**Appendix 1-10: Summary of Malathion Monitoring Data**

# **1 Field-level Aquatic Monitoring**

Malathion is water soluble and therefore has the potential to be dissolved in rain water and transported in runoff water from application sites. The Boll Weevil Eradication Program (BWEP) has monitored malathion in runoff from rain events following malathion applications from fields with known application rates (USDA 1996 and 1997). Though runoff concentrations are not directly applicable to concentrations in aquatic bins as spray drift is not considered, this targeted monitoring effort characterizes run-off concentrations for the given use conditions.

Levels of malathion in runoff water have been examined using automatic runoff sampling equipment which consists of collection bottles with funnels recessed in the ground at sites where runoff is expected. The amount of malathion in runoff is expected to be affected by numerous variables including the soil type, half-life on the particular soil, the amount of time between application and precipitation, the amount of precipitation, and vegetation. **Table B 1-10.1** below shows runoff monitoring data from six treated cotton fields in the Boll Weevil program close to bodies of water. Sampling was performed close to the field (0-20 feet) and farther from the field (40-110 feet from the field). In most cases, malathion concentrations were lower when the interval between application and rainfall was longer and/or distance from the field was farther. These observations are expected since increasing the time interval since application allows for more degradation to occur and longer runoff travel distances allow malathion to leach or adsorb to soil particles before reaching surface water. All samples were taken the day after the first rain event after malathion application except where noted. These results should be caveated with the understanding that no spiked samples were tested as a positive control in BWEP monitoring efforts. Other studies on natural waters found recoveries ranging from 29% to 72% for malathion and 9% to 61% for malaoxon likely due to degradation prior to analysis (MRID 45526201).

**Table B 1-10.1. Field monitored runoff from aerial ultra-low volume application of 0.75 lb malathion/A in the cotton boll weevil control program (USDA 1996 and 1997)**

|  |  |  |
| --- | --- | --- |
| Field Number | Time from Application to Rain (days) | Field Runoff Malathion Concentrations (µg/L) |
| Closer to Field(Distance in Feet) | Farther from Field(Distance in Feet) |
| 1806-502 | 1 | 9.3 (20')  |  1.9 (110') |
| 3 | 7.5 (20')1 | 3.5 (110')1 |
| 6 | >0.3 (20')1  | >0.3 (110')1 |
| 1806-504 | 1 | 70 (20')  | 33 (40') |
| 6 | 0.48 (20')1 | nd (40')1 |
| 502 | 3 | 1.1 (20')  | 1.1 (110') |
| 7 | 0.3 (20')  | 0.5(110') |
| 504 | 1 | 10.9 (20')  | nd (40') |
| 3 | 41.8 (20')  | 15.6 (40') |
| 7 | 146 (20')  | 93.5 (40') |
| 7806 | ? | 0.9 (0')  | 0.5 (45') |
| 6 | 1.7 (0')  | 1.1 (45') |
| 14 | <0.3 (0')  | 0.3 (45') |
| 325 | 2 | 8.54 (15')  | 0.82 (60') |
| 9 | 35.8 (15')  | 16.2 (60') |

1 Sample collection made more than one day after rain event

Malathion concentrations in water in and around urban medfly treatment areas in California and Florida have been measured. In urban areas not involved in medfly control measures, malathion can be found in runoff water at higher levels than agricultural areas. It is likely that residential uses will result in aquatic contamination. Residential malathion uses include outdoor home and garden and commercial use as well as residential mosquito control. However, the monitoring studies associated with this use provide information on malathion fate and transport in residential settings prior to residential use mitigation. This mitigation included the elimination of residential lawn (broadcast), residential pressurized can formulation, and residential dust formulation uses but maintains residential house perimeter and garden treatments (USEPA, 2006). Home use formulations may be applied as a “... spray to lower foundation of house, patios and garbage cans ... along fences; to firewood piles; and other infested areas” (Ortho Malathion 50 Plus Insect Spray label). Malathion on the surfaces described on this label is likely to persist longer and be more available for runoff than malathion on soil. Fyfanon ULV formulation is applied at 0.2 - 0.23 lbs/A aerially at 150 mph over residential areas for mosquito control. In addition to covering anthropogenic surfaces it is likely that small to moderate sized bodies of water receive direct spray during normal aerial mosquito control use as smaller waterbodies can co-occur with residential aeras. Large waterbodies are avoided during malathion applications for public health mosquito control and buffers to waterbodies are required for agricultural uses. In medfly treatments, malathion is mixed with a bait mixture and applied aerially at nearly the same rate as in mosquito control but with large buffers to waterbodies (up to 200 feet). Thus, contaminated water bodies presumably received insecticide residues by drift and runoff. On average, reservoirs in the treatment area which were flagged to avoid direct spray contained 0.16 µg/L before treatments and 2.59 µg/L immediately after treatment. All waters in and around the treatment area, whether protected or not, showed increased malathion levels immediately after treatment. In general, applications were performed approximately weekly with no noted aggregate accumulation of malathion in water.

Rainwater runoff in California medfly treatment area contributed greatly to malathion levels in a stream passing through the treatment area. After precipitation, inflow into the treatment area contained less than 1 µg/L while downstream water contained up to 203 µg/L malathion.

Maxima in 1990 and 1981 were 44.1 and 583 µg/L, respectively (CEPA 1996). Residential uses that are no longer supported also potentially contributed to these concentrations. Residential settings are expected to be composed of numerous surfaces which may be physically and biologically impervious to malathion. Although the maximum application rate for mosquito control is low relative to agricultural use (0.20 - 0.6 lbs/A for aerial mosquito control versus 0.175 – 7.5 lbs/A for agricultural pest control), application over wide areas may be concentrated in storm drain systems along with malathion from home and garden and commercial site use. Furthermore, the baited formulation for medfly control effort produced a mean droplet size significantly larger than current non-agricultural broadcast uses. The mean droplet size for the medfly program was 200-300 µm while ULV non-agricultural broadcast uses require a mean droplet size of 30 µm (ground) or 60 µm (aerial). The larger droplet size from the medfly program increases deposition near areas of application and decreases offsite drift. The highest levels of aquatic malaoxon found in a search of available data were a result of medfly control efforts in California (CDFG 1982). **Table B 1-10.2** below is derived from the monitoring study during the malathion spraying in the Santa Clara Valley. Samples were taken 2 - 3.5 hours after the first rainfall six days after the last application in the medfly control effort. These runoff concentrations are much higher than agricultural runoff levels or non-targeted residential runoff levels, however, the study includes spiked sample positive controls validating recoveries. This indicates reported concentrations accurately reflect concentrations in water at the time of sampling.

**Table B 1-10.2. Malathion and Malaoxon Concentrations in Creeks after Malathion Applications in the Santa Clara Valley (0.13 lb a.i./A; DV0.5 = 200-300 µm)**

|  |  |
| --- | --- |
| Sampling Location | Average Concentration (Std. Dev.) |
| Malathion (µg/L) | Malaoxon (µg/L) |
| Adobe Creek | 50’ Upstream | 449 (17.7)  | 164 (33.2) |
| Drain | 583 (40.3)  | 328 (18.4) |
| 100’ Downstream | 361 (20.5)  | 169 (-) |
| Stevens Creek | 50’ Upstream | 159 (-)  | 68.0 (-) |
| Drain | 434 (73.5)  | 147 (4.2) |
| 150’ Downstream | 156 (23.3)  | 68.0 (-) |
| Guadalupe Creek, Site 1 | 50’ Upstream | 1.9 (0.2)  | 0.8 (0.3) |
| Drain | 142 (-)  | 147 (4.2) |
| 150’ Downstream | 23.5 (2.1)  | 22.0 (-) |
| Guadalupe Creek, Site 2 | 50’ Upstream | 137 (25.4)  | 212 (9.2) |
| Drain | 188 (12.0)  | 250 (8.5) |
| 150’ Downstream | 169 (6.4)  | 231 (8.5) |

In the registrant aquatic field dissipation study located in Missouri, malathion was applied at a

maximum rate of 0.58 lb ai/A in three weekly applications to a flooded rice paddy (soil pH 6.1,

water pH not stated). Samples were collected prior to the subsequent weekly application and tested for malathion and malaoxon. Malathion residues detected in water samples collected after the first and second application dissipated to below the detection limit (10 μg/L) in samples taken prior to the second and third applications. In water samples collected one day after the last application, malathion concentrations averaged 17 μg/L and had decreased to 10 μg/L by the second sampling day. Malaoxon residues were <10 μg/L at all sampling dates. The data indicate a very rapid dissipation of malathion in water, with a likely half-life less than one day. An accurate half-life could not be determined because of the rapid dissipation and high detection limit (MRID 42058402, 43166301).

# **General Monitoring Data**

## Clean Water Act Programs

Malathion is identified as a cause of impairment for four water bodies listed as impaired under section 303(d) of the Clean Water Act in California and Idaho and detailed in **Table B 1-10.3**. There are no Total Maximum Daily Loads (TMDL) listed for malathion.  Section 304(a) ambient water quality criteria (0.1 µg/L), Aquatic life benchmarks (**Table B 1-10.4**), and Health Advisory levels (**Table B 1-10.5**), have been established for malathion.  Monitoring data and impaired waters for malathion, demonstrate that the use of malathion may result in transport of malathion to surface water at levels that may cause risk to human health and/or ecological receptors.

**Table B 1-10.3. 303(d) Impaired waters for malathion**

|  |  |  |  |
| --- | --- | --- | --- |
| **Name** | **Watershed** | **State** | **Reach ID** |
| Arcade Creek | Lower American | California | CAR5192100019980813113546 |
| Colusa Basin Drain | Sacramento-Stone Corral | California | CAR5202100019980813170249  |
| Orestimba Creek | [Middle San Joaquin-Lower Merced-Lower Stanislaus](http://iaspub.epa.gov/tmdl_waters10/attains_watershed.control?p_huc=18040002&p_state=CA&p_cycle=2010&p_report_type=) | California | CAR5355000020021209154446  |
| Mason Creek | Lower Boise | Idaho | ID17050114SW006\_02 |

**Table B 1-10.4. Aquatic life benchmarks for malathion (µg/L)1**

|  |  |  |  |
| --- | --- | --- | --- |
| **Fish** | **Invertebrates** | **Nonvascular Plants** | **Vascular Plants** |
| Acute | Chronic | Acute | Chronic | Acute | Chronic |
| 16.5 | 8.6 | 0.295 | 0.035 | 2400 | > 9630 |

1 http://www.epa.gov/oppefed1/ecorisk\_ders/aquatic\_life\_benchmark.htm#benchmarks

**Table B 1-10.5. Office of Water health advisories for malathion1**

|  |
| --- |
| **Health Advisories2** |
| **10-kg Child** | **70-kg Adult** |
| 1-day(µg/L) | 10-day (µg/L) | RfD (mg/kg/day) | DWEL (µg/L) | Life-time (µg/L) | mg/L at 10-4 Cancer Risk |
| *0.2* | *0.2* | *0.07* | *2* | *0.5* | *-* |

DWEL=Drinking Water Equivalent Level

RfD=Reference Dose

1 The 2012 Edition of the Drinking Water Standards and Health Advisories is available at:  http://water.epa.gov/action/advisories/drinking/upload/dwstandards2012.pdf  (accessed 2/28/2015)

2 Health advisories, sponsored by the EPA’s Office of Water (OW), are concentrations of drinking water contaminants at which adverse health effects are not anticipated to occur over specified exposure durations.

## 3 Open Literature studies retrieved through ECOTOX

There were628 ECOTOX studies for malathion that were assigned the FATE rejection code. Because the laboratory fate dataset is well characterized, the dataset was searched for dissipation and monitoring studies only, excluding groundwater monitoring and international studies. This exclusion criteria resulted in 26 studies. 24 of these monitoring studies did not appear to be targeted monitoring and were therefore not thought to add significant value. Further, the 24 studies included an author affiliated with the USGS and study results are therefore likely included in the USGS NAWQA database, discussed in the monitoring data summary. The remaining targeted monitoring studies are Petreas *et al* (1992) and Pederson *et al* (2006). Petreas *et al* addresses the dissipation of a malathion aerial spray and transformation products on teflon and filter paper and resulting volatilization. Degradation was most rapid on filter paper (DT50 = 39 hours) and longest on teflon (DT50 = 92 days) with malaoxon concentrations increasing over time on all surfaces. Nine days after application, malaoxon concentrations had increased to 10% to 20% of the concentration of original malathion deposition. Malaoxon air concentrations were at their maximum between 24 and 48 hours after application and malathion and malaoxon were still detectable in air at the end of the 10 day study. Pederson *et al* (2006) monitored runoff to the Calleguas Creek after precipitation events with known usage volume of malathion in a mixed residential and agricultural watershed. Runoff samples were collected at 15 to 60 minute intervals over the course of rain events of more than 15 millimeters. No difference in event mean concentration was found between agricultural irrigation, agricultural runoff, and residential runoff events and no first flush spike in malathion concentration was found. Generally, more variation was found between runoff sites than could be explained by the controlled variables in the study. Malathion concentrations were under 0.1 ppb.

## USGS NAWQA and CDPR

Extensive monitoring data is available for malathion through the Water Quality Portal (<http://www.waterqualitydata.us/>) which includes malathion monitoring data from the USGS National Water-Quality Assessment (NAWQA) along with data from 20 other national, state, and local organizations. Many high concentrations prior to the 1988 Registration Standard which imposed label restrictions to reduce exposure resulting from indoor applications were found. However, 62,538 surface water samples have been taken since 1988 with 3,354 detections between one part per trillion and one part per billion (detection frequency of 5%) and 25 detections between 1.0 and 9.58 ppb. California Department of Pesticide Regulation (CDPR) has also performed extensive monitoring with 11,417 samples, 355 detections, and 28 detections above one ppb since 1995.Both NAWQA data and CDPR data for detects over one ppb are combined and presented in **Table B 1-10.6** below. High concentrations were found in areas with developed, agricultural, and mixed landcovers (determined through Google Maps) and in many areas around the U.S. and territories therefore significant correlation between high concentrations and use pattern is not likely. This demonstrates that agricultural and non-agricultural uses are both substantial contributors to aquatic exposure. Highest flows in waters found with concentrations more than one ppb is 762 cubic feet per second. This flow is higher than those assumed for the low flow bin (0.035 cfs) and moderate-flow bin (35 cfs) but is significantly lower than the high-flow bin (3,500 cfs). NAWQA reports 12 detections of malaoxon in surface water in 8 states across the South, Midwest, and Northwest (detection frequency of 0.1%) with the highest concentration of 0.204 ppb. Monitoring targeted to runoff from cotton fields applied with malathion under the Boll Weevil Eradication Program demonstrated runoff 20 feet from the edge of field can have concentrations as high as 146 ppb (USDA, 1996 and 1997).

**Table B 1-10.6. All water quality portal concentrations higher than 1 ppb since 1988**

| **State** | **Waterbody** | **Concentration (ppb)** | **Average flow in month of detection13** | **Drainage area** | **Watershed Composition** |
| --- | --- | --- | --- | --- | --- |
| Alabama | Three Mile Branch | 9.6 | --- | 14 mi21 | Developed |
| Mountain Fork | 4.8 | --- | 84 mi22 | Agriculture |
| Flat Creek (FLTL-1) | 3.4 | --- | 9 mi23 | Agriculture |
| Goose Creek (GOOM-1) | 2.5 | --- | 14 mi24 | Developed |
| Arkansas | Canal No. 43 near Hailey | 8.5 | --- | 72 mi25 | Agriculture |
| Clay Bayou near Hailey | 1.7 | --- | 168 mi26 | Agriculture |
| California | Calaveris River at Pezzi Rd | 1.4 | --- | --- | Mixed |
| Warm Creek near San Bernadino | 1.4 | 1.5 cfs | --- | Developed |
| Newman Wasteway near Gustine | 1.1 | --- | 8 mi27 | Agriculture |
| Alamo River near Niland | 1.1 | 762 cfs | --- | Agriculture |
| Colusa Basin Drain #5 | 1.21.063.3 | --- | --- | --- |
| Hines Channel | 2.6 | --- | --- | --- |
| Marshburn Slough | 2.41.0 | --- | Small enough there is sometimes no flow8  | --- |
| Westcliff Park | 5.6 | --- | --- | --- |
| Verde Drain | 4.1 | --- | --- | --- |
| Orcutt/Solomon Canyon Creek | 2.01.63.7 | --- | --- | --- |
| Orcutt Creek | 5.6 | 0.3 | --- | --- |
| Reclamation Ditch in Monterey County | 2.822.5 | 2.72.0 | --- | --- |
| Alisal Creek | 1.03.91.811.9 | --- | --- | --- |
| Main St. Ditch | 13.0 | --- | --- | --- |
| Oso Flaco Creek | 5.21.1 | --- | --- | --- |
| Rice Drain 3  | 5.4 | --- | --- | --- |
| Tembladero Slough  | 1.7 | --- | --- | --- |
| Connecticut | Naugatuck River at Beacon Falls | 4.3 | 560 cfs | --- | Mixed |
| Florida | 10B Lateral near Vineland | 5.3 | Flows as high as 250 cfs in month of detection; typically <100 cfs | --- | Developed |
| Mullock Creek in Fort Myers | 1.9 | --- | 77 mi29 | Developed |
| Iowa | English River in Riverside | 1.2 | 60 cfs 7 miles upstream | --- | Agriculture |
| Kansas | Unnamed Tributary in Fort Leavenworth | 2.6 | --- | --- | Mixed |
|  | 1.5 | --- | --- | Mixed |
| Mississippi | Deer Creek at Rolling Fork | 5.4 | 9 cfs | --- | Agriculture |
| New York | Stone Hill River Tributary at Bedford Hills | 2 | --- | --- | Mixed |
|  | 1.4 | --- | --- | Mixed |
|  | 1.1 | --- | --- | Mixed |
| Puerto Rico | Rio de la Plata near Toa Alta | 2 | --- | 45 mi210 | Mixed |
| Rio de Bayamon at Bayamon | 1.8 | --- | 34 mi211 | Developed |
| Tennesse | Fletcher Creek in Memphis | 1.8 | 34 cfs | --- | Developed |
| Texas | Unnamed tributary to Oso Creek near Corpus Christi | 2.6 | 26 cfs in Oso Creek | --- | Mixed |
| Arroyo Colorado at Harlingen | 1.2 | --- | 706 mi212 | Mixed |

1 <http://adem.alabama.gov/programs/water/wqsurvey/table/2005ThreeMileBranch-LowerWetumpkaRoad.pdf>

2 <http://adem.alabama.gov/programs/water/wquality/tmdls/FinalHesterCreekMtnForkPathogensTMDL.pdf>

3 <http://adem.alabama.gov/programs/water/wqsurvey/table/2009/2009FlatCk.pdf>

4 <http://adem.alabama.gov/programs/water/wquality/tmdls/FinalGooseCreekPathogenTMDL.pdf>

5 <http://watersheds.cast.uark.edu/reports/pdf/0805000202hydro_sub.pdf>

6 <http://watersheds.cast.uark.edu/reports/pdf/0805000202hydro_sub.pdf>

7 <http://iaspub.epa.gov/tmdl/attains_waterbody.control?p_list_id=CAR5412000020011211151440&p_cycle=2010&p_report_type>=

8<http://www.cdpr.ca.gov/docs/>emon/epests/rifa/1208\_99n.pdf

9 <http://blogs.fgcu.edu/mullochcreek/wp-content/uploads/sites/30/2014/07/SCP-FFY-grant-proposal-2007.pdf>

10 <https://ofmpub.epa.gov/waters10/attains_impaired_waters.show_tmdl_document?p_tmdl_doc_blobs_id=75535>

11 <http://iaspub.epa.gov/tmdl_waters10/attains_waterbody.control?p_list_id=PRER12A1&p_cycle=2012&p_report_type>=

12http://arroyocolorado.org/about-the-watershed/

13Average monthly flow from month of detection taken from <http://waterdata.usgs.gov/nwis/sw>

# 5 Long-range Transport

A number of studies have documented atmospheric transport and re-deposition of pesticides

from the Central Valley to the Sierra Nevada Mountains (Fellers *et al.*, 2004; LeNoir *et al.*, 1999;

McConnell *et al.*, 1998; Sparling *et al.*, 2001). Prevailing winds blow across the Central Valley

eastward to the Sierra Nevada Mountains, transporting airborne industrial and agricultural

pollutants into the Sierra Nevada ecosystems, where they are deposited in rain and snow.

McConnell *et al.* (1998) detected malathion in rain and snow samples collected from the Sierra

Nevada Mountains at 500 m elevation near the entrance of the Sequoia National Park, at 1920 m in the Sequoia National Park, and at 2,200m at Ward Creek, west of Lake Tahoe. Measured

concentrations ranged from <0.046 to 24 ng/L. No malathion was detected in the surface water

samples taken in this study. LeNoir et al. (1999) detected malathion in three air samples taken at

200 m and 533 m in Sequoia National Park. Concentrations in these samples ranged from 0.15

to 0.29 ng/m3. They also detected malathion in water samples taken from a transect that ran

from 200 m to 2,040 m at concentrations ranging from 66 to 83 ng/L. These results indicate that

prevailing winds blowing from the Central Valley may transport and re-deposit malathion in

higher elevations of the Sierra Nevada Mountains. Other studies have detected malathion in rainwater and air in urban areas within the Central Valley. Majewski *et al.* (2005) monitored pesticides in rainwater collected near Modesto, California between 2001 and 2004. They report a mean and maximum concentration of malathion of 0.031 and 0.383 μg/L, respectively, with a detection frequency of 43%. Majewski and Baston (2002) report on pesticides in air samples taken near Sacramento, California in 1996 and 1997. They detected malathion but at relatively low frequency (0.0 – 10.8%). Mean air concentrations were 1.13-2.89 ng/m3 and maximum concentrations were 1.13-3.77 ng/m3. The magnitude of transport via secondary drift depends on malathion’s ability to be mobilized into air and its eventual removal through wet and dry deposition of gases/particles and photochemical reactions in the atmosphere. In general, deposition of drifting or volatilized pesticides is expected to be greatest close to the site of application. Air and precipitation monitoring studies in the ECOTOX bibliography reported concentrations of the same magnitude as those reported above (Vogel *et al.*, 2008; Harman-Fetcho *et al.*, 2000; Majewski *et al*., 1998).

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