time the organisms were handled, mortality occurred in test samples and control. The life stage most similar to the mysid shrimp life stage during guideline testing is the mysis stage. Although the 36-hr LC<sub>50</sub> value for the mysis stage is 8 ppt, the reviewer did not use that value for risk assessment because of the low survival rate in the controls after 24-hr. Therefore the 24 hr. LC<sub>50</sub> value (160 ppt) for the mysis stage is used. This study tested the shrimp at the naupliae, protozoa, and mysis stage and determined LC<sub>50</sub> values for each stage at 24 and 36 hr. The LC<sub>50</sub> values range from 0.6 ppt for 36 hr. Naupliae stage to 800 ppt for 12 hr. mysis stage.

(2) Juarez, L.M., J. Sanchez, 1989. Toxicity of the Organophosphorous Insecticide Methamidophos (O,S-Dimethyl Phosphoramidothioate) to Larvae of the Freshwater Prawn, *Macrobrachium rosenbergii* (DeMan) and the Blue Shrimp, *Penaeus stylirostris* Stimpson. Bull. Environ. Contam. Toxicol. (1989) 43:302-309.



Since the  $LC_{50}/EC_{50}$  falls in the range of <1 to 100 ppm, methamidophos is categorized as highly toxic to slightly toxic to estuarine/marine invertebrates on an acute basis. The guideline (72-3b and 72-3c) is fulfilled.

#### **iv. Estuarine and Marine Invertebrate, Chronic**

An estuarine/marine invertebrate life-cycle toxicity test using the TGAI is required for Methamidophos because the end-use product is expected to be transported to this environment from the intended use site (cotton and tomato), and the following conditions have been met: (1) the pesticide is intended for use such that its presence in water is likely to be recurrent regardless of toxicity due to several applications and (2) aquatic acute  $LC_{50}$  for mysid shrimp is 1 mg/L. The preferred test species is mysid shrimp. The guideline (72-4) is not fulfilled.

#### **d. Toxicity to Plants**

##### **i. Terrestrial Plants**

Currently, terrestrial plant testing is not required for pesticides other than herbicides except on a case-by-case basis (*e.g.*, labeling bears phytotoxicity warnings incident data or literature that demonstrate phytotoxicity). Methamidophos is known to cause phytotoxicity to terrestrial plants. Methamidophos is also a more toxic degradate of methamidophos. There is concern that the methamidophos may be the cause of this phytotoxicity rather than the methamidophos. Therefore, a tier I seedling emergence and vegetative vigor tests (122-1) are needed to assess risk to non-target terrestrial plants.

For seedling emergence and vegetative vigor testing the following plant species and groups should be tested: (1) six species of at least four dicotyledonous families, one species of which is soybean (*Glycine max*) and the second is a root crop, and (2) four species of at least two monocotyledonous families, one of which is corn (*Zea mays*).

##### **ii. Aquatic Plants**

Currently, aquatic plant testing is not required for pesticides other than herbicides and fungicides except on a case-by-case basis (*e.g.*, labeling bears phytotoxicity warnings, incident data or literature that demonstrate phytotoxicity). EFED is not aware of any phytotoxicity of methamidophos to aquatic plants. Therefore, phytotoxicity testing for non-target aquatic plants is not needed at this time.

### e. Terrestrial Field Testing and Literature Findings

Menkens, G. et al. 1989. MRID 41548801.

This supplemental residue study is an aerial application made 4 times over 7-9 day interval schedule with application of 1.0 lb ai/A using Monitor 4 on potatoes in Idaho.

<u>Crops</u>	<u>Mean (ppm)</u>	<u>Maximum (ppm)</u>
Potato leaves	82	161
Non-crop foliage (drift)	4	19
Non-crop foliage (overruns)	3.5	15
Non-crop inflorescence (drift and overruns)	4.3	8.5
Soil	1.1	1.3
Flying insects (crop)	18.6	53.0
Flying insects (drift and overruns)	1.1	3.1
Ground insects (crop)	none found	none found
Ground insects (drift and overruns)	0.9	4.2

The study was considered supplemental because of the compositing of samples. The registrant-calculated methamidophos half-life on foliage is 2.2 days for field interior sweep net invertebrates and 5.5 days for foliage.

Menkens, G. et al. 1989. MRID 41548802.

This supplemental residue study is an aerial application of Monitor 4 over sugar beets in California with 1.0 lb ai/A with 5 applications on a 14 day spray schedule. The following table provides residue information:

<u>Crops</u>	<u>Mean (ppm)</u>	<u>Maximum (ppm)</u>
Sugar beets leaves	46.4	69
Non-crop foliage (drift)	39.4	80
Non-crop foliage (overruns)	31	126
Non-crop inflorescence (drift and overruns)	15.3	50
Crop inflorescence	49.3	89
Soil (field)	0.54	1.2
Soil (drift)	0.25	0.80
Flying insects (crop)	13	23
Flying insects (drift)	3.6	7.6
Flying insects (overruns)	9.6	13
Ground insects (crop)	23.4	70

Ground insects (drift	23.3	59
Ground insects (overruns)	15.8	53

The author calculated half-lives for the residues, which ranged from 3 days for foliage to 23 days in soil. The study was considered supplemental because the residues were composited.

Perritt, J.E., D.A. Palmer, H. Krueger, and M. Jaber. 1990. MRID 41548803.

This supplemental residue study was an aerial application on cotton of Monitor 4 at 1 lb ai/A with 8 day intervals applied 7 times in Alabama. The following table provides residue information:

<u>Residue Medium</u>	<u>Mean (ppm)</u>	<u>Maximum (ppm)</u>
Crop foliage	132	452
Non-crop foliage	35	154
Soil invertebrates	1.6	16
Soil invertebrates (crop)	1.4	4
Flying insects	20	43
Soil	0.86	2.8
Small mammals (fur and skin)	>0.10	2.9 (hisip cotton rat)

EFED concluded that thirty-four casualties were found during the study at eight test fields. Ten of the casualties were found during preapplication periods, and six were found post application under circumstances that did not indicate that exposure to Monitor 4 Spray was a potential cause of mortality. Only one casualty was found under circumstances suggesting that it was likely treatment related. Cause of death could not be determined for another seventeen casualties, but exposure to Monitor 4 Spray could not be precluded as a potential cause of mortality.

Blus, L.J., C.S. Stanley, C.J. Henny, G.W. Pendleton, T.H. Craig, E.H. Craig, D.K. Halford. 1989. *Effects of organophosphorous Insecticides on Sage Grouse in Southeastern Idaho*. J. Wildl. Manage. 53(4): 1139-1146.

Die-offs of sage grouse (*Centrocercus urophasiannus*) were noted in 1981 near potato fields sprayed with methamidophos. Five intoxicated sage grouse were collected and inhibition of brain ChE activity ranged from normal to 61%.

Data collected in 1983 show brain ChE depressions of 40-65% in sage grouse collected near potato fields shortly after spraying with methamidophos. Although most of the mortalities occurred from the nearby alfalfa fields, 2 depredated grouse contained 39%

and 43% ChE inhibition of which one had 18  $\mu\text{g/g}$  of methamidophos in the crop of the grouse. The authors of the study concluded that since "the 2 depredated sage grouse found in or near the potato field sprayed with methamidophos had brain ChE activity depressed <50%, recent experimental evidence supports the probability that their deaths resulted from the spraying."

This study radioed-collared sage grouse near potato and alfalfa fields. Surveys and radio tracking found that the grouse frequented the potato and alfalfa fields as well as the non-cropland sagebrush up to 4 Km away. Many of the grouse were observed using the potato fields extensively. After spraying, the crops of the grouse collected as dead or shot in the potato fields contained foliage of weeds and small amounts of insect materials. Two radio-tagged sage grouse were found in or near a potato field the day it was sprayed with methamidophos. One of the dead grouse was found to contain 18 ppm methamidophos detected in the crop contents. This finding rebukes some of the popular ideas that the odor of methamidophos would offend the birds to cause them to look for alternative sources of food. Predation on the intoxicated sage grouse was noted. Approximately 35% of the intoxicated grouse may have survived if they had not been depredated.

Although methamidophos half-life is <4 days, low levels of methamidophos may persist for several weeks in plants. Thus, intoxicated grouse may be exposed to additional residues when ChE reversal is initiated and the grouse resumes feeding on the contaminated foliage.

According to the authors, these findings suggest that OP insecticides may adversely affect sage grouse populations whose summer range include cropland. The authors also noted that this study may provide some evidence for the claim that pesticides are partly responsible for the declining populations of upland game birds in the U.S. and Europe.

Temple, D. And D. Palmer, 1995. *An Evaluation of the Effects of Monitor 4 Liquid Insecticide on the Nestling Ecology of European Starlings Associated with Cabbage Fields in East-Central Wisconsin.* MRID 43740301.

This study concludes that methamidophos applications (1 lb ai/A) have equal or less adverse impact on avian reproduction than the permethrin insecticide (which is practically not toxic to vertebrates) which was used as the control. This study was limited to the European Starling reproduction and did not address the other species in the area. This study also is designed not to look at acute toxicity but focused on reproductive endpoints. There was some avian mortalities in the study but it is not apparent if these mortalities are chemical related. Fourteen percent of the post application blood samples  $\geq 50\%$  ChE inhibition. These findings suggest that animals

that have greater exposure to contaminated food, or are more sensitive to OP pesticides than are starlings, could die from ChE inhibition.

Hussain, M.A., R.B. Mohamad, P.C. Oloffs. 1985. *Studies on the Toxicity, Metabolism, and Anticholinesterase Properties of Acephate and Methamidophos*. J. Environ. Sci. Health, B20 (1), p. 129-147. (1985).

Backswimmer (aquatic insect) and rainbow trout have ChE inhibition for 4 hours before recovery begins. This suggests that aquatic insects and fish that are exposed to acephate/methamidophos may not recover by spontaneous reactivation of AchE. Therefore aquatic insects or fish may be stressed for some time because of physiological effects caused by inhibition of AchE.

### **Terrestrial Incidents Reported to EPA**

- I002680-001. California Dept. Of Fish and Game reports in 10/27/87 that 4 California quail were found dead in a farm yard near a broccoli field. Methamidophos and oxydem-methyl were found as residues on broccoli leaves in the crops of the dead birds. The nearby broccoli field was sprayed with the above chemicals.
- An incident was reported to EFED by the Wisconsin Dept. Of Agriculture, Trade and Consumer Protection concerning a cabbage field. On July, 1980, nine dead starlings and house sparrows were found dead in a residential yard. Further search of the residential area revealed another 4 house sparrows, a killdeer and a barn swallow. A cabbage field nearby was sprayed with Monitor 4. Lab analysis showed methamidophos residues in 4 sparrows and a killdeer. Foliage samples were taken and methamidophos residues were detected on the following plants: willow tree leaves (0.075 ppm) 80-100 feet from cabbage field, maple leaves (1.3 ppm) 150 feet from field, six other samples within and around the edges of the field (ranges from 0.08 to 24.0 ppm), grass (upto 57 ppm), and walnut leaves (11 ppm) of methamidophos. The application was made at 6:30 pm with wind speeds measured at 3.5 to 6 mph. There was also a cat found dead in the field from exposure to methamidophos. Brain ChE inhibition in the birds were found to range from 39% to 76% with 0.6 to 3.8 ppm residues in the brain.
- EPA research lab at Corvallis, Oregon reported to EFED on 3/16/87 of a general sage grouse population decline in Idaho due to habitat destruction. OP insecticides were also being blamed for the die-offs and the population declines for the pass 10 years. There was no proof presented of the OPs contribution to the population decline until 8/81 when sage grouse were collected. ChE assays found uniform brain ChE inhibition upto 61%. In 1983, survey of potato farmers show that there has been several sage grouse and other wildlife die-offs on their property. Several farmers have indicated a disenchantment with the chemical sprays because of the wildlife causalties. In 1983, the EPA lab found that several birds in and near potato

fields had brain ChE inhibition ranges from 50% to 65% after methamidophos spraying in the potato fields.

- Chevron Chemical Co. reported an incident concerning a cauliflower field sprayed with Monitor 4 in 4/24/85. Approximately 100 to 200 starlings were died from ingesting invertebrates from soil and foliage contaminated with methamidophos. The digestive tracts contained 5.1 ppm of methamidophos residues. The forty acre cauliflower field was sprayed by ground application.

- In Los Banos, CA, during the summer of 1997, more than 700 colonies of bees were damaged or destroyed from alfalfa sprayed with Monitor, Dorsban, and Dibrom. Residues were not collected from the bees due to urgency of getting the trucks to move the colonies out of harms way by the beekeepers. By the time that bees were collected for analysis, the residues were not detectable.

### 3. Exposure and Risk Characterization

Risk characterization integrates the results of the exposure and ecotoxicity data to evaluate the likelihood of adverse ecological effects. The means of this integration is called the quotient method. Risk quotients (RQs) are calculated by dividing exposure estimates by acute and chronic ecotoxicity values.

$$RQ = \text{EXPOSURE/TOXICITY}$$

RQs are then compared to OPP's levels of concern (LOCs). These LOCs are used by OPP to analyze potential risk to nontarget organisms and the need to consider regulatory action. The criteria indicate that a pesticide used as directed has the potential to cause adverse effects on nontarget organisms. LOCs currently address the following risk presumption categories: (1) **acute high** -- potential for acute risk is high; regulatory action may be warranted in addition to restricted use classification, (2) **acute restricted use** -- the potential for acute risk is high, but may be mitigated through restricted use classification, (3) **acute endangered species** - endangered species may be adversely affected, and (4) **chronic risk** - the potential for chronic risk is high regulatory action may be warranted. Currently, EFED does not perform assessments for chronic risk to plants, acute or chronic risks to nontarget insects, or chronic risk from granular/bait formulations to birds or mammals.

The ecotoxicity test values (measurement endpoints) used in the acute and chronic risk quotients are derived from required studies. Examples of ecotoxicity values derived from short-term laboratory studies that assess acute effects are: (1)  $LC_{50}$  (fish and birds), (2)  $LD_{50}$  (birds and mammals), (3)  $EC_{50}$  (aquatic plants and aquatic invertebrates) and (4)  $EC_{25}$  (terrestrial plants). Examples of toxicity test effect levels derived from the results of long-term laboratory studies that assess chronic effects are: (1) LOEC (birds, fish, and aquatic invertebrates), (2) NOAEC (birds, fish and aquatic invertebrates), and (3) MATC (fish and

aquatic invertebrates). For birds and mammals, the NOAEC generally is used as the ecotoxicity test value in assessing chronic effects, although other values may be used when justified. Generally, the MATC (defined as the geometric mean of the NOAEC and LOAEC) is used as the ecotoxicity test value in assessing chronic effects to fish and aquatic invertebrates. However, the NOAEC is used if the measurement end point is production of offspring or survival.

Risk presumptions and the corresponding RQs and LOCs, are tabulated below.

#### Risk Presumptions for Terrestrial Animals

Risk Presumption	RQ	LOC
<b>Birds</b>		
Acute High Risk	EEC <sup>1</sup> /LC50 or LD50/sqft <sup>2</sup> or LD50/day <sup>3</sup>	0.5
Acute Restricted Use	EEC/LC50 or LD50/sqft or LD50/day (or LD50 < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC50 or LD50/sqft or LD50/day	0.1
Chronic Risk	EEC/NOEC	1
<b>Wild Mammals</b>		
Acute High Risk	EEC/LC50 or LD50/sqft or LD50/day	0.5
Acute Restricted Use	EEC/LC50 or LD50/sqft or LD50/day (or LD50 < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC50 or LD50/sqft or LD50/day	0.1
Chronic Risk	EEC/NOEC	1

<sup>1</sup> abbreviation for Estimated Environmental Concentration (ppm) on avian/mammalian food items

<sup>2</sup>  $\frac{\text{mg}}{\text{ft}^2}$       <sup>3</sup>  $\frac{\text{mg of toxicant consumed}}{\text{day}}$   
 LD50 \* wt. of bird      LD50 \* wt. of bird

#### Risk Presumptions for Aquatic Animals

Risk Presumption	RQ	LOC
Acute High Risk	EEC <sup>1</sup> /LC50 or EC50	0.5
Acute Restricted Use	EEC/LC50 or EC50	0.1
Acute Endangered Species	EEC/LC50 or EC50	0.05
Chronic Risk	EEC/MATC or NOEC	1

<sup>1</sup> EEC = (ppm or ppb) in water

## Risk Presumptions for Plants

Risk Presumption	RQ	LOC
Non-Target Plants in Terrestrial and Semi-Aquatic Areas		
Acute High Risk	EEC <sup>1</sup> /EC25	1
Acute Endangered Species	EEC/EC05 or NOEC	1
Aquatic Plants		
Acute High Risk	EEC <sup>2</sup> /EC50	1
Acute Endangered Species	EEC/EC05 or NOEC	1

<sup>1</sup> EEC = lbs ai/A

<sup>2</sup> EEC = (ppb/ppm) in water

### a. Exposure and Risk to Nontarget Terrestrial Animals

For pesticides applied as a nongranular product (*e.g.*, liquid, dust), the estimated environmental concentrations (EECs) on food items following product application are compared to LC50 values to assess risk. The predicted 0-day maximum and mean residues of a pesticide that may be expected to occur on selected avian or mammalian food items immediately following a direct single application at 1 lb ai/A are tabulated below.

Estimated Environmental Concentrations on Avian and Mammalian Food Items (ppm) Following a Single Application at 1 lb ai/A)

Food Items	EEC (ppm) Predicted Maximum Residue <sup>1</sup>	EEC (ppm) Predicted Mean Residue <sup>1</sup>
Short grass	240	85
Tall grass	110	36
Broadleaf/forage plants and small insects	135	45
Fruits, pods, seeds, and large insects	15	7

<sup>1</sup> Predicted maximum and mean residues are for a 1 lb ai/a application rate and are based on Hoerger and Kenaga (1972) as modified by Fletcher *et al.* (1994).

Predicted residues (EECs) resulting from multiple applications are calculated in various ways. For the purpose of Methamidophos the following procedure was used: using the maximum Kenaga nomogram as modified by Fletcher with a FATE program that uses first order degradation.



## i. Birds

The acute risk quotients for broadcast applications of nongranular products are tabulated below.

Methamidophos Avian Acute and Chronic Risk Quotients for Multiple Applications (ground applications) of Nongranular Products (Broadcast) Based on a Northern bobwhite quail (*Colinus virginianus*) LC<sub>50</sub> of 42 ppm and a Northern bobwhite quail (*Colinus virginianus*) of 3 ppm NOAEC.

Site Appl. Rate/No. Appl./Interval	Food Items	Maximum EEC <sup>2</sup> (ppm)	Peak Mean EEC <sup>2</sup> (ppm)	Acute RQ (EEC/LC <sub>50</sub> )	Chronic RQ (EEC/NO AEC)	Average EEC over application period
Tomato 1/5/7	Ground and Aerial					
	Short Grass	256	91	6.10	30.22	37
	Tall Grass	117	38	2.79	12.80	16
	Broad Leaf	144	48	3.43	16.00	19
	Seed/ Fruit	16	7	0.38	2.49	3
Tomato <sup>1</sup> 1/9/5	Ground and Aerial					
	Short Grass	278	99	6.63	32.87	57
	Tall Grass	128	42	3.04	13.92	24
	Broad Leaf	157	52	3.73	17.4	30
	Seed/ Fruit	17	8	0.41	2.71	5
Potatoes, Cotton 1/4/7	Ground and Aerial					
	Short Grass	256	91	6.10	30.22	36
	Tall Grass	117	38	2.79	12.80	15
	Broad Leaf	144	48	3.43	16.00	19
	Seed/ Fruit	16	7	0.38	2.49	3

<sup>1</sup> Tomato in Florida only

<sup>2</sup> The EEC is based on Kenaga as modified by Fletcher and on the FATE model. The peak mean value is the highest value after enter the mean value from Fletcher.

An analysis of the results indicate that for multiple broadcast applications of methamidophos, avian acute high, restricted use, and endangered species levels of concern are exceeded at registered maximum application rates equal to 1 pound ai/A, respectively. Supplemental data for redwing blackbird (LD<sub>50</sub> = 1.78 mg/kg) suggest risk to passerines and other small birds may be much higher compared with the bobwhite (LD<sub>50</sub> = 8 mg/kg).

## ii. Mammals

### Acute Risk to Mammals

Estimating the potential for adverse effects to wild mammals is based upon EEB's draft 1995 SOP of mammalian risk assessments and methods used by Hoerger and Kenaga (1972) as modified by Fletcher *et al.* (1994). The concentration of methamidophos in the diet that is expected to be acutely lethal to 50% of the test population (LC<sub>50</sub>) is determined by dividing the LD<sub>50</sub> value (usually rat LD<sub>50</sub>) by the % (decimal of) body weight consumed. A risk quotient is then determined by dividing the EEC by the derived LC<sub>50</sub> value. Risk quotients are calculated for three separate weight classes of mammals (15, 35, and 1000 g), each presumed to consume

four different kinds of food (grass, forage, insects, and seeds). The acute risk quotients for broadcast applications of nongranular products are tabulated below.

Mammalian (Herbivore/Insectivore) Acute Risk Quotients Multiple Applications of Nongranular Products (Broadcast)  
Based on a laboratory rat (*Rattus norvegicus*) LD<sub>50</sub> of 13 mg/kg.

Site/ App. Method/ Rate in lbs ai/A (No. of Apps.)	Body Weight (g)	% Body Weight Consumed	Rat LD <sub>50</sub> (mg/kg)	EEC (ppm) Short Grass	EEC (ppm) Forage & Small Insects	EEC (ppm) Large Insects	Acute RQ <sup>1</sup> Short Grass	Acute RQ Forage & Small Insects	Acute RQ Large Insects
Tomatoes									
1 (5)	15	95	13	256	144	16	18.7	10.5	1.2
1 (5)	35	66	13	256	144	16	13.0	7.3	0.8
1 (5)	1000	15	13	256	144	16	2.6	1.7	0.2
Tomatoes <sup>1</sup>									
1(9)	15	95	13	278	157	17	20.3	11.5	1.2
1(9)	35	66	13	278	157	17	14.1	8.0	0.9
1(9)	1000	15	13	278	157	17	3.2	1.8	0.2
Potatoes, Cotton									
1(4)	15	95	13	256	144	16	18.7	10.5	1.2
1(4)	35	66	13	256	144	16	14.1	11.5	0.9
1(4)	1000	15	13	256	144	16	2.6	1.7	0.2

<sup>1</sup> Tomatoes in Florida only.

Mammalian (Granivore) Acute Risk Quotients for Multiple Applications of Nongranular Products (Broadcast) Based  
on a laboratory rat (*Rattus norvegicus*) LD<sub>50</sub> of 13 mg/kg.

Site/ App. Method/ Rate in lbs ai/A (No. of Apps.)	Body Weight (g)	% Body Weight Consumed	Rat LD <sub>50</sub> (mg/kg)	EEC (ppm) Seeds	Acute RQ <sup>1</sup> Seeds
Tomatoes					
1 (5)	15	21	13	16	0.3
1 (5)	35	15	13	16	0.2
1 (5)	1000	3	13	16	<0.1
Tomatoes <sup>1</sup>					
1(9)	15	21	13	17	0.3
1(9)	35	15	13	17	0.2
1(9)	1000	3	13	17	<0.1
Potatoes, Cotton					
1(4)	15	21	13	16	0.3
1(4)	35	15	13	16	0.2
1(4)	1000	3	13	16	<0.1

<sup>1</sup> Tomatoes in Florida only.

An analysis of the above results indicate that for broadcast applications of nongranular methamidophos the following mammalian acute high risk, restricted use (R), and endangered species (ES) levels of concern (LOC) are exceeded:

Crops	herbivore/insectivore.....			granivore.....		
	15 gram	35 gram mammal	1000 gram mammal	15 gram	35 gram	1000 gram
Tomatoes, Potatoes, Cotton	All LOCs	All LOCs	All LOCs	R, ES	R, ES	No LOCs
Tomatoes in Florida	All LOCs	All LOCs	All LOCs	R, ES	R, ES	No LOCs

### Chronic Risk to Mammals

Chronic risk quotients can be calculated based on the Fletcher mean residues on food items. Mean residues result from the pesticide being applied repeatedly, but degrading over the course of time from the first application to the last application. Avian chronic risk quotients based on average residues for multiple, broadcast applications of non-granular products are tabulated below.

Mammalian Chronic Risk Quotients for Multiple Applications of Nongranular Methamidophos (Broadcast) Based on a laboratory mouse (*Mus musculus*) NOEC of 10 ppm in a 2-generation reproductive.

Site	Application Rate in lbs ai/A (No. of Apps)	Food Items	Peak Mean EEC <sup>1</sup> (ppm)	NOAEC (ppm)	Chronic RQ (Ave. EEC/NOAEC)	Average EEC over application period
Tomatoes	1 (5)	Short Grass	90.67	10	9.10	37.00
		Tall Grass	38.40	10	3.80	16.00
		Broadleaf Plants & Insects	48.00	10	4.80	19.00
		Seeds	7.47	10	0.75	3.00
Tomatoes <sup>2</sup>	1 (9)	Short Grass	98.61	10	9.86	57.00
		Tall Grass	41.76	10	4.18	24.00
		Broadleaf Plants & Insects	52.20	10	5.22	30.00
		Seed	8.1	10	0.08	5
Potatoes, Cotton	1 (4)	Short Grass	90.67	10	9.07	36
		Tall Grass	38.40	10	3.84	15
		Broadleaf Plants & Insects	48.00	10	4.80	19
		Seed	7.47	10	0.75	3

<sup>1</sup> The EEC is based on Kenaga as modified by Fletcher and on the FATE model. The peak mean value is the highest value after enter the mean value from Fletcher.

<sup>2</sup> Tomato in Florida only

An analysis of the results indicate that for a single broadcast application of nongranular products, mammalian acute and chronic high risk, restricted use, and endangered species levels of concern are exceeded at registered maximum application rates equal to or above one lb ai/A.

### iii. Insects

Currently, EFED does not assess risk to nontarget insects. Results of acceptable studies are used for recommending appropriate label precautions. Methamidophos is highly toxic to bees and other beneficial insects.

### b. Risk to Nontarget Aquatic Animals

EECs calculated using the GENERIC Expected Environmental Concentration Program (GENEEC) are used for assessing acute and chronic risks to aquatic organisms. Acute risk assessments are performed using peak EEC values for single and multiple applications. Chronic risk assessments are performed using the 21-day EECs for invertebrates and 56-day EECs for fish. Details on the GENEEC model assumptions and the environmental fate parameters used in the model are discussed in Section 2.d.ii. EECs (in parts per million) for methamidophos applications to various crops are tabulated below.

Methamidophos Estimated Environmental Concentrations (EECs) For Aquatic Exposure

Site	Application Method	Appl. Rate (lbs ai/A)	# of Appls./ Interval Between Appls.	Initial (PEAK) EEC (ppb)	21-day average EEC (ppb)	56-day average EEC (ppb)
<b>GENEEC</b>						
Tomatoes	ground .....	1	5/7	61	48	33
	aerial.....	1	5/7	63	50	34
Tomatoes (Florida)	ground.....	1	9/5	67	53	36
	aerial.....	1	9/5	77	61	42
Potatoes, Cotton	ground.....	1	4/7	61	48	33
	aerial....	1	4/7	65	51	35
<b>PRZM-EXAMS<sup>1</sup></b>						
Cotton	aerial.....	1	4/7	40	6.8	2.9
Potatoes	aerial.....	1	4/7	30	8	3.7

<sup>1</sup> Values for PRZM-EXAMS were presented in Section 2.d. They are presented here for purposes of comparison.

## ii. Aquatic Animal Species

Acute and chronic risk quotients are tabulated below.

Methamidophos Acute Risk Quotients for Freshwater Fish (rainbow trout  $LC_{50}$  = 25000 ppb), Aquatic Invertebrates (*Daphnia magna*  $LC_{50}$  = 26 ppb), Estuarine Fish (*Cyprinodon variegatus*  $LC_{50}$  = 5600 ppb), and Estuarine/Marine Invertebrates (*Americamysis bahia*  $LC_{50}$  = 1050 ppb).

Site/Application Method/Rate in lbs ai/A (No. of Apps.)	Type of Application	Freshwater Acute RQ		Estuarine Acute RQ	
		Rainbow trout	<i>Daphnia Magna</i>	Sheepshead minnow	<i>Americamysis bahia</i> (Mysid shrimp)
Tomatoes	ground.....	<0.05	2.3	<0.05	<0.05
	aerial.....	<0.05	2.4	<0.05	<0.05
Tomatoes	ground.....	<0.05	2.6	<0.05	0.06
	aerial....	<0.05	3.0	<0.05	0.07
Cotton,	ground....	<0.05	2.3	<0.05	<0.05
	aerial....	<0.05	1.5	<0.05	<0.05
Potatoes	ground....	<0.05	2.3	<0.05	<0.05
	aerial....	<0.05	1.1	<0.05	<0.05

An analysis of the results indicate that aquatic acute high risk, restricted use, and endangered species levels of concern are exceeded for freshwater and estuarine invertebrates fish at a registered maximum application rate equal to or above one lb ai/A. There are no chronic risk assessment since there are no chronic data for aquatic species.

### d. Risk to Nontarget Plants

There are no non-target plant risk assessment since there are no plant toxicity data.

## 5. Endangered Species

Endangered species of birds, mammals, reptiles, amphibians, and freshwater and estuarine invertebrates LOCs are exceeded for Methamidophos.

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.

## **6. Risk Characterization**

Risk characterization is a qualitative assessment of risks that expands on the environmental fate and ecological effects risk assessments. It includes discussions of other factors that may affect risk but were not considered in the quantitative risk assessments.

### **Use Characterization**

Methamidophos is a restricted-use insecticide with use sites limited to cotton, potatoes, and tomatoes. Methamidophos is applied as a post-emergence foliar application during the growing season. Its pesticidal activity is locally systemic, with a long-lasting biological effect (up to 14 days). Crops with a high percentage of acreage treated are fresh tomatoes (46%) and potatoes (21%). The trend shows increasing cotton acreage treated by methamidophos from a current treated acreage of 1% (BEAD usage data up to 1996) to a projected usage of 10% (registrant-provided information, 1997).

Please see Section 1 for details on poundages applied and the uses considered in the risk assessment.

### **Environmental fate assessment**

Methamidophos is not persistent in aerobic environments but may be persistent in anaerobic aquatic environments where it will be associated with the aqueous phase. Aerobic soil metabolism is the main degradative process for methamidophos ( $t_{1/2} < 1$  day) with the final degradates being carbon dioxide and unextractable residues. Methamidophos is very soluble (at nearly kg/L) and highly mobile ( $K_d < 0.1$ ), so it can move to aquatic environments by runoff; its persistence in aquatic environments is not known.

### **Ground Water**

Based on environmental fate data, methamidophos is not persistent but is very mobile in the soil. The environmental fate characteristics of methamidophos and ground water modeling support the conclusion that methamidophos is not expected to leach to ground water. Results from the SCI-GROW screening model predicted that the maximum chronic concentration of methamidophos in shallow ground water is not expected to exceed  $0.03 \mu\text{g/L}$ . This is considered to be an "upper bound" for residues of methamidophos in ground water.

Methamidophos was modeled using a 9 lb ai/acre/season application to tomatoes. Typical use rates of methamidophos for potatoes and cotton are less than this amount; therefore, any methamidophos residues reaching ground water should be less than predicted.

This prediction is supported by the ground water monitoring data for methamidophos, in which there were only four detections of methamidophos in ground water reported out of 779 wells sampled (PGWDB); when wells with detections were resampled the next year, none showed any residues. Results were reported for 1303 samples in STORET with no detections reported; however, uncertainty is high for the STORET data because it is not known what the actual detection limit of the analytical method was and whether samples were taken in areas where methamidophos was not in use.

### **Surface Water**

Modeling results suggest methamidophos will persist for short periods in surface waters following transport by surface runoff or spray drift. However, modeling estimates are conservative, due to the lack of data on the persistence in aquatic environments. Methamidophos will be found primarily in the water column because binding to suspended and bottom sediments is not expected, due to the low  $K_d$  ( $<0.1$ ). Monitoring data show that there are no records for methamidophos sampling from lakes, ocean, estuary, or reservoir sites; there are records of 11 sediment and 241 water samples from canals and 87 water samples from ambient streams with no detections reported. However, it is uncertain what the actual detection limit was and if samples were taken from an area where methamidophos was not in use.

The Tier 2 modeling assumes a single 10-hectare field generates runoff following pesticide application made on the entire field during a single day. This runoff is then collected in a 1-hectare pond with no outlet. Other surface water bodies may exhibit considerable flow-through (rivers, streams) or turnover (reservoirs, lakes). Methamidophos concentrations in such waters would be expected to be considerably less than the predicted values; however, the amount of dilution is unknown.

Aquatic invertebrates are very sensitive to methamidophos. Furthermore, risk to freshwater invertebrates from methamidophos is at least 5X greater than that for marine and estuarine invertebrates due to the apparent greater sensitivity of freshwater species.

Methamidophos is used in areas where runoff from agricultural fields could flow into freshwater rivers, streams, and inland lakes. It is possible that methamidophos residues may be diluted to insignificant amounts by the time they reached these water bodies; in addition, methamidophos may degrade en route.

Methamidophos is used in areas where runoff from agricultural fields could flow into estuaries. It is possible that methamidophos residues may be diluted to insignificant amounts by the time

they reached any estuaries; in addition, methamidophos may degrade en route. Areas where there is a risk to marine and estuarine areas are the lower Rio Grande Valley in Texas, southern Florida, the Delmarva peninsula, and the North and South Carolina coasts. High amounts of rainfall in these areas exacerbate the risk to estuarine habitats in these areas.

However, the lack of information on dilution volumes and on the persistence of methamidophos residues in freshwater and estuarine environments reduces the certainty of a decrease in risk. Therefore, the risk to fresh water and estuarine invertebrates should not be discounted.

## **Risk to Terrestrial Ecosystems**

### **Birds**

#### **Acute Risk**

#### **RQ Shows High Risk**

Risk Quotients (RQs) based on laboratory dietary data (Bobwhite  $LC_{50}$  = 42 ppm) range from 5.6X to 12.2X over the level of concern for high acute risk to forage- and small insect-eating birds. Oral acute dose data on redwing blackbird ( $LD_{50}$  = 1.78 mg/kg) suggest that the RQ is underestimated by 4 times when compared to the bobwhite ( $LD_{50}$  = 8.0 mg/kg). This would suggest that the RQ may range from 22.4X to 48.8X over the level of concern.

#### **Field Study and Incidents Show Mortality From Methamidophos Use**

Field studies (Blus et al., 1989) showed that data collected from sage grouse near potato fields show brain ChE depressions of 40-65% shortly after spraying with methamidophos. These amounts of ChE depressions are considered to be mortality related. One field study found two depredated sage grouse found in or near potato fields contain depressed brain ChE activity <50% and one of the grouse had 18  $\mu$ g/g methamidophos residues in its crop. The two birds were considered to be killed as a result of the methamidophos spraying.

In section 3.e., there are several incidents of bird kills reported involving California quail, starlings, killdeer, barn swallows, house sparrows with methamidophos detections in their bodies and nearby foliage and water. One of the incident reports is an EPA investigation (1983) of extensive die-offs of sage grouse in potato-growing areas of the Northwest. The EPA investigation revealed that bird kills are common among many farmers using methamidophos although most of the bird kills are not reported. This incident report contributed to the 1989 Blus study.

#### **Diversity of Bird Populations in Cotton Growing Areas**



Major use states for methamidophos use on cotton are California, Arizona, Mississippi, and Louisiana. Methamidophos use on cotton in these states is expected to affect resident bird populations (non-migratory birds) with nests near treated fields. Mortality and reproductive impairment of survivors pose important risk to the maintenance of viable populations of avian species. Because these species are representative of the more than 50 avian species known to occur in and around cotton fields, the potential for adverse population impacts to many avian species from methamidophos exposure is great. The table below from the National Biological Service (Saber et al. 1997) presents trends in breeding bird populations of several avian species relevant to this risk characterization. All the species shown exhibit downward trends in population in three or more cotton states since 1966. Four species (white-eyed vireo, mourning dove, northern cardinal, and red-winged blackbird) showed population declines that were statistically significant ( $p < 0.05$ ) in three or more states. While these data do not establish causality for population declines (a variety of factors are likely to contribute to population declines), they do suggest that populations of many bird species at a state-wide level of resolution could be sensitive to additional acute or reproductive effects from exposure to methamidophos.

**Population Status of Important Bird Species in Cotton States**

State	Trends in Breeding Bird populations 1966-1996					
	Carolina Wren	White-Eyed Vireo	Northern Cardinal	Blue Grosbeak	Mourning Dove	Red-Winged Blackbird
AL	negative	positive	negative	positive	negative	negative*
AR	negative	negative*	positive	positive	negative	positive*
AZ	no data	no data	negative	positive	negative	positive
CA	no data	no data	no data	positive	negative*	positive
FL	positive	negative	negative	positive	positive	negative*
GA	positive	negative	negative*	positive	negative	negative*
LA	positive	negative	negative	positive	positive	negative
MO	positive	negative	negative*	positive	negative*	positive
MS	positive	positive	negative	negative	negative	negative*
NC	positive	positive	negative	positive	negative	negative
NM	no data	no data	no data	positive	negative	negative
OK	positive	positive	positive	negative	negative*	positive
SC	negative	stable	negative*	positive	negative	negative*
TN	positive	negative*	negative*	positive	negative	positive
TX	positive	negative*	positive	negative	negative*	negative
VA	positive	positive	negative*	positive	negative	negative*

\* denotes significant decline in population ( $p < 0.05$ )

### **Measured Residues of Methamidophos Show High Acute and More Persistent Exposure**

A number of studies submitted to the Agency show that the amounts of methamidophos residues on food items poses high acute risk to birds. In a supplemental study using Monitor 4 on potatoes in Idaho (MRID 41548801), sugar beets in California (MRID 41548802), and cotton in Alabama (MRID 41548803) with applications similar to that of the cotton and potato

maximum labeled, methamidophos residues were compared with the modeled terrestrial EEC provided in the table below:

Table . Methamidophos residues on food items in a potato (ID), sugar beet (CA) and cotton fields (AL).				
Food Items	Mean/Max. (ppm) ID	Mean/Max. (ppm) CA	Mean/Max. (ppm) AL	EEC Mean/Max (ppm)
crop leaves	82 / 161	46/ 69	132 / 452	48 / 144 (broadleaf)
Non-crop foliage (overruns)	3.5 / 15	31 / 126	35 / 154	38 / 117 (tall grass)
Inflorescence	4.3 / 8.5	49 / 89 (1); 15 / 50 (2)	not provided	7 / 16 (seed and fruit)
Flying insects (crop)	18.6 / 53	13 / 23	20 / 43	48 / 144 (small insects)
Flying insects (overruns)	1.1 / 3.1	10 / 13	not provided	48 / 144 (small insects)
Ground insects or soil invertebrates	0.9 / 7	23 / 70 (1); 23 / 59 (3)	17 / 7	7 / 16 (large insects)

(1) crop

(2) non-crop inflorescence from drift and over runs.

(3) drift

The consistency between the reported residues and the modeled EEC create a higher certainty for our terrestrial EEC models. Cotton and potatoes in the risk assessment used a 7-day interval in the terrestrial EEC models to estimate the residue numbers presented above. The application rates and the intervals used in the studies were comparable to those used in the risk assessment. The half-lives were calculated by the authors of the residue studies. They are as follows:

Idaho  $t_{1/2}$  is 2.2 days for field interior sweep net invertebrates and 5.5 days for foliage.

California  $t_{1/2}$  ranges from 3 days for foliage to 23 days in soil.

Alabama  $t_{1/2}$  is 8.2 days for foliage and 7.5 days for soil invertebrates.

Based on the information presented above, there would be sufficient residues that will persist to cause repeated adverse acute effects to birds ingesting these food items. It is concluded that there is high certainty that methamidophos presents high acute risk to birds.

### Chronic risk

Laboratory data indicate that methamidophos affects the reproductive capacity of birds by thinning of eggshells at concentrations greater than 3 ppm. There are no field data available to corroborate this. Risk quotients calculated from the NOAELs for methamidophos and the average methamidophos residues predicted from FATE exceed the LOC for birds by up to 33X for tomatoes in Florida, 30X for potatoes, cotton, and tomatoes outside of Florida. The above residue data indicate that there would be sufficient residues that will persist to cause adverse chronic effects to birds ingesting these food items. It is concluded that there is high certainty that methamidophos presents high chronic risk to birds.

## **Mammals**

### **Acute risk**

#### **RQ Shows High Risk**

The lab data and exposure indicate that methamidophos is classified in laboratory studies as highly toxic for oral acute, dermal, and inhalation exposure. RQs show that the LOCs for acute risk to mammals from exposure to methamidophos are 40X for tomatoes in Florida, 37X for potatoes, cotton, and tomatoes outside of Florida.

There is a single incident reported to OPP concerning an adverse impact to mammals. A cat died in a cabbage field that had recently been sprayed with methamidophos (see Section 3.e for details on this incident).

The high risk attributed to mammals from methamidophos may have been underestimated. This is because the highly toxic acute effects to mammals from dermal and inhalation exposure of methamidophos were not considered with the RQ which considered only the oral exposure route. The above residue data indicate that there would be sufficient residues that will persist to cause adverse acute effects to mammals ingesting these food items. It is concluded that there is high certainty that methamidophos presents high acute risk to mammals.

#### **Chronic Risk to Mammals**

Laboratory data indicates that methamidophos affects the reproductive capacity of mammals by reducing the viability of pups and body weight at concentrations greater than 10 ppm. There are no field data available to corroborate this. Risk quotients calculated from the NOAELs for methamidophos and the average methamidophos residues predicted from FATE exceed the LOC for mammals by up to 20X for tomatoes in Florida, and 18X for potatoes, cotton, and tomatoes outside of Florida. It is concluded that the use of methamidophos poses a high chronic risk to mammals.

The environmental fate assessment clearly indicates that methamidophos is not persistent in the environment, which decreases the concern for chronic risk. Laboratory studies indicate that methamidophos is mobile and rapidly degrades, and field dissipation studies confirmed that methamidophos residues will not persist in soil (apparent half-lives were much less than 3 days). However, the above residue data indicate that there would be sufficient residues that will persist ( $t_{1/2}$  = 7.5 days in foliage and invertebrates) to cause adverse chronic effects to mammals ingesting these food items. It is concluded that there is high certainty that methamidophos presents high chronic risk to mammals.

#### **Risk to Beneficial Insects and Other Arthropods**

Methamidophos is highly toxic to honey bees and beneficial predatory insects. There were no residue toxicity studies on bees, so it is assumed that bees will be adversely affected when exposed to methamidophos residues on foliage.

There is one incident reported to OPP concerning an adverse impact to 700 bee colonies from methamidophos (see Section 3.e for details on this incident). Bees and other beneficial insects/arthropods are expected to be at high risk to methamidophos exposure.

## **Risk to Aquatic Ecosystems**

### **Freshwater environments**

#### **Acute Effects**

Methamidophos is slightly toxic for freshwater fish; risk quotients indicate that there would be minimal effects to freshwater fish.

Laboratory studies show methamidophos to be very highly toxic to freshwater invertebrates (Daphnid); LOCs calculated using Tier I EECs are exceeded by 4.6X to 6X. However, supplemental information from a laboratory study conducted in Mexico (Juarez and Sanchez, 1989) on a commercial variety of freshwater prawns produced an  $LC_{50}$  of 42 ng/L (42 parts per trillion). If this value were used to calculate an RQ, the LOC would be exceeded by 4000X. However, there is some uncertainty associated with the level of risk posed by methamidophos to fresh water invertebrates because this supplemental study that has not been corroborated. There are also uncertainty associated with exposure due to a lack of aerobic aquatic metabolism for methamidophos that could be used to estimate persistence in aquatic environments. Therefore, the risk to freshwater invertebrates cannot be discounted and may be higher than indicated from the RQs.

The exposure to freshwater habitats may be underestimated from tomato use because most of the tomato production is done under black plastic mulch. Methamidophos is not expected to bind to the plastic mulch and could be present in runoff in higher concentrations than modeled for cotton and potatoes. However, these uncertainties do not preclude high acute risk to freshwater invertebrates and indirectly to other freshwater aquatic organisms from lack of food items.

#### **Chronic effects**

No data on the chronic effects of methamidophos to freshwater fish and invertebrates are available to assess chronic risk. A freshwater invertebrate study (72-b) using *Daphnia magna* is needed to assess chronic risk to fresh water invertebrates.

## **Estuarine environments**

### **Acute Risk**

Methamidophos is moderately toxic to estuarine fish; risk quotients indicate that there would be minimal effects to estuarine fish from methamidophos for the currently labeled uses.

Methamidophos is slightly toxic to very highly toxic to estuarine invertebrates; LOCs for endangered species calculated using Tier I EECs generated for the current uses are exceeded for mysid shrimp. However, supplemental information from a laboratory study conducted in Mexico (Juarez and Sanchez, 1989) on a commercial variety of blue shrimp produced an  $LC_{50}$  of 160 ng/L (160 parts per trillion). If this value were used to calculate an RQ, the LOC would be exceeded by 1000X. However, there is some uncertainty associated with the level of risk posed by methamidophos to estuarine invertebrates because the other species of estuarine invertebrate (mysid shrimp) tested does not appear to be as sensitive. In addition, the study conditions (static renewal) may have adversely affected the species tested. Therefore, the risk to estuarine invertebrates cannot be discounted and may be higher than indicated from the RQs. However, since shrimp nurseries are located in shallow estuaries that could receive runoff from fields treated with methamidophos, the risk to commercial shrimp production in Florida, North Carolina, and the Gulf areas from methamidophos cannot be discounted.

The exposure to estuarine habitats may be underestimated from tomato use because most of the tomato production is done under black plastic mulch. Methamidophos is not expected to bind to the plastic mulch and could be present in runoff in higher concentrations than modeled for cotton and potatoes. Since shrimp nurseries are located in shallow estuaries that could receive runoff from fields treated with methamidophos, the high acute risk to commercial shrimp production in Florida, North Carolina, and the Gulf areas from methamidophos cannot be discounted.

### **Chronic Risk**

No data on the chronic effects of methamidophos to estuarine fish and invertebrates are available to assess chronic risk. An estuarine invertebrate study (72-4b) using mysid shrimp (*Americamysis bahia*) is needed to assess chronic risk to estuarine invertebrates.

### **Plants**

Risk to terrestrial plants cannot be determined because no acceptable phytotoxicity studies of methamidophos on plants are available. Acephate, which degrades to methamidophos, is known to cause phytotoxicity to terrestrial plants; methamidophos is also generally more toxic than acephate. There is concern that the methamidophos may be the cause of this phytotoxicity rather than the acephate. Because of the lack of information, it is assumed that terrestrial plants will be adversely affected when exposed to methamidophos.

Currently, aquatic plant testing is not required for pesticides other than herbicides and fungicides except on a case-by-case basis (*e.g.*, labeling bears phytotoxicity warnings, incident data or literature that demonstrate phytotoxicity). EFED is not aware of any phytotoxicity of methamidophos to aquatic plants. Therefore, phytotoxicity testing for non-target aquatic plants is not needed at this time.

## References

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**APPENDICES / SUPPORTING DOCUMENTATION  
FOR EFED METHAMIDOPHOS RED CHAPTER**

## APPENDIX A

### PRZM 3.1/2.3 and EXAMS 2.97.5 Chemical-Specific Input Parameters

#### Chemistry

Aerobic soil metabolism is the main degradative process for methamidophos. The laboratory half-life was 14 hours in a sandy loam soil, producing the intermediate degradate O-desmethyl methamidophos, which is itself rapidly metabolized by soil microorganisms to carbon dioxide and microbial biomass (half-life of < 5 days). Methamidophos not stable against hydrolysis at neutral and alkaline pH's and photodegrades more rapidly on soil than in water. Methamidophos is somewhat persistent in anaerobic sandy loam sediment:pond water systems in the laboratory, with a  $DT_{50}$  of 41 days. Non-volatile degradates formed under anaerobic conditions were DMPT (O,S-dimethyl phosphorothioate) and O-desmethyl methamidophos; because of an incomplete material balance at sampling intervals > 3 months, it was not possible to determine their persistence. There are no acceptable data for the aerobic aquatic metabolism of methamidophos.

Methamidophos is very soluble (>200g/100 mL) and very mobile ( $K_{oc} = 0.88$ ) in the laboratory. Only one  $K_{oc}$  value is available, because methamidophos was adsorbed in only one of the five soils (a clay loam) used in the batch equilibrium studies. When tested in the same soils, DMPT was determined to be similarly mobile to methamidophos; again, only one  $K_{oc}$  value is available ( $K_{oc} = 0.9$  in the clay loam soil).

No acceptable field studies are available for methamidophos. Information of marginal value comes from a terrestrial field dissipation study in which methamidophos could not be detected at 3 days following a single and the last of 6 applications of methamidophos to potato plants in two sites in California. However, the study was not scientifically valid because methamidophos could not be detected at the first sampling interval after application. In addition, the formation and decline of degradates were not followed.

Based upon both the laboratory and field data, ground water effects are expected to be minimal. In surface waters, in the absence of acceptable aerobic aquatic metabolism, degradation is assumed to proceed at a rate slower than aerobic soil metabolism, thus methamidophos is predicted to persist over a longer interval. Methamidophos is persistent under anaerobic aquatic conditions ( $DT_{50} = 41$  days), which indicates that it would be more stable in deep waters or anaerobic sediments.

Laboratory studies showed that bioaccumulation of methamidophos in largemouth bass was insignificant; the maximum bioconcentration factor of 0.09X in whole fish occurred on day 28 and decreased to <0.014 ppm (quantification limit) after one day depuration.

The data in Tables 1, 2, and 3 were used for input into the PRZM-EXAMS modeling for Parent Methamidophos. Below is a brief discussion of how the fate information was integrated.

**Degradation:** For PRZM-EXAMS environmental fate parameters from the submitted studies for methamidophos were used as inputs according to approved parameter selection criteria<sup>1</sup>. Hydrolysis and soil and aqueous photolysis half-life were incorporated because the studies indicated that methamidophos was not stable to these processes. The single metabolism half-life (14 hours) was multiplied by 3 according to approved parameter selection criteria. The half-lives were converted to a daily rate constant for PRZM using the formula  $\text{Ln } 2 / (3 \times T_{1/2})$ . The water solubility of 200000 mg/L was used as an upper bound.

**Soil-Water Partition Coefficient.** Data on soil adsorption and desorption are reported in Table 1. The Freundlich  $K_{\text{ads}}$  value of 0.029 for methamidophos was used because only a single soil (clay loam soil) showed any adsorption.

**Soil Volatilization.** The soil volatilization routines in PRZM 3.1 and PRZM 2.3 were deactivated by setting the relevant parameters (Vapor diffusion rate, Henry's Law Constant and the enthalpy of Vaporization) to zero. The ability to estimate some of the necessary parameters, particularly the enthalpy of vaporization for methamidophos and its metabolite, is very poor, and there is lack of confidence in the validity of the PRZM 3.1 and PRZM 2.3 volatilization routines.

Table 1. Environmental fate parameters for Methamidophos			
Fate Parameter	Value	Source	Quality of Data
Molecular Mass	141.14 g · mol <sup>-1</sup>	EFGWB One-Liner	Good
Aerobic Soil Metabolism Rate Constant	0.396 d <sup>-1</sup>	MRID 41372201	Good - Fair
$K_p$ n (adsorption)	0.029 (clay loam), n=0.64	MRID 40504811	Good - Fair
Solubility	> 200000 mg L <sup>-1</sup>	MRID 43661003	Good
Vapor Pressure	1.725 x 10 <sup>-5</sup> torr	MRID 43661003	Good
Hydrolysis Rate Constant at pH 7	2.53 x 10 <sup>-2</sup> d <sup>-1</sup>	MRID 00150609	Good
Aqueous Photolysis Constant	3.46 x 10 <sup>-4</sup> d <sup>-1</sup>	MRID 00150610	Fair
Soil Photolysis Constant	0.266 d <sup>-1</sup>	MRID 00150611	Fair

<sup>1</sup>Draft Internal Guidance: Model Parameter Selection Criteria for PRZM and EXAMS, Environmental Fate and Effects Division, August 5, 1997.

Table 2. PRZM 3.1/2.3 input parameters for Methamidophos			
Input Parameter	Value	Source	Quality of Data
Foliar Volatilization (PLVKRT)	0 d <sup>-1</sup>		Poor
Foliar Decay Rate (PLDKRT)	0 d <sup>-1</sup>		Poor
Foliar Washoff Extraction Coefficient (FEXTRC)	0.5 cm <sup>-1</sup>		Poor
Plant Uptake Fraction (UPTKF)	0		Poor
Soil-Water Partition Coefficient (KD) for all crops	0.029 L kg <sup>-1</sup>	MRID 40504811	Good
Dissolved Phase Decay Rate: Upper Horizons (DWRATE)	0.396 d <sup>-1</sup>	MRID 41372201	Fair
Adsorbed Phase Decay Rate: Upper Horizons (DSRATE)	0.396 d <sup>-1</sup>	MRID 41372201	Fair
Dissolved Phase Decay Rate: Lower Horizons (DWRATE)	0.396 d <sup>-1</sup>	MRID 41372201	Fair
Adsorbed Phase Decay Rate: Lower Horizons (DSRATE)	0.396 d <sup>-1</sup>	MRID 41372201	Fair
Vapor Phase Decay Rate (DGRATE) (all horizons)	0 d <sup>-1</sup>		Poor

Table 3. EXAMS 2.97.5 Input parameters for Methamidophos			
Input Parameter	Value	Source	Quality
Aerobic Aqueous Metabolism Constant (KBACW)	1.65x10 <sup>-2</sup> h <sup>-1</sup>	MRID 41372201	good
Sediment Metabolism Constant (KBACS)	0		poor
Neutral Hydrolysis Rate Constant (KNH)	9.8 x 10 <sup>-4</sup> h <sup>-1</sup>	MRID 00150609	good
Partition Coefficient (KPS) for all modeled crops	0.029 mL g <sup>-1</sup>	MRID 40504811	fair
Molecular Mass (MWT)	141.14 g · mol <sup>-1</sup>	EFGWB One-Liner	excellent
Solubility (SOL)	>200000 mg · L <sup>-1</sup>	MRID 43661003	good
Vapor Pressure (VAPR)	1.725 x 10 <sup>-3</sup> torr	MRID 43661003	good
Henry's Law Constant (calculated)	1.6 x 10 <sup>-11</sup> Atm.M <sup>3</sup> Mole <sup>-1</sup>	EFGWB One-Liner	fair
Q10 For The water Column (QTBAW)	0		poor
Q10 For Sediment (QTBAS)	0		poor

## Models Used

The EECs were calculated using two versions of the PRZM model: 3.1, (Carsel, et.al., undated; executable dated October 17, 1997) and 2.3 (Carsel, et.al., undated; executable dated April 30, 1997) to simulate the transport of the pesticide off the field, and EXAMS 2.97.5, (Burns, L.A., 1997; executable dated June 19, 1997), to simulate the fate of the chemical in the water body. The PRZM 3.1 version used is an interim release that has been modified to provide improved pesticide extraction into runoff and additional application capacity. All post-processing analysis were handled by Table20 (executable dated May 27, 1998).

## Procedure

All PRZM simulations were run from January 1 through December 31 for each year of meteorological data available for the Major Land Resource Areas (MLRA). EXAMS was run for all the scenarios. The 10 year return EECs (or 10% yearly exceedence EECs) listed in Table 4 were calculated by linear interpolation between the third and fourth largest values using the Table20 program. The upper 90% confidence bound of the overall means were estimated by Table20.

## Scenarios

The scenarios chosen represent high exposure sites for methamidophos. The weather data and agricultural practices are simulated at each site over multiple (36) years so that the probability of an EEC occurring at that site can be estimated. The modeled sites are 10 hectare fields draining into a 1 hectare pond, 2 m deep with no outlet (20,000,000 liter volume). The site was selected so as to generate exposures to aquatic organisms greater than for most sites (about 90%) used for growing the modeled crops. Table 4 provides a summary of the scenario for each modeled crop. The simulations were made with a maximum application rate of 1.0 lb a.i./acre with the maximum number of yearly applications being four. Intervals between applications were 7 days for cotton and tobacco, based on the reapplication intervals specified on the Monitor 4 product label. The EECs have been calculated so that in any given year there is a 10% probability the maximum average concentration of that duration in that year will equal or exceed the EEC at the site. The Loring silt loam soil was classified as a Group C, which is more prone to runoff than leaching. Eginbench loamy sand soil (Group D) was used for the Idaho potato scenario because it is one of the Idaho soils used for potato production.

Table 4. Usage Practices used for modeling Methamidophos on various crops.		
Crop	Location, (Soil), Hydrologic Group, and (MLRA)	Maximum Labeled Rate (lb ai/A), App. Dates, Pre-Harvest Interval (PHI)
Cotton	Yazoo County, MS (Loring silt loam), Group C, (MLRA 134)	1.0 lb acephate (4 x 1.0 lbs ai) at 7 day interval June 19 - July 10; PHI=NA
Potatoes	Bingham County, ID (Eginbench loamy sand), Group D, (MLRA 11)	1.0 lb (4 x 1.0 lbs ai) at 7 day interval June 20 - July 11; PHI=NA

The PRZM 3.1 scenario parameters for each site are provided in Appendix B. The EXAMS non-chemical specific parameters describing the pond are listed in Appendix C.

## PRZM-EXAMS RESULTS

Crop specific consecutive PRZM-EXAM simulations were conducted to evaluate the cumulative probability distribution for peak, 4-day, 21 day, 60 day, and 90 day EECs. The one-in-10 year PRZM-EXAMS Peak EECs for methamidophos for the two scenarios modeled are presented in Table 5. No accumulation in water bodies is expected.

Table 5. Tier II upper tenth percentile EECs for Methamidophos ( $\mu\text{g/L}$ )**							
Crop	Peak	4-Day	21-Day	60-day	90-day	Over-all Mean	90% CB Mean*
Cotton, Mississippi	40	20	6.8	2.9	2.0	1.1	??
Potatoes, Idaho	30	17	8	3.7	2.7	0.8	0.7

\* Upper 90th percent confidence bound on the overall mean concentration.

\*\* EECs rounded to 2 significant figures.

The model simulations use historical precipitation as an input, and did not take into account irrigation which is often used in dry (e.g., California) regions to supplement rainfall. Virtually all pond residues were associated with the aqueous phase. Aerobic aquatic metabolism data were not available for input, so the model used the contributions of hydrolysis and aqueous photolysis to estimate persistence in the pond; by 4 days, the EEC's decreased to approximately one-half the peak concentrations

Runoff is the source of methamidophos loading to aquatic environments in all of these scenarios. Transport with eroded sediment was only a small source of loading for acephate. Mitigation strategies need to consider the relative risks of ground water versus surface water contamination, and the relative risks of alternative pesticides to aquatic, and terrestrial environments, as well as human health.

It should be remembered in interpreting these results that they represent the upper limit for possible exposure from these use patterns to aquatic environments at a single high exposure site. In actual practice, the true environmental concentrations will probably be less than indicated by this analysis because most sites will produce less loading to aquatic environments than these scenarios.

## **Appendix B**

### **PRZM Scenario Parameters**

This section provides a brief description of each crop site used to produce the Tier II EECs for methamidophos. The soils descriptions are summaries of the Official Soil Series Descriptions provided on-line by Iowa State University<sup>2</sup>. The PRZM parameters that describe each site more fully are provided in Tables B-1 through B-6.

#### **Scenario Sites**

The field used to grow Mississippi cotton is located in Yazoo County, Mississippi. The soil is a Loring silt loam, a fine-silty, mixed, mesic Thermic Typic Fragiudalf, in MLRA O-134. The Loring silt loam is a moderately well drained soil with a fragipan formed in loess on level to strongly sloping upland and stream terraces on slopes of 0-20 percent. The Loring silt loam is a Hydrologic Group C soil with SCS curve numbers that were measured on a real field in Yazoo County, Mississippi under cotton culture. There are approximately 101,000 acres of cotton grown in Yazoo County, which is the most of any county in Mississippi and among the top 10 percent in the U.S. (US Department of Commerce, 1994a). USLE C Factors were developed by George Foster at the University of Mississippi in consultation with Ronald Parker of the US EPA to represent a cotton field with one year tilled followed by two years under conservation tillage using RUSLE. The weather data used was for MLRA 134.

The field used to grow Idaho potatoes is located in Bingham County. The soil is a Eginbench loamy sand, a coarse, mixed, frigid, Xeric, Torripsamment in MLRA E-11. Eginbench loamy sand is a very deep, somewhat poorly drained, rapidly permeable soil that formed on mixed alluvium with an aeolian mantle. Runoff is very slow. These soils have water tables of 1 to 6 feet which are highest during the irrigation season. The water table can be artificially induced to allow subirrigation by perching water on top of bedrock. The series is located on level river terraces with slopes of 0-2 percent. The MAP is 12 inches and the MAT is 43°F. The soils are used for irrigated potatoes, small grains, and hay. The soil is characterized as a Group D hydrologic soil. The series is not extensive in southeast Idaho. The series was established in Madison County, Idaho in 1977. The weather data used was for MLRA 11.

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<sup>2</sup>Official Soil Series Descriptions, USDA-NRCS Soil Survey Division; Iowa State University; WEB Page: <http://www.statlab.iastate.edu/soil/osd>. 1998.



Table B-1 PRZM climate and time parameters for Idaho potatoes and Mississippi cotton.				
	Mississippi Cotton	Idaho Potatoes		
Parameter	Value	Value	Source	Quality
Starting Date*	January 1, 1948	January 1, 1948		
Ending Date*	December 31, 1983	December 31, 1983		
Pan Evaporation Factor (PFAC)	0.74	0.720	PIC	good
Snowmelt Factor (SFAC)	0.150 cm · K <sup>-1</sup>	0.30 cm · K <sup>-1</sup>	PIC	good
Minimum Depth of Evaporation (ANETD)	17.0 cm	17.0 cm	PIC	good
Average Duration of Runoff Hydrograph (TR)	5.8 h	4.5 h	PIC	good
* These values are in the RUN file rather than the INP file.				

Table B-2. PRZM model state flags for modeled scenarios.	
Parameter	Value
Pan Factor Flag (IPEIND)	0
Foliar Application Model Flag (CAM); foliar application	2
Bulk Density Flag (BDFLAG)	0
Water Content Flag (THFLAG)	0
Kd Flag (KDFLAG)	0
Drainage model flag (HSWZT)	0
Method of characteristics flag (MOC)	0
Irrigation Flag (IRFLAG)	0
Soil Temperature Flag (ITFLAG)	0
Thermal Conductivity Flag (IDFLAG)	0
Biodegradation Flag (BIOFLAG)	0
Erosion Calculation Flag (ERFLAG)	4 (cotton) / 1 (potatoes)

Table B-3. Erosion and landscape parameters for Mississippi cotton and Idaho potatoes				
	Mississippi Cotton	Idaho Potatoes		
Parameter	Value	Value	Source	Quality
USLE K Factor (USLEK)	0.49 tons EI <sup>-1</sup> *	0.1 tons EI <sup>-1</sup> *	PIC	good
USLE LS Factor (USLELS)	0.40	1.5	PIC	fair
USLE P Factor (USLEP)	1.00	1.00	**	fair
Field Area (AFIELD)	10 ha	10 ha	standard	
NRCS Hyetograph (IREG)	3	***		good
Slope (SLP)	6%	***		fair
Hydraulic Length (HL)	354 m	***		good
* EI = 100 ft-tons * in/ acre*hr ** P Factor represent compromise for 1 year of conventional tillage and two years of no till. *** Not an input in PRZM 2.3				

**Table B-4. PRZM crop parameters for Mississippi cotton and Idaho potatoes**

	Mississippi Cotton	Idaho Potatoes		
Parameter	Value	Value	Source	Quality
Initial Crop (INICRP)	1	1	PIC	good
Initial Surface Condition (ISCOND)	3	1	PIC	fair
Number of Different Crops (NDC)	3	1		fair - good
Number of Cropping Periods (NCPDS)	36	36	Standard	
Maximum rainfall interception storage of crop (CINTCP)	0.2	0.10	PIC	fair
Maximum Active Root Depth (AMXDR)	125 cm	30.0 cm	PIC	fair
Maximum Canopy Coverage (COVMAX)	98	90	PIC	fair
Soil Surface Condition After Harvest (ICNAH)	3	3	PIC	fair
Date of Crop Emergence (EMD, EMM, IYREM)	5/01	5/21		fair - good
Date of Crop Maturity (MAD, MAM, IYRMAT)	9/07	10/01		fair - good
Date of Crop Harvest (HAD, HAM, IYRHAR)	9/22	10/16		fair - good
Maximum Dry Weight (WFMAX)	0.0	0.0	PIC	fair
SCS Curve Number (CN)	92-99 (Year 1) 83-94 (Years 2,3)	91-94	PIC	fair
Manning's N Value (MNGN)	0.02	*	PRZM Manual	good
USLE C Factor (USLEC)	0.63,0.16,0.18 (Year 1) 0.16,0.13,0.13 (Year 2) 0.16,0.13,0.09 (Year 3)	0.43, 0.27, 0.43	PIC	fair
* Not an input for PRZM2.3				

**Table B-5. PRZM 3.1 soil parameters for a cotton field in Yazoo County, Mississippi.**

Parameter	Value	Source	Quality
Total Soil Depth (CORED)	125 cm	PIC	good
Number of Horizons (NHORIZ)	3	PIC	good
First, Second and Third Soil Horizons (HORIZN = 1, 2, 3)			
Horizon Thickness (THKNS)	10 cm (HORIZN = 1, 2) 105 cm (HORIZN = 3)	PIC	good
Bulk Density (BD)	1.60 g · cm <sup>-3</sup> (HORIZN = 1, 2) 1.80 g · cm <sup>-3</sup> (HORIZN = 3)	PIC	good
Initial Water Content (THETO)	0.294 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 1) 0.294 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 2) 0.147 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 3)	PIC	good
Compartment Thickness (DPN)	0.1 cm (HORIZN = 1) 2.0 cm (HORIZN = 2) 5.0 cm (HORIZN = 3)	standard	
Field Capacity (THEFC)	0.191 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 1, 2) 0.249 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 3)	PIC	good
Wilting Point (THEWP)	0.086 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 1, 2) 0.109 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 3)	PIC	good
Organic Carbon Content (OC)	1.16% (HORIZN = 1, 2) 0.174% (HORIZN = 3)	PIC	good

**Table B-6. PRZM 2.3 soil parameters for a potato field in Bingham County, Idaho.**

Parameter	Value	Source	Quality
Total Soil Depth (CORED)	100 cm	PIC	good
Number of Horizons (NHORIZ)	3	PIC	good
First, Second and Third Soil Horizons (HORIZN = 1, 2, 3)			
Horizon Thickness (THKNS)	15 cm (HORIZN = 1) 80 cm (HORIZN = 2) 5 cm (HORIZN = 3)	PIC	good
Bulk Density (BD)	1.8 g · cm <sup>-3</sup> (HORIZN = 1, 2, 3)	PIC	good
Initial Water Content (THETO)	0.107 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 1) 0.104 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 2) 0.057 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 3)	PIC	good
Compartment Thickness (DPN)	0.1 cm (HORIZN = 1) 2.0 cm (HORIZN = 2) 5.0 cm (HORIZN = 3)	standard	
Field Capacity (THEFC)	0.107 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 1) 0.104 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 2) 0.057 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 3)	PIC	good
Wilting Point (THEWP)	0.047 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 1) 0.044 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 2) 0.017 cm <sup>3</sup> · H <sub>2</sub> O · cm <sup>-3</sup> · soil (HORIZN = 3)	PIC	good
Organic Carbon Content (OC)	0.58% (HORIZN = 1) 0.29% (HORIZN = 2) 0.174% (HORIZN = 3)		

## Appendix C

### EXAMS Scenario Input Parameters

The pond used to generate the Tier II EECs for methamidophos is modified for generic use from the Richard Lee pond that was distributed with EXAMS and is the standard pond used for all EEC calculations. Modifications were made to convert the pond from 1 acre, 6 ft deep to 1 ha, 2 m deep. Additionally, adjustments were made to the standard pond by changing the water temperature to that which was more appropriate for the region being simulated. The temperature in the pond each month was set to the average monthly air temperature over all years calculated from the meteorological file that was used in the simulation. Additionally, the latitude and longitude were changed for each pond to values appropriate for the site selected. Finally, all transport into and out of the pond has been set to zero.

**Table C-1. EXAMS II pond geometry for standard pond.**

	Littoral	Benthic
Area (AREA)	10000 m <sup>2</sup>	10000 m <sup>2</sup>
Depth (DEPTH)	2 m	0.05 m
Volume (VOL)	20000 m <sup>3</sup>	500 m <sup>3</sup>
Length (LENG)	100 m	100 m
Width (WIDTH)	100 m	100 m

**Table C-2. EXAMS II dispersive transport parameters between benthic and littoral layers in each segment for standard pond.**

Parameter	Pond*	Stream 1**	Stream 2***
Turbulent Cross-section (XSTUR)	10000 m <sup>2</sup>	300 m <sup>2</sup>	1200 m <sup>2</sup>
Characteristic Length (CHARL)	1.01, 1.025 m	0.275 m	0.275 m
Dispersion Coefficient for Eddy Diffusivity (DSP)	$3.0 \times 10^{-5}$	$3.0 \times 10^{-5}$	$3.0 \times 10^{-5}$
* JTURB = 1, ITURB = 2; ** JTURB = 3, ITURB = 4; *** JTURB = 5, ITURB = 6			

**Table C-3. EXAMS II sediment properties for standard pond.**

	Littoral	Benthic
Suspended Sediment (SUSED)	30 mg L <sup>-1</sup>	
Bulk Density (BULKD)		1.85 g cm <sup>-3</sup>
Per cent Water in Benthic Sediments (PCTWA)		137%
Fraction of Organic Matter (FROC)	0.04	0.04

Table C-4. EXAMS II external environmental parameters for standard pond.	
Precipitation (RAIN)	90 mm · month <sup>-1</sup>
Atmospheric Turbulence (ATURB)	2.00 km
Evaporation Rate (EVAP)	90 mm · month <sup>-1</sup>
Wind Speed (WIND)	1 m · sec <sup>-1</sup>
Air Mass Type (AMASS)	Rural (R)

Table C-5. EXAMS II biological characterization parameters for standard pond.		
Parameter	Limnic	Benthic
Bacterial Plankton Population Density (BACPL)	1 cfu · cm <sup>-3</sup>	
Benthic Bacteria Population Density (BNBAC)		37 cfu · (100 g) <sup>-1</sup>
Bacterial Plankton Biomass (PLMAS)	0.40 mg · L <sup>-1</sup>	
Benthic Bacteria Biomass (BNMAS)		6.0x10 <sup>-3</sup> g · m <sup>-2</sup>

Table C-6. EXAMS water quality parameters for standard pond.	
Parameter	Value
Optical path length distribution factor (DFAC)	1.19
Dissolved organic carbon (DOC)	5 mg · L <sup>-1</sup>
chlorophylls and pheophytins (CHL)	5x10 <sup>-3</sup> mg · L <sup>-1</sup>
pH (PH)	7
pOH (POH)	7

**Table C-7. EXAMS mean monthly water temperatures and location parameters for a field pond in Yazoo County, Mississippi.**

Month	Temperature (Celsius)
January	6
February	9
March	12
April	16
May	20
June	24
July	26
August	28
September	25
October	18
November	13
December	10
Latitude	34° N
Longitude	83° W

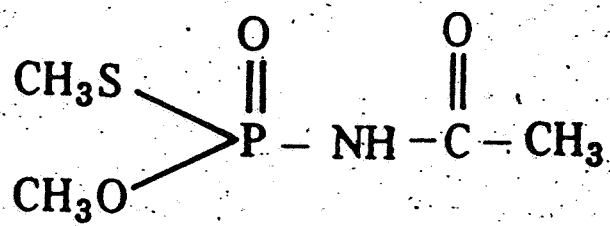
## Appendix D Input File Names

Table D-1. Input files archived for Methamidophos Tier 2 EECs.		
File Name	Date	Description
MET134.MET	March 22, 1991	MLRA 134 weather data for Mississippi cotton
MET11.MET	March 22, 1991	MLRA 11 weather data for Idaho potatoes
Input Data File Sets		
MSCOTT4	October 7, 1998	File set for Methamidophos on cotton in Mississippi, 4 aerial applications of 1 lb/A at 7 day intervals, starting June 19 each year
IDPOTAT4	October 8, 1998	File set for Methamidophos on potatoes in Idaho, 4 aerial applications of 1 lb/A at 7 day intervals, starting June 20 each year

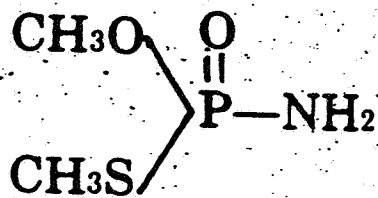


## **APPENDIX E**

### **Structures of Methamidophos and Major Degradates**



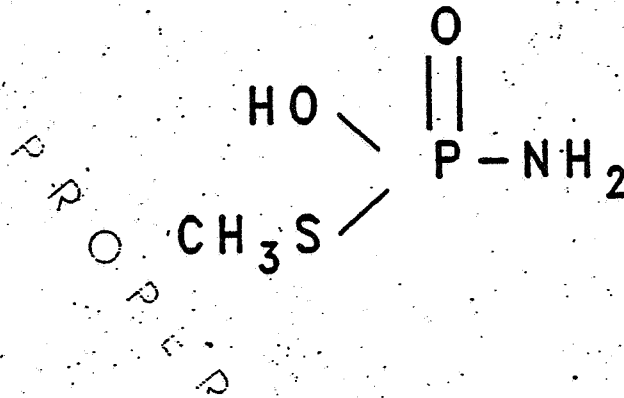
Acephate



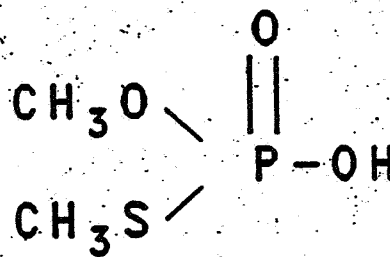
Methamidophos

## FIGURE 3

Chemical Structures of the Degradation Products of  
<sup>14</sup>C-Methamidophos



O-Desmethyl-Methamidophos  
(S-methyl phosphoramidothioate)



Desamino-Methamidophos  
(O,S-dimethyl phosphorothioate)

ABC LABS NO. 39665-44

**APPENDIX F**  
**Proposed Degradation Pathways**  
**for Methamidophos**

Figure 18

Proposed Pathway for the Degradation of  
Methamidophos during Soil Metabolism

