# Appendix J
# Pesticides Technical Analysis



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## CORRELATIONS FOUND IN PREVIOUS STUDIES

Water column concentrations of several pesticides of concern were found by USGS to correlate with suspended solids concentrations. Since much of the sediment which enters streams comes from sediment washed off fields during storm events, pesticides associated with sediment may be controlled by reducing surface erosion.

The USGS found during Willamette River Basin Water Quality Study (WRBWQS) that in-stream DDT concentrations in the Willamette Basin correlate with suspended solids concentrations (Anderson, et al, 1996). The USGS also found that atrazine correlates with suspended solids concentrations (Spearman's $\rho=0.42$[1], $p<0.05$[2]) (Anderson, et al, 1997).

One pesticide of concern which strongly associates with sediment is DDT. DDT and its metabolites preferentially associate with the suspended phase because they are hydrophobic, with organic carbon-water partitioning coefficients ($K_{oc}$) of 770,000 for DDD, 4,400,000, for DDE and 243,000 for DDT. Theoretical computations performed by USGS predicted that 55 to 81 percent of the mass of DDT and metabolites should have been associated with the suspended phase if the systems were at equilibrium. In all cases measured by USGS, observed amounts in the suspended phase were only slightly greater than predicted (Anderson, et al, 1996).

Like DDT, dieldrin sorbs to sediment. However, dieldrin sorbs to sediment to a lesser degree than DDT which is reflected in lower observed organic carbon-water partitioning coefficients, $K_{oc}$. The USGS found that empirical data from the Willamette River Basin was consistent with a $K_{oc}$ of 1,700 mL/g reported by USEPA (Anderson, et al, 1996; Anderson, et al, 1997). This is much lower than the $K_{oc}$ values for DDT and its metabolites (770,000 mL/g for DDD, 4,400,000 mL/g, for DDE and 243,000 mL/g for DDT). Based on this 1,700 mL/g value, dieldrin would be almost completely associated with the dissolved phase, whereas most of DDT would be sorbed to sediment (from 58% to 96% of total DDT would be sorbed to sediment, based on a suspended organic concentration of 5.7 mg/L). However, more recently EPA determined that a more appropriate estimate of $K_{oc}$ for dieldrin is 190,546 mL/g. Based on this updated $K_{oc}$, 52% of dieldrin would be sorbed to sediment (U.S. EPA, 2003).

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. 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 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 ($p < 0.05$).

[1] Spearman's ρ (rho) is analogous to Pearson's correlation coefficient, r, but calculated using the ranks of data. Spearman's ρ can range from -1 to 1 to indicate negative or positive relationships, respectively, with a value of 1 indicating a perfect positive correlation and -1 indicating a perfect negative correlation. Spearman's ρ is appropriate for both normally and non-normally distributed data, whereas Pearson's r is appropriate only for normally distributed data.

[2] The p-value is the probability that there is no correlation between the parameters. This should be compared to a predetermined error level which represents the chance we are willing to accept of an incorrect conclusion, known as the significance level (α). A significance level of 0.05 (alternatively known as a confidence level of 95%) indicates that we are willing to accept a 0.05 maximum probability of error. A correlation is typically considered significant if the p-value is less than a significance level of 0.05 ($p < 0.05$). However, if a lower confidence level is acceptable, then a higher p-value may be considered an acceptable indication of correlation. For example, for a 90% confidence level a p-value < 0.10 would indicate a statistically significant correlation (Aroner, 2000).

# MODEL DEVELOPMENT

## CORRELATIONS

Most of the pesticides of concern in the Pudding River watershed are associated with agriculture. Therefore, the relationships between pesticides, suspended solids, and flow for the two Pudding River watershed agricultural streams with large amounts of data; Zollner Creek and Little Pudding River; were examined.

### Evaluation of Data Sets - Differences between streams

Recent (2005 to 2007) TSS and DDT data for Zollner Creek and Little Pudding River was examined to determine if the data could be combined in a single data set for purposes of developing relationships between DDT, TSS, and flow, or whether the data from the streams needed to be treated independently.

Total DDT (t-DDT) concentrations are much higher in Little Pudding River than in Zollner Creek and Pudding River. A comparison Zollner Creek near Mt. Angel and Little Pudding River at Rambler Road, which are both agriculture sites, to Pudding at Aurora, an integrator site located downstream from both Zollner and Little Pudding River, is presented in Table J- 1. Total DDT for this analysis is the sum of observed DDT, DDE, and DDD concentrations, with concentrations below detection levels set to ½ the MRL. Therefore, if neither DDT, DDE, nor DDD was detected, t-DDT was set to 0.0015 µg/L, since the detection level for each is 0.001 µg/L.

Table J- 1: t-DDT at 2 agriculture and 1 integrator sites - 2005 to 2007

| t-DDT | n | Median | IQR | 95% CI of Median | |
|---|---|---|---|---|---|
| Pudding River at Aurora | 10 | 0.0015 | 0.00000 | 0.0015 | 0.0015 |
| Zollner Creek nr Mt. Angel | 10 | 0.0015 | 0.00063 | 0.0015 | 0.0090 |
| Little Pudding River at Rambler Rd | 10 | 0.0085 | 0.01188 | 0.0040 | 0.0640 |

The Mann-Whitney test showed that differences between Little Pudding River and Zollner Creek Pudding River DDT concentrations are statistically significant (1 tailed p = 0.0093 and p = 0.0002, respectively). It also showed that differences between Zollner Creek and Pudding River DDT concentrations are not statistically significant (1 tailed p = 0.2179).

Some of the greater concentration of DDT in the Little Pudding River appears to be due to the higher suspended solids concentrations in the Little Pudding River (Figure J- 1 and Table J- 2). It is unclear whether differences between Zollner Creek and Little Pudding River TSS concentrations are statistically significant.

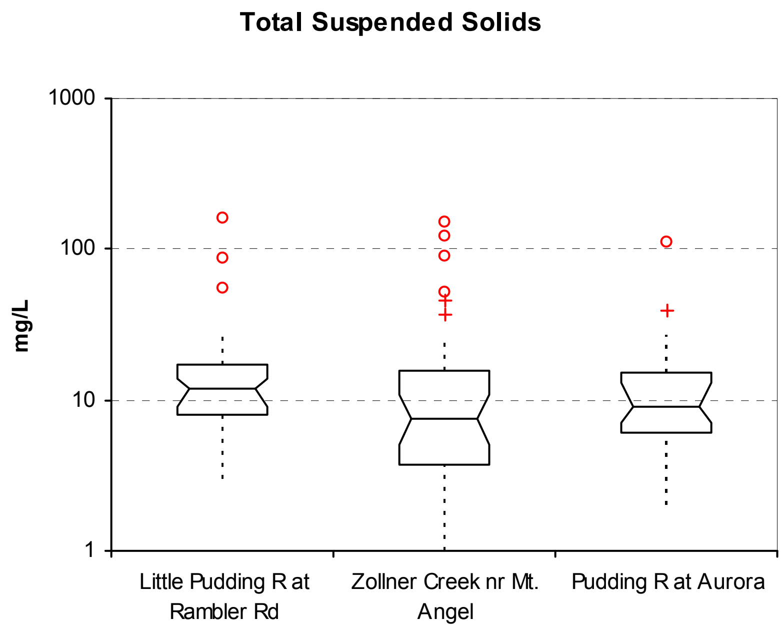


Figure J- 1:  ODEQ TSS data for 3 sites - 2005 to 2007

Table J- 2:  ODEQ TSS data for 3 sites

| Total Suspended Solids (mg/L) 2005-2007 | n | Mean | SD | SE | 95% CI of Mean | |
|---|---|---|---|---|---|---|
| Little Pudding R at Rambler Rd | 46 | 17.674 | 25.5117 | 3.7615 | 10.098 | 25.250 |
| Zollner Creek nr Mt. Angel | 63 | 15.349 | 26.2397 | 3.3059 | 8.741 | 21.958 |
| Pudding R at Aurora | 45 | 12.511 | 16.4464 | 2.4517 | 7.570 | 17.452 |

| Total Suspended Solids (mg/L) 2005-2007 | Median | IQR | 95% CI of Median | |
|---|---|---|---|---|
| Little Pudding R at Rambler Rd | 12.000 | 9.000 | 9.000 | 14.000 |
| Zollner Creek nr Mt. Angel | 7.000 | 10.000 | 5.000 | 10.000 |
| Pudding R at Aurora | 9.000 | 9.000 | 7.000 | 13.000 |

The logs of the TSS data sets are normally distributed, but variances of Zollner Creek and Little Pudding River ln [TSS] are not the same (Excel F-Test two-sample for variances, p =  0.005).  Therefore t-test assuming unequal variances was performed on the log-transformed data to determine whether TSS concentrations in Little Pudding R differ from those in Zollner Creek.  The t-test indicated that the null hypothesis that the mean in Zollner Creek (mean ln TSS = 1.974) is equal to the mean in Little Pudding River (mean ln TSS = 2.481) cannot be rejected (p=0.007).  Therefore, the means of the data sets may be the same.  Note that this is supported by the overlapping of the 95% confidence intervals of the means (Table J- 3, Figure J- 2).

The data sets were also compared using the Mann-Whitney test. This suggests that differences between TSS concentrations in the Little Pudding R and Zollner Creek are statistically significant (p = 0.009). This is also the case for Little Pudding R vs. Pudding River TSS concentrations (p = 0.043).

Table J- 3: Statistics for natural log of TSS for 3 ODEQ sites

| ln TSS | n | Mean | SD | SE | 95% CI of Mean | |
|---|---|---|---|---|---|---|
| Pudding R at Aurora | 45 | 2.153 | 0.8229 | 0.1227 | 1.906 | 2.401 |
| Zollner Creek nr Mt. Angel | 52 | 2.045 | 1.1631 | 0.1613 | 1.721 | 2.368 |
| Little Pudding R at Rambler Rd | 46 | 2.481 | 0.7728 | 0.1139 | 2.251 | 2.710 |

| ln TSS | Median | IQR | 95% CI of Median | |
|---|---|---|---|---|
| Pudding R at Aurora | 2.197 | 0.916 | 1.946 | 2.565 |
| Zollner Creek nr Mt. Angel | 2.013 | 1.425 | 1.609 | 2.398 |
| Little Pudding R at Rambler Rd | 2.485 | 0.754 | 2.197 | 2.639 |

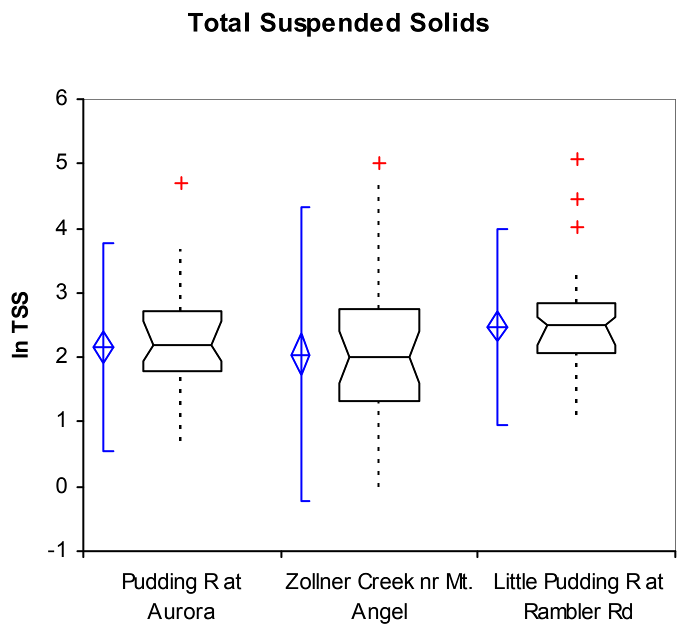


Figure J- 2: ODEQ TSS data for 3 sites - 2005 to 2007 - log transformations

The greater concentration of DDT in the Little Pudding River also appears to be because there is more mass of DDT associated with each gram of sediment in the Little Pudding River than in the other streams. As shown below (Figure J- 3 and Table J- 4), Little Pudding River sediment contains about twice the DDT as Zollner Creek sediment and three to four times the DDT as Pudding River sediment.

Table J- 4: ODEQ t-DDT:TSS ratios for 3 sites

| Ratio t-DDT to TSS (ng DDT per mg TSS) | n | Mean | SD | SE | 95% CI of Mean | |
|---|---|---|---|---|---|---|
| Little Pudding R at Rambler Rd | 9 | 0.9686 | 0.73837 | 0.24612 | 0.4010 | to 1.5361 |
| Zollner Creek nr Mt. Angel | 9 | 0.5479 | 0.57769 | 0.19256 | 0.1039 | to 0.9920 |
| Pudding R at Aurora | 8 | 0.290 | 0.2365 | 0.0836 | 0.0921 | to 0.4874 |

| Ratio t-DDT to TSS (ng DDT per mg TSS) | Median | IQR | 95% CI of Median | |
|---|---|---|---|---|
| Little Pudding R at Rambler Rd | 0.8182 | 0.6607 | 0.4444 | to 1.7500 |
| Zollner Creek nr Mt. Angel | 0.3750 | 0.6250 | 0.0294 | to 0.8182 |
| Pudding R at Aurora | 0.201 | 0.362 | 0.0769 | to 0.7500 |

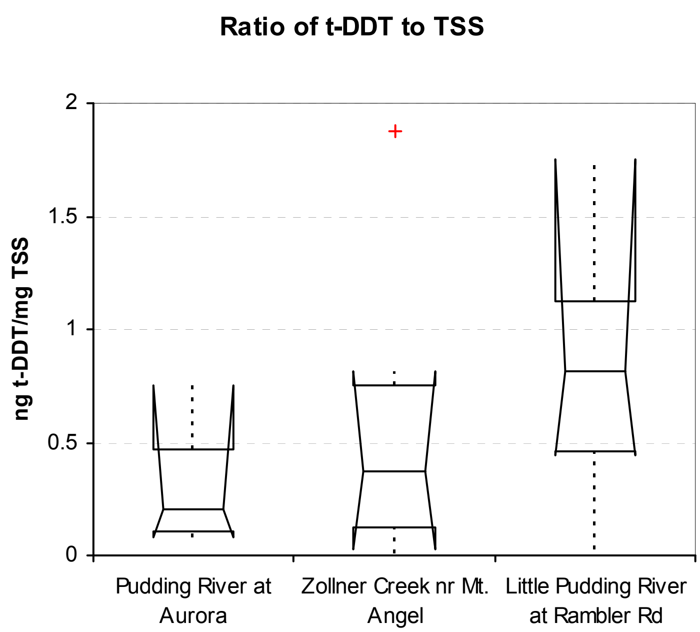


Figure J- 3: ODEQ t-DDT:TSS ratios for 3 sites

The Mann-Whitney test suggests that the ratio of t-DDT to TSS in the Little Pudding River is greater than in Zollner Creek, but with only a 90% confidence level (p = 0.08). The test also indicates that the ratio in Little Pudding River is greater than in Pudding River (p = 0.01).

Since the DDT and TSS concentrations and DDT/TSS ratios in Zollner Creek and Little Pudding River differ, the streams were analyzed independently.

### Little Pudding River Correlations

DDT concentrations in the Little Pudding River were compared to TSS and other parameters to determine if any parameters correlate. Analyses were performed to determine if the data varies seasonally.

*Seasonality*

Table J- 4 shows the 3 years of Little Pudding River ODEQ Total DDT data plotted vs. month. As shown, most of the data was collected during the spring. Kruskal-Wallis test for seasonality (WQHydro) indicated that there are no seasonal differences in the DDT data when data values are compared on either a monthly (Figure J- 5) or quarterly basis (Figure J- 6and Figure J- 7) (p > 0.10). This may be because of the relatively small amount of data available.

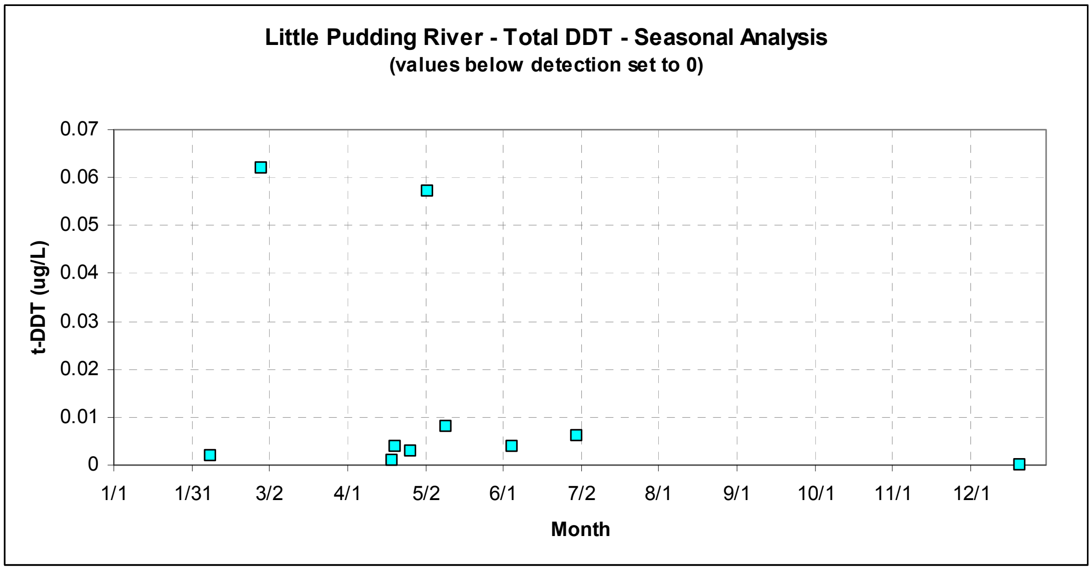


Figure J- 4: Little Pudding River - Total DDT by month

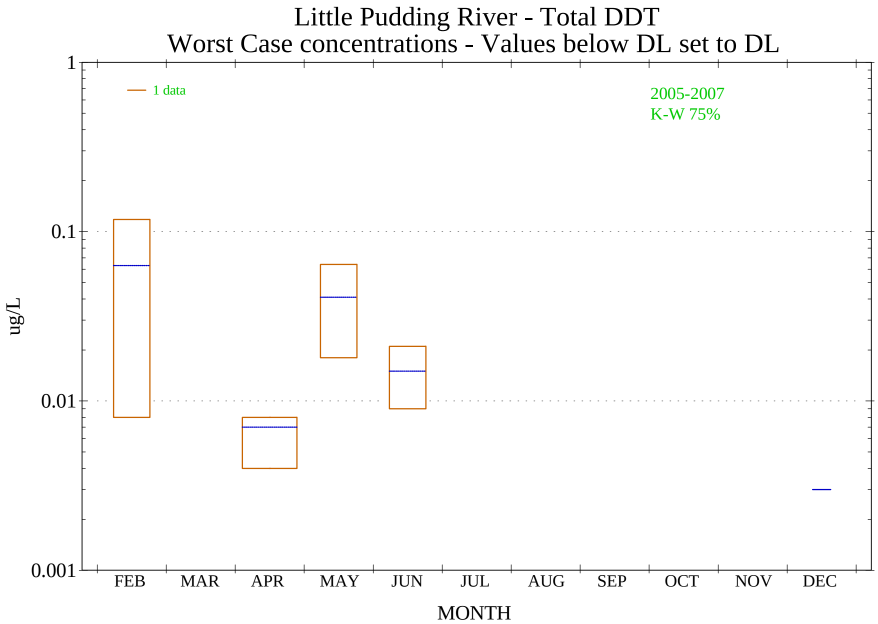


Figure J- 5: Little Pudding River - Total DDT - Aggregated by month

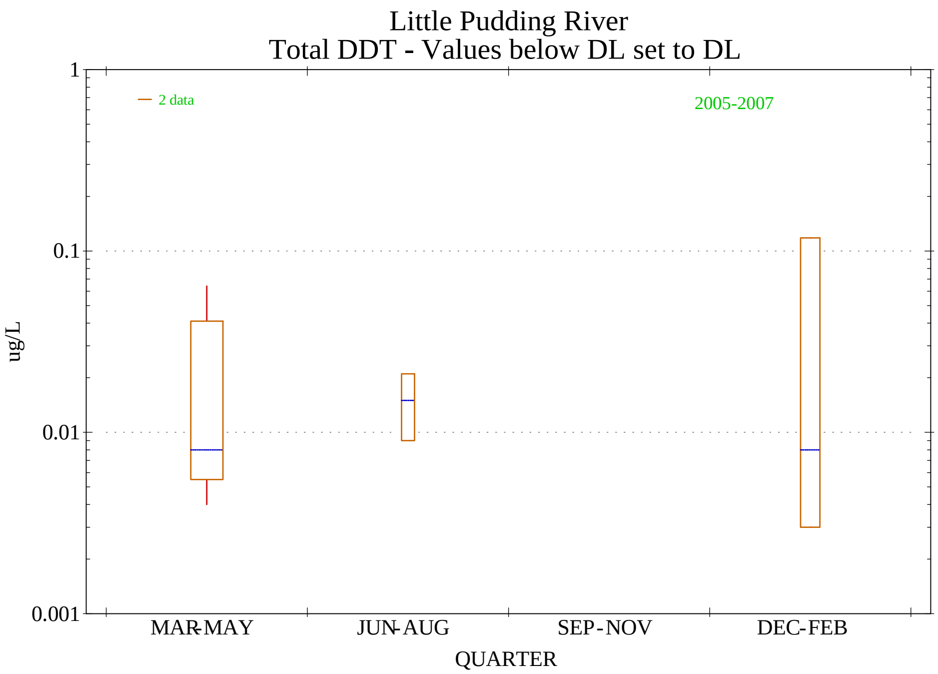


Figure J- 6: Little Pudding River - Total DDT - Aggregated by quarter (starting Mar)

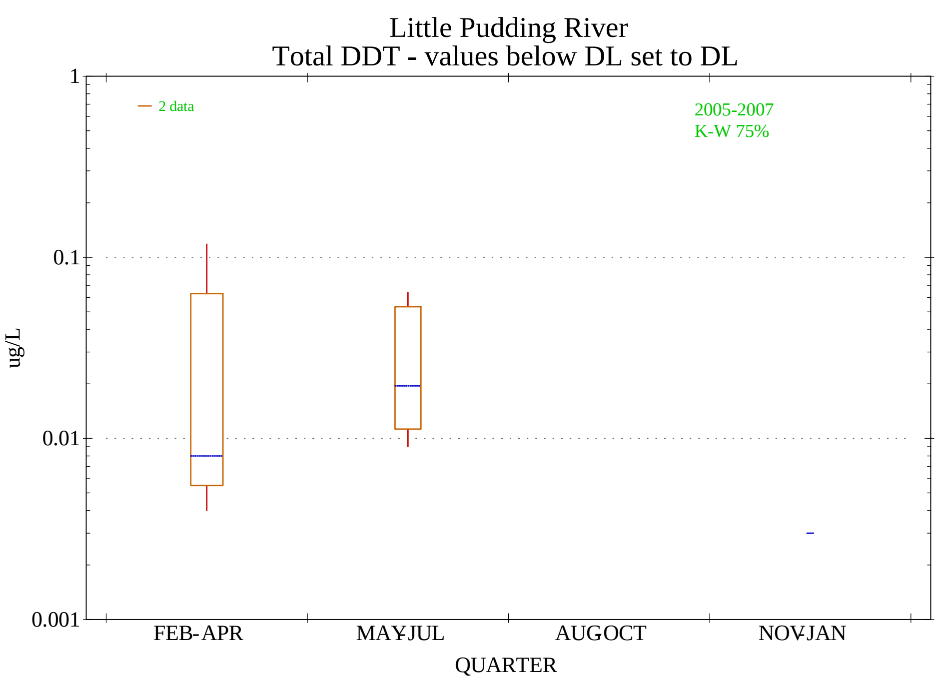


Figure J- 7: Little Pudding River - Total DDT - Aggregated by quarter (starting Feb)

Since DDT tends to be associated with solids, total suspended solids (TSS) concentrations were also examined. The Kruskal-Wallis test for seasonality indicated that seasonal differences are significant for TSS (99% confidence level) (Figure J- 8 and Figure J- 9). TSS concentrations tend to be greater in March through May than in June, possibly due to runoff of solids during spring precipitation events.

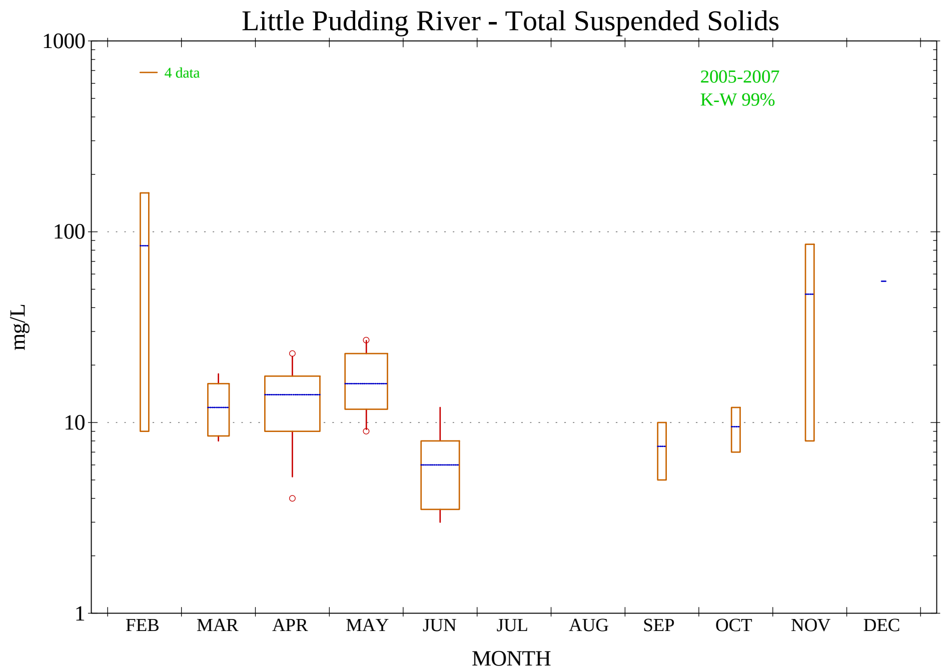


Figure J- 8: Little Pudding River - TSS - Aggregated by month

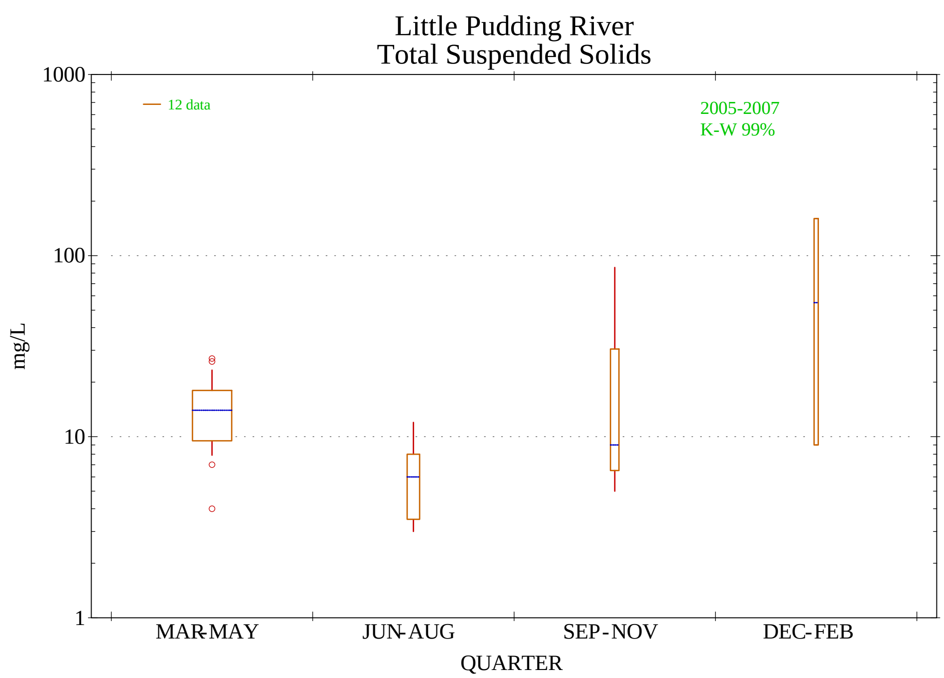


Figure J- 9: Little Pudding River - TSS - Aggregated by quarter

## *Correlations of DDT with other parameters*

DDT concentrations in the Little Pudding R were compared to TSS, total organic carbon (TOC), stream discharge, and precipitation in order to determine if any these parameters correlate with DDT. Little Pudding River is not gaged, so flow at Zollner Creek near Mt. Angel (USGS gage 14201300) was used instead. It is assumed that flow in Little Pudding River correlates with flow in Zollner Creek since both are low elevation, agriculture dominated watersheds.

Since none of the parameters of interest are normally distributed, the data was transformed to distributions that are more normally distributed by taking natural logarithms of the data before calculating Pearson's correlation coefficients (except for precipitation, which was not transformed due to the large amount of zero values). Resultant correlation coefficients, r, and correlations of determination, $r^2$ or $R^2$, are presented in Table J- 5. In addition to DDT, other pesticides of potential concern were included to see if efforts to reduce concentrations of DDT would likely result in reductions in other pesticides.

Only a few parameters were found to potentially be correlated. These are total suspended solids (TSS) with total organic carbon (TOC) ($R^2$ = 0.99), discharge ($R^2$ = 0.17), precipitation ($R^2$ = 0.30), and detected DDT concentrations ($R^2$ = 0.73, r = 0.86, p=0.0067). Note that, except for dieldrin, DDT could not be compared to other pesticides due to insufficient data.

In 9 out of 10 Little Pudding River samples, DDT was detected. The correlation between these DDT values and TSS is statistically significant. However, when the sample in which DDT was not detected is added to the dataset, the correlation is not statistically significant. This is because, even though this sample had a relatively high 55 mg/L concentration of TSS, it was not found to contain detectable concentrations of DDT.

Since even the log transformed data is generally not normally distributed, the Spearman rank method was used to verify likely correlations. Correlations found to be statistically significant at a 90% or near 90% confidence level are presented in Table J- 6. As shown, detected concentrations of DDT correlate with TSS. In addition, TSS correlates with TOC, discharge, and precipitation (88% confidence level). However, DDT correlates with neither discharge nor precipitation. Correlations between discharge and precipitation, not surprisingly, are also statistically significant.

Note that Spearman's method is a non-parametric method and, therefore, results are the same regardless of whether or not the data is log or otherwise transformed. Plots of parameters for which correlations are statistically significant are presented in Figure J- 10 to Figure J- 13.

Table J- 5: Little Pudding River Correlations - Pearson's correlation coefficients, r, and coefficients of determination, $R^2$

| | **ln TSS** | **ln TOC** | **ln Q Zollner** | **Precip via Silverton (in)** | **ln Chlorpyrifos (µg/L)** | **ln Dieldrin (µg/L)** | **ln Malathion (µg/L)** | **ln Diazinon (µg/L)** | **ln Atrazine (µg/L)** |
|---|---|---|---|---|---|---|---|---|---|
| **Pearson's r** | | | | | | | | | |
| ln TSS | 1 | | | | | | | | |
| ln TOC | **0.99** | 1 | | | | | | | |
| ln Q Zollner | 0.41 | 0.30 | 1 | | | | | | |
| Precip via Silverton (in) | **0.54** | **0.86** | **0.41** | 1 | | | | | |
| ln Chlorpyrifos (µg/L) | 0.18 | NA | 0.35 | 0.09 | 1 | | | | |
| ln Dieldrin (µg/L) | -0.35 | NA | **-0.56** | -0.06 | NA | 1 | | | |
| ln Malathion (µg/L) | -0.07 | NA | -0.03 | -0.05 | 0.14 | NA | 1 | | |
| ln Diazinon (µg/L) | -0.08 | NA | -0.10 | -0.03 | -0.07 | NA | 0.18 | 1 | |
| ln Atrazine (µg/L) | -0.03 | NA | 0.00 | 0.17 | 0.09 | NA | -0.06 | -0.11 | 1 |
| ln t-DDT (max) | **0.53** | -0.35 | -0.10 | 0.43 | NA | -0.11 | NA | NA | NA |
| ln t-DDT (min) Detected Only | **0.86** | **1.00** | 0.16 | **0.76** | NA | -0.17 | NA | NA | NA |
| ln t-DDT (Min) | 0.27 | **-0.72** | -0.28 | 0.18 | NA | -0.04 | NA | NA | NA |
| ln t-DDT (Min) w < DL = 1/2 MRL | 0.42 | **-0.56** | -0.18 | 0.33 | NA | -0.08 | NA | NA | NA |
| **Pearson's $r^2$** | | | | | | | | | |
| ln TSS | 1 | | | | | | | | |
| ln TOC | **0.99** | 1 | | | | | | | |
| ln Q Zollner | 0.17 | **0.09** | 1 | | | | | | |
| Precip via Silverton (in) | **0.30** | **0.75** | **0.17** | 1 | | | | | |
| ln Chlorpyrifos (µg/L) | 0.03 | NA | 0.12 | 0.01 | 1 | | | | |
| ln Dieldrin (µg/L) | 0.12 | NA | **0.32** | 0.00 | NA | 1 | | | |
| ln Malathion (µg/L) | 0.00 | NA | 0.00 | 0.00 | 0.02 | NA | 1 | | |
| ln Diazinon (µg/L) | 0.01 | NA | 0.01 | 0.00 | 0.00 | NA | 0.03 | 1 | |
| ln Atrazine (µg/L) | 0.00 | NA | 0.00 | 0.03 | 0.01 | NA | 0.00 | 0.01 | 1 |
| ln t-DDT (max) | 0.28 | 0.12 | 0.01 | 0.19 | NA | 0.01 | NA | NA | NA |
| ln t-DDT (min) Detected Only | **0.73** | **1.00** | 0.03 | **0.57** | NA | 0.03 | NA | NA | NA |
| ln t-DDT (Min) | **0.07** | **0.52** | 0.08 | 0.03 | NA | 0.00 | NA | NA | NA |
| ln t-DDT (Min) w < DL = 1/2 MRL | 0.18 | **0.31** | 0.03 | 0.11 | NA | 0.01 | NA | NA | NA |

Table J- 6:  Little Pudding River - Spearman's Rank Coefficients

| Spearmans ρ | TSS | Q Zollner |
|---|---|---|
| **TOC** | 1.00 (p=<0.0001) | |
| **Q Zollner** | 0.34 (p=0.03) | |
| **Precip via Silverton (in)** | 0.23 (p=0.12) | 0.51 (p=0.001) |
| **t-DDT (min) Detected Only** | 0.69 (p=0.056) | |

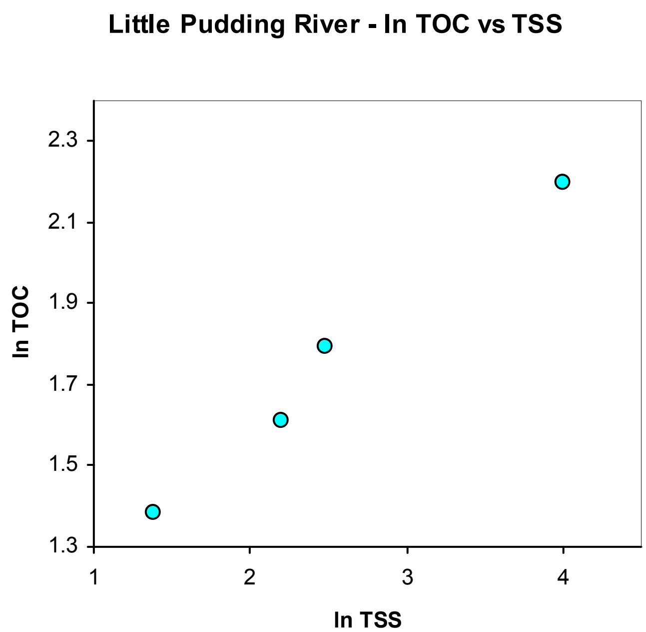


Figure J- 10:  Little Pudding River - Ln TOC vs. Ln TSS

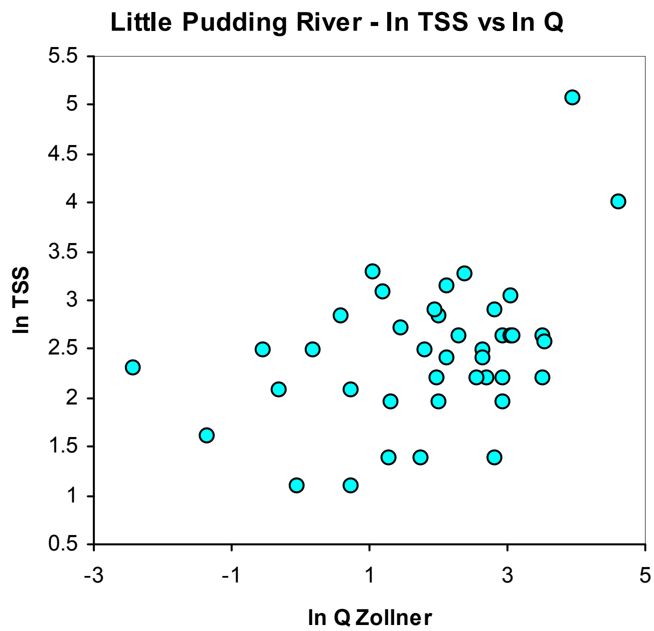


Figure J- 11: Little Pudding River - Ln TSS vs. Ln Discharge

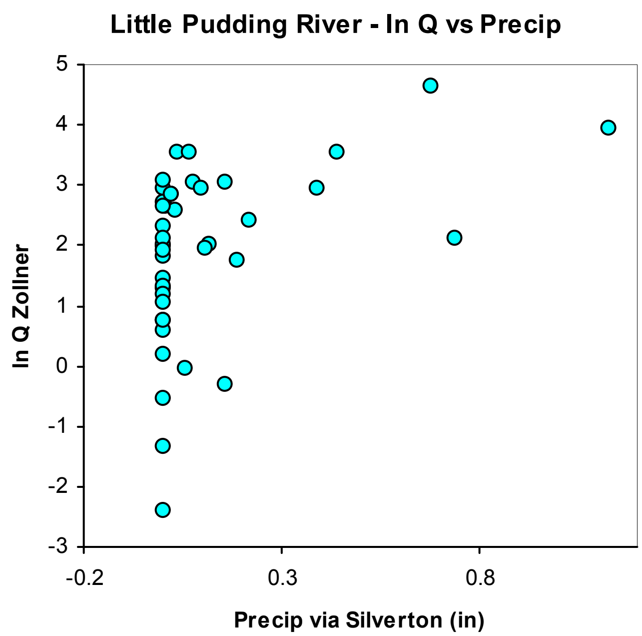


Figure J- 12: Little Pudding River - Ln Discharge vs. Precipitation

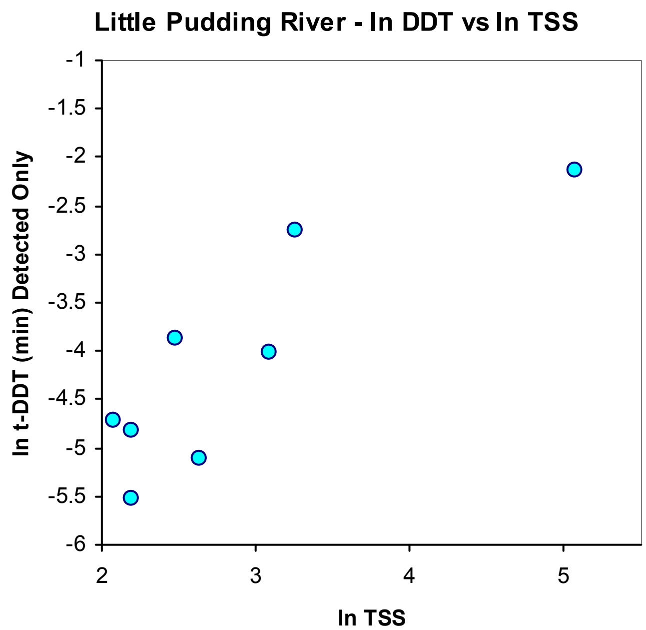


Figure J- 13: Little Pudding River - Ln DDT vs. Ln TSS

### Zollner Creek Correlations

DDT was detected in 3 of the 10 samples collected by ODEQ at Zollner Creek near Mt. Angel from 2005 through 2007 that were analyzed for DDT (prior to this, no samples collected in Zollner by either ODEQ or USGS were analyzed for DDT since the early 1990's). Pearson's correlation coefficients of log transformed data are shown in Table J- 7. As shown, detected total DDT concentrations correlate with TSS (Spearman's $\rho = 1$, $p < 0.0001$) (Figure J- 14). However, the correlation of DDT with precipitation is not statistically significant (Spearman's $\rho = 0.87$, $p = 0.33$).

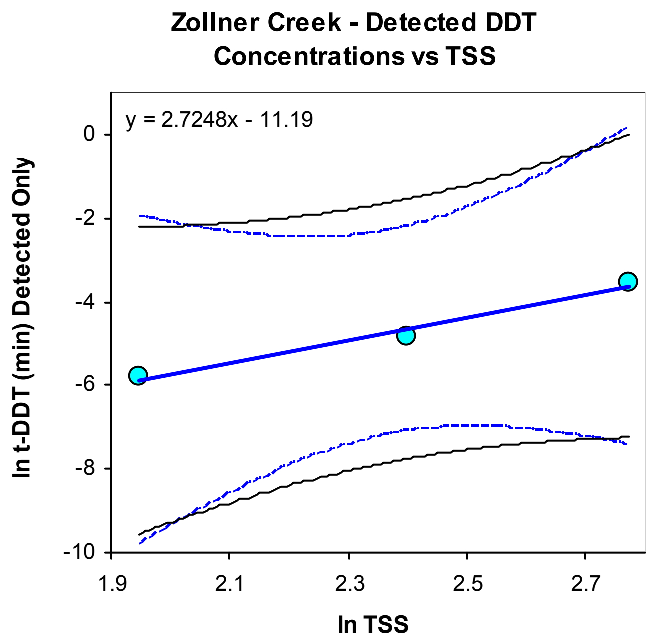


Figure J- 14:  Zollner Creek - DDT vs. TSS for detected concentrations only

Table J- 7:  Zollner Creek - Pearson's correlation coefficients, r, and coefficients of determination, $R^2$

| | **ln TSS** | **ln TOC** | **ln Q Zollner** | **Precip via Silverton (in)** |
|---|---|---|---|---|
| Pearson's r | | | | |
| **ln TSS** | 1 | | | |
| **ln TOC** | 0.03 | 1 | | |
| **ln Q Zollner** | **0.69** | -0.50 | 1 | |
| **Precip via Silverton (in)** | **0.41** | 0.24 | 0.44 | 1 |
| **ln t-DDT (max)** | 0.07 | NA | -0.05 | -0.14 |
| **ln t-DDT (min) Detected Only** | **0.99** | NA | -0.29 | **0.90** |
| **ln t-DDT (Min)** | 0.03 | NA | -0.04 | -0.20 |
| **ln t-DDT (Min) w < DL = 1/2 MRL** | 0.05 | NA | -0.04 | -0.17 |
| Pearson's $R^2$ | | | | |
| **ln TSS** | 1 | | | |
| **ln TOC** | 0.00 | 1 | | |
| **ln Q Zollner** | **0.47** | 0.25 | 1 | |
| **Precip via Silverton (in)** | **0.17** | 0.06 | 0.19 | 1 |
| **ln t-DDT (max)** | 0.00 | NA | 0.00 | 0.02 |
| **ln t-DDT (min) Detected Only** | **0.98** | NA | 0.08 | **0.81** |
| **ln t-DDT (Min)** | 0.00 | NA | 0.00 | 0.04 |
| **ln t-DDT (Min) w < DL = 1/2 MRL** | 0.00 | NA | 0.00 | 0.03 |

Although the $R^2$ for the correlation between detected concentrations and TSS is a high 0.98, the relationship is not reliable, as indicated by the 95% confidence interval of the slope, which ranges from -1.8686 to 7.3183. Statistics for the relationship are as follows:

| **Term** | **Coefficient** | **SE** | **p** | **95% CI of Coefficient** | |
|---|---|---|---|---|---|
| Intercept | -11.1896 | 0.8662 | 0.0492 | -22.1959 | to -0.1833 |
| Slope | 2.7248 | 0.3615 | 0.0840 | -1.8686 | to 7.3183 |

When non-detected DDT concentrations are included, no correlation is indicated between DDT and TSS. This is illustrated by Figure J- 15, in which the 7 DDT values less than the MRL were set to the MRL and plotted along with the 3 detected values. As shown, DDT was not detected in two samples with high TSS concentrations. Note, however, that one of these high TSS values was an estimate only and, therefore, may not be reliable.

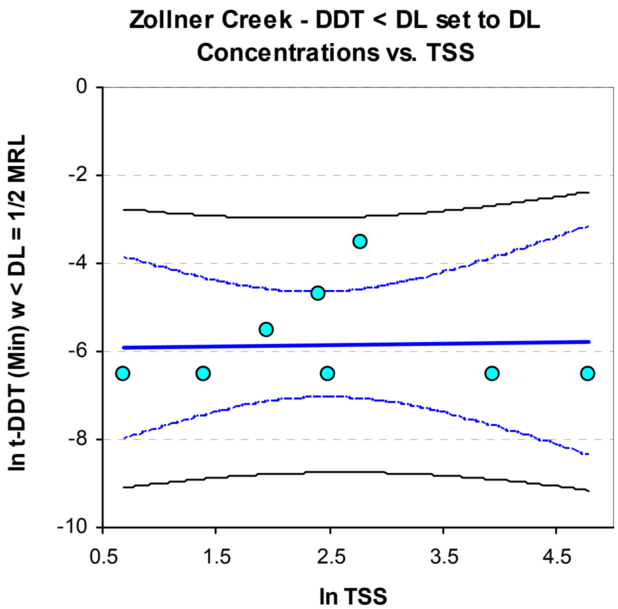


Figure J- 15: Zollner Creek - DDT vs. TSS - both detected and non-detected concentrations

## LITTLE PUDDING RIVER MULTIPLE LINEAR REGRESSION DDT MODEL

The following describes a multiple linear regression (MLR) model developed which relates Little Pudding River DDT to TSS and Zollner Creek discharge. The model was developed using only A+ rated ODEQ data from 2005 through 2007.

The relationship between detected total DDT concentrations and TSS is shown in Figure J- 16. The first plot shows the untransformed data, while the second natural log transformed data. While $R^2$ for the log transformed data ($R^2$ = 0.75, Adjusted $R^2$ = 0.72, SE = 0.5720) is less than for the untransformed data ($R^2$ = 0.85), the relationship via the transformed data is the appropriate model because both the log transformed t-DDT and TSS datasets are normally distributed (Kolmogorov-Smirnov p > 0.15), whereas the untransformed datasets are not. Note also that log transformed data is less influenced by individual data values. Statistics for the 1-parameter model are presented in Table J- 8.

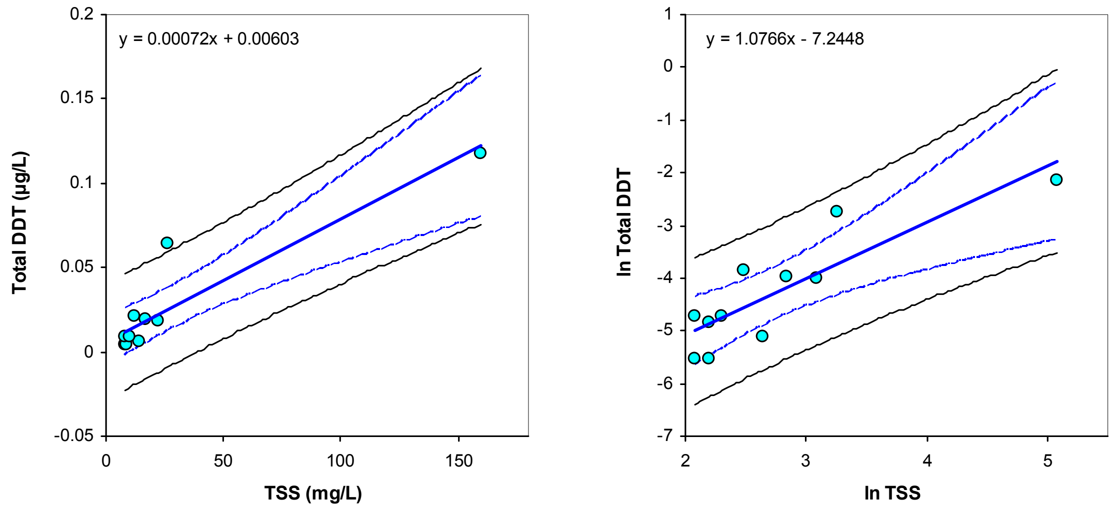


Figure J- 16: Little Pudding River 1-parameter DDT model

Table J- 8: Statistics for 1-parameter model.

| Term | Coefficient | SE | p | 95% CI of Coefficient | |
|---|---|---|---|---|---|
| Intercept | -7.2448 | 0.5965 | <0.0001 | -8.5942 | -5.8953 |
| Slope | 1.0766 | 0.2077 | 0.0006 | 0.6067 | 1.5466 |

The residuals for this 1-parameter model are normally distributed (Kolmogorov-Smirnov p >0.15) and correlate with discharge (Pearson r = -0.60, p=0.05) but not with precipitation (Table J- 9). This suggests that the model can be improved by the addition of discharge.

Table J- 9: Pearson's r values for 1-parameter model residuals

| | Residuals | ln Q Zollner | Precip Silverton |
|---|---|---|---|
| Residuals | 1 | | |
| ln Q Zollner | -0.60 | 1 | |
| Precip Silverton | -0.08 | 0.38 | 1 |

Adding discharge results in a statistically significant MLR model (p for both TSS and discharge < 0.05) with an improved $R^2$ and standard error ($R^2$ = 0.85, adjusted $R^2$ = 0.82, and SE = 0.4643). Statistics for the model are as follows (Table J- 10):

Table J- 10: Statistics for adding discharge to MLR model.

| Term | Coefficient | SE | P | 95% CI of Coefficient | |
|---|---|---|---|---|---|
| Intercept | -7.2650 | 0.4843 | <0.0001 | -8.3818 | -6.1481 |
| ln TSS | 1.2301 | 0.1806 | 0.0001 | 0.8137 | 1.6465 |
| ln Q Zollner | -0.2273 | 0.0955 | 0.0446 | -0.4476 | -0.0069 |

Note that Zollner Creek discharge was not available for the 6/14/07 sample (data missing from 6/12/07 to 6/17/07). For Pudding River at Aurora, discharge gradually declined during this period from 243 cfs to 191 cfs (provisional data). The average flow for 6/11/07 of 243 cfs and 6/18/2007 of 191 cfs nearly equaled the 6/14/2007 flow of 210 cfs. Is was assumed that Zollner Creek flow behaved similarly, so flow for 6/11/07 and 6/18/07 were averaged to estimate a flow of 1.24 for 6/14/07 (both values provisional).

The relationship, ln(tDDT) = 1.2301 ln(TSS) – 0.2273 ln($Q_{Zollner}$) – 7.2650 may be further explained as follows:

Model

$$\ln DDT = b_o + b_1 \ln TSS + b_2 \ln Q + \varepsilon$$
$$e^{\ln DDT} = e^{(b_o + b_1 \ln TSS + b_2 \ln Q + \varepsilon)}$$
$$DDT = e^{b_o} e^{b_1 \ln TSS} e^{b_2 \ln Q} e^{\varepsilon}$$
$$DDT = e^{b_o} (e^{\ln TSS})^{b_1} (e^{\ln Q})^{b_2} e^{\varepsilon}$$
$$DDT = e^{b_o} TSS^{b_1} Q^{b_2} e^{\varepsilon}$$
$$b_o = \text{intercept} = \text{-}\,7.2650$$
$$b_1 = \text{TSS coefficient} = 1.2301$$
$$b_2 = \text{Q coefficient} = \text{-}\,0.2273$$
$$DDT = e^{-7.2650} TSS^{1.2301} Q^{-0.2273} e^{\varepsilon}$$
$$DDT = 7.00x10^{-4} \cdot TSS^{1.2301.} Q^{-0.2273} e^{\varepsilon}$$

The term $e^{\varepsilon}$ in the above is a bias term. Since TSS required a log transformation to derive a normal distribution, such a bias term should be included (Helsel and Hirsch, 2002; Koch 2005).

An empirical estimate of bias calculated from residuals (differences between model calculated ln t-DDT values and observed ln t-DDT values) is a follows:

Bias = $\frac{1}{n}\sum_{i=1}^{n} e^{\varepsilon_i}$ = 1.066

Model with Bias Term included :

$$DDT = 7.00x10^{-4} \cdot TSS^{1.2301.} Q^{-0.2273} e^{\varepsilon}$$
$$DDT = 1.066(7.00x10^{-4} \cdot TSS^{1.2301.} Q^{-0.2273})$$
$$DDT = 7.456x10^{-4} \cdot TSS^{1.2301.} Q^{-0.2273}$$

where :

$DDT$ = total DDT, $\mu$g/L

$TSS$ = total suspended solids, mg/L

$Q$ = Discharge via Zollner Creek Gage 14201300, cfs

Model error statistics for the model with and without the bias term are provided in Table J- 11. As shown, inclusion of the bias term nearly eliminates model bias, as indicated by the mean error (ME), and reduces both absolute mean and RMS error.

Table J- 11: Error statistics for 2-parameter Little Pudding R MLR DDT model

| | **Without bias term** | **With Bias term** |
|---|---|---|
| **Mean Error (ME)** | -0.025 | 0.001 |
| **Absolute Mean Error (AME)** | 0.025 | 0.010 |
| **Root Mean Square Error (RMS)** | 0.046 | 0.017 |

A plot of model calculated vs. observed Total DDT is shown in Figure J- 17 ($R^2$ = 0.85).

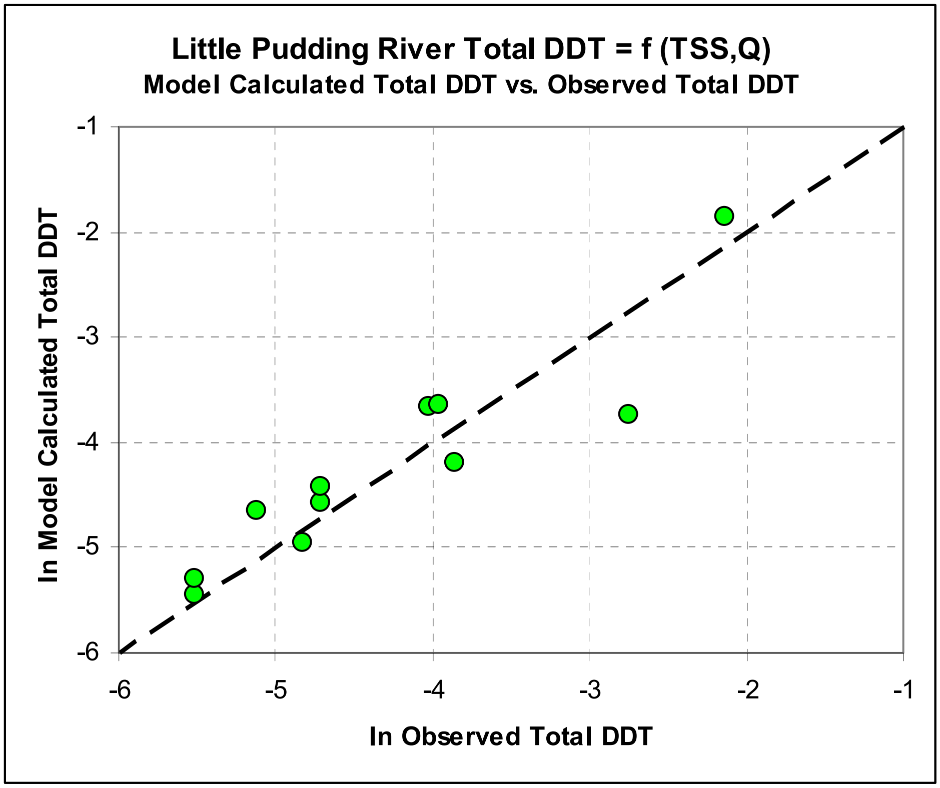


Figure J- 17: Little Pudding River DDT model – Calculated t-DDT vs. Observed t-DDT

### LITTLE PUDDING RIVER LOAD DURATION CURVES

In order to develop a load duration curve for the Little Pudding River, the flow rate of the stream is needed. Unfortunately, the stream is ungaged. Marion Soil and Water Conservation District has a gage on the Little Pudding River at Rambler Road (LPR1). However, only water level is measured, not discharge.

Table J- 12: Watershed areas, Little Pudding River and Zollner Creek

| **Watershed** | **Area (acres)** |
|---|---|
| Upper Little Pudding River | 19,318 |
| Lower Little Pudding River | 18,827 |
| Zollner Creek near Mt. Angel Gage 14201300 | 9,600 |

Nearby Zollner Creek is gaged and has similar characteristics to Little Pudding River, so some insight into Little Pudding flow may be obtained from Zollner. Little Pudding River drainage area is 4 times that of Zollner, so natural flow in Little Pudding could be up to 4 times that of Zollner (Table J- 12). Note, however, that during the irrigation season, nearly all of the available flow is diverted at times from both streams, so applying a 4x factor to Zollner Creek during the summer could overestimate flow in Little Pudding. The only instantaneous Little Pudding River discharge measurement that could be located that was collected during a time period that the Zollner Creek gage was operating was an 8/16/94 USGS measurement. On this date, Little Pudding River near Rambler Road flow discharge was 0.24 cfs, and daily average Zollner Creek discharge was 0.27 cfs, which indicates a 1:1 relationship.

Allocated water withdrawals for Little Pudding are 1.7 times the allocated withdrawals for Zollner Creek (Table J- 13). This may suggest that roughly 1.7 times the Zollner Creek flow is available during the summer.

Table J- 13: Allocated diversions, Little Pudding River and Zollner Creek watersheds

| Watershed | Allocated Diversions (cfs) |
|---|---|
| Little Pudding River Watershed | 23.9 |
| Zollner Creek Watershed | 14.1 |

In calibrating a mass-balance model of the Pudding River (described below), it was found a 2:1 relationship between Little Pudding R and Zollner Creek worked well. Therefore, for purposes of generating a load duration curve for Little Pudding River, the discharge was set to twice the gaged Zollner Creek discharge. While this may overestimate flow during the summer and underestimate it during other times of the year, overall, it should provide a reasonable estimate of DDT load provided by the stream to the Pudding River. The resultant load duration curve is shown in Figure J- 18.

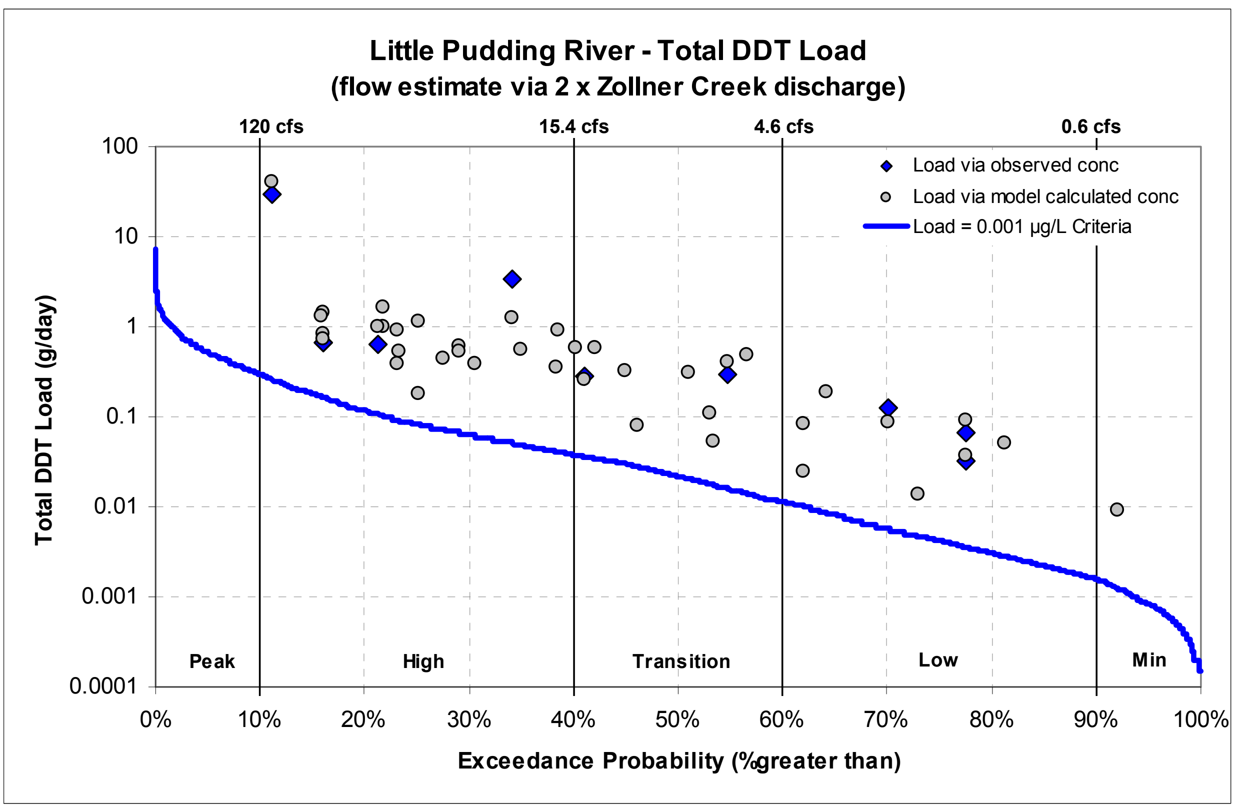


Figure J- 18: Little Pudding River t-DDT load duration curve

## LITTLE PUDDING RIVER DDT REDUCTIONS IN RESPONSE TO TSS REDUCTIONS

The median TSS concentration in the Little Pudding River for the 2005 to 2007 ODEQ data set was 12 mg/L and the mean was 17.5 mg/L.  MLR model calculated total DDT concentrations for a 17.5 mg/L TSS concentration for the range of flow conditions is shown by the uppermost curve in Figure J- 19. The impacts of reducing TSS by percentages ranging from a 32% to 94% are shown by the remaining curves.  While the distributions of DDT for various overall percent reductions in TSS will not match these curves exactly, since 17% of TSS variability is due to flow ($R^2$ for correlation of TSS vs. discharge = 0.17; p = 0.007), they should provide reasonable estimates of DDT concentrations to be expected.  Note that Figure J- 20 is identical to Figure J- 19, except that a log scale is used to allow for easier comparisons to water quality criteria.

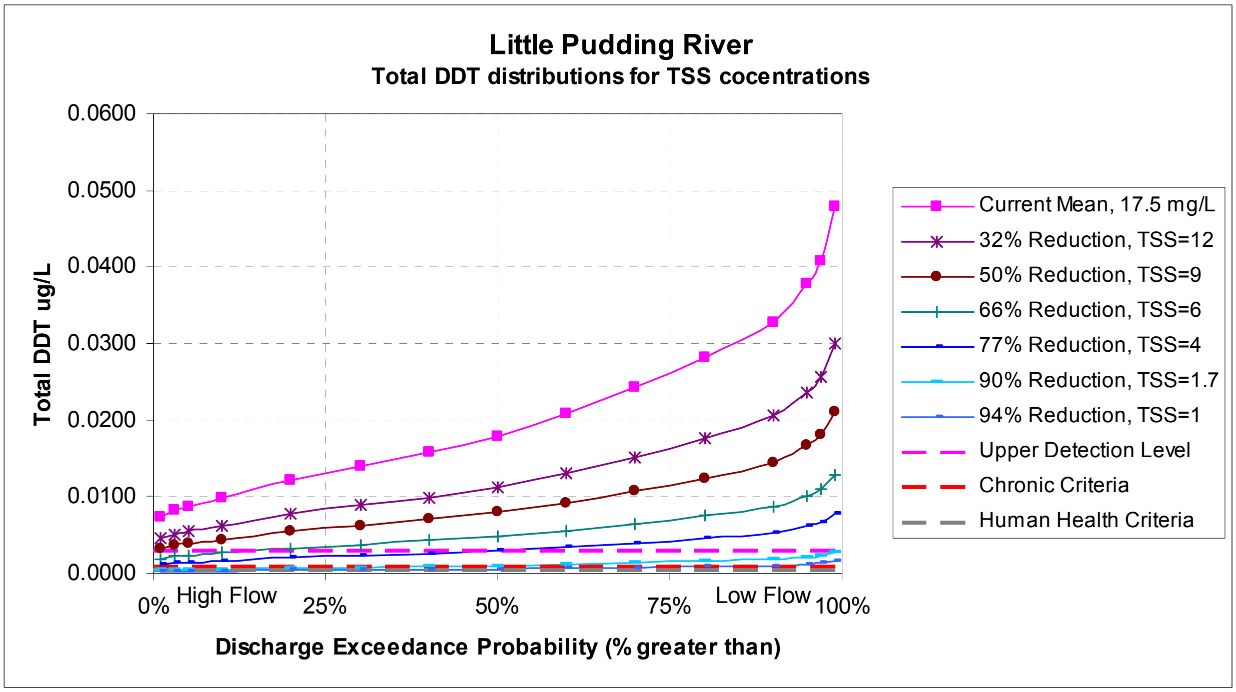


Figure J- 19:  Little Pudding River – MLR Model calculated t-DDT vs. discharge and TSS concentration

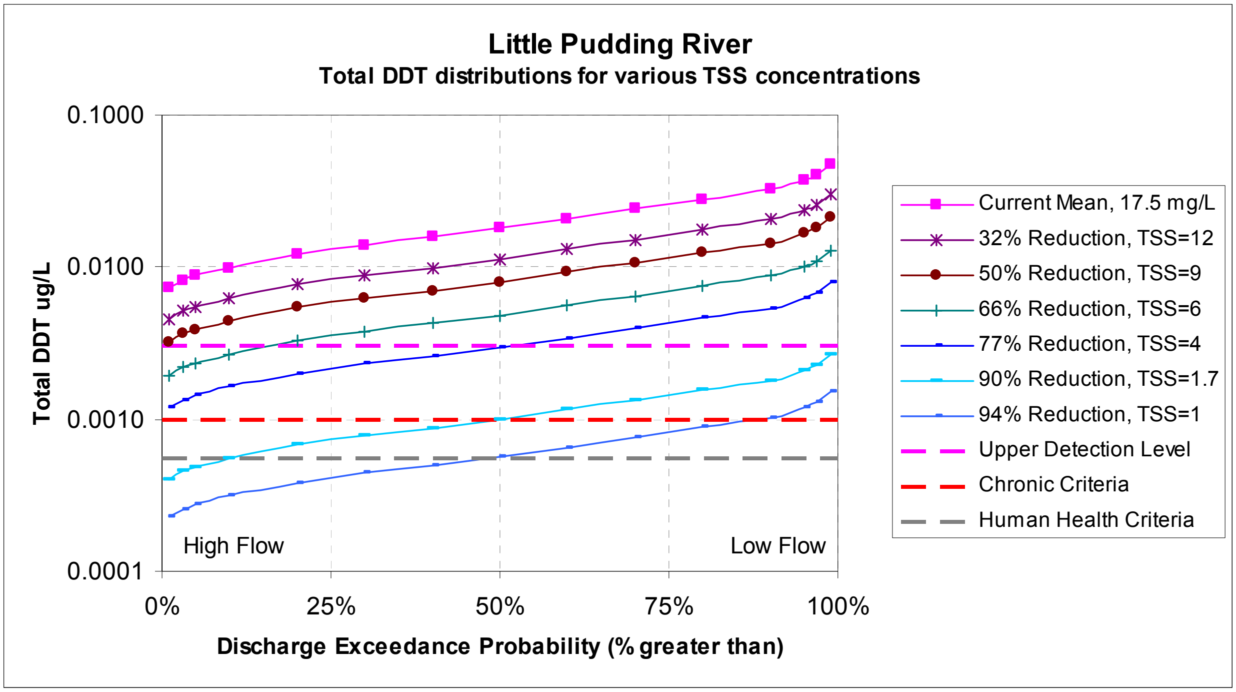


Figure J- 20:  Little Pudding River – MLR Model calculated t-DDT vs. discharge and TSS concentration

As shown, total DDT concentrations are currently above detection for all flow conditions. By reducing TSS by 77%, t-DDT concentrations will be less than 0.003 µg/L half the time. This suggests that by reducing TSS 77%, as many as half of the t-DDT measurements could be below detection. This is because the detection levels for DDT, DDE, and DDD are all 0.001 µg/L, so the t-DDT concentration could approach 0.003 µg/L without DDT or its metabolites being detected.

In order to meet the 0.001 µg/L criteria, further reductions in TSS are needed. By reducing TSS by 90%, the model suggests that the 0.001 µg/L chronic toxicity criteria will be met half the time. In addition, DDT will be below the 0.003 µg/L upper detection level for all flow conditions. Note, however, that DDT could still possibly be detected at concentrations less than 0.003 µg/L. For example, if the DDE were detected at 0.002 µg/L, while DDT and DDD were both <0.001 µg/L, the measured t-DDT concentration would be 0.002 µg/L. However, the model suggests that for a 90% reduction in TSS, such detections would be infrequent.

Finally, in order to meet a human health based target for total DDT of 0.000554 µg/L half the time, a 94% reduction in TSS to 1 mg/L would be needed.[3] This means that at least half the time, TSS would have to be less than the 1 mg/L detection level for TSS. While interesting from an academic standpoint, such a TSS reduction would likely be highly improbable under the best of conditions and impossible in an agricultural watershed like the Little Pudding River.

## MASS-BALANCE MODEL CALIBRATION

In order to derive appropriate total suspended solids maximum concentration targets for Zollner Creek, Little Pudding River, and other agriculture dominated streams of concern, a simple mass-balance model was developed for the Pudding River. The model was developed using 37 paired sets of TSS data collected by ODEQ from 2005 through 2007 at 3 sites: Little Pudding River at Rambler Road, Zollner Creek near Mt. Angel (Monitor-McKee Road), and Pudding River at

[3] The t-DDT concentration to be met is 0.000554 µg/L, which is the sum of Table 20 human health criterion for 4-4'DDT, the Table 33A human health criterion for 4-4'-DDE, and the Table 33A human health criterion for 4-4'-DDD (0.000024 + 0.00022 + 0.00031 = 0.000554 µg/L).

Aurora (Hwy 99E). Since DDT was only measured for 8 of 37 sample dates with TSS data available for all 3 sites and flow data available for both Zollner Creek and Pudding River at Aurora and since, in many cases, concentrations were below detection, t-DDT concentrations are not available for most of the samples. Therefore, t-DDT was estimated for Little Pudding River using the MLR model, or, in the case of Zollner Creek and "background" concentrations, relationships between TSS and flow.

Since most of the data for other locations, including the Pudding River and Zollner sites is "censored" (i.e., below detection), such relationships cannot be determined directly from the data for these sites. The only statistically significant relationship for DDT vs. TSS is the one for Little Pudding River (Figure J- 21). Therefore, for modeling purposes, it was assumed that the slope for the relationship for this site (slope = 1.0766 via Ln t-DDT = 1.0766 Ln TSS – 7.2448) also applies for Zollner Creek and the Pudding River. The intercept term was then adjusted to derive relationships for the other sites.

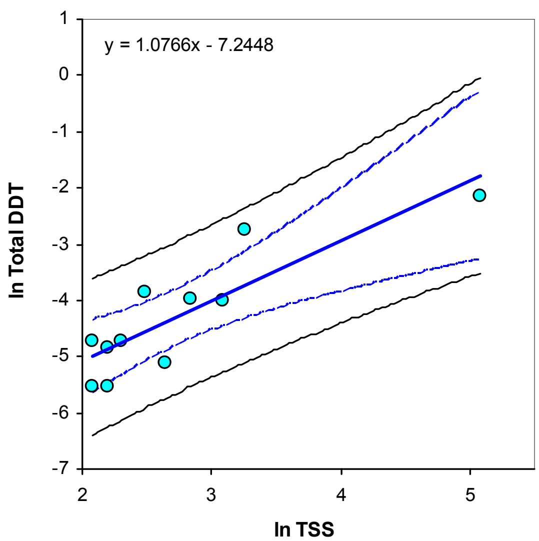


Figure J- 21: Little Pudding R at Rambler Rd - DDT vs. TSS

For Zollner Creek, the intercept term was adjusted so that the average of the calculated t-DDT concentrations equaled the average of the observed values, with values below detection set to 0.0015 µg/L (half the max detection level of 0.003 µg/L). The resultant equation is: Ln [t-DDT] = 1.0766 x Ln [TSS] – 8.46 (Figure J- 22).

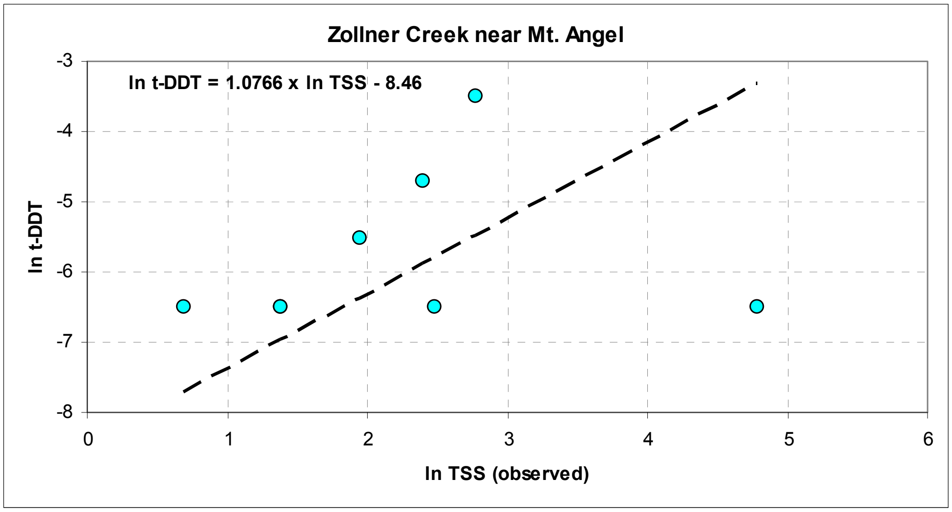


Figure J- 22: Assumed relationship between t-DDT and TSS for Zollner Creek

For the Pudding River, only one value is above detection. For this site the intercept term was adjusted to intersect this value. The resultant equation is: Ln [t-DDT] = 1.0766 x Ln [TSS] – 9.70 (Figure J- 23).

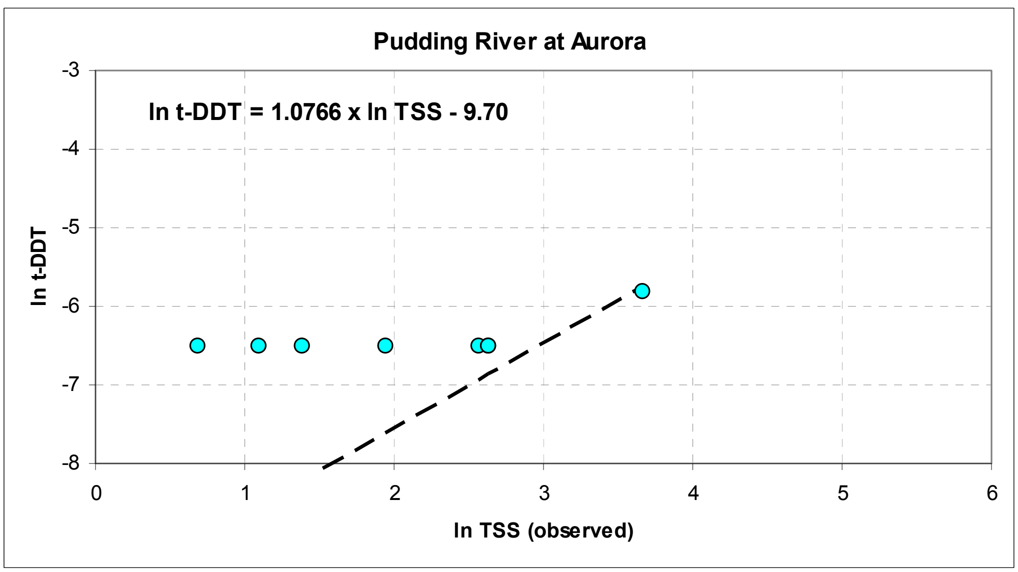


Figure J- 23: Assumed relationship between t-DDT and TSS for Pudding River

The Pudding River equation was not used to calculate DDT at the Pudding River at Aurora site. Instead, it was used as a reference for estimating a relationship for background Pudding River DDT concentrations, that is, Pudding River concentrations in the absence of Zollner Creek and Little Pudding River loads. The intercept term for Pudding River background was derived iteratively using the model. It is the primary calibration "knob" for the model. This term was adjusted from 9.70 until the model calculated a frequency of detection that is similar to that observed at the Pudding River at Aurora site. This resulted in the following relationship to apply to background Pudding River concentrations: Ln [t-DDT] = 1.0766 x Ln [TSS] – 9.90. Resultant relationships between t-DDT and TSS for Zollner Creek, Pudding River at Aurora, and Pudding River background are shown in Figure J- 24.

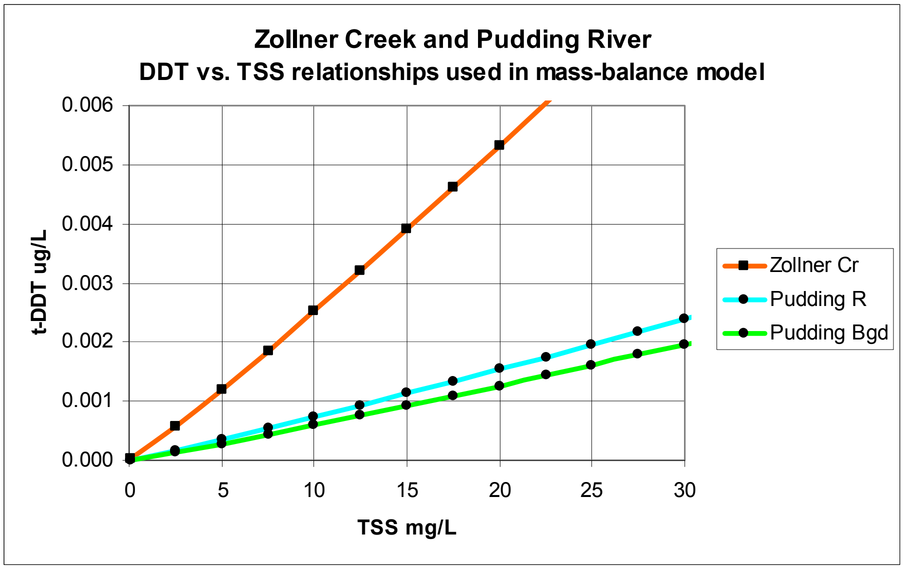


Figure J- 24:  t-DDT vs TSS for Zollner Creek, Pudding River and Background

Background Pudding River TSS concentrations are also unknown and had to be estimated.  A review of the TSS data for the 37 paired data values for Zollner Creek, Little Pudding R, and Pudding River shows that, on average, 5% of the TSS load for Pudding R at Aurora is due to Little Pudding and Zollner Creek (assuming Little Pudding discharge is 2 x Zollner discharge). Therefore, background TSS was set to 95% of TSS at Aurora.

Little Pudding River is not gaged, so discharge was estimated from Zollner Creek discharge.  As described above, a 2:1 ratio of Little Pudding River to Zollner Creek discharge was found to be appropriate.

Since DDT was detected in only 1 of 11 ODEQ Pudding River at Aurora samples, actual DDT concentrations are unknown.  This makes calibration of a model difficult.  Rather than calibrating on concentration, the model calibration focused on frequency of detection.  The goal was to adjust “background” concentrations, i.e., concentrations not associated with Little Pudding River or Zollner Creek, until the frequently of detection matched the roughly 10% detection frequency observed by DEQ.

Since the detection levels for DDT, DDE and DDD are each 0.001 µg/L, t-DDT concentrations greater than 0.003 µg/L will be detected (assuming laboratory analytical methods are accurate), concentrations less than 0.001 µg/L will not be detected, and concentrations in the range 0.001 to 0.003 µg/L may or may not be detected, depending how the t-DDT is proportioned between DDT and its metabolites.  For modeling purposes, it was assumed that calculated t-DDT concentrations greater than 0.002 µg/L would be detected, while those less than 0.002 ug//L would not.

A concentration duration curve of model calculated current t-DDT concentrations vs. flow exceedance probability is shown in Figure J- 25.

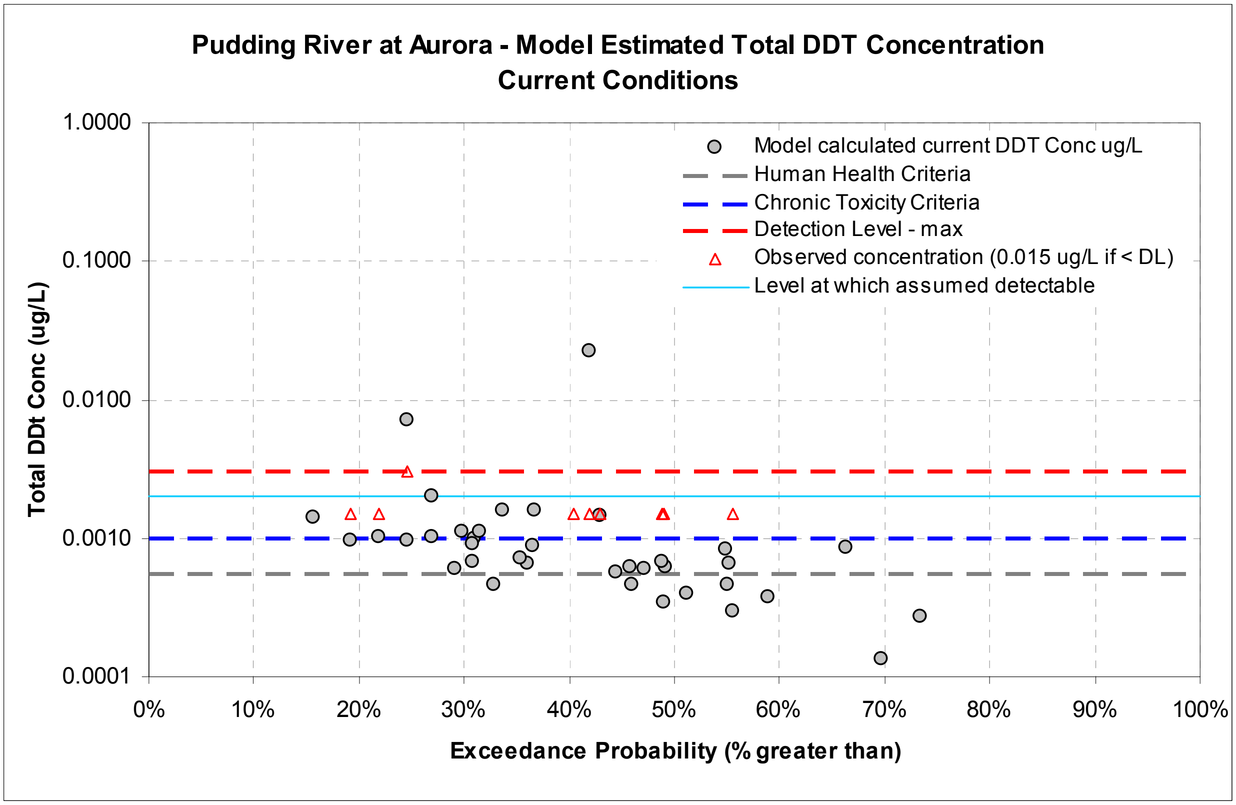


Figure J- 25: Duration plot of model estimated t-DDT concentrations – current conditions

Observed average TSS and t-DDT concentrations, t-DDT to TSS ratios, and flow rates for the 8 dates with paired TSS, DDT and flow data are shown in Table J- 14. For Zollner Creek and Pudding River, mean t-DDT concentrations and tDDT:TSS ratios are estimates only, since most observed t-DDT concentrations were below detection (values below detection were set to 0.0015 µg/L to calculate means).

Table J- 14: Averages for 8 dates with paired DDT, TSS and Flow data; Current conditions

| | **TSS** (mg/L) | **t-DDT** (µg/L) | **Discharge** (cfs) | **tDDT:TSS** (ng/g) | **tDDT:TSS via means** (ng/g) |
|---|---|---|---|---|---|
| Little Pudding R at Rambler Rd | 38.4 | 0.0300 | 58.2 | 0.947 | 0.782 |
| Zollner Creek nr Mt. Angel | 27.9 | 0.0063 | 29.1 | 0.570 | 0.226 |
| Pudding River at Aurora | 12.8 | 0.0017 | 1144.4 | 0.210 | 0.132 |
| Pudding River Background | 12.11 | 0.0008 | 1057.1 | 0.059 | 0.062 |
| Averages for paired ODEQ 2005-2007 data (8 dates with flow, TSS and DDT data). Values for streams are observed values. Pudding River Background is a model calculated value for the Pudding River without Little Pudding R and Zollner Creek. Little Pudding R discharge is an estimate based on an assumed 2:1 ratio between Little Pudding River and Zollner Creek. tDDT for tDDT:TSS ratio derived by setting values of DDT, DDE, and DDD to ½ the 0.001 µg/L detection level if < detection. tDDT:TSS via means calculated from other averages in table. | | | | | |

Observed average TSS concentrations and flow rates and model calculated average t-DDT concentrations and t-DDT:TSS ratios for the 37 dates with paired TSS and flow data, (including the 8 dates with DDT) are shown in Table J- 15. As shown, TSS concentrations for Little Pudding River and Zollner Creek are similar, but the load of DDT carried by sediment in the Little Pudding River is about 3 times greater than in Zollner. For these 37 dates, the average t-DDT concentration was about 15 times the chronic criteria in the Little Pudding River, 5 times the criteria in Zollner Creek, and about 1.5 times the criteria in the Pudding River at Aurora. Modeling suggest that, in the absence of loads from Little Pudding R and Zollner Creek, t-DDT concentrations in Pudding River would not exceed the chronic criteria, but would still exceed the 0.554 ng/L (0.000554 µg/L) human health based target.

Surrogate measures for load allocations developed from this mass balance model are presented in Chapter 4 – Pesticides.

Table J- 15: Averages for 37 dates with paired TSS and Flow data; Current Conditions

| | **TSS** (mg/L) | **t-DDT** (µg/L) | **Discharge** (cfs) | **tDDT:TSS** (ng/g) | **tDDT:TSS via means** (ng/g) |
|---|---|---|---|---|---|
| Little Pudding R at Rambler Rd | 17.5 | 0.0155 | 30.6 | 0.834 | 0.884 |
| Zollner Creek nr Mt. Angel | 17.2 | 0.0048 | 15.3 | 0.249 | 0.282 |
| Pudding River at Aurora | 10.6 | 0.0016 | 1009.8 | 0.171 | 0.148 |
| Pudding River Background | 10.04 | 0.0006 | 964 | 0.059 | 0.061 |
| Averages for paired ODEQ 2005-2007 data (37 dates with flow and TSS data). DDT concentrations are model calculated values. Pudding River Background values are model calculated values for the Pudding River without Little Pudding R and Zollner Creek. | | | | | |

## REFERENCES

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