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This Appendix evaluates current-use pesticides of concern in the Molalla-Pudding Subbasin in order to determine if water column, fish or shellfish tissue, or sediment concentrations are high enough to potentially adversely impact aquatic life or human health.

# **OVERVIEW OF CURRENT USE PESTICIDE DETECTIONS**

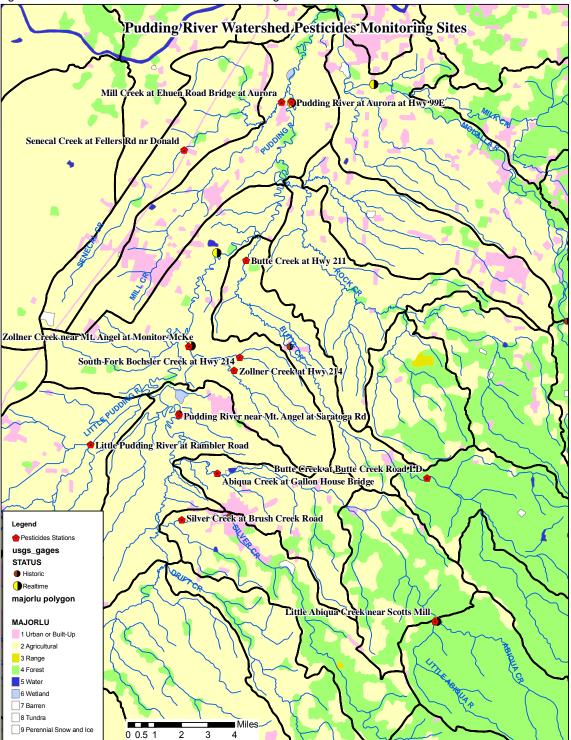
A 1998 USGS report describes April 1993 to September 1995 pesticides monitoring in the Willamette Basin, including extensive monitoring in the Pudding River watershed (Rinella and Janet, 1998). Sampling was performed by USGS as part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program (Bonn, et al, 1995) and the Willamette River Basin Water Quality Study (Anderson, et al, 1996 and Anderson, et al, 1997). The studies suggest that a number pesticides may be present in the Willamette Basin in concentrations which may exceed either State of Oregon water quality criteria or, if State of Oregon water quality criteria have not been established, then in concentrations which may exceed criteria established by the National Academy of Sciences and National Academy or Engineering (NAS/NAE), the Canadian Council of Resources and Environmental Ministers (CCRM), or the U.S. Environmental Protection Agency (USEPA).

Janet and Rinella (1998) concluded that the largest concentrations for 27 of the 50 different pesticides detected in the Willamette Basin occurred at the Zollner Creek near Mt. Angel site in the Molalla-Pudding Subbasin . The following current-use pesticides were found to occasionally exceed water quality criteria: atrazine, azinphos-methyl, carbaryl, carbofuran, chlorpyrifos, diazinon, diuron, gamma-HCH (lindane), and malathion. The largest concentrations were observed at predominantly agricultural sites, including Zollner Creek.

Frequent monitoring of water column pesticides concentrations was performed by USGS at three locations in the Pudding River watershed: Little Abiqua Creek Near Scotts Mills (14200400, 1992 To 2004), Pudding River At Aurora (14202000, 1992 To 1997), and Zollner Creek Near Mt Angel (14201300, 1992 To 2006) (Figure I - 1 and Table I - 1). Occasionally monitoring was also done by USGS at other sites. Frequent monitoring of water column pesticides was performed by ODEQ at 10 sites from 2005 to 2007, listed in Table I - 2. Concentrations measured were compared to applicable criteria or guidelines (Table I - 3).

| Gage<br>Number | NAME   | RM   | Drainage<br>Area<br>(sq.mi.) | Periods                       | LAT     | LONG      | STATUS   | ELEV<br>(ft) |
|----------------|--|------|------------------------------|-------------------------------|---------|-----------|----------|--------------|
| 14202000       | Pudding River at Aurora<br>(Hwy 99E, u/s from Mill Cr) | 8.1  | 479                          | 1928-64, 93-97,<br>02-present | 45.2333 | -122.7489 | Realtime | 72           |
| 14201340       | Pudding River near<br>Woodburn                         | 23.4 | 314                          | 1997-present                  | 45.1514 | -122.8031 | Realtime | 130          |
| 14201300       | Zollner Creek near Mt.<br>Angel                        | 0.4  | 15.0                         | 1993-present                  | 45.1006 | -122.8206 | Realtime | 240          |
| 14200000       | Molalla River near Canby                               | 6.0  | 323                          | 1928-59, 63-78,<br>00-present | 45.2444 | -122.6861 | Realtime | 94           |
| 14200300       | Silver Creek near Silverton                            | 3.0  | 47.9                         | 1963-79                       | 45.0094 | -122.7875 | Historic | 218          |
| 14200400       | Little Abiqua at Scotts Mills                          | 0.1  | 9.8                          | 1993-2004                     | 44.9558 | -122.6272 |          | 800          |
| 14201000       | Pudding River near Mt. Angel<br>(Saratoga Rd)          | 40.7 | 204                          | 1939-66                       | 45.0361 | -122.8292 | Historic | 120          |
| 14201500       | Butte Cr at Monitor                                    | 5.9  | 58.7                         | 1936-85                       | 45.1017 | -122.7450 | Historic | 155          |

Table I - 1: Active and historic USGS discharge gages and water quality monitoring sites.





| Table I - 2: | ODEQ water quality mo | nitoring sites |
|--------------|-----------------------|----------------|
|--------------|-----------------------|----------------|

| Station Name and Lab Analytical<br>Storage and Retrieval (LASAR)<br>number | % Urban | % Ag | % Forest | River Mile | Drainage Area<br>u/s from station |
|--|---------|------|----------|------------|-----------------------------------|
| Pudding River at Aurora (Hwy 99E)  |         |      |          | mi         | (mi <sup>2</sup> )<br>479.        |
| (Gage 14202000, 10917)   | 5       | 58   | 36       | 8.1        | -73.<br>0                         |
| Pudding River near Mt. Angel (Saratoga Rd) (old Gage 14201000, 31877)      | 3       | 47   | 50       | 40.<br>7   | 204.<br>0                         |
| Abiqua Creek at Gallon House Bridge (31872)                                | 2       | 29   | 68       | 1.9        | 76.0                              |
| Butte Creek at Hwy 211 (10896)   | 1       | 24   | 75       | 1.3        | 67.8                              |
| Silver Creek at Brush Creek Road (10646)                                   | 6       | 17   | 77       | 1.3        | 54.4                              |
| Little Pudding River at Rambler Road (31875)                               | 22      | 74   | 3        | 2.9        | 52.9                              |
| Zollner Creek Near Mt Angel (Monitor-<br>McKee Rd) (Gage 14201300, 10899)  | 1       | 99   | 0        | 0.4        | 15.0                              |
| Zollner Creek at Hwy 214 (11515)   | 1       | 98   | 1        | 1.0        | 6.9                               |
| South Fork Bochsler Creek at Hwy 214 (11514, tributary to Zollner Cr)      | 1       | 98   | 1        | 0.6        | 2.6                               |
| Senecal Creek at Fellers Rd<br>(trib to Mill Cr to Pudding R)              | 8       | 89   | 3        | 3.1        | 9.7                               |
| Little Abiqua Creek near Scotts Mill (Gage 14200400)                       | 0       | 4    | 96       | 0.4        | 9.8                               |
| Butte Creek at Butte Creek Road LD (31874)                                 | 0       | 4    | 96       | 15.<br>8   | 49.2                              |

Agriculture sites include sites in the Zollner Creek and Little Pudding River watersheds. Currentuse pesticides detected at these sites include atrazine, chlorpyrifos, diazinon, lindane, and malathion. Zollner Creek is a small watershed which, as of 1995, consisted of 46% row crops and less than 50% grass and wheat (Anderson, et al, 1997). Zollner Creek and its tributary Bochsler Creek are the only streams with land use > 90% agriculture. All pesticides of concern, except for chlordane, were detected in these streams. State criteria for chlorpyrifos and malathion were all exceeded. In addition, the CCRM criteria for atrazine and the NAS/NAE criteria for diazinon were exceeded.

Integrator sites showed pesticide concentrations that appear to relate more to whether the site is impacted by Zollner Creek and Little Pudding River than the percent agriculture. Atrazine, chlorpyrifos, diazinon, and malathion, which have been detected in Zollner Creek or the Little Pudding River, have also been detected downstream at the Pudding River at Aurora (RM 8.1) site. However, upstream at the Pudding River near Mt. Angel site, no pesticides of concern were detected, even though this site has a percent agriculture that is similar to the Aurora site (47% vs. 58%). Note, however, that monitoring was performed at the Mt. Angel site only for current-use pesticide lindane; and not for atrazine, chlorpyrifos, diazinon, or malathion; which may explain some of discrepancy.

There were no detections of chlordane, chlorpyrifos, diazinon, dieldrin, lindane, or malathion at the sites representing forestry land use (Butte Creek at Butte Creek Road and Little Abiqua Creek near Scotts Mill, USGS gage No. 14200400).

USGS and ODEQ measured water column concentrations of the current use pesticides detected were compared to criteria to determine if concentrations could potential adversely aquatic life or human health (Table I - 4). Parameters in concentrations in excess of applicable criteria are shown as "> Std." Parameters detected but not in concentrations in excess of applicable criteria as shown as "> DL." Parameters all or virtually all below detection are shown as "OK." GS and Q in table indicate whether the dataset is via USGS (GS) or ODEQ (Q).

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|  |                               |                  |                                 |                 |   |                |  |                                     | Alternative Criteria for   | <u>Drinking</u> |
|--|-------------------------------|------------------|---------------------------------|-----------------|---|----------------|--|-------------------------------------|--|-----------------|
|  |                               |                  |                                 |                 |   | Huma           | n Health   | protection of freshwater<br>aquatic | <u>Water</u>   |                 |
|  |                               | <u>Frest</u>     | nwater                          | 1               |   | For Cons       | sumption of:                                       | life from chronic toxicity          | MCLs   |                 |
| <u>Compound</u>                        | <u>Acute</u><br>(CMC)<br>μg/L |                  | <u>Chronic</u><br>(CCC)<br>μg/L |                 | <u>Water +</u><br><u>Organism<sup>B</sup></u><br>µg/L |                | <u>Organism</u><br><u>only<sup>B</sup></u><br>µg/L |                                     | (via USEPA, CCRM,<br>NAS/NAE, or Rinella; see<br>footnote)<br>µg/L | µg/L            |
| Atrazine                               |                               |                  |                                 |                 |   |                |  |                                     | 2 (CCRM)   | 3               |
| Azinphos-<br>methyl                    |                               |                  |                                 |                 |   |                |  |                                     | 0.01 (USEPA)   |                 |
| Carbaryl                               |                               |                  |                                 |                 |   |                |  |                                     | 0.02 (NAS)   | 40              |
| Carbofuran                             |                               |                  |                                 |                 |   |                |  |                                     | 1.75 (CCRM)  |                 |
| Chlordane                              | 2.4                           | Table 33A        | 0.0043                          | Table 33A       | 0.00046   | Table 20       | 0.00048  | Table 20                            |  | 2               |
| Chlorpyrifos                           | 0.083                         | Table 33A        | 0.041                           | Table 33A       |   |                |  |                                     |  |                 |
| DDD 4,4'-                              |                               |                  |                                 |                 | 0.00031   | Table 33A      | 0.00031  | Table 33A                           |  |                 |
| DDE 4,4'-                              |                               |                  |                                 |                 | 0.00022   | Table 33A      | 0.00022  | Table 33A                           |  |                 |
| DDT 4,4'-                              | 1.1 т                         | Table 33A        | 0.001 т                         | Table 33A       | 0.000024  | Table 20       | 0.000024   | Table 20                            |  |                 |
| Diazinon                               |                               |                  |                                 |                 |   |                |  |                                     | 0.009 (NAS)  |                 |
| Dicamba                                |                               |                  |                                 |                 |   |                |  |                                     | 10 (CCRM)  |                 |
| Dieldrin                               | 0.24                          | Table 33A        | 0.0019                          | Table 20        | 0.000052  | Table 33A      | 0.000054   | Table 33A                           |  |                 |
| Diuron                                 |                               |                  |                                 |                 |   |                |  |                                     | 1.6 (Rinella)  |                 |
| Lindane (γ-<br>HCH)                    |                               |                  |                                 |                 |   |                |  |                                     | 0.08 (USEPA)   | 0.2             |
| Malathion                              |                               |                  | 0.1                             | Table 33A       |   |                |  |                                     | 0.008 (NAS)  |                 |
| Metribuzin                             |                               |                  |                                 |                 |   |                |  |                                     | 1 (CCRM)   |                 |
| 2,4-D                                  |                               |                  |                                 |                 |   |                |  |                                     | 4 (CCRM)   | 70              |
| T - This criterion a                   |                               |                  |                                 |                 |   |                |  |                                     |  |                 |
| MCL - Maximum (<br>best available trea |                               |                  |                                 |                 |   |                |  | ICLs are set as                     | close to MCLGs as feasible u                                       | sing the        |
| NAS - National Ac                      | ademy of Sc                   | iences and Nat   | ional Academy                   | / of Engineerii | ng (NAS/NAE   | , 1973) (And   | erson, et al, 19                                   | 997, p.39)                          |  |                 |
| CCRM - Canadiar                        |                               |                  |                                 |                 |   | 98, pp.22-23)  |  |                                     |  |                 |
| USEPA - U.S. Env                       |                               | 0                |                                 |                 | ,   |                |  |                                     |  |                 |
| Rinella - Water qu                     | uality criteria               | specified in Rin | ella and Janet                  | (1998) - Sour   | ce not specifie                                       | ed - either U. | S. EPA, CCR  | M, or NAS                           |  |                 |

### Table I - 4: Comparisons of observed concentrations to water quality criteria or other levels of concern.

|   | % Urban | % Ag   | % Forest | t-DDT                               | Atrazine             | Chlordane         | Chlorpyrifos         | Diazinon                        | Dieldrin                 | Lindane            | Malathion                |
|---|---------|--------|----------|-------------------------------------|----------------------|-------------------|----------------------|---------------------------------|--------------------------|--------------------|--------------------------|
| Integrator Sites (mix of agriculture, fores                                       | try a   | nd url | ban la   | and uses):                          |                      |                   | •                    | •                               | •                        | -                  |                          |
| Pudding River at Aurora (Hwy 99E)<br>(Gage 14202000, LASAR 10917)                 | 5       | 58     | 3<br>6   | >Std<br>(GS)<br>OK (Q) <sup>1</sup> | >DL (GS)<br>>DL (Q)  | OK (GS)<br>OK (Q) | >DL (GS)<br>OK (Q)   | >DL (GS)<br>OK (Q) <sup>2</sup> | >Std<br>(GS)<br>OK (Q)   | OK (GS)<br>OK (Q)  | >DL (GS)<br>OK (Q)       |
| Pudding River near Mt. Angel<br>(Saratoga Rd) (old Gage 14201000,<br>LASAR 31877) | 3       | 47     | 5<br>0   | OK (Q)                              |                      | OK (Q)            |                      |                                 | OK (Q)                   | OK (Q)             |                          |
| Abiqua Creek at Gallon House Bridge (31872)                                       | 2       | 29     | 6<br>8   |                                     | OK (Q)               |                   | OK (Q)               | OK (Q)                          |                          |                    | OK (Q)                   |
| Butte Creek at Hwy 211 (near mouth) (10896)                                       | 1       | 24     | 7<br>5   | >Std (Q)                            |                      |                   |                      |                                 | OK (Q)                   | OK (Q)             |                          |
| Silver Creek at Brush Creek Road (10646)  | 6       | 17     | 7<br>7   | OK (Q)                              |                      |                   | OK (Q)               | OK (Q)                          |                          |                    | OK (Q)                   |
| Agriculture Sites:  |         |        |          |                                     |                      |                   | •                    | -                               | -                        | -                  |                          |
| Little Pudding River at Rambler Road (RM 2.9) (31875)                             | 2<br>2  | 74     | 3        | >Std (Q)                            | >DL (Q)              | OK (Q)            | >DL (Q)              | OK (Q)                          | OK (Q)                   | OK (Q)             | OK (Q)                   |
| Zollner Creek Near Mt Angel<br>(Monitor-McKee Rd) (Gage<br>14201300, 10899)       | 1       | 99     | 0        | >Std<br>(GS)<br>>Std (Q)            | >Alt (GS)<br>>DL (Q) | OK (GS)           | >DL (GS)<br>>Std (Q) | >Alt (GS)<br>>Alt (Q)           | >Std<br>(GS)<br>>Std (Q) | >DL (GS)<br>OK (Q) | >Std<br>(GS)<br>>Std (Q) |
| Zollner Creek at Hwy 214 (11515)  | 1       | 98     | 1        |                                     | >DL (Q)              |                   | >Std (Q)             | >Alt (Q)                        |                          |                    | OK (Q)                   |
| South Fork Bochsler Creek at Hwy 214 (11514, tributary to Zollner Cr)             | 1       | 98     | 1        |                                     | >DL (Q)              |                   | >DL (Q)              | >Alt (Q)                        |                          |                    | OK (Q)                   |
| Senecal Creek at Fellers Rd (trib to<br>Mill Cr to Pudding R)                     | 8       | 89     | 3        |                                     | >DL (GS)             |                   | OK (GS)              | >Alt (GS)                       | OK (GS)                  | OK (GS)            | OK (GS)                  |
| Forestry Sites:   |         |        |          |                                     |                      |                   | ·                    |                                 | ·                        | ·                  |                          |
| Little Abiqua Creek near Scotts Mill (Gage 14200400)                              | 0       | 4      | 96       | OK (GS)                             | OK (GS)              | OK (GS)           | OK (GS)              | OK (GS)                         | OK (GS)                  |                    | OK (GS)                  |
| Butte Creek at Butte Creek Road LD  | 0       | 4      | 9        | >Std (Q) <sup>3</sup>               |                      | OK (Q)            |                      |                                 | OK (Q)                   | OK (Q)             |                          |

## DETAILS OF CURRENT USE PESTICIDE MONITORING

#### ATRAZINE

Atrazine has been one of the most heavily applied pesticides in the Willamette Basin and was one of the most frequently detected pesticides in USGS studies (Anderson, et al, 1997). Atrazine was detected in 99% of USGS samples collected as part of Phase III Willamette River Basin Water Quality Study (Anderson, et at, 1997). The USGS found that atrazine concentrations in the Willamette Basin correlate highly with agricultural land use (spearman correlation coefficient,  $\rho$ , for atrazine versus the percent of drainage area in agricultural land use = 0.86, p<0.05) (Rinella and Janet, 1998).

The highest concentrations of atrazine observed by USGS in the Willamette Basin during its National Water-Quality Assessment (NAWQA) surveys were in Zollner Creek, a small (15 mi<sup>2</sup>) watershed with intensive agriculture and diverse crop types (46% row crops, less than 50% grass and wheat, 4% forested) (Anderson, et al, 1997). Atrazine also correlates well with suspended solids concentrations (p=0.42, p<0.05), as well as with a number of other pesticides (Anderson, et al, 1997). In addition, ODEQ's monitoring in the watershed between 2005-2007 showed frequent detections of Atrazine in Zollner Creek. However, atrazine concentrations do not correlate with discharge, i.e., in-stream concentrations are similar regardless of flow. High concentrations during low flows, when suspended solids concentrations are low, may indicate groundwater contamination or the presence of pesticides in irrigation return flows. High concentrations during high flows could indicate the association of atrazine with suspended solids that wash off during rainfall events.

According to Anderson, et al, 1997, the sale of most formulations of atrazine has been restricted since 1993. Nonetheless, at the time of the 1997 report, atrazine remained available for purchase by individuals with pesticide application licenses, a group that included commercial applicators and many growers (Anderson, et al, 1997).

Atrazine has urban, in addition to agricultural, applications. But concentrations of Atrazine detected in the Willamette Basin during the Phase III Willamette River Basin Water Quality Study were significantly higher at agricultural sites than at urban sites (Anderson, et at, 1997).

The USGS found that median concentrations of atrazine and suspended sediment were significantly higher in the late fall than in the summer. Median concentrations of atrazine as high as in the fall or spring were maintained well past any periods of initial flushing, suggesting that a steady supply of atrazine is retained in soils in the Willamette Basin (Anderson, 1997, p.2).

Atrazine has a half-life in the range 1 to 3 months. Because it degrades relatively slowly, it may build up in the soil and be carried into streams with every storm, even if applied earlier in the year. This may explain the high frequency at which atrazine is detected in streams (Anderson, et al, 1997).

While there no State of Oregon standard for atrazine, the Canadian Council of Resources and Environmental Ministers (CCRM) has established a chronic toxicity based criterion for atrazine of 2  $\mu$ g/L. In addition, the USEPA MCL for drinking water for atrazine is 3.0  $\mu$ g/L.

Simazine is now increasingly used as a substitute for atrazine in agricultural operations, partially in response to recent EPA crop use restrictions on atrazine. The EPA drinking water MCL is similar to the atrazine MCL and the two chemicals are in the same herbicide class (triazine). DEQ's recently collected data in the Molalla-Pudding Subbasin reflect a shift toward increased simazine use, with more frequent stream detections and higher maximum and median concentrations of simazine during 2005 - 2007 monitoring. DEQ has measured numerous

detections over 1  $\mu$ g/L of simazine, and in 2006 detections were 13  $\mu$ g/L, 9.5  $\mu$ g/L L, and 9.2  $\mu$ g/L – all exceeding the MCL.

#### Integrator Sites

As shown in Figure I - 2, atrazine was frequently detected by USGS in the early to mid 1990's and recently by ODEQ at the Pudding River at Aurora (RM 8.1) site. However, all observed concentrations are significantly less than CCRM criteria.

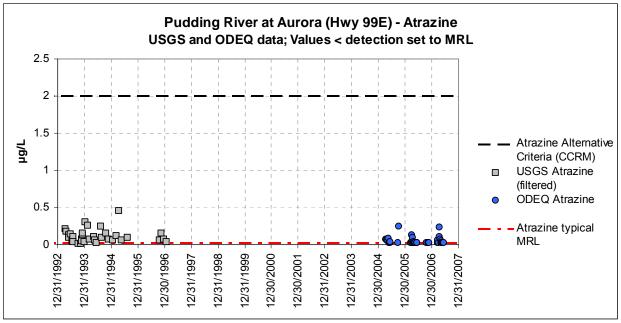


Figure I - 2: Pudding River at Aurora - Atrazine concentrations

The only other integrator site for which samples were analyzed for atrazine was Abiqua Creek at Gallon House Bridge (RM 1.9). Atrazine was detected in none of the 39 samples collected by ODEQ at this site.

It's quite likely that much of the atrazine found at the Pudding River at Aurora site is contributed by Zollner Creek and Little Pudding River.

#### Agriculture Sites

Atrazine was frequently detected by USGS in Willamette Basin streams that are heavily impacted by agriculture. The largest concentrations of atrazine observed by USGS for high flow conditions during its National Water-Quality Assessment (NAWQA) study of the Willamette Basin were at its Zollner Creek near Mt. Angel site (RM 0.4) (Rinella and Janet, 1998).

Atrazine was frequently detected by ODEQ in agricultural streams recently sampled by ODEQ. As shown in Figure I - 3, Zollner Creek atrazine concentrations frequently exceeded the CCRM criterion as well as the drinking water MCL in the early to mid 1990's. However, all recent concentrations in the Little Pudding River and Zollner Creek, as well as in all other Pudding River Watershed streams, have been found to be significantly less than these criteria (Figure I - 4 to Figure I - 6).

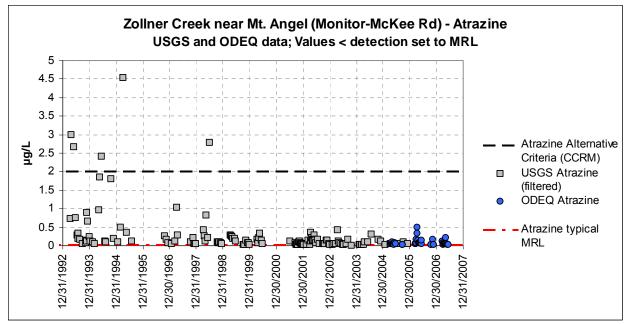


Figure I - 3: Zollner Creek near Mt. Angel – Atrazine concentrations

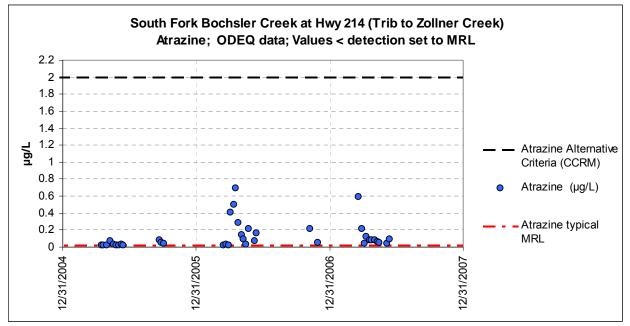


Figure I - 4: South Fork Bochsler Creek at Hwy 214 (tributary to Zollner Creek) - Atrazine concentrations

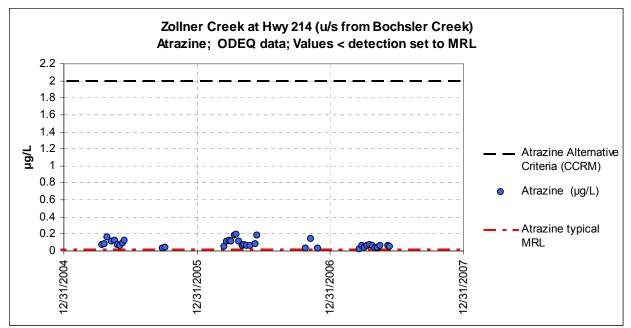


Figure I - 5: Zollner Creek at Hwy 214 (upstream from Bochsler Creek) – Atrazine concentrations

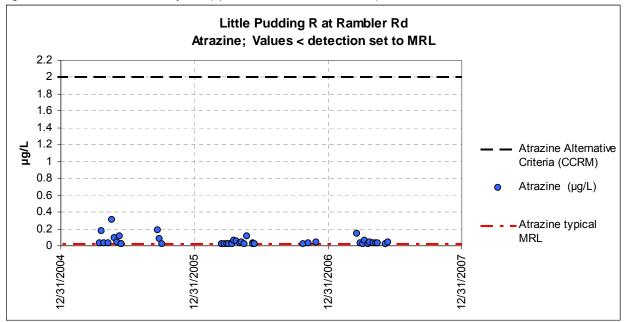


Figure I - 6: Little Pudding River at Rambler Road – Atrazine concentrations

#### **Forestry Sites**

Atrazine was not detected at forestry sites. During its NAWQA study of the Willamette Basin, in 11 samples collected at 6 predominately forested sites in the Willamette Basin, only 2 detections of atrazine and 1 detection of its degradation product, desethylatrazine, were observed at very low concentrations (Rinella and Janet, 1998).

#### CHLORPYRIFOS

The insecticide chlorpyrifos ranked 5<sup>th</sup> in the total estimated load of targeted pesticides applied in the Willamette Basin (Anderson, 1997). Chlorpyrifos was detected in 14% of USGS samples collected as part of Phase III Willamette River Basin Water Quality Study (Anderson, et at, 1997).

Chlorpyrifos concentrations were not found by USGS to correlate with percent of a watershed as agricultural land (Anderson, et al, 1997). This may be because chlorpyrifos may be applied to only a limited number of crops in the watersheds studied. Chlorpyrifos concentrations were found, however, to correlate with seasonal application rates of chlorpyrifos (Spearman's  $\rho$  = 0.23, p = 0.05).

#### **Integrator Sites**

The only integrator site where chlorpyrifos was detected was the Pudding River at Aurora (RM 8.1). Chlorpyrifos was detected occasionally in samples collected by USGS. However, chlorpyrifos was found in none of 37 samples collected recently by ODEQ (Figure I - 7), perhaps because the detection level for ODEQ was higher than for USGS.

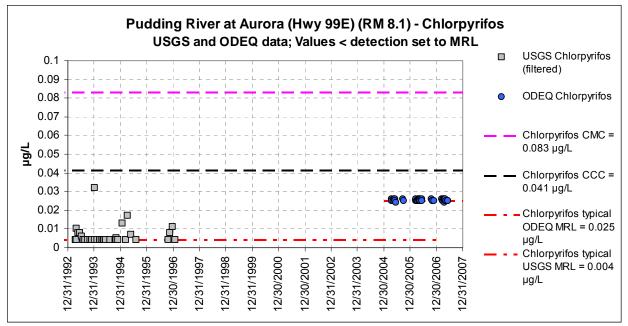


Figure I - 7: Zollner Creek near Mt. Angel – Chlorpyrifos concentrations

Chlorpyrifos were detected in none of 39 samples collected by ODEQ at Abiqua Creek at Gallon House Bridge (1.9) and in none of 38 samples collected by DEQ at Silver Creek at Brush Creek Road (RM 1.3). As with atrazine, it's quite likely that much of the chlorpyrifos found at the Pudding River at Aurora site is contributed by Zollner Creek and Little Pudding River.

#### **Agriculture Sites**

Chlorpyrifos was frequently detected by ODEQ in agricultural streams recently sampled by ODEQ, with concentrations often in excess of chronic criteria in Zollner Creek (Figure I - 8 to Figure I - 11) and Little Pudding River (Figure I - 12)

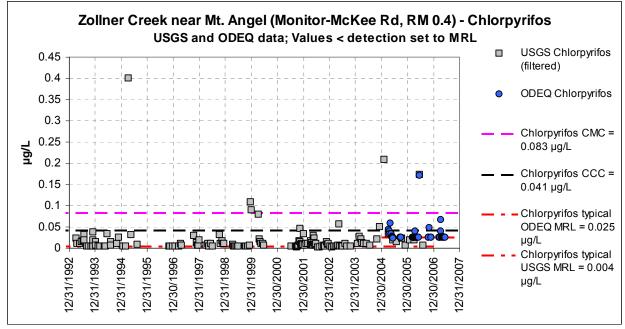


Figure I - 8: Zollner Cr near Mt. Angel (RM 0.4) – Chlorpyrifos concentrations

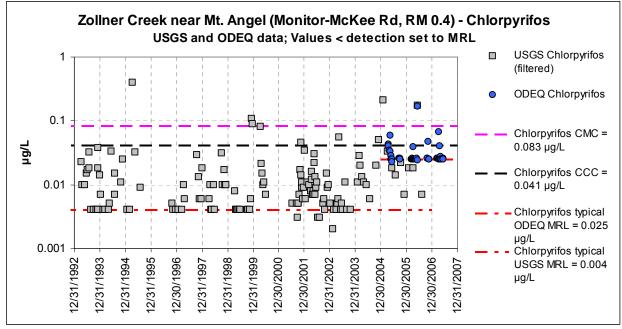


Figure I - 9: Zollner Creek near Mt. Angel (RM 0.4) – Chlorpyrifos concentrations - Logarithmic scale

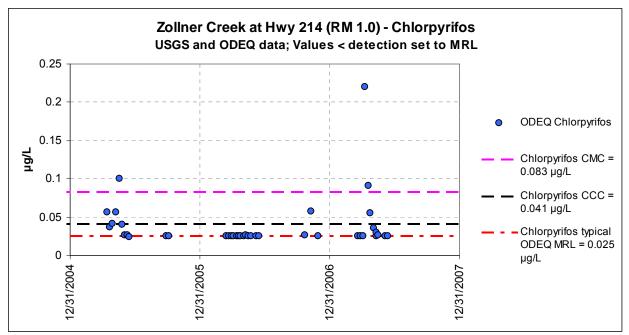


Figure I - 10: Zollner Creek at Hwy 214 (RM 1.0) - Chlorpyrifos concentrations

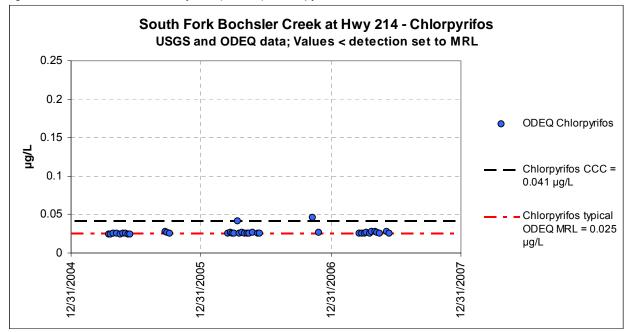


Figure I - 11: South Fork Bochsler Creek at Hwy 214 - Chlorpyrifos concentrations

The highest concentrations of chlorpyrifos observed by USGS for high flow conditions during its National Water-Quality Assessment (NAWQA) study of the Willamette Basin were at its Little Pudding River at Sunnyview Road site (RM 14.4). This site is located upstream from the Little Pudding River at Rambler Road site (RM 2.9). 89% the Sunnyview Road site drainage area is agricultural land use (Rinella and Janet, 1998).

ODEQ also detected chlorpyrifos in the Little Pudding River. Four of 43 (slightly less than 10%) of samples collected in Little Pudding R at Rambler Rd exceeded the State of Oregon 0.041  $\mu$ g/L chronic criterion.

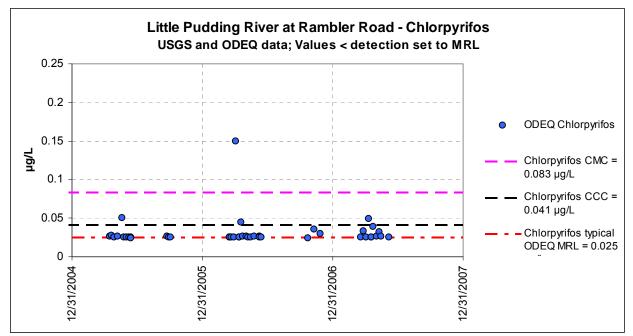


Figure I - 12: Little Pudding River at Rambler Road - Chlorpyrifos concentrations

#### Seasonality

The Kruskal-Wallis test for seasonality (WQHydro) indicated that the observed seasonal differences in chlorpyrifos concentrations are significant in the Little Pudding River (Figure I - 13). Concentrations are significantly greater in the spring than in the rest of the year, presumably because the pesticide is applied in the spring and runs off during spring rains.

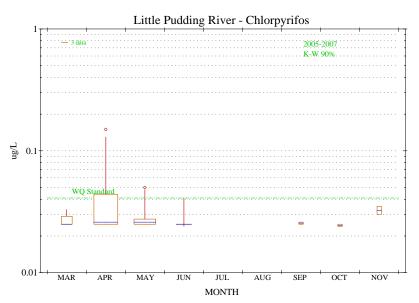


Figure I - 13: Little Pudding River - Chlorpyrifos seasonality

#### **Forestry Sites**

Chlorpyrifos was not detected at forestry sites.

#### **ETHOPROP (PROPHOS)**

Similar to the situation with atrazine and simazine, ethoprop may be replacing chlorpyrifos for certain crop uses. Like chlorpyrifos, ethoprop is an organophosphate insecticide. Recent DEQ sampling in the Molalla-Pudding Subbasin found concentrations of ethoprop approaching or exceeding 1  $\mu$ g/L.. Median and maximum concentrations of ethoprop between 2005 and 2007 generally were higher than corresponding chlorpyrifos values. There is no water quality criterion from ethoprop, but it has a similar mode of action as chlorpyrifos, and could have similar impacts on aquatic life (Kevin Masterson, DEQ Toxics Coordinator, personal communication, July 2008)

#### AZINPHOS-METHYL

Recent DEQ sampling in the Molalla-Pudding Subbasin resulted in four detections of azinphosmethly in 2005, including one sample at 4.5  $\mu$ g/l from Zollner Creek. Two of the four detections were found in the mainstem of the Pudding River. Azinphos-methyl was not detected in 2006 or 2007, but the laboratory method detection limit (0.025  $\mu$ g/L) was higher than the water quality criterion of 0.01 $\mu$ g/L.

#### DIAZINON

The insecticide diazinon was detected in 26% of USGS samples collected as part of Phase III Willamette River Basin Water Quality Study. During this study diazinon was found more frequently and at higher concentrations at urban sites than at agricultural sites (Anderson, et al, 1997). As of 1996, diazinon was readily available though retail sales to homeowners and was used by commercial landscapers, and, therefore, may occur in streams draining areas of commercial and residential development (Anderson, et al, 1997). It was also used by growers on a variety of fruit and vegetable crops.

There is no State of Oregon standard for diazinon, although, Oregon does have a guidance value of 0.05  $\mu$ g/L for diazinon listed in Table 33C of OAR 340-41-0033. The guidance values in Table 33C can be used to invoke narrative water quality criteria. The NAS/NAE criteria for diazinon for protection of freshwater aquatic life from chronic toxicity is 0.009  $\mu$ g/L. This provides a point of reference above which toxicity could be considered a concern. Monitoring performed by USGS shows that this criteria was occasionally exceeded in the 1990's. Since then, the frequency of criteria exceedance has declined, but significant exceedances still occur.

Diazinon was detected by USGS somewhat more frequently at urban sites than agricultural sites during Phase I and II of the WRBWQS (Anderson, 1996). Additionally, recent DEQ sampling resulted in 17 detections of diazinon in 2007, as well as several detections in 2006. Many of these detections were over the 0.05  $\mu$ g/l guidance value in Table 33C.

#### **Integrator Sites**

Diazinon was frequently detected by USGS in the Pudding River in the early 1990s, with detected concentrations occasionally in excess of the NAS/NAE criterion. Diazinon was detected in only 1 of 37 samples collected 2005 through 2007 by ODEQ at the Pudding River sites, but much of the reason it was detected infrequently compared to USGS data may be that the ODEQ detection level is much higher than the USGS detection level (Figure I - 14). The single ODEQ detection of 0.088 µg/L was greater than the maximum concentration observed by USGS. This concentration also exceeds the NAS/NAE criterion.

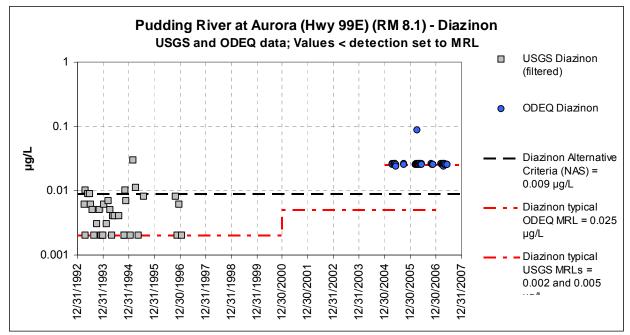


Figure I - 14: Pudding River at Aurora (RM 8.1) - Diazinon concentrations

Diazinon were detected in none of 39 samples collected by ODEQ at Abiqua Creek at Gallon House Bridge (1.9) and in none of 38 samples collected by DEQ at Silver Creek at Brush Creek Road (RM 1.3).

#### **Agriculture Sites**

Monitoring performed by USGS shows that NAS/NAE criteria for protection of freshwater aquatic life from chronic toxicity life of 0.009  $\mu$ g/L was frequently exceeded in the 1990's (Figure I - 15) at Zollner Creek near Mt. Angel (RM0.4) Since then, the frequency of criteria exceedance has declined, but significant exceedances still occur. All exceedances occur during the spring.

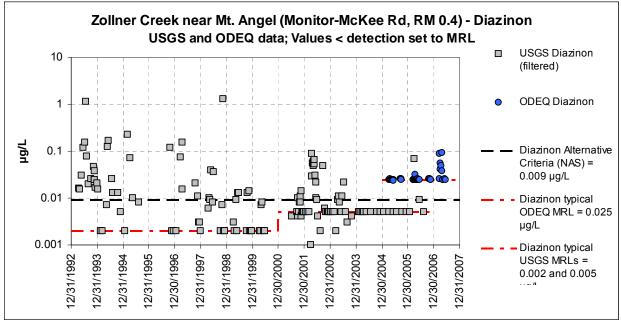


Figure I - 15: Zollner Creek near Mt. Angel (RM 0.4) - Diazinon concentrations

Recent data from Zollner Creek and Boschler Creek, at tributary to Zollner, shows that both Zollner and Boschler Creeks occasionally contain high springtime diazinon concentrations (Figure I - 16 to Figure I - 18).

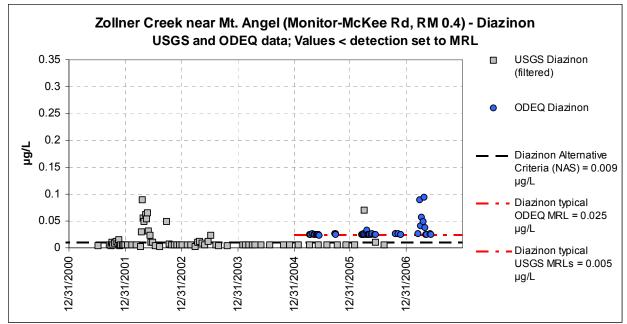


Figure I - 16: Zollner Creek near Mt. Angel (RM 0.4) - Recent diazinon concentrations

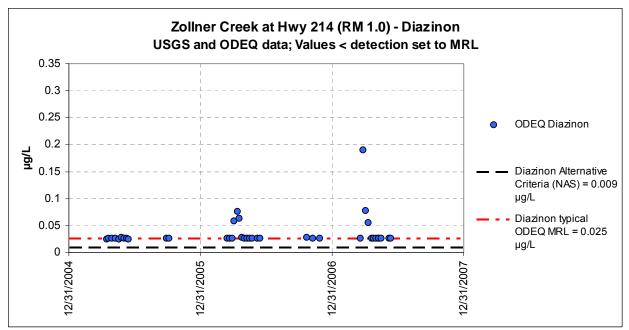


Figure I - 17: Zollner Creek at Hwy (RM 1.0) - Diazinon concentrations

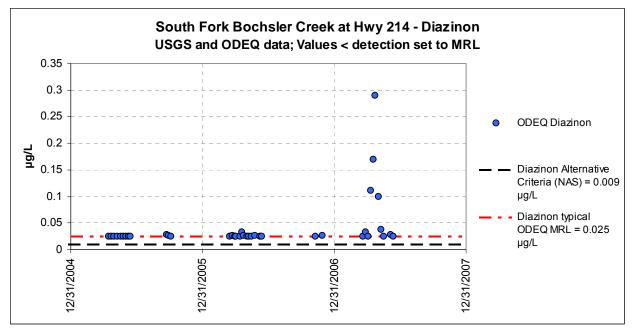


Figure I - 18: South Fork Bochsler Creek at Hwy 214 - Diazinon concentrations Similar exceedances were not observed in the Little Pudding River, where no diazinon was detected.

#### **Forestry Sites**

Diazinon was not detected at forestry sites.

#### LINDANE

Lindane (γ-HCH) is another pesticide which may be present in Willamette Basin streams in concentrations which exceed levels of concern. Lindane was one of the most frequently detected organochlorine compounds in samples collected from 39 Willamette Basin sites during Phase I and Phase II of the Willamette River Basin Water Quality Study (WRBWQS) (Anderson, et at, 1996). However, lindane was not detected by USGS anywhere in the Willamette Basin during Phase III of the WRBWQS (Anderson, et at, 1997).

There are no State of Oregon water quality criteria for lindane, however, the U.S. EPA has established a chronic toxicity criterion for lindane of 0.08  $\mu$ g/L (Gilliom, 1998).

#### **Integrator Sites**

Lindane was not detected in any samples collected by either USGS or ODEQ at any of the integrator site stations, although it was detected by USGS in Zollner Creek.

#### Agriculture Sites

Lindane was frequently detected in Zollner Creek in the early 1990's by USGS but, since then, the pesticide has rarely has been detected (Figure I - 19). Only one detected concentration, a measurement from 1994, exceeded the U.S. EPA criterion. Lindane has not been detected at other monitoring sites in the Pudding River watershed.

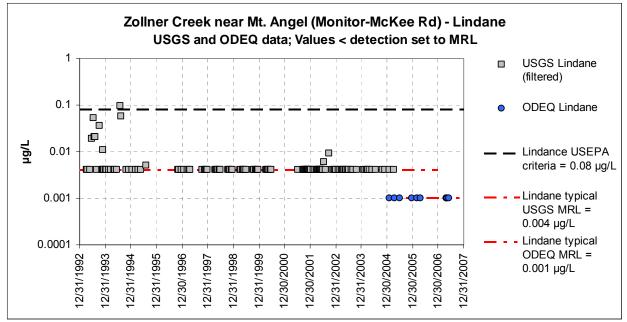


Figure I - 19: Zollner Creek near Mt. Angel (RM 0.4) - Lindane concentrations

### **Forestry Sites**

Lindane was not detected at forestry sites.

#### MALATHION

Malathion is another pesticide which has historically been detected frequently in the Willamette Basin, but which recently has rarely been detected. Malathion was detected in only 1% of USGS samples collected as part of Phase III Willamette River Basin Water Quality Study (Anderson, et at, 1997).

Only one ODEQ sample contained concentrations in excess of the State of Oregon chronic toxicity criterion of 0.1  $\mu$ g/L.

#### **Integrator Sites**

In the early 1990s, Malathion was detected occasionally in the Pudding River by USGS, although no concentrations exceeded State of Oregon criteria (Figure I - 20). Since 1993, the pesticide has not been detected at any of the integrator sites. Malathion was detected in none of 37 ODEQ Pudding River at Aurora samples collected 2005 through 2007.

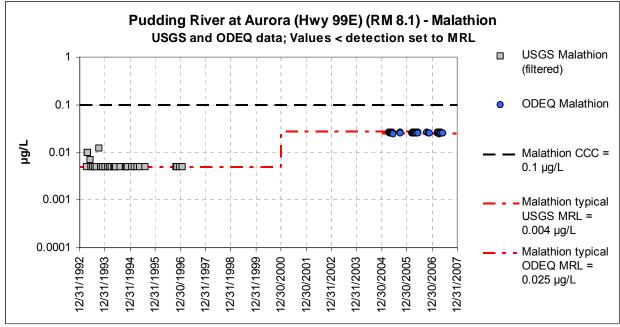


Figure I - 20: Pudding River at Aurora (RM 8.1) - Malathion concentrations

Malathion was not detected in Abiqua Creek or Silver Creek. The only detection of malathion in the Pudding River watershed was a single Zollner Creek detection.

### **Agriculture Sites**

Malathion was detected in only 1 of 38 measurements from 2005 though 2007 at the Zollner Creek near Mt. Angel site (Figure I - 21). However, this single detection of 0.19  $\mu$ g/L exceeds the chronic criterion. Malathion was not detected in any of 38 ODEQ samples from South Fork Bochsler Creek at Hwy 214 (Zollner Creek tributary site) or in any of 37 ODEQ samples from Zollner Creek at Hwy 214 (RM 1.0).

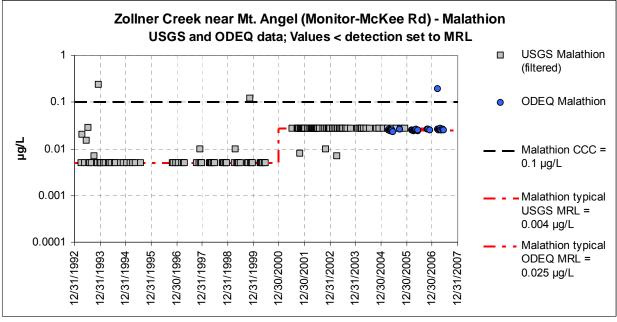


Figure I - 21: Zollner Creek near Mt. Angel (RM 0.4) - Malathion concentrations

#### **Forestry Sites**

Malathion was not detected at forestry sites.

# CORRELATIONS

Several current-use pesticides of concern were found by USGS not to correlate with suspended solids. These include chlorpyrifos and diazinon (Anderson, et al, 1996; Anderson, et al, 1997).

Pesticides were generally found by USGS not to correlate with stream discharge. In other words, in-stream concentrations were found to be similar regardless of flow. This is surprising considering that suspended solids concentrations tend to correlate with stream discharge and that several pesticides were found to correlate with suspended solids. Specifically, concentrations of atrazine, chlorpyrifos, and diazinon were found not to correlate with discharge. Part of this was that the relationship found by USGS between suspended solids and discharge is not very strong ( $\rho = 0.25$ , p = 0.06) (Anderson, et al, 1997). The only pesticide found by USGS to correlate with discharge was metribuzin (( $\rho = 0.24$ , p = 0.04).

Regarding atrazine, which was found by USGS to correlate with suspended solids but not to discharge, the USGS speculated that the presence of high concentrations of atrazine during low flows, when suspended solids concentrations are low, may indicate groundwater contamination or the presence of pesticides in irrigation return flows. The presence of high concentrations of atrazine during high flows could indicate the association of atrazine with suspended solids that wash off during rainfall events. The USGS also found that atrazine correlates well with several other pesticides. This suggests that when atrazine is transported from fields to streams, many other compounds may be transported as well. (Anderson, et al, 1997).

The USGS also found that pesticides correlate highly with the percent of watershed as agriculture. For example, USGS found for the Willamette Basin that spearman correlation coefficients ( $\rho$ ) for atrazine vs. percent of drainage areas in agricultural land use ranged from 0.71 to 0.91 (p < 0.05).

### PARAMETERS TO BE EVALUATED FOR TMDLS IN THE FUTURE

#### **CHLORPYRIFOS**

One pesticide not currently included on the 303(d) list which could possibly be added is chlorpyrifos. Unlike currently listed pesticides (DDT, dieldrin, and chlordane) chlorpyrifos is a current use pesticide. Chlorpyrifos was frequently detected in agricultural streams sampled recently by ODEQ, with concentrations often in excess of chronic criteria in Zollner Creek and Little Pudding River. Since neither of these streams are currently 303(d) listed for this pesticide, TMDLs have not been developed to address the high concentrations. Since DDT is not a current use pesticide, it's appears unlikely that TSS reductions developed in the TMDL to address DDT concerns will eliminate chlorpyrifos standards violations, particularly since USGS concluded that chlorpyrifos does not correlate with suspended solids (Anderson, et al, 1996; Anderson, et al, 1997).

While adding both Zollner Creek and Little Pudding River to the 303(d) list for chlorpyrifos standard exceedances may be necessary, DEQ does not recommend the development of a TMDL for chlorpyrifos as a short-term action. DEQ is currently working closely with OSU Extension Service, the Marion Soil and Water Conservation District, agricultural interests and other stakeholders in the Pudding Watershed on a Pesticide Stewardship Partnership (PSP). The PSP involves stream monitoring of current use pesticides, such as chlorpyrifos, and using the monitoring data to focus collaborative efforts to implement best management practices that will reduce drift and runoff of pesticides into streams with elevated levels of pesticides. Follow up monitoring is conducted to determine if the concentrations of pesticides is decreasing over time. This approach has worked successfully in the Hood River watershed, and DEQ would like to

provide adequate time for the Pudding River PSP to produce positive results. If this collaborative approach does not result in generally decreasing levels of chlorpyrifos in the next 2-3 years, DEQ will re-evaluate the need to initiate development of a chlorpyrifos TMDL.

### AZINPHOS-METHYL

Azinphos-methyl (Guthion) was detected five times by DEQ in 2005, including one sample with a concentration of 4.5 µg/L. Azinphos-methyl was not detected in 2006 or 2007 pesticide samples, although the DEQ detection limit (0.025 µg/L) has been higher than the water quality criterion of 0.01µg/L. In 2008 the DEQ Laboratory's detection limit for azinphos-methyl was reduced to 0.01 µg/L, and the Pudding watershed pesticide monitoring data from 2008 will be evaluated to determine if the chemical was present in any samples. Like chlorpyrifos, azinphos-methyl is a current use pesticide included in DEQ's Pudding watershed Pesticide Stewardship Partnership. In addition, EPA will be prohibiting almost all uses of azinphos-methyl after 2012. Since azinphos-methyl is not a persistent pesticide like DDT and other organochlorines, it's likely that it will be detected very infrequently after 2012. Given these circumstances, DEQ does not recommend proceeding with development of a TMDL for azinphos-methyl at this time. If detections of this pesticide continue after 2-3 years, DEQ will re-evaluate the need to develop a TMDL.

### REFERENCES

The references cited in this Appendix can be found in the reference section for Chapter 4 – Pesticides.