January 15, 2005

Attachment A to the Calleguas Creek Watershed Toxicity TMDL

Toxicity TMDL Linkage Analysis for the Calleguas Creek Watershed

Submitted to:

Calleguas Creek Watershed Management Plan

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INTRODUCTION

In a preliminary analysis performed for the Source Analysis (LWA 2004a), compounds likely to impose toxicity include ammonia and organophosphate (OP) pesticides. To assist the development of the Toxicity TMDL for the Calleguas Creek Watershed (CCW), a numerical model is employed to estimate loading, movement, and effects of reductions of constituents thought to impose toxicity on the receiving waters in the watershed. As discussed in the Toxicity TMDL Modeling Approach (LWA 2004c), the Toxicity TMDL will not exclude other compounds, but will focus primarily on OP pesticides, as there is an adopted TMDL for Nitrogen Compounds, and a TMDL for Historic Pesticides and PCBs is in development. The following is a description of the Toxicity TMDL Mass Balance Model (TTMBM) developed to provide decision support of source loading and implementation effectiveness for the Toxicity TMDL.

SCOPE OF THE TOXICITY TMDL MASS BALANCE MODEL

The National Research Council (NRC, 2001) provides some guidance for determining the appropriate level of complexity for modeling efforts in support of TMDL development: “There is a common belief that the expected realism in the model can compensate for a lack of data, and the complexity of the model gives the impression of credibility. Starting with simple analyses and iteratively expanding data collection and modeling as the need arises is the best approach.” Following the recommendation of the NRC, the first step in the TTMBM development is a review and critical evaluation of the available OP pesticide data collected in the CCW.

Discussions of the TTMBM development and applicability require a preface describing data and time constraints. The TTMBM uses the available information to determine source loadings and contributions to receiving waters in the CCW. Currently, there are no data available describing the quality of native space (undeveloped, vacant, open space) runoff, however, if drift and atmospheric deposition are important processes, there will be a significant contribution from the native space to the receiving waters. If scavenging from the atmosphere by precipitation is an important process in the CCW, the data analysis will indicate a runoff problem, when in-fact there would be an air pollution problem. Groundwater contribution to the receiving waters may be a significant fraction of flow during dry-weather, however there are no available detected data describing the concentrations of OP pesticides in the groundwater basins of the CCW. An estimate of groundwater contribution is included in the TTMBM. There are entire subwatersheds in the CCW without in-stream data or with extremely limited data on OP pesticides. The TTMBM developed herein represents the most complete model possible based on available information. Continued monitoring and future model refinement are recommended.

Chlorpyrifos is known to readily partition to the organic fraction/coating of sediment. Except for a limited number of samples, available sediment data is limited to samples collected in the late 80’s and early 90’s. Water column data only exist from mid 90’s to present. Sediment data are being collected as part of the current TMDL effort but data from a sufficient number of events are not currently available to perform the analysis. Consequently, sediment partitioning is not currently included as a mechanism in the TTMBM. Once recent sediment data become available, the model may be expanded to incorporate partitioning effects to account for phase transfer.

The time frame for model development is an important consideration for any modeling investigation. A sophisticated hydrologic model simulation using HSPF is now available for the CCW, however the calibration of HSPF was finalized after the TTMBM was developed. Output from a model such as HSPF would be required for flow inputs to alternate water quality models such as WASP. The time available for the CCW Toxicity TMDL development is less than the time that would be required to use a canned model such as WASP.

Limited data set size and scatter has a great influence on the model development and validation. A summary of data available in the CCW by TTMBM Subwatershed is presented in Table 1. The number of chlorpyrifos and diazinon samples collected by runoff or receiving water type and the percent detected are listed in the Table. Also listed in the Table is the percent of samples where the constituent was either detected or non-detected at a detection level sufficiently low to evaluate compliance with water quality objectives. Detection levels for the majority of chlorpyrifos samples are too high to be environmentally relevant. Environmentally relevant detection levels for diazinon are utilized on a far greater percentage of samples than chlorpyrifos.

Data summaries for receiving water data that could be used for validation are listed in Table 2. To further limit the usefulness of the data, several subwatersheds only have detected data corresponding to dry-weather sampling, meaning the wet-weather performance of the model is unverifiable for several subwatersheds. A minimum of 3 unique detected data and more than 20% of data detected are needed to perform the statistical analysis of the data. Statistics generated from data sets with less than 40% detected values should be considered estimates and are subject to error. Nearly all runoff or receiving water data sets available contain less than 40% detected values.

Because of limited available data, grab and composite samples are treated in the analyses as being equivalent and equally representative of conditions in the CCW. Estimated and qualified data are used below in the analysis as normal detected values. Both uses of the data may introduce errors into the analysis, as grab samples may not be equivalent to composite samples and may not be representative of the source. Estimated values, while being a better estimate of the true sample value than the reporting limit, may not reflect the true value accurately.

In the simplified reality of the TTMBM, it is assumed that the receiving water data are representative of surface waters in the entire subwatershed. A related simplifying assumption is that it is assumed that the agricultural runoff and urban characterization sites are representative of all like land uses everywhere across the CCW.

An analysis of pesticide use reports (PUR) conducted for the Source Assessment (LWA, 2004a) yielded agriculture and urban uses as the predominant source of OP pesticides applied to the watershed. A link between the application rates of OP pesticides to runoff water quality was not established for the TTMBM. There are currently too few data for a temporal analysis of runoff water quality.

CCW is a small flashy watershed, so the storm-runoff model that is the heart of the Dynamic Calleguas Creek Modeling System (DCCMS), which is detailed in LWA 2004d, works well to estimate runoff and in-stream flows.

An explicit margin of safety (MOS) cannot be determined for the TTMBM, as there is insufficient receiving water data to fully characterize the performance of the model.

Many of the above qualifications on the TTMBM can be removed through continuing monitoring efforts using environmentally relevant detection limits.

Table 1: Chlorpyrifos and Diazinon Data Summaries by Source Type in CCW.

	Clorpyrifos		Diazinon	
Source	n	Detected	n	Detected
Agricultural Runoff	75	37.3%	66	22.7%
Urban Runoff (1)	47	10.6%	50	54.0%
Pumped Groundwater	4	0.0%	4	0.0%
Effluent Discharge	18	5.6%	19	36.8%
Receiving Water	213	25.8%	239	45.2%

(1) Samples from out-of-watershed characterization site.
(2) Samples from in-watershed characterization sites/
(3) Combination of (1) and (2)
(4) Includes the samples from Urban and Agriculture; and Agriculture and Open Space.
(5) Includes the samples Residential, Commercial, and Industrial runoff.

Table 2: Chlorpyrifos and Diazinon Summary Statistics for Receiving Waters in the CCW by Toxicity TMDL Modeling Subwatershed.

	Chlorpyrifos			Diazinon		
TMDL Reach	n	Detected	Percentile @ 0.014 μg/L	n	Detected	Percentile @ 0.1 μg/L
Arroyo Simi	39	12.8%	NC (1)	42	50.0%	73.9%
Las Posas	10	30.0%	79.8%	10	60.0%	80.6%
Conejo Creek	55	5.5%	NC	73	39.7%	90.6%
Calleguas Creek	52	19.2%	NC	57	56.1%	78.3%
Revolon Slough	54	61.1%	23.0%	54	37.0%	79.7%
Mugu Lagoon	3	33.3%	NC	3	0.0%	NC

(1) Not Calculated: Statistical analysis requires a minimum of three unique data point and greater than 20% detected to calculate distribution. Distributions calculated with less than 40% detected data should be considered estimates.
(2) Neglecting 6 early data points with detection limits of 2 ug/L allows a sufficient number of detected values (20.5%) to estimate the probability distribution.

MODELING APPROACH OVERVIEW

The framework for the CCW Toxicity TMDL modeling effort is a spreadsheet-based mass balance water quality model. The newly developed model dubbed the Toxicity TMDL Mass Balance Model (TTMBM) represents a preliminary modeling effort to track selected constituents through the CCW. The TTMBM utilizes the flowrate calculations and precipitation data processing of the Dynamic Calleguas Creek Modeling System (DCCMS) developed in support of the Calleguas Creek Salts TMDL (LWA 2004d).

To model the desired constituents in the CCW, the entire watershed is divided into 6 subwatersheds based on the major drainages within the watershed, specifically: Arroyo Simi, Conejo and Calleguas Creeks, Revolon Slough, and Mugu Lagoon. The subwatersheds are displayed in Figure 1. General information about each of the TTMBM subwatersheds including: TMDL Reaches circumscribed by the subwatershed boundaries, listing of publicly owned treatment works (POTW) are encompassed, and general size parameters are listed in Table 3. Each subwatershed is considered a single complete-mix computational element for determining in-stream flow and calculating the water quality due to processes present along stream reaches circumscribed by the sub-watersheds.

Table 3: Toxicity TMDL Mass Balance Model Subwatershed Description.

Subwatershed	TMDL Reaches	POTWs	Area		Perimeter mi.
			acres	sq. mi.	
Arroyo Simi	7, 8	Simi Valley WQCP Moorpark WRP	82,951	129.6	66.5
Las Posas	Upper 6	---	21,570	33.7	31.2
Conejo Creek	9B, 10, 11, 12, 13	Hill Canyon WWTP Olsen Rd. (1)	46,812	73.1	49.5
Calleguas Creek	2, 3, 6, 9A	Camarillo WRP Camrosa WRP	17,239	26.9	35.5
Revolon Slough	4, 5	---	39,466	61.7	47.3
Mugu Lagoon	1	---	11,924	18.6	32.0

(1) Olsen Rd decommissioned in 2002, all flow currently diverted to Hill Canyon.

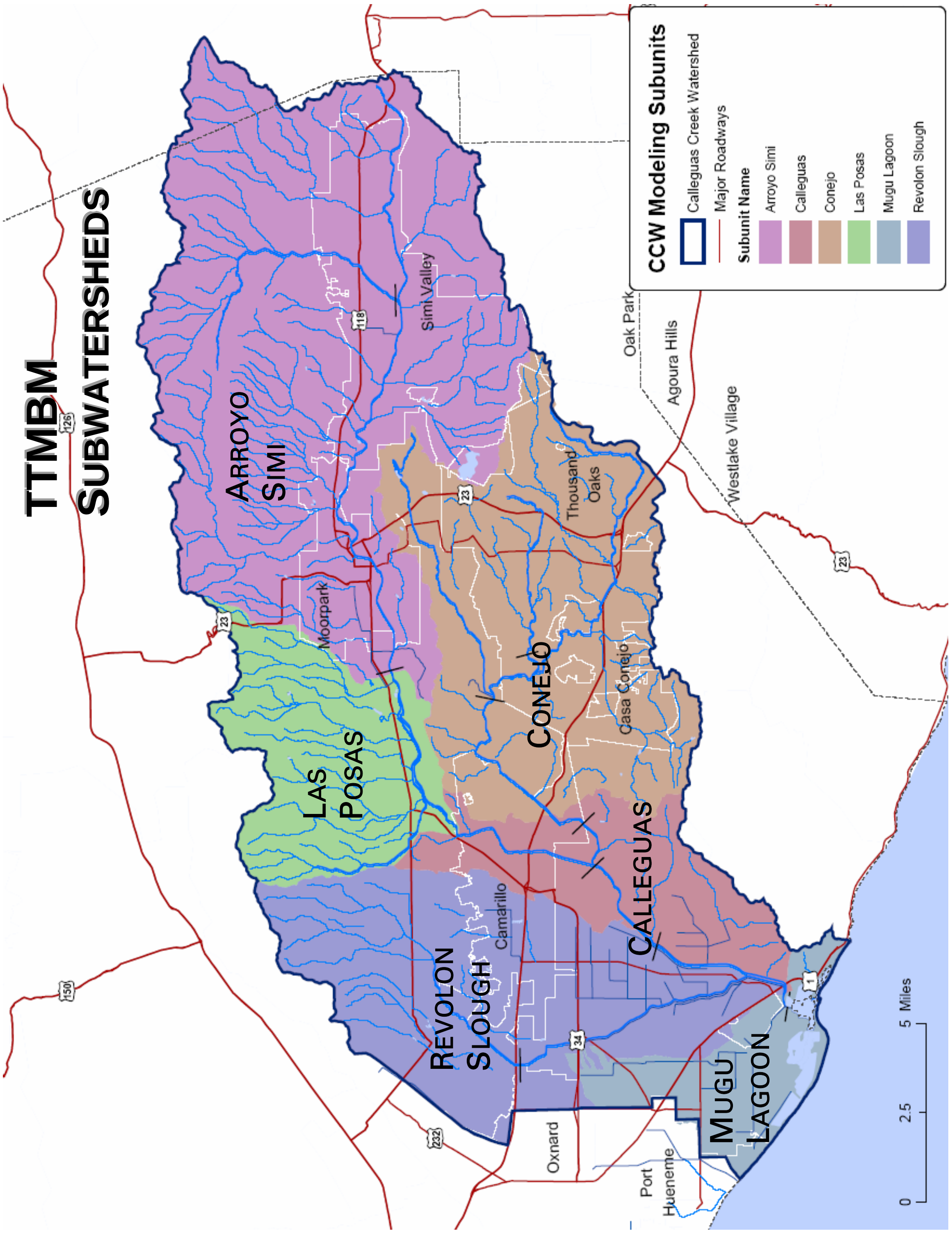

Figure 1: Subwatershed Definition Sketch for the Toxicity TMDL Modeling Effort.

Length scales for the receiving waters in the CCW are listed in Table 4. Manning's equation is used to calculate in-stream depth at any desired flowrate using the depths in Table 4, and the nominal flowrate of the reach. The stream width is assumed to remain constant. Only volatilization is affected by the stream width. By assuming a constant width will underestimate volatilization during high flow events, conservatively overestimating in-stream concentrations.

Table 4: Nominal Receiving Water Characteristic Dimensions.

Subwatershed	Length (ft)	Length (mi)	Width (ft)	Depth (ft)	Surface Area (ft^2)
Arroyo Simi	96,307	18.2	40.0	0.55	3,853,954
Las Posas	29,779	5.6	29.7	0.43	731,296
Conejo Creek	130,258	24.7	17.0	0.67	707,801
Calleguas Creek	50,635	9.6	97.4	2.54	2,350,128
Revolon Slough	88,704	16.8	50.0	0.50	4,435,200
Mugu Lagoon	38,438	7.3	55.5	2.65	880,994

Land-use patterns for each of the TTMBM subwatersheds are listed in Table 5. In the Table, the areas of native (undeveloped), agricultural, and urban land uses are listed in terms of percentages of the subwatershed, percentages of the total land use in the entire CCW, and the actual areas in acres and square miles for each subwatershed. The calculations are based on the Department of Water Resources (DWR) 2000 land use GIS data. Based on the information in Table 5, the Arroyo Simi subwatershed encompasses a total of 82,951 acres (129.6 sq. mi.), and is 72.6% covered by undeveloped native land which is 55.8% of the total native land in the entire CCW. Arroyo Simi and Conejo Creek subwatersheds each contain just under 40% of the total urban area in the watershed. Revolon Slough is covered by over 65% agricultural lands and contains nearly half of all the land in the CCW used for agricultural purposes.

Crop penetration for each TTMBM subwatershed is listed in Table 6. Because the analysis performed for the Interim Source Assessment (LWA 2004a) revealed a large portion of the total chlorpyrifos and diazinon agricultural use is on lemon, strawberry, broccoli, corn, beans, onions and garlic, and lettuce they are explicitly separated from general citrus, nut, truck, field, and grain crops. In the Arroyo Simi Subwatershed, 35.1% of the agricultural land is used for lemon groves, however the Arroyo Simi groves only account for 6.1% of the total lemon grove area in the entire CCW. The Las Posas and Revolon Slough Subwatersheds together account for over 75% of the land used for lemon groves. In the whole CCW, over 50% of the lemon groves, over 50% of the strawberry fields, and over 60% of the broccoli fields are located in the Revolon Slough Subwatershed. Together, lemons, strawberries, and broccoli crops account for over 90% of the agricultural chlorpyrifos use. Application to beans and onions account for 63% of the agricultural diazinon use. Revolon Slough Subwatershed accounts for over 70% of the beans and over 60% of the onion and garlic plantings in the whole watershed.

Table 5: Land Use in each TTMBM Subwatershed.

Subwatershed	Land Use	Percent of Sub-watershed	Percent of Land Use in CCW	Area (1)	
				Acres	Sq. mi.
Arroyo Simi	Native	72.6	55.8	60,243	94.1
	Agriculture	3.6	5.2	2,958	4.6
	Urban	23.8	35.8	19,749	30.9
	Total	100.0	37.7	82,951	129.6
Las Posas	Native	41.8	8.4	9,018	14.1
	Agriculture	54.5	20.6	11,751	18.4
	Urban	3.7	1.5	800	1.3
	Total	100.0	9.8	21,570	33.7
Conejo Creek	Native	47.3	20.5	22,165	34.6
	Agriculture	7.8	6.4	3,657	5.7
	Urban	44.8	38.1	20,990	32.8
	Total	100.0	21.3	46,812	73.1
Calleguas Creek	Native	42.4	6.8	7,315	11.4
	Agriculture	40.2	12.2	6,926	10.8
	Urban	17.4	5.4	2,998	4.7
	Total	100.0	7.8	17,239	26.9
Revolon Slough	Native	12.6	4.6	4,965	7.8
	Agriculture	66.5	46.1	26,260	41.0
	Urban	20.9	14.9	8,240	12.9
	Total	100.0	17.9	39,466	61.7
Mugu Lagoon	Native	35.1	3.9	4,187	6.5
	Agriculture	45.1	9.4	5,374	8.4
	Urban	19.8	4.3	2,363	3.7
	Total	100.0	5.4	11,924	18.6
Whole CCW	Native	49.1	100.0	107,894	168.6
	Agriculture	25.9	100.0	56,926	88.9
	Urban	25.1	100.0	55,141	86.2
	Total	100.0	100.0	219,961	343.7

(1) As per Department of Water Resources, 2000

Table 6: Crop Penetration in each TTMBM Subwatershed.

Subwatershed	Crop[1]	Percent of Ag in Sub-watershed	Percent of Crop in Whole CCW	Area	
				Acres	Sq. mi.
Arroyo Simi	Lemon	35.1	6.1	1,039	1.6
	Strawberry	1.2	0.7	37	0.1
	Broccoli	1.8	7.4	54	0.1
	Corn	0.0	0.0	0	0.0
	Beans	0.0	0.0	0	0.0
	Onion and garlic	5.4	10.4	158	0.2
	Lettuce	0.0	0.0	0	0.0
	Other Citrus and Nuts	35.3	11.0	1,044	1.6
	Other Truck, Field, and Grain	16.4	3.3	486	0.8
	Pasture and Livestock	4.8	19.1	141	0.2
	Vineyard and Turf	0.0	0.0	0	0.0
	Idle	0.0	0.0	0	0.0
Las Posas	Lemon	38.7	26.5	4,543	7.1
	Strawberry	0.2	0.3	19	0.0
	Broccoli	0.6	9.8	71	0.1
	Corn	0.0	0.0	0	0.0
	Beans	0.0	0.0	0	0.0
	Onion and garlic	0.7	5.8	88	0.1
	Lettuce	0.2	2.0	21	0.0
	Other Citrus and Nuts	44.6	55.3	5,239	8.2
	Other Truck, Field, and Grain	10.9	8.6	1,284	2.0
	Pasture and Livestock	3.7	58.5	431	0.7
	Vineyard and Turf	0.0	0.0	0	0.0
	Idle	0.5	45.2	55	0.1

Continued

Table 6 continued

Subwatershed	Crop[(1)]	Percent of Ag in Sub-watershed	Percent of Crop in Whole CCW	Area	
				Acres	Sq. mi.
Conejo	Lemon	33.7	7.2	1,232	1.9
	Strawberry	0.0	0.0	0	0.0
	Broccoli	0.0	0.0	0	0.0
	Corn	1.6	8.9	58	0.1
	Beans	0.0	0.0	0	0.0
	Onion and garlic	0.0	0.0	0	0.0
	Lettuce	2.6	9.2	96	0.1
	Other Citrus and Nuts	18.7	7.2	682	1.1
	Other Truck, Field, and Grain	41.6	10.2	1,521	2.4
	Pasture and Livestock	1.0	4.8	36	0.1
	Vineyard and Turf	0.0	0.0	0	0.0
	Idle	0.9	26.3	32	0.1
Calleguas	Lemon	18.6	7.5	1,292	2.0
	Strawberry	16.1	20.0	1,117	1.7
	Broccoli	2.0	19.4	141	0.2
	Corn	5.7	60.7	395	0.6
	Beans	4.5	9.3	313	0.5
	Onion and garlic	2.9	13.4	204	0.3
	Lettuce	4.2	28.1	292	0.5
	Other Citrus and Nuts	9.2	6.7	639	1.0
	Other Truck, Field, and Grain	35.8	16.7	2,479	3.9
	Pasture and Livestock	0.2	1.7	13	0.0
	Vineyard and Turf	0.6	2.4	41	0.1
	Idle	0.0	0.0	0	0.0

Continued

Table 6 continued

Subwatershed	Crop [1]	Percent of Ag in Sub-watershed	Percent of Crop in Whole CCW	Area	
				Acres	Sq. mi.
Revolon Slough	Lemon	32.7	50.1	8,575	13.4
	Strawberry	11.0	51.8	2,889	4.5
	Broccoli	1.8	63.5	463	0.7
	Corn	0.8	30.3	197	0.3
	Beans	9.2	72.1	2,422	3.8
	Onion and garlic	3.7	63.3	962	1.5
	Lettuce	2.2	55.1	572	0.9
	Other Citrus and Nuts	6.7	18.7	1,769	2.8
	Other Truck, Field, and Grain	29.1	51.4	7,642	11.9
	Pasture and Livestock	0.3	10.2	76	0.1
	Vineyard and Turf	2.5	37.9	658	1.0
	Idle	0.1	28.5	35	0.1
Mugu Lagoon	Lemon	8.0	2.5	432	0.7
	Strawberry	28.1	27.1	1,511	2.4
	Broccoli	0.0	0.0	0	0.0
	Corn	0.0	0.0	0	0.0
	Beans	11.6	18.6	624	1.0
	Onion and garlic	2.0	7.1	108	0.2
	Lettuce	1.1	5.6	58	0.1
	Other Citrus and Nuts	1.9	1.1	100	0.2
	Other Truck, Field, and Grain	27.2	9.8	1,460	2.3
	Pasture and Livestock	0.8	5.7	42	0.1
	Vineyard and Turf	19.3	59.8	1,039	1.6
	Idle	0.0	0.0	0	0.0

(1) As per Department of Water Resources, 2000

WATER SOURCES AND OP PESTICIDE LOADING TO THE WATERSHED

Precipitation, deep aquifer transfers, and imported water are all major sources of water to the watershed.

Precipitation

Areal precipitation values for a subwatershed are calculated by using the percent of subwatershed area listed in to form a weighted average of the precipitation measurements recorded at the local gages. All precipitation information is post-processed from the DCCMS to match the TTMBM subwatersheds.

Table 7: Precipitation Station General Statistics. See Figure 2 for Station Location within the CCW.

Station ID	Start Date	End Date	Average Annual (in) (1)	Max Daily Precip (in)
128	1/21/1943	2/26/2004	15.20	5.74
141	10/18/1948	3/2/2004	14.58	5.54
154	10/11/1947	3/2/2004	14.71	4.88
169	12/5/1956	3/2/2004	16.24	5.52
177	1/5/1957	3/2/2004	12.71	5.02
187	1/27/1956	2/26/2004	33.20	6.05
188	1/21/1956	3/2/2004	14.97	6.58
189	1/21/1956	2/3/2004	16.01	5.14
190	11/14/1955	2/3/2004	15.31	5.02
191	11/14/1955	2/3/2004	17.47	5.25
192	11/14/1955	2/4/2004	14.04	5.07
193	12/4/1980	2/4/2004	29.26	4.9
194	11/14/1955	2/3/2004	12.93	5.27
196	11/6/1977	2/4/2004	20.23	5.1
206	11/4/1960	2/6/2004	17.23	4.31
219	10/28/1964	2/26/2004	14.43	4.2
223	10/13/1946	1/28/2004	12.07	4.77
227	9/19/1966	2/4/2004	28.49	4.75
234	10/4/1968	2/4/2004	30.50	4.7
238	11/5/1970	2/3/2004	20.85	8.7
239	12/4/1972	9/29/2002	16.46	4.98
242	10/25/1971	2/3/2004	43.16	5.61
250	10/20/1976	2/3/2004	19.68	4.76
259	10/1/1981	1/3/2004	14.07	4.46
263	10/17/1984	2/3/2004	11.87	3.77
3	10/21/1902	7/12/1992	13.22	4.6
49	1/16/1929	1/28/2004	13.68	4.7

(1) Average based on annual precipitation for period of record for individual precipitation stations.

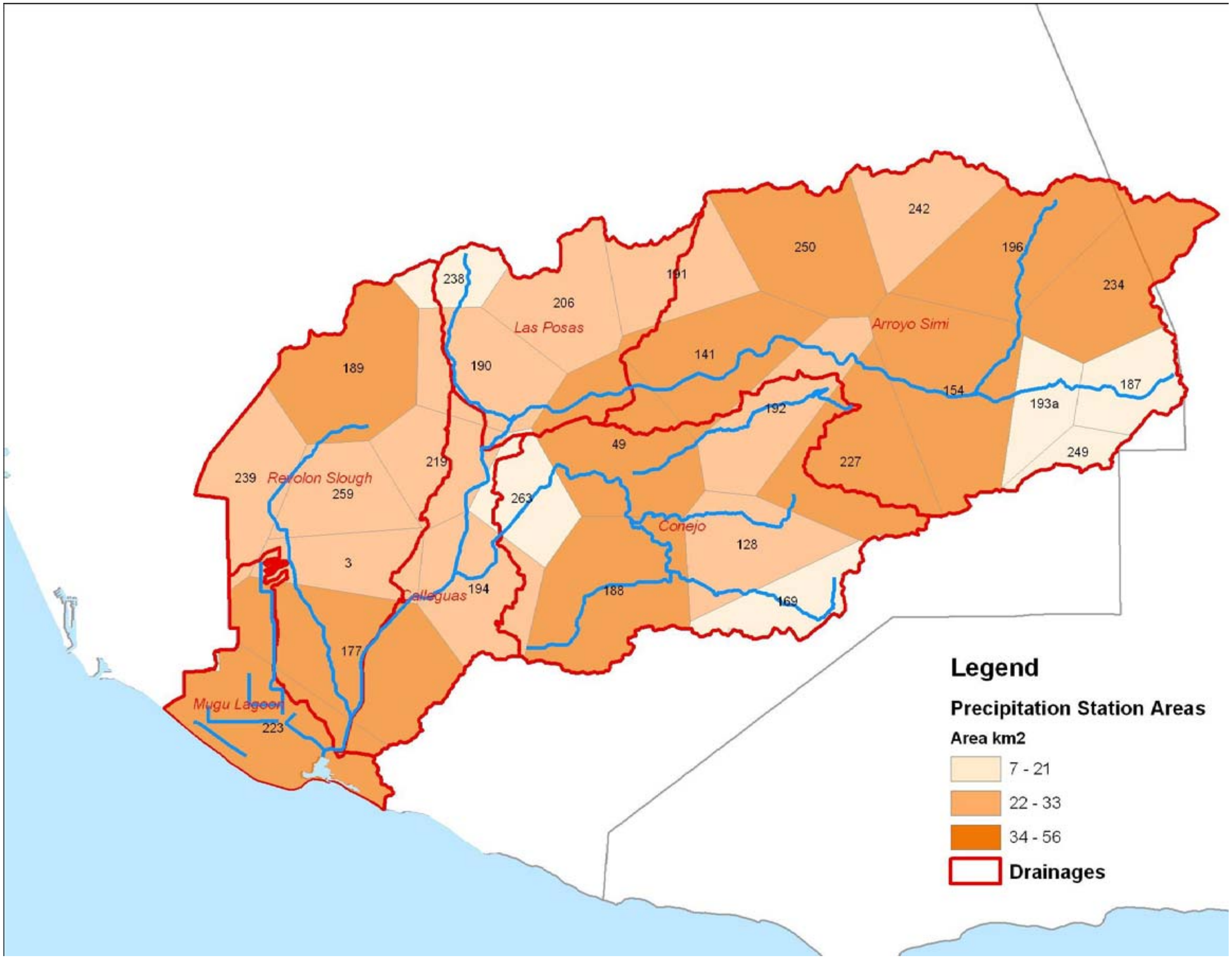

Figure 2: Relation of Precipitation Stations to CCW Toxicity TMDL Mass Balance Model Subwatersheds.

Table 8: Subwatershed Percent Coverage by Precipitation Stations.

Subwatershed	Precipitation Station	Percent of Subwatershed
Arroyo Simi	154	15.61
	187	6.73
	192	2.94
	193a	5.89
	196	12.81
	227	8.25
	234	11.66
	242	8.01
	141	10.63
	191	4.10
	250	11.57
	49	1.71
Las Posas	141	1.22
	190	27.35
	191	15.65
	206	32.29
	219	1.08
	238	9.6
	263	0.4
	49	12.39
Conejo Creek	141	0.50
	192	12.22
	227	10.14
	49	16.41
	128	16.19
	169	9.75
	188	24.75
	194	1.98
	263	7.91

Continued

Table 8: Continued

Subwatershed	Precipitation Station	Percent of Subwatershed
Calleguas	177	32.77
	190	2.27
	194	38.52
	219	14.3
	223	3.15
	263	5.07
	3	3.72 (1)
Revolon Slough	177	15.81
	189	24.92
	190	4.49
	219	8.32
	223	2.47
	238	2.02
	239	15.67
	259	26.29 (1)
	3	
Mugu Lagoon	177	15.57
	223	80.2
	239	1.58
	3	2.76 (1)

(1) Data for Station 3 used prior to 10/1/1990, data for Station 259 used post 10/1/1990.

Precipitation driven flows are calculated in the DCCMS by the rational method (Chow et al., 1988). The fraction of the total subwatershed area comprising the various land use types similar to the list in Table 5 are used to form a weighted average precipitation driven runoff. Runoff from urban, agricultural, and open space land-use areas are calculated separately. Characteristic water quality may be assigned to each land use type to reflect concentrations of constituents in the respective runoff.

Atmospheric Deposition

Wet and dry deposition of OP pesticides are known to be a source of constituents to wet and dry weather runoff. The TTMBM implicitly includes atmospheric deposition in the estimates of OP pesticide loading from wet and dry weather runoff for each land use type. While allowing calculation of receiving water quality, the method will not attribute the true source of constituents. Wet and dry weather monitoring stations should be installed around the CCW in a strategic manner to test the true level of atmospheric deposition contribution to agricultural, urban, and native space runoff.

Direct measurements of pesticide deposition in urban areas have not been measured. Estimates have been determined using ambient concentrations and assumed deposition rates, but the determined rates carry a high degree of uncertainty and may be unrealistic (Ross, 2002).

A study conducted by Dow AgroSciences (1998) at Orestimba Creek around agricultural sites in Stanislaus County, CA involved surface water monitoring for a year. The researchers found that some concentration peaks detected for several OP pesticides could be associated with specific pesticide application events, and that the most probable transport process could be determined. For chlorpyrifos, nine of thirteen attributable concentration peaks were a result of drift from the application site. For diazinon, five of fourteen attributable peaks were a result of drift from the application site (SRWP, 2000).

Majewski and Baston (2002) conducted ambient air quality monitoring for OP pesticides in the Sacramento urban area and nearby agricultural areas during the period 1996-1997. Of 17 pesticides monitored during the study, chlorpyrifos, diazinon, and trifluralin accounted for 24 percent of the agricultural and 76 percent of the non-agricultural/urban pesticides used during the two-year study period. Molinate and thiobencarb offer the clearest example of pesticides used in agriculture that drift into urban areas, because they are used exclusively in rice cultivation, but were measured in the Sacramento urban area (Majewski and Baston, 2002).

The Southern California Coastal Water Research Project (SCCWRP) is beginning a study to determine the impact of atmospheric deposition of pesticides transported from sources within the airshed to waterbodies of interest in selected regions of Southern California. Results from the study will help quantify deposition pesticide deposition rates in urban areas.

There is no clear path to incorporate the finding of the above studies into the CCW to determine the local deposition rate of OP pesticides for modeling purposes. Monitoring of wet and dry deposition rates of OP pesticides would provide the clearest information to incorporate the atmospheric contribution to the runoff water quality.

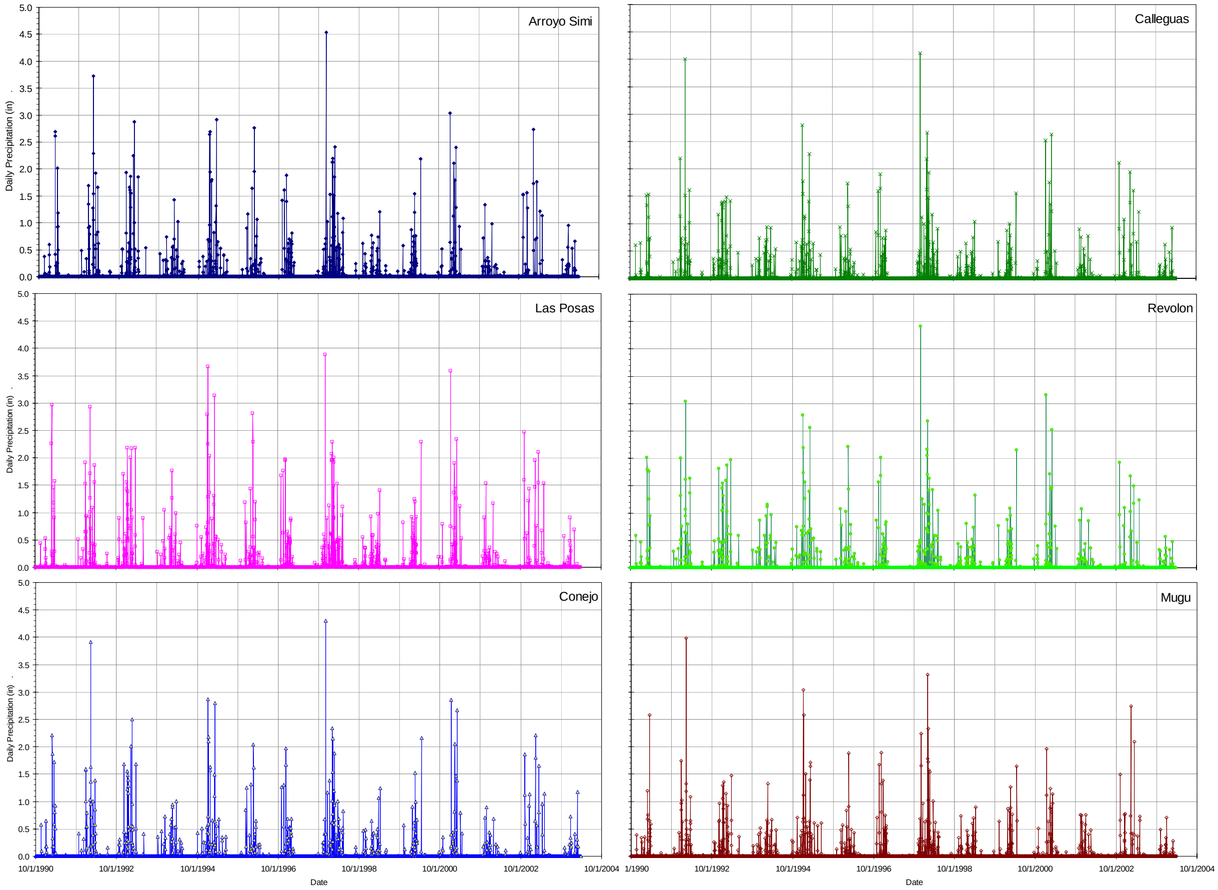

Figure 3: Daily Precipitation Over the TTMBM Subwatersheds from Oct 1, 1990 to March 1, 2004.

Imported Water Supplies

Imported water from the State Water Project and Freeman Diversion are accountable for essentially all the imported water to the CCW. Deep groundwater wells drawing water from the lower confined aquifer underlying the CCW are producing water from the Fox Canyon Aquifer which is replenished with water from outside the watershed. There is no direct linkage between the Imported Water Supplies and the TTMBM.

As there is no evidence to the contrary, it is assumed in the TTMBM development that there is no chlorpyrifos or diazinon in any imported water source.

COMPUTATIONAL ELEMENT

Each computational element balances the inflow and outflow of water and mass with conservation equations to calculate changes in in-stream flow and concentration across a subwatershed. The computational elements used by the TTMBM to model conditions in the CCW are displayed in Figure 1. Over each time step, the stream reach within any subwatershed is assumed to behave as a complete-mix system in equilibrium. Because of the relatively short reach length, stream geometry, and daily time step; flows can be considered in equilibrium on a daily basis, so long as the routing of peak flows is not of critical importance. Assuming that each subwatershed behaves as a complete-mix reactor implies that the in-stream concentration is constant at all locations within a subwatershed (Tchobanoglous and Schroeder, 1985). Because the concentration is modeled as constant for the entire subwatershed, all withdrawals from the reach, including the discharge to the downstream reach will have the same concentration by definition. A schematic of the computational element is displayed in Figure 4. Each input and output considered is represented in Figure 4 with an arrow pointing into the reach for additions, and pointing out from the reach to represent withdrawals. In Figure 4, flows from upstream reaches enter from the right and flow to downstream reaches exit to the left. Details of the flows are discussed in subsequent subsections. Scour and deposition, sorption and desorption, and sediment content are not currently included in the TTMBM, but may be incorporated when paired sediment and water column data are available.

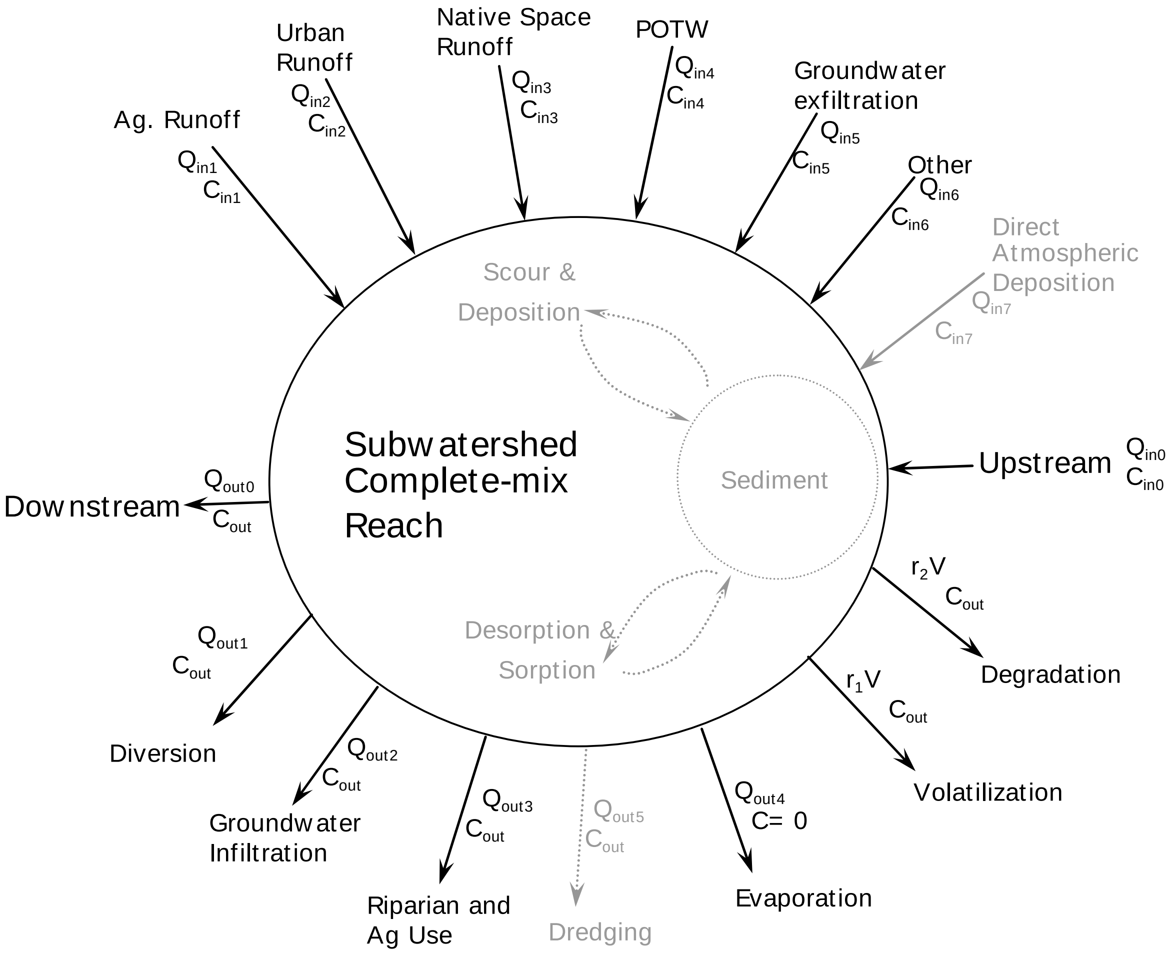

Figure 4: Schematic of Inputs and Outputs for a General Computational Element used in the CCMS Mass Balance Model to Estimate Water Flow and Quality within Surface Water Reaches. Direct Atmospheric Deposition, Sediment Interaction, and Dredging are Not Included in the Current Version of the TTMBM.

Mass Balance Calculations

To calculate the stream discharge flow and in-stream concentration for a computational element, all inflow rates and concentrations must be specified along with all other of the outflow rates. Normally, the outflow to the downstream reach will be calculated with the conservation of flow equation. If all inflow rates and concentrations, and all outflow rates except the downstream discharge rate are known, the in-stream concentration and downstream discharge may be calculated. Because of the complete-mix assumption, the concentration in the outflows will equal the in-stream concentration, except in the case of evaporation (Tchobanoglous and Schroeder, 1985), where only water is assumed to be removed from the system by evaporation implying that the concentration of constituents in evaporated water is equal to zero. The general conservation law is captured in Equation (1).

$$\text{accumulation} = \text{in} - \text{out} + \text{generation} \tag{1}$$

Each of the daily time steps is assumed to be in steady-state. By making the steady-state assumption the ability to model peak flood routing is lost; however because of the relatively small size of the CCW, a smaller time step than one day would be required to capture a flood wave moving through the watershed. The steady assumption specifies no accumulation of flow or mass in the surface water within a subwatershed, simplifying the mass balance equation by setting the left hand side of Equation (1) to zero, in effect requiring the sum of the inputs to equal the sum of the outputs plus and generation within the subwatersheds (Tchobanoglous and Schroeder, 1985), resulting in Equation (2). The mass loading of a constituent may be represented by Equation (3), where $Q_{in}C_{in}$ is the sum total of mass loads to the subwatershed, $Q_{out}C_{out}$ is the sum total of loads leaving the subwatershed, and rV is the generation of constituents within the subwatershed, where r is the reaction rate and V is the in-stream volume of water.

$$\text{in} = \text{out} - \text{generation} \tag{2}$$

$$\sum Q_{in}C_{in} = \sum Q_{out}C_{out} - \sum rV \tag{3}$$

A first order reaction is represented in Equation (3) by replacing the rate, r, with kC_{out}., where k is the first order reaction rate in 1/s and C_{out} is the in-stream concentration within the subwatershed. If k is a negative value, the reaction will represent degradation of the constituent. Volatilization is represented in Equation (3) by replacing rV with $-K_LaC_{out}hA_{surface}$, where K_L is the liquid-film transfer rate (ft/s), a is the ratio of the surface area to the volume (1/ft), h is the nominal stream depth (ft), C_{out} is the in-stream concentration, and $A_{surface}$ is the surface area of the stream within the subwatershed, and the term is negative because constituents are volatilizing from the water surface. The form of the volatilization term is derived assuming a zero atmospheric concentration above and around the stream. For most slightly soluble constituents, the transfer rate K_La is essentially the total mass transfer rate K divided by the depth, h, allowing the volatilization to be represented by $KC_{out}A_{surface}$.

The sum of all inflows (reference Figure 4) is set equal to the sum of all outflows forming the flow balance for each subwatershed and is defined by Equation (4). Flows discharged downstream from the computational element may be calculated using algebra to solve Equation (4) for the flowrate leaving the subwatershed, Q_{out0}., yielding Equation (5).

$$Q_{in0} + Q_{in1} + Q_{in2} + Q_{in3} + Q_{in4} + Q_{in5} + Q_{in6} = Q_{out0} + Q_{out1} + Q_{out2} + Q_{out3} + Q_{out4} \tag{4}$$

$$Q_{out0} = Q_{in0} + Q_{in1} + Q_{in2} + Q_{in3} + Q_{in4} + Q_{in5} + Q_{in6} - Q_{out1} - Q_{out2} - Q_{out3} - Q_{out4} \tag{5}$$

The constituent concentration within the subwatershed may be calculated by inserting the mass loadings indicated in Figure 4 into the conservation of mass equation, Equation (2), while recalling that the concentrations are equal for all outflows, except evaporation which by definition equals zero. The conservation of mass equation for a computational element is given by Equation (6). Rearranging Equation (6) for the outflow concentration yields Equation (7).

$$\begin{aligned} &C_{in0}Q_{in0} + C_{in1}Q_{in1} + C_{in2}Q_{in2} + C_{in3}Q_{in3} + C_{in4}Q_{in4} + C_{in5}Q_{in5} + C_{in6}Q_{in6} \\ &= C_{out}Q_{out0} + C_{out}Q_{out1} + C_{out}Q_{out2} + C_{out}Q_{out3} + (0)Q_{out4} - kVC_{out} - KA_{surface}C_{out} \end{aligned} \tag{6}$$

$$C_{out} = \frac{C_{in0}Q_{in0} + C_{in1}Q_{in1} + C_{in2}Q_{in2} + C_{in3}Q_{in3} + C_{in4}Q_{in4} + C_{in5}Q_{in5} + C_{in6}Q_{in6}}{Q_{out0} + Q_{out1} + Q_{out2} + Q_{out3} - kV - KA_{surface}} \tag{7}$$

In general, the derived equations listed above will hold for each of the subwatersheds in the CCW, but not all flows will be present for each reach and if not present would be set to zero. Derivations of the individual flows are presented in the following sections.

The in-stream volume and surface area required for the degradation and volatilization calculations are determined from the information in Table 4 and adjusted to different flowrates via Manning's Equation.

Upstream Subwatersheds

Inflow and mass loading from the upstream subwatershed are added as inputs to the computational element. If the sub-watershed is located at the top of a stream's drainage, there will be no upstream subwatershed and the TTMBM will assign a 0.0 for the flow and mass loading. If multiple upstream subwatersheds contribute to the computational element, the sum of the upstream outflows and sum of the mass loadings are inserted in Q_{in0} and $C_{in0}Q_{in0}$. A definition sketch of the case where multiple upstream reaches contribute to the computational element is displayed in Figure 5. The inflow to the computational element is a simple sum of the flowrates from the upstream reaches, as indicated in Equation (8).

$$Q_{in0} = Q_{out0\,A} + Q_{out0\,B} \tag{8}$$

The inflow of mass and concentration of the inflow are calculated in Equation (9), which may be rearranged into Equation (10) for calculating the concentration in the inflow.

$$C_{in0}Q_{in0} = C_A Q_{out0\,A} + C_B\, Q_{out0\,B} \tag{9}$$

$$C_{in0} = \frac{C_A Q_{out0\,A} + C_B\, Q_{out0\,B}}{Q_{in0}} \tag{10}$$

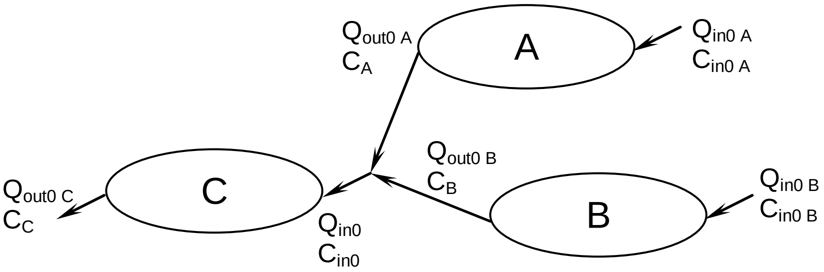

Figure 5: Schematic of Case where Two Upstream Subwatersheds, A and B, Contribute to the Inflow of a Computational Element, C.

Subwatershed Inflows of Constituents

Possible inflows include: agriculture returns, urban runoff, native (open space) runoff, publicly owned treatment works (POTWs), groundwater exfiltration, and any other flows. Each computational element includes provisions to include a generation component, which would be necessary if the constituents were being generated chemio-physio-biologically in the reach. The generation component is set to zero as no reactions producing OP Pesticides are assumed to occur in the CCW surface waters, i.e. no degradation products are tracked.

Agriculture Returns to Computational Elements

Agricultural runoff flowrate is calculated via the rational method within the DCCMS. Dry weather runoff is calculated using an average flow per unit area of agriculture land. Wet weather runoff is calculated similarly to the dry-weather agricultural runoff, except the precipitation over the subwatershed is multiplied by a runoff coefficient and fraction of agricultural land use to determine the runoff flowrate. Provisions are included in the DCCMS model to mimic tailing of runoff following precipitation events. For the CCW, only large rain events will cause appreciable, increased in-stream flow for more than one day. Flow duration curves for agricultural return and runoff flowrates calculated from DCCMS output are plotted in Figure 6. In general, Revolon Slough Subwatershed produces the greatest amount of agricultural runoff, followed by the Las Posas Subwatershed. Both watersheds contain significant agricultural activities as is evidenced in the land use Table 5. The 86th percentile level is called out on Figure 6 as an estimate of the maximum non-stormwater agricultural runoff flows. The Revolon Slough subwatershed contains the bulk of the agricultural runoff data.

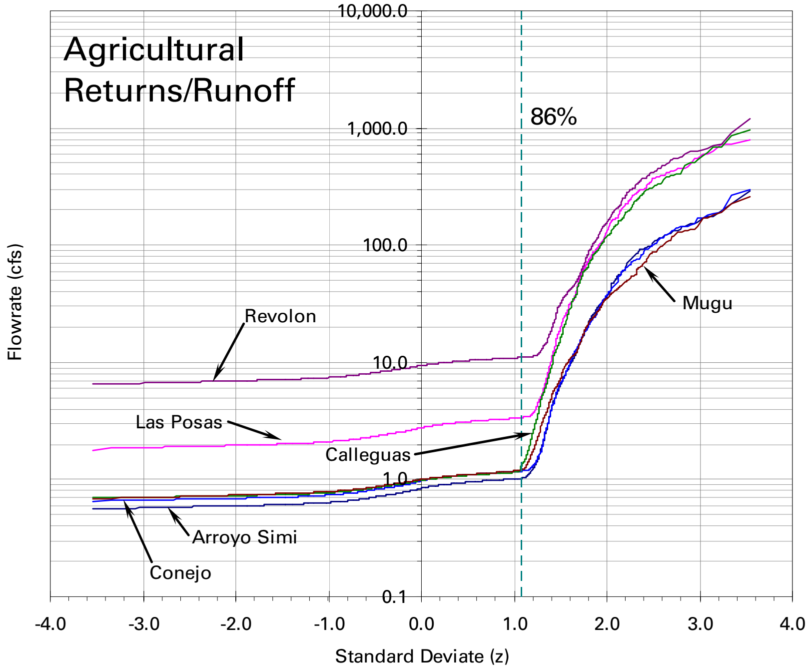

Figure 6: Flow Duration Curves of Agricultural Returns and Runoff for the TTMBM Subwatersheds.

Data from all agricultural runoff sites across the entire CCW are aggregated to determine characteristic concentrations of OP pesticides in the return flows. Regression on order statistics (ROS), used throughout the TTMBM development, utilizes the non-detected data in an analysis to estimate the distribution of the concentrations. The concentration log-normal probability distributions for chlorpyrifos and diazinon are plotted in Figure 7. Superimposed on the Figure are the 95th probability level, and the probabilities associated with the in-stream water quality criteria. The probability distribution functions (PDFs) corresponding to the distribution lines are included in the plots. The PDFs illustrate how plotting by the standard deviate allows a straight line to correspond to a “bell curve” shaped normal distribution.

Assuming that any individual sample is representative of agricultural runoff from any given location in the CCW, the concentration measurements may be paired with the DCCMS calculated agricultural runoff flows. Specifically, the calculated agricultural runoff flowrate for the entire Revolon Slough Subwatershed is used to calculate the load from agricultural runoff to Revolon Slough. Ideally, the specific land use, area drained, and actual flowrate corresponding to the sample times and locations would be used to scale-up the sampling information to reflect loadings of similar areas in the subwatersheds. Furthermore, it would be best to have sufficient sampling to cover the range of crop types and farming practices. However, the required detail and numbers of sampling do not exist at the current time and a complete analysis is not possible. The greatest error would potentially occur using the selected methodology if each sample represented drainage from a different crop type. The method utilized here would not be in great error if each sampling location drained a representative mix of crops and agricultural practices.

Using the Revolon Slough Subwatershed-wide agricultural runoff flowrate to calculate the load and to act as the abscissa, Figure 8 is a plot of the OP pesticide loading from agricultural areas. In an analysis inspired by Stow and Borsuk (2003), a power curve was used as a regression for the data. A power relationship describes the increase in loading for increasing runoff flowrate, because concentrations increase as flowrates increase. For instance, if concentration doubled with doubling flowrate, the load would increase by a factor of 4, or a 2.0 power relationship. Chlorpyrifos load is seen in Figure 8 to increase with slightly greater than a 1.3 power of flowrate indicating concentrations in agricultural runoff increase with increasing runoff flowrate. Diazinon loading increases with essentially a 1.0 power reflecting diazinon concentrations remaining relatively constant with increasing runoff flowrate, so that increasing runoff load is solely a function of the increasing flowrate.

The relationships defining the agricultural runoff load of constituents as a function of runoff flowrate displayed in Figure 8 are the input parameters to the TTMBM. Given the agricultural runoff flowrate in cfs, Equations (11) and (12) are used in the TTMBM to determine the agricultural runoff chlorpyrifos and diazinon loads in lb/d, respectively.

$$\mathrm{Load}_{\mathrm{ag\,runoff}}^{\mathrm{chlorpyrifos}} = 0.00231 \cdot \mathrm{Q}_{\mathrm{ag\,runoff}}^{1.310} \tag{11}$$

$$\mathrm{Load}_{\mathrm{ag\,runoff}}^{\mathrm{diazinon}} = 0.00127 \cdot \mathrm{Q}_{\mathrm{ag\,runoff}}^{1.052} \tag{12}$$

Both Equations (11) and (12) correspond to the upper 90th percentile prediction interval of the regression. Because the acute conditions are the important conditions to model, the upper prediction interval is used in the TTMBM to estimate peak loads and concentrations of OP pesticides in the CCW. Appendix A is a summary of TTMBM results using the regression equations instead of the prediction interval to determine the average loads and concentrations found in the CCW.

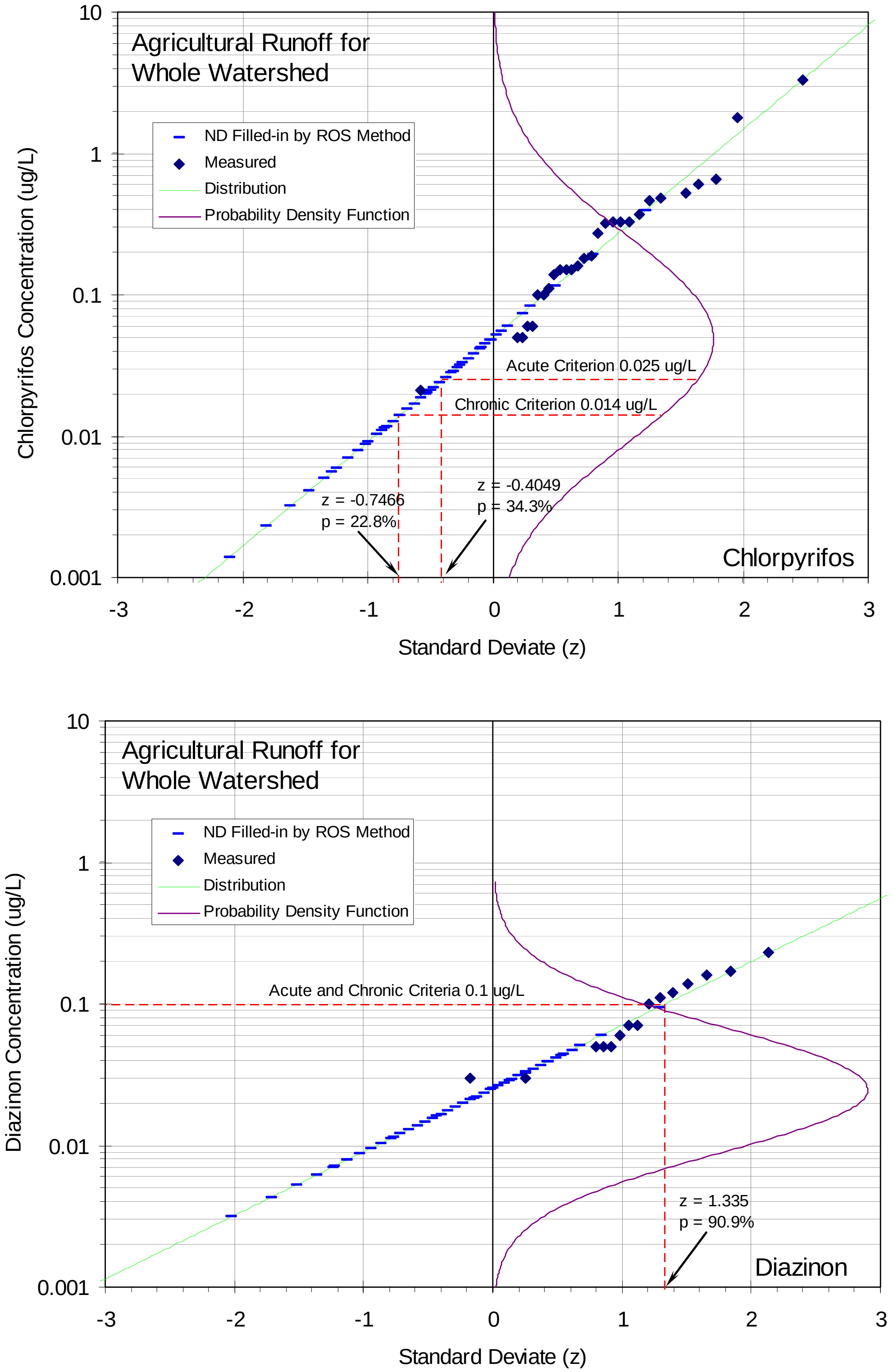

Figure 7: Agricultural Runoff Chlorpyrifos and Diazinon Concentration Log-Normal Probability Distributions.

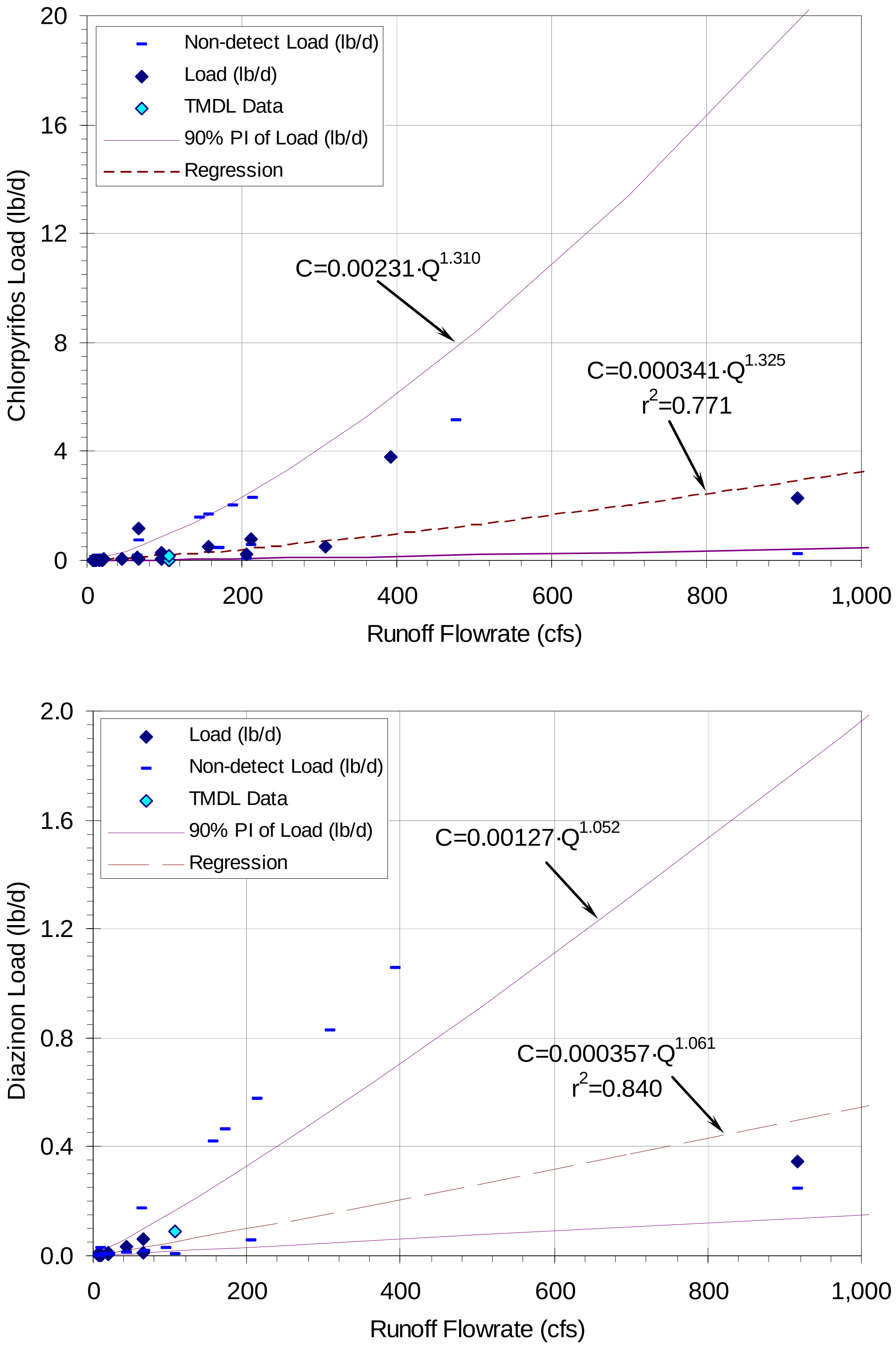

Figure 8: OP Pesticide Load as a Function of Agricultural Runoff Flowrate.

Urban Runoff to Computational Elements

To the extent possible, urban runoff has been analyzed akin to the agricultural runoff. Many of the details discussed above apply to the urban runoff, but have not been repeated in the interest of brevity.

Urban runoff is calculated as a mix of runoff from residential, commercial, and industrial land uses. Urban runoff flowrate is calculated via the rational method within the DCCMS. Dry weather runoff is calculated using an average flow per urban area. Wet weather runoff is calculated similarly to the dry-weather urban runoff, except the precipitation over the subwatershed multiplied by a runoff coefficient is used to determine the runoff flowrate and provisions are included in the model to mimic tailing of the runoff. The flow duration curves of daily urban runoff in the CCW for the period 10/1/1990 to 3/1/2004 are plotted in Figure 9. The Arroyo Simi and Conejo Subwatersheds produce the greatest amount of urban runoff as they contain significant urbanized areas as reported in Table 5. The 86th percentile flows are called out on Figure 9 as an estimate of the maximum non-stormwater urban runoff flows.

OP pesticide data for urban runoff were collected at selected characterization sites, while all sites are located in Ventura County, not all sites are located in the CCW. The underlying assumption is that the selected characterization sites are representative of all urban sites in the CCW. Probability plots of available chlorpyrifos and diazinon data are presented in Figure 10. Only 5 of 47 chlorpyrifos data were detected, so a distribution plot could not be calculated. The probability plot of diazinon reveals the concentrations in urban runoff exceed receiving water quality objectives approximately 30% of the time.

The loading of chlorpyrifos and diazinon given an urban runoff flowrate is presented in Figure 11. Equations (13) and (14), given an urban runoff flowrate in cfs, a urban runoff load is calculated in lb/d for chlorpyrifos and diazinon, respectively.

$$\mathrm{Load}_{\text{urban runoff}}^{\text{chlorpyrifos}} = 0.0224 \cdot \mathit{ln}\left(\mathrm{Q}_{\text{urban runoff}}\right)^{2.230} \tag{13}$$

$$\mathrm{Load}_{\text{urban runoff}}^{\text{diazinon}} = 0.00811 \cdot \mathit{ln}\left(\mathrm{Q}_{\text{urban runoff}}\right)^{2.667} \tag{14}$$

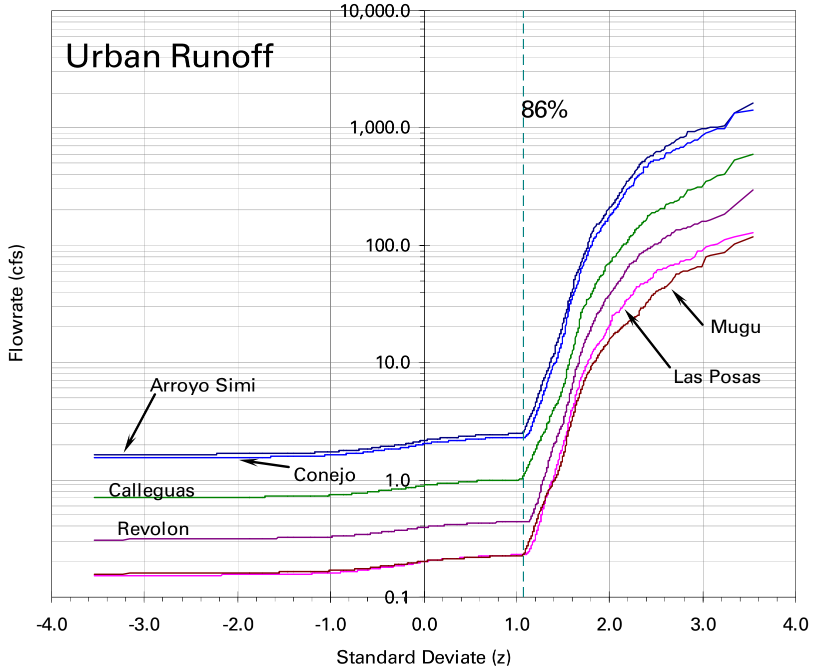

Figure 9: Urban Runoff Flowrate Distributions by TTMBM Subwatershed.

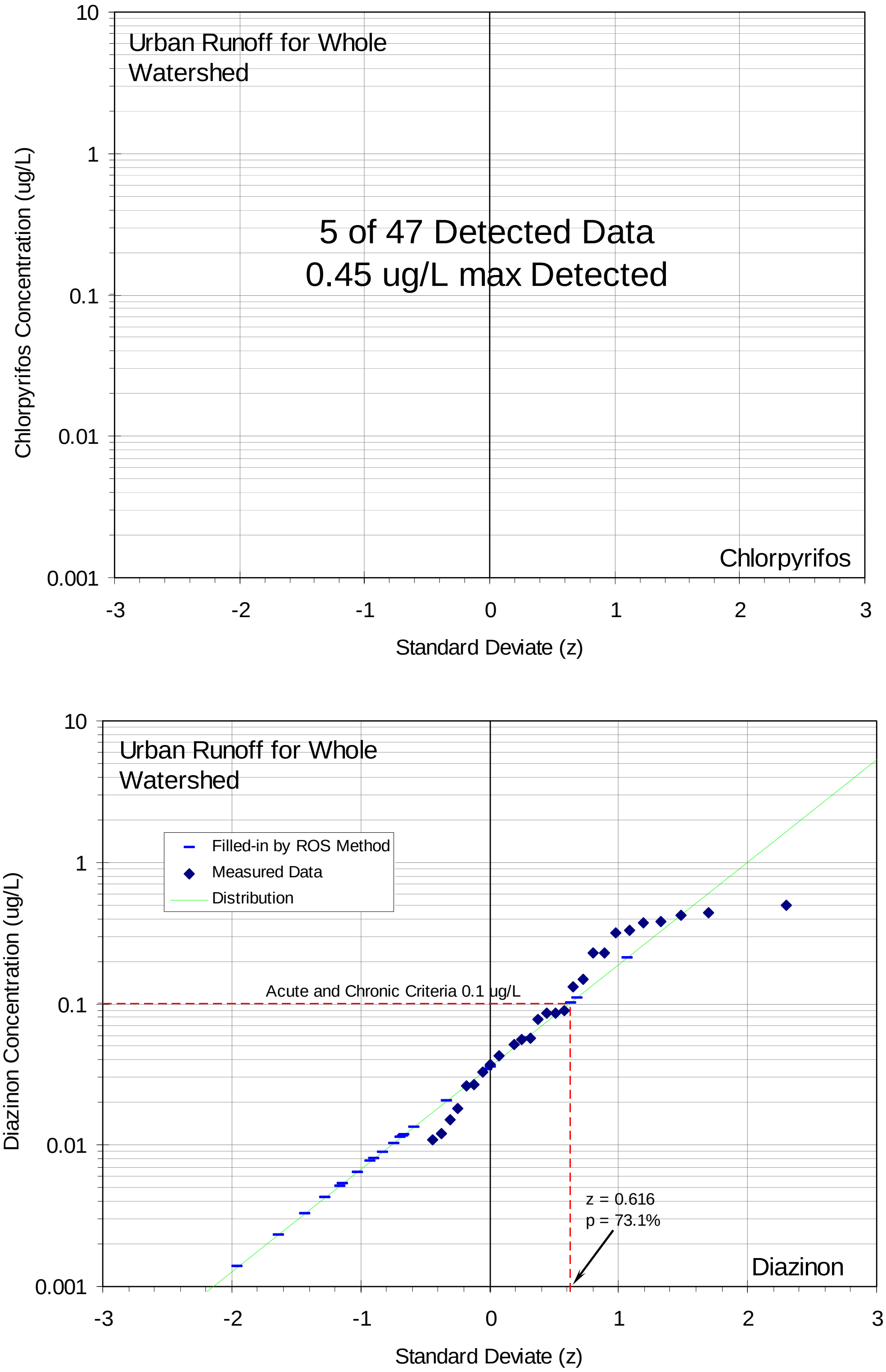

Figure 10: Distributions of Chlorpyrifos and Diazinon Concentrations Sampled from Urban Runoff. Data from all Urban Characterization Sites Combined. ND Filled-in Values Represent the Calculated Estimate of the Non-Detected Values via the ROS Method and Do Not Correspond to Physical Measurements.

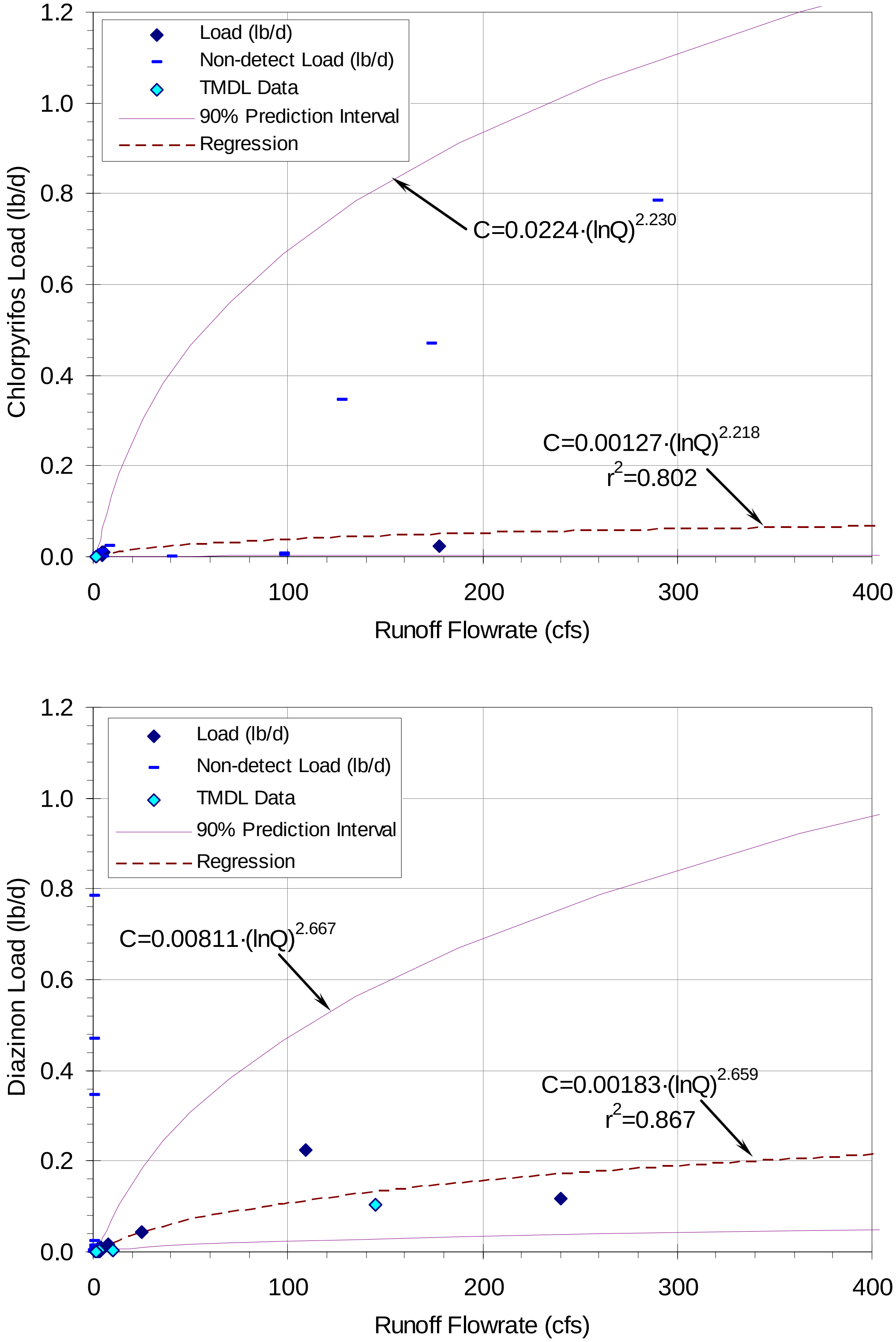

Figure 11: Chlorpyrifos and Diazinon Load Estimated for Urban Runoff.

Native (Open Space) Runoff to Computational Elements

The runoff from native areas of vacant, undeveloped, open space is calculated in a manner similar to urban runoff. Wet-weather runoff flows are calculated similarly to the urban runoff. No information is currently available describing the native runoff OP pesticide concentration or loads in the CCW. The loading of OP pesticides to the receiving waters would provide an indication of drift, and wet and dry deposition. To date, there are no data quantifying pesticides in runoff from natural space in the CCW.

The DCCMS calculated flowrates for native flowrates are presented in Figure 12. Arroyo Simi and Conejo Subwatersheds yield the greatest native runoff, as would be expected as the two subwatersheds contain the majority of native area in the CCW. Currently, the load of chlorpyrifos and diazinon are set to zero in native space runoff.

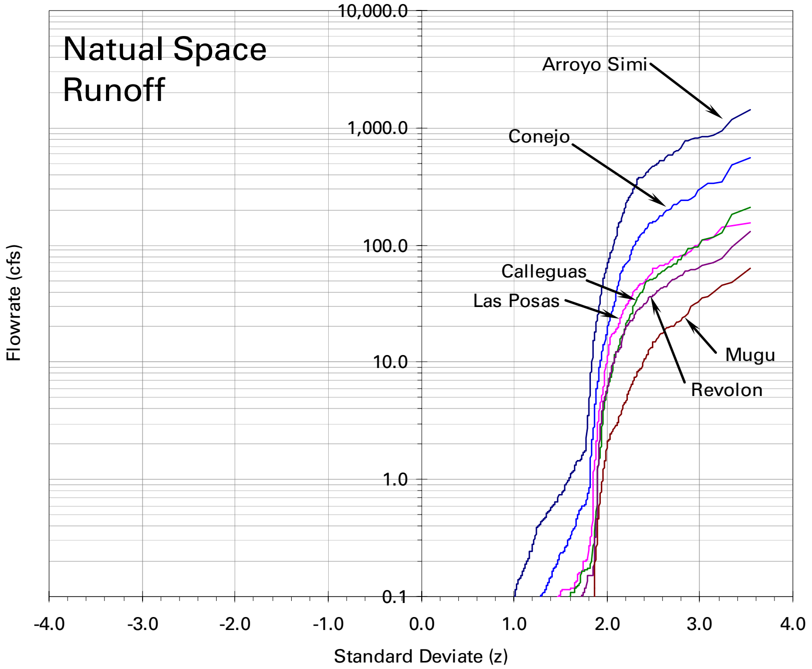

Figure 12: Flow Duration Curves for Native Runoff Flowrates.

POTW Inflows to Computational Elements

Only the subwatersheds containing wastewater treatment plants that discharge to surface waters will have non-zero Q_{in4} and C_{in4}. The flow duration curves of the DCCMS calculated POTW effluent flowrates are plotted in Figure 13.

For the DCCMS, effluent monitoring data from the treatment plants are used to develop statistical descriptions of the effluent flowrate. On review and analysis of flow data from the Simi Valley, Hill Canyon, and Camarillo POTWs there was an observed pattern of monthly variations in flowrates. Because the variations in flowrate could not be conclusively linked to external variables, separate distributions for flowrates from each POTW were calculated from the available data for each month of the year. Flowrates from POTWs are generally higher after precipitation. Insufficient data from the Moorpark POTW precluded performing a similar analysis for that treatment plant. The details of the analysis are included in the DCCMS documentation.

All available data for OP pesticides in POTW effluent are listed in Table 9. A maximum of four samples are available for each treatment plant. The combined chlorpyrifos and diazinon data are plotted in Figure 14.

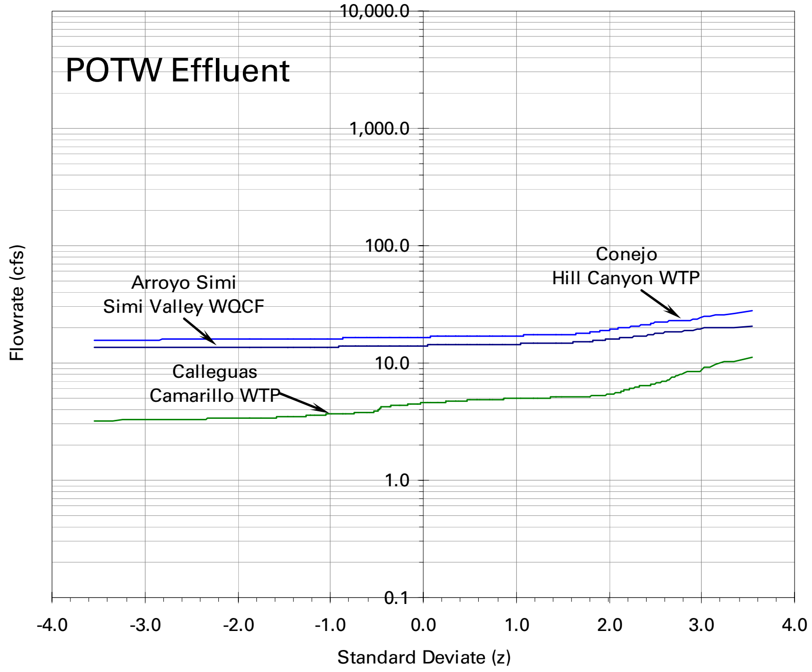

Figure 13: Flow Duration Curves for the POTWs in the CCW.

Because so few data exist characterizing each POTW effluent, the concentrations of chlorpyrifos and diazinon are set in the TTMBM to the chronic water quality criteria of 0.014 µg/L, and 0.1 µg/L, respectively. The values used in the TTMBM are listed in Table 10 as an order of magnitude guide for POTW contribution. While a constant concentration is used for each POTW, the DCCMS calculated effluent flowrates are used to determine the loading for chlorpyrifos and diazinon to the surface waters in the CCW.

Table 9: Chlorpyrifos and Diazinon Detected Values for POTW Discharge in the CCW.

	Chlorpyrifos			Diazinon		
POTW	n	Detected	Detected Values μg/L	n	Detected	Detected Values μg/L
Simi Valley	4	0%	---	4	75%	0.025 0.025 0.14
Moorpark	2	0%	---	3	67%	0.11 0.17
Olsen Rd. (1)	4	25%	0.03	4	0%	---
Hill Canyon	4	0%	---	4	50%	0.09 0.25
Camarillo	4	0%	---	4	0%	---
Camrosa	0	---	---	0	---	---

(1) Olsen Rd decommissioned in 2002, all flow currently diverted to Hill Canyon.

Table 10: Chlorpyrifos and Diazinon Nominal Loadings for POTW Discharges in the CCW.

	Chlorpyrifos			Diazinon		
POTW	Flowrate (cfs)	Conc. (μg/L)	Load (lb/d)	Flowrate (cfs)	Conc. (μg/L)	Load (lb/d)
Simi Valley	14.1	0.014	0.00106	14.1	0.1	0.0076
Moorpark (1)	2	0.014	0.00015	2	0.1	0.0011
Olsen Rd. (2)	0	---	---	0	---	---
Hill Canyon	16.7	0.014	0.00126	16.7	0.1	0.0090
Camarillo	4.6	0.014	0.00035	4.6	0.1	0.0025
Camrosa (3)	0	---	---	0	---	---

(1) In general, Moorpark does not discharge to surface waters of the United States and is not included in the TTMBM.

(2) Olsen Rd decommissioned in 2002, and is not included in the TTMBM.

(3) In general, Camrosa does not discharge to surface waters of the United States and is not included in the TTMBM.

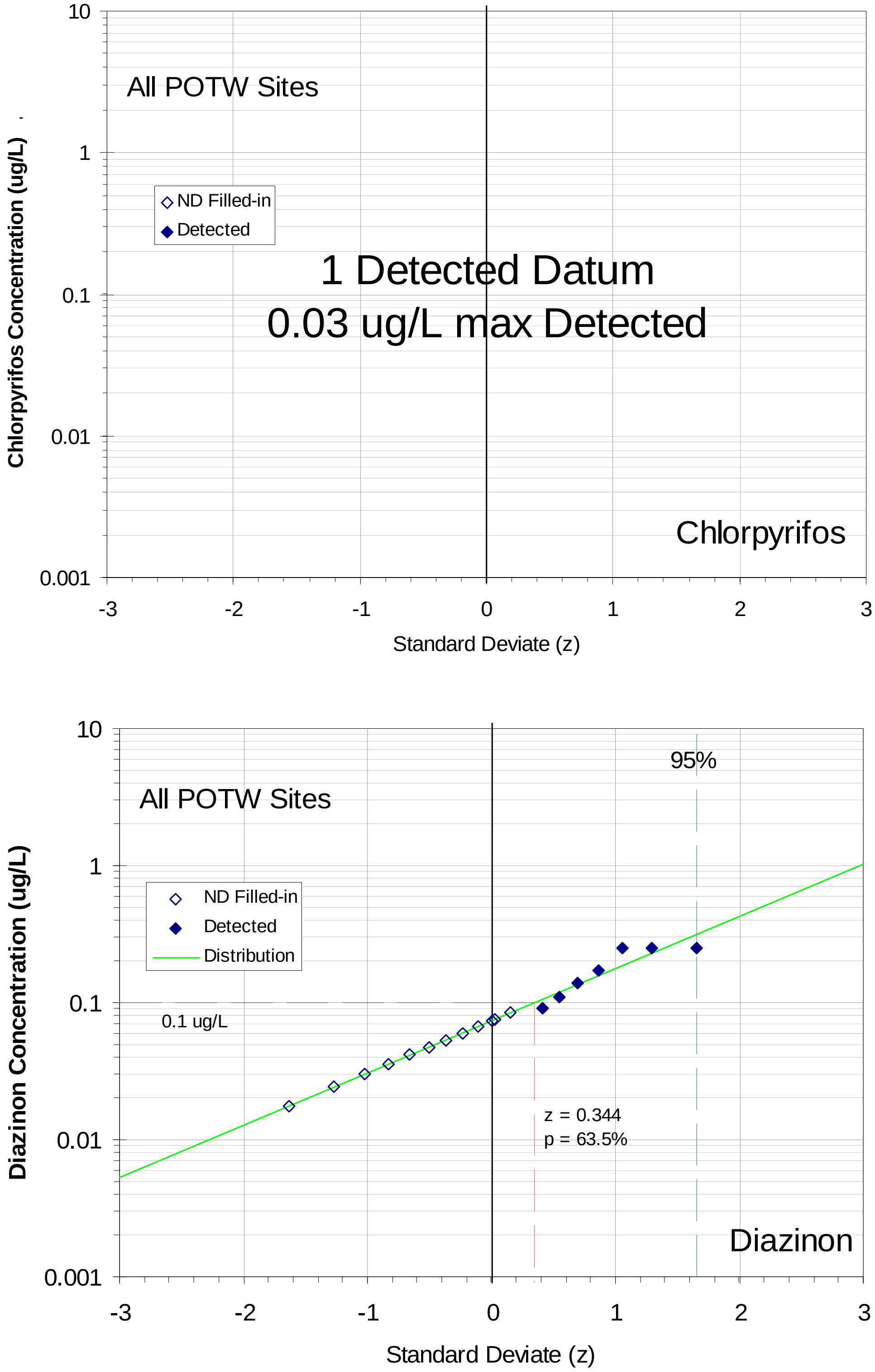

Figure 14: Distributions of Chlorpyrifos and Diazinon Concentrations Sampled from POTW Treated Effluent. Data from all CCW POTWs Combined. ND Filled-in Values Represent the Calculated Estimate of the Non-Detected Values via the ROS Method and Do Not Correspond to Physical Measurements.

Groundwater Inputs to Computational Elements

Groundwater exfiltration and groundwater dewatering discharges are included under the general heading of groundwater inputs to computational elements. Currently, the only dewatering wells included in the model are located in the Simi Valley area of the watershed. The groundwater flows in the Simi Valley are largely due to continuous pumping to lower the groundwater table. From a modeling perspective, the dewatering well discharges affect the CCW system in an equivalent manner to the natural exfiltration of groundwater providing baseflow to the stream.

Analysis of available data revealed that dry-season groundwater exfiltration rates are related to the previous wet-season total precipitation. A relationship between annual precipitation and groundwater exfiltration has been developed for the Upper Arroyo Simi, Conejo Creek, and Calleguas Creek sections of the CCW (LWA 2004d). For dates between April 1st and September 30th for a given water year, the cumulative precipitation for the water year is used to calculate groundwater exfiltration using the developed relationships. For dates between October 1st and March 31st, a weighted average between the total precipitation in the previous water year and the cumulative precipitation for the current water year are used in the calculations. Flow duration curves for groundwater exfiltration are presented as Figure 15.

Groundwater well water quality data were reviewed to develop updated estimates of exfiltration water quality. Dewatering well discharge water quality measurements have not revealed chlorpyrifos or diazinon in the Arroyo Simi groundwater. There is little information available on OP pesticide concentrations in the groundwater in other areas of the CCW. Average groundwater concentrations were input into the TTMBM on a trial and error basis to increase dry-weather in-stream loadings to match measured values. Estimated groundwater concentrations are 0.001 µg/L of chlorpyrifos and 0.002 µg/L of diazinon. For the current model, it is assumed that there are no OP pesticides present in the groundwater baseflow contribution to the surface water streams. Groundwater exfiltration as implemented in the TTMBM will serve to dilute the receiving water concentrations of OP pesticides.

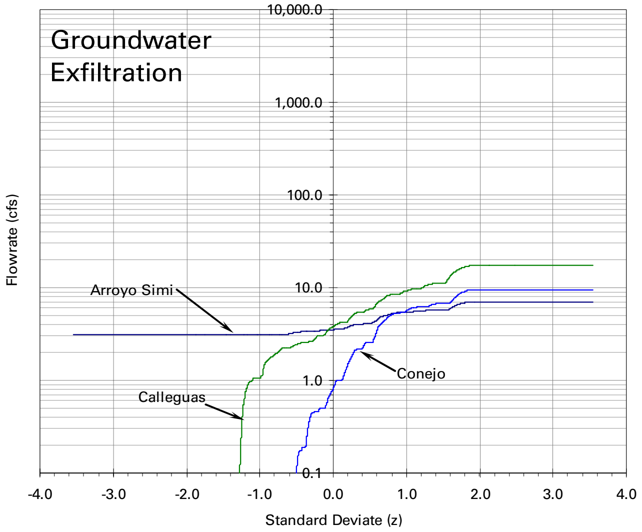

Figure 15: Flow Duration Curves of Groundwater Exfiltration by TTMBM Subwatershed.

Other Inflows to Computational Elements

Other processes possibly included in the future will account for management practices and diversions resulting from the implementation of control strategies. Other inflows are reserved for the implementation of potential control strategies. In the Conejo Subwatershed, State Import Water will be used to replenish the North and South Forks of the Arroyo Conejo once the Hill Canyon WTP effluent is removed from the stream as part of the salts implementation plan. The replenishment flows would be added to the TTMBM under the other flows catagory. State Import Water is assumed to contain no OP pesticides.

In-stream Generation within Computational Elements

No in-stream processes are included that generate chlorpyrifos or diazinon. Currently, TTMBM does not include desorption for sediment, so no phase transfer is included in the model. Degradation products are not tracked in the TTMBM, so no other species are generated. The description of the degradation and volatilization reactions is included in the In-stream Degradation Section.

Subwatershed Outflows

Possible withdrawals or outflows from the CCW reaches include groundwater infiltration and diversions, agricultural use, and evaporation. First order degradation (combination of microbial and hydrolysis reactions) and volatilization from the surface waters are included in the TTMBM for both chlorpyrifos and diazinon. Because of the complete-mix assumption, the concentration in each of the outflows is equal to the concentration calculated in the reach that is discharged to downstream subwatersheds.

Groundwater Infiltration from Computational Elements

The groundwater infiltration rate for the Northern CCW is 1.1 cfs/reach mile, and in the Conejo Creek region the rate is 0.3 cfs/reach mile. To ensure the Arroyo Las Posas goes dry during dry-weather, the rate of infiltration may be increased in the Las Posas Subwatershed up to five times the nominal value. The infiltration rate is checked internally by the DCCMS to ensure negative flowrates are not produced if the streambed becomes dry. Infiltration removes a load of the constituents from the stream. The groundwater infiltration flows are plotted in Figure 16.

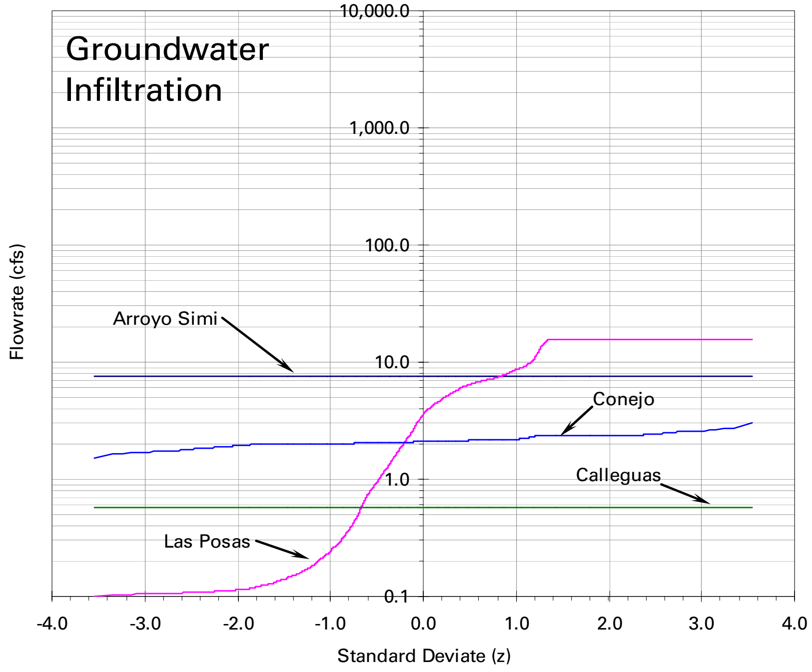

Figure 16: Flow Duration Curves of Groundwater Infiltration for the CCW.

Riparian Vegetation Demand from Computational Elements

Natural stream draw-down for riparian habitat support and agricultural withdrawals are accounted for in the Riparian Vegetation Demand. In the DCCMS calculations, the rate of riparian vegetation consumption is modified by the ratio of the daily evaporation to the annual average evaporation, as in Equation (15).

$$\text{Riparian ET} = \text{Riparian ET}_{\text{steady}} \frac{\text{daily evap (in/d)}}{0.164\text{ (in/d)}} \qquad (15)$$

The calculated lost flow is checked against the available flow to ensure that a negative flowrate for the subwatershed does not result from including the riparian consumptive loss. All riparian use flows are plotted in Figure 17. Water is drawn from the streams to satisfy the evapotranspiration demand of riparian vegetation. Because the water is drawn from the stream before evaporating, constituents are carried from the stream to the root-zone. Constituents may accumulate in the root zone and would be subject to leaching back into the stream with baseflow, however, the back leaching is not currently included in the model. Once the Conejo Creek Diversion began operation, there was a significant drop of water available for stream-side use, as is evidenced by the off-scale jump the Conejo flows take for the percentage of time the diversion has been in operation.

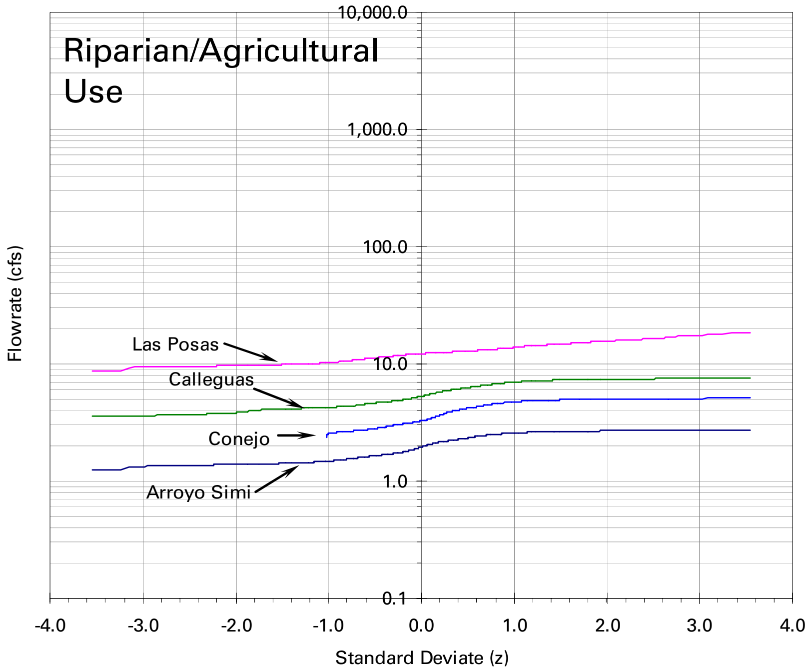

Figure 17: Flow Duration Curves for Riparian and Agricultural Use.

Evaporation from Computational Elements

Daily evapotranspiration values for coastal and inland areas of the CCW were developed in LWA 2004c. The variability within each month of the year of available daily evaporation is used to perturb the daily evaporation values calculated in LWA 2004c. Regression of historic evaporation against daily maximum temperatures in Camarillo or Oxnard would provide a mechanism for forming a daily estimate based on daily watershed conditions rather than rely on a constant value.

Evaporation from the reaches is calculated from the evaporation rate data multiplied by the estimated water surface area, and so is strictly the evaporative loss from the stream surface. The calculated lost flow from evaporation is checked against the available flow in the subwatershed to ensure that a negative flowrate does not result from including the evaporation loss.

Mugu Lagoon, Revolon Slough, and Calleguas Subwatersheds are calculated using the coastal areas evaporation rates in Figure 18. Evaporation from surface waters in Conejo, Las Posas, and Arroyo Simi Subwatershed is calculated using the interior valley information in Figure 18. The evaporative rates for the CCW are plotted in Figure 19.

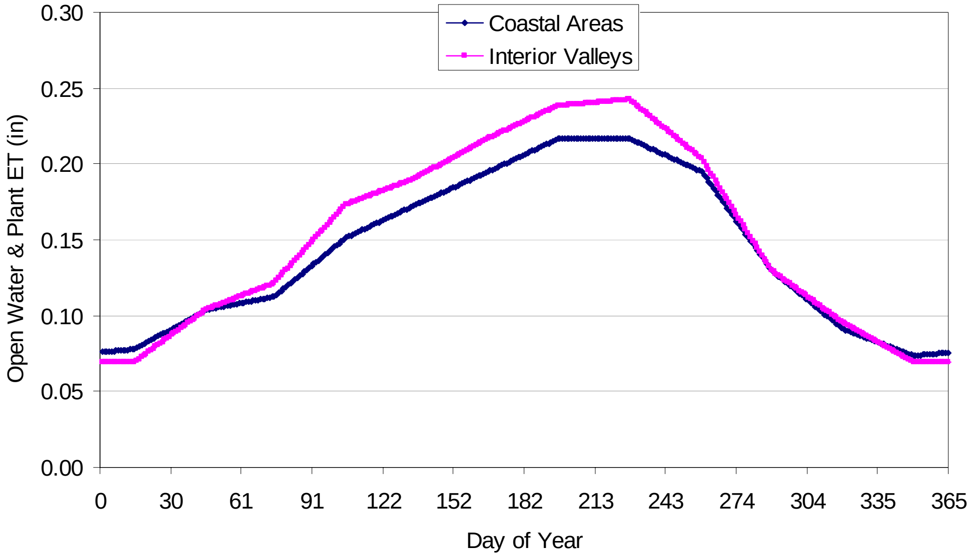

Figure 18: Base evapotranspiration from coastal and inland areas of the CCW.

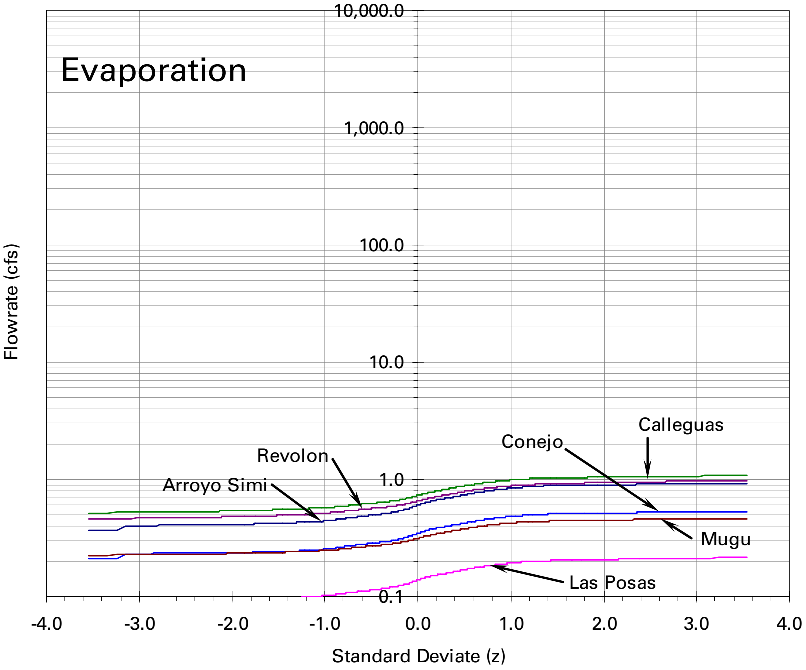

Figure 19: Flow Duration Curves for Evaporation from Receiving Waters in the CCW.

In-stream Consumption within Computational Elements

First order degradation rates are included in each of the constituent mass balances to account for microbial degradation and hydrolysis. Volatilization is included in each mass balance. The rates are small in comparison to the hydrologic movement through the watershed, so the degradation and volatilization do not greatly affect loadings in receiving waters.

Downstream Subwatersheds

The calculated outflow and mass load are used as input to the next most downstream computational element. As above, the reach discharge to downstream subwatersheds and outflow concentrations are calculated by Equations (16), and (17), respectively:

$$Q_{out0} = Q_{in0} + Q_{in1} + Q_{in2} + Q_{in3} + Q_{in4} + Q_{in5} + Q_{in6} - Q_{out1} - Q_{out2} - Q_{out3} \tag{16}$$

$$C = \frac{C_{in0}Q_{in0} + C_{in1}Q_{in1} + C_{in2}Q_{in2} + C_{in3}Q_{in3} + C_{in4}Q_{in4} + C_{in5}Q_{in5} + C_{in6}Q_{in6}}{Q_{out0} + Q_{out1} + Q_{out2} - kV - KA_{surface}} \tag{17}$$

TTMBM VALIDATION

The loads to the receiving waters in the CCW are calibrated above using available data and information. For validation, the TTMBM model output for calculated in-stream loads and concentrations are compared to measured in-stream values. The flowrate range of 0-25 cfs highlights typical dry-weather conditions, whereas the flowrates greater than approximately 25 cfs reveal wet-weather behavior. Additionally, the different scales give two views on the scatter and data availability. Unfortunately, there are subwatersheds where insufficient in-stream data exist to make strong judgments of the TTMBM behavior.

In each of the loading plots, the available data are represented by solid diamond shapes. For samples collected with no detected chlorpyrifos or diazinon, the detection level is used with the receiving water flow to estimate a corresponding non-detected load. The only meaning attributable to the non-detect load is that the actual receiving water load would be some value less than the value plotted. The TTMBM calculated loads are plotted as open squares, and the agricultural contribution to the load are plotted as plus symbols. The difference between the total and agricultural contribution is the total urban contribution which is composed of urban runoff and POTW flows. The TTMBM calculated concentrations are compared to the measured in-stream concentrations for each subwatershed.

Inspection of the following plots reveals that the measured in-stream concentrations of chlorpyrifos and diazinon can vary by more than two orders of magnitude for any given set of runoff conditions. By using the 90th percentile prediction interval to estimate loading to the receiving waters, the TTMBM is designed to estimate the high end of concentrations for any given flow condition. Calculated concentrations of chlorpyrifos and diazinon for each of the TTMBM subwatersheds are presented in Figure 20. The available measured concentrations are superimposed on the plots.

Appendix A contains Figures similar to the validation presented below for the conditions of using the regression functions for estimating the discharge chlorpyrifos and diazinon loads. Using the regression is essentially utilizing the 50th percentile prediction interval.

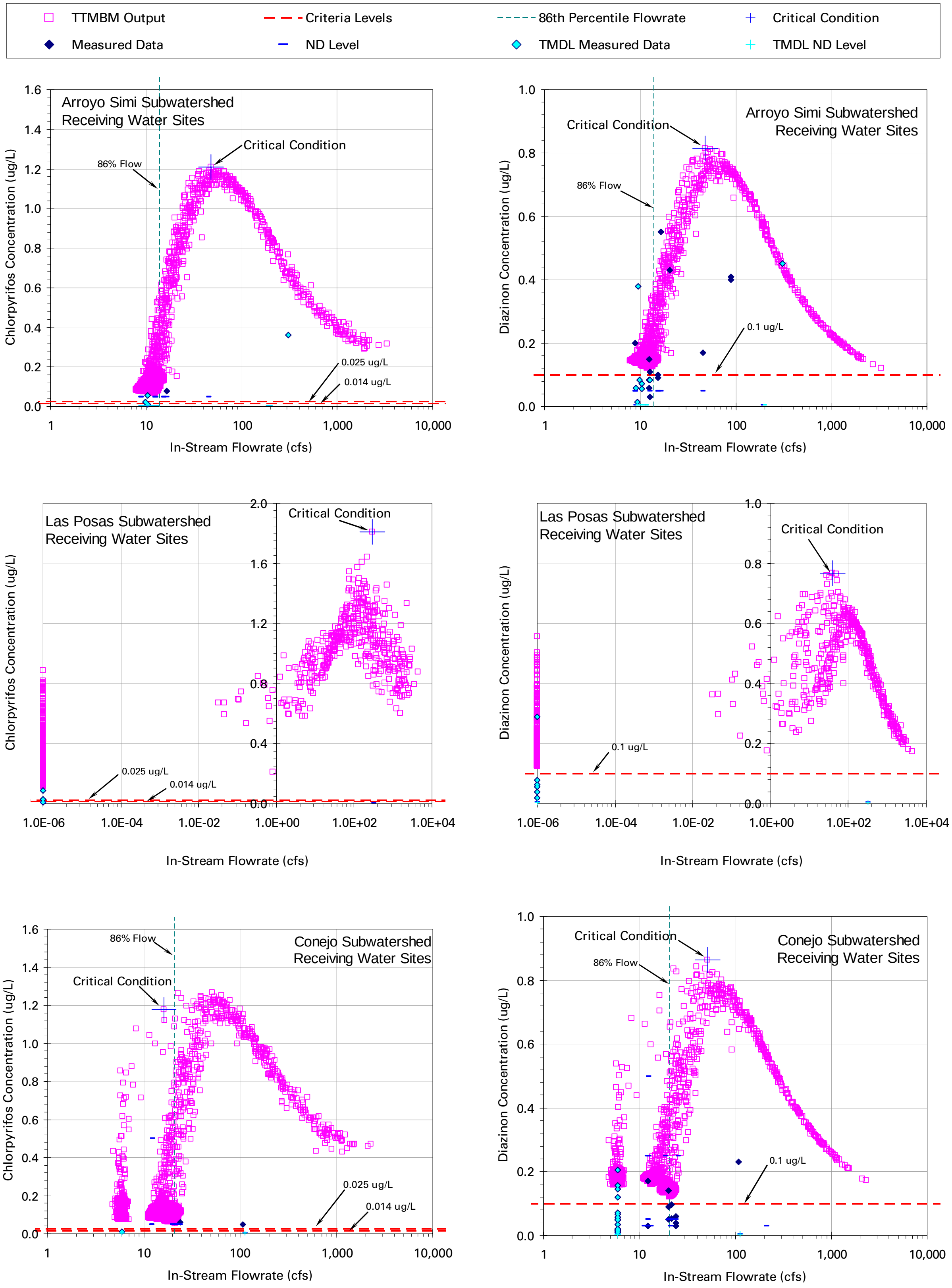

Figure 20 Continued

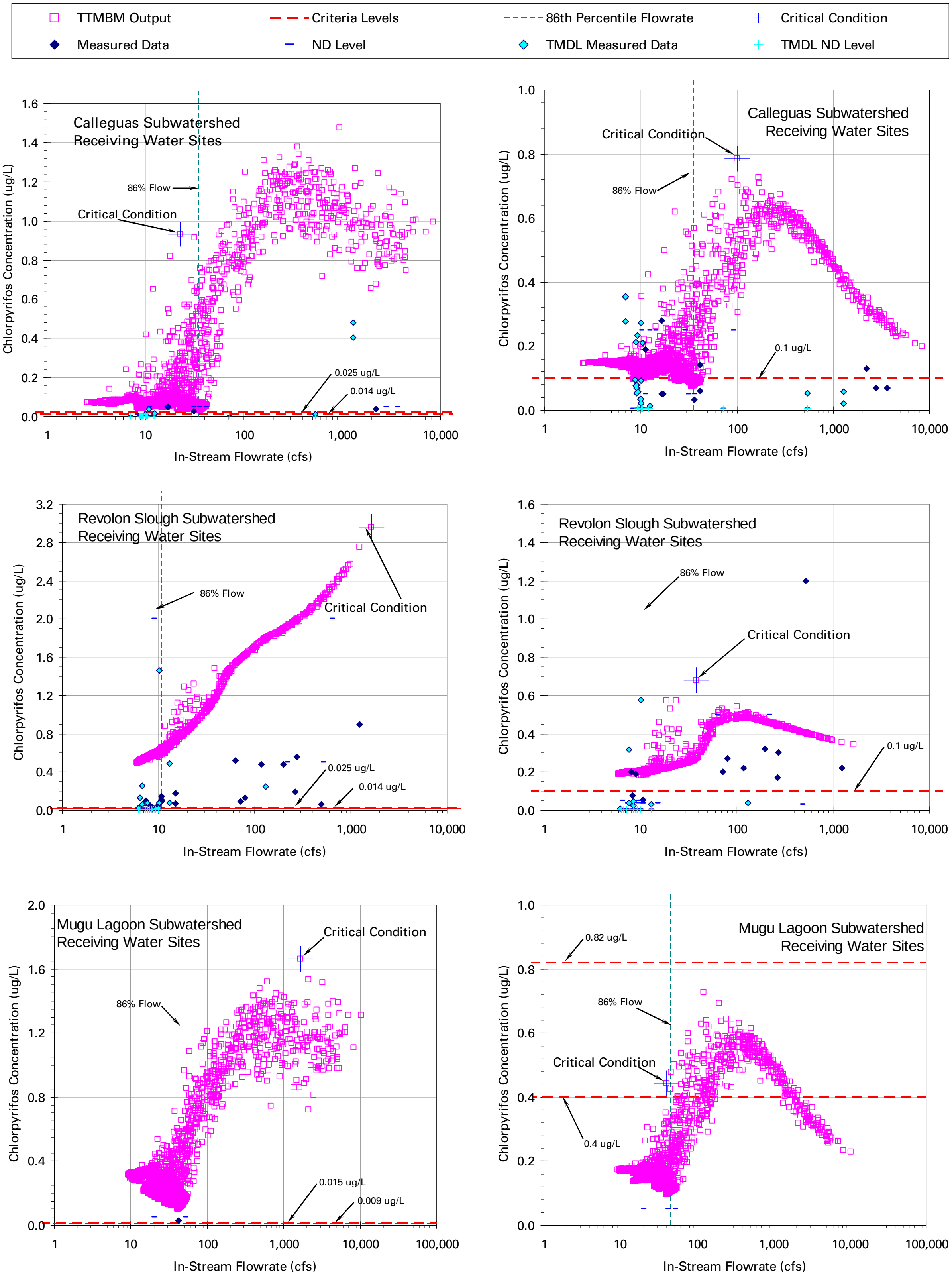

Figure 20: Measured Receiving Water Chlorpyrifos and Diazinon Concentrations Compared to TTMBM Output. Note not all Figures Plotted o the Same Scale.

Arroyo Simi Subwatershed

The pesticide loads are plotted in Figure 21. The comparison between the TTMBM calculated and measured concentrations is plotted as Figure 22. TTMBM output over-predicts the measured chlorpyrifos. Diazinon calculations from the TTMBM match the observed data fairly well. There are no Arroyo Simi receiving water chlorpyrifos or diazinon samples for higher flow wet weather events, so a comparison is not possible. The TTMBM Runoff Model calculates relatively constant concentrations of chlorpyrifos and diazinon, in the Arroyo Simi Subwatershed with slightly elevated values during wet-weather events.

Las Posas Subwatershed

The pesticide loads are plotted in Figure 23. The comparison between the TTMBM calculated and measured concentrations is plotted as Figure 24. The available receiving water data in the Las Posas Subwatershed is more limited than for the Arroyo Simi Subwatershed. A meaningful comparison of model performance to measured values is not possible.

Conejo Subwatershed

The pesticide loads are plotted in Figure 25. The comparison between the TTMBM calculated and measured concentrations is plotted as Figure 26. The TTMBM in general over-predicts chlorpyrifos loading and diazinon. There are no available measurements for higher flow events. There are too few chlorpyrifos data for a meaningful comparison to TTMBM performance for wet or dry weather conditions. Concentration comparisons for diazinon are fair, however available data only represent dry-weather, so a wet-weather comparison is not possible.

Calleguas Subwatershed

The pesticide loads are plotted in Figure 27. The comparison between the TTMBM calculated and measured concentrations is plotted as Figure 28. As with the Conejo Subwatershed TTMBM output over-predicts chlorpyrifos and diazinon loads. Wet-weather chlorpyrifos loads are significantly over-predicted. Wet-weather diazinon loads are slightly over-estimated but match the data well. Chlorpyrifos and diazinon concentrations match well, but there are some measured diazinon concentrations significantly higher than the TTMBM.

Revolon Subwatershed

The pesticide loads are plotted in Figure 29. The comparison between the TTMBM calculated and measured concentrations is plotted as Figure 30. Chlorpyrifos and diazinon dry-weather loads match the trends of measured loads well. There are significant scatter in the measured data that are not reflected in the TTMBM model calculations. Wet weather chlorpyrifos loads match quite well to the trend of the measured data. Chlorpyrifos loads are significantly over estimated. Diazinon loads are over-estimated by the TTMBM for wet-weather flows. Chlorpyrifos concentrations in general match well, but diazinon concentrations are estimated as relatively constant, where the measured concentrations are quite variable.

Mugu Lagoon Subwatershed

The pesticide loads are plotted in Figure 31. The comparison between the TTMBM calculated and measured concentrations is plotted as Figure 32. There are too few chlorpyrifos and diazinon values in the Mugu Lagoon Subwatershed for a meaningful comparison of TTMBM output to measured values. Concentration comparisons are similar to other subwatersheds.

Load Apportionment by Subwatershed

To facilitate scenario development, the in-stream load of chlorpyrifos and diazinon are apportioned to POTW, agricultural runoff, and urban runoff as a function of in-stream flowrate for each subwatershed in Figure 33 to Figure 38. In each subwatershed except Revolon Slough, POTW effluent is the major source of both chlorpyrifos and diazinon to the receiving waters for low in-stream flowrates typical of dry weather. As in-stream flowrates increase, agricultural runoff becomes the dominant source of chlorpyrifos and urban runoff becomes the dominant source of diazinon to the receiving waters. In the Revolon Slough Subwatershed, agricultural runoff is the dominant source of both chlorpyrifos and diazinon at all flows according to TTMBM calculations.

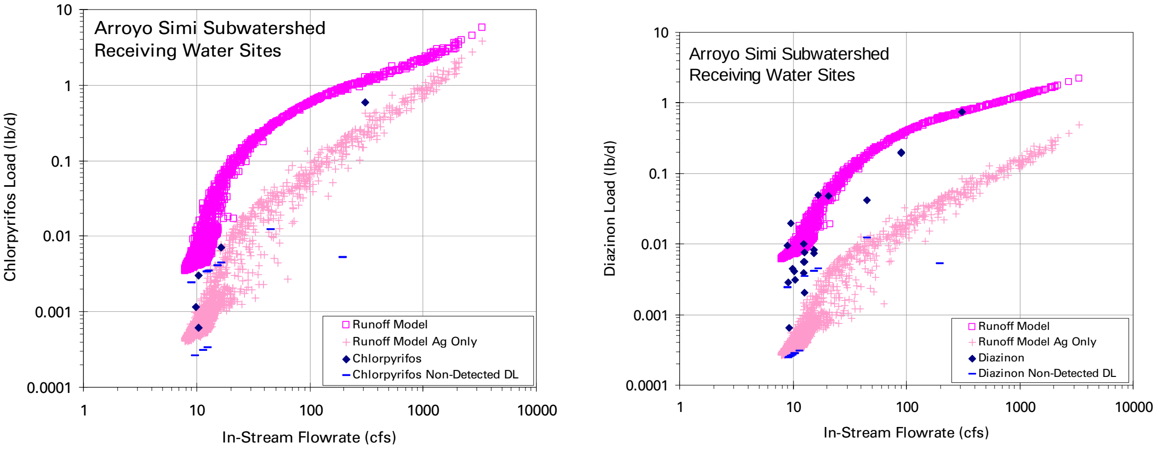

Figure 21: Chlorpyrifos and Diazinon Load in the Arroyo Simi Subwatershed.

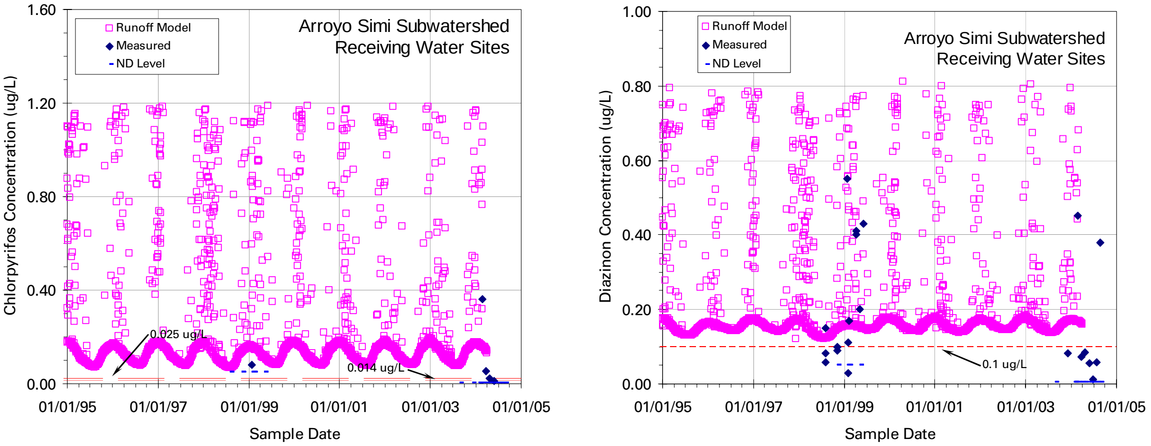

Figure 22: Chlorpyrifos and Diazinon Concentrations in the Arroyo Simi Subwatershed.

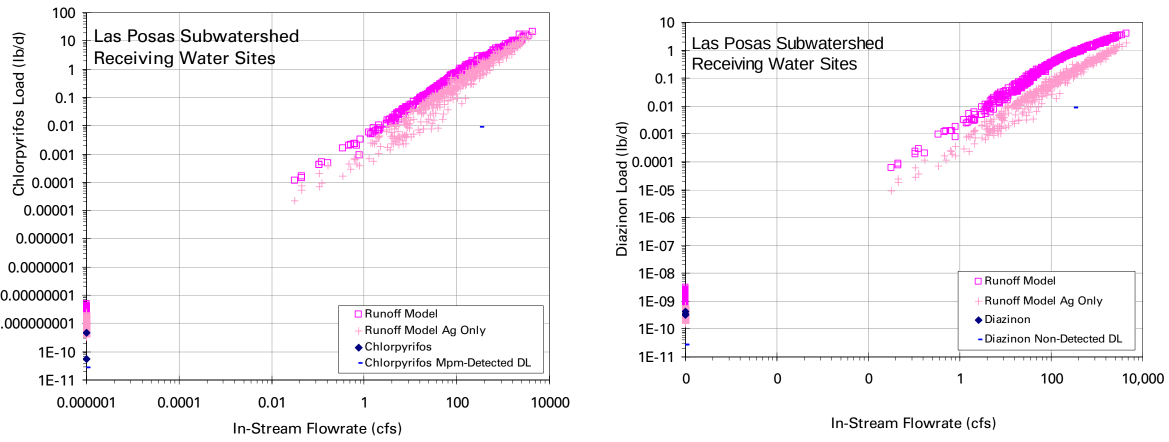

Figure 23: Chlorpyrifos and Diazinon Load in the Las Posas Subwatershed.

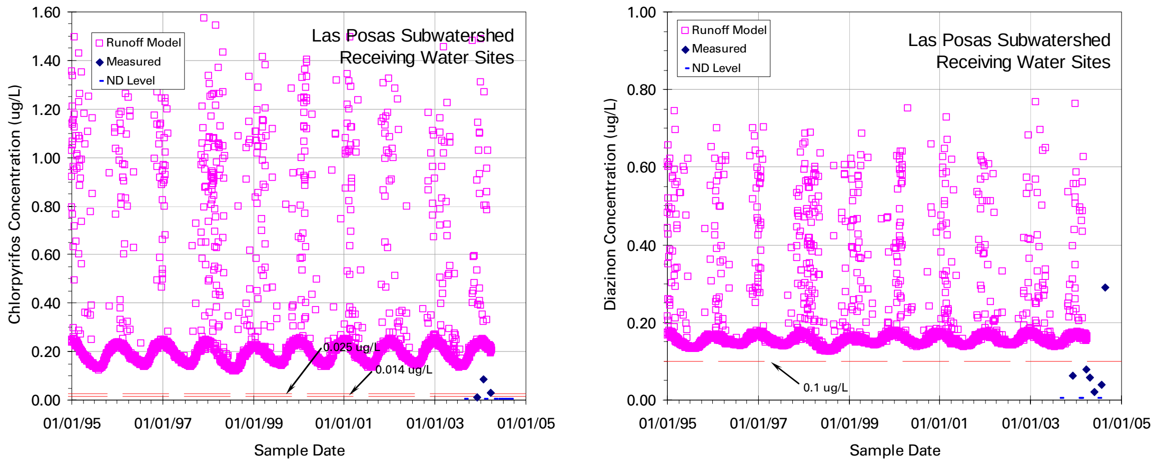

Figure 24: Chlorpyrifos and Diazinon Concentrations in the Las Posas Subwatershed.

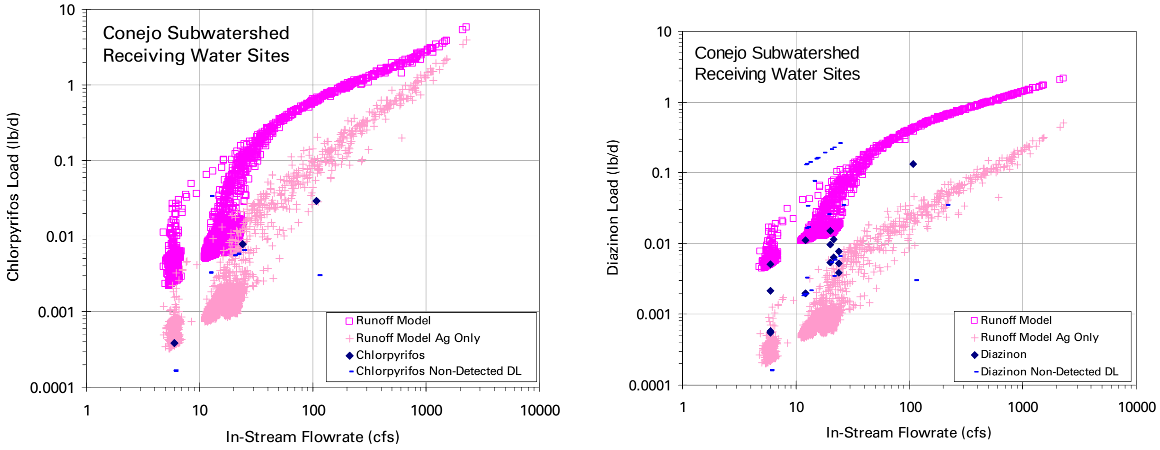

Figure 25: Chlorpyrifos and Diazinon Load in Conejo Subwatershed.

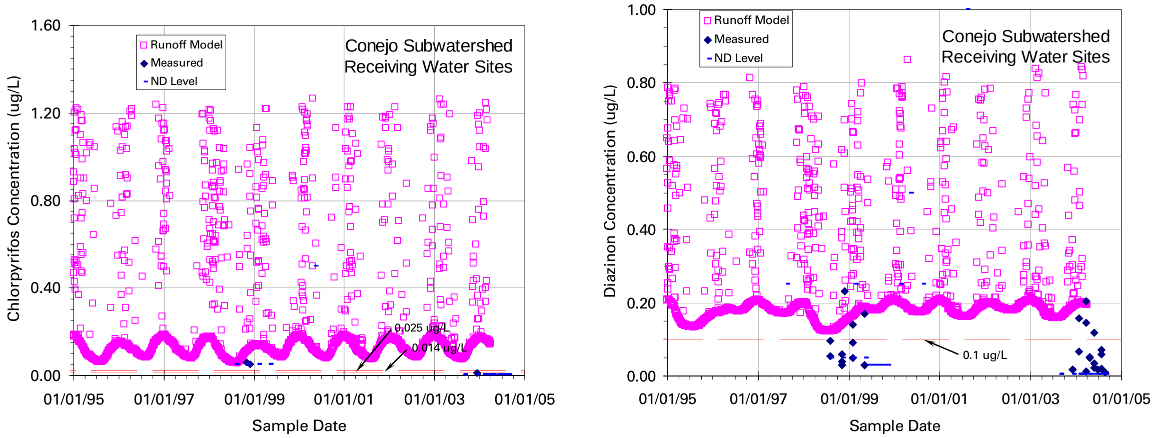

Figure 26: Chlorpyrifos and Diazinon Concentration in the Conejo Subwatershed.

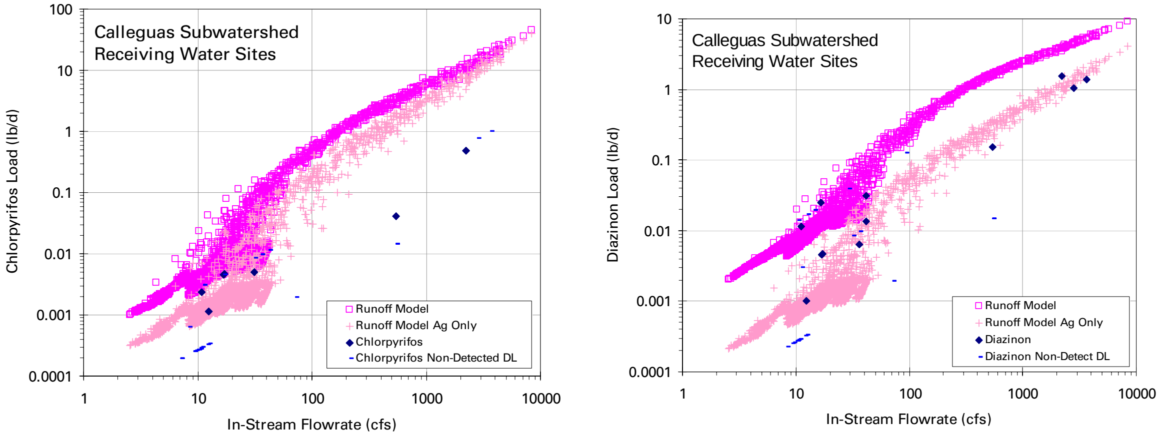

Figure 27: Chlorpyrifos and Diazinon Load in the Calleguas Subwatershed.

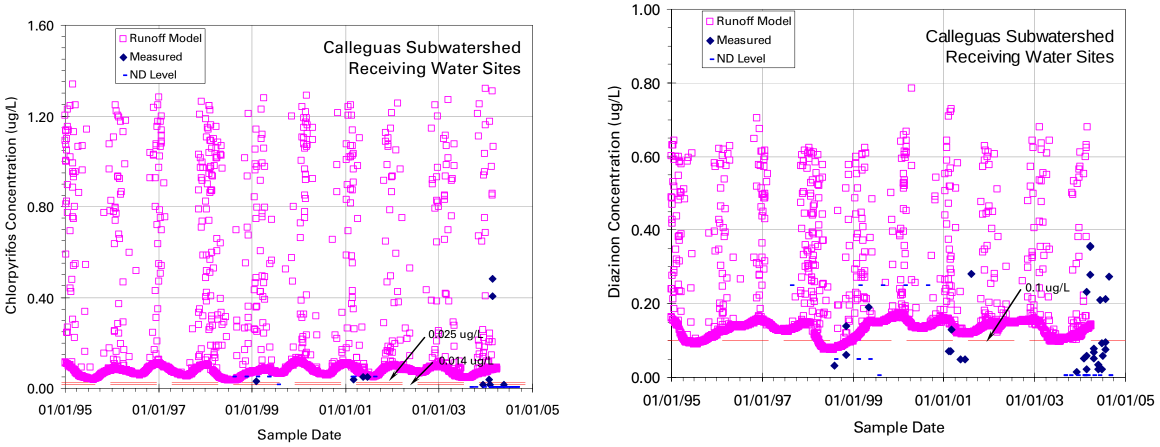

Figure 28: Chlorpyrifos and Diazinon Concentrations in the Calleguas Subwatershed.

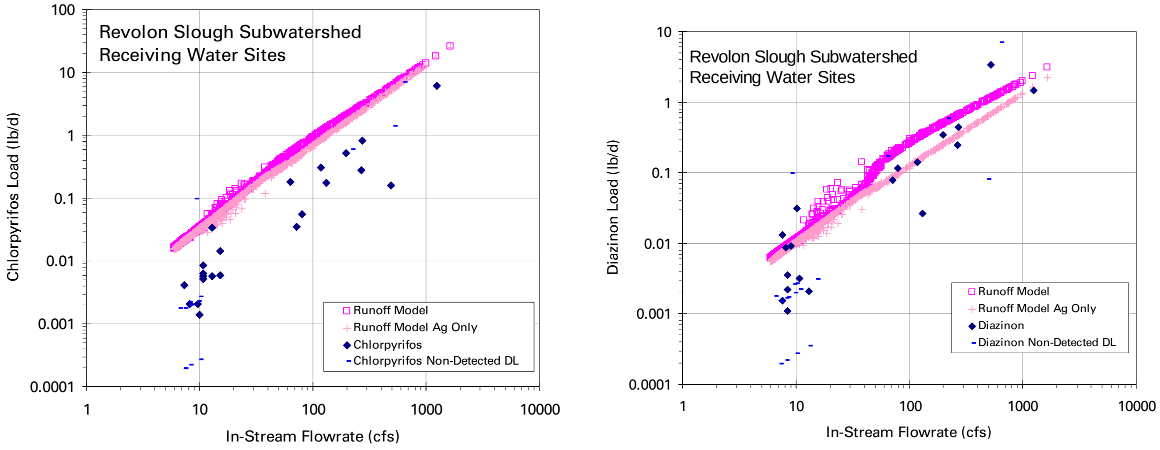

Figure 29: Chlorpyrifos and Diazinon Load in the Revolon Slough Subwatershed.

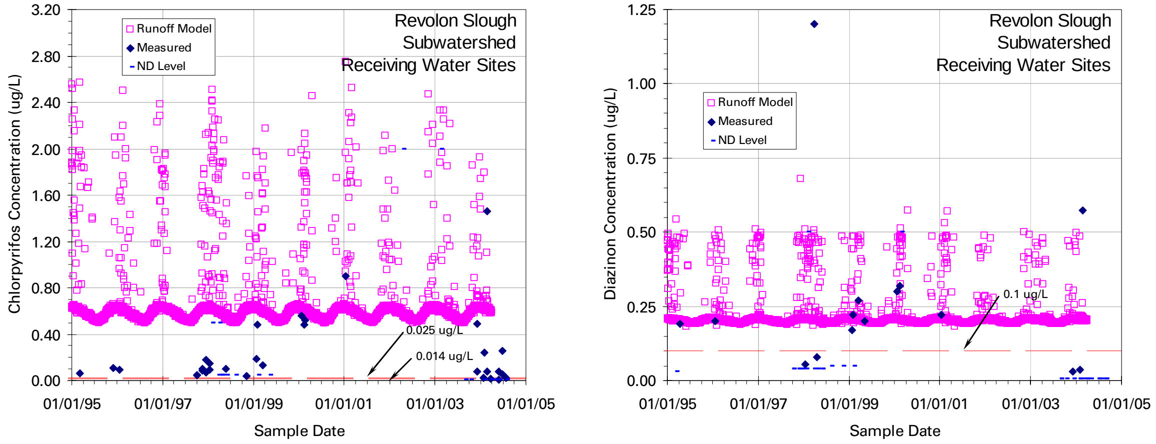

Figure 30: Chlorpyrifos and Diazinon Concentrations in Revolon Slough Subwatershed.

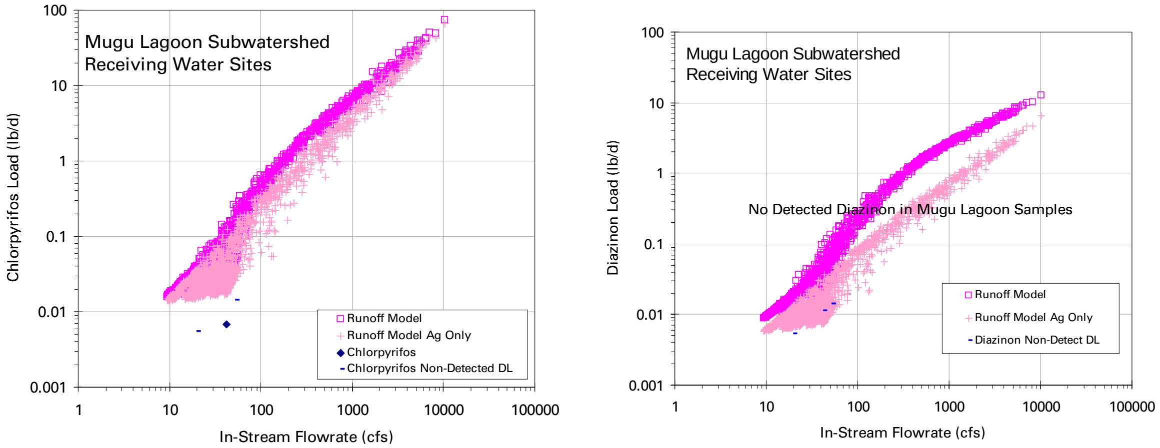

Figure 31: Chlorpyrifos and Diazinon Loads in the Mugu Lagoon Subwatershed.

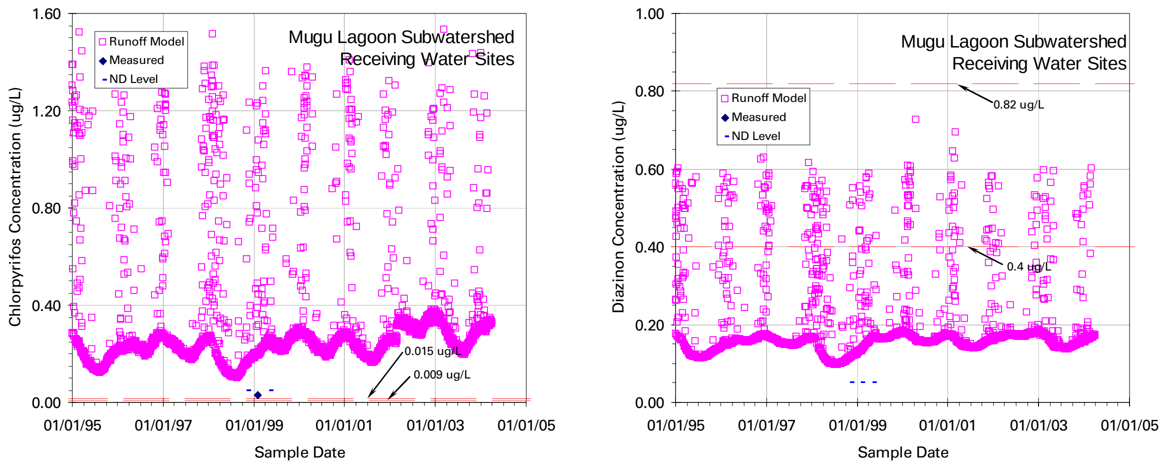

Figure 32: Chlorpyrifos and Diazinon Concentrations in the Mugu Lagoon Subwatershed.

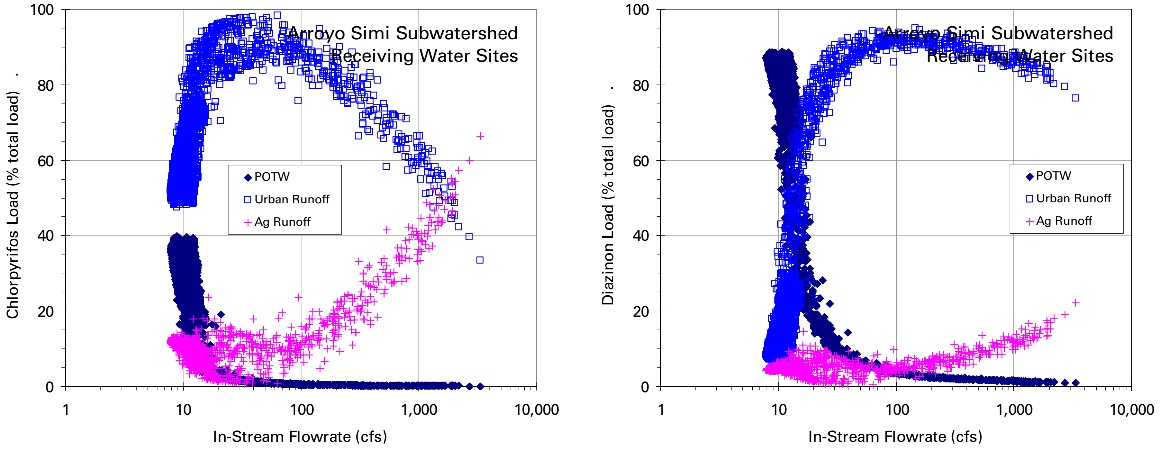

Figure 33: Chlorpyrifos and Diazinon Load Apportionment Arroyo Simi Subwatershed.

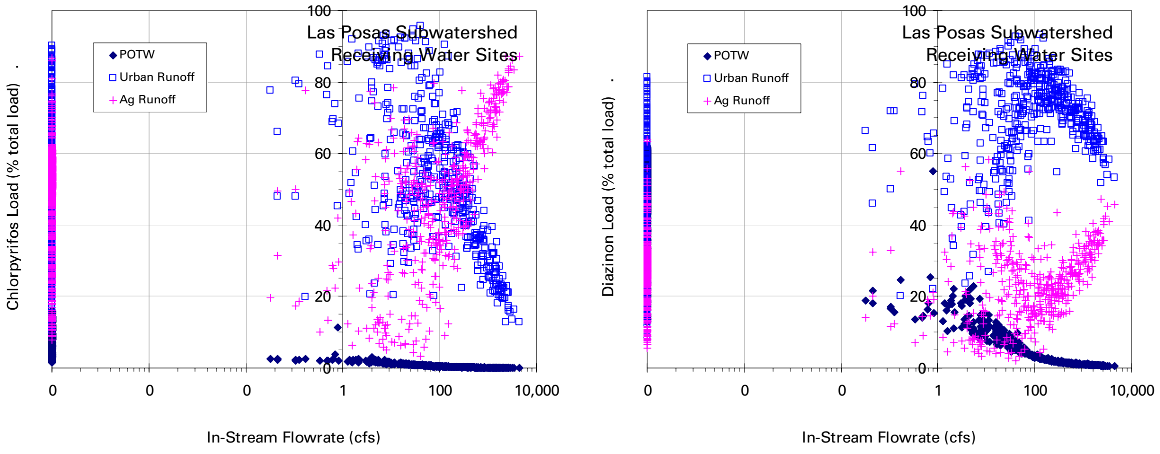

Figure 34: Chlorpyrifos and Diazinon Load Apportionment for Las Posas Subwatershed.

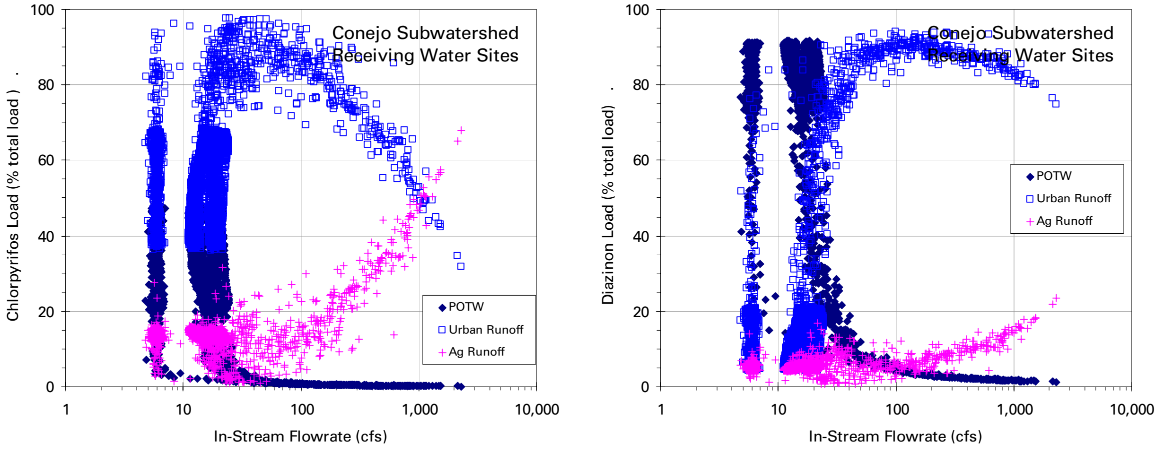

Figure 35: Chlorpyrifos and Diazinon Load Apportionment for Conejo Subwatershed.

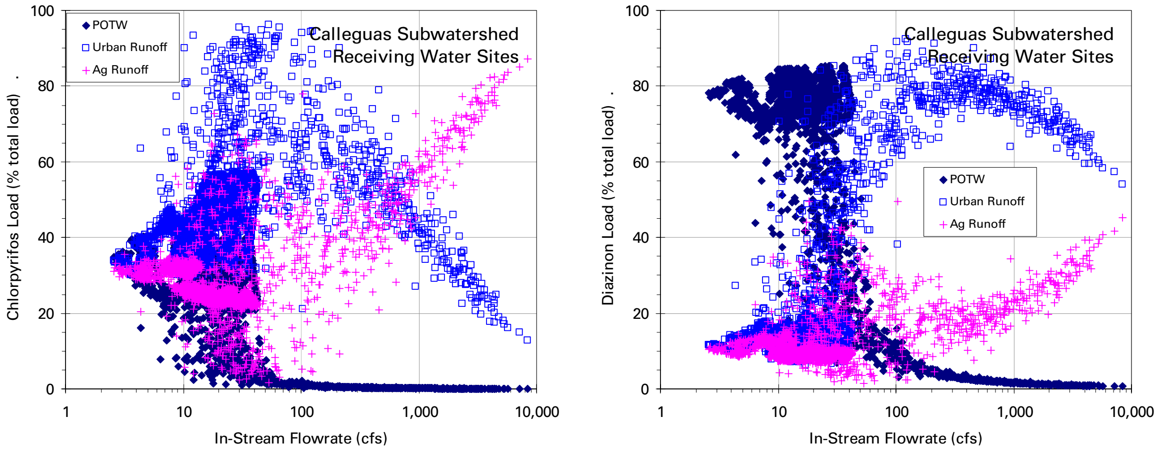

Figure 36: Chlorpyrifos and Diazinon Load Apportionment for Calleguas Subwatershed.

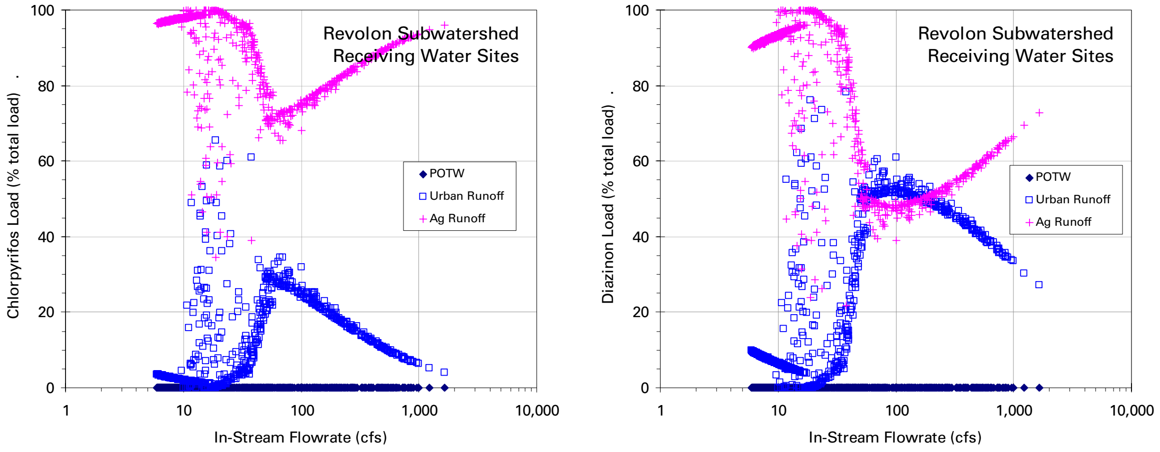

Figure 37: Chlorpyrifos and Diazinon Load Apportionment for Revolon Slough Subwatershed.

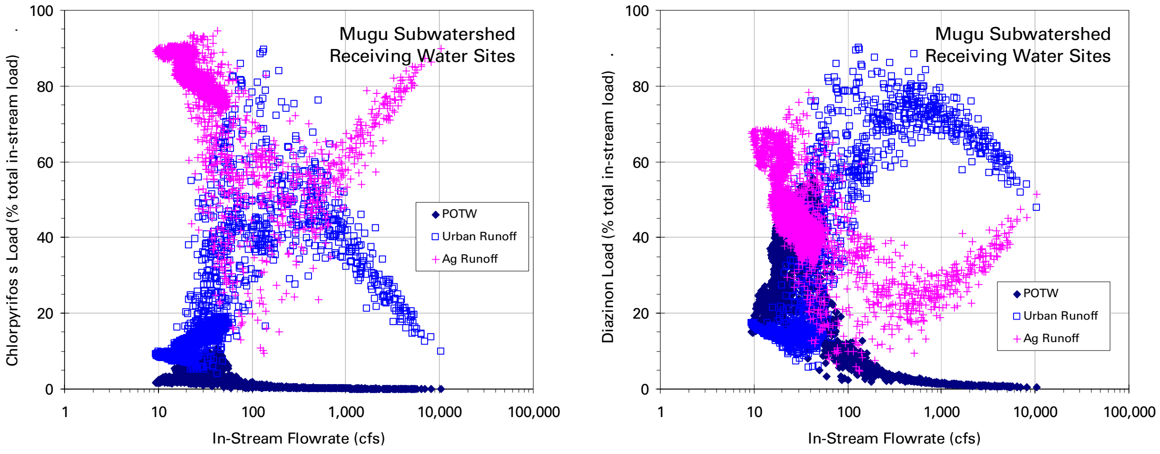

Figure 38: Chlorpyrifos and Diazinon Load Apportionment in Mugu Lagoon Subwatershed.

CRITICAL CONDITIONS

The critical conditions for diazinon and chlorpyrifos include both dry and wet conditions, however the exact quantification of those conditions needs further analysis. During dry weather, specific events appear to lead to high loadings in the receiving water. A linkage between flows, use and runoff quality has not yet been established and it may not be possible to determine the connection. However, it is likely that peak dry weather concentrations and loads will occur during periods of maximum source flows. Additional analysis will be conducted to identify this period and determine whether any other linkages exist that can be used to clarify dry weather critical conditions.

During wet weather events, concentrations of chlorpyrifos are typically much greater than nominal dry weather values. In-stream diazinon concentrations are typically observed to be greater during wet-weather events than for dry-weather. Consequently, wet weather is also a critical condition for these pesticides. Higher concentrations appear to be driven by larger storm events. The larger amount of discharge of these pesticides during storm events does not appear to be diluted significantly by runoff from native spaces. Therefore, all storm events are potentially of concern. Wet weather wasteload and load allocations will be defined for wet weather conditions to account for this critical condition.

MARGIN OF SAFETY (MOS)

A TMDL analysis involves uncertainty. To address the uncertainty, a TMDL is to include a margin of safety, which can be explicit, implicit, or both. Conservative assumptions are incorporated throughout the development of the linkage analysis and calculation of the required reductions. The analysis includes an implicit margin of safety by relying on a generally conservative approach through the entire development. The implicit MOS based on conservative analysis and requiring receiving water targets for the major sources follows the approach of other chlorpyrifos and diazinon TMDLs developed recently in California (SFBRWQCB 2004, CVRWQCB 2004) The following is a list of the conservative assumptions made during the development of the TTMBM and calculations of required reductions:

- All runoff data were used in regression calculations potentially biasing the results high in comparison to present conditions.
- Loading equations are based on the 90% prediction interval of the load vs. runoff flowrate regressions. Calculations of discharge quality effectively estimate the 95th percentile measurement.
- Total measurements of chlorpyrifos and diazinon implicitly include and incorporate sediment associated loading to the receiving waters.
- WLAs to urban stormwater and POTWs are set to the numeric target, but use of both constituents is banned in urban areas so the concentrations should drop below target levels.
- Implicit in the development of the numeric water quality targets is a margin of safety.
- The WLAs and LAs are set to the numeric water column target. Because the contributions to receiving water are dependent on the environmental conditions and behave differently, maximum contribution is a blend of all sources none of which are discharging at the target concentration simultaneously.
- Agricultural return flows, urban runoff, and POTWs are the dominant sources of chlorpyrifos and diazinon to the receiving waters in the CCW. Applying the numeric receiving water target to the discharges will ensure the major sources of chlorpyrifos and diazinon to receiving waters are at or below the targets.

Basing the loading equations on the 90% prediction level of the regression captures a large portion of the observed variability in the discharge data, thereby calculating the receiving water quality based on the peak loadings for a given set of conditions. The TTMBM output, in general, over-predicts the in-stream concentrations. Required reductions based on the TTMBM output are a conservative estimate of the required reductions necessary to achieve numeric targets in-stream and as such are an implicit MOS. By requiring a limit of the receiving water numeric target for all controllable discharges results in the maximum TTMBM calculated receiving water concentrations under the target by 5 to 72%.

SENSITIVITY ANALYSIS

Because the TTMBM suffers from significant data limitations, a formal sensitivity analysis is not performed at the current time. It is anticipated that the TTMBM will be updated when additional data are available and the update will potentially alter the rates of loading used in the model. Any sensitivity analysis performed now would be invalidated when the model is updated with additional data. For example, it is possible that the rate of urban loading should be a super-linear function of runoff flowrate, instead of the sub-linear and linear rates assumed for the current version of TTMBM. If runoff loading is found to be super-linear, the model will be much more sensitive to perturbations of the loading rate than for linear loading rates.

Urban runoff, POTW effluent, and agricultural returns provide the bulk of the OP pesticide loading to the system. Loading of chlorpyrifos and diazinon from urban runoff and POTW effluent to the watershed are expected to decrease substantially due to implementation of the restrictions. Model sensitivity to urban runoff and POTW effluent is neutered do to the anticipated reductions stemming from the bans on use. The potential atmospheric drift contribution to urban runoff is expected to be dramatically altered due to restrictions on which crops chlorpyrifos and diazinon may be applied to, and re-labeling for application procedures and allowable dose applied. Because the magnitude of reductions required in both the agricultural returns and the receiving waters, the calculated percent required reduction is not sensitive to the exact load in either compartment. To illustrate the insensitivity of percent required reduction, Table 11 lists the change in the required reduction if the actual initial load is found to be either 50% greater or less than the TTMBM calculation. If the TTMBM calculated required reduction is 99%, the required reduction would be 99.3% if the initial load is found to be 50% greater than TTMBM calculations. Also, for a 99% required reduction, even after the loads are reduced by 50%, there is still a need for a 98% reduction. Due to the magnitude of the required reductions, the ultimate answers derived from TTMBM calculations are insensitive to precise load calculations, as the implementation proceeds there will be an increasing need for model refinement and formal sensitivity analysis.

Table 11: Change in Required Reduction Given a Change in the Calculated Load.

Initial Required Reduction (%)	Required Reduction Given Change in Load	
	50% Greater	50% Less
99	99.3	98
98	98.7	96
95	96.7	90
90	93.3	80
80	86.7	60

SCENARIO INVESTIGATIONS

To perform implementation scenario investigations, changes affecting flows should be input into a new DCCMS scenario to determine CCW flows for the new scenario. The new flows would be copied into the TTMBM spreadsheet. Finally, estimates of loading modifications would be used to change the TTMBM input values.

IMPROVEMENTS REMAINING

In general, the TTMBM output under-estimates the OP pesticide concentrations. Currently, atmospheric contribution is encapsulated in the agricultural and urban runoff loads of pesticides. There are no measurements of OP pesticides in the native space runoff in the CCW. Measurement of OP pesticide native space runoff would provide the most direct way of incorporating atmospheric deposition into the TTMBM. Incorporation of atmospheric drift/direct deposition and wet and dry deposition on the watershed may improve the comparison between TTMBM output and measured in-stream values. Chlorpyrifos is known to have a high affinity for the organic fraction of sediment. As current TMDL data become available, a linkage will be investigated between the constituents and TSS, Sediments, etc. Incorporation of the pesticide use information into the model to the extent possible will provide a means to relax the assumption that each agricultural runoff sample is representative of all agricultural runoff across the entire CCW. Specifically, determining if a link can be established between the rate and timing of pesticide use and runoff water quality will ideally account for a large portion of the variability in the observed measurements.

When improvements are made to the DCCMS, the applicable results should be carried over to the Toxicity TMDL model.

Because of the TTMBM structure, adding additional constituents essentially requires additional columns to be inserted into the spreadsheet based model, and addition of the appropriate runoff loading parameters.

As discussed in the Scope of the Toxicity TMDL Mass Balance Model section, continued monitoring for OP pesticides in the CCW using environmentally relevant detection limits would greatly benefit any subsequent modeling effort. Each additional piece of information listed above will likely increase the resolution of apportioning loads under wider range of conditions. Due to the application-runoff nature of OP pesticide loading to the receiving water, an extremely detailed model would be required to exactly match the variability of the observed data. A detailed model would require more data to develop, calibrate, and validate as well as consume time and monetary resources. For the purposes of TMDL development, it is unclear that the increased level of detail is necessary. If the expected range of variability around the TTMBM model output were know (i.e “error bars” for a range of in-stream flowrates), through additional data gathering, sufficient information would exist to develop wasteload and load allocations that would be protective of all beneficial uses in each of the receiving waters.

CONCLUSIONS

Conservation of mass is the basis of the TTMBM water quality model. Flowrates of various water streams in the CCW are calculated by the DCCMS model. By assuming that each reach is steady for any given time step, reach outflow and concentration may be calculated from algebraic equations. The effect of using a daily time step and the steady-state assumption is to generate a series of daily average snapshots of the conditions likely to exist in the CCW. Both the TTMBM and DCCMS are built on the principles of mass conservation forming a simple, robust, and defensible method of modeling constituent flows through the CCW.

The current development of the TTMBM represents utilizing the available information to the extent possible to construct a defensible model. Due to limitations in the available data, there are components of the TTMBM that could be improved. Currently, the TTMBM illuminates which sources of the constituents contribute the greatest fraction of in-stream load, and under what conditions. Because of data limitations, the TTMBM output should be considered estimates of field conditions. Through continued monitoring and additional investigations, the additional information could greatly improve the predictive capability of the TTMBM.

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CONVERSIONS

Area

$$0.004047 \frac{\text{km}^2}{\text{acre}}$$

Volume

$$7.481 \frac{\text{gal}}{\text{ft}^3}$$

Flow

$$1.008 \frac{\text{acre} \cdot \text{in}/\text{hr}}{\text{cfs}}$$

$$0.0013813 \frac{\text{cfs}}{\text{acre} \cdot \text{ft}/\text{yr}}$$

$$0.5042 \frac{\text{cfs}}{\text{acre} \cdot \text{ft}/\text{d}}$$

$$1.547 \frac{\text{cfs}}{\text{MGD}}$$

Mass Loading

$$5.394 \frac{\text{lb}/\text{d}}{\text{cfs} \cdot \text{mg}/\text{L}}$$

$$0.005394 \frac{\text{lb}/\text{d}}{\text{cfs} \cdot \mu\text{g}/\text{L}}$$

APPENDIX A: TTMBM USING NOMINAL REGRESSION RESULTS

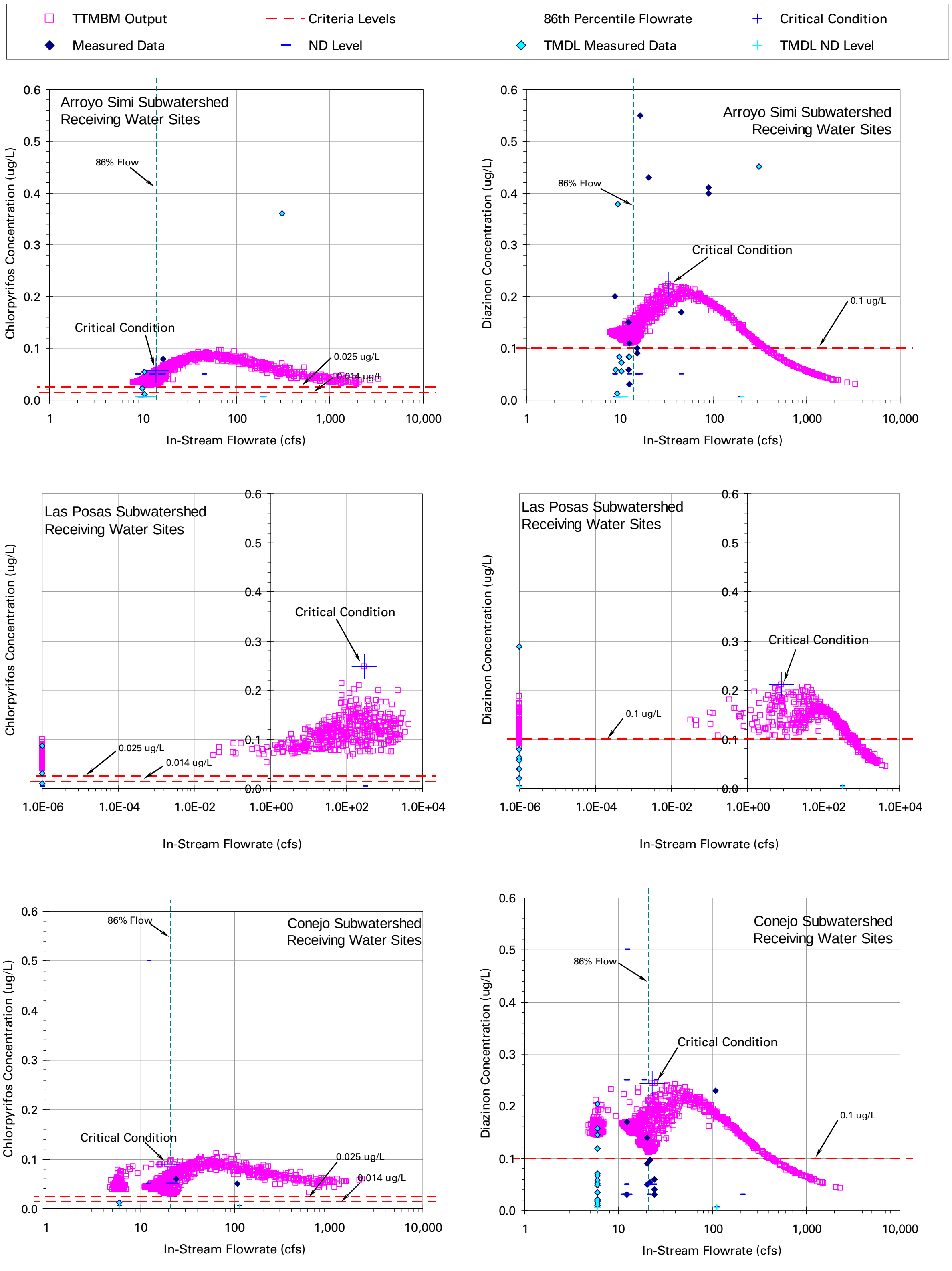


Figure 39 Continued

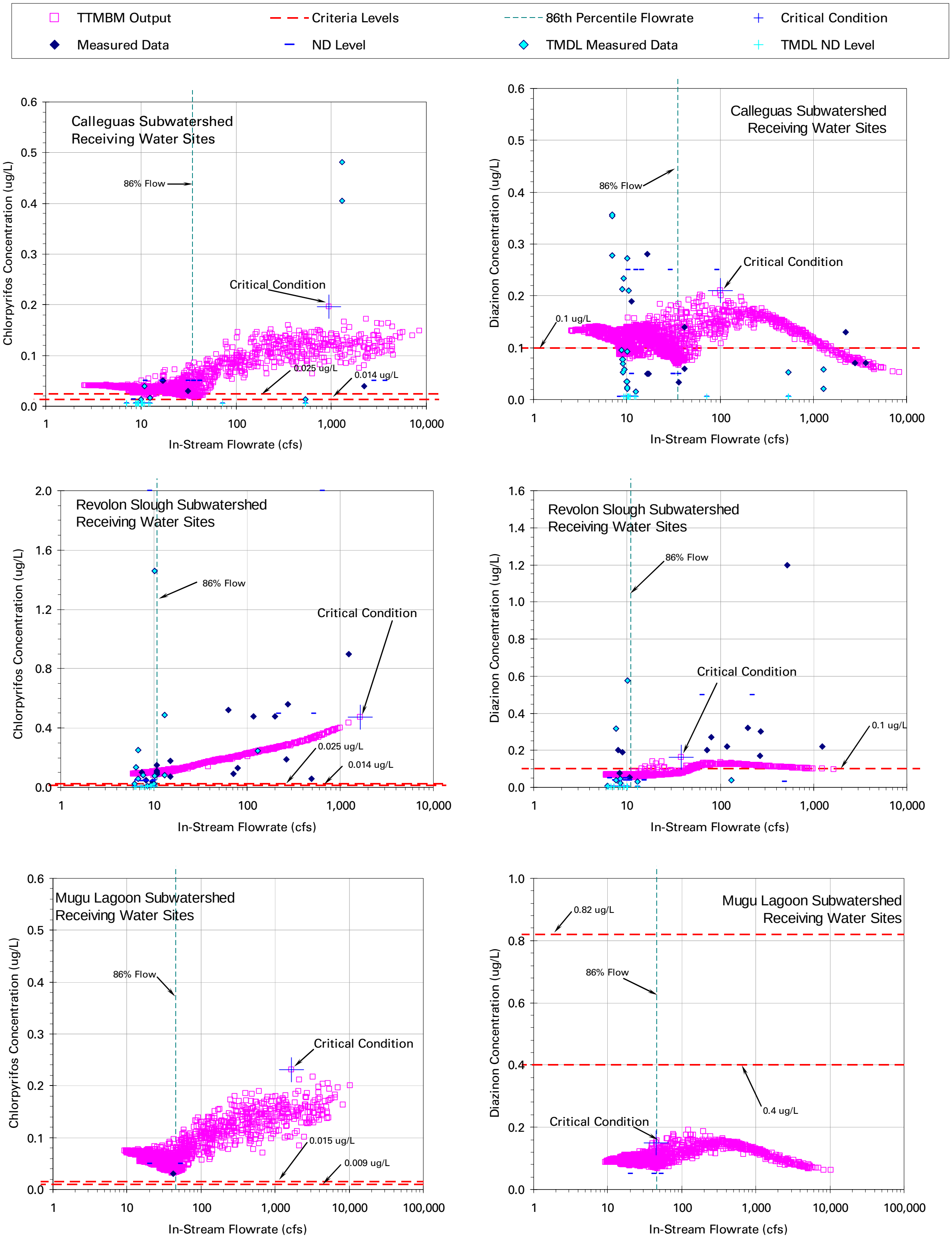
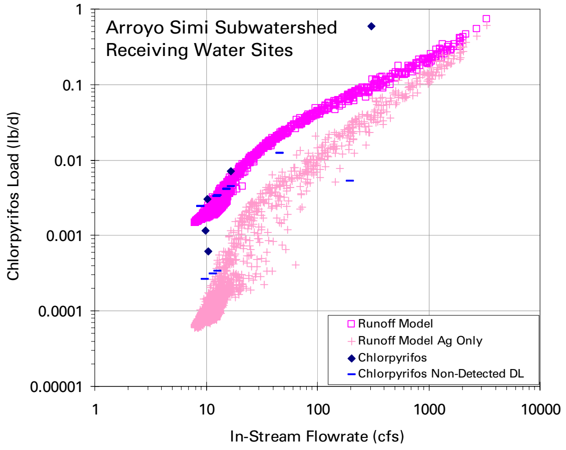
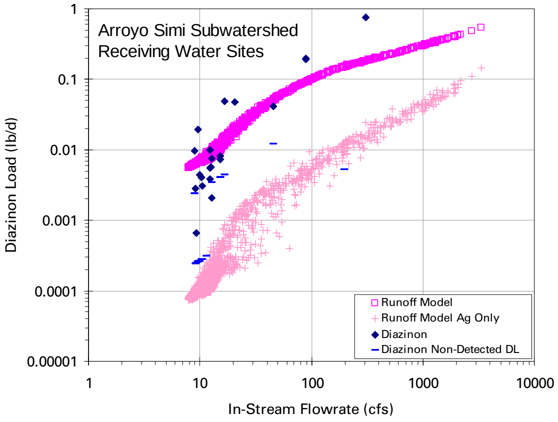
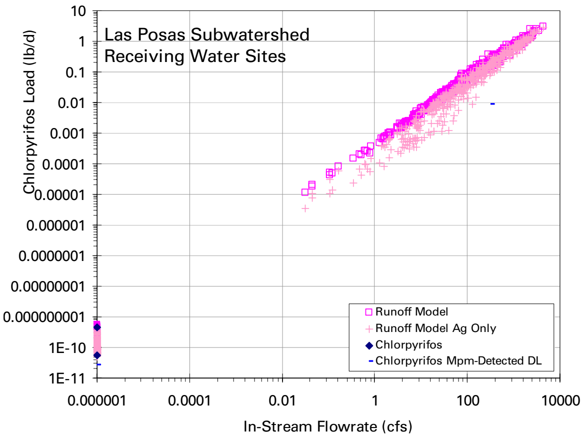
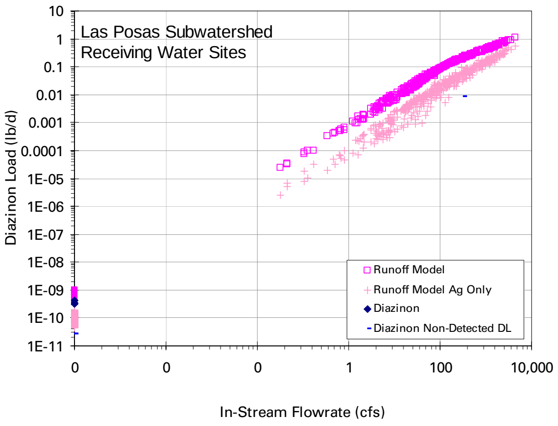


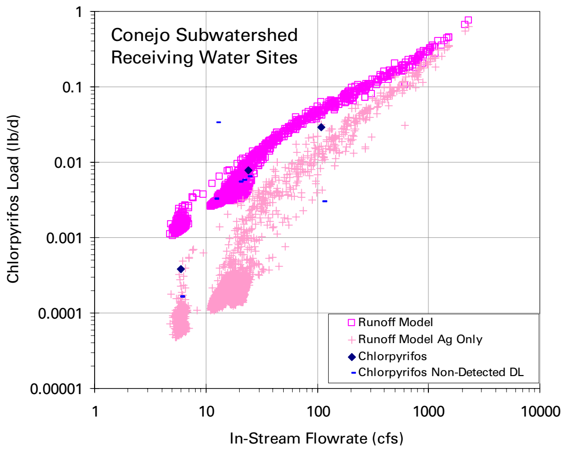
Figure 39: Chlorpyrifos and Diazinon Concentrations as a function of receiving water flowrates. Discharge loads calculated via regression.

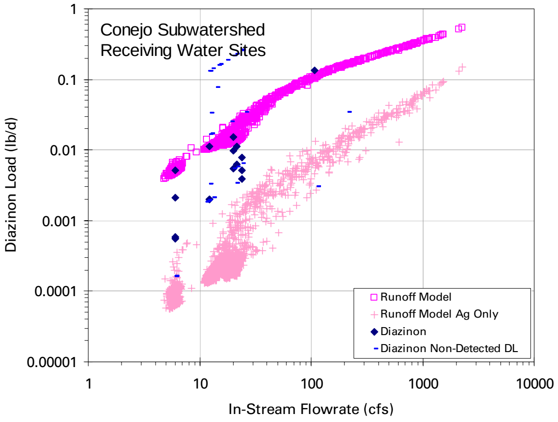

Arroyo Simi Subwatershed
Receiving Water Sites
Chlorpyrifos Load (lb/d)
1
0.1
0.01
0.001
0.0001
0.00001
1
10
100
1000
10000
In-Stream Flowrate (cfs)
Runoff Model
Runoff Model Ag Only
Chlorpyrifos
Chlorpyrifos Non-Detected DL


Arroyo Simi Subwatershed
Receiving Water Sites
Diazinon Load (lb/d)
1
0.1
0.01
0.001
0.0001
0.00001
1
10
100
1000
10000
In-Stream Flowrate (cfs)
Runoff Model
Runoff Model Ag Only
Diazinon
Diazinon Non-Detected DL


Las Posas Subwatershed
Receiving Water Sites
Chlorpyrifos Load (lb/d)
10
1
0.1
0.01
0.001
0.0001
0.00001
0.000001
0.0000001
0.00000001
0.000000001
1E-10
1E-11
0.000001
0.0001
0.01
1
100
10000
In-Stream Flowrate (cfs)
Runoff Model
Runoff Model Ag Only
Chlorpyrifos
Chlorpyrifos Mpm-Detected DL


Las Posas Subwatershed
Receiving Water Sites
Diazinon Load (lb/d)
10
1
0.1
0.01
0.001
0.0001
1E-05
1E-06
1E-07
1E-08
1E-09
1E-10
1E-11
0
0
0
1
100
10,000
In-Stream Flowrate (cfs)
Runoff Model
Runoff Model Ag Only
Diazinon
Diazinon Non-Detected DL


Conejo Subwatershed
Receiving Water Sites
Chlorpyrifos Load (lb/d)
1
0.1
0.01
0.001
0.0001
0.00001
1
10
100
1000
10000
In-Stream Flowrate (cfs)
Runoff Model
Runoff Model Ag Only
Chlorpyrifos
Chlorpyrifos Non-Detected DL


Conejo Subwatershed
Receiving Water Sites
Diazinon Load (lb/d)
1
0.1
0.01
0.001
0.0001
0.00001
1
10
100
1000
10000
In-Stream Flowrate (cfs)
Runoff Model
Runoff Model Ag Only
Diazinon
Diazinon Non-Detected DL

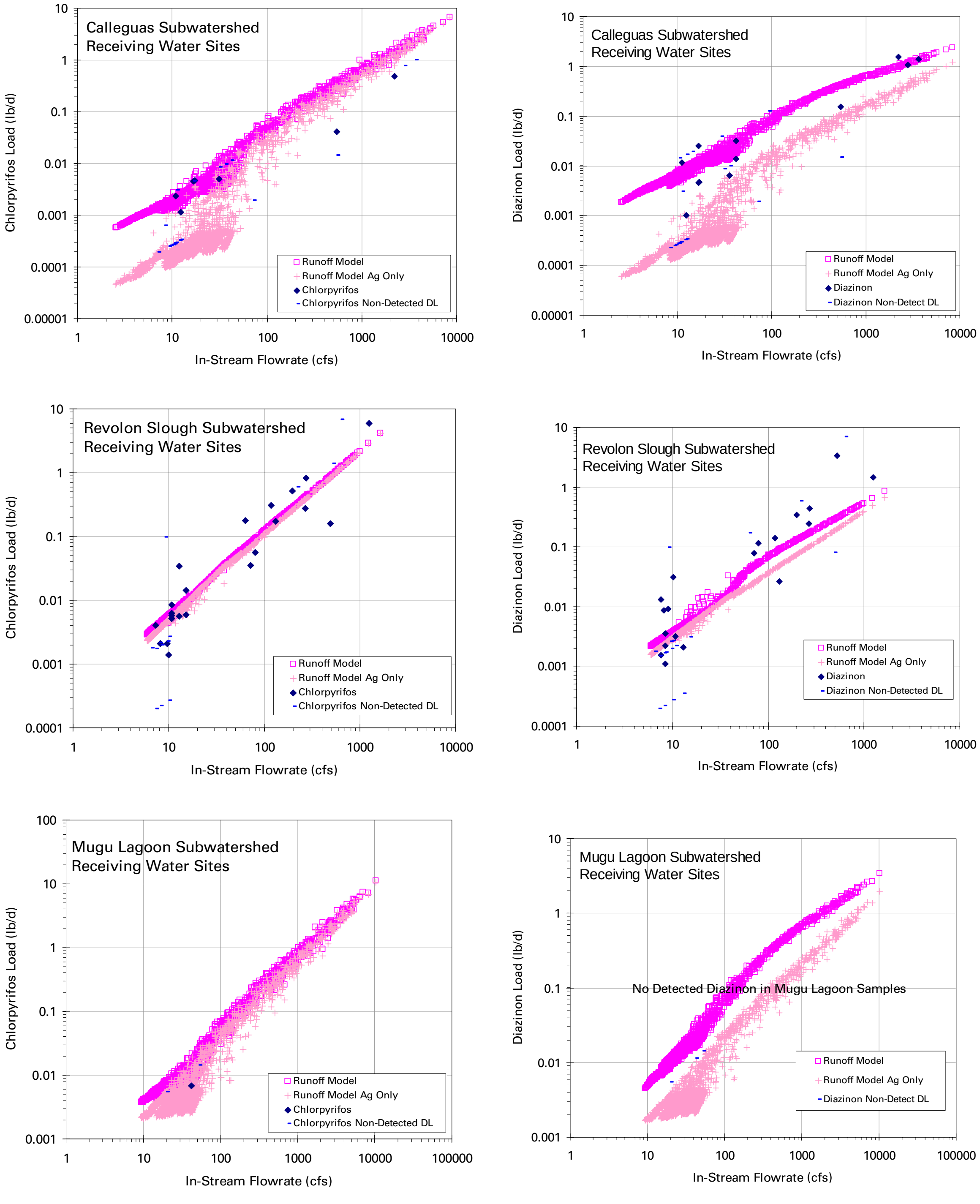


Figure 40: Chlorpyrifos and Diazinon Load as a Function of Flowrate and Compared to Receiving Water Data.

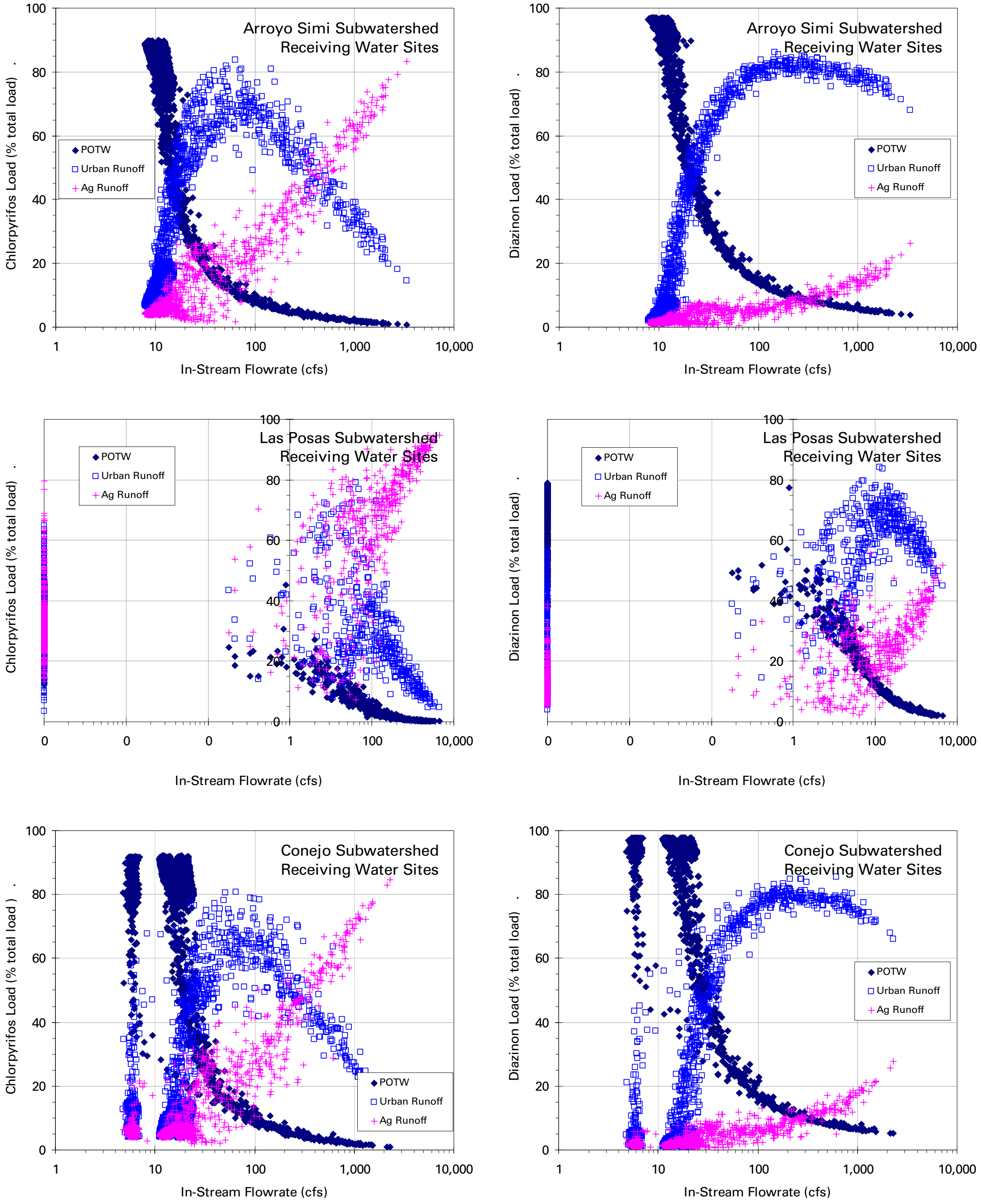


Figure 41 Continued

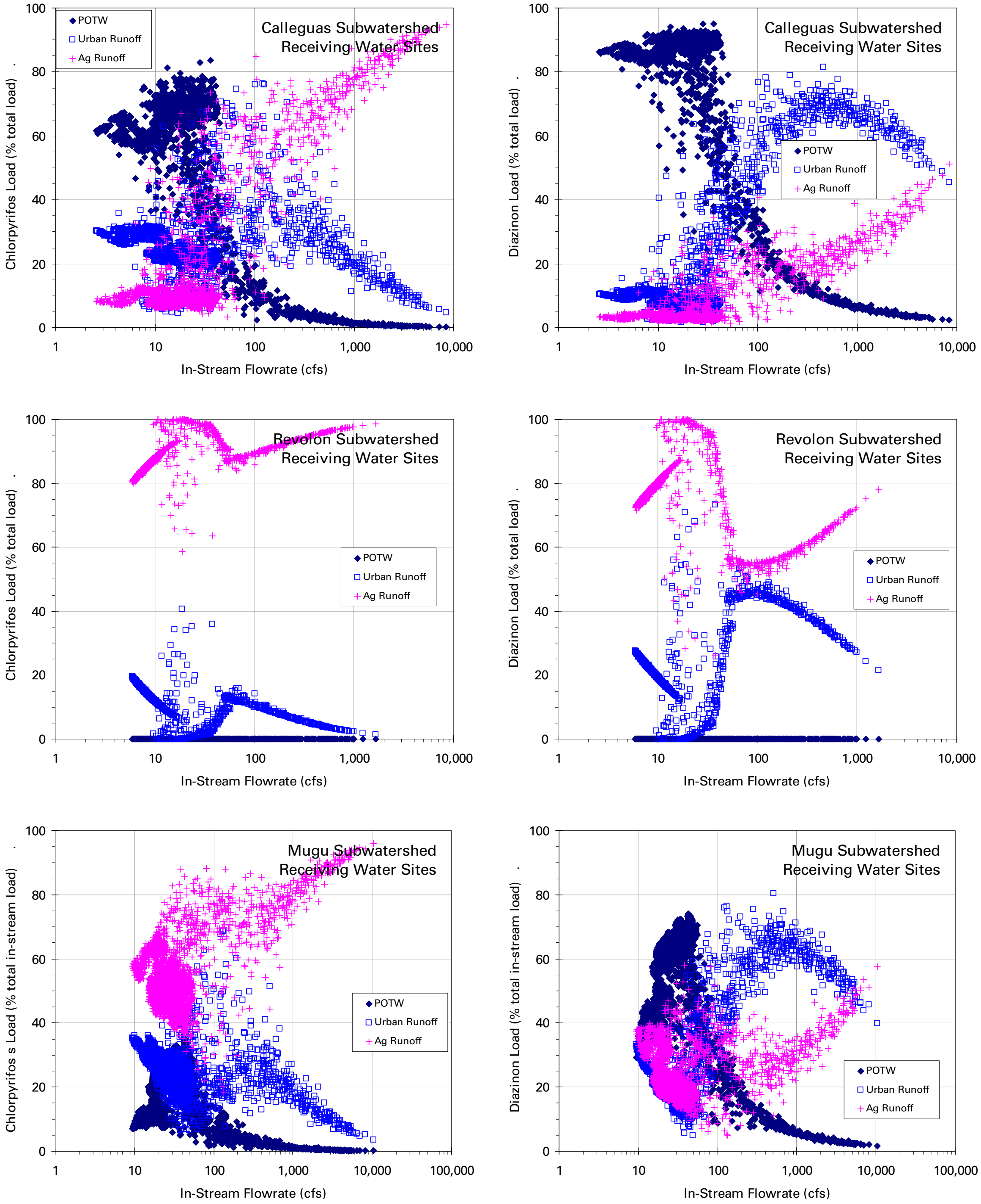


Figure 41: Apportionment of in-stream load using regression discharge loading equations.