Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, California 95812

Study 306. Surface Water Monitoring for Pesticides in Agricultural Areas of Northern California, 2016.

April R. DaSilva, Ph.D.
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1. INTRODUCTION

For years, the California Department of Pesticide Regulation (CDPR) has monitored for agricultural pesticides through long-term monitoring in the Central Coast and Imperial Valley. However, the northernmost part of the state (*e.g.,* forest land) has only been monitored through various short-term special studies. Although much of Northern California is forested, there are concentrated areas of farmland located in Del Norte, Modoc and Siskiyou counties. According to CDPR's pesticide use reports (CDPR 2013), commodities grown within these counties include outdoor transplants, greenhouse plants in containers, potato, wheat, onion, alfalfa, and strawberries. These crops are associated with a variety of pesticides that are potential candidates for monitoring.

Limited monitoring data, reported by the California Environmental Data Exchange Network (CEDEN 2016) and CDPR's Surface Water Database (SURF; CDPR 2015), are available for these three counties. In recent years, the Regional Water Board (Region 1 - North Coast) has reported pesticide detections in Smith River and Klamath River (Del Norte County), whereas in Pit River (Modoc County) no measurable pesticide concentrations have been reported. In Siskiyou County, a wider range of pesticides have been detected in the Shasta River, Klamath River, Scott River and Yreka Creek; however, these sites are not located near the agriculturally-dominated area around the town of Tulelake. The lack of available data illustrates the need to expand monitoring efforts to the northern part of the state in order to capture the effects of current pesticide use and irrigation practices.

For 2016, agricultural monitoring in Northern California will focus on high-use areas with limited historical data. This study is a preliminary investigation to determine the presence of pesticides in surface waters located in the Smith River and Tulelake watersheds. New data from Study 306 will be used to evaluate runoff and receiving waters in these agriculturally-dominated areas of Northern California. Monitoring sites in these locations were selected based on high pesticide use at the watershed level. Using CDPR's Surface Water Monitoring Prioritization Model (Luo et al. 2013, 2014, 2015), specific pesticides were identified for the watersheds of interest, thus focusing the pesticide priority list for a given region.

2. OBJECTIVES

The goal of this project is to assess pesticide concentrations in agricultural runoff and receiving waters in Northern California. Specific objectives include:

1) Prioritize pesticide monitoring candidates based on current use reports at the watershed level;
2) Determine the presence and concentrations of prioritized pesticide active ingredients in surface waters in the Smith River and Klamath River watersheds;
3) Analyze chemistry data to evaluate potential impacts on aquatic life.

3. PERSONNEL

This study will be conducted by staff from the Environmental Monitoring Branch, Surface Water Protection Program. Key personnel are listed below:

Project Leader:	April DaSilva, Ph.D.
Field Coordinator:	Kaylynn Newhart
Reviewing Scientist:	Xin Deng, Ph.D.
Statistician:	Dan Wang, Ph.D.
Laboratory Liaison:	Sue Peoples
Analytical Chemistry:	Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

Questions concerning this monitoring project should be directed to April DaSilva, Environmental Scientist, at (916) 445-0113 or by email at april.dasilva@cdpr.ca.gov.

4. STUDY PLAN

4.1 Selection of pesticides

Pesticides selected for monitoring were based on results from CDPR's Surface Water Monitoring Prioritization Model (Luo et al. 2013, 2014, 2015). This model identifies pesticide active ingredients and degradates according to use and aquatic toxicity benchmark data. The model was run to determine pesticides at both the county and watershed (HUC12) levels using pesticide use data from 2012 to 2014.

To better understand pesticide use in both the Smith River and Tulelake watersheds throughout the year and growing season, monitoring priority lists were generated. May and July were identified to not only represent two months during the growing season that have different pesticides applied, but they also have different irrigation methods and schedules. Northern California agriculture is aided by cooler temperatures and increased rainfall compared to the rest of the state, thus the growing season is shorter and depending on the crop (i.e., alfalfa), harvest may occur a few times per season. As summer temperatures rise, irrigation increases. Thus, sampling during May and July will not only reflect a difference in pesticide use but also the variation in runoff volumes.

Active ingredients, for the three counties and representative watersheds, were chosen based on the following criteria:

1. Pesticides with a final ranking score ≥9 are of high priority and shall be considered for monitoring. Those with a final score <9, are considered to be low priority due to either low use (use score <2) and/or low toxicity (toxicity score <3).

2. Pesticides with a use score ≥2 shall be considered for monitoring. Pesticides that were not in the priority lists or had use scores < 2 may be monitored because they will be concurrently analyzed with analytical groups (Table 4, Appendix 1) that contain pesticides in the final monitoring list.

3. Pesticides that were ranked very low by the model are not included in the final monitoring list (Table 4), unless they are in the chosen analytical method groups. Historical monitoring data and/or availability of analytical methods were additional factors to help arrive at a final list for monitoring.

Pesticide use in these regions is much lower compared to other agriculturally-dominated areas in California. The resultant prioritization lists, therefore, are heavily based on pesticides with lower use scores. The final monitoring list will be optimized to consider a broader range of pesticides with lower use scores in order to increase monitoring candidates.

4.2 Selection of monitoring sites

Water quality monitoring will be conducted at eight sites within agriculturally-dominated areas of Del Norte, Modoc and Siskiyou counties. These locations, which include creeks, drainage canals and irrigation canals were selected 1) due to limited historical monitoring data as reported by CDPR's SURF database, 2) have pesticide use patterns that warrant monitoring, and 3) are publically accessible.

Del Norte County

Ambient surface water monitoring will be conducted at two sites (SR_Ritmer and SR_Morrison) within the Smith River watershed (Figure 1) in May and July of 2016. The monitoring priority list for the Smith River watershed was generated using pesticide data from 2012–2014 (Table 1). Due to lower pesticide use in the spring (May), monitoring will be limited to phenoxy herbicides, diuron and imidacloprid, whereas, in the summer (July), monitoring will include phenoxy herbicides, organophosphates and imidacloprid. There is use of other pesticides such as chlorothalonil, iprodione and maneb; however, they will not be monitored due to 1) low use or low detection frequency in previous monitoring studies, 2) prioritization model did not recommend monitoring or 3) analytical methods are not available. The complete list of pesticides to be monitored is provided in Table 4.

Modoc and Siskiyou Counties

Ambient surface water monitoring will be conducted in the following watersheds: Anderson Rose Diversion Dam-Lost River, Copic Bay, Mills Creek-Tule Lake Valley, The Panhandle and Tule Lake Valley-Lost River in May and July of 2016. These watersheds contain a variety of private and leased lands that grow alfalfa, onion, wheat, potato and horseradish.

There will be six sites (plus a planned back-up site) that represent the Tulelake region (Figure 2, Table 3). Two sites (Oregon_In_1 and Oregon_In_2) along the California-Oregon border will be monitored to identify pesticide inputs originating from Oregon. These sites are important to include as the Tulelake Irrigation District (TID) receives their surface water supplies from the Klamath River via the Lost River Diversion Channel, which travels into California from Oregon. Moreover, many agricultural fields along the diversion channel and the state-line (Oregon side) receive tailwater from fields within the Klamath Irrigation District that may contribute unknown pesticides, thus potentially impacting irrigation waters prior to use in California.

The TID delivers surface water from its J-Canal (23 miles long) through a channelized lateral canal system that extends south-east, before turning back west; it is the main water system for the Copic Bay Watershed. Irrigation tailwater is collected into drainage systems and discharge is either pumped back into the canal system or into Tule Lake Wildlife Refuge (Sump 1A or Sump 1B).Water stored within the sumps may be re-diverted for irrigation or discharged into the P-Canal, which enters the Lower Klamath National Wildlife Refuge (MBK Engineers 2013). A representation of the TID and drainage network is provided in Figure 3.

Two sites (TL_Main_1 and TL_Main_2) along the main drain that runs along the north side of the Tule Lake Wildlife Refuge (Sump 1A) will be sampled. Both sites are separate and will collect runoff from different large blocks of fields without overlap. Sites within the main drains will be sampled near water pump stations to identify what is in the runoff and what may be redeposited onto other fields when water is redistributed for use.

Two sites (Copic_Bay_In and Copic_Bay_Out) will represent the Copic Bay Watershed, which receives water towards the end of the J-Canal. At the input, irrigation water includes water from the J-Canal and tailwater that has been collected into the nearest lateral drain and pumped for use. The output of Copic Bay is pumped into Sump 1B. This section of land is important to monitor as irrigation return flow from the north-eastern part of the Tulelake region may impact the fields within Copic Bay.

In order to understand pesticide use in the Tulelake region, each of the six sites will be monitored for the same pesticides. The monitoring priority list for these watersheds was generated using pesticide data from 2012–2014 (Table 2). In the spring (May), monitoring will be limited to phenoxy herbicides, triazines, dinitroanilines and imidacloprid, whereas, in the summer (July), monitoring will include phenoxy herbicides, triazines, dinitroanilines, and organophosphates. There is use of other pesticides such as paraquat dichloride, glyphosate and oxamyl; however, they will not be monitored for due to either 1) low use or low detection frequency in previous monitoring studies, 2) prioritization model did not recommend monitoring or 3) analytical methods are not currently available. The complete list of pesticides to be monitored is provided in Table 4.

4.3 SAMPLING

Surface water grab samples will be collected into 1-L amber glass bottles from each field site. Samples will be transported on ice and stored in a refrigerator (4°C) until analyzed. CDPR staff

will transport samples following procedures outlined in CDPR SOP QAQC004.01 (Jones, 1999). A chain-of-custody record will be completed for each sample.

4.4 FIELD MEASUREMENTS

Water quality measurements (pH, temperature, dissolved oxygen, turbidity, and specific conductivity) will be collected *in situ* during each sampling trip. Using a YSI-EXO 1 multi-parameter Sonde unit to collect measurements, methods outlined in Doo and He (2008) will be followed (https://www.ysi.com/productsdetail.php?EXO1-Water-Quality-Sonde-89).

5. CHEMICAL ANALYSIS

The Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA; Sacramento, CA) will conduct the chemical analyses for this study. CDFA will analyze five pesticide classes, which will include 34 chemical compounds (Table 4, Appendix 1). Laboratory QA/QC will follow CDPR guidelines provided in the Standard Operating Procedure QAQC001.00 (Segawa 1995). Extractions will include laboratory blanks and matrix spikes. The analytical methods, method detection limits, reporting limits and detected compounds will be reported by the lab for each sample set.

6. DATA ANALYSIS

Concentrations of pesticides in water will be reported as micrograms per liter (µg/L)/parts per billion (ppb) or nanograms per liter (ng/L)/parts per trillion (ppt). Data generated from this study will be entered into a Microsoft Office Access database that will hold all field measurements and laboratory data. Resulting pesticide concentrations will be evaluated against aquatic life toxicity benchmark values, water quality limits or other toxicity data (CCVRWQCB 2012; US EPA 2016). As data are collected, a multi-year data assessment may identify patterns and trends in detections.

7. TIMETABLE

Field Sampling:	May 2016–September 2016
Chemical Analysis:	May 2016–October 2016
Draft Report:	March 2017

8. BUDGET

The estimated cost for the CDFA chemical analyses is $59,580 (Table 5). This cost includes a lab verification study (15 samples) for metribuzin.

9. REFERENCES

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CDPR (California Department of Pesticide Regulation) 2013. Pesticide Use Reporting. http://www.cdpr.ca.gov/docs/pur/pur13rep/13_pur.htm.

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US EPA 2016. Aquatic Life Benchmark Table. Benchmark table updated January 2016. http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm

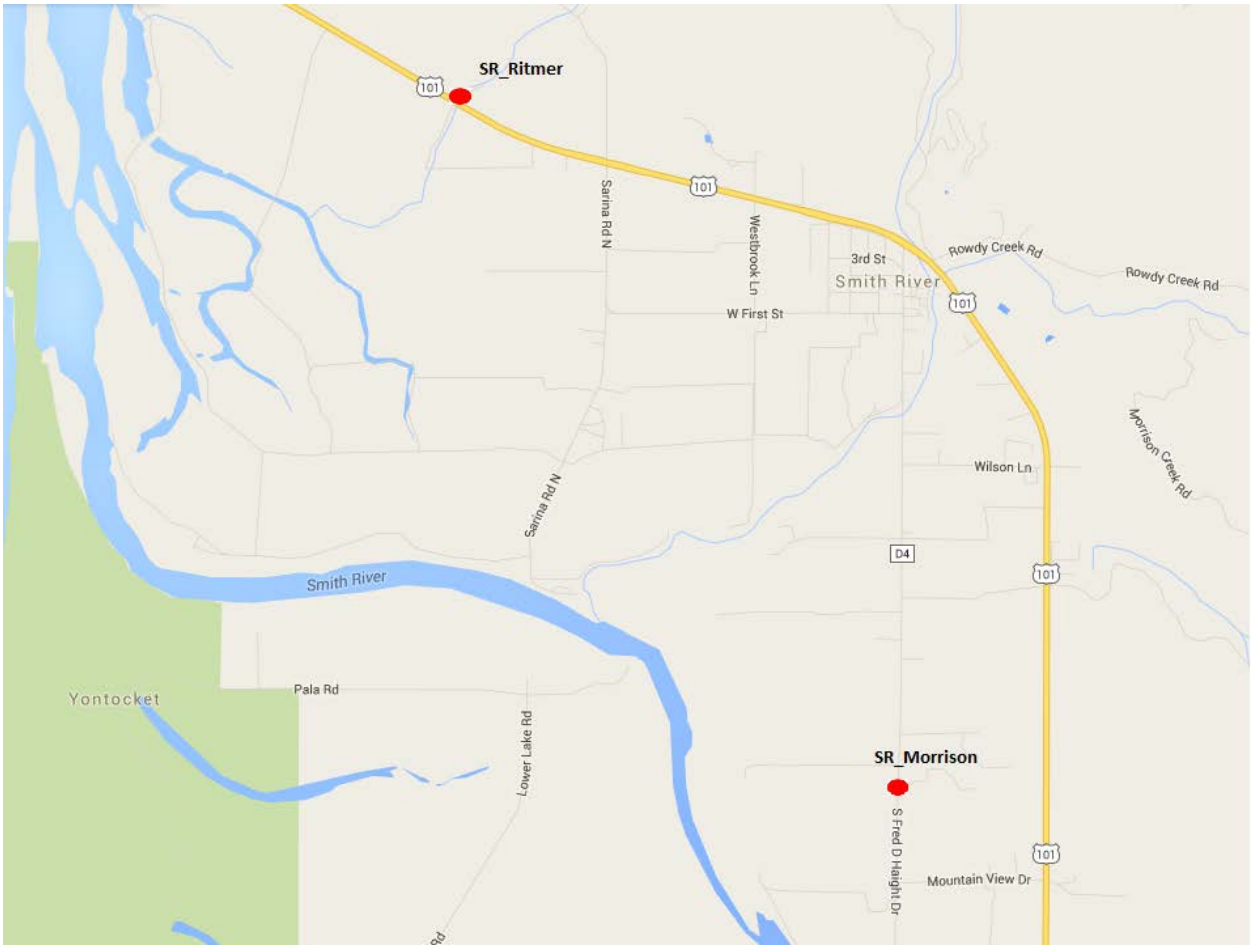

Figure 1. Monitoring sites in Ritmer Creek and Morrison Creek in Del Norte County.

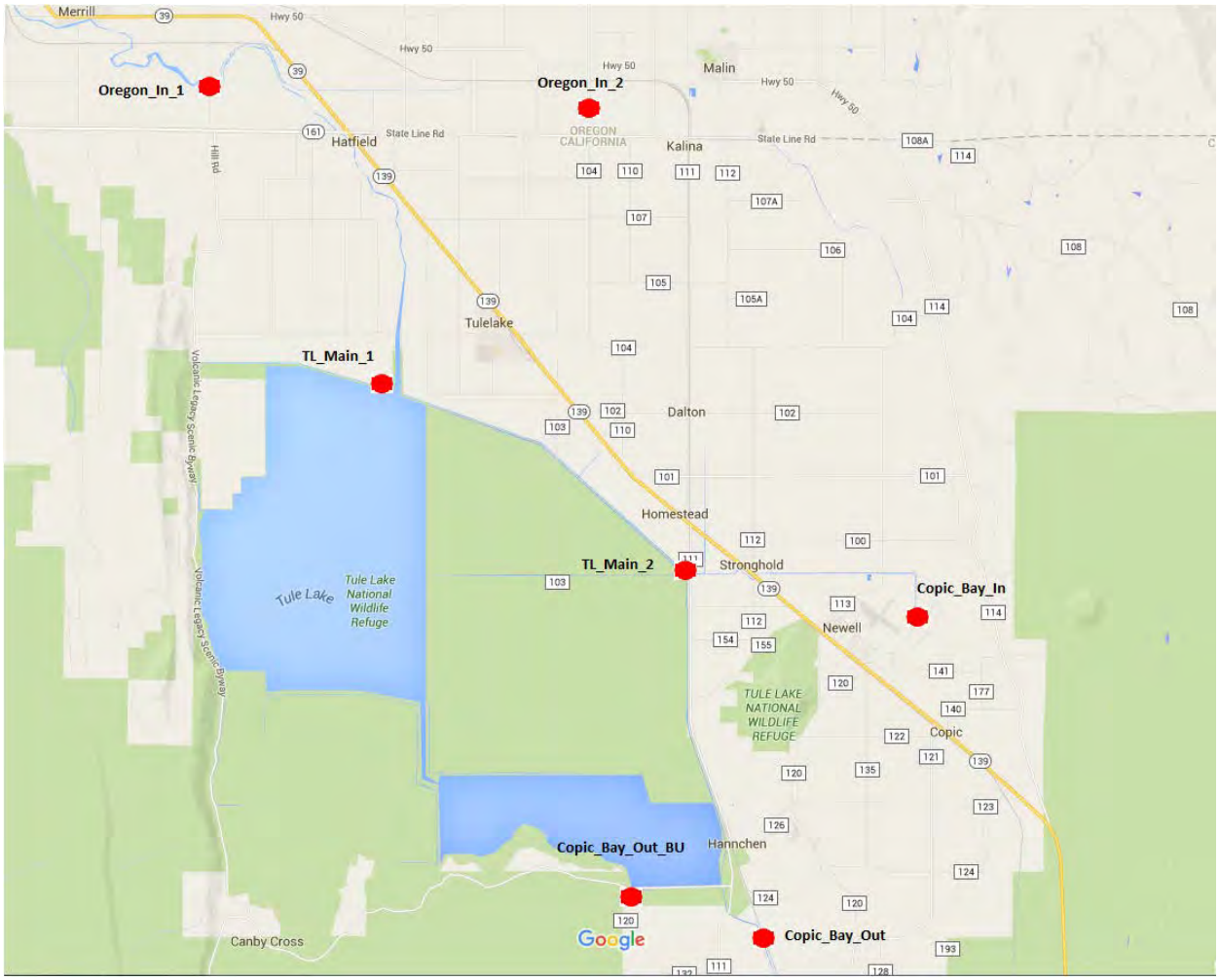

Figure 2. Monitoring sites of Tulelake in Modoc and Siskiyou Counties.

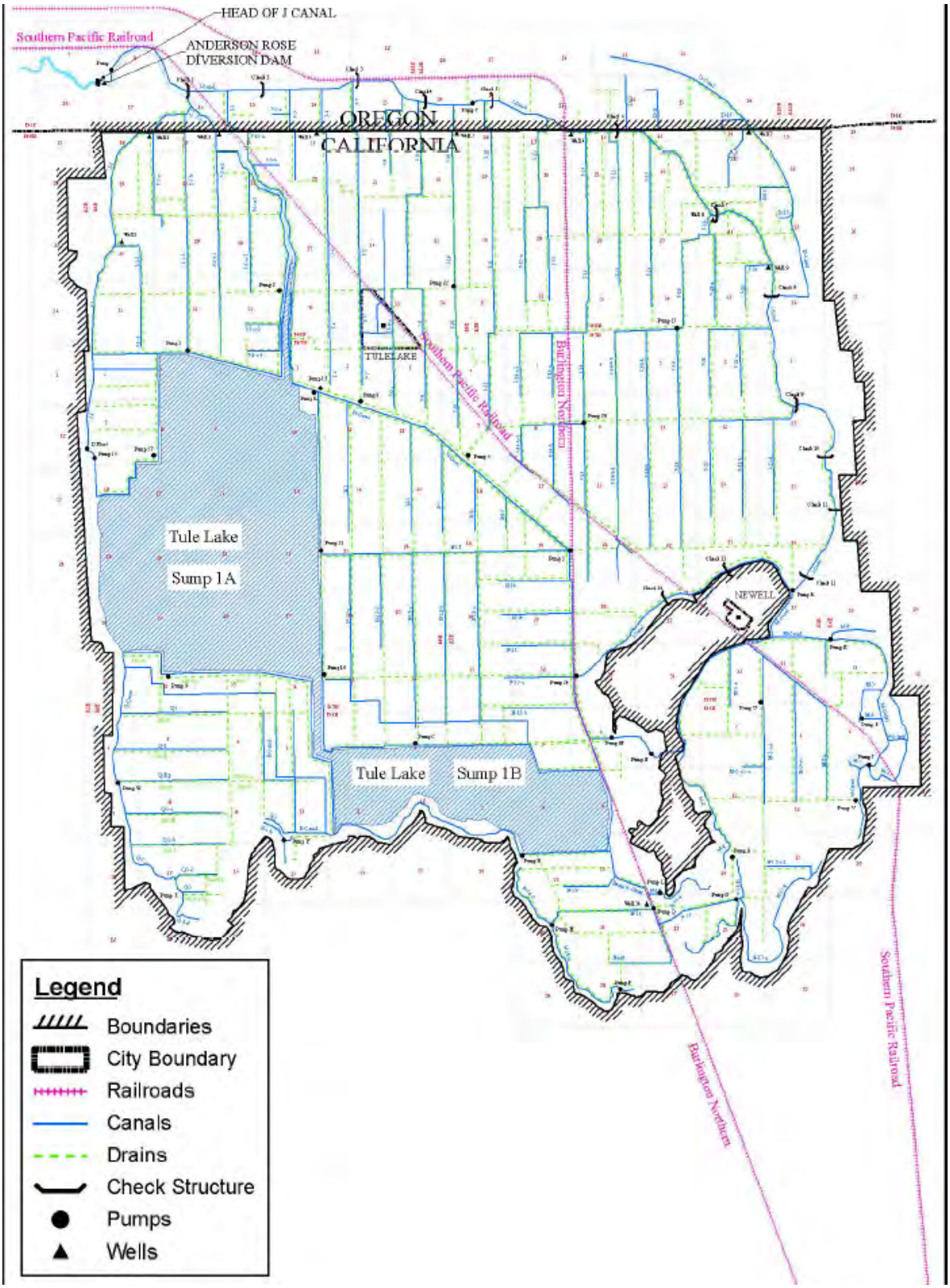

Figure 3. Representation of the Tulelake Irrigation District's drainage system.

Table 1. Pesticide prioritization model results (2012–2014 use) for surface water monitoring in Del Norte County (Smith River, CA).

Smith River Watershed, Drainage Area = 102 km^2 HUC12: 180101010404				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Model Recommended Monitoring**
PHORATE[(b)]	4	5	20	YES
CHLOROTHALONIL	5	4	20	NO[2]
PERMETHRIN	2	6	12	YES
DISULFOTON[(b)]	3	4	12	YES
DIURON[(a)]	3	4	12	YES
ETHOPROP[(b)]	3	3	9	YES
DDVP[(b)]	1	6	6	YES
CARBARYL	1	5	5	YES
IMIDACLOPRID	1	3	3	YES

[1)] Low use.
[2)] Short persistence defined by the prioritization model.
[3)] Low bioavailability in water-sediment system.
[4)] Analytical method not currently available.

[(a)] Pesticides that will be monitored for in May only
[(b)] Pesticides that will be monitored for in July only

Table 2. Pesticide prioritization model results (2012–1014 use) for surface water monitoring in Modoc and Siskiyou counties (Tulelake, CA).

Anderson Rose Diversion Dam-Lost River Watershed, Drainage Area = 96 km^2 HUC12: 180102040903				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Model Recommended Monitoring**
METRIBUZIN	4	4	20	YES
DIQUAT DIBROMIDE	2	5	10	NO[3]
2,4-D	3	3	9	YES
MCPA	1	2	2	YES
DICAMBA, DIMETHYLAMINE SALT	1	1	1	YES
Copic Bay Watershed, Drainage Area = 87 km^2 HUC12: 180102041109				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Model Recommended Monitoring**
METRIBUZIN	4	4	16	YES
DIMETHOATE	5	3	15	YES
CHLORPYRIFOS	2	6	12	YES
CHLOROTHALONIL	3	4	12	NO[2]
PENDIMETHALIN	3	4	12	YES
MALATHION	2	5	10	YES
PARAQUAT DICHLORIDE	2	5	10	YES
2,4-D	3	3	9	YES
METHOMYL	2	4	8	YES
MANCOZEB	2	3	6	NO[2]
OXYFLUORFEN	1	5	5	YES
HEXAZINONE	1	4	4	YES
MCPA	2	2	4	YES
Mills Creek-Tule Lake Valley Watershed, Drainage Area = 224 km^2 HUC12: 180102040906				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Model Recommended Monitoring**
METRIBUZIN	5	4	20	YES
CHLORPYRIFOS[(b)]	3	6	18	YES
PARAQUAT DICHLORIDE	3	5	15	YES[1,4]
2,4-D	5	3	15	YES
PENDIMETHALIN	3	4	12	YES
DIMETHOATE[(b)]	4	3	12	YES
MALATHION[(b)]	2	5	10	YES
DIQUAT DIBROMIDE	2	5	10	NO[3]
MANCOZEB	3	3	9	NO[2]
BENTAZON, SODIUM SALT	3	3	9	YES[4]

CHLOROTHALONIL	2	4	8	NO[2]
AZOXYSTROBIN	2	3	6	YES
OXYFLUORFEN	1	5	5	YES
MCPA	2	2	4	YES
The Panhandle Watershed, Drainage Area = 196 km^2 HUC12: 180102041001				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Model Recommended Monitoring**
PENDIMETHALIN	4	4	16	YES
METRIBUZIN	4	4	16	YES
DIMETHOATE[(b)]	5	3	15	YES
CHLORPYRIFOS[(b)]	2	6	12	YES
2,4-D	3	3	9	YES
MANCOZEB	3	3	9	NO[2]
CHLOROTHALONIL	2	4	8	NO[2]
AZOXYSTROBIN	2	3	6	YES
MCPA	3	2	6	YES
Tule Lake Valley-Lost River Watershed, Drainage Area = 167 km^2 HUC12: 180102040904				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Model Recommended Monitoring**
PENDIMETHALIN	5	4	20	YES
METRIBUZIN	5	4	20	YES
PARAQUAT DICHLORIDE	3	5	15	YES[1,4]
CHLORPYRIFOS[(b)]	2	6	12	YES
CHLOROTHALONIL	3	4	12	NO[2]
2,4-D	4	3	12	YES
DIMETHOATE[(b)]	4	3	12	YES
MALATHION[(b)]	2	5	10	YES
DIQUAT DIBROMIDE	2	5	10	NO[3]
MANCOZEB	3	3	9	NO[2]
BENTAZON, SODIUM SALT	3	3	9	YES[4]
DIURON	2	4	8	YES
IMIDACLOPRID[(a)]	2	3	6	YES
AZOXYSTROBIN	2	3	6	YES
OXAMYL	2	3	6	NO[2]
MCPA	3	2	6	YES

[1)] Low use.
[2)] Short persistence defined by the prioritization model.
[3)] Low bioavailability in water-sediment system.
[4)] Analytical method not currently available.

[(a)] Pesticides that will be monitored for in May only
[(b)] Pesticides that will be monitored for in July only

Table 3. Sampling site information for study 306 in 2016.

Site ID	Site Location	County	Watershed	Latitude	Longitude
SR_Morrison	Morrison Creek at S Fred D Haight Dr	Del Norte	Smith River	41.903200	-124.146505
SR_Ritmer	Ritmer Creek at Hwy 101			41.937004	-124.175233
Copic_Bay_In	Canal near County Rd 141	Modoc	Mills Creek-Tule Lake Valley	41.890151	-121.350086
Copic_Bay_Out	Canal at County Rd 131 (east) near railroad tracks		The Panhandle	41.817061	-121.394928
Copic_Bay_Out_BU	Wildlife Refuge entrance at Rim Rd		The Panhandle	41.830194	-121.435749
TL_Main_2	Main Drain at County Rd 111 and North Dike Rd East Side		Tule Lake Valley-Lost River and Mills Creek-Tule Lake Valley	41.900527	-121.418707
Oregon_In_1	J-Canal at Malone Road	Siskiyou	Anderson Rose Diversion Dam-Lost River	42.010562	-121.561211°
Oregon_In_2	J-Canal at Harpold Road		Tule Lake Valley-Lost River	42.003344	-121.447338
TL_Main_1	Main Drain at North Dike Rd West Side			41.941178	-121.506828

Table 4. Analytical chemical suites to be monitored for.

Phenoxy Screen (PX)	Organophosphates Screen (OP-U)	Triazine Long Screen(TR)	Dinitroaniline Screen (DN)	Imidacloprid (IMD)
2,4-D Dicamba MCPA Triclopyr	Chlorpyrifos DDVP (Dichlorvos) Dimethoate Disulfoton Ethoprop Fenamiphos Malathion Methidathion Methyl Parathion Thimet (Phorate)	Atrazine ACET Bromacil DACT DEA Diuron Hexazinone Metribuzin Prometon Prometryn Norflurazon Simazine	Benfluralin Ethalfluralin Oryzalin Oxyfluorfen Pendimethalin Prodiamine Trifluralin	Imidacloprid

Table 5. Analytical cost estimate for agricultural samples collected in Northern California.

Analytical Screen	Total samples*	Cost/sample	Cost Estimate
Phenoxy (PX)	18	690	12,420
Organophosphates (OP-U)	9	780	7,020
Triazines long (TR)	15	864	12,960
Dinitroanilines (DN)	13	960	12,480
Imidacloprid (IMD)	11	600	6,600
Metribuzin lab verification	15	540	8,100
Total			**$59,580**

*QC samples included in the total number of samples

Appendix 1. CDFA analytical method details.

Analytical Suite	Chemical	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Phenoxy (PX) Instrument: GC/MS Method#: EMON-SM-05-012	2,4-D	0.015	0.05
	Dicamba	0.017	0.05
	MCPA	0.022	0.05
	Triclopyr	0.020	0.05
Organophosphates (OP) Instrument: GC/FPD/MS Method#: EMON-SM-46	Azinphos-methyl	0.0099	0.05
	Chlorpyrifos	0.0109	0.04
	Diazinon	0.0110	0.04
	Dichlorvos	0.0098	0.05
	Dimethoate	0.0079	0.04
	Disulfoton	0.0093	0.04
	Ethoprophos	0.0098	0.05
	Fenamiphos	0.0125	0.05
	Fonofos	0.0080	0.04
	Malathion	0.0117	0.04
	Methidathion	0.0111	0.05
	Methyl Parathion	0.0080	0.03
	Phorate	0.0083	0.05
	Propenofos	0.0114	0.05
	Tribufos (DEF)	0.0142	0.05
Triazines (TR) Instrument: LC/MS Method#: EM 62.9	Atrazine	0.016	0.05
	Bromacil	0.031	0.05
	Cyanazine	0.013	0.05
	Diuron	0.022	0.05
	Hexazinone	0.040	0.05
	Metribuzin	0.025	0.05
	Norflurazon	0.019	0.05
	Prometon	0.016	0.05
	Simazine	0.013	0.05
	Prometryn	0.016	0.05
	Deethyl Atrazine (DEA)	0.010	0.05
	Deisopropyl Atrazine (ACET)	0.030	0.05
	Diamino Chlorotraizine (DACT)	0.016	0.05
Dinitroanilines (DN) Instrument: GC/MS/MS or LC/MS Method#: EMON-SM-05-06	Benfluralin	0.0135	0.05
	Ethalfluralin	0.0160	0.05
	Oryzalin	0.0210	0.05
	Oxyfluorfen	0.0166	0.05
	Pendimethalin	0.0155	0.05
	Prodiamine	0.0162	0.05
	Trifluralin	0.0147	0.05
Imidacloprid Instrument: LC/MS Method#: EMON-SM-05-023	Imidacloprid	0.0394	0.05