Surface Water Monitoring for Rainy Season Use Herbicides in 2009, California, USA

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Abstract Several herbicides with low toxicity benchmarks have high use during California's rainy season. In 2009 the California Department of Pesticide Regulation initiated a monitoring study at the end of seasonal use to determine the presence of these herbicides in surface water. Water samples were collected from 10 sites in Napa, Sonoma, and Yolo Counties and analyzed for dinitroaniline, diphenyl ether, and photosynthetic inhibitor herbicides. Diuron was the most frequently detected herbicide (52%), followed by hexazinone (43%), simazine (33%), oryzalin (24%), oxyfluorfen (19%), pendimethalin (14%), bromacil (10%), and trifluralin (5%). Diuron and hexazinone were detected with about equal frequency in February (high rainfall) and March (no rain 4-5 days prior to sampling); all other herbicides were only detected during February sampling. Hexazinone, pendimethalin, and trifluralin detections were attributed to agricultural use, bromacil detections were attribute to non-agricultural use, and diuron, oryzalin, oxyfluorfen, and simazine detections were attributed to both uses. Diuron and oxyfluorfen were detected above their United States Environmental Protection Agency's Aquatic Life Benchmarks.

Keywords Diuron – Oxyfluorfen – Hexazinone – Simazine – Surface Water

Introduction

Herbicides account for the largest use of synthetic pesticides[1] applied in California. The top 100 pesticides listed in the California Department of Pesticide Regulation's (CDPR) 2008 – 2009 pesticide use reports included more than 7.5 million kg active ingredient (ai) of herbicides. Excluding glyphosate's 3.1 million kg ai use, herbicide use is still more than double that of insecticides and fungicides combined (CDPR 2010). A subset of the herbicides in the top 100 list has high use in California's rainy season. In an analysis by Starner (2008), diuron, oryzalin, oxyfluorfen, pendimethalin, simazine, and trifluralin warrant monitoring based on high use during California's rainy season and high toxicity (low U.S. Environmental Protection Agency (EPA) aquatic benchmark). There have been numerous monitoring studies in California with diuron, pendimethalin, simazine, and trifluralin whereas monitoring for oryzalin and oxyfluorfen has been more limited (Ensminger 2010).

Because of oxyfluorfen's high use, high toxicity, and limited monitoring, it was the focus of this study. In California, oxyfluorfen is mainly used to control grass and broadleaf weeds in tree crops (a total of 28 crops, but mainly almonds), grapes, and rights of way. In tree crops and vines, oxyfluorfen is frequently applied preemergence to bare soil when trees are dormant; greater than 75% of oxyfluorfen applications occurred in October through February (Table 1). Similar to other herbicides applied in the rainy season, a subsequent rainfall is needed to incorporate it into the soil. Oxyfluorfen strongly adsorbs to soil but can be transported to surface waters (Riley et al. 1994, US EPA 2002). Oxyfluorfen is a potential surface water concern because of its low U.S. EPA aquatic benchmark (0.29 μL^{-1} to non-vascular plants; US EPA 2002, 2012). In 2009, during the rainy season, CDPR conducted a surface water monitoring program for oxyfluorfen. Photosynthetic inhibitor herbicides and dinitroaniline herbicides were included in this

[1] Organic synthetic chemicals used in crop agriculture, excluding fumigants and surfactants.

study because these herbicides were in the same chemical analysis or have high rainy season use with toxicity concerns (Table 1; see Appendix Table 1 for herbicide characteristics). The objective of this study was to document the occurrence and concentrations of these herbicides in three counties of California, to assess their potential for aquatic toxicity using U.S. EPA aquatic life benchmarks, and to compare detected herbicides to reported pesticide use in California.

Material and Methods

Surface water monitoring was conducted at ten sites in Napa, Sonoma, and Yolo Counties (Table 2; Appendix Figures 1-3). Five of the sites were rivers or larger creeks; the remaining sites were small agricultural streams in Yolo County. The sampled water bodies primarily receive input from agricultural areas. Location of the sites and the timing of sample collection were based on oxyfluorfen seasonal use. During February and March of 2009, water samples were collected during rainstorm and nonstorm events. Water samples were collected with an extendable pole or by hand directly into 1-L glass amber bottles, sealed with Teflon®-lined lids, and stored on wet ice for transport. Upon arrival at the laboratory, water samples were refrigerated (4°C) until extracted for chemical analysis. Water physiochemical properties (dissolved oxygen, electrical conductivity, pH, turbidity, and temperature; Appendix Table 2) were measured *in situ* during all sampling events with a calibrated YSI 6920 V2 meter (YSI Incorporated, Yellow Springs, OH, USA) (Doo and He 2008). The California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry conducted the chemical analysis. Photosynthetic inhibitor herbicides were eluted with 5% ammonium hydroxide in methanol, filtered, concentrated, reconstituted in 1:3 methanol/water and analyzed by APCI/LC/MS/MS. Oxyfluorfen and dinitroaniline herbicides were extracted with methylene chloride, passed through sodium sulfate, evaporated on a rotary evaporator, and concentrated to a final volume of 1 mL. One-half of the volume was injected into a GCMS-SIM (gas chromatography with mass spectrometer operated in the single ion monitoring mode) or GCMS/MS. The remaining 0.5 mL was evaporated to dryness, brought up to a final volume of 0.5 mL with methanol, and analyzed for oryzalin on LCMS. The reporting limit for all herbicides was 0.05 $\mu g\ L^{-1}$; method detection limits were between 0.005 – 0.04 $\mu g\ L^{-1}$ CDFA 2007, 2009).

Quality control for this study followed CDPR guidelines (Segawa 1995). Laboratory quality control consisted of laboratory reagent blanks, matrix spikes, blind spikes, and surrogate spikes. Laboratory blanks and matrix spikes were analyzed in each extraction set. There were no detections in any of the 60 reagent blanks. Of the 60 matrix spikes, recoveries ranged from 62%-114% (Appendix Table 3). Propazine was added as a surrogate spike in the photosynthetic inhibitor analyses; recovery of the 25 surrogates ranged from 73%-92% (Appendix Table 4). One blind spike (benfluralin) recovery (85%) was acceptable. Field QC comprised of field blanks and duplicates (combined, 15% of all samples). There were no detections in the field blanks and there was less than 12% difference in the field duplicates.

Analytical results were compared to the US EPA Office of Pesticide Programs' Aquatic Life Benchmarks (US EPA 2012). Benchmark values are based on the most sensitive aquatic toxicity data for each pesticide and are estimates of the concentrations below which pesticides are not expected to harm aquatic life. These values assist in identifying pesticides, and monitoring sites, that may warrant further research (US EPA 2012). For this analysis, the lowest benchmark reported by the US EPA was used. If a lower water quality criteria value exists, the results were compared to this value (Tjeerdema 2012). Results were also compared to pesticide use reporting (CDPR 2010). CDPR requires pesticide applicators to report most pesticide uses in California. This includes production agriculture (agriculture commodities including rangeland and pastures), non-production agriculture (parks, golf courses, cemeteries, and along roadside and railroad rights of way), and non-agricultural pesticide uses (outdoor industrial and institutional uses for pesticides listed in section 6800(b) of the California Code of Regulations and structural pest control). Homeowner use and most industrial and institutional use are not reported. Production agricultural pesticide use is reported on a one-mile section basis using the meridian-range-township-section designation whereas non-production agriculture and non-agricultural pesticide use is only reported by county (CDPR 2010). For the purposes of this review, non-production agriculture and non-agricultural uses will be discussed together as non-agricultural pesticide use and production agriculture will be referred to as agriculture use; use period for this analysis was from October 2008 through February 2009.

Results and Discussion

Herbicides were detected at all sites except one (site Y6). Across all sampling sites and dates, a median of two herbicides were detected per collected water sample, ranging between 0 – 7 herbicides. Diuron was the most frequently detected herbicide, with a 52% detection frequency for the entire study. Hexazinone was second most frequently detected (43%), followed by simazine (33%), oryzalin (24%), oxyfluorfen (19%), pendimethalin (14%), bromacil (10%), and trifluralin (5%) (Figure 1). These detection frequencies are similar to statewide detection frequencies compiled in CDPR's surface water database except for hexazinone and oryzalin, which were much higher in this study (Ensminger 2010). Diuron and hexazinone had similar number of detections in February and March but simazine, oryzalin, oxyfluorfen, pendimethalin, bromacil, and trifluralin were only detected in February. These latter herbicides were detected during or immediately after rainfall. In February, more rain fell during the week preceding sampling (up to 139 mm rainfall, with some rain most days) than in the March sampling (up to 27 mm rainfall, no rain four to five days prior to sampling). The rainfall differences may account for the differences in detections; pesticide detection frequency increases with rainfall (Ensminger et al. 2012). More detailed data is available (analytical data, Appendix Table 5; rainfall data, Appendix Figure 4).

Bromacil, hexazinone, oxyfluorfen, pendimethalin, and trifluralin were only detected in agricultural tributary streams whereas diuron, simazine, and oryzalin were detected in both tributary streams and mainstem rivers. All mainstem rivers (except site Y6) were in Sonoma and Napa Counties and all tributary streams were located in Yolo County.

Although dilution in the larger water bodies can account for fewer detections (Spurlock 2002) pesticide use patterns also influence detections. Of the five herbicides detected in tributary streams in Yolo County, bromacil, hexazinone, and trifluralin only had reported use in Yolo County. For hexazinone and trifluralin, this was mostly agricultural use. Pendimethalin had both agricultural and non-agricultural use in all three counties, but there was little agricultural use near the Napa and Sonoma sampling sites and little non-agricultural use in Yolo County (Figure 2 and Table 3). Thus for hexazinone, pendimethalin, and trifluralin it seems likely that their detections arose from agricultural use. However, non-agricultural use can contribute to runoff so its potential cannot be disregarded (Powell et al. 1996; DaSilva and Troiano 2010). Bromacil was strictly non-agricultural use. Because this type of use is only reported to the county level, it is difficult to ascertain how close to the sampling sites the bromacil applications occurred or how the limited use of bromacil resulted in two detections.

With oxyfluorfen, all three counties had moderate to high agricultural use near, or upstream of, the sampling sites (Figure 2). However, oxyfluorfen was only detected in Yolo County. Yolo County did have much higher county wide non-agricultural use than did Napa and Sonoma Counties and this use, as well as the agricultural use, may have contributed to the detections. Based on overall use in the three counties we would have expected more detections, especially in Napa County where the use is heavily concentrated along the Napa River. Recent studies have reported higher detections of oxyfluorfen in Monterey, Santa Barbara, and San Luis Obispo Counties but not in Imperial County (Starner 2011; Smalling and Orlando 2011). There may have been various reasons for the absence of detections, as the lack of oxyfluorfen runoff during sampling events due to application timings, dilution effects in Napa River and Sonoma Creek, different reporting limits, or watershed differences.

Diuron, oryzalin, and simazine were detected in tributary streams and mainstem rivers; these detections were likely from mixed use. There were no diuron detections, and very little use, in Sonoma County (Figure 3 and Table 3). Diuron was detected four times in Napa County. Except for two locations distant from the sampling sites (about 25 km and in a different watershed; Figure 3), Napa County only had non-agricultural use (2143 kg ai). This non-agricultural use likely contributed to the detections in Napa County; diuron applied to roadsides can be detected in surface water (Powell et al. 1996; DaSilva and Troiano 2010). In Yolo County, diuron had some agricultural use near the sampling sites (Figure 3). In addition, there was moderate county-wide non-agriculture use (369 kg ai) that may have contributed to the detections (Table 2). Oryzalin was detected at both sites in Sonoma County and at two sites in Yolo County. There was some, albeit minor, agricultural use in both of these counties that may have accounted for these detections. Oryzalin also had county wide non-agricultural use in these counties which also may have contributed to the detections. Like oxyfluorfen, oryzalin had use in Napa County along the Napa River (Figure 3), but was not detected. For simazine, all three counties had agricultural use near or upstream of the sampling sites as well as county-wide non-agricultural use (minimal in Sonoma County). Both types of use could have contributed to the detections.

Comparing to the US EPA aquatic life benchmarks, two diuron detections (10%) and one oxyfluorfen detection (5%) were above their benchmarks for non-vascular plants (US EPA 2012). The US EPA benchmark for diuron is 2.4 µg L^{-1}; the two exceedances were 4.6 and 4.1 µg L^{-1}. These were also exceedances of the recent diuron water quality criteria (1.3 µg L^{-1}, four day average; Fojut et al. 2012). The US EPA benchmark for oxyfluorfen is 0.29 µg L^{-1}; the one exceedance was 1.14 µg L^{-1}. These exceedances occurred in Yolo County at sites Y4 (diuron) and Y5 (diuron, oxyfluorfen), during the February sampling. Both of these sites are small agricultural creeks that run alongside agricultural fields.

Statewide, many of the herbicides in this study are some of the most widely used herbicides in California, with up to 760,000 kg ai annual use. Much of this use is during the rainy season. Based on results from this study, these herbicides move offsite into surface waters; in many cases, rainfall accentuates this transport. Intermittently surface waters contain herbicides at concentrations that may be harmful to aquatic organisms. In addition, little is known about toxicological interactions among multiple stressors (herbicides, insecticides, fungicides, and other contaminates) as many of these interactions are synergistic (Lydy and Belden 2006). Additional herbicide monitoring of high use herbicides with the potential for aquatic toxicity is warranted to determine the scope of surface water contamination, as is research on the aquatic toxicity of pesticide mixtures containing these herbicides.

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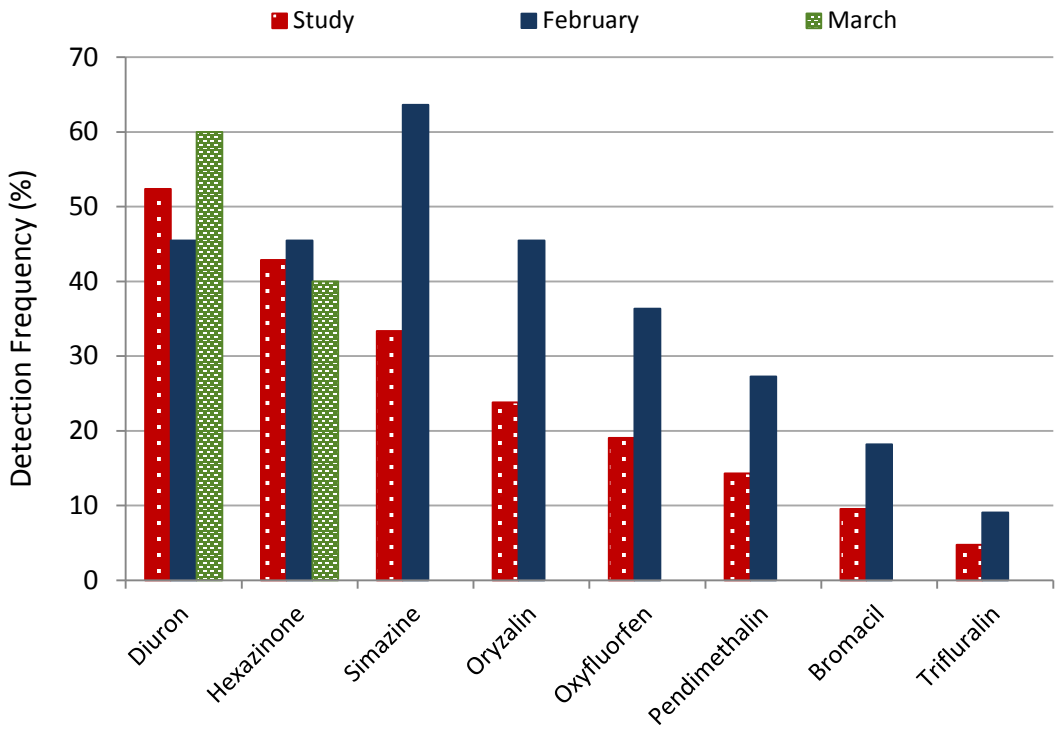


Figure 1 Herbicide detection frequencies for the study compared to the February and the March 2009 sampling events (February 15 and 19 sampling dates were compiled and reported as one sampling event (February) as both dates received rainfall)

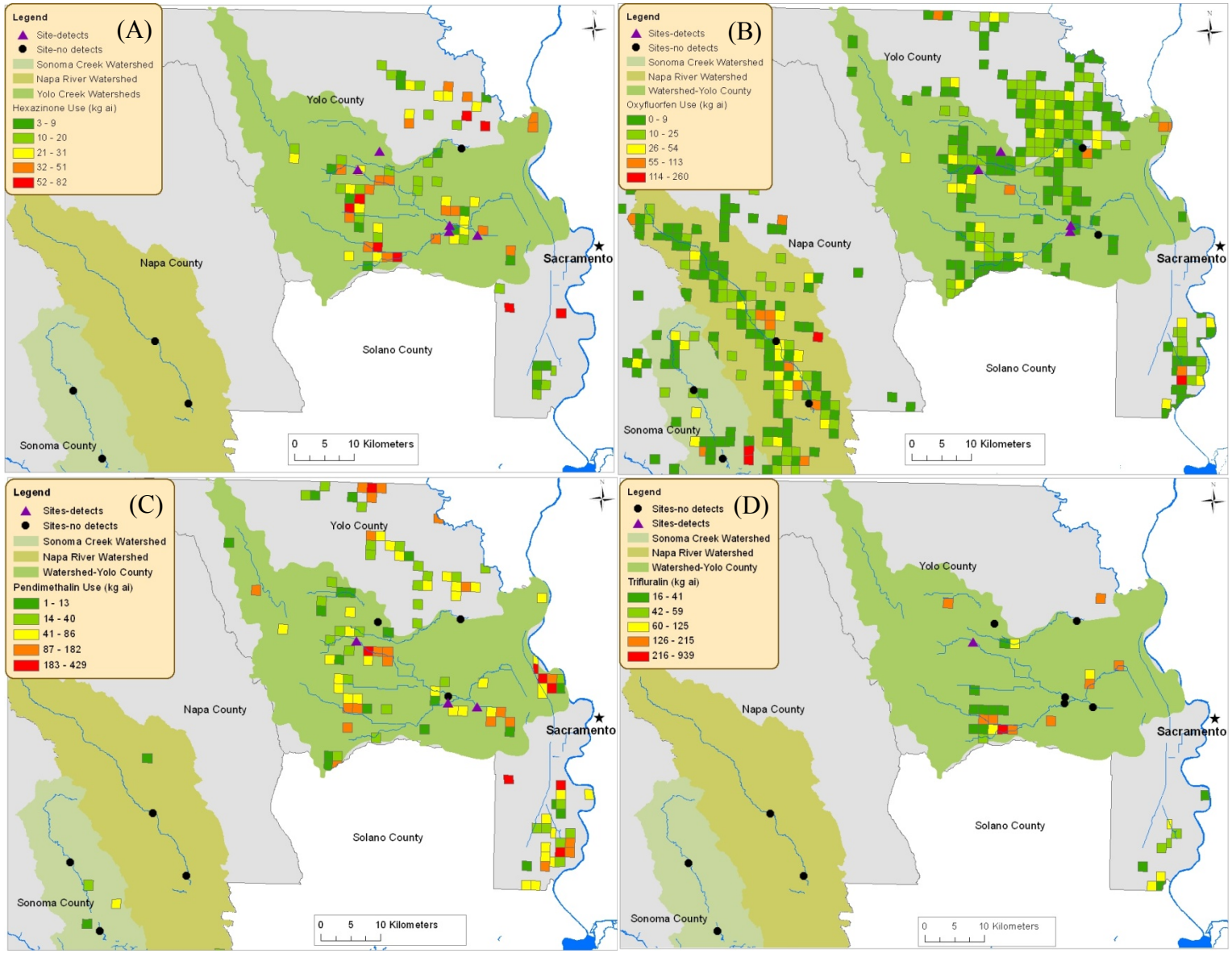


Figure 2 Reported agricultural herbicide use of hexazinone (A), oxyfluorfen (B), pendimethalin (C), and trifluralin (D) in Napa, Sonoma, and Yolo Counties (there in no reported bromacil use)

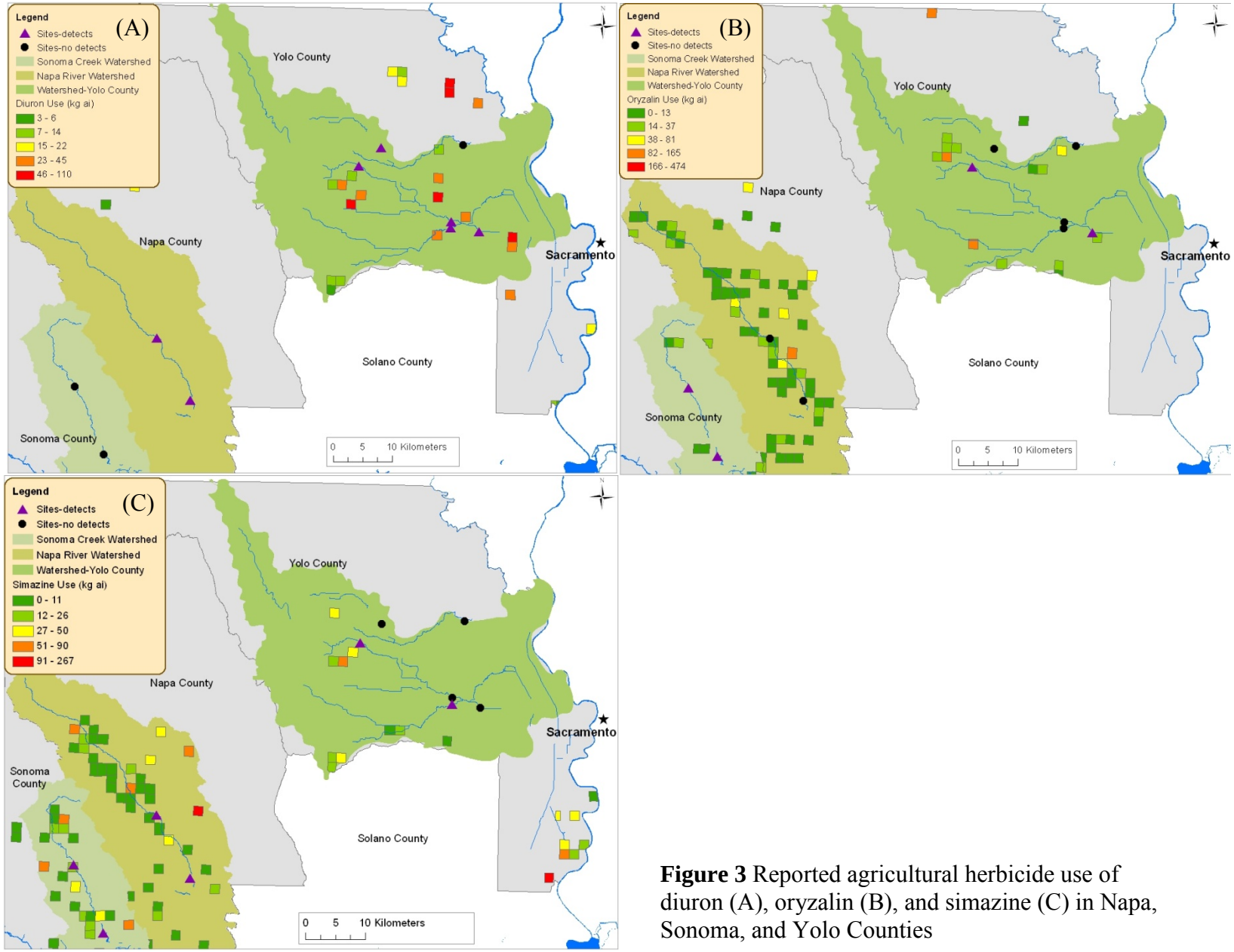


Figure 3 Reported agricultural herbicide use of diuron (A), oryzalin (B), and simazine (C) in Napa, Sonoma, and Yolo Counties

Table 1 Rainy season herbicide use in California and lowest U.S. EPA aquatic benchmark for herbicides in the study[a]

Herbicide	Pesticide Use (kg ai)[b] Year Total	Rainy Season	Lowest benchmark (μL^{-1})[c]
Bromacil	22,867	16,644	6.8
Diuron	282,512	242,065	2.4
Hexazinone	48,445	44,956	7.0
Oryzalin	204,377	155,995	15.4
Oxyfluorfen	422,555	335,765	0.29
Pendimethalin	768,215	560,788	5.2
Simazine	189,691	149,610	36.0
Trifluralin	243,959	63,619	1.14

[a]Year total is for 2008 water year (October 2008 – September 2009). Rainy season use: October 2008, November 2008, December 2008, January 2009, February 2009.

[b]CDPR 2010

[c]US EPA 2012

Table 2 Monitoring sites in Napa, Sonoma, and Yolo counties, California USA

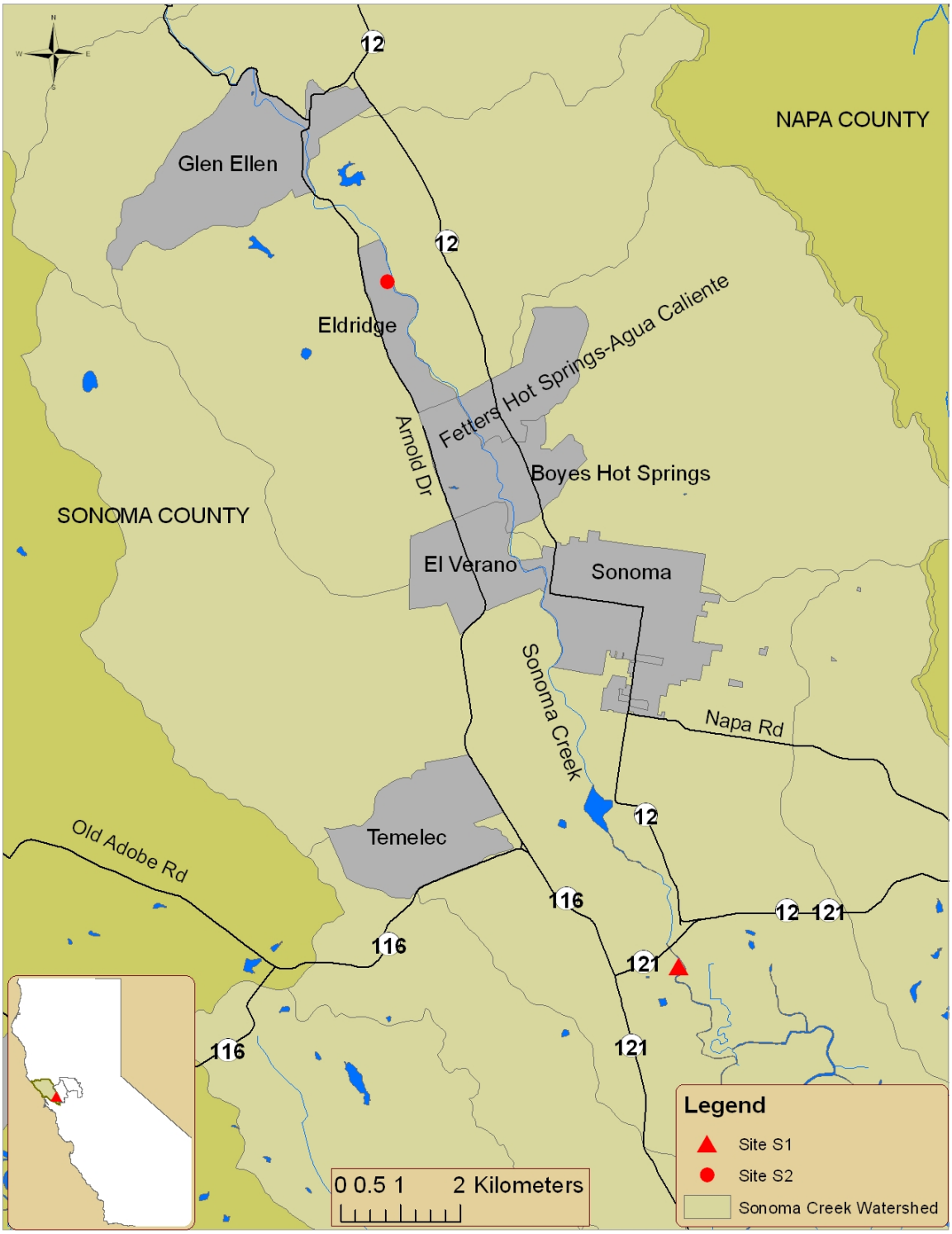
Site Code	Site Type[a]	Description	County	Latitude	Longitude
S1	R	Sonoma Creek near Highway 121	Sonoma	38.23791	-122.44811
S2	R	Sonoma Creek at Madrone Rd (Eldridge, CA)	Sonoma	38.34009	-122.50755
N1	R	Napa River at Trancas Street (Napa, CA)	Napa	38.32462	-122.28398
N2	R	Napa River at Yountville Cross Rd	Napa	38.41816	-122.3513
Y1	T	Dry Slough at County Rd 99 (Plainfield, CA)	Yolo	38.59532	-121.78574
Y2	T	Willow Slough at County Rd 99 (Plainfield, CA)	Yolo	38.60468	-121.78503
Y3	T	Willow Slough at County Rd 102	Yolo	38.59021	-121.73042
Y4	T	County Rd 89 and Highway 16	Yolo	38.68633	-121.96621
Y5	T	County Rd 19 near County Rd 91B	Yolo	38.71466	-121.92443
Y6	R	Cache Creek at Highway 113	Yolo	38.72107	-121.76448

[a]R, river; T, tributary stream

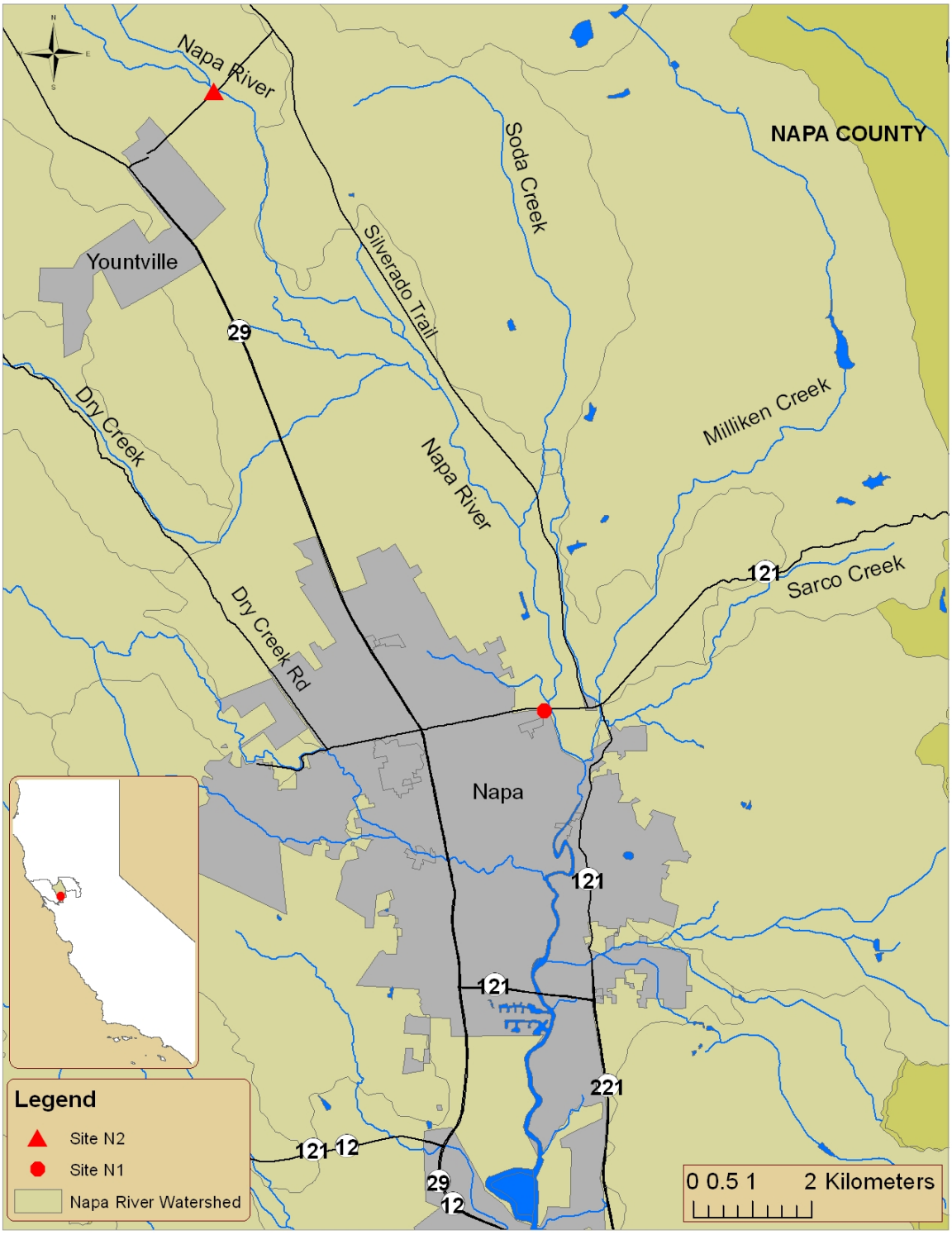
Table 3 Non-agriculture use (kg ai; includes non-production agriculture) of herbicides detected in the study (October 2008 through February 2009)

Herbicide	Napa	County Sonoma	Yolo
Bromacil	0	0	11
Diuron	2143	205	815
Hexazinone	0	0	1
Oryzalin	57	119	279
Oxyfluorfen	5	32	426
Pendimethalin	171	248	20
Simazine	195	2	76
Trifluralin	0	0	19

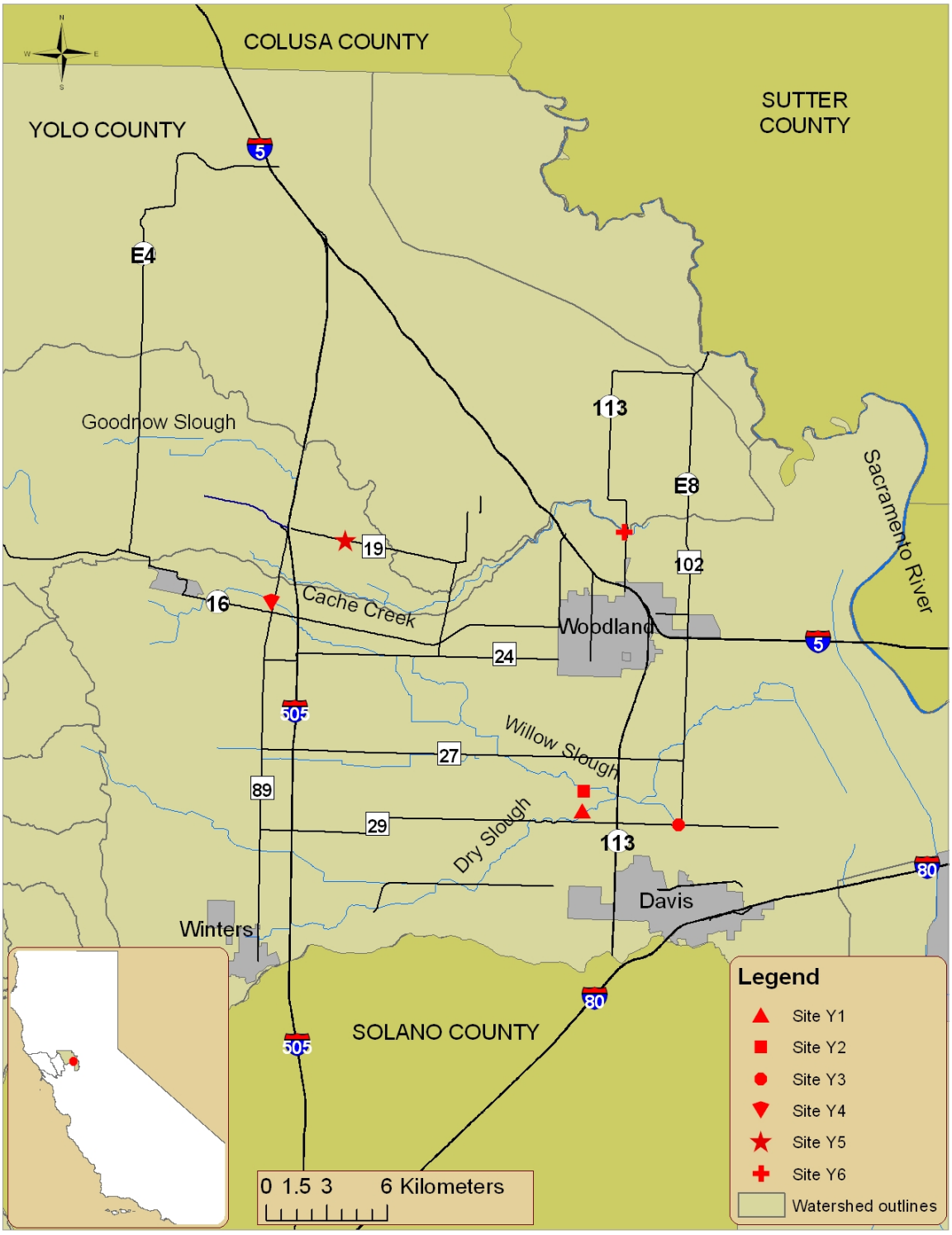
Appendices



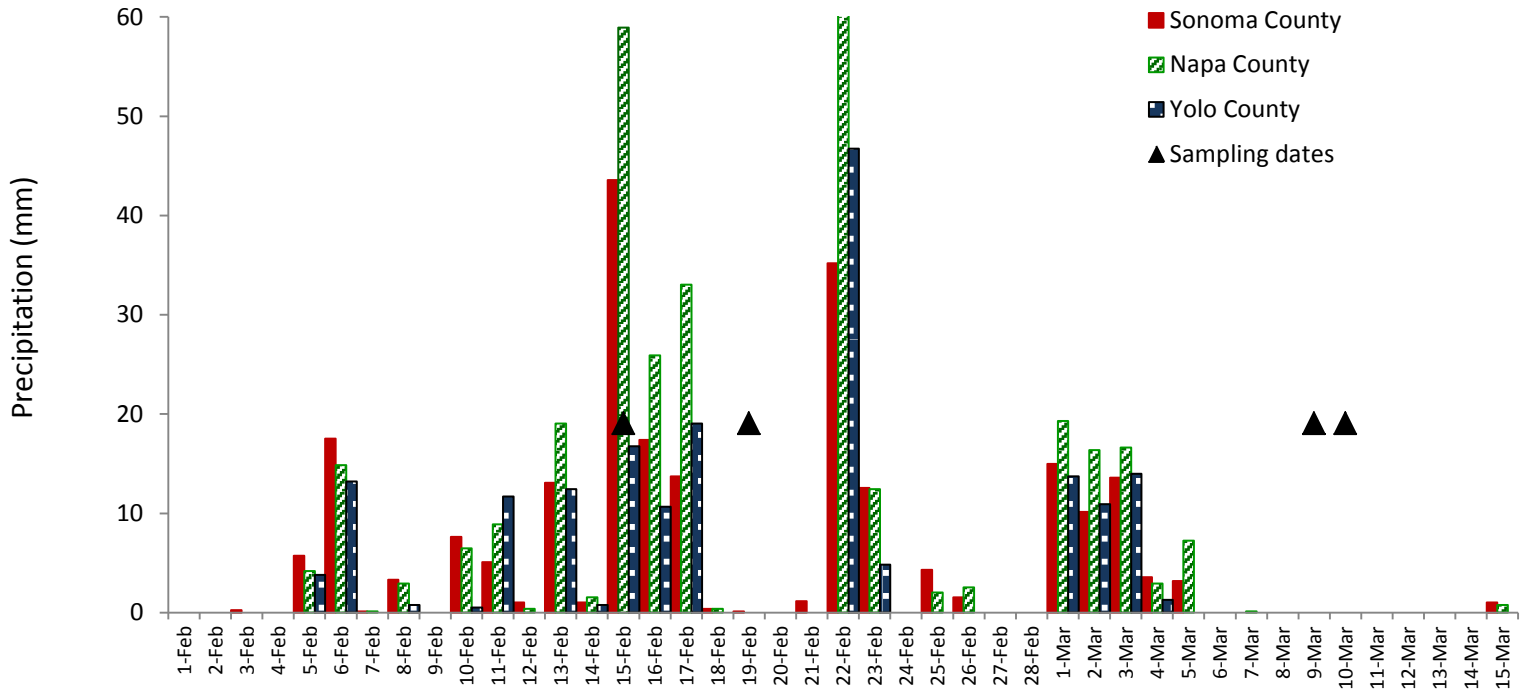
Appendix Figure 1 Sampling sites S1 and S2 in Sonoma County



Appendix Figure 2 Sampling sites N1 and N2 in Napa County



Appendix Figure 3 Sampling sites Yolo County



Appendix Figure 4 Precipitation totals for Sonoma and Yolo Counties, February 1 – March 15, 2009. Yolo rainfall was recorded at Davis, California, Sonoma rainfall was recorded at Santa Rosa and Petaluma, California, and Napa rainfall was recorded at Oakville and Carneros, CA (http://www.cimis.water.ca.gov/cimis/frontLogonData.do)

Appendix Table 1 Herbicide characteristics of detected herbicides[a]

Herbicide Group/ Herbicide	Common Trade Names	Application[b]	Main Use (California)	Weed Control
Dinitroaniline				
Oryzalin	Surflan A.S. Oryzalin 4 A.S.	PRE	Nut crops (almonds, pistachio, walnut), grapes, rights of way	Annual grass and broadleaf weeds
Pendimethalin	Prowl H2O Herbicide	PRE PPI	Nut crops (almonds, pistachio, walnut), grapes, cotton	Annual grass and small seeded broadleaf weeds
Trifluralin	Treflan (TR-10, 4D), Triflurex HFP, Trifluralin HF, Tenkoz Trifluralin 4 EC	PPI	Alfalfa, almond, apricots, vegetables	Annual grass and small seeded broadleaf weeds
Diphenylether				
Oxyfluorfen	Goal 2XL, Goaltender, Goal 2XL, Galigan 2E Oxfluorfen, Pindar GT	PRE POST-directed	Nut crops (almonds, pistachio, walnut), grapes	Broadleaf weeds
Photosynthesis Inhibitor				
Bromacil	Krovar I DF Herbicide[c]	PRE	Rights of ways, oranges, landscape maintenance, tangerines	Annual and perennial grasses, sedges, and broadleaf weeds
Diuron	Karmex (XP, DF), Krovar I DF[c], (Dupont) Direx (4L, 80 DF), (Drexel) Diuron (80, 4L)	PRE POST-directed	Rights of ways, oranges, alfalfa, landscape maintenance, tangerines, walnuts, grapes	Annual broadleaf and grass weeds
Hexazinone	Dupont Velpar (ULW, DF, L) herbicide	PRE POST	Alfalfa, forest trees, rights of way	Annual and perennial broadleaf and grass weeds
Simazine	Princep Caliber 90, Simazine 90 DF, Sim-trol (90 DF, 4L), Princep 4L, Drexel Simazine 4L	PRE	Oranges, grapes, nut crop (almond, walnut)	Annual broadleaf and grass weeds

[a]CDPR 2010; Vencill 2002

[b]PRE, preemergence; PPI, preplant incorporated into the soil; POST, postemergence

[c]Contains both bromacil and diuron

Appendix Table 2 Field water quality measurements at the time of sampling

Sampling Date	Site	Time	pH	DO (mg L^{-1})	EC (µS cm^{-1})	Water Temp (ºC)	Turbidity (NTU)
2/15/2009	S2	15:10	7.51	10.79	0.126	8.79	133.1
2/15/2009	Y1	9:30	7.93	8.88	0.241	7.49	118.0
2/15/2009	Y2	10:15	8.59	11.66	0.748	8.03	30.2
2/15/2009	Y3	9:15	8.39	10.01	1.319	9.13	15.9
2/15/2009	Y4	12:15	8.36	10.52	0.756	8.79	121.4
2/15/2009	Y5	11:45	8.36	10.89	0.324	8.32	236.0
2/15/2009	Y6	10:45	8.55	11.14	0.663	8.47	8.0
2/19/2009	N1	11:00	7.61	9.87	0.235	10.18	18.0
2/19/2009	N2	9:30	7.64	10.14	0.245	9.7	17.1
2/19/2009	S1	13:40	7.58	9.72	0.212	9.83	15.5
2/19/2009	S2	12:50	7.81	10.41	0.202	9.94	15.1
3/9/2009	N1	15:00	7.62	9.8	0.272	11.83	3.9
3/9/2009	N2	14:20	7.58	9.91	0.273	11.68	3.8
3/9/2009	S1	12:25	7.53	9.76	0.29	9.98	3.8
3/9/2009	S2	11:20	7.88	10.7	0.214	9.46	4.7
3/10/2009	Y1	12:21	8.03	10.43	0.376	9.43	56.7
3/10/2009	Y2	12:50	8.39	11.49	0.851	12.43	21.1
3/10/2009	Y3	14:02	8.22	10.03	0.802	13.04	28.3
3/10/2009	Y4	9:50	8.25	--	0.721	8.34	33.8
3/10/2009	Y5	10:35	7.64	7.29	0.623	7.12	40.3
3/10/2009	Y6	11:16	8.36	10.91	0.706	10.3	8.0

Appendix Table 3 Recovery of matrix spikes in surface water samples (there were no detections in any of the 60 blank spikes)

QC Sample Number	Extraction Date	Analysis Date	CDFA EMON Method Number	Analyte	Spike Level (ppb)	Result (ppb)	Recovery (%)
20082173	2/19/2009	2/19/2009	05-006	Benfluralin	0.15	0.117	78.0
20082173	2/19/2009	2/19/2009	05-006	Ethalfluralin	0.15	0.120	80.0
20082173	2/19/2009	2/19/2009	05-006	Oryzalin	0.15	0.093	62.0
20082173	2/19/2009	2/19/2009	05-006	Oxyfluorfen	0.15	0.129	86.0
20082173	2/19/2009	2/19/2009	05-006	Pendimethalin	0.15	0.128	85.3
20082173	2/19/2009	2/19/2009	05-006	Prodiamine	0.15	0.118	78.7
20082173	2/19/2009	2/19/2009	05-006	Trifluralin	0.15	0.118	78.7
20082210	2/24/2009	2/26/2009	62.9	ACET[a]	0.2	0.170	85.0
20082210	2/24/2009	2/26/2009	62.9	Atrazine	0.2	0.163	81.5
20082210	2/24/2009	2/26/2009	62.9	Bromacil	0.2	0.212	106
20082210	2/24/2009	2/26/2009	62.9	DACT[a]	0.2	0.175	87.5
20082210	2/24/2009	2/26/2009	62.9	DEA[a]	0.2	0.172	86.0
20082210	2/24/2009	2/26/2009	62.9	Diuron	0.2	0.209	105
20082210	2/24/2009	2/26/2009	62.9	Hexazinone	0.2	0.209	105
20082210	2/24/2009	2/26/2009	62.9	Metribuzin	0.2	0.203	102
20082210	2/24/2009	2/26/2009	62.9	Norflurazon	0.2	0.197	98.5
20082210	2/24/2009	2/26/2009	62.9	Prometon	0.2	0.176	88.0
20082210	2/24/2009	2/26/2009	62.9	Prometryn	0.2	0.174	87.0
20082210	2/24/2009	2/26/2009	62.9	Propazine	0.2	0.167	83.5
20082210	2/24/2009	2/26/2009	62.9	Simazine	0.2	0.182	91.0
20082222	2/24/2009	2/26/2009	62.9	ACET	0.2	0.195	97.5
20082222	2/24/2009	2/26/2009	62.9	Atrazine	0.2	0.181	90.5
20082222	2/24/2009	2/26/2009	62.9	Bromacil	0.2	0.220	110
20082222	2/24/2009	2/26/2009	62.9	DACT	0.2	0.190	95.0
20082222	2/24/2009	2/26/2009	62.9	DEA	0.2	0.192	96.0
20082222	2/24/2009	2/26/2009	62.9	Diuron	0.2	0.202	101
20082222	2/24/2009	2/26/2009	62.9	Hexazinone	0.2	0.227	114[b]
20082222	2/24/2009	2/26/2009	62.9	Metribuzin	0.2	0.221	111
20082222	2/24/2009	2/26/2009	62.9	Norflurazon	0.2	0.221	111[b]
20082222	2/24/2009	2/26/2009	62.9	Prometon	0.2	0.185	92.5
20082222	2/24/2009	2/26/2009	62.9	Prometryn	0.2	0.177	88.5
20082222	2/24/2009	2/26/2009	62.9	Propazine	0.2	0.182	91.0
20082222	2/24/2009	2/26/2009	62.9	Simazine	0.2	0.193	96.5
20082171	2/25/2009	3/5/2009	05-006	Benfluralin	0.15	0.131	87.3
20082171	2/25/2009	3/5/2009	05-006	Ethalfluralin	0.15	0.135	90.0
20082171	2/25/2009	3/5/2009	05-006	Oryzalin	0.15	0.106	70.7

QC Sample Number	Extraction Date	Analysis Date	CDFA EMON Method Number	Analyte	Spike Level (ppb)	Result (ppb)	Recovery (%)
20082171	2/25/2009	3/5/2009	05-006	Oxyfluorfen	0.15	0.144	96.0
20082171	2/25/2009	3/5/2009	05-006	Pendimethalin	0.15	0.140	93.3
20082171	2/25/2009	3/5/2009	05-006	Prodiamine	0.15	0.154	103
20082171	2/25/2009	3/5/2009	05-006	Trifluralin	0.15	0.140	93.3
20082380	3/13/2009	3/16/2009	05-006	Benfluralin	0.150	0.123	82.0
20082380	3/13/2009	3/16/2009	05-006	Ethalfluralin	0.150	0.123	82.0
20082380	3/13/2009	3/16/2009	05-006	Oryzalin	0.150	0.107	71.3
20082380	3/13/2009	3/16/2009	05-006	Oxyfluorfen	0.150	0.140	93.3
20082380	3/13/2009	3/16/2009	05-006	Pendimethalin	0.150	0.131	87.3
20082380	3/13/2009	3/16/2009	05-006	Prodiamine	0.150	0.138	92.0
20082380	3/13/2009	3/16/2009	05-006	Trifluralin	0.150	0.119	79.3
20082389	3/17/2009	3/19/2009	62.9	ACET	0.2	0.156	78.0
20082389	3/17/2009	3/19/2009	62.9	Atrazine	0.2	0.167	83.5
20082389	3/17/2009	3/19/2009	62.9	Bromacil	0.2	0.219	110
20082389	3/17/2009	3/19/2009	62.9	DACT	0.2	0.176	88.0
20082389	3/17/2009	3/19/2009	62.9	DEA	0.2	0.171	85.5
20082389	3/17/2009	3/19/2009	62.9	Diuron	0.2	0.221	111
20082389	3/17/2009	3/19/2009	62.9	Hexazinone	0.2	0.221	111
20082389	3/17/2009	3/19/2009	62.9	Metribuzin	0.2	0.209	105
20082389	3/17/2009	3/19/2009	62.9	Norflurazon	0.2	0.208	104
20082389	3/17/2009	3/19/2009	62.9	Prometon	0.2	0.172	86.0
20082389	3/17/2009	3/19/2009	62.9	Prometryn	0.2	0.166	83.0
20082389	3/17/2009	3/19/2009	62.9	Propazine	0.2	0.160	80.0
20082389	3/17/2009	3/19/2009	62.9	Simazine	0.2	0.171	85.5

[a]ACET, deisopropyl atrazine; DACT, diamino chlorotraizine; DEA, deethyl atrazine
[b]Above upper control limit. All other recoveries were within QC control limits

Appendix Table 4 Recovery of propazine surrogates in surface water samples; all surrogates were spiked with 0.2 ppb propazine and were recovered within QC control limits

CDFA No.	Extraction Date	Analysis Date	Result (ppb)	Recovery (%)
20082147	2/24/2009	2/25/2009	0.179	89.5
20082148	2/24/2009	2/25/2009	0.146	73.0
20082149	2/24/2009	2/25/2009	0.161	80.5
20082150	2/24/2009	2/25/2009	0.149	74.5
20082151	2/24/2009	2/25/2009	0.157	78.5
20082152	2/24/2009	2/25/2009	0.153	76.5
20082153	2/24/2009	2/25/2009	0.183	91.5
20082154	2/24/2009	2/25/2009	0.162	81.0
20082216	2/24/2009	2/25/2009	0.166	83.0
20082217	2/24/2009	2/25/2009	0.172	86.0
20082218	2/24/2009	2/25/2009	0.161	80.5
20082219	2/24/2009	2/25/2009	0.151	75.5
20082220	2/24/2009	2/25/2009	0.149	74.5
20082325	3/17/2009	3/19/2009	0.162	81.0
20082326	3/17/2009	3/19/2009	0.167	83.5
20082327	3/17/2009	3/19/2009	0.177	88.5
20082328	3/17/2009	3/19/2009	0.156	78.0
20082329	3/17/2009	3/19/2009	0.159	79.5
20082330	3/17/2009	3/19/2009	0.169	84.5
20082331	3/17/2009	3/19/2009	0.162	81.0
20082332	3/17/2009	3/19/2009	0.180	90.0
20082333	3/17/2009	3/19/2009	0.176	88.0
20082334	3/17/2009	3/19/2009	0.161	80.5
20082335	3/17/2009	3/19/2009	0.174	87.0
20082336	3/17/2009	3/19/2009	0.162	81.0

Appendix Table 5 Rainy season herbicide monitoring results, California, 2009

Date	Site Code	Time	----------Herbicide Concentration (µg L^{-1})[a]----------							
			Diuron	Hexazinone	Simazine	Oryzalin	Oxyfluorfen	Pendimethalin	Bromacil	Trifluralin
2/15/09	S2	15:10	nd	nd	0.828	0.627	tr	tr	nd	nd
	Y1	9:30	tr	0.089	0.218	nd	0.195	0.07	nd	nd
	Y2	10:15	tr	0.073	nd	nd	0.081	tr	nd	nd
	Y3	9:15	0.172	0.222	nd	0.05	nd	0.06	0.051	nd
	Y4	12:15	4.64	1.35	0.05	0.251	0.15	0.304	nd	0.067
	Y5	11:45	4.08	0.987	tr	nd	1.139	tr	0.163	nd
	Y6	10:45	nd	nd	nd	nd	nd	tr	nd	nd
2/19/09	S1	13:40	nd	nd	0.169	0.094	nd	nd	nd	nd
	S2	13:00	nd	nd	0.136	0.129	nd	nd	nd	nd
	N1	11:00	0.056	nd	0.058	tr	nd	nd	nd	nd
	N2	9:30	0.109	nd	0.07	tr	nd	nd	nd	nd
3/09/09	S1	12:35	nd	nd	tr	tr	nd	nd	nd	nd
	S2	11:20	nd	nd	tr	tr	nd	nd	nd	nd
	N1	15:15	0.053	nd	tr	tr	nd	nd	nd	nd
	N2	14:30	0.087	nd	tr	nd	nd	nd	nd	nd
3/10/09	Y1	12:30	0.371	0.44	nd	nd	tr	tr	nd	nd
	Y2	13:00	0.245	0.509	nd	nd	nd	tr	nd	nd
	Y3	14:20	0.406	0.73	nd	nd	nd	tr	nd	nd
	Y4	10:00	tr	nd	nd	nd	tr	nd	nd	nd
	Y5	10:45	0.183	0.057	nd	nd	nd	nd	nd	nd
	Y6	11:45	nd	nd	nd	nd	nd	nd	nd	nd

[a]nd, nondetection (< MDL); tr, trace detection, RL - MDL. Nondetections and trace detections are not included in the detection frequency. There were no detections of atrazine, benfluralin, deethyl atrazine (DEA), deisopropyl atrazine (ACET), diamino chlorotraizine (DACT), ethalfluralin, metribuzin, norflurazon, prodiamine, prometon, or prometryn.