tdc environmental

MEMO

TO:	Elissa Callman	**DATE:**	February 8, 2012
FROM:	Kelly D. Moran	**PROJECT:**	56c
SUBJECT:	Thiobencarb Monitoring Data Evaluation		

This memorandum was prepared to summarize and evaluate thiobencarb monitoring data for the Sacramento River Source Water Protection Program water utilities. It includes background on thiobencarb and drinking water, an overview of management practices to protect surface water quality in the Sacramento Valley, the history of thiobencarb use and thiobencarb formulations, a summary of Sacramento valley thiobencarb monitoring data, and an analysis of factors that have affected surface water thiobencarb concentrations.

Background

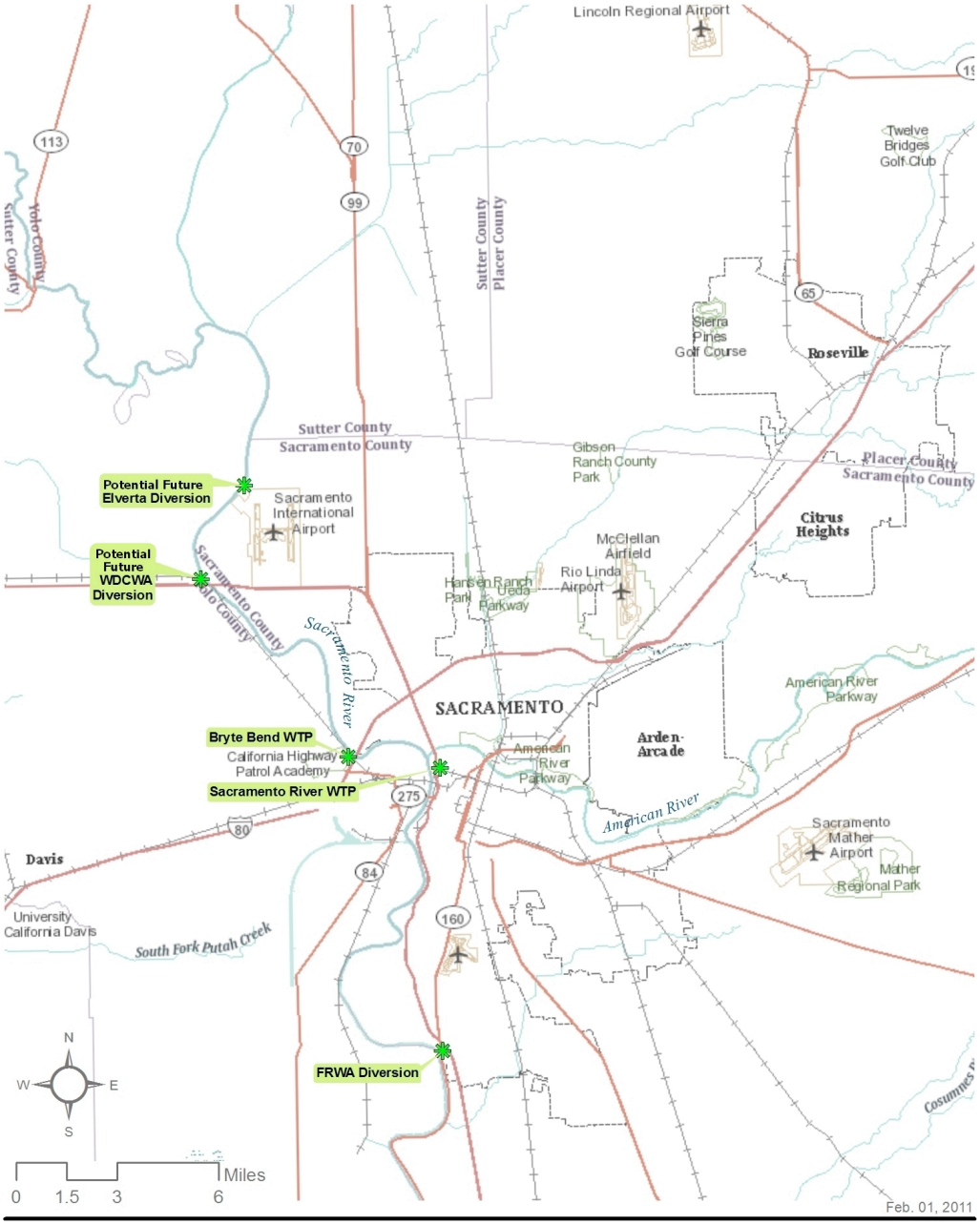
Thiobencarb is of interest to Sacramento River drinking water utilities because it causes drinking water to have an unpleasant bitter taste at concentrations that have occurred in the Sacramento River. Recognizing this unpleasant taste, the state of California's drinking water program established an enforceable secondary Maximum Contaminant Level for thiobencarb of 1 part per billion. This level was based on water supplier complaint records, which show customer complaints begin when thiobencarb concentrations reach 0.1 parts per billion (ppb) and always occur when concentrations reach 1 ppb (OEHHA 2000; DPR 2002).

Figure 1 shows the current and potential future drinking water supply intake locations on the Sacramento River. The three currently operating intakes are Bryte Bend (City of West Sacramento), Sacramento River (City of Sacramento), and FRWA (Freeport Regional Water Authority), serving Sacramento County and the East Bay Municipal Utilities District in the San Francisco Bay area. These five locations are all downstream from the Sacramento Valley rice-growing region, where almost all California rice is grown. The operating drinking water supply intakes supply drinking water to more than half a million Californians.

Starting shortly after U.S. EPA registered thiobencarb for use on rice in the 1980s, late each spring the City of Sacramento began receiving complaints about a foul taste in the drinking water. Subsequent investigation identified thiobencarb as the cause of the unpleasant taste. Drinking water treatment forms bitter tasting thiobencarb oxidation products. Over the following years, California rice growers, California Department of Pesticide Regulation (DPR), California's Central Valley Water Quality Control Board (Water Board), thiobencarb registrants, and the Sacramento River water utilities worked together to develop the Rice Pesticide Program (RPP) to address thiobencarb and several other pesticides.

Through the RPP, the participants developed an adaptive management program involving pesticide and water quality regulation, rice grower management practices, water quality monitoring, and annual coordination meetings. The adaptive management program has developed improved management practices over the years to address the latest conditions.

Figure 1. Sacramento River Drinking Water Supply Intake Locations.



Current thiobencarb management practices are reflected in DPR recommended restricted use permit conditions (which are implemented by all County Agricultural Commissioners in the Sacramento Valley watershed), the Central Valley Water Board Rice Pesticide Program resolution, and any additional grower-initiated measures reflected in an annual California Rice Commission memorandum.

Sacramento Valley Thiobencarb Monitoring

Annual thiobencarb monitoring in the Sacramento Valley watershed began before 1990. The monitoring program has included monitoring by water utilities, California state agencies, and rice growers. The cities of Sacramento and West Sacramento have monitored thiobencarb concentrations at their Sacramento River intakes (see Figure 1). Upstream monitoring was initially conducted by DPR and California Department of Fish and Game. Starting in 2003, the California Rice Commission took over the upstream monitoring under the oversight of the Central Valley Water Board. Upstream monitoring has occurred at locations shown in Figure 2.

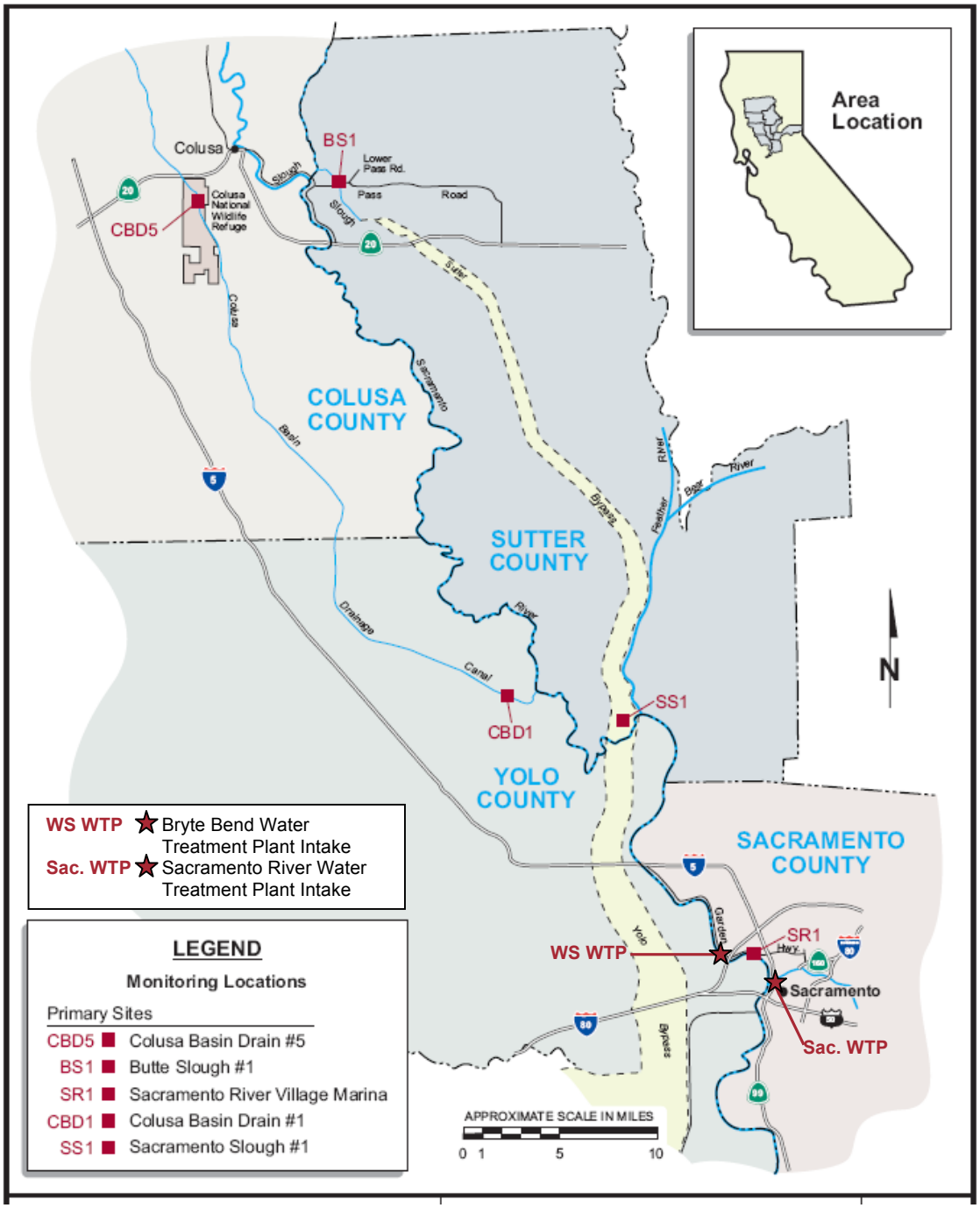
For the last 20 years, the water utilities have provided their monitoring data to the organization that conducted the upstream monitoring (DPR or the California Rice Commission), which prepared annual monitoring reports (DPR 1990-2002; CRC 2003-2011). These data are summarized and evaluated in this memorandum. Limited additional monitoring has been conducted by the USGS in 2002-2003 (Orlando and Kuivila 2004) with results similar to those described here and in 2010, when USGS measured somewhat higher peak thiobencarb levels (Hladik et al. 2011; Kuivila et al. in preparation).

Figure 3 summarizes the last six years of thiobencarb monitoring data in the watershed. Over the entire history of the monitoring, the highest thiobencarb levels occurred in the early 1980s and between 1992 and 2002. The lowest levels occurred between 2003 and 2007. Starting in 2008, thiobencarb concentrations increased. This memorandum includes an exploration of the potential causes of the higher thiobencarb levels, which correlate with a change in product formulation in 2008. Summaries of 2008-2011 monitoring data are attached. Full reports of all Rice Pesticide Program monitoring data are available from California DPR (1990-2002 reports are on the web at http://www.cdpr.ca.gov/docs/emon/surfwtr/riceprog.htm) and the Central Valley Water Board (1995-2010 reports are on the web at http://tinyurl.com/73fuggd).

To protect the drinking water supply quality in the Sacramento River, the Water Board established a performance goal of 1.5 ppb (this value is not supposed to be exceeded). The focus of adaptive management has been to eliminate exceedances of the performance goal, which were prevalent in the early 1980s, and between 1992 and 2002. Although there were no exceedances of the Central Valley Water Board's performance goal of 1.5 ppb between 2004 and 2007, upstream samples exceeded the performance goal on six occasions between 2008-2010. Continued occurrence of periods of increased thiobencarb concentrations shows the importance of continued adaptive management to control thiobencarb concentrations.

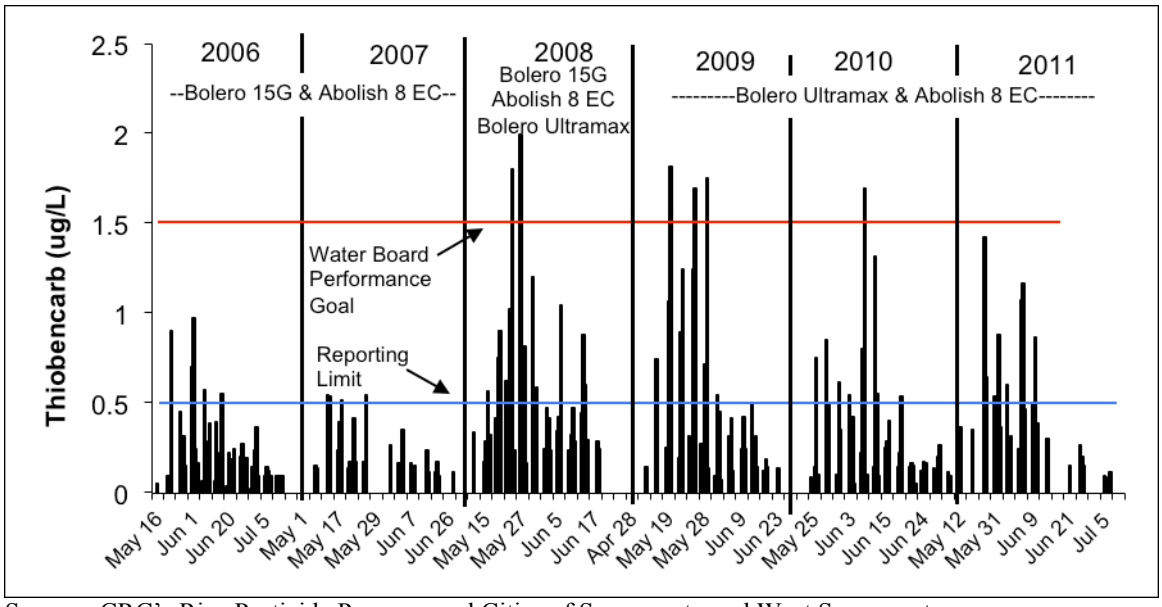
Figure 4 summarizes Sacramento River thiobencarb monitoring data since 1995. Since 1994, the highest Sacramento River thiobencarb concentrations occurred in 2002, when a

Figure 2. Sacramento Valley Thiobencarb Monitoring Locations.



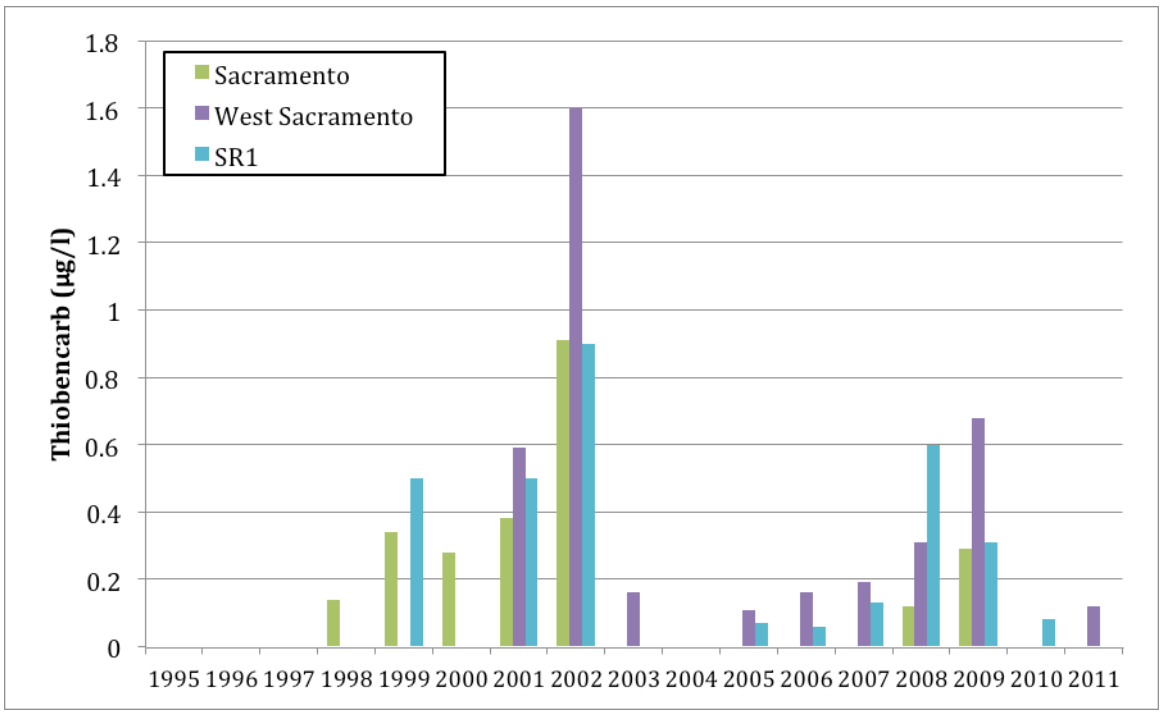
Source: CRC 2004 RPP Report, prepared by Kleinfelder Inc. Modified with permission of CRC. Scale is approximate.

Figure 3. Thiobencarb Monitoring Data Summary 2006-2011



Source: CRC's Rice Pesticide Program and Cities of Sacramento and West Sacramento

Figure 4. Sacramento River Peak Thiobencarb Measurements 1995-2011



Source: CRC's Rice Pesticide Program, DPR, and Cities of Sacramento and West Sacramento

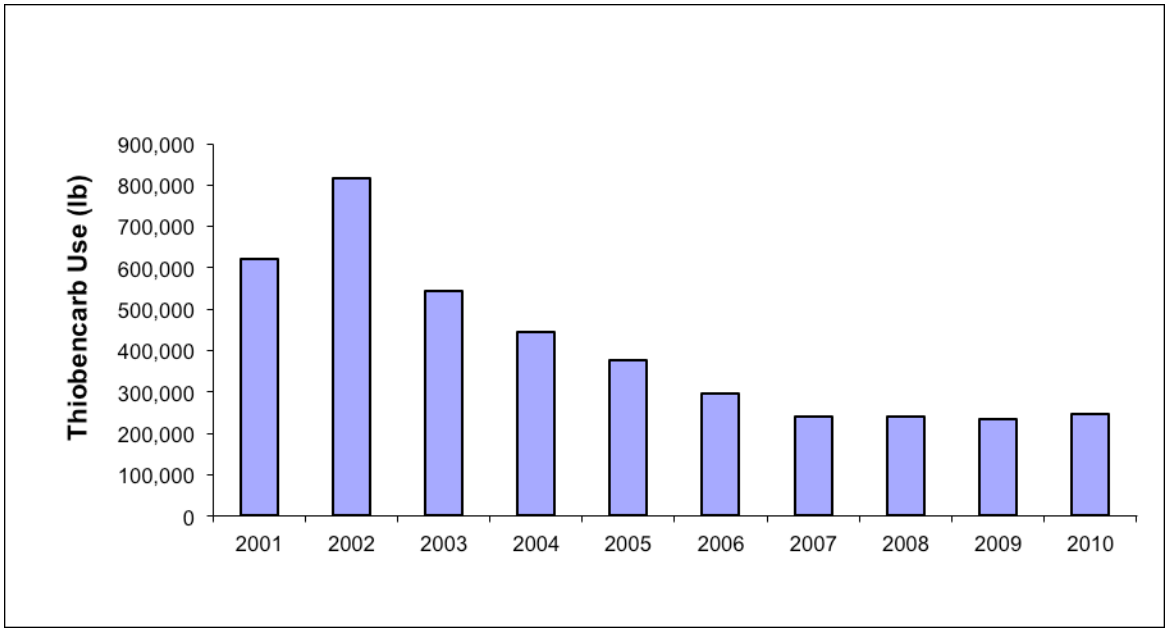
storm triggered emergency releases of water from many thiobencarb-treated rice fields. Concentrations increased again in recent years. The May 26, 2009 (Memorial Day) Sacramento River sample near the City of West Sacramento's Bryte Bend Water Treatment Plant intake contained 0.68 ppb.

Table 1 lists monitoring samples between 2001 and 2011 with thiobencarb concentrations greater than 1 part per billion. One ppb is the Water Board water quality objective for the Sacramento River; the California secondary Maximum Contaminant Level for drinking water, and U.S. EPA's aquatic life benchmark for the most sensitive class of aquatic species (aquatic invertebrates).

Sacramento Valley Thiobencarb Use

After declining steadily in the early 2000s, thiobencarb use in the Sacramento Valley has stabilized in recent years (see Figure 5). Early reports to DPR (CRC 2011) indicate that in 2011, Sacramento Valley rice growers applied about 180,000 pounds of thiobencarb. According to DPR, the geographic distribution of thiobencarb usage may have shifted south in recent years, moving it nearer to drinking water supply intakes (Luo 2010).

Figure 5. Sacramento Valley Rice Thiobencarb Use 2001-2010



Source: DPR and CRC Rice Pesticide Program Annual Reports, 2001-2010.

Sacramento Valley Rice Thiobencarb Management Practices

The RPP has focused on implementation of management practices to control the four pathways by which thiobencarb may reach surface water:

- off-target application (e.g., drift),
- emergency discharges,
- water seeping through dikes around fields, and
- water discharges from treated fields (discharge is allowed after hold time).

**Table 1. Thiobencarb Sampling 2001 – 2011:
Summary of Values ≥1 Microgram/Liter**

Sampling Location	Date	Concentration (µg/l)
Colusa Basin Drain - CBD5	May 3, 2001	1.3 1.27 (duplicate sample)
Colusa Basin Drain - CBD5	May 8, 2001	5.1
Colusa Basin Drain - CBD5	May 10, 2001	5.9 5.1 (duplicate sample)
Colusa Basin Drain - CBD5	May 15, 2001	2.2
Colusa Basin Drain - CBD5	May 17, 2001	2.7
Colusa Basin Drain - CBD5	May 22, 2001	4.8
Colusa Basin Drain - CBD5	May 24, 2001	5.5
Colusa Basin Drain - CBD5	May 29, 2001	4.0
Butte Slough - BS1	May 29, 2001	2.6
Colusa Basin Drain - CBD5	May 31, 2001	3.0
Colusa Basin Drain - CBD5	June 5, 2001	2.1
Butte Slough - BS1	June 5, 2001	1.5
Colusa Basin Drain - CBD5	June 7, 2001	1.6
Colusa Basin Drain - CBD5	June 12, 2001	1.6
Colusa Basin Drain - CBD5	June 14, 2001	1.4
Colusa Basin Drain - CBD5	June 19, 2001	1.1
Colusa Basin Drain - CBD5	June 21, 2001	1.2
Colusa Basin Drain - CBD5	May 7, 2002	3.7
Colusa Basin Drain - CBD5	May 9, 2002	5.3 5.75 (duplicate sample)
Colusa Basin Drain - CBD5	May 14, 2002	7.2
Colusa Basin Drain - CBD5	May 16, 2002	3.6 3.41 (duplicate sample)
Butte Slough - BS1	May 16, 2002	1.4
Colusa Basin Drain - CBD5	May 21, 2002	5.1
Butte Slough - BS1	May 21, 2002	2.3
Colusa Basin Drain - CBD5	May 23, 2002	8.2 6.96 (duplicate sample)
Butte Slough - BS1	May 23, 2002	3.4
Colusa Basin Drain - CBD5	May 28, 2002	7.3
Butte Slough - BS1	May 28, 2002	2.0
Colusa Basin Drain - CBD5	May 30, 2002	2.9 3.79 (duplicate sample)
Butte Slough - BS1	May 30, 2002	1.8
Colusa Basin Drain - CBD5	June 4, 2002	2.2
Colusa Basin Drain - CBD5	June 6, 2002	2.0 2.23 (duplicate sample)
Colusa Basin Drain - CBD5	June 11, 2002	1.1
Colusa Basin Drain - CBD1	May 30, 2002	6.2

**Table 1. Thiobencarb Sampling 2001 – 2011:
Summary of Values ≥1 Microgram/Liter (Continued)**

Sampling Location	Date	Concentration (µg/l)
Colusa Basin Drain - CBD1	June 4, 2002	4.7
Colusa Basin Drain - CBD1	June 6, 2002	2.8
Colusa Basin Drain - CBD1	June 11, 2002	2.0
Colusa Basin Drain - CBD1	June 13, 2002	1.4
West Sacramento	May 24, 2002	1.6
Colusa Basin Drain - CBD5	June 12, 2003	1.3
Colusa Basin Drain - CBD1	June 12, 2003	1.7
Colusa Basin Drain - CBD1	June 17, 2003	2.3
Colusa Basin Drain - CBD1	June 19, 2003	1.4
Colusa Basin Drain - CBD5	May 4, 2004	3.6
Colusa Basin Drain - CBD1	May 25, 2004	1.1
Colusa Basin Drain - CBD1	May 27, 2004	1.6
Colusa Basin Drain - CBD5	May 22, 2008	1.0
Colusa Basin Drain - CBD1	May 22, 2008	1.8
Butte Slough - BS1	May 27, 2008	2.0
Butte Slough - BS1	May 29, 2008	1.2
Colusa Basin Drain - CBD1	June 5, 2008	1.0
Colusa Basin Drain - CBD5	May 19, 2009	1.1
Colusa Basin Drain - CBD1	May 19, 2009	1.8
Colusa Basin Drain - CBD1	May 21, 2009	1.2
Colusa Basin Drain - CBD5	May 26, 2009	1.2
Colusa Basin Drain - CBD1	May 26, 2009	1.5 1.8 (duplicate sample)
Colusa Basin Drain - CBD1	May 28, 2009	1.75
Colusa Basin Drain - CBD1	June 8, 2010	1.6 1.8 (duplicate sample)
Colusa Basin Drain - CBD5	June 10, 2010	1.1 1.5 (duplicate sample)
Colusa Basin Drain - CBD5	May 24, 2011	1.4
Colusa Basin Drain - CBD5	June 7, 2011	1.1
Colusa Basin Drain - CBD1	June 7, 2011	1.2

Source: CRC's Rice Pesticide Program, DPR, and Cities of Sacramento and West Sacramento

Monitoring Site Locations:
CBD5 - Colusa Basin Drain within the Colusa National Wildlife Refuge south of Highway 20
BS1 - Butte Slough on Lower Pass Road northeast of Meridian
CBD1 - Colusa Basin Drain at Road 99E and near Road 108 west of Knights Landing
SSB - Sacramento Slough downstream of the Karnack pumps
SR1 - Sacramento River at the Village Marina on Garden Highway
Sacramento - Sacramento River Water Treatment Plant Intake
West Sacramento - Bryte Bend Water Treatment Plant Intake

Since 2003, the RPP has included best management practices to address each of these four pathways. Current thiobencarb management practices, which are detailed in DPR recommended restricted use permit conditions and the Central Valley Water Board Rice Pesticide Program resolution include drift minimization practices; minimum water hold times; maximum seepage rates; limitations on emergency discharges; application, seepage, and water hold time compliance inspections (partially funded by growers and a registrant); and mandatory annual thiobencarb stewardshipsessions.

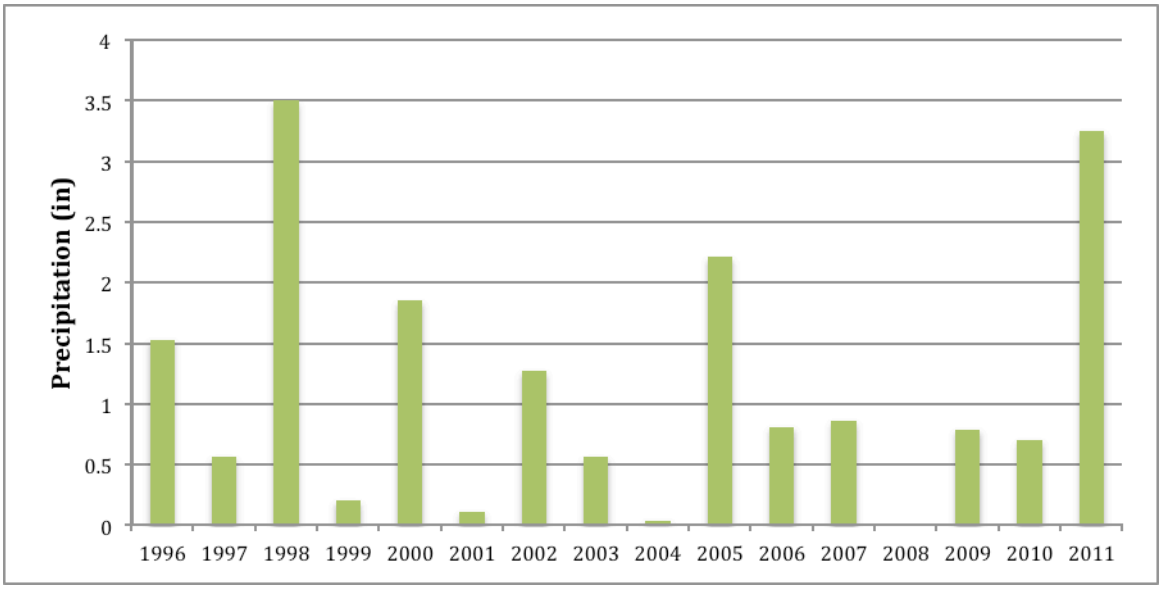
RPP participants strengthened management practices in 2009 and 2010 in response to increases in upstream and river thiobencarb monitoring concentrations and multiple thiobencarb performance goal exceedances. In 2010, the California Rice Commission (CRC) increased its outreach to pesticide applicators, dealers, and distributors and provided funding to increase County Agricultural Commissioner surveillance inspections. Other 2010 changes include increased attention from regulatory agencies (particularly DPR) and improved thiobencarb (Bolero) product labeling that clarified water hold times in treated fields.

Evaluation of Sacramento Valley Thiobencarb Monitoring Data

Rain Events

During the California rice-growing season, rainfall amounts can vary quite significantly (see Figure 6). Rainfall, particularly heavy storms, can cause growers to releases water from thiobencarb-treated fields prior to the required hold time. In the 1990s, early releases were relatively common. A major thrust of RPP management practices has been to develop grower practices that limit the potential for early releases. Since 2003, reported early releases have been fairly rare.

Figure 6. Total Precipitation in Colusa County May 1-June 30



Source: University of California Statewide Integrated Pest Management Program California weather database, Colusa A Station, Colusa California.

In 2002, there was a significant rain event in mid-May that was associated with 33 emergency releases of water from thiobencarb treated rice fields. After the storm event, monitoring found the highest Sacramento River thiobencarb concentrations measured since the early 1990s—as high as 1.6 ppb.

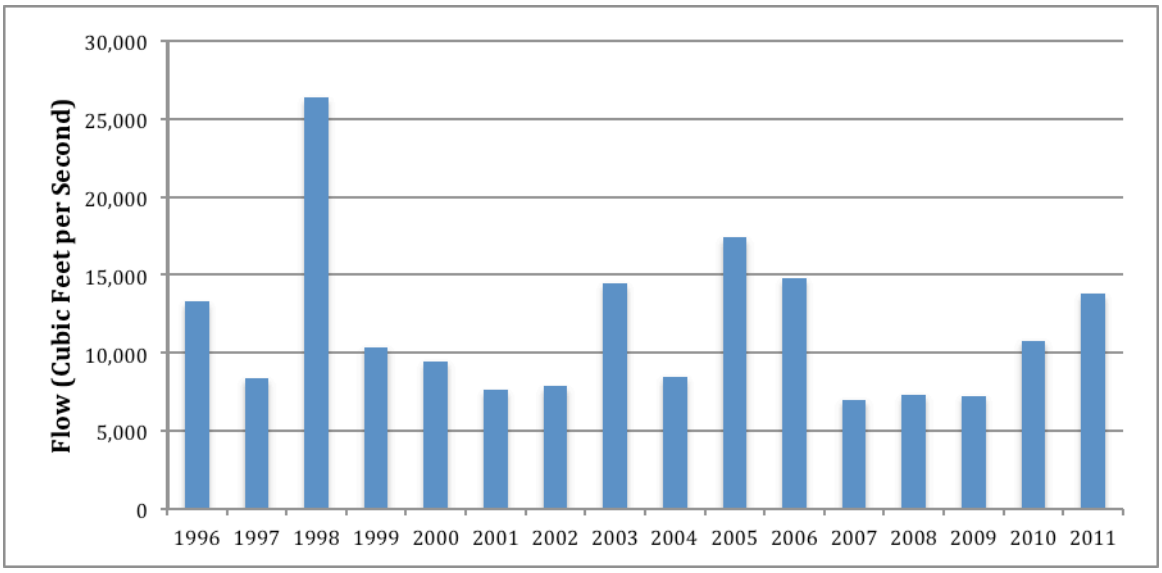
Since 2003, rainfall levels during the thiobencarb season have been relatively low and no significant rain events have occurred during the main part of the thiobencarb application season. In both 2005 and 2011 relatively high amounts of rainfall occurred, but rainfall was spread out—rain occurred in multiple small events separated by short dry periods. In 2011, a significant (about one inch) rain event occurred on June 28, at the very end of the thiobencarb season. This event had limited impact on thiobencarb concentrations. In 2005 and 2011, growers reported 2 (2005) and zero (2011) emergency discharges of water from thiobencarb treated rice fields, probably because spread out rainfall is easier for growers to manage than a single intense storm like the one in 2002. Unlike 2002, when Sacramento River flows were relatively low, in 2005 and 2011, high river flows offered significant opportunity for dilution of any thiobencarb releases.

Water Flow

Monitoring data demonstrate the importance of dilution of thiobencarb by water flowing in the Sacramento River. As shown in Figure 7, the flows in the Sacramento River vary significantly from year to year. In 2011 and 2010, higher Sacramento River flows reduced Sacramento River thiobencarb concentrations. In the 2011 peak application period (May 15 through June 14), 2011 flows were twice the average flows in 2007-2009. In the peak application period in 2010 (May 15 through June 14), flows were 60% higher than average flows in 2007-2009.

Higher flows increase dilution of thiobencarb, reducing measured concentrations. Because no flow data are available at the Colusa Basin Drain, Butte Slough, and Sacramento Slough monitoring locations, while it is possible

Figure 7. Average Sacramento River Flow at Colusa County, May 15- June 14



Source: California Department of Water Resources, California Data Exchange Center, Sacramento River gauge at Colusa, California.

to infer from the high river flows that dilution may have reduced upstream thiobencarb concentrations, this hypothesis cannot be confirmed.

Table 2 and Figure 8 summarize the relationship of peak annual thiobencarb concentration and average annual Sacramento River flow. Since 1998, when river flows have been high, thiobencarb concentrations have not exceeded 0.2 micrograms per liter (µg/L). Every time that river thiobencarb concentrations exceeded 0.5 µg/L, river flows were low to median (less than 11,000 cubic feet per second [cfs]).

The highest Sacramento River concentration measured between 1998 and 2011 occurred subsequent to a large (>1 inch) rain event during a low-flow year (2002). Large rain events appear to correlate to increased thiobencarb concentrations in the Sacramento River. The relationship between storm events and River thiobencarb concentrations cannot be fully analyzed because river monitoring has not been timed to capture flows subsequent to major storm events. Sometimes multi-day gaps occurred between storm events and the next river samples.

Wind

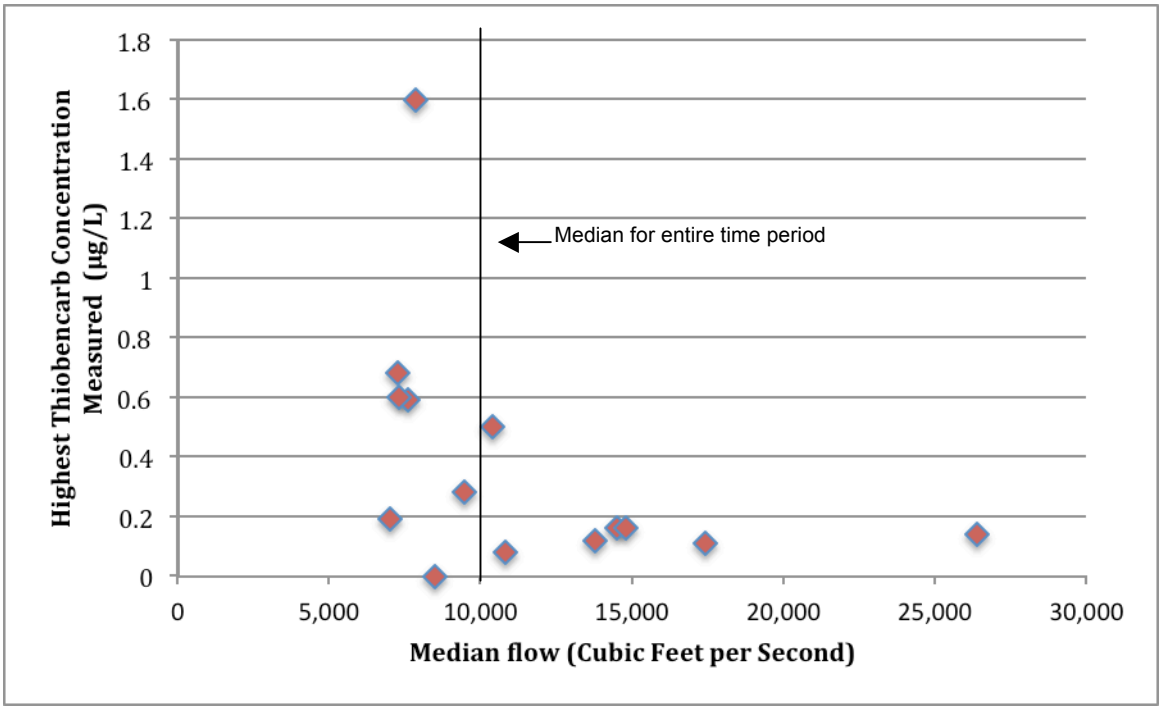
High wind puts pressure on levees. Early releases may be used by growers to protect levee integrity. Figure 9 shows daily peak wind levels recorded in Colusa County from 2006 through 2009. In 2008, the wind levels were reportedly problematic for growers. In 2008, one early release was reported. Data from past years has not been evaluated.

Table 2. Peak Annual Sacramento River Thiobencarb Concentrations, River Flow, and Storm Events 1998-2011

Year	Peak Sacramento River Thiobencarb Concentration(µg/L)	Average River Flow May 15-June 14 (cfs)	Largest Storm Event Between May 15 and June 14 (in)	Dates of Largest Storm Event	Date of Peak Thiobencarb Concentration
2002	**1.6**	7,997	**1.23**	**May 19-21**	**24-May**
2009	0.68	7,315	0.22	June 3-5	26-May
2008	0.6	7,242	<0.01	N/A	22-May
2001	0.59	7,797	<0.01	N/A	29-May
1999	0.5	10,312	0.12	Jun 2-3	8-Jun
2000	0.28	9,609	**1.04**	**May 14-15**	**22-May**
2007	0.19	7,166	0.43	5-Jun	23-May
2003	0.16	14,568	<0.01	N/A	16-Jun
2006	0.16	15,247	0.63	May 21-22	14-Jun
1998	0.14	28,235	**1.9**	**May 27-29**	**1-Jun**
2011	0.12	14,786	0.67	May 25-26	1-Jun
2005	0.11	21,349	0.47	May 17-18	14-Jun
2010	0.08	11,355	0.45	27-May	25-May
2004	<0.1	8,962	0.04	19-May	N/A

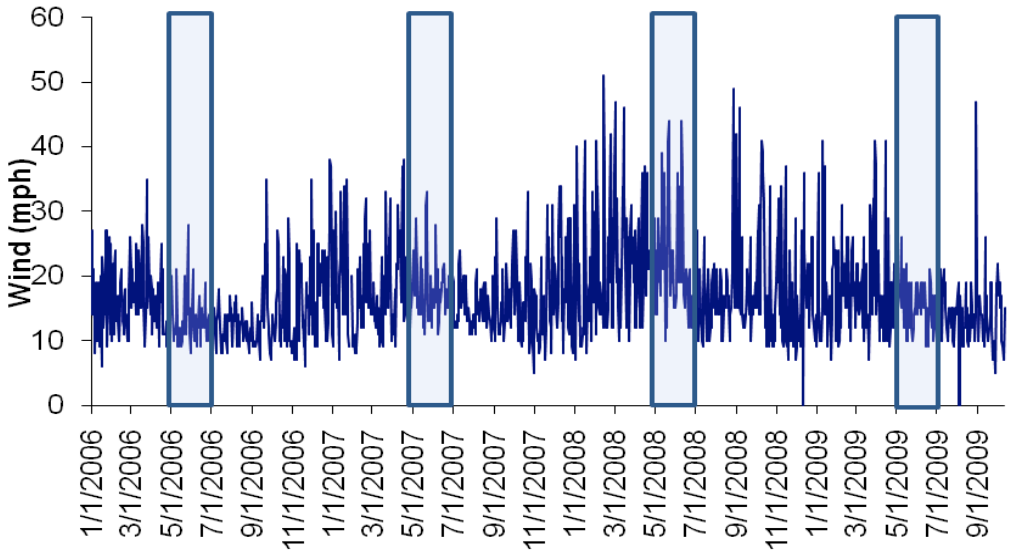
Notes: "Storm Event" defined as sum of rainfall totals on consecutive days with measurable rain reported at Colusa Station A. Bold values indicate “major storm events,” defined as at involving at least one inch of precipitation.
Source: DPR 1998-2002; CRC 2003-2010. Precipitation from University of California Statewide Integrated Pest Management Program California weather database, Colusa A Station, Colusa California. Flow from California Department of Water Resources, California Data Exchange Center, Sacramento River gauge at Colusa, California.

Figure 8. Relationship of Average River Flow to Highest Measured River Thiobencarb Concentration, 1998-2011



Source: Data in Table 2. Non-detects graphed as zero.

Figure 9. Maximum Daily Wind Speeds, Colusa County 2006-2009 Highlighted areas show approximate RPP monitoring time period.



Source: University of California Statewide Integrated Pest Management Program California weather database, data collected at Nickels Soil Laboratory, Arbuckle California

Formulation Change - Potential Causes of Thiobencarb Concentration Increases Starting in 2008?

A thiobencarb product formulation used only between 2003 and 2007 (15G) correlates with the lowest thiobencarb concentrations measured during the entire history of thiobencarb monitoring in the Sacramento Valley watershed. In 2008, the new Ultramax formulation was introduced. That year, watershed thiobencarb concentrations increased. Potential causes for the 2008-2011 increase in thiobencarb concentration were examined:

- Thiobencarb use. Thiobencarb use was relatively stable during this period. DPR noted a possible southward shift in usage within the Sacramento valley.
- Thiobencarb management practices. Practices were not significantly changed until new measures were added in response to 2008-2009 monitoring data.
- Rain Events. No significant rain events occurred during the peak thiobencarb application season, except for a late event in 2011 that was not associated with elevated thiobencarb levels.
- Water Flow. River levels were relatively low in 2007-2009. These low flows may have contributed to higher concentration measurements during this period.
- Wind. High winds occurred during the application period in 2008, but did not recur in 2009-2011.
- Emergency releases. The level of emergency releases did not increase.
- Violations of water hold or seepage requirements. Violation rates did not increase.

Except for a change in product formulation, no other significant change was identified between 2003 and 2011 that would have cause thiobencarb concentration increases after 2008.

These topics were discussed with the California Rice Commission (CRC) and DPR at the RPP Coordination meeting in October 2009. To ensure that all possible causes were considered, the following factors were specifically reviewed by meeting participants: drift, emergency releases, wind, rain, seepage, hold time, application quantity/acreage, application locations, river flow, and formulation. Other than the change in the granular thiobencarb formulation, no change was identified that correlated with the increased Sacramento River thiobencarb concentrations.

History of Recent Thiobencarb Formulations

In California, thiobencarb is available in two formulations: a granular form that may be applied to flooded fields, and an emulsifiable concentrate that is applied to soil (which requires draining of flooded fields prior to application). Granular products are sold under the name "Bolero;" the emulsifiable concentrate is sold under the brand name "Abolish." Attachment 2 contains a list of California-registered thiobencarb products. The granular Bolero comprises 70-80% of the total quantity of California thiobencarb used (Acosta 2011). Since 1993, the granular product has been reformulated twice. The emulsifiable concentrate has not been reformulated.

From 1993-2002, the 10G formulation was used. This formulation contains a great deal of fine dust that was thought to increase drift of aerially applied materials. After high levels of thiobencarb that occurred across Sacramento valley rice growing areas and

flowed to the Sacramento River drinking water intakes after a rainstorm in 2002, DPR, rice growers, and the registrant implemented a series of management measures to reduce thiobencarb levels in surface waters. Among these 2002 measures was termination of all use of the 10G formulation in Sacramento valley rice growing areas.

In 2003, the 10G formulation was replaced with the less dusty 15G formulation in 2003. The 15G formulation was the sole granular formulation used between 2003 and 2007. The lowest Sacramento Valley watershed thiobencarb concentrations (2003-2007) correlate with the years when the 15G formulation was used.

In 2007, both U.S. EPA and the California Department of Pesticide Regulation (DPR) approved a slightly reformulated version of the granular thiobencarb Bolero product called "Bolero Ultramax," which became available for use in the 2008 California rice-growing season. The Ultramax formulation largely replaced 15G in 2008 and was the sole granular formulation available starting in 2009

Difference between 15G and Ultramax Formulations

On the basis of publicly available information, it appears that the difference between Bolero 15 G and the new Ultramax product is a change in the carrier (granule) material, which is a relatively inert solid material. According to the Material Safety Data Sheets for the two products, the carrier is either silica or talc. The exact nature of the formulation change is not clear. It is possible that the change involved the physical properties of the carrier material rather than its chemical composition. Since the chemical composition of pesticides is considered trade secret under both California and Federal law, the details of the actual formulation change are not available to the public.

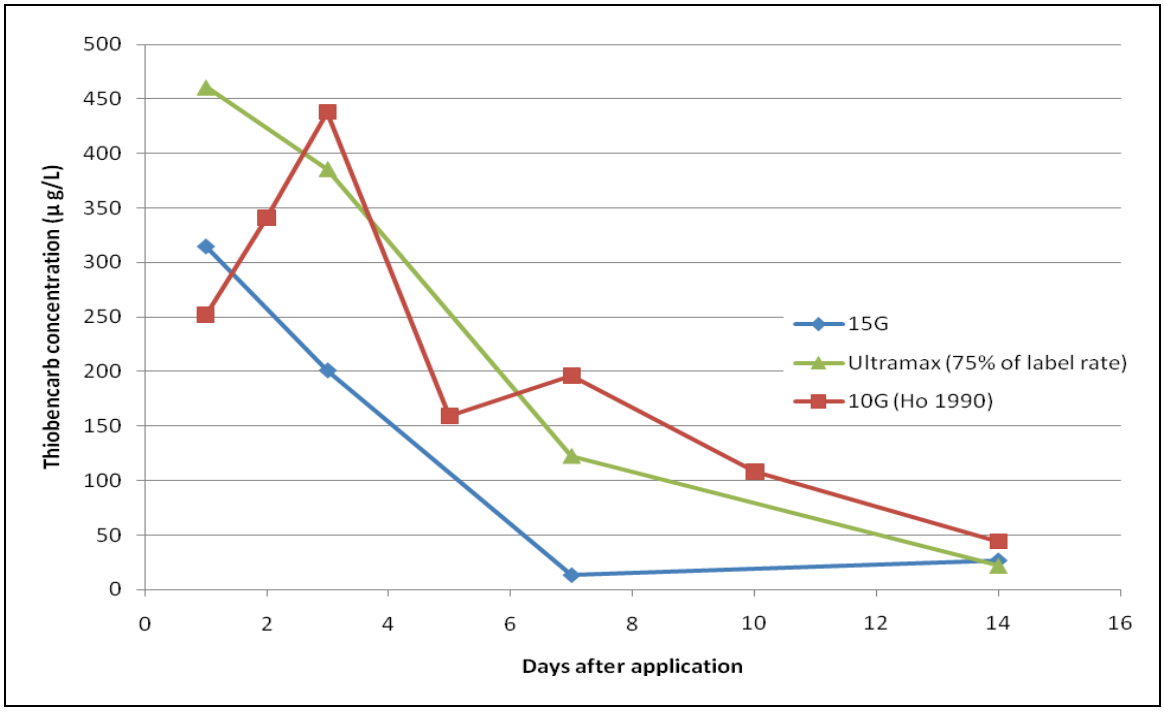
Water Quality Implications of Formulation Change

According to Valent Corporation data summarized in Figure 10, Bolero Ultramax releases thiobencarb into the water column at higher concentrations after initial application than does 15G. As shown in Figure 10, the 10G formulation used prior to 2003 also appeared to release higher concentrations of thiobencarb in water than 15G in the first days after application.

With the Ultramax formulation, rice field water thiobencarb concentrations do not appear to decline as expected. Water hold times for thiobencarb-treated rice fields were established on the basis of data for the 10G formulation linking hold time to thiobencarb degradation (Ho 1990). For the 10G formulation, the longer the hold time, the lower the thiobencarb concentration in rice field water. As shown in Figure 11, available data for the new Ultramax product do not show that thiobencarb concentrations consistently decrease in rice field water with longer hold times (Valent 2007).[1]

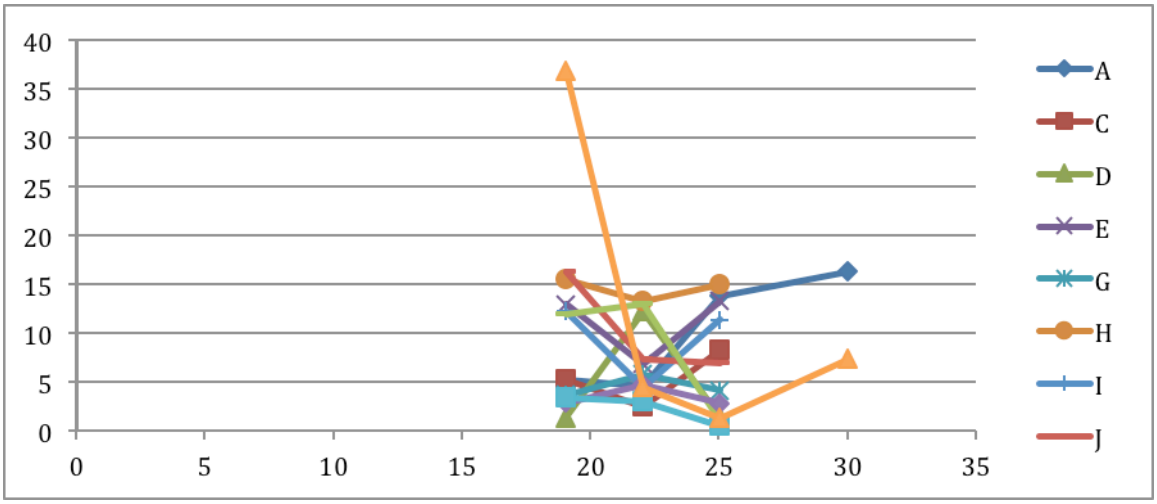
[1] Available data for the Ultramax formulation (Valent 2007) have significant limitations. No samples were taken prior to 19 days. Only two of the fields that were managed in accordance with label directions were sampled at 30 days. The report did not examine the source of the high variability in samples, nor did it assess other factors that typically affect thiobencarb concentrations in fields (e.g., soil type, water depth, total suspended solids in samples, wind speed, temperature).

Figure 10. Initial Thiobencarb Water Concentrations in Treated Rice Fields – Three Formulations Compared (Ultramax applied at only 75% of rate specified on label)



Note: Data are from a relatively small number of samples: an average of two values (one field each) for 15G and Ultramax; an average of one sample from each of 4 fields for 10G. Application rates were 4 pounds thiobencarb per acre for 10G and 15G and three pounds thiobencarb per acre for Ultramax.
Source: Valent 2008 (presentation included a table of the data that are graphed above.) and Ho 1990.

Figure 11. Thiobencarb Concentration Vs. Time from Valent Hold Time Study (Concentration in ppb; time in days)



Notes: Values are averages of two samples per field; non-detects graphed at 0.5 times detection limit. No samples were taken before 19 days. Data for test fields where water management was inconsistent with the product label are omitted.
Source: Valent 2007

Available data, though limited, suggests that the fate of thiobencarb in the new Ultramax product could be different than the 10G and 15G formulations. There are various ways that the change in formulation could cause rice field thiobencarb concentrations to differ from the pattern for previous products. For example, the new formulation could release thiobencarb into water more easily not only at the time of application—but also when the granules are disturbed. If this is the case, wind and water flows would increase thiobencarb concentrations in rice field water. Another possibility is that the new granule material could reduce the rate of thiobencarb degradation.

The transition from the 15G formulation to the Ultramax formulation may have been a major factor in increased Sacramento Valley surface water thiobencarb concentrations from 2008-2011. Since the Ultramax formulation creates higher concentrations of thiobencarb immediately after application, it increases the thiobencarb concentrations associated with drift from aerial applications, seepage (if field levees are not controlled properly), and emergency discharges. The potential change in thiobencarb concentrations in permitted field discharges (if any) is unclear from available data.

Conclusions

There are four pathways by which thiobencarb may reach surface water: off-target application (e.g., drift), emergency discharges, water seeping through dikes around fields, and water discharges from treated fields (discharge is allowed after hold time).

Annual thiobencarb monitoring in the Sacramento Valley watershed began before 1990. In this long monitoring history, surface water thiobencarb concentrations during the thiobencarb use season often exceeded 1 part per billion. The highest thiobencarb levels occurred in the early 1980s and between 1992 and 2002. The lowest levels occurred between 2003 and 2007. Starting in 2008, thiobencarb concentrations again increased.

Surface water thiobencarb concentrations are affected by a variety of factors, including drift, emergency releases, wind, rain, seepage, hold time, application quantity/acreage, application locations, product formulation, and water flow levels in receiving waters.

California rice growers, California Department of Pesticide Regulation (DPR), California's Central Valley Water Quality Control Board (Water Board), thiobencarb registrants, and the Sacramento River water utilities worked together to develop the Rice Pesticide Program (RPP) in the 1990s. After more than 20 years, this program continues to adapt management practices in its effort to control thiobencarb levels in Sacramento valley surface waters.

The thiobencarb granular formulation change from 15G to Ultramax could have significantly contributed to the increase in Sacramento valley surface water thiobencarb concentrations in 2008-2011. This potential merits further examination by the manufacturer and pesticide regulators.

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ATTACHMENT 1

Sacramento Valley Thiobencarb Monitoring Data Summaries 2008-2011

Cities of Sacramento and West Sacramento
2008 Thiobencarb Monitoring Data Summary

Date	Thiobencarb Concentration (µg/L)		
	West Sacramento	**Sacramento**	**% Sacto. River at SRR Intake**
29-Apr	<0.1	<0.1	71.2
15-May	0.31	0.12	70.3
26-May	<0.1*	<0.1	66.6
29-May	0.16	<0.1	64.2
5-Jun	<0.1	<0.1	82.8

[a] Analysis done by TestAmerica Laboratory
Source: Values provided by City of Sacramento's Water Quality Laboratory

Monitoring Site Locations:
Sacramento - Sacramento River Water Treatment Plant Intake
West Sacramento - Bryte Bend Water Treatment Plant Intake (except for * = sample taken at Crawdad's marina, which is slightly downstream from the water treatment plant, just downstream of the Natomas main drain, and near the junction with the American River).

California Rice Commission, 2008 Thiobencarb Monitoring Data Summary

Sampling Date	Thiobencarb Concentration (µg/L)				
	CBD5	BS1	CBD1	SSB	SR1
29-Apr	BRL	BRL	BRL	BRL	BRL
6-May	0.33	BRL/BRL*	BRL	BRL	BRL
13-May	0.28	0.17	0.56	0.32	BRL
20-May	0.75	0.41	0.90	BRL	BRL/BRL*
22-May	1.02	0.38	1.80	0.23	0.62
27-May	0.78	1.99	0.81/0.80*	0.16	BRL
29-May	0.34	1.2	0.58	BRL	BRL
3-Jun	0.47	0.24	0.41	0.23	BRL
5-Jun	0.42	0.34	1.04	BRL/BRL*	BRL
10-Jun	0.32	0.23/BRL*	0.47	0.28	BRL
12-Jun	0.88	0.44	0.6	0.29	BRL
17-Jun	BRL	BRL	0.28	0.24	BRL
24-Jun	BRL	BRL	BRL	BRL	BRL/BRL*
1-Jul	BRL/BRL*	BRL	BRL	BRL	BRL

BRL = Below laboratory reporting limits
Table includes values below laboratory detection limits (Valent - 0.5 µg/L, EMA - 0.5 µg/L).
All samples were analyzed by Valent except for data marked with "*." These values are from split samples analyzed by Environmental Micro Analysis, Inc.
Source: Values provided by CRC.

Monitoring Site Locations:
CBD5 - Colusa Basin Drain within the Colusa National Wildlife Refuge south of Highway 20
BS1 - Butte Slough on Lower Pass Road northeast of Meridian
CBD1 - Colusa Basin Drain at Road 99E and near Road 108 west of Knights Landing
SSB - Sacramento Slough downstream of the Karnack pumps
SR1 - Sacramento River at the Village Marina on Garden Highway

Cities of Sacramento and West Sacramento
2009 Thiobencarb Monitoring Data Summary

Date	Thiobencarb Concentration (µg/L)		
	West Sacramento	Sacramento	% Sacto. River at SRR Intake
24-Apr	<0.2 [a]	<0.2 [a]	82
1-May	<0.1	<0.1	53.8
8-May	<0.1	<0.1	69.7
15-May	<0.1	<0.1	75.2
22-May	0.11	<0.1	77.8
26-May	0.68*	0.29	77.9
29-May	0.22	0.18	83.8
5-Jun	<0.1	<0.1	80.5
12-Jun	<0.1	<0.1	87.5

[a] Analysis done by TestAmerica Laboratory
Source: Values provided by City of Sacramento's Water Quality Laboratory

Monitoring Site Locations:
Sacramento - Sacramento River Water Treatment Plant Intake
West Sacramento - Bryte Bend Water Treatment Plant Intake (except for * = sample taken at Crawdad's marina, which is slightly downstream from the water treatment plant, just downstream of the Natomas main drain, and near the junction with the American River).

California Rice Commission, 2009 Thiobencarb Monitoring Data Summary

Sampling Date	Thiobencarb Concentration (µg/L)				
	CBD5	**BS1**	**CBD1**	**SSB**	**SR1**
28-Apr	BRL	BRL	BRL	BRL	BRL
5-May	BRL	BRL/BRL*	0.14	BRL	BRL
14-May	0.74	BRL	BRL	BRL	BRL
19-May	1.06	0.25	1.81	BRL	BRL/BRL*
21-May	0.89	0.19	1.24	BRL	BRL
26-May	1.24	BRL	1.54/1.84*	BRL	0.31
28-May	0.71/BRL*	0.15	1.75	0.13	0.27
2-Jun	0.54	0.09	0.45	0.07	BRL
4-Jun	0.31	BRL	0.41	0.12/BRL*	BRL
9-Jun	0.24	BRL	0.42	0.24	BRL
11-Jun	0.21	0.5	0.31	0.14	BRL
16-Jun	0.18	0.12	0.14	BRL	BRL
23-Jun	0.13	BRL	BRL	BRL	BRL

BRL = Below laboratory reporting limits
Table includes values below laboratory detection limits (Valent - 0.5 µg/L, EMA - 0.5 µg/L).
All samples were analyzed by Valent except for data marked with "*." These values are from split samples analyzed by Environmental Micro Analysis, Inc.
Source: Values provided by CRC.

Monitoring Site Locations:
CBD5 - Colusa Basin Drain within the Colusa National Wildlife Refuge south of Highway 20
BS1 - Butte Slough on Lower Pass Road northeast of Meridian
CBD1 - Colusa Basin Drain at Road 99E and near Road 108 west of Knights Landing
SSB - Sacramento Slough downstream of the Karnack pumps
SR1 - Sacramento River at the Village Marina on Garden Highway

Cities of Sacramento and West Sacramento
2010 Thiobencarb Monitoring Data Summary

Date	Thiobencarb Concentration (μg/L)		
	West Sacramento	Sacramento	% Sacto. River at SRR Intake
29-Apr	<0.1	<0.1	78.2
11-May	<0.1	<0.1	71.1
18-May	<0.1	<0.1	70.6
20-May	<0.1	<0.1	49.5
26-May	<0.1	<0.1	47.6
27-May	<0.1	<0.1	48.6
29-May	<0.1[a]	<0.1	49.0
31-May	<0.1[b]	<0.1	60.5
7-Jun	<0.1	<0.1	58.4
9-Jun	<0.1	<0.1	56.2
16-Jun	<0.1	<0.1	56.6
21-Jun	<0.1	<0.1	56.0
1-Jul	<0.1	<0.1	80.8
6-Jul	<0.1	<0.1	74.2

[a] Sample taken at Crawdad's marina, which is slightly downstream from the water treatment plant, just downstream of the Natomas main drain, and near the junction with the American River
[b] Sample taken at Sand Cove Park, which is across the river and slightly downstream from the water treatment plant.
Source: Values provided by City of Sacramento's Water Quality Laboratory

Monitoring Site Locations:
Sacramento - Sacramento River Water Treatment Plant Intake
West Sacramento - Bryte Bend Water Treatment Plant Intake (except for as noted above).

California Rice Commission, 2010 Thiobencarb Monitoring Data Summary

Sampling Date	Thiobencarb Concentration (µg/L)				
	CBD5	**BS1**	**CBD1**	**SSB**	**SR1**
11-May	BRL	BRL	BRL	BRL	BRL
18-May	BRL	BRL	BRL	BRL	BRL
25-May	0.14	BRL	0.75	0.10	0.08
27-May	0.85	BRL	0.50	BRL	BRL
1-Jun	0.61	0.10	0.35	BRL	BRL/BRL*
3-Jun	0.24	0.28/0.80*	0.42	0.05	BRL
8-Jun	0.8	0.22	1.58/1.8*	0.10	BRL
10-Jun	1.12/1.5*	0.14	0.55	0.09	BRL
15-Jun/ 16-Jun	0.28	0.25	0.40	BRL	BRL
17-Jun	0.22	0.14	0.53	BRL/BRL**	BRL
22-Jun	0.16	0.14	0.15	0.05	BRL
24-Jun	0.17	0.12	0.16	BRL	BRL/BRL**
29-Jun	0.06	0.13	0.20	0.26	BRL
6-July	0.11	BRL	0.09	BRL	BRL

BRL = Below laboratory reporting limits
Table includes values below laboratory detection limits (Valent - 0.5 µg/L, EMA - 0.5 µg/L).
All samples were analyzed by Valent except for data marked with "*" or "**"
* Indicates values are from split samples analyzed by McCampbell Analytical
** Indicates values from California Laboratory Services.
Source: Values provided by Valent and CRC.

Monitoring Site Locations:
CBD5 - Colusa Basin Drain within the Colusa National Wildlife Refuge south of Highway 20
BS1 - Butte Slough on Lower Pass Road northeast of Meridian
CBD1 - Colusa Basin Drain at Road 99E and near Road 108 west of Knights Landing
SSB - Sacramento Slough downstream of the Karnack pumps
SR1 - Sacramento River at the Village Marina on Garden Highway

Cities of Sacramento and West Sacramento
2011 Thiobencarb Monitoring Data Summary

Date	Thiobencarb Concentration (µg/L)		
	West Sacramento	Sacramento	% Sacto. River at SRR Intake
25-Apr	<0.1	<0.1	65.6
5-May	<0.1	<0.1	62.3
9-May	<0.1	<0.1	58.7
17-May	<0.1	<0.1	58.6
18-May	<0.1	<0.1	70.6
23-May	<0.1	<0.1	67.2
26-May	<0.1	<0.1	64.2
30-May	<0.1 (0.096)[a]	<0.1	67.0
31-May	<0.1	<0.1	70.9
1-Jun	0.12	<0.1	70.1
2-Jun	<0.1	<0.1	73.6
6-Jun	<0.1	<0.1	67.5
7-Jun	<0.1	<0.1	70.0
13-Jun	<0.1	<0.1	55.2
20-Jun	<0.1	<0.1	43.1

[a]Sample taken at Riverbank Marina, which is slightly downstream from the water treatment plant, just downstream of the Natomas main drain, and near the junction with the American River
Source: Values provided by City of Sacramento's Water Quality Laboratory

Monitoring Site Locations:
Sacramento - Sacramento River Water Treatment Plant Intake
West Sacramento - Bryte Bend Water Treatment Plant Intake (except for as noted above).

California Rice Commission, 2011 Thiobencarb Monitoring Data Summary

Sampling Date	Thiobencarb Concentration (µg/L)				
	CBD5	BS1	CBD1	SSB	SR1
12-May	0.36	BRL	BRL	BRL	BRL
17-May	0.35/BRL*	BRL	BRL	BRL	BRL
24-May	1.42	BRL	0.64	BRL	BRL
31-May	0.48	0.53	0.88	0.36	BRL
2-Jun	0.25	0.6	0.35	0.31/BRL*	BRL/BRL*
7-Jun	1.07	0.24/BRL*	1.16	0.46	BRL
9-Jun	0.49	BRL	0.86	0.38	BRL/BRL*
14-Jun	BRL	BRL	0.30	BRL	BRL
16-Jun	BRL	BRL	BRL/BRL*	BRL	BRL
21-Jun	0.15	BRL	BRL	BRL	BRL
23-Jun	0.20	0.26	0.15	BRL/BRL*	BRL
28-Jun	BRL	BRL	BRL	BRL	BRL
5-July	BRL	0.09	0.08	0.11	BRL
12-July	BRL	BRL	BRL	BRL	BRL

BRL = Below laboratory reporting limits
Table includes values below laboratory detection limits (Valent - 0.5 µg/L, CLS - 0.5 µg/L).
All samples were analyzed by Valent except for data marked with "*"
*Indicates values are from split samples analyzed by California Laboratory Services.
Source: Values provided by Valent and CRC.

Monitoring Site Locations:
CBD5 - Colusa Basin Drain within the Colusa National Wildlife Refuge south of Highway 20
BS1 - Butte Slough on Lower Pass Road northeast of Meridian
CBD1 - Colusa Basin Drain at Road 99E and near Road 108 west of Knights Landing
SSB - Sacramento Slough downstream of the Karnack pumps
SR1 - Sacramento River at the Village Marina on Garden Highway

ATTACHMENT 2
California Registered Thiobencarb Products

Product Name	Date registered	Registration #	% Thiobencarb	Formulation	Notes
Bolero Technical	12/10/07	63588-4-AA	97.4%	Liquid (Manufacturing Concentrate)	This manufacturing-use material is only for formulating products. It cannot be used on fields.
Abolish 8 EC Rice Herbicide	03/11/93	59639-79-ZA	84%	Liquid (Emulsifiable Concentrate)	
Bolero 8 EC	03/11/93	59639-79-AA	84%	Liquid (Emulsifiable Concentrate)	
Bolero 10 G	04/29/93	59639-80-AA	10%	Granules	The use of this formulation is prohibited in Sacramento Valley rice growing counties due to dusts associated with the formulation.
Bolero 15 G	09/26/01	59639-112-AA	15%	Granules	
Bolero 15 G Ultramax Rice Herbicide	02/02/07	59639-112-ZA	15%	Granules	"New formulation"
Bolero Ultramax Herbicide	11/29/07	59639-112-ZB	15%	Granules	"New formulation"

Note: Registration numbers starting with "59639" are associated with Valent Corporation. Registration numbers starting with "63588" are associated with K-I Chemical.