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Review of the Environmental Fate and Use Patterns of Propanil in California

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Introduction

Propanil (*N*-(3,4-dichlorophenyl) propanamide; CAS 709-98-8; Figure 1) is a synthetic anilide herbicide used to control grasses and broad-leaf weeds primarily during the production of rice. Propanil is registered as a restricted material in California for use on rice and other field crops under the trade names Duet®, Riceshot®, Stam 80®, Superwham! ®, and Willowood®. Its major degradate, 3,4-dichloroaniline (3,4-DCA), has similar toxicity to that of propanil and is often found in the environment. However, this degradate is an intermediate used in the manufacturing of herbicides such as diuron, linuron and propanil (Crossland 1990), thus its detection in the environment may not always be directly related to one of those herbicides. A review of the environmental fate and ecotoxicology of propanil has been published in 2016 by Kanawi et al. Here, I summarized the environmental fate and toxicology of propanil and reviewed its use and environmental detections in California.

Environmental fate overview

Although propanil is used primarily on California rice, a majority of environmental fate studies were not conducted in California . However, the environmental fate of propanil can be estimated for California based on the findings of propanil's fate in other parts of the U.S. and the world. Here, the environmental fate and toxicology of propanil is summarized below.

Physical-chemical properties

Propanil is soluble in water (S = 95 mg/L at 20°C) and considered hydrophilic according to its octanol-water partition coefficient (log $K_{ow} = 2.29$); however, it is highly soluble in organic solvents such as acetone (1,700,000 mg/L at 20°C). Its vapor pressure indicates it is non-volatile (VP = 0.019 mPa at 25°C), whereas its organic carbon normalized partition coefficient (K_{oc} = 152-800) shows propanil has an affinity to bind to soils (PPDB 2016).

Chemodynamics

Based on propanil's vapor pressure (VP = 0.019 mPa at 25°C) and Henry's law constant (H = 4.4 x 10^{-4} Pa m^3/mol) volatilization is not a major dissipation pathway from either water or moist soils; Carvalho et al. (2010) confirmed volatilization is negligible. Although volatilization does not impact propanil's dissipation, airborne droplets may drift potentially impacting surrounding crops, waterbodies or human populations. Sanderson et al. (1997) used three formulations, with and without non-ionic surfactant, to measure droplet size and drift potential. They found a significant difference in droplet size for liquid flowable (235 µm), water dispersible granule (218 µm), and emulsifiable concentrate (177 µm), respectively; addition of a surfactant reduced the droplet size. Moreover, a fivefold change in drift potential was observed between the formulations. The authors state that an applicator's nozzle tip size, pressure and flow rate should be considered to control drift of formulated propanil.

Propanil has a variable soil sorption capacity (K_{oc} range from 152 to 800) and movement throughout soil has been found to be dependent on soil type and infiltration rate (Kanawi et al. 2016). In addition, changes in organic matter have been found to accelerate propanil transformation (Konstantinou et al. 2001b). The sorption of degradate 3,4-DCA has been studied. In soil containing approximately 47% silt, the soil sorption capacity identified 3,4-DCA to be mobile in soil (Fava et al. 2005). However, Albers et al. (2008) note that 3,4-DCA binds irreversibly to soils containing humic acid and/or fulvic acid, thus reducing its environmental risk. Gonzalez-Pradas et al. (2005) observed an increase in 3,4-DCA adsorption onto dissolved organic carbon extracts from peat and tannic acid. Overall, the sorption and corresponding leachability of 3,4-DCA is dependent on soil type.

Propanil has been identified as a potential groundwater pollutant in California and studies throughout the United States have been conducted to identify its persistence in groundwater. Water collected from three Arkansas wells were fortified with herbicide mixtures (1 and 5 µg/L; 15 and 22°C incubations), and herbicide concentrations were analyzed over 18 months. By 18 months, 75-90% of propanil, respectively, at both fortification levels was degraded. However, degradation was observed to occur after a 6 month lag phase, thus it is assumed that microflora were acclimating to the contaminant (Cavalier et al. 1991). Although 3,4-DCA is mobile and capable of reaching groundwater, its measured soil half-life (DT_{50} = 1.59 days, respectively) indicates rapid degradation will limit its potential to contaminate groundwater (Fava et al. 2005).

Environmental degradation

Photolysis has been determined to be a major degradation pathway. Photocatalytic degradation has been studied under various irradiation lengths and in the presence of a catalyst. Dhahir (2011) found that use of zinc oxide (ZnO; 10 mg per 75 mL solution; natural sunlight), as a catalyst, increased degradation with complete degradation occurring within 180 minutes of irradiation. Using titanium dioxide (TiO_2; 100 and 500 mg/L) as a catalyst, aqueous solutions were irradiated (xenon arc lamp; 1500 W; 240 min) to evaluate the disappearance of propanil under simulated sunlight. Konstantinou et al. (2001a) found that in the presence of TiO_2, first-order degradation resulted; a half-life of 4.3 minutes was measured (500 mg/L TiO_2 solution). A multi-step degradation pathway including hydroxylation, dechlorination, dealkylation and oxidation has been proposed; multiple byproducts have been observed.

Microbial degradation has also been determined to be a major degradation pathway. When applied with other herbicides (20°C; 14 days) Smith (1984) found that 95% of propanil degraded within 7 days and that degradation was not impacted by the presence of other herbicides. Kanawi et al. (2016) reviewed studies that measured degradation also occurring within a matter of days, under varying soil types. Microbial degradation results in the major degradation product 3,4-DCA. Other studies have not only identified 3,4-DCA but have further identified the minor degradate 3,3',4,4'-tetrachloroazobenzene (TCAB). Using sandy loam soil (pH 5.3), Bartha and Pramer (1967) identified the formation of TCAB via condensation of 3,4-DCA, thus concluding that 3,4-DCA is an intermediate of propanil biochemical transformation. Soil microorganisms capable of degrading the herbicide were identified by Kaufman and Blake (1973). Two soil microorganisms (*Pseudomonas striata* and *Achromobacter* sp.) were found to degrade the aniline moiety of propanil within 6 days by 55 and 58%, respectively. A total of nine microorganisms were isolated from the soil samples (75% organic matter and 3% organic matter, respectively), each having specificity for the aniline moiety. Carvalho et al. (2010) found diverse microbial communities more efficiently degrade the herbicide and 3,4-DCA degradate compared to isolated organisms. However, they did note that some organisms within the studied community were more specific for 3,4-DCA degradation resulting in higher removal efficiencies. Bacterial isolates (*Acidovorax* sp. TA2, *Acidovorax* sp. TA35, *Comamonas testosterone* TB1, *C. testosterone* TB18 and *C. testosterone* TB30), capable of degrading 3,4-DCA have been identified in topsoil (A-horizon; heavy sand loam, sandy loam, or sandy soils; Dejonghe et al. (2002)). These isolates contain a plasmid (IncP-1ß) capable of degrading chlorinated aromatic compounds like 3,4-DCA.

The fate of 3,4-DCA was investigated through use of rice-paddy microecosystems. The downward movement in soil, uptake by rice plants and distribution to aquatic organisms were evaluated by Isensee et al. (1982). The microecosystems contained ^{14}C-3,4-DCA treated soil (10 mg/L), sand and Metapeke soil (loam, sand, silt and clay), in which planted rice seeds were grown. After 13 days, additional water was added and on day 14, mosquito fish, algae and daphnids were introduced; the test terminated on day 115. This study found 3% of the ^{14}C-3,4-DCA leached, however within 15 days 39-55% respectively, was accumulated into the rice plant tissue. The degradate did accumulate in aquatic organisms with algae accumulating the most when compared to the other organisms (Isensee et al. 1982).

Hydrolysis is not a significant route of degradation. Kanawi et al. (2016) notes that studies have indicated that little to no hydrolysis occurs if light, microbes or organic matter are absent. Thus, both photolysis and microbial degradation are the major routes of propanil degradation.

Ecotoxicology

Propanil disrupts the electron transport chain by inhibiting the photosystem II, ultimately impacting plant growth. Although rice has a tolerance for the herbicide, observed toxicity to plants such as duckweed and phytoplankton, has been noted in Kanawi et al. (2016). Propanil resistance has been observed in plant species found in California rice cultivation and one notorious rice weed, *Cyperus difformis* L., has been identified as resistant. Valverde et al. (2014) identified four resistant populations collected from Sacramento Valley rice fields. They also found that these plants showed resistance to other commonly used rice herbicides such as bensulfuron-methyl and imazosulfuran. Propanil resistance has been identified to result in *Echinochloa* spp., due to aryl acylamidase enzymes which hydrolyze the herbicide (Preston 2004). To enhance propanil's ability to combat resistant weeds, synergistic pesticides (e.g., piperophos and anilophos) have been mixed with propanil. These synergists are known to inhibit the enzymes while being selective for rice (Preston 2004). Inclusion of synergists or using alternative herbicides are ways rice growers can address weed resistance.

Propanil, within aquatic environments, has been found to adversely impact non-target organisms such as fish and invertebrates. *Oreochromis niloticus* fingerlings exposed under static conditions to various propanil concentrations displayed erratic swimming and other abnormal behaviors (Okayi et al. 2013). Moraes et al. (2009) observed adverse toxicological and metabolic impacts when *Leporinus obtusidens* were exposed to rice paddy water (90 days; 1644 µg/L propanil, respectively; commercial formulation). The authors do suggest that other ingredients in the formulation (*e.g.*, surfactants) are contributing to the observed adverse effects. The degradate 3,4-DCA has been found to illicit adverse effects on juvenile goby (*Pomatoschistus microps*). When exposed for 96 hours to concentrations ranging from 0.5 to 1.5 mg/L, muscle lactate dehydrogenase and gill glutathione S-transferase activity were altered; in addition alterations to the spleen were observed (Monteiro et al. 2006).

Toxicity studies using invertebrates have also been conducted. The effects propanil elicits on gene transcription was investigated by Pereira et al. (2010). *Daphnia magna*, exposed to 363 µg/L propanil, respectively, experienced alterations to moulting, protein biosynthesis, energy metabolism, and oxygen transport. Although the authors did observe toxic responses, they do note that these responses are not restricted to the genes associated with propanil's target site. *D. magna* were also studied to investigate changes in energy stores in relation to herbicide exposure. As a response to environmental stress, a reduction in glycogen (28%) and caloric content (27%) resulted (Villarroel et al. 2013). Such changes in energy stores may impact growth and reproduction.

To determine the effects of herbicide spray on plankton communities, Perschbacher et al. (2002) simulated direct spraying of ponds and drift capable of impacting ponds. Stam® (4.5 kg a.i./ha), was sprayed directly onto the mesocosm pond surfaces and resulted in a significant reduction in oxygen production (75%) and a stimulation of chlorophyll *a* production. Drift simulated exposures did not significantly impact oxygen levels, but did stimulate chlorophyll *a* production to a lesser degree and increased zooplankton concentrations (Perschbacher et al. 2002). Toxicity towards other non-target species has been reported. Additional toxicity data has been reviewed in Kanawi et al. (2016).

In vitro studies have been conducted to determine the potential for propanil to impact kidney cells (Rankin et al. 2008). Isolated rat renal cortical cells (IRCC) from male Fischer 344-rats were exposed to a range of propanil and 3,4-DCA concentrations; cytotoxicity was observed. Propanil was identified to be a more potent nephrotoxicant compared to 3,4-DCA; both are nephrotoxic *in vitro*. In addition, the hydrolysis derived degradate does not appear to induce most of the toxicity, although it does contribute to propanil's *in vitro* toxicity (Rankin et al. 2008). Dose-dependent adverse effects in male mice, caused by 3,4-DCA exposure have been studied by Eissa et al. (2012). Mice were orally dosed with 3,4-DCA (13.8, 27.7 or 55.3 mg/kg bw/day; 30 days) and the effects of bone-marrow cells and spermatocytes were observed. This study identified chromosome malformations, a significant reduction in sperm count and motility, and alterations in liver and testes of exposed mice compared to control mice. Zhang and Lin (2009) also observed reproductive impairment of male Wister rats dosed with 3,4-DCA.

Rice cultivation in California

California commercial rice production encompasses roughly 500,000-600,000 acres that are highly concentrated in the Sacramento Valley (Figure 2; Summers Consulting, 2012). It is grown under a Mediterranean type climate (no summer rainfall, high solar radiation and cold overnight temperatures), and on acidic to moderately alkaline clay and/or silty-clay soils (pH 4.5-8). Fields are often irrigated with surface water from nearby rivers or reservoirs; however, groundwater may be pumped for irrigation. Pesticides may be applied by airplane, however often ground applications of herbicides take place to minimize drift. The growing season varies from 130 to 165 days from April to October (Hill et al. 2006).

Rice herbicide use and detections in California

In 1983, the California Department of Pesticide Regulation (CDPR) implemented the Rice Pesticides Program. This program was designed to minimize the discharge of popular rice herbicides molinate and thiobencarb into surrounding surface waters (Newhart 2002). By 1990, the Central Valley Regional Water Quality Control Board amended their Water Quality Control Plan to include the two rice herbicides and the insecticides carbofuran, methyl parathion and malathion (CDPR 1994). CDPR continued monitoring efforts while managing the program, however in 2003 the California Rice Commission took over the program and continues the monitoring, sampling, analysis and reporting of thiobencarb (CRC 2016). In 2008, propanil was placed on CDPR's Groundwater Protection List (3CCR section 6800(b); CDPR 2013a) due to its mobility, persistence or ground-based application method.

Over the last decade, statewide use of propanil has steadily increased, whereas use of thiobencarb has gradually decreased (Figure 3); surface water and groundwater propanil contamination is of concern. Although statewide use shows a steady increase every year, on the county level, use has been variable. In the Sacramento Valley (Figure 4), specifically Colusa County, more than 700,000 lb. a.i. were applied in 2013. However, in other rice growing regions of the Sacramento Valley, use barely topped 100,000 lb. a.i. (*e.g.*, Yolo County). In the Central Valley (Figure 5), use has continued to drop since 2000 and may reflect a change in crops grown in these counties or a change to other herbicides. In addition, the total acreage being treated with propanil has continued to slowly grow throughout the state, yet remains highly concentrated in the Sacramento Valley (Table 1).

With the popularity of propanil use, monitoring of both surface water and groundwater has been conducted. CDPR's Surface Water Database (SURF; CDPR 2016b) contains monitoring results of approximately 2,561 samples, analyzed for propanil, that have been collected throughout the state since 1992. Out of these samples, propanil has only been detected in 170 surface water samples, with the highest detections being from Colusa, Sacramento, Sutter and Yolo counties (Table 2). Out of these detections, three samples exceeded the US EPA aquatic life benchmark for fish (chronic) of 9.1 µg/L and the nonvascular plant benchmark of 16 µg/L (US EPA 2016); these three samples were collected from Colusa County in 2001, 2006 and 2009. The degradate 3,4-DCA has also been monitored for. According to the SURF database, 429 samples collected from 2005 to 2012 had no detectable amounts of the degradate. The lack of detections may be related to the sampling of large rivers which may have contributed to diluting the concentration below detection limits. Future monitoring of 3,4-DCA, in waterways adjacent to field sites where propanil has been applied, may result in increased detections.

Groundwater wells in California have been monitored for propanil from 2000 to 2014. Approximately 1,202 well samples have been collected (Table 3); 2 detections (Butte and Sutter counties) were reported by the State Water Resources Control Board. Overall the sampled wells have had no detectable amounts of propanil. The degradate 3,4-DCA has been detected in groundwater in California. Samples collected in 2011 and 2012 resulted in 99 detections. However, one cannot confidently assume these detections were related to propanil use, as diuron was detected in 73 samples and may be the contributing parent pesticide.

Summary

Propanil is the most highly used synthetic anilide herbicide in rice culture for the control of weeds and grasses. It disrupts the electron transport chain by inhibiting the photosystem II and ultimately impacts plant growth. Although rice plants are tolerant to propanil, other common rice-field plants are becoming resistant to the herbicide. In California, resistant rice-field plants have been identified and are also gaining resistance to other commonly used herbicides. Studies have confirmed that use of propanil, in combination with synergists, can combat the resistance issue. Also, using alternative herbicides, specific for use on rice, may limit the growth of resistance over time.

Propanil has a low vapor pressure and Henry’s law constant, thus volatilization is not considered a major dissipation pathway. It does have a moderate sorption capacity to soil, yet it has been identified to have the potential to leach to groundwater. In California, propanil has been detected in two groundwater samples over 14 years of sampling, however the major degradate 3,4-DCA has been detected more frequently. The movement of propanil throughout soil has been found to be dependent on soil type and organic matter content; leaching may vary among rice-growing areas in California and worldwide.

Hydrolysis is not a significant route of degradation. However, both microbial and photolytic degradation have been identified as major degradation pathways, with degradation occurring within a matter of hours to days. Bacterial isolates, from a variety of soils, have been identified to degrade both propanil and 3,4-DCA. Similarly, the presence of a catalyst has been found to accelerate photolysis.

Propanil toxicity to non-target organisms has been identified by many researchers. Studies using fish and invertebrates have observed changes in swimming behavior and metabolic alterations.

The degradate 3,4-DCA elicits similar results, with changes in enzymes and histopathological alterations.

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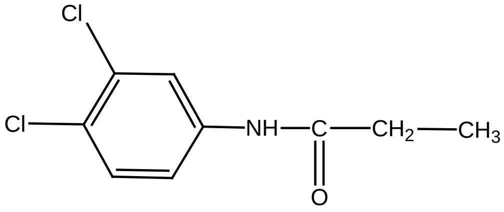

Figure. 1 Propanil structure.

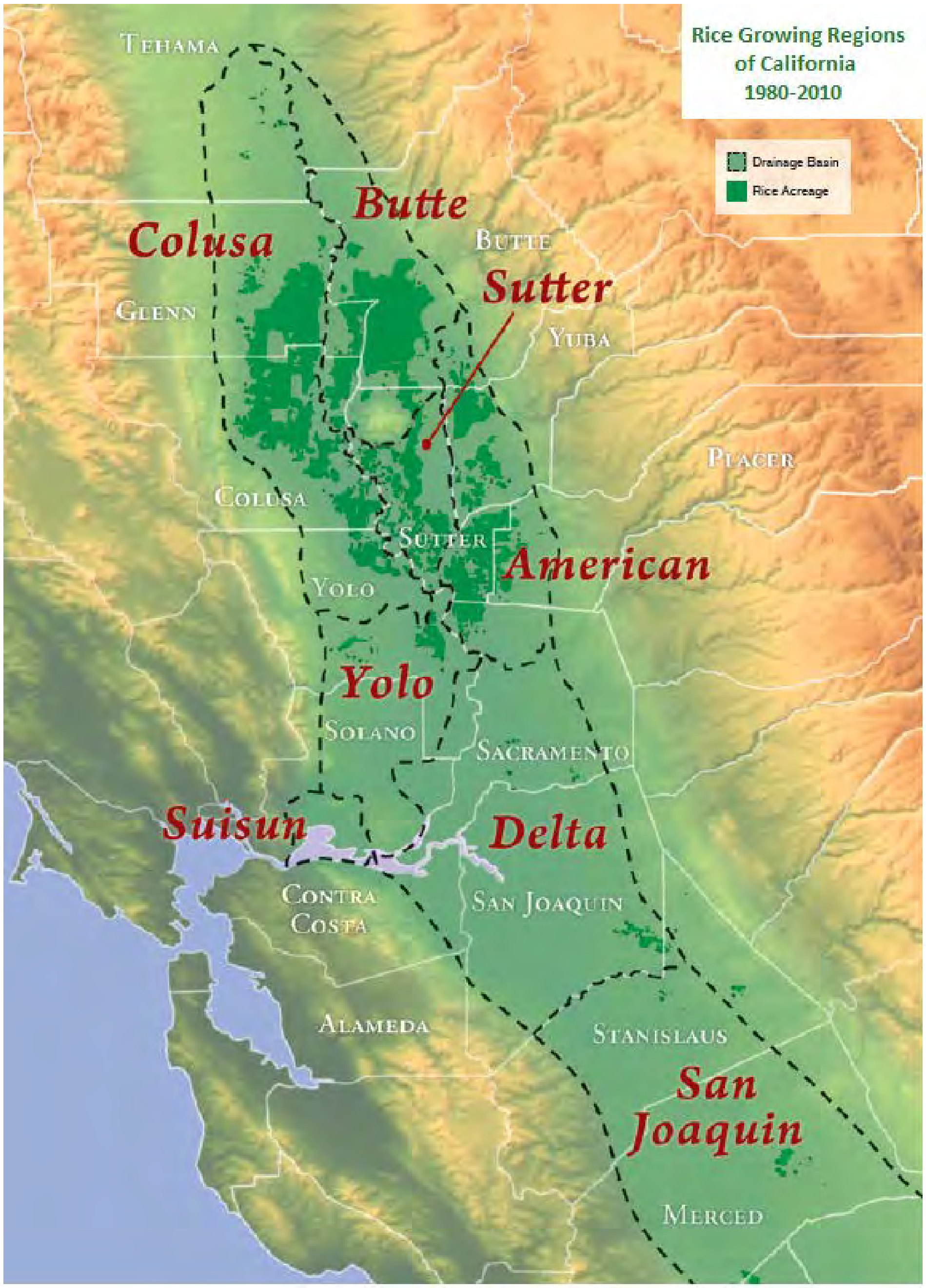

Figure 2. California rice growing regions from 1980-2010 (map is adopted from Summers Consulting, LLC, 2012).

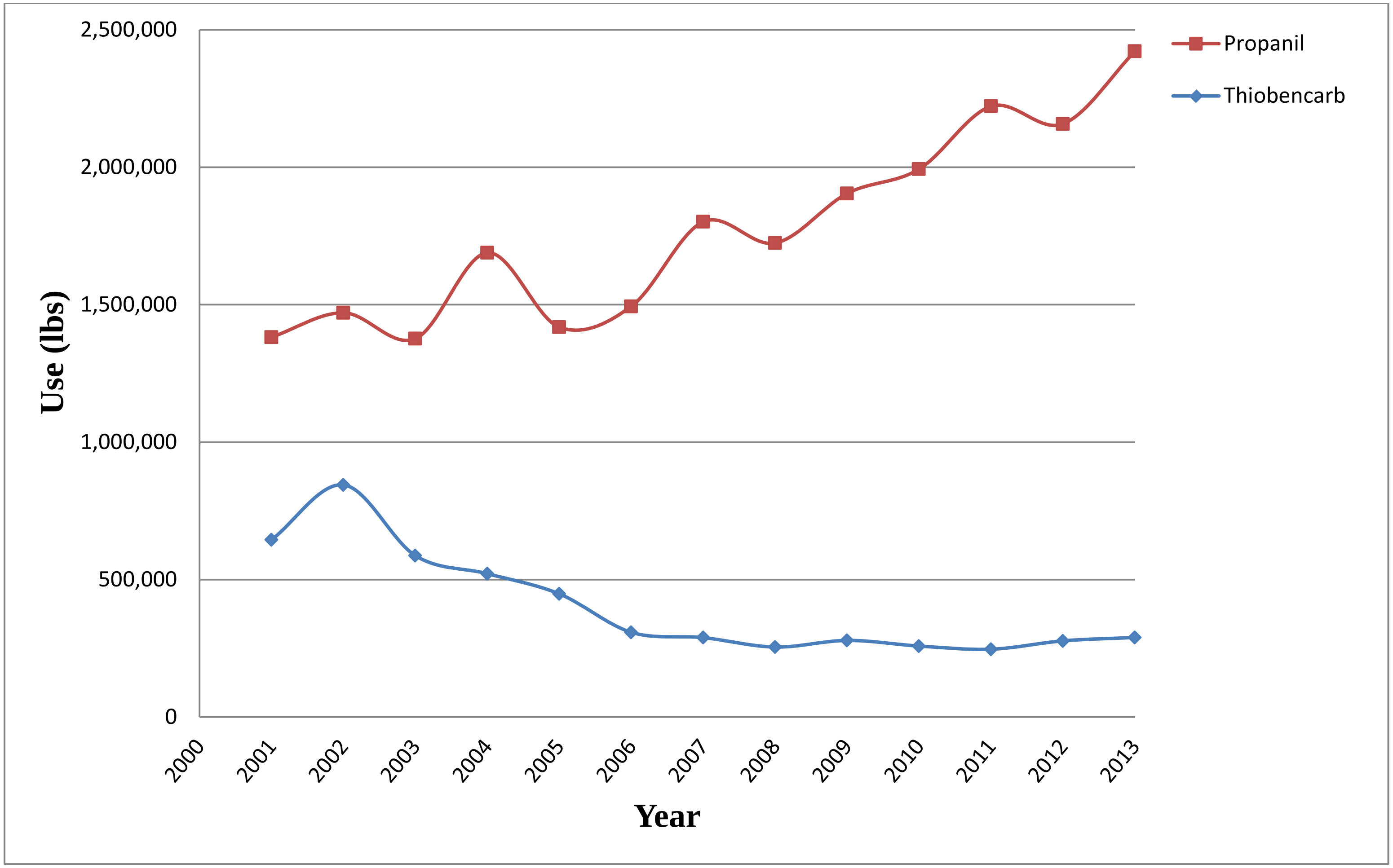

Figure 3. Statewide use comparison of propanil and thiobencarb from 2001 to 2013.

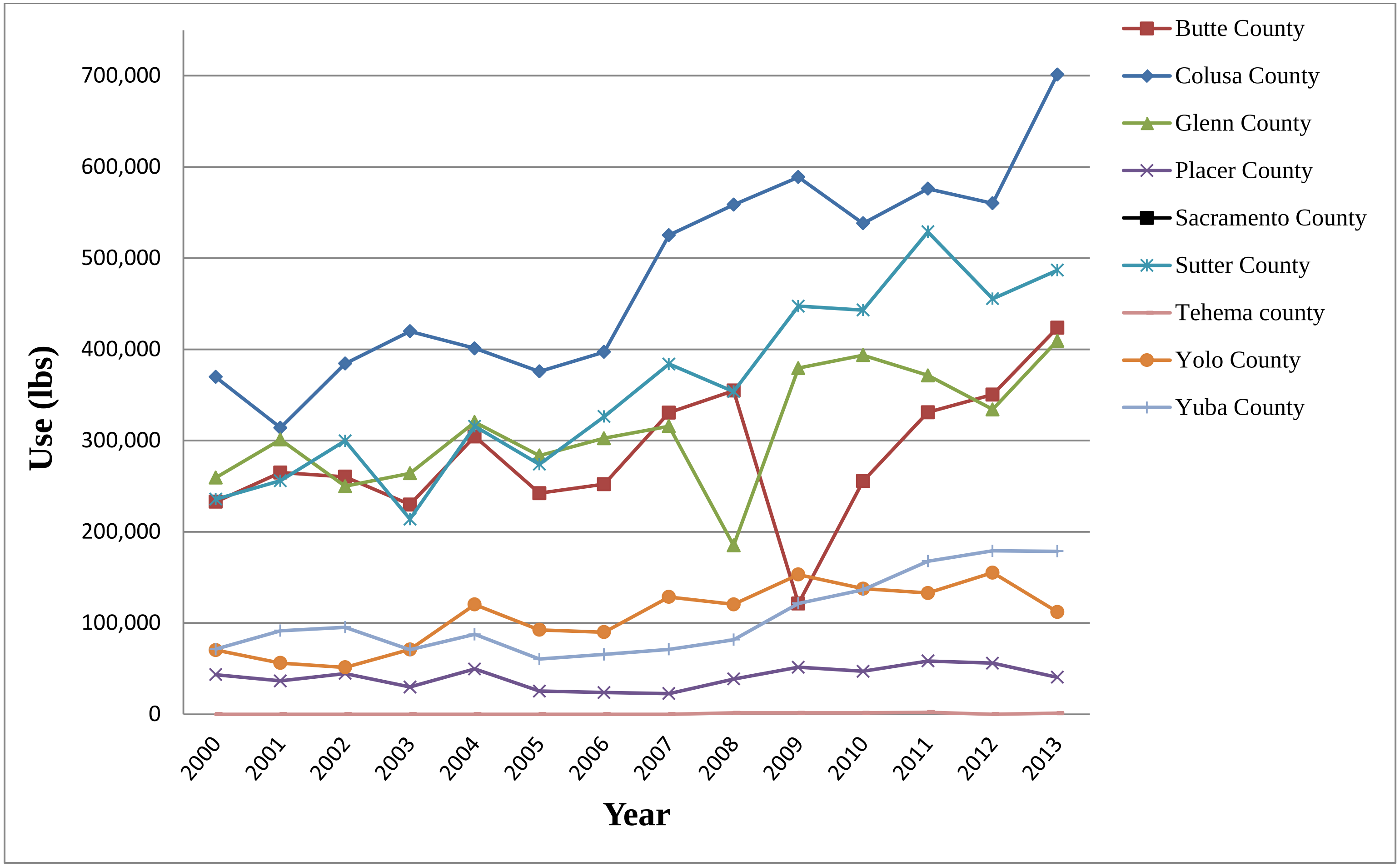

Figure 4. Use of propanil on rice in the Sacramento Valley from 2000 to 2013.

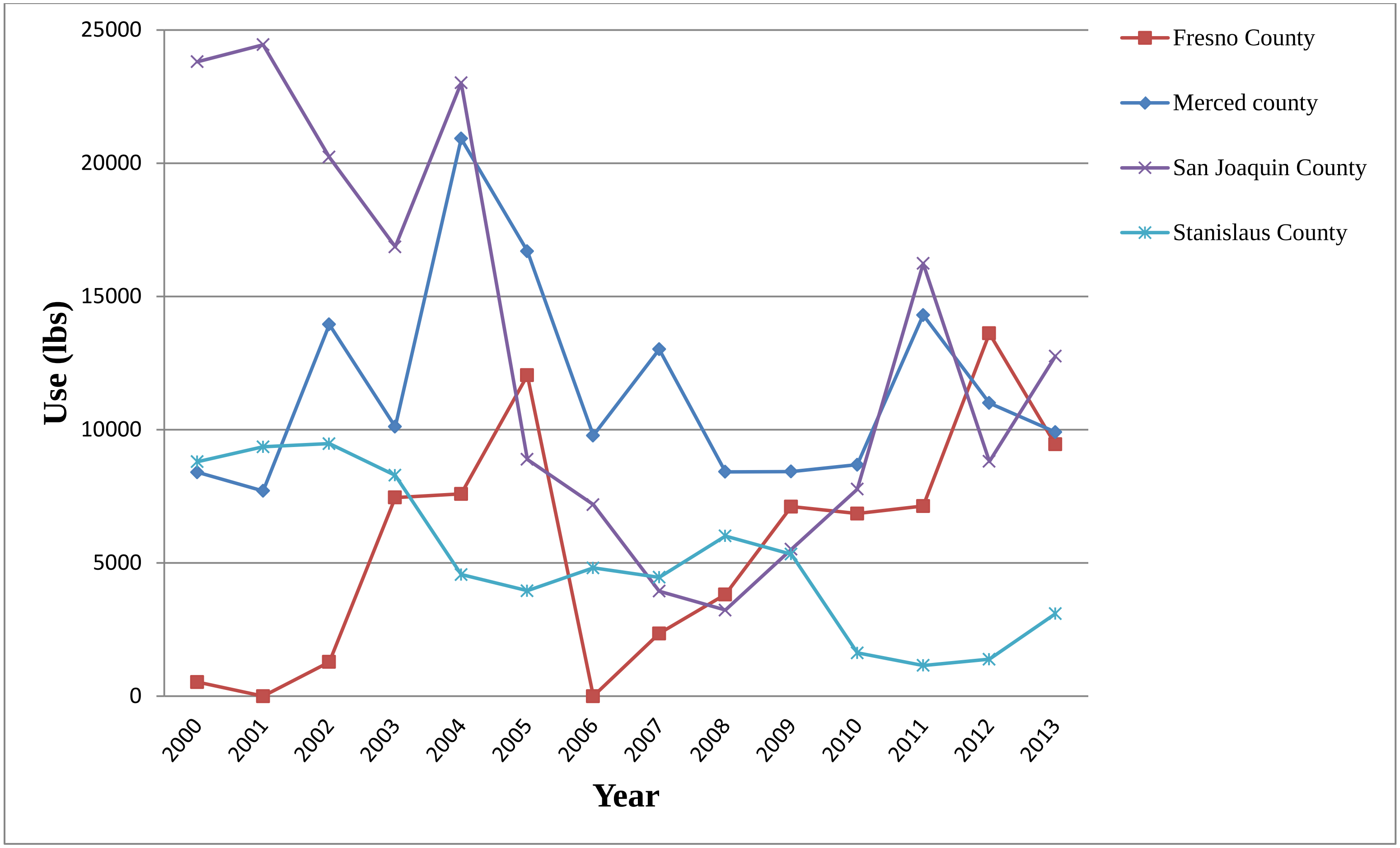

Figure 5. Use of propanil on rice in the Central Valley from 2000 to 2013.

Table 1. Average amount of rice or other agriculture acres treated with propanil from 2000-2013 in each county[†].

County	Average Acres Treated (Rice)	Average Acres Treated (Other)*
Butte	62,621	0
Colusa	95,392	94
Fresno	1,388	0
Glenn	61,778	49
Merced	2,648	71
Placer	9,117	10
Riverside	0	2
Sacramento	5,627	20
San Joaquin	2,855	0
Stanislaus	1,231	15
Sutter	76,741	123
Tehema	290	0
Ventura	0	2
Yolo	22,086	0
Yuba	23,188	0
Total	**364,962**	**386**

*Other includes: rights of way, prune, sunflower, wheat, wild rice, safflower, soil, corn, walnut, barley, alfalfa, uncultivated ag, N-outdoor flower, unknown.

[†] Data obtained from the CDPR Pesticide Use Reports 2000-2013 (CDPR 2014a).

Table 2. Propanil detections in surface water collected throughout California (data collected from 1992-2013)[†].

County	No. Collected Samples	No. Detections	Detection frequency (%)
Alpine	4	0	0.0
Butte	2	0	0.0
Colusa*, ¥	123	62	50.4
Contra Costa	50	0	0.0
El Dorado	4	0	0.0
Merced*, ¥	426	4	0.9
Nevada	4	0	0.0
Orange	42	0	0.0
Riverside*, ¥	160	1	0.6
Sacramento*¥	371	41	11.1
San Bernardino	97	0	0.0
San Joaquin	370	0	0.0
Solano	20	0	0.0
Stanislaus*, ¥	666	5	0.8
Sutter*, ¥	150	40	26.7
Yolo*, ¥	71	17	23.9
Yuba	1	0	0.0
Total	**2561**	**170**	**6.6**

[†] Data obtained from the CDPR Surface Water Database (CDPR 2016b).

[¥] Concentration ranges of detected samples: 0.07-47 µg/L (Colusa), 0.004-0.009 µg/L (Merced), 0.014 µg/L (Riverside), 0.006-1.45 µg/L (Sacramento), 0.004-0.013 µg/L (Stanislaus), 0.02-4.4 µg/L (Sutter), and 0.05-3.3 µg/L (Yolo).

*Median concentrations from detected samples: 1.4 µg/L (Colusa), 0.006 µg/L (Merced), 0.014 µg/L (Riverside), 0.071 µg/L (Sacramento), 0.011 µg/L (Stanislaus), 0.41 µg/L (Sutter), and 0.23 µg/L (Yolo).

Table 3. Propanil detections in groundwater collected throughout California (data collected from 2000-2014)[†].

Year	No. Counties Sampled	No. Collected Samples	No. Detections	Detection frequency (%)
2000	0	0	0	0
2001	0	0	0	0
2002	9	76	0	0
2003	20	187	0	0
2004	2	5	0	0
2005	0	0	0	0
2006	0	0	0	0
2007	0	0	0	0
2008	0	0	0	0
2009	0	0	0	0
2010	0	0	0	0
2011	29	736	2[°,*,¥]	0.3
2012	5	59	0	0
2013	4	80	0	0
2014	4	59	0	0
Total		**1202**	**2**	**0.2**

[†] Data obtained from the CDPR Annual Well Sampling Reports (CDPR 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014b, 2015, 2016a).

[°] reported by the State Water Resources Control Board.

[¥] Concentration ranges of detected samples: 0.006-0.097 µg/L.

*Median concentrations from detected samples: 0.097 µg/L (Butte) and 0.006 µg/L (Sutter).