

Rice Pesticides Monitoring in the Sacramento Valley, 1995

by

K. P. Bennett, N. Singhasemanon, N. Miller, and R. Gallavan

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ABSTRACT

The presence of rice pesticides in surface waterways of the Sacramento Valley is of continuing concern to those charged with the task of protecting quality of the region's waters. In the late 1970's, some waterways in this region were found to have contained some rice pesticide residues at levels high enough to be acutely toxic to aquatic organisms. Thus, an annual monitoring program was implemented in 1980 to measure the concentrations of selected rice pesticides and assess their potential toxicity in three of the Sacramento Valley's waterways: the Colusa Basin Drain, Butte Slough, and the Sacramento River near the City of Sacramento.

The 1995 monitoring program focused on five rice pesticides – molinate, thiobencarb, carbofuran, methyl parathion, and malathion – in the same three waterways. In addition, mass transport of pesticides in the Sacramento River was estimated using measured concentrations and discharge. Samples were collected prior to and during the period of peak discharge from flooded rice fields. Additionally, weekly samples from the Colusa Basin Drain were tested by the California Department of Fish and Game for acute toxicity using the test organism, *Ceriodaphnia dubia*.

In 1995, maximum concentrations in the Colusa Basin Drain were measured at 25 ug/L for molinate, 3.5 ug/L for thiobencarb, 0.70 ug/L for carbofuran, 0.08 ug/L for methyl parathion, and 1.0 ug/L for malathion. In Butte Slough, the maximum concentrations were 8.5 ug/L for molinate, 1.3 ug/L for thiobencarb, 0.57 ug/L for carbofuran, 0.19 ug/L for methyl parathion, and 0.64 ug/L for malathion. The maximum concentration of molinate in the Sacramento River was measured at 0.16 ug/L. There were no detections of thiobencarb, carbofuran, methyl parathion, or malathion in the Sacramento River. Background levels in the waterways, measured two to three weeks prior to the applications of these chemicals, indicated no detectable residues for all pesticides. The total estimated amount of molinate transported by the Sacramento River past the City of Sacramento was 83.7 kg, down 23 percent from 1994 (109 kg) and 96 percent from 1993 (2,007 kg). Waters collected from the Colusa Basin Drain were not acutely toxic to the test organism, *Ceriodaphnia dubia*, in seven of eight samples. The source of toxicity in the one sample was undetermined and did not appear related to the pesticides measured.

Pesticides used in the production of rice were detected at levels which exceeded the State's prescribed performance goals in both the Colusa Basin Drain and Butte Slough during May and June. Specifically, molinate, thiobencarb, carbofuran, and malathion performance goals were exceeded on at least one occasion in the Colusa Basin Drain. Also, carbofuran, methyl parathion, and malathion performance goals were exceeded on at least one occasion in Butte Slough. As rice pesticide levels in the agricultural drains and sloughs of the Sacramento Valley are dependent on numerous and dynamic variables (e.g. use patterns, water management, and weather), accurate prediction of those levels is difficult, and continued monitoring is recommended during future rice growing seasons to verify compliance with performance goals and narrative objectives.

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DISCLAIMER

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such product.

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CONVERSION FACTORS AND ABBREVIATIONS

Conversion Factors

Multiply	By	To obtain
hectare	2.471	acre
kilometers ²	0.3861	miles ²
cubic meters per second	35.31	cubic feet per second
meter	3.281	feet
kilometer	0.6214	mile
kilogram	2.204	pound

Temperature can be converted from degrees Celsius (°C) to degrees Fahrenheit (°F) with the following equation: $^{\circ}\text{F} = 1.8(^{\circ}\text{C}) + 32$

Abbreviations

g, gram	mg, milligram	kg, kilogram
L, liter	ml, milliliter	km, kilometer
ug/L, microgram per liter	mg/L, milligram per liter	ha, hectare
ppm, parts per million	ppb, parts per billion	cms, cubic meter per sec.

INTRODUCTION

California is one of the largest rice producers in the United States and has consistently maintained the highest yield per hectare in the nation (CDFA, 1995). In 1994, California produced 1,869,879 metric tons of rice on 196,425 hectares of land. Specifically, the Sacramento Valley comprises over 95 percent of that yearly rice production (Figure 1). Critical to this high yield in rice production is the use of pesticides to control weeds and insect damage. Of the pesticides used in rice production, the herbicides molinate and thiobencarb and the insecticides carbofuran, methyl parathion, and malathion are regularly used in the Sacramento Valley. In 1995, California growers applied 489,292 kg of molinate, 148,453 kg of thiobencarb, 25,699 kg of carbofuran, 12,443 kg of methyl parathion, and 4,590 kg of malathion on the state's rice crops (DPR, 1997). There is concern about their use due to their potential to cause aquatic toxicity.

Major agricultural drains in the Sacramento Valley's rice producing regions are tributaries of the Sacramento River. Since 1980, various sites have been evaluated annually for the presence of pesticides used in rice production. The annual evaluations were conducted in response to observed fish kills (primarily carp), which occurred in the late 1970's and early 1980's. Investigations from 1980 to 1982 by the California Department of Fish and Game (CDFG) concluded that these fish kills were due to the rice herbicide, molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbothioate)(Finlayson *et al.*, 1982). Additionally, another rice herbicide, thiobencarb (*S*-[(4-chlorophenyl)methyl] diethylcarbamothiate) was found to have caused an objectionable taste in Sacramento City drinking water during May and June of 1981 and 1982 (DHS, 1987). Both herbicides are used to control graminaceous weeds found in rice fields, particularly barnyard grass (*Echinochloa crus-galli*).

In 1990, the Central Valley Regional Water Quality Control Board (CVRWQCB) and the Department of Pesticide Regulation (DPR) established performance goals for the two herbicides and three insecticides also used in rice production- carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate), methyl parathion (*O,O*-dimethyl 0-4-nitrophenyl phosphorothioate), and malathion (*O,O*-dimethyl phosphorodithioate of diethyl

mercaptosuccinate). Performance goals are target concentrations that were developed to protect the beneficial uses of surface water in the state from rice pesticide contamination and provide a level by which compliance with a monitoring program could be measured. With the newly established performance goals, a more formal Rice Pesticides Monitoring Program began in 1991 to track the levels of these chemicals at selected sites. The current performance goals and selected physicochemical properties of the rice pesticides are listed in Table 1.

To reduce the amount of pesticide residues in the agricultural drains and sloughs of the Sacramento Valley, “holding times” were developed and adopted. A holding time is a management tool which involves holding flooded rice field waters on the rice paddies for a period of time sufficient to allow the pesticide in solution to degrade to a level suitable for discharge. [For a complete description of the rice monitoring program, including holding times, see Gorder and Lee (1995).]

The objective of the monitoring program has been to measure concentrations of selected pesticides in surface water of the rice growing regions in the Sacramento Valley. This year’s monitoring program measured concentrations of molinate, thiobencarb, carbofuran, methyl parathion, and malathion. In addition, basic water quality parameters and discharge were recorded. Sampling was conducted at four sites by several entities. The Colusa Basin Drain was sampled by DPR, Butte Slough and the Sacramento River at Village Marina by the California Rice Industry Association, and Sacramento’s raw water intake on the Sacramento River by the City of Sacramento. Additionally, acute toxicity tests were performed by CDFG on samples collected from the Colusa Basin Drain only. Data were used to verify compliance with performance goals and narrative toxicity objectives, and to identify the need for any programmatic changes to future monitoring efforts.

MATERIALS AND METHODS

Study Area

This year’s monitoring efforts were focused at four sites, two in immediate proximity to Sacramento’s rice growing region, and two downstream on the Sacramento River (Figure 2). The Colusa Basin Drain is a western tributary of the Sacramento River, and Butte Slough is an

eastern tributary. The drain and slough were chosen for several reasons: 1) they are major conduits of the majority of rice field effluent from the west side and Butte County (east side) in Sacramento Valley's rice growing region, 2) they have been used previously as water sampling sites in the monitoring program, and 3) they have historically contained measurable concentrations of the selected pesticides. The two sites located on the Sacramento River are indicative of water quality downstream of rice growing areas, where dilution for the Sacramento and American Rivers has occurred. These sites have also been monitored for rice pesticides in prior years.

The monitoring site on the Colusa Basin Drain was located within the Colusa National Wildlife Refuge. This site, approximately 64 km north of the City of Sacramento, has been traditionally referred to as Colusa Basin Drain Five (CBD5). Water flowing past CBD5 represents the majority of surface drainage from rice growing regions west of the Sacramento River. The terminus of the Colusa Basin Drain is the Sacramento River near Knights Landing. Data in previous reports (Lee, 1994; Lee and Gorder, 1993, 1992) have shown that the highest measured rice pesticide concentrations were consistently found at CBD5. Discharge into the drain consists of rice field effluent, localized drainage, and controlled releases from the Glenn-Colusa Irrigation District.

Butte Slough lies approximately 11 km east of CBD5. The monitoring site was located at Lower Pass Road and has been traditionally referred to as Butte Slough One (BS1). The BS1 site represents the culmination of Butte County's surface drainage from rice growing regions east of the Sacramento River, and via the Sutter Bypass, its terminus is also the Sacramento River. Lee (1994) and Lee and Gorder (1993) have also shown that rice pesticides are present in Butte Slough during the rice growing season. Butte Slough discharge consists of localized drainage, rice field effluent, and natural flow from Butte Creek.

The first of two monitoring sites on the Sacramento River was located at the Village Marina, approximately 1.5 km upstream from the confluence of the Sacramento and American Rivers. It has been traditionally referred to as SRI, and data collected there were used to integrate pesticide residue results from both CBD5 and BS1 after Sacramento River dilution.

The second site on the Sacramento River was the City of Sacramento's raw water intake (SRRAW), which is located 0.3 km downstream from the American River confluence. The SRRAW site is the collection point for the city's drinking water supply. As part of the City's monitoring program, they collected and analyzed water samples for molinate and thiobencarb from May to July.

Additionally, the Natomas East Drainage Canal (NEDC) was used as a sampling site in response to an emergency release granted to the Natomas Mutual Water District. This site is 2.8 km east of the Sacramento River at Northgate Boulevard and discharges to the river between SRI and SRRAW. Staff from DPR collected samples here during this emergency release period.

Sample Collection

Background samples were collected at CBD5, BS1, and SRI on April 14, approximately three weeks before the normal application period of the five pesticides in the region. These samples were used to determine if residual rice pesticides were present from prior years.

Bi-weekly sample collection then occurred at CBD5 over a 10-week period from May 16 to July 20, 1995, coinciding with the period of most intensive rice drainage releases upstream. Personnel from DPR collected water samples from a canal bridge using the equal-width-increment sampling method (Edwards and Glysson, 1988). Sampling points were determined by dividing the width of the drain into equal sections. Ten sampling points were selected, each at 2.5-meter intervals. A 3-liter Teflon® bottle attached to a depth-integrated sampler (D-77) was then lowered into the water at an equal speed for each point. With this method, a greater sample volume is collected at points with higher flow and represents a greater percentage of the total volume. A volume of 10-11 liters was collected and composited in a 38-liter stainless steel container, then stored on wet ice for transportation to DPR's West Sacramento Field Office. The sample was then immediately split into equivalent volumes using a 10-port water splitter (Geotech, dekaport model) and placed in 1-liter, amber glass bottles sealed with Teflon®-lined lids. Samples that were to be analyzed for carbofuran, methyl parathion, and malathion were first acidified to a pH between 3.0 and 3.5 with 3N hydrochloric acid to increase

sample stability during transportation and storage. Chain of custody records were completed for each sample.

Sampling at **BS1** and **SRI** was conducted by a CRIA consultant at a slightly different frequency from that at **CBD5**. Water samples were collected during the same period of weeks as was for **CBD5**, but during weeks one, two, nine, and ten, water was collected only once per week. Sampling frequency was increased to twice a week during the middle six weeks of the program when pesticide concentrations in previous years had been found to be highest. Additionally, samples were collected by the consultant at **CBD5** on three occasions to allow for a qualitative comparison of sampling results with DPR. The sampling point for **BS1** had originally been proposed to be from the center of a bridge at Lower Pass Road. However, record rainfall during the winter months and resultant flooding washed out the Lower Pass Road bridge. Therefore, **BS1** samples were collected from the slough's edge. Water samples at **SRI** were collected from the edge of a floating dock at the Village Marina along the east bank of the Sacramento River in Sacramento.

The CRIA consultant collected water samples with a Kemmerer-type water bailer. The weighted collection device, constructed of stainless steel and Teflon[®], was lowered into the water to the desired depth, and a weighted tripping mechanism was sent down the carrier cable to seal the unit when the unit's capacity (1.2 liters) was reached. Multiple grab samples were collected from the same point and stored in a stainless steel container until 8 to 9 liters were obtained. The composite sample was then mixed and poured into 1-liter amber bottles, filling the bottles in sequence by 1/3 liter each to best simulate a true split sample. Preservation, storage, and administrative procedures were completed as described for **CBD5** above.

The City of Sacramento collected faucet samples while the intake pump was running.

Unusually intense rains in June caused stresses on the Natomas Mutual Water District's recirculation system, and water was pumped from the system into Natomas Drain on June 17 and 18 to avoid levee failure. Personnel from DPR collected samples daily, June 17 through 19. The effective width and depth of the drain was too restrictive to collect a cross-sectional sample. **Therefore, center channel samples were collected from the Northgate Boulevard**

bridge using a D-77 sampler and processed as described above for CBD5.

As a standard operating procedure, all sampling personnel wore rubber gloves during sampling. If contamination was suspected while sampling, the gloves were replaced. Gloves were changed at each site to avoid cross contamination of samples. Every attempt was made to avoid both disturbing the bottom of the agricultural drain/slough and sampling areas with no observable flow. All sampling equipment used by DPR personnel at CBD5 was thoroughly cleaned by rinsing several times with deionized water. Detergents or alcohols were not used due to their potential for toxicity in the bioassays. Sampling equipment used by CRIA's consultant was thoroughly cleaned with Liquidnox (washing detergent) and deionized water following each sampling event. As a measure of decontamination effectiveness, both crews submitted rinse blanks for selected pesticides on a semi-weekly basis throughout the program. Rinse blanks were prepared by pouring four to five liters of deionized water over and through all sampling equipment and collecting it in a stainless steel container. The rinse water was then poured into four 1-liter amber bottles, acidified when necessary, and forwarded to the appropriate analytical laboratory as previously described.

Environmental Measurements

During each sampling event, environmental parameters were measured *in situ* and included pH and dissolved oxygen (DO). At CBD5, pH was measured with a Sentron (model 1001) pH meter. DO and water temperature were measured with a Yellow Springs Instruments (model 57) DO meter at center channel. At BS1 and SRI, water temperature and pH were measured with a Fisher multi-meter. An Engineered Systems and Designs (oxan model) oxygen analyzer was used to measure DO. Measurements and notes were recorded in a water quality log.

Pesticide Analyses

Five analytical laboratories performed chemical analyses on the samples collected. Zeneca Ag Products analyzed samples for molinate, Valent USA Corporation for thiobencarb, FMC Corporation for carbofuran, California Department of Food and Agriculture (CDFA) Center for Analytical Services for methyl parathion and malathion, and Alta Analytical Laboratory, Inc. for

quality control samples of methyl parathion and malathion. In addition, CDFA's Center for Analytical Services performed molinate, thiobencarb, and carbofuran analyses on quality control samples. Brief descriptions of the analytical methods used by the primary laboratories and the Quality Assurance/Quality Control program are described in the following text. Detailed analytical methods for all laboratories except Zeneca, whose procedure is proprietary, can be found in Appendix A. For a complete description of Zeneca's molinate analytical method, contact Zeneca Ag Products, Western Research Center, 1200 South 47th Street, Box Number 4023, Richmond, CA 94804-0023. Method validation data are presented in Appendix B.

Analytical Methods

Molinate samples were extracted with toluene. The extract was then shaken for an hour and its phases allowed to separate. The extract was then analyzed using a Hewlett-Packard model 5890 gas chromatograph (GC) equipped with a J&W DB-17 capillary column (15m x 0.55mm i.d. x 1.0 μ m), and a nitrogen/phosphorus detector. This method achieved a reporting limit (RL) for molinate of 1.0 μ g/L.

Thiobencarb samples were extracted with a hexane solution. The extract was then concentrated to dryness with a rotary evaporator. The thiobencarb residue was then redissolved in ethyl acetate. This extract was later analyzed using a Hewlett-Packard mode 5890 GC equipped with a J&W DB-17 capillary column (15m x 0.53mm i.d. x 1.0 μ m), and a nitrogen/phosphorus detector. This method achieved a RL for thiobencarb of 0.5 μ g/L.

Carbofuran samples were concentrated by passing the sample through a C-18 solid phase extraction column. The column was then washed with water and the bound carbofuran was removed from the column with acidified methanol followed by water. The extract was then analyzed using a high performance liquid chromatograph (HPLC) equipped with a Pickering C-18 column (4.6mm i.d. x 250mm). Post column derivatization was performed and the extract was quantified by a fluorescence detector. The RL for carbofuran using this method was 0.35 μ g/L.

Methyl parathion and malathion samples were extracted using methylene chloride. The extract

was passed through sodium sulfate to remove any residual water. The methylene chloride was evaporated to dryness in a rotary evaporator. The extract was then analyzed using a Hewlett-Packard model 5890 GC equipped with an HP-1 methyl silicone gum column (10m x 0.53mm i.d. x 2.65 µm) and a flame photometric detector. The RL for both methyl parathion and malathion in this method was 0.05 µg/L.

Quality Assurance/Quality Control

As an inter-laboratory quality assurance measure, each week one split sample was analyzed by a second laboratory; CDFA Center for Analytical Services analyzed for molinate, thiobencarb, and carbofuran to verify results by Zeneca, Valent and FMC. Alta Analytical Laboratory analyzed for methyl parathion and malathion, assuring CDFA's results. Rinse blanks and blind matrix spikes were submitted throughout the study under the auspices of the Quality Assurance Officer to check for contamination and measure laboratory accuracy. Details of the Laboratory Project Plan including method validation and continuing quality control data are discussed further in the "Results and Discussion" section.

Toxicity Testing

The CDFG Aquatic Toxicology Laboratory performed a total of eight toxicity tests during the monitoring program. An unacidified split sample from CBD5 was used to conduct toxicity testing. An aquatic toxicity test was conducted on the background sample from CBD5 to determine if toxicity existed prior to the application of rice pesticides. Toxicity tests were also performed on one sample each, from weeks one through seven, which corresponded to high water discharges from rice fields. Bioassays (96-hour exposure tests) were performed with *Ceriodaphnia dubia* in accordance with U.S. Environmental Protection Agency guidelines (US EPA, 1985).

RESULTS AND DISCUSSION

There are numerous and dynamic variables that make it difficult to quantitatively assess the success of this year's monitoring program based on pesticide concentrations alone; they include pesticide use patterns, application methods, timing of applications and releases,

proximity of fields to sampling sites, weather conditions, water management, etc. An evaluation of the program can, however, be determined by examining trends in pesticide use, concentrations, mass transport, and aquatic toxicity. The results of this monitoring program consist of the following sections: environmental measurements, pesticide concentrations, pesticide transport, and aquatic toxicity. Basic environmental parameters were measured *in situ* and examined in a historical context. Pesticide loads (concentration x discharge volume) were estimated for those pesticides detected in the Sacramento River and compared to similar data from previous years. Finally, toxicity test results were examined with respect to pesticide residues present in these samples.

Environmental Measurements

pH

Water collected for the background sample and during the ten week monitoring period at CBD5 had pH values ranging from 7.4 to 8.2 (Table 2). The CVRWQCB has set the water quality criteria for pH as a range of values from 6.5 to 8.5 (CVRWQCB, 1994). Additionally, U.S. EPA's (1986) recommended freshwater criteria for pH for aquatic life is expressed as a range of values from 6.5 to 9.0. All pH measurements met the water quality criteria established by the CVRWQCB. In addition, CDFG measured pH at CBD5 in 1993 and 1994 for the rice monitoring program. Their raw data indicated that pH ranged from 7.4 to 8.7 in 1994 and 7.0 to 8.2 in 1993, and were consistent with this year's values.

Environmental parameters for Butte Slough and the Sacramento River were measured *in situ* by a CRIA environmental consultant, and the pH values ranged from 5.8 to 8.3 at BS1 (Table 3) and 5.7 to 9.3 at SRI (Table 4). Measured pH values at BS1 fell below the CVRWQCB water quality criteria on three occasions, June 20, 22, and July 3. In comparison, pH data collected *in situ* by CDFG for the rice monitoring program in the 1994 and 1993 indicate that pH at BS1 typically ranges from 7.4 to 8.9, rarely exceeding the CVRWQCB higher limit of 8.5.

Measured pH values at SRI fell outside the criteria on five occasions, April 14, June 20, 27, 29, and July 3. This site was not monitored in 1994, but data collected, as part of the rice monitoring program, by CDFG in 1993 indicate that pH ranged from 7.6 to 8.0, well within the **CVRWQCB's specified water quality criteria. Additionally, raw data from water samples**

collected at SRRAW, by the City of Sacramento, showed pH values at 7.4 to 7.6 during June and July of 1995. It is unclear why pH values at both BS1 and SRI were atypically low on the aforementioned dates. pH measurements at BS1 and SRI should be given additional attention during future monitoring programs to identify any potential trend towards more acidic conditions.

No water quality measurements were made at the NEDC site.

Dissolved Oxygen

Dissolved Oxygen at CBD5 ranged from 5.1 to 9.1 mg/L (63 and 93% saturation, respectively). U.S. EPA (1986) has recommended a minimum ambient DO concentration for the protection of freshwater aquatic life of 3.0 mg/L for warm waters and 4.0 mg/L for cold waters. The CVRWQCB (1994) has set the water quality criteria for DO at a minimum of 5.0 mg/L for waters designated warm and 7.0 mg/L for waters designated spawning habitat. Flow from the Colusa Basin Drain has been identified by the CVRWQCB as essential to the spawning habit of several warm water species of game fish, including striped bass (*Morone saxatilis*) and white sturgeon (*Acipenser transmontanus*). In the Sacramento Valley, striped bass spawn from April to June, and white sturgeon spawn from March to June. Historically, these species have not spawned in the drain itself, but the drain's confluence with the Sacramento River is located within the upper spawning range for striped bass (CDFG, 1987) and the lower spawning range for white sturgeon (S.Siepmann, 9/96, percomm). Water quality of Colusa Basin Drain discharge may affect water quality of the Sacramento River depending on the volume of water discharging to the Sacramento River.

Dissolved oxygen at CBD5 fell below the criterion for spawning habitat on 9 of 20 occasions (Table 2). DO is inversely proportional to water temperature (Hynes, 1970); to expect values between 3.0 and 7.0 mg/L, in shallow, warmer waters (>20°C), such as that at CBD5 during late May, June and July, is reasonable. Additionally, low flows resulted in near static conditions during some periods of sampling this year and may have contributed to low DO readings (Figure 3). The DO values at CBD5 were consistent with data collected by CDFG during the 1994 and 1993 monitoring programs, which indicated that DO values ranged from 4.9 to 11 mg/L, and fell below 7.0 mg/L on seven occasions over two monitoring seasons.

The CRIA consultant reported DO at **BS1** ranged from 1.8 to 16 mg/L (Table 3). As was the case for the Colusa Basin Drain, Butte Slough, historically, has not been spawning habitat for striped bass or white sturgeon, but the quality of Butte Slough water may affect water quality of the Sacramento River, known spawning habitat for both species of fish. Using the 7.0 mg/L criterion, DO fell below the standard on 14 of 15 occasions. In comparison, *in situ* DO data collected by CDFG in the 1994 and 1993 monitoring programs indicated that values at **BS1** ranged from 4.1 to 10 mg/L and fell below the standard on five of 16 occasions in 1994 and 14 of 16 occasions in 1993.

The SRI site had DO values from 2.2 to 7.8 mg/L (Table 4). As presented, DO values fell below the water quality criterion of 7.0 mg/L on 14 of 15 occasions during the monitoring program. **SR1** DO values ranged from 7.7 to 11 mg/L in 1993, the last year that data was collected at that site. On three dates – April 14, June 6, and June 8 – DPR and the CRIA consultant collected samples and measured DO at **CBD5** for a comparison of results. There was less than five percent difference between two of the three pairs of DO measurements. The third pair was off by more than 50 percent. The variability in DO measurements by the CRIA consultant during this season and discrepancy in the data between 1995 and 1993 may have been due to instrument failure. Therefore, DO values from the 1993 and 1994 monitoring programs may be a more accurate indicator of conditions at **BS1** and **SRI**. Different DO equipment was recommended and measurements will be observed again during future monitoring programs. An additional summary of the data collected by the CRIA consultant is available under separate cover (Findlay, 1995).

Pesticide Concentrations

Pesticide Use

In the Sacramento Valley during the 1995 rice season, 633,576 kg of molinate, 256,505 kg of thiobencarb, 29,051 kg of carbofuran, 19,052 kg of methyl parathion, and 17,315 kg of malathion were applied (DPR, 1997). In comparison to 1994 use, there was a 7.3 percent decrease in molinate use, a 41 percent increase in thiobencarb use, an 8.2 percent decrease in carbofuran use, a 27 percent increase in methyl parathion use, and a 14 percent decrease in malathion use (Table 5).

In the drainage basin represented by sampling at CBD5 (Colusa and Glenn Counties) and compared to 1994, molinate use decreased by 7.4 percent, thiobencarb use increased by 39 percent, carbofuran use increased by less than 1 percent, methyl parathion use decreased by 49 percent, and malathion use increased by 2.2 percent. In the drainage basin represented by sampling at BS1 (Butte County) and compared to 1994, molinate use decreased by 15 percent, thiobencarb use increased by 25 percent, carbofuran use decreased by 5.6 percent, methyl parathion use increased substantially by 147 percent, and malathion use decreased by 50 percent (Table 6). Pesticide use pattern changes occur due to several factors including pest pressures, resistance, and product availability.

Colusa Basin Drain

No pesticide residues were detected in background samples collected on April 14 nor were they detected in any of the rinse blanks (Table 7). Molinate residues were detected throughout the monitoring period at CBD5 and ranged from 2.8 to 25 ug/L. The performance goal for molinate of 10 ug/L was exceeded on 9 of 20 occasions (45 %)(Figure 4). In comparison, the same performance goal for molinate was exceeded at CBD5 in 63 percent of the samples collected in each of the two prior years.

Though the performance goal for molinate was exceeded in a lower number of samples than in 1994, the issue of meeting the prescribed performance goal needs to be addressed. The temporal pattern of molinate field applications in areas of Colusa and Glenn Counties, discharging to the Colusa Basin Drain, is presented in Figure 4. Applications of molinate began on April 24. Given its 28-day holding time, molinate residues should not have been detected at CBD5 until May 22. However, residues were found in samples collected on May 16 and 18. Though the detections were below the performance goal, it suggests that the source of the contamination was due to activities other than scheduled releases.

Other potential sources of rice pesticide residues include illegal and emergency releases. [A detailed discussion of the rice program's enforcement plan, including procedures for requests of emergency releases, can be found in Gorder and Lee (1995)]. A review of DPR's Pesticide Enforcement Branch records indicated that 18 growers were cited for water-holding violations

(illegal releases), ten of which had potential for contamination of the Colusa Basin Drain. Of 12 emergency releases granted in the Sacramento Valley by agricultural commissioners for the pesticides of interest, two could potentially have contributed to peak concentrations of molinate at CBD5 but were not attributable to the early detections on May 16 and 18. These emergency releases occurred in Colusa County on May 21 and June 4 and may have contributed to molinate detections during the period of May 23 through June 6.

Two additional potential sources of molinate residues at CBD5 include seepage through rice field levees and aerial drift. Data addressing both seepage and aerial drift of rice pesticides as sources of contaminants in surface waterways are limited. However, it has been shown that molinate migrates with seepage water through levee banks of rice fields, with the resultant seepage water having molinate concentrations as high as 720 µg/L (Pino, 1992). In addition, it has been shown that off-site deposition via aerial drift can contribute to pesticide contamination of adjacent waterways (Pino *et al.*, 1992). Both seepage and aerial drift could have contributed to molinate contamination of CBD5 during this year's program in addition to the above mentioned releases. Efforts to reduce seepage were increased this year via an educational thrust. Details of this voluntary program are presented in Appendix C.

Thiobencarb residues were also detected during the monitoring period at CBD5 and ranged from none detected to 3.5 ug/L (Table 7). The performance goal for thiobencarb of 1.5 ug/L was exceeded on 4 of 20 occasions (20%)(Figure 5). In comparison, the same performance goal for thiobencarb was exceeded at CBD5 in 10 percent of the samples collected in 1994 and 16 percent of the samples in 1993.

No water-holding violations or emergency releases were reported for thiobencarb in Colusa or Glenn Counties. The pattern of detections for thiobencarb was similar to molinate, in that residue was found prior to the first scheduled releases (Figure 5). The vertical line in Figure 5 depicts 30 days after the first reported application of thiobencarb in the watershed. Though the reported level during this early period was below the performance goal, the detection suggests a source of contamination other than scheduled releases.

Data on thiobencarb seepage and aerial drift have not been collected. Thiobencarb seepage is

not as likely as molinate to contribute to contamination because of its relatively low solubility and higher soil adsorption coefficient (Table 1). Thiobencarb is applied to rice in a similar manner that molinate is applied, however, there are both liquid and granular formulations of thiobencarb. Liquid formulations tend to have smaller particle size and therefore, have greater drift potential. For this reason, the contribution of thiobencarb mass to surface waters, from aerial drift, was not compared to that of molinate.

Detected carbofuran residues at CBD5 ranged from 0.39 to 0.70 ug/L (Table 7). The performance goal for carbofuran of 0.40 ug/L was exceeded on 5 of 20 occasions (25%)(Figure 6). In comparison, use from 1993 to 1995 has remained relatively constant with the same performance goal exceeded in 57 percent of the samples collected in 1994 and 31 percent in 1993.

The first scheduled discharges of carbofuran were May 1, but there were no samples collected between the background sample and that date (Figure 6). Detections of carbofuran above the performance goal were however, found on May 16, 18, 23, June 1, and June 6. There were no emergency releases for carbofuran reported or water holding violations that could have been attributed to these measured residues.

Carbofuran is typically applied to the edges of rice fields which are sometimes in close proximity to agricultural drains and poses the potential for off-site deposition. Additionally, carbofuran has a relatively high solubility (351 mg/L) and may migrate beyond the field perimeter with seepage water, as does molinate (solubility=970 mg/L). A combination of these two factors may have contributed to carbofuran concentrations during this monitoring period.

Additionally, carbofuran was also used on sunflowers, alfalfa and sugar beets in the region. Though rice constituted the largest use of carbofuran in the watershed, runoff from sunflower crops containing carbofuran residues may have occurred during the April/May time frame when it was applied in the watershed. Thus, irrigation runoff from this crop may have contributed to the contamination at CBD5 during May. Carbofuran was applied to sugar beet crops in April and may have also contributed to the contamination at CBD5 during May. A single alfalfa application of less than 10 pounds was made in late March, and given carbofuran's 30-day field

dissipation half-life, it was an unlikely contributor of contamination.

Three methyl parathion detections were reported in samples collected from **CBD5**, all of which were below the performance goal of 0.13 ug/L (Table 7, Figure 7). In comparison, methyl parathion was detected three times in 1994 and exceeded the performance goal once, near the end of the monitoring period. In 1993, the performance goal was exceeded in 32 percent of the samples collected.

There were two malathion detections, May 16 and 18. Both detections exceeded the performance goal of 0.10 ug/L (Table 7, Figure 7). In comparison, malathion was detected once above the performance goal in 1994 and once in 1993, but the highest concentration of 1.03 ug/L this season was higher than the maximum in the previous two years (0.32, 0.15 ug/L respectively). In 1995, malathion was used in Colusa and Glenn Counties on a variety of crops during the monitoring period with the largest amounts being applied to alfalfa in March and April. These crop sites may have contributed to the detections of malathion at **CBD5**. Malathion has a short hydrolysis half-life (6.21 days) and has not remained in this waterway for any appreciable length of time during the monitoring period.

Concern about the variation of results produced from the collection of samples using two different methods (equal-width-increment vs. point) was investigated by having samples collected by DPR and CRIA's consultant, simultaneously at **CBD5**, on four occasions, April 14, June 6, 8, and 13. Results from the point sampling method are in parentheses in Table 7. There were insufficient data to quantify variation in results between the methods. However, a qualitative analysis of the results suggests that **CBD5** was a well-mixed sampling site, and point sampling may have been sufficient. In contrast, **BS1** and **SRI** had physical restraints that necessitated use of the point sampling method.

Butte Slough

No pesticide residues were detected in background samples nor were they detected in any of the rinse blanks. Detected molinate residues at **BS1** ranged from 2.1 to 8.5 ug/L, which met the performance goal of 10 ug/L (Table 8, Figure 8). In 1994 and 1993, the performance goal was exceeded in 30 and 42 percent of the samples collected, respectively.

There were two thiobencarb detections at **BS1** which occurred during the midpoint of the monitoring period and were beneath the prescribed performance goal (Table 8, Figure 8). In comparison, thiobencarb was detected on one occasion in 1994 and six times in 1993, all at levels below the performance goal of 1.5 ug/L.

Residues of carbofuran were detected on four occasions at **BS1**, and ranged from 0.37 to 0.57 ug/L (Table 8). Concentrations in 2 of 16 samples (12%) collected exceeded the performance goal (Figure 9). In comparison, the performance goal was exceeded in zero percent of the samples collected in 1994 and 23 percent in 1993. There were no emergency or illegal releases for carbofuran reported in 1995 that could have been attributed to the measured residues.

Methyl parathion was detected once at a concentration of 0.19 ug/L; malathion was also detected once at a concentration of 0.64 ug/L. The detections exceeded methyl parathion and malathion performance goals of 0.13 ug/L and 0.10 ug/L, respectively (Figure 9). There was a single detection of methyl parathion at **BS1** in 1994 and two detections in 1993, all of which were below the performance goal. In contrast, malathion has been absent at **BS1** in 1994 and 1993.

There were no emergency releases reported that could have been attributed to the detection of methyl parathion or malathion. Methyl parathion has a low water solubility and a short field dissipation half-life (Table 1) which suggests that its contribution to contamination of **BS1** from seepage may have been small. In contrast, Pino and others (1992) have shown that off-site deposition of methyl parathion from aerial applications to rice fields has resulted in concentrations as high as 16 ug/L in adjacent agricultural drains. The source of the malathion detection is uncertain, but 1995 Pesticide Use Report data suggests that the contamination may have been partially attributed to applications on other crops other than rice. In particular, malathion was applied to walnuts, upstream of the sampling site, in June and July.

Sacramento River

No pesticide residues were detected in background samples from SRI nor were they detected in any of the rinse blanks. **No rice pesticide residues were detected in the Sacramento River at**

SR1 during the monitoring period. The City of Sacramento did, however, find molinate residues in their samples from SRRAW on two occasions. The detections were on May 29 and June 22 at 0.12 and 0.16, respectively and were well below the performance goal of 10 ug/L. The molinate reporting limit for the City of Sacramento was 0.10 ug/L, versus the 1.0 ug/L reporting limit utilized by analytical laboratories in this monitoring program. Thus, both detections reported by the City were below the reporting limit of the monitoring program's primary laboratory. In comparison, there were three detections of molinate at SR1 in 1993, all of which were below the performance goal. SR1 was not monitored in 1994. The City detected molinate at SRRAW on 4 occasions in 1994 and 12 occasions in 1993, all of which were also below the performance goal.

Natomas East Drain Canal

Unusually intense rains in June caused stress on the water delivery and drainage system in the areas just north of Sacramento, and an emergency release was granted to the Natomas Mutual Water District. Water was pumped from that system into the NEDC on June 17 and 18 to avoid levee damage. DPR personnel collected samples on June 17 through 19, from NEDC at Northgate Boulevard, located 2.8 km east of the Sacramento River. Detections of molinate, thiobencarb and methyl parathion occurred on June 18, but their concentrations declined below reporting limits by the following day (Table 9). Only methyl parathion exceeded its performance goal during the monitoring of this emergency release.

Quality Assurance/Quality Control

A quality assurance program was in place throughout the monitoring program to measure precision of the analytical methods (Appendix D). Before the onset of field sampling, method validation studies were completed by each laboratory performing chemical analyses (Appendix B). Warning and control limits were established from these recoveries in order to determine if continuing quality control (QC) sample results fell within the precision range established during method validation.

Blank water samples and spiked water samples were analyzed with each set of field samples. Mean recoveries and standard deviations for the primary laboratories are presented in Table 10. Additionally, blind spikes were prepared by CDFA and delivered to DPR for undisclosed

submission as field samples. The blank, spike-recovery, and blind spike-recovery data accompanying these analyses are included in Appendices E and F. There were no significant anomalies (i.e. results outside control limits) in the continuing quality control data from any of the primary analytical laboratories, indicating the primary laboratories performed within the variation established during method validation.

- Interlaboratory Comparison -

As an additional quality control measure, split samples were collected at CBD5 to compare primary laboratory results with QC laboratory results for each pesticide. The reported concentrations are presented in Table 7. When quantitative data were reported, regression analysis was used to investigate differences between the two sets of results. The assumption that method precision did not vary with concentration was made in order to complete the regression analyses.

Molinate concentrations from eleven split samples were available for comparing laboratory results. The samples collected on April 14 were reported "none detected" (ND) and the observation was assigned one-half the value of the reporting limit for each laboratory in order to complete the regression analysis. A regression of quality control laboratory results on primary laboratory results indicated that the calculated slope did not differ significantly from one, and the calculated intercept did not differ significantly from zero at the five percent level of significance (Figure 10A). The correlation coefficient was 0.96. The sample collected on May 25 (primary=25 ug/L, QC=32.9 ug/L) was flagged as an observation having a large standardized residual (2.11) in comparison to other samples. Upon further investigation of sampling and chemical analytical procedures, nothing unusual about this observation was found. The regression analysis, with or without this observation, indicated there was no evidence of systematic differences between the two laboratories.

A similar procedure was used on the set of thiobencarb results, but in this case, results from two samples were reported ND by both laboratories. The result from one additional sample was reported as ND by the primary laboratory. One-half the value of the reporting limit for each laboratory was substituted for ND data in order to complete the regression analysis. A regression of QC results on primary laboratory results indicated that the calculated slope did not

differ significantly from one, and the calculated intercept did not differ significantly from zero at the five percent level of significance (Figure 10B). The correlation coefficient was 0.97. The sample collected on June 8 (primary=3.5 ug/L, QC=3.7 ug/L) was flagged as an observation whose x-value gives it large influence in the calculation of regression coefficients (slope and intercept). The sample collected on June 29 (primary=1.4ug/L, QC=2.17ug/L) was flagged as an observation having a large standardized residual (2.08) in comparison to other samples. The regression analysis, with or without these observations, indicated there was no evidence of systematic differences between the two laboratories.

Another consideration with the thiobencarb data set was the assignment of a quantitative value to semi-qualitative data (i.e., ND's) for use in regression analysis. Using quantitative results only, results from eight samples were available for comparing primary laboratory results with QC results. Again, there was no evidence of systematic differences between the two sets of results; the correlation coefficient was also 0.97. No unusual observations were cited. The regression analysis, with both eight and 11 split samples, indicated there was no evidence of systematic differences between the two sets of results. In addition to favorable continuing QC results, results from the interlaboratory comparisons for molinate and thiobencarb further substantiate the reproducibility of the data reported by the primary laboratories.

Data from split samples for carbofuran, methyl parathion, and malathion were primarily ND's and not suitable for regression analysis. Though the data for these three pesticides did not lend themselves to quantitative statistical analysis, there was qualitative agreement between the primary laboratories and QC laboratories on the absence of residues in the collected samples (i.e. both labs showed NDs).

Pesticide Mass Transport

Another method used to measure the success of the rice program is to calculate mass transport of rice pesticides in the Sacramento River. In this method, pesticide concentration at a specific site is multiplied by the discharge at that site, summed over the monitoring period, and

compared to monitoring programs from previous years. This method therefore takes into account variability in concentrations and discharge from year to year.

The mass of rice pesticides transported in the Sacramento River was estimated with detected concentrations in the river and discharge measurements from the USGS gaging station at Freeport. Concentrations were corrected to account for flows from the American River just upstream of the station and to more accurately represent average daily concentrations. This step helps address the effects of tides on the mixing dynamics of the American and Sacramento Rivers. Yearly totals of pesticide mass transport can be expressed as the following:

$$\sum (\text{conc.} \times \text{SR}_i / \text{SR}_o \times \text{flow}_{sr} \times \text{K})$$

where conc. = concentration of contaminant detected daily by the City of Sacramento at SRRAW in ug/L;

SR_i = theoretical average daily percentage of Sacramento River water at SRRAW that had its origins in the Sacramento River upstream of the confluence of the American River, based on average daily releases from Nimbus Dam on the American River and average daily flows in the Sacramento River at Freeport;

SR_o = observed percentage of Sacramento River water at SRRAW that had its origins in the Sacramento River upstream of the confluence of the American River at the time the water sample was taken for determination of pesticide concentration, based on results of daily comparative analysis of conductivity performed on water samples drawn from the Sacramento and American Rivers;

flow_{sr} = average daily flow, measured in cubic meters per second, of the Sacramento River at Freeport; and

K = a conversion factor ($10^{-3} \text{ L/m}^3 \times 60 \text{ sec/min} \times 60 \text{ min/hr} \times 24 \text{ hr/day} \times 1 \text{ kg}/10^9 \text{ ug}$)

In the case of isolated detections which have NDs on sampling days immediately preceding and following the date of detection, one-half the detection limit was used to calculate the pesticide mass for those days. Concentrations outside this criterion and less than the reporting limit were regarded as zero.

Based on the two molinate detections at SRRAW and their corrected concentrations, the mass of molinate transported in the Sacramento River during the monitoring period was 231 kg. In

comparison, the mass of molinate transported was 109 kg in 1994 and 2,007 kg in 1993. The estimated mass transported in the Sacramento River of both molinate and thiobencarb since 1982 is presented in Figure 11. No thiobencarb has been detected in the River since 1000. These data illustrate a marked decrease in rice herbicide mass transported past the City of Sacramento. This trend has been attributed to the implementation of water-holding times, which allows the pesticides to degrade before discharge into neighboring waterways (Lee, 1994).

Aquatic Toxicity

Another method for evaluating the success of the rice program is the use of aquatic toxicity test results. To address the State's narrative water quality objectives for toxicity, acute toxicity testing (96-hour) was performed on one sample per week from CBD5 with *Ceriodaphnia dubia* during the first seven weeks of the monitoring period. As a check for toxicity prior to the onset of the rice season, a similar background toxicity test was performed on water from CBD5 collected on April 14. The results of the toxicity testing are presented in Appendix G. A *t* test ($p < 0.05$) was used to determine that significant mortality occurred in one sample, collected on May 30. This sample displayed 55 percent survival with 95 percent survival in the control.

Of the five rice pesticides analyzed in the May 30 sample, only molinate and thiobencarb were detected; respective concentrations were 19 and 1.2 ug/L. Acute toxicity (96-hr) data with *Ceriodaphnia dubia* are lacking for these rice pesticides. However, the *C. dubia* 48-hr LC₅₀ for molinate has been observed by the CDFG Aquatic Toxicology Laboratory to be greater than 9,000 ug/L (R. Fujimura, 9/95, percomm). The 48-hr LC₅₀ values for the remaining rice pesticides are: thiobencarb = 510 ug/L, carbofuran = 2.6 ug/L, methyl parathion and malathion = 2.6 ug/L (Norberg-King, 1991). Detected concentrations of both molinate and thiobencarb in the May 30 sample were well below their respective 48-hr LC₅₀ values, however 96-hour toxicity values would be expected to be lower than those listed above. Water quality data did not indicate any specific situation that could be considered harmful to the test organism (e.g. low DO, high ammonia). Consequently, a definitive conclusion on the source of the toxicity can not be drawn with available data. There was no significant toxicity found in any of the samples collected in 1994.

CONCLUSIONS

Environmental parameters (pH and DO) measured at the western Sacramento Valley monitoring site (CBD5) were consistent with measurements from prior years. The same parameters measured at the eastern Valley monitoring site (BS1) and the Sacramento River (SRI) were not typical and consistently fell outside the State's water quality criteria. The cause of the resultant atypical values remains undetermined but may have been the result of equipment malfunction. Different equipment was recommended to CRIA and additional attention will be paid to future water quality measurements at those sites.

Pesticides used in the production of rice were detected in both the Colusa Basin Drain and Butte Slough. Sources of contamination included scheduled and emergency releases, and potentially illegal releases, aerial drift, and levee seepage. Herbicide residues measured in water from the western Sacramento Valley were detected throughout the monitoring period at levels exceeding performance goals. Specifically, molinate and thiobencarb exceeded their performance goals in 45 and 20 percent of the samples collected, respectively. Carbofuran detections exceeded the performance goal in 25 percent of the samples collected.

There was no direct relationship between the change in the amount of pesticide applied in the drainage basin and the percentage change of pesticide detections above their respective performance goals for 1993 to 1995. This was probably due to multiple factors affecting pesticide levels including total use in the drainage basin, relative time of releases, flow in the waterway at time of releases, actual length of holding time, proximity of release to sampling site, drift, seepage, and yearly variability between samples.

East side drainage water typically contained less rice pesticide residues, and the herbicides did not exceed the prescribed performance goals. Thiobencarb concentrations in the east Valley have not exceeded the performance goal since 1992. Insecticide detections were few and short-lived. Historically, detections of malathion or methyl parathion residues have not been found with any regularity on either side of the Sacramento Valley during the monitoring period.

No pesticides were detected in the Sacramento River at SR1. There were, however, two molinate detections from Sacramento River samples collected by the City of Sacramento at SRRAW. (Note: Reporting limits for molinate at SR1 were 1.0 ug/L (analyzed by Zeneca) vs. 0.10 ug/L at SRRAW (analyzed by the City of Sacramento)). Both detections were two orders of magnitude below the performance goal. With the exception of molinate, monitoring results indicated that rice pesticide transport in the Sacramento River was negligible, i.e. data were below the program's reporting limits. The total mass of molinate transported past SR1 for the season was estimated to be 231 kg, up 53 percent from 1994.

Acute aquatic toxicity occurred in one of eight samples collected at CBD5 during the monitoring period. The toxic event did not appear to be attributable to any of the five rice pesticides, however, no final determination could be made because of lacking toxicological data. In general, rice pesticide residues from the west Valley were higher in concentration and more persistent than those from the east Valley or the Sacramento River. This suggests that aquatic toxicity due to rice pesticides may not be problematic in Butte Slough and the Sacramento River during the rice growing season. It is difficult to predict from year to year what pesticide levels will be found in the waterways of the Sacramento Valley due to the factors mentioned above. Therefore, continued yearly monitoring is recommended during the rice growing season to verify compliance with narrative toxicity criteria and numerical performance goals.

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