



## Methoprene Concentrations in Surface Water Samples from Grant County Mosquito Control District No. 1

### Abstract

The Washington State Department of Ecology monitored methoprene concentrations in surface water samples from Grant County Mosquito Control District No. 1 during the 2005 application season. Methoprene (trade name Altosid) is a mosquito larvicide that mimics a juvenile growth hormone, thereby preventing the larvae from maturing into adults.

Methoprene was detected in only 6% of the samples collected (4 out of 68). The maximum concentrations recorded were in the range of 0.1 – 0.6 ug/L (parts per billion). A breakdown product, methoprene acid, was also analyzed and only detected in one instance.

The results of this study are briefly compared to available water quality criteria and to data from similar monitoring programs.

*Acknowledgements:* The authors very much appreciate the cooperation with this study extended by Jim Thompson, manager of the mosquito control program for Grant County. We also thank Jo Wisniewski and Steve Germaine of the Washington Department of Fish and Wildlife for their role in collecting samples from the Westlake Pond Area. The methoprene analyses were conducted by Bob Carrell of the Ecology Manchester Environmental Laboratory. We appreciate his good work.

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E-mail: [ecypub@ecy.wa.gov](mailto:ecypub@ecy.wa.gov)

Phone: (360) 407-7472

Address: PO Box 47600, Olympia WA 98504-7600

Authors: Art Johnson and Kristin Kinney  
Washington State Department of Ecology  
Environmental Assessment Program  
E-mail: [arjo461@ecy.wa.gov](mailto:arjo461@ecy.wa.gov)  
Phone: (360) 407-6766  
Address: PO Box 47600, Olympia WA 98504-7600

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## Background

Methoprene<sup>1</sup> (trade name Altosid) is permitted for use to control mosquitoes in Washington State. Methoprene mimics a juvenile growth hormone, preventing mosquito larvae from maturing into adults. Unable to metamorphose, the mosquitoes die in the pupal stage. Methoprene comes in liquid, granular, pellet, or briquette form and is applied directly to the water where mosquito larvae are found.

Grant County Mosquito Control District No. 1 (MCD #1) began using methoprene in 1983 as a replacement for organophosphate insecticides. MCD #1 currently uses about 400 gallons of methoprene annually to control mosquitoes over a 1,000 square mile area (Figure 1.) The application season stretches from early April to mid-October. Most of the application is done by aerial spraying, often in combination with *Bacillus thuringiensis* (Bt), a naturally occurring bacterium which is also active against mosquito larvae. Grant County is the largest user of methoprene in Washington State and may be one of the largest users in the nation.

Methoprene has low toxicity to humans, is practically non-toxic to birds, and has only slight toxicity to fish. It is, however, highly toxic to some freshwater invertebrates, although the effects are not permanent and populations recover (Ecology, 2002). Methoprene degrades rapidly in sunlight, both in water and on inert surfaces. Half-lives range from 30 hours to 14 days, depending on environmental conditions (Suffolk County, 2005).

In commenting on the current National Pollution Discharge Elimination System (NPDES) permit for aquatic mosquito control, the Washington Department of Fish and Wildlife (WDFW) raised concerns about possible adverse impacts of methoprene on several wildlife species (Beach, 2003). One of these was the northern leopard frog, which is found only in Grant County.

The northern leopard frog (*Rana pipiens*) is a Washington State endangered species. Leopard frogs were historically present at more than 18 locations in eastern Washington, with occupied areas primarily distributed along the Columbia River and its tributaries. Leopard frogs have declined for unknown reasons, with dams, non-native fish and bullfrogs, and agriculture (chemicals and land conversion) all potential factors. Surveys conducted in Washington since 1992 have documented northern leopard frogs at only two areas, both in the Crab Creek drainage in Grant County (Leonard et al., 1999; McAllister et al., 1999). Both populations occur on land administered by WDFW: one at the Gloyd Seeps Wildlife Area (GWA) and one at the Columbia Basin Wildlife Area (CWA) at Potholes Reservoir, which is jointly administered with the U.S. Bureau of Reclamation. The CWA population is larger with more potentially suitable habitat, and may therefore have greater likelihood for persistence. However, both populations are small, spatially restricted, and considered highly vulnerable to extinction. CWA is located in the Westlake area, to the west of Moses Lake and south of I-90 (see Figure 1). (Germaine, 2004)

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<sup>1</sup> 2,4-Dodecadienoic acid, 11-methoxy-, 3,7,11-trimethyl-, 1-methylethyl ester; CAS No. 40596-69-8

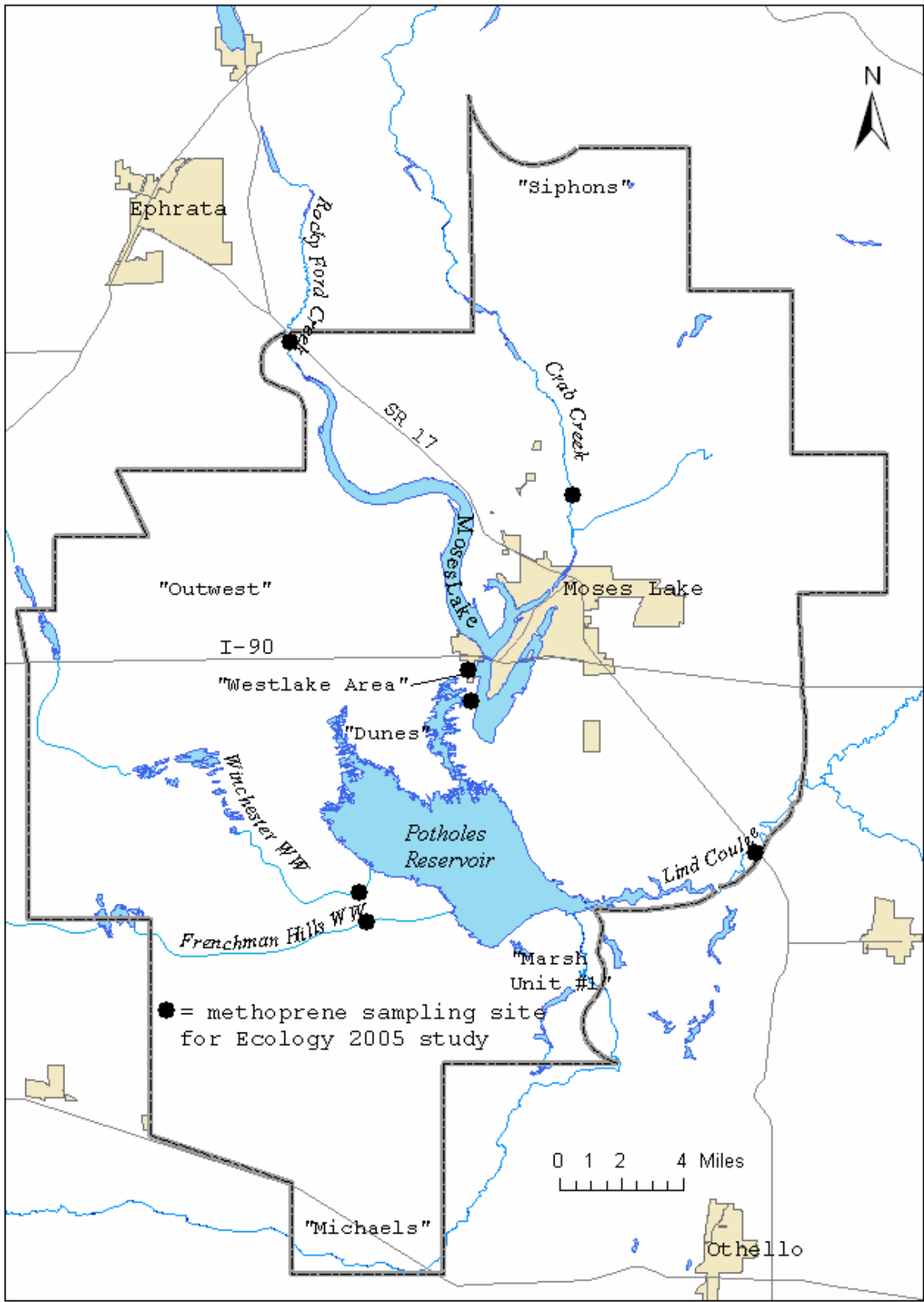


Figure 1. Approximate Boundary of Grant County Mosquito Control District #1

WDFW has recommended that only Bt be used in northern leopard frog habitats (Beach, 2003). However, section S1.4 of the NPDES permit states that: Methoprene is restricted in areas designated by the Washington Department of Fish and Wildlife except when a health threat exists in those areas as determined by the state and local health departments. With the concurrence of the Washington State Department of Health, Grant County Health District granted a temporary lifting of the methoprene restriction that has allowed Grant County to apply methoprene to ponds in the Westlake area.

The Washington State Department of Ecology (Ecology) Water Quality Program requested that Ecology’s Environmental Assessment Program monitor methoprene concentrations in the surface waters of MCD #1 during the 2005 application season. The Water Quality Program wanted to know what kind of methoprene concentrations occur when there is treatment on this scale and to verify that the concentrations are not a significant concern for aquatic life. This information was needed for the next issuance of the NPDES permit, scheduled for May 2007.

## Sampling Design

The weekly schedule that MCD #1 typically follows for methoprene applications is summarized below (see Figure 1):

Day	Locations
Monday	Winchester Wasteway (upper), Rocky Ford Creek, Moses Lake, “Outwest”
Tuesday	Frenchman Hills Wasteway, Winchester Wasteway (lower), “Michaels”, “Marsh Unit #1”
Wednesday	Potholes Reservoir Dunes, “Westlake Area”
Thursday	Crab Creek
Friday	Lind Coulee, “Siphons”, “Deadman’s Corner” (west of Figure 1)

The decision on specific areas to be sprayed within the above locations is based on surveys (i.e., dip samples) to determine larval densities. MCD #1 decides where to spray based on the previous day’s survey. Methoprene applications begin at first light and are normally completed by approximately 10 AM.

Depending on the time of year, water levels, and other conditions, certain watersheds are more heavily sprayed than others. In general, the periods when the most methoprene is applied are as follows:

Watershed	Maximum Application Period
Crab Creek	June – August
Moses Lake	All season
Rocky Ford Creek	June – August
Potholes Reservoir Dunes	April – May
Winchester Wasteway	April – May
Frenchman Hills Wasteway	April – May
Lind Coulee	June – August
Westlake Area	April – May

It was initially proposed that methoprene monitoring be done in May during the period when Potholes Reservoir, Winchester Wasteway, Frenchman Hills Wasteway, and the Westlake Ponds are most heavily treated, and again in August when Crab Creek, Rocky Ford, and Lind Coulee are most heavily treated. However, the weather was cooler than normal during the early part of the 2005 application season, delaying development of the mosquito population. Therefore, the initial set of samples was collected in June rather than May.

The specific sites for the monitoring program were as follows:

Waterbody	Waterbody Number	Sampling Site
Winchester Wasteway	WA-41-1110	Road C S.E.
Frenchman Hills Wasteway	WA-41-1120	Road C S.E.
Moses Lake	WA-41-9250	Outlet at Sand Dunes Road
Crab Creek	WA-41-1030	Road 7 S.E.
Rocky Ford Creek	WA-41-2010	State Route 17
Lind Coulee	WA-41-3500	State Route 17
West Lake Area Ponds	--	Ponds A13d, B8d, F11

The creek and wasteway sampling sites are at the downstream end of their respective watersheds. Results for these sites were intended to integrate the effects of upstream spraying. Except for the Moses Lake outlet, where only a few discrete shoreline areas are treated, methoprene applications occur within close proximity to each of these sites. There was no easily accessible and representative sampling location for the Potholes Dunes applications, so no samples were taken in that waterbody.

Samples for the creeks and wasteways were collected over a three-week period in June and a three-week period in August. In most cases, the week-1 samples were collected on Monday, the week-2 samples on Wednesday, and the week-3 samples on Friday. For sites where spraying was being done the same day, the samples were collected after the applications were completed. This sampling design was intended to give results that are broadly representative of methoprene concentrations in MCD #1 during the peak application periods. Under this schedule, the delay between methoprene application and sample collection for any given site typically varied from several hours to several days. Forty-two samples were collected for this part of the study, including replicates and field blanks. The sampling was done by Ecology personnel.

The peak application period for the Westlake Area Ponds overlaps the period when early stage tadpoles are present. Ponds A13, B8d, and F11 were selected for sampling by WDFW. The pond samples were taken from the shoreline. The general approach was to sample on day-0 (day of application), day-1, day-3, and day-6 or-7 prior to the second application, and then to repeat the same schedule the following week. Thirty samples were collected for this part of the study. The ponds were sampled by WDFW personnel.

All samples were analyzed for methoprene and methoprene acid. Methoprene acid is one of several toxic breakdown products reported to have greater persistence than methoprene (Degitz et al., 2003).

Table 1. Sampling Schedule for Methoprene Study (number of samples)

Agency	Locations	No. of Sites	Jun-05			Aug-05			Total Samples
			week 1	week 2	week 3	week 1	week 2	week 3	
Ecology	Creeks and Wasteways	6	8*	6	7 <sup>†</sup>	8*	6	7 <sup>†</sup>	42
WDFW	Westlake Ponds	3	15**	15**	--	--	--	--	30

\* includes one field blank and one replicate sample

<sup>†</sup> includes one replicate sample

\*\*includes one field blank and two replicate samples

## Methods

### Field

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Methoprene samples were collected as simple grabs using 1-liter amber glass bottles provided by the Ecology Manchester Environmental Laboratory. Amber glass was used to minimize methoprene degradation by UV light. The sampling procedure was to shove the inverted bottle straight downward into the water and gain the remainder of the sample underwater.

Each bottle was filled to the shoulder and a label attached showing the site name, sample number, date, time, and name of sample collector. Each bottle was wrapped in bubble wrap, put in a plastic bag, and placed on ice in a cooler immediately after collection. The temperature of each waterbody was recorded at the time of sample collection. The latitude and longitude of each sampling site was determined from a GPS receiver (Appendix A).

The samples were returned to Ecology Headquarters on the day of collection and transported by Ecology courier to Manchester Laboratory on the following day. Chain-of-custody was maintained.

### Laboratory

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The water samples were analyzed for methoprene and methoprene acid by the Manchester Laboratory. The samples were extracted following Manchester SOP #730098. The samples were pH adjusted to 5 and then poured through a J.T. Baker C18 Speedisk with a 5 psi vacuum applied. The disk was then dried at full vacuum for 30 minutes and extracted with methylene chloride and derivatized with diazomethane. The extracts were analyzed by Gas Chromatography with Mass Spectroscopy detection (GS/MS) using a modification of EPA method 8270.



## Data Quality

Manchester Laboratory prepared written case narratives assessing the quality of the data collected for this project. These reviews include a description of analytical methods and assessments of holding times, initial and continuing calibration and degradation checks, method blanks, surrogate recoveries, matrix spike recoveries, laboratory control samples, and laboratory duplicates. The reviews and the complete Manchester data reports are available from the author on request. The data are also available electronically through the Ecology Environmental Information Management System (EIM) at [www.ecy.wa.gov/eim/index.htm](http://www.ecy.wa.gov/eim/index.htm).

Replicate samples were collected to provide estimates of the total variability (field + laboratory) associated with the data obtained during this project. The replicates were collected at the same site within a few minutes of each other. The results, Table 2, showed good agreement. In the two instances where methoprene was detected, the replicates agreed within 7% or better.

Table 2. Results on Replicate Samples (ug/L)

Site	Date	Sample Numbers	Methoprene			Methoprene Acid		
			Rep. #1	Rep. #2	RPD	Rep. #1	Rep. #2	RPD
Winchester	6-Jun	234400/05	0.091 U	0.10 U	--	0.091 UJ	0.10 UJ	--
Wasteway	24-Jun	254030/31	0.097 U	0.099 U	--	0.097 UJ	0.099 UJ	--
Crab Creek	1-Aug	314024/25	0.11 U	0.10 U	--	0.11 UJ	0.10 UJ	--
	26-Aug	344044/46	0.11 U	0.10 U	--	0.11 UJ	0.10 UJ	--
Pond A13d	3-Jun	224402/03	<b>0.13</b>	<b>0.14</b>	7%	0.10 UJ	0.10 UJ	--
	13-Jun	244424/25	0.10 U	0.095 U	--	0.10 UJ	0.095 UJ	--
Pond B8d	10-Jun	234418/19	<b>0.19</b>	<b>0.19</b>	0%	0.10 UJ	0.095 UJ	--
Pond F11	6-Jun	234408/09	0.10 U	0.095 U	--	0.10 UJ	0.095 UJ	--

RPD = relative percent difference (replicate range as percent of average)

U = Not detected above the reported quantitation limit

UJ = Not detected above the reported estimated quantitation limit

Field blanks were analyzed to detect contamination arising from the sample bottles, collection procedures, or during transport. The blanks were prepared at selected sampling sites by transferring organic-free water from one sample container to another. The blank water was provided by Manchester Laboratory. Results showed no evidence of contamination in the samples (Table 3).

The replicate and blank samples were submitted blind to the laboratory.

Table 3. Results on Field Blanks (ug/L)

Site	Date	Sample Number	Methoprene (ug/L)	Methoprene Acid (ug/L)
Winchester Wasteway	6-Jun	234406	0.095 U	0.095 UJ
Crab Creek	1-Aug	314026	0.10 U	0.10 UJ
Pond F11	3-Jun	224401	0.10 U	0.10 UJ
Pond A13d	10-Jun	234417	0.10 U	0.10 UJ

U = Not detected above the reported quantitation limit

UJ = Not detected above the reported estimated quantitation limit

In light of methoprene’s vulnerability to degradation, Manchester Laboratory conducted a study to determine what holding time would be appropriate for field samples. Sample bottles containing blank water were spiked with methoprene at 1 and 10 ug/L and maintained at 4°C in the dark. The following recoveries were obtained:

Spiking Level	Day-1	Day-3	Day-7
1 ug/L	80%	69%	70%
10 ug/L	79% / 80%	109% / 91%	0% / 92%

The laboratory suspects that the lack of methoprene recovery in one of the Day-7 samples was due to a failure to spike it (Bob Carrell, personal communication). None of the degradation compounds were observed in that or any other of the samples. All samples for the present study were analyzed within seven days.

## Results and Discussion

### Results of Sampling

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The results from analyzing methoprene and methoprene acid in water samples from selected locations in MCD #1 are in Tables 4 (creeks and wasteways) and 5 (Westlake Area ponds). Appendix B shows the dates and locations when methoprene was applied during the period these samples were being collected.

Of the 40 creek and wasteway samples collected by Ecology in June and August, methoprene and methoprene acid were only detected in a single sample from Lind Coulee. Concentrations in that sample were estimated at 0.64 and 0.52 ug/L (parts per billion), respectively. Neither methoprene nor methoprene acid were detected in any other samples at or below approximately 0.1 ug/L.

Table 6 shows the correspondence between dates when methoprene was applied and dates when the creek and wasteway samples were collected. As noted previously, the applications begin at first light and are normally completed by 10 AM.

Table 4. Methoprene Data Collected by Ecology in Grant County Mosquito Control District No. 1 During 2005: Creeks and Wasteways

Site	Date	Time	Sample Number	Temp. (°C)	Methoprene (ug/L)	Methoprene Acid (ug/L)
Winchester Wasteway	6-Jun	1204	234400	17.7	0.091 U	0.091 UJ
	6-Jun	1206	234405	NA	0.10 U	0.10 UJ
	15-Jun	0950	244060	16.6	0.097 U	0.097 UJ
	24-Jun	1310	254030	20.6	0.097 U	0.097 UJ
	24-Jun	1315	254031	NA	0.099 U	0.099 UJ
	1-Aug	1530	314021	25.2	0.11 U	0.11 UJ
	11-Aug	0850	324030	20.3	0.10 U	0.10 UJ
	26-Aug	1230	344041	19.2	0.11 U	0.11 UJ
Frenchman Hills Wasteway	6-Jun	1253	234401	18.3	0.10 U	0.10 UJ
	15-Jun	0940	244061	16.0	0.11 U	0.11 UJ
	24-Jun	1335	254032	21.2	0.10 U	0.10 UJ
	1-Aug	1515	314020	24.0	0.11 U	0.11 UJ
	11-Aug	0900	324031	21.8	0.10 U	0.10 UJ
	26-Aug	1215	344040	19.8	0.10 U	0.10 UJ
Moses Lake Outlet	6-Jun	1205	234402	20.0	0.095 U	0.095 UJ
	15-Jun	1156	244062	19.5	0.098 U	0.098 UJ
	24-Jun	1520	254034	22.0	0.10 U	0.10 UJ
	1-Aug	1830	314027	25.9	0.10 U	0.10 UJ
	11-Aug	1105	324032	25.5	0.097 U	0.097 UJ
	26-Aug	1500	344043	24.3	0.10 U	0.10 UJ
Crab Creek	6-Jun	1050	234403	15.3	0.10 U	0.10 UJ
	15-Jun	1049	244063	16.0	0.10 U	0.10 UJ
	24-Jun	1630	254035	22.4	0.10 U	0.10 UJ
	1-Aug	1745	314024	23.9	0.11 U	0.11 UJ
	1-Aug	1750	314025	NA	0.10 U	0.10 UJ
	11-Aug	1000	324033	18.4	0.099 U	0.099 UJ
	26-Aug	1415	344044	19.6	0.11 U	0.11 UJ
	26-Aug	1425	344046	NA	0.10 U	0.10 UJ
Rocky Ford Creek	6-Jun	1118	234404	16.8	0.10 U	0.10 UJ
	15-Jun	1108	244064	17.4	0.10 U	0.10 UJ
	24-Jun	1655	254036	22.0	0.10 U	0.10 UJ
	1-Aug	1700	314023	23.0	0.10 U	0.10 UJ
	11-Aug	1020	324034	19.5	0.10 U	0.10 UJ
	26-Aug	1345	344045	19.4	0.10 U	0.10 UJ
Lind Coulee	6-Jun	1355	234407	17.3	0.10 U	0.10 UJ
	15-Jun	1022	244065	NA	<b>0.64 NJ</b>	<b>0.52 J</b>
	24-Jun	1420	254033	NA	0.097 U	0.097 UJ
	1-Aug	1620	314022	21.3	0.10 U	0.10 UJ
	11-Aug	0935	324035	18.3	0.10 U	0.10 UJ

Site	Date	Time	Sample Number	Temp. (°C)	Methoprene (ug/L)	Methoprene Acid (ug/L)
	26-Aug	1300	344042	17.7	0.10 U	0.10 UJ

U = Not detected above the reported quantitation limit.

UJ = Not detected above the reported estimated quantitation limit.

J = Analyte positively identified; the associated numerical value is its approximate concentration.

NJ = Analyte tentatively identified; the associated numerical value is its approximate concentration.

NA = not analyzed

Table 5. Methoprene Data Collected by Ecology and WDFW in Grant County Mosquito Control District No. 1 During 2005: West Lake Area Ponds

Site	Date	Time	Sample Number	Temp. (°C)	Methoprene (ug/L)	Methoprene Acid (ug/L)
Pond A13d	3-Jun	1259	224402	21±2	<b>0.13</b>	0.10 UJ
	3-Jun	1300	224403	21±2	<b>0.14</b>	0.10 UJ
	4-Jun	1253	224406	21±2	0.10 U	0.10 UJ
	6-Jun	1002	234410	19±2	0.10 U	0.10 UJ
	9-Jun	1259	234413	21±2	0.10 U	0.10 UJ
	10-Jun	1401	234416	21.5	0.10 U	0.10 UJ
	11-Jun	1335	234421	22.0	0.098 U	0.098 UJ
	13-Jun	1126	244424	20.5	0.10 U	0.10 UJ
	13-Jun	1127	244425	20.5	0.095 U	0.095 UJ
	16-Jun	1419	244428	21.0	0.097 U	0.097 UJ
Pond B8d	3-Jun	1346	224404	19±2	0.10 U	0.10 UJ
	4-Jun	1333	224407	19±2	0.095 U	0.095 UJ
	6-Jun	1048	234411	17±2	0.10 U	0.10 UJ
	9-Jun	1354	234414	19±2	0.10 U	0.10 UJ
	10-Jun	1458	234418	20.2	<b>0.19</b>	0.10 UJ
	10-Jun	1459	234419	20.2	<b>0.19</b>	0.095 UJ
	11-Jun	1425	234422	20.5	<b>0.14</b>	0.10 UJ
	13-Jun	1206	244426	18.5	0.095 U	0.095 UJ
	16-Jun	1505	24429	23.5	0.095 U	0.095 UJ
Pond F11	3-Jun	1151	224400	20±2	0.095 U	0.095 UJ
	4-Jun	1215	224405	20±2	0.10 U	0.10 UJ
	6-Jun	0912	234408	17±2	0.10 U	0.10 UJ
	6-Jun	0913	234409	17±2	0.095 U	0.095 UJ
	9-Jun	1216	234412	20±2	0.095 U	0.095 UJ
	10-Jun	1318	234415	21.5	0.095 U	0.095 UJ
	11-Jun	1235	234420	22.0	0.095 U	0.095 UJ
	13-Jun	1015	244423	17.0	0.10 U	0.10 UJ
	16-Jun	1335	244427	20.0	0.098 U	0.098 UJ

U = Not detected above the reported quantitation limit

UJ = Not detected above the reported estimated quantitation limit

NA = not analyzed

Table 6. Correspondence Between Methoprene Applications and Ecology Water Samples from Creeks and Wasteways

Sampling Site	June 2005 Sampling Period		August 2005 Sampling Period	
	Application Date	Sample Date	Application Date	Sample Date
Winchester Wasteway	6-Jun	6-Jun	29-Jul	--
	15-Jun	15-Jun	30-Jul	1-Aug
	23-Jun	--	9-Aug	11-Aug
	24-Jun	24-Jun	18-Aug	26-Aug
Frenchman Hills Wasteway	3-Jun	6-Jun	29-Jul	--
	7-Jun	--	30-Jul	1-Aug
	9-Jun	15-Jun	9-Aug	11-Aug
	23-Jun	--	18-Aug	26-Aug
	24-Jun	24-Jun		
Moses Lake Outlet	6-Jun	6-Jun	29-Jul	1-Aug
	14-Jun	--	8-Aug	11-Aug
	15-Jun	15-Jun	16-Aug	26-Aug
	23-Jun	24-Jun		
Crab Creek	5-May	6-Jun	30-Jul	1-Aug
	9-Jun	--	8-Aug	11-Aug
	15-Jun	15-Jun	16-Aug	26-Aug
	24-Jun	24-Jun		
Rocky Ford Creek	6-Jun	6-Jun	23-Jul	1-Aug
	15-Jun	15-Jun	2-Aug	--
	--	24-Jun	9-Aug	11-Aug
			16-Aug	26-Aug
Lind Coulee	27-May	6-Jun	22-Jul	1-Aug
	9-Jun	15-Jun	5-Aug	11-Aug
	20-Jun	--	15-Aug	26-Aug
	23-Jun	24-Jun		

Most of the June samples were taken within one day of methoprene application. Approximately half of the August samples were collected within three days of application, while the remainder were collected six-to-eleven days following application.

WDFW began sampling Westlake Area Ponds A13d, B8d, and F11 immediately following the methoprene application of June 3. Sampling continued for two weeks, during which time a second and a third application occurred on June 4 and 10.

Detection frequency was slightly greater in the ponds, where methoprene was detected in 5 of the 28 samples analyzed. The June 3 replicate samples from Pond A13d had methoprene concentrations of 0.13 – 0.14 ug/L. The June 10-11 samples from Pond B8d had 0.14 – 0.19 ug/L. Methoprene applications had occurred the same or previous day these samples were taken.

Neither methoprene nor methoprene acid were detected in any of the other pond samples at or below approximately 0.1 ug/L, including several samples collected on days when methoprene was applied. Table 7 shows the correspondence between application and sampling dates for the ponds. The Westlake Pond Area had been sprayed on four occasions prior to the initial set of samples collected on June 3.

Table 7. Correspondence Between Methoprene Applications and WDFW Water Samples from Westlake Area Ponds

Sampling Site	June 2005	
	Application Date	Sample Date
Westlake Area Ponds	23-May	--
	1-Jun	--
	2-Jun	--
	3-Jun	3-Jun
	4-Jun	4-Jun
	--	6-Jun
	--	9-Jun
	10-Jun	10-Jun
	--	11-Jun
	--	13-Jun
	--	16-Jun

## Results from Other Monitoring Programs

An effort to identify similar monitoring programs for methoprene yielded the following:

The Ontario Ministry of Environment monitors methoprene in surface waters where it is used for mosquito control. Detection limits have been in the range of 0.005-0.020 ug/L. They report “almost never finding methoprene in open waters over the course of hundreds of samples”. Methoprene has been detected in municipal catch basins, but concentrations have been highly variable. Most catch basin detections have been in the vicinity of 0.005 ug/L. (Tim Fletcher, Ecological Standards Section, Ontario Ministry of Environment, personal communication)

New York’s Suffolk County Department of Health Services has analyzed methoprene in hundreds of surface and well water samples as part of their mosquito control program. At a detection limit of 0.2 ug/L, methoprene has never been detected (Martin Trent and Sam Jackling, Suffolk County Health Department, personal communication). A recent study employing lower detection limits of approximately 0.01 ug/L has detected methoprene when samples were collected immediately after spraying. These data are not yet available (Martin Trent, personal communication).

## Water Quality Criteria for Methoprene

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As far as could be determined, there are no state or federal water quality criteria for methoprene. The Ontario Ministry of Environment (OMOE) has, however, developed Interim Provincial Water Quality Objectives (IPWQO) for this compound (OMOE, 2005).

The OMOE IPWQOs are maximum desirable concentrations of contaminants which ensure surface waters are satisfactory for aquatic life and recreation. They were developed to protect the most sensitive aquatic life stage of an organism for an indefinite exposure, based on toxicity data for fish, amphibians, and aquatic invertebrates. The type of endpoints evaluated for methoprene included LC-50s, embryo development, swimming behavior, and fecundity. A safety factor of 10 was employed. In addition to the IPWQO, OMOE established lowest effects levels as benchmarks for fish, amphibians, and aquatic invertebrates.

The draft IPWQO for methoprene, 0.2 ug/L, is the amphibian benchmark for chronic exposure, 1.6 ug/L, divided by 10. The 1.6 ug/L value comes from a study where significant abnormalities (missing hind limbs and eyes) were produced in Southern leopard frog juveniles exposed to an average methoprene concentration of 1.6 ug/L during a 90-day field exposure (Sparling 2000).

The OMOE benchmarks and draft IPWQO are listed in Table 8.

Table 8. OMOE Interim Draft Benchmarks for Methoprene

Organism	Benchmark (ug/L)
Fish	84
Invertebrates	10
Amphibians	1.6
draft IPWQO	0.2

IPWQO = Interim Provincial Water Quality Objective

## Conclusions

The present study found that methoprene levels in surface water samples from Grant County Mosquito District No. 1 rarely exceeded 0.2 ug/L, even when collected close to the time of application. Overall, the detection frequency for methoprene was 4 out of 68 samples or 6% (replicate samples pooled).

A low detection frequency for methoprene has also been reported by other surface water monitoring programs in the U.S. and Canada. A comparison of study results with draft Ontario Ministry of Environment (OMOE) water quality criteria suggests that the levels observed in Grant County would not be expected to have adverse effects on aquatic life.

## Recommendations

1. If further methoprene monitoring is done in connection with mosquito control in Grant County or other areas of Washington State, sampling should be closely confined to the location and time of application.
2. The derivatization step employed in the analytical method used in this study resulted in interferences. Detection limits could potentially be lowered by analyzing methoprene and methoprene acid separately or by employing additional clean-up of the extract.



## References

Beach, R., 2003. Comments on the National Pollution Discharge Elimination System Permit (NPDES) for Aquatic Mosquito Control – Permit No. WQG-992000 and Best Management Practices for Mosquito Control (BMPs): Recommendation for Restricted Use of Methoprene. Memorandum to K. Emmett. Washington Department of Fish and Wildlife, Olympia, WA.

Degitz, S.J., E.J. Durhan, J.E. Tietge, P.A. Kosian, G.W. Holcombe, and G.T. Ankley, 2003. Developmental Toxicity of Methoprene and Several Degradation Products in *Xenopus laevis*. *Aquat. Toxicol.* 62:97-105.

Ecology, 2002. Fact Sheet for Aquatic Mosquito Control General NPDES Permit. 4/17/2002.

[http://www.ecy.wa.gov/programs/wg/pesticides/final\\_pesticide\\_permits/mosquito/mosquito\\_index.html](http://www.ecy.wa.gov/programs/wg/pesticides/final_pesticide_permits/mosquito/mosquito_index.html)

Germaine, S.S., 2004. Ecology of Northern Leopard Frogs (*Rana pipiens*) at Potholes Reservoir, Grant County, Washington: Relationships with Habitat, Water Level, and Non-native Fish and Amphibians: A Funding Proposal submitted to the USDI Bureau of Reclamation Ephrata Field Office by the Washington Department of Fish and Wildlife Region 2 District Team, and Diversity and Science Divisions.

Johnson, A., 2005. Quality Assurance Project Plan: Methoprene Monitoring in Grant County Mosquito Control District #1. Washington State Department of Ecology, Olympia, WA. Publication No. 05-03-108. [www.ecy.wa.gov/biblio/0503108.html](http://www.ecy.wa.gov/biblio/0503108.html)

Leonard, W.P., K.R. McAllister, and R.C. Friesz, 1999. Survey and Assessment of Northern Leopard Frog (*Rana pipiens*) Populations in Washington State. *Northwestern Naturalist* 80: 51-60.

McAllister, K.R., W.P. Leonard, D.W. Hays, and R.C. Friesz, 1999. Washington State Status Report for the Northern Leopard Frog. Washington Department of Fish and Wildlife, Wildlife Management Program, Olympia, WA.

OMOE, 2005 (peer review draft). Scientific Criteria Document for the Development of a Provincial Water Quality Objective for Methoprene. Standards Development Branch, Ontario Ministry of the Environment, Toronto, ON.

Sparling, D.W., 2000. Effects of Altosid and Abate-4E on Deformities and Survival in Southern Leopard Frogs Under Semi-natural Conditions. *J. Iowa Acad. Sci.* 107(3):90-91.

Suffolk County, 2005. Suffolk County Vector Control and Wetlands Management Long-term Plan and Environmental Impact Statement. Suffolk County, NY.

**Appendix A. Location of Sampling Sites for 2005 Methoprene Study (NAD 83)**

Waterbody	Sampling Site	Latitude	Longitude
Winchester Wasteway	Road C S.E.	46 59 42	119 25 31
Frenchman Hills Wasteway	Road C S.E.	46 58 27	119 25 45
Moses Lake	Outlet at Sand Dunes Road	47 05 01	119 20 01
Crab Creek	Road 7 S.E.	47 11 23	119 15 59
Rocky Ford Creek	State Route 17	47 15 42	119 27 21
Lind Coulee	State Route 17	47 00 34	119 08 21
West Lake Area Ponds	Pond A13d	47.09471	119.43857
	Pond B8d	47.08136	119.3710
	Pond F11	47.08914	119.34246

**Appendix B. Methoprene Applications in MCD #1 During the Period When Water Samples were Being Collected by Ecology and WDFW in 2005.**

(Prepared by Jim Thompson, Grant County Mosquito Control, October 28, 2005)

Westlake Ponds	<u>23 May thru 16 June</u> May23, Jun1, Jun2, June3, Jun4, Jun10	
Lower Crab Creek	<u>5 May thru 24 June</u> May5, Jun9, Jun15, Jun24	<u>26 July thru 26 August</u> July30, Aug8, Aug16
Rocky Ford Creek	<u>30 May thru 24 June</u> Jun6, Jun15	<u>23 July thru 26 August</u> July23, Aug2, Aug9, Aug16
Moses Lake	<u>30 May thru 24 June</u> Jun6, Jun14, Jun15, Jun23	<u>26 July thru 26 August</u> Jul29, Aug8, Aug16
Frenchman Hills W.W.	<u>30 May thru 24 June</u> Jun3, Jun7, Jun9, Jun23, Jun24	<u>26 July thru 26 August</u> Jul29, Jul30, Aug9, Aug18
Winchester W.W.	<u>30 May thru 24 June</u> Jun6, Jun15, Jun23, Jun24	<u>26 July thru 26 August</u> Jul29, Jul30, Aug9, Aug18
Lind Coulee W.W.	<u>27 May thru 24 June</u> May27, Jun9, Jun20, Jun23	<u>22 July thru 26 August</u> July22, Aug5, Aug15