Occurrence of Aquatic Toxicity and Dormant-Spray Pesticide Detections in the Sacramento River Watershed, Winter 1996-97

BY

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ABSTRACT

This study was initiated to monitor the concentrations of dormant spray pesticides and the occurrence of acute and chronic aquatic toxicity in portions of the Sacramento River watershed. This is the first year of a multi year study planned for the Sacramento River watershed. Resulting data will help DPR scientists evaluate the effectiveness of programs designed to decrease the offsite movement of dormant spray insecticides. An acute toxicity monitoring site, located on the Sutter Bypass, was sampled twice per week collecting water for two 96-hour toxicity tests. A chronic toxicity monitoring site, located along the Sacramento River at Bryte, was sampled three times per week collecting the initial water and replacement renewal water for one 7-day chronic toxicity test. Background samples were collected during the first week of December, 1996. Flooding caused by heavy rains prevented sampling until January 20; sampling then continued until March 7, 1997. No significant rain fell after January 29, but river discharge remained high until mid-February. Diazinon and methidathion usage were 30% lower than in previous years, largely due to heavy rains and flooding. Of the 10 pesticides analyzed, only the organophosphates diazinon and methidathion were detected. Diazinon was detected in 7 of 16 samples collected from the Sutter Bypass in late January and late February at levels from 0.04 to 0.08 ppb. Methidathion was detected there on January 27 at 0.07 ppb. Diazinon was detected at approximately 0.06 ppb in 4 of 24 samples collected in late January from the Sacramento River at Bryte. Methidation was detected there on January 27 at 0.05 ppb. No significant toxicity was detected in any of the 16 acute or 8 chronic toxicity tests. This year's results are comparable only to other years which exhibit the same unusual rainfall pattern. The heavy rainfall and subsequent flooding likely disrupted normal dormant spray applications and runoff patterns.

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DISCLAIMER

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INTRODUCTION

Recent pesticide monitoring studies of the Sacramento River (Figure 1) have provided information on the annual occurrence of pesticides in the river. Two studies by scientists from the U.S. Geological Survey (USGS) and the Department of Pesticide Regulation (DPR) provided data on the yearly distribution of pesticides in the main stem of the Sacramento River (MacCoy et al., 1995; Nordmark, 1995). These studies have shown that diazinon was the most commonly detected organophosphate pesticide and that most detections were observed during the dormant spray season. The USGS study also detected low levels of methidathion during this season. Other studies on various agricultural tributaries of the Sacramento River have shown higher concentrations of the same pesticides which may have caused mortality to the water flea, *Ceriodaphnia dubia.* In a monitoring study conducted by the Central Valley Regional Water Quality Control Board (CVRWQCB), diazinon concentrations as high as 5 µg/L[1] were detected in the Sacramento Slough in January 1996 (personal communication, Chris Foe, CVRWQCB, 1996). In a separate study (Foe and Sheipline, 1993), acute toxicity to *C. dubia* in conjunction with high diazinon and methidathion concentrations was found at Gilsizer Slough, which drains some of the area west of the Feather River and flows into the Sutter Bypass (Figure 2).

In the Sacramento Valley, the organophosphorus insecticides diazinon and methidathion are the primary dormant season insecticides used on stone fruit and nut trees (DPR 1993; DPR 1994; DPR 1995). The peak use of these pesticides occurs in January and they are primarily applied using ground equipment. This dormant spray application period coincides with the bulk of the seasonal rainfall, providing the potential for these pesticides to wash off target areas and migrate with surface runoff to the Sacramento River.

The objective of this study was to monitor the concentrations of dormant spray insecticides and the occurrence of aquatic toxicity, both acute and chronic, in portions of the Sacramento River watershed. A companion study was also conducted to monitor pesticide levels and toxicity in the San Joaquin River (Bennett, 1997) watershed and these results will be presented in a separate report. Long-term monitoring of acute and chronic toxicity in these watersheds will help scientists at DPR evaluate the effectiveness of programs designed to decrease the runoff of dormant spray insecticides.

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[1] One µg/L is equivalent to one part per billion (ppb)

MATERIALS AND METHODS

Study Area Hydrology

The Sacramento River is the largest river in California both in volume of water and in drainage area (Friebel et al., 1995). From Mount Shasta in the north to the Sacramento-San Joaquin Delta in the south, the river flows for 327 miles and drains approximately 27,000 square miles including agricultural, urban and undeveloped land areas (Domagalski and Brown, 1994). The primary source of water entering the system is surface runoff from the Sierra Nevada Mountains to the east and Cascade Range to the north (CSLC, 1993). Runoff from rain events occurring in the Sacramento Valley and Coastal Range Mountains provides short-term increases in river flow. Seasonal rains occur from October to March with little significant rain from June to September. River flow during the summer is composed of dam releases of snow-melt water for agricultural, urban, recreational and wildlife purposes.

The primary dormant spray areas above the city of Sacramento are located in the counties of Butte, Colusa, Glenn, Sutter, Tehama, and Yuba. Within these counties there are two major areas of dormant spray applications. The first is along the Sacramento River in southeastern Tehama, northeastern Glenn and northwestern Butte counties. The second area is along the Feather River from southern Butte County to the Bear River with most applications within 6 miles to the west of the Feather River. Runoff from orchard areas west of the Sacramento River chiefly flows into the Colusa Basin Drain which enters the Sacramento River at Knights Landing (Figure 2). Runoff from dormant spray areas east of the Sacramento River principally flows into Butte Creek, which has been engineered to drain into the Sutter Bypass via the Butte Slough. Runoff from the west side of the Feather River also drains into the Sutter Bypass. During periods of normal flow, the Sutter Bypass enters the Sacramento River via the Sacramento Slough at Karnak. During periods of high flow, the Sutter Bypass channel fills completely with runoff from this area plus water diverted from the Sacramento River. This flow merges with the Feather River 8 miles prior to entering the Sacramento River, forming a 2 mile wide channel which inundates the Sacramento Slough. During floods, a large portion of the flows of the Sacramento River and the Sutter Bypass/Feather River are diverted into the Yolo Bypass. Runoff from areas east of the Feather River drains into the Feather River above Nicolaus.

Study Site Description

Sutter Bypass

A small bridge across the western channel of the Sutter Bypass at the Karnak Pumping Station, just prior to the Sacramento Slough, was selected as the acute toxicity monitoring site. This site receives runoff water from most of the agricultural areas between the Sacramento and Feather Rivers. Previous studies have indicated the potential for high concentrations of pesticides in this area (personal communication, Chris Foe, CVRWQCB, 1996, Wofford and Lee, 1995).

Extensive flooding occurred in late December and early January which inundated the Sutter Bypass at Karnak. Therefore, the acute toxicity monitoring was done at an alternate site along the western edge of the Sutter Bypass at Kirkville Road, approximately 9 miles upstream. Sampling continued at this alternate site until February 17, when water levels had receded enough to allow sampling at the original site.

Sacramento River

The chronic toxicity monitoring site was located on the right bank of the Sacramento River at the water intake for the West Sacramento Water Treatment Plant at Bryte. This site receives discharge from all major agricultural tributaries but is above the confluence of the largely non-agricultural American River and the discharge of urban runoff from the cities of Sacramento and West Sacramento (Figure 2).

Sample Collection

Background sampling was conducted during the week of December 2, 1996, prior to the onset of the dormant spray season. Sampling was originally scheduled to resume on January 6, 1997, and continue through early March, 1997. However, due to flooding throughout the region in January, sampling did not resume until January 20. Sampling continued until March 7 when no more dormant spray applications were reported.

Chemical analyses were performed on each water sample collected for both acute and chronic tests. Selected organophosphate and carbamate insecticides were analyzed in two separate analyses with diazinon being analyzed in a third analysis (Table 1). Pesticides included in our analyses were chosen based on pesticide use reports indicating historical use during the dormant spray season in the Central Valley, previous detections in the watershed, the availability of analytical methods in the organophosphate or carbamate screens, and to standardize analyses between the Sacramento and San Joaquin River studies.

Acute toxicity tests were performed twice per week, with samples collected on Monday and Wednesday. One chronic toxicity test was conducted weekly using water samples collected on Monday, Wednesday, and Friday. Water collected on Monday was used to begin the chronic toxicity tests. Water collected on Wednesday and Friday was used to renew chronic test water (see "Pesticide Analysis and Toxicity Tests" section below).

Originally, water samples were to be collected at both sites, from as close to center channel as possible, using a depth-integrated sampler (D-77) with a 3-liter Teflon® bottle and nozzle. The initial background samples were collected using this method but it was unsuitable for use in the Sutter Bypass at Kirkville Road (acute toxicity site). At this site, samples were collected using a subsurface grab method utilizing a 1-liter bottle on the end of a 4-meter pole. Sample collection using the subsurface grab method continued when sampling resumed in the Sutter Bypass at Karnak on February 17.

During the course of the study, the nozzles for the D-77 sampler were lost due to exceptionally high flows and snagging on underwater debris. Therefore, changes were made in the sampling methods used in the Sacramento River at Bryte (chronic toxicity site). The February 14 sample was started using the full D-77 assembly, but due to the loss of equipment during sampling, sample collection was completed using a grab sample. All subsequent samples from this site were subsurface grab samples.

Normally, eight to ten 1-liter splits were required for each sampling event. At least 12 liters of water were collected and composited in a stainless steel 10-gallon (38-liter) milk can. The composited sample was placed on wet ice for transportation back to the DPR sample handling facility at West Sacramento for splitting. All samples were split on the day of collection into 1-liter amber glass bottles, with Teflon® lined caps, using a (USGS designed) Geotech® 10-port splitter. Two pairs of 1-liter samples were submitted for acute toxicity testing and one pair of 1-liter samples was submitted for chronic toxicity testing. Three 1-liter samples were submitted for chemical analyses: one each for the organophosphate, carbamate and diazinon analyses. Two 1-liter backups were stored at West Sacramento. Additional sample splits from sampling events on

February 3 and 24 were provided to the CVRWQCB for acute toxicity testing and chemical analysis to augment their continued research in the region.

Samples designated for organophosphate and carbamate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH of between 3.0 to 3.5. Most organophosphate and carbamate pesticides are sufficiently preserved at this pH (Ross et al. 1996). Diazinon, however, rapidly degrades under acidic conditions and was therefore analyzed from a separate, unacidified, sample. Samples were stored in a 4° C refrigerator until transported to the appropriate laboratory (on wet ice) for analysis. All samples were delivered to the testing laboratory within 24 hours of collection.

Environmental Measurements

Water quality parameters measured on site included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) for each collection event. Water pH was measured using a Sentron® (model 1001) pH meter. EC was measured using an Orion® salinity-conductivity-temperature meter (model 142). Water temperature and DO were measured using a Yellow Springs Instruments® dissolved oxygen meter (model 57). Additionally, ammonia, alkalinity and hardness were measured by the Department of Fish and Game (DFG) Aquatic Toxicity Laboratory (ATL) upon delivery of the toxicity samples. Totals of alkalinity and hardness were measured with a Hach® titration kit. Total ammonia was measured with an Orion multi-parameter meter (model 290A) fitted with an Orion® ammonia ion selective electrode (model 95-12).

Precipitation and discharge information were also gathered for the study area. Precipitation data was averaged from two sites: a Department of Forestry station located near Chico and a National Weather Service station located at the Sacramento Post Office (stations CHI and SPO, respectively on the California Data Exchange Center) to approximate rainfall in the Sacramento Valley.

Discharge records for the Karnak/Sacramento Slough site were unavailable due to flooding from January until the February 17 sample. Instead, discharge data for the Butte-Slough-near-Meridian gage was used to provide flow estimates for the Sutter Bypass sites. The flow through the Tisdale Weir is not gaged but can provide over 16,000 cubic feet per second (cfs) to the Sutter Bypass during periods of extreme flow. The contribution of the Tisdale Bypass was estimated using data from the gage immediately below the weir, Wilkins Slough, and historical hand measurements of flows through the Tisdale Bypass conducted by Department of Water Resources (DWR) personnel. Flow through the Tisdale Bypass begins when discharge at the Wilkins Slough gage exceeds about 23,000 cfs (Friebel et al., 1995). Six other gaging records (personal communication with Stephen Graham, DWR) taken since 1993 in the Tisdale Bypass were plotted against the corresponding discharge at Wilkens Slough and a simple equation developed using TableCurve 2D© by Jandel Scientific@. This equation was used to predict approximate discharge through the Tisdale Bypass when flows exceeded 23,000 cfs at Wilkins Slough. Discharge data used in this study for the Sutter Bypass was a combination of data from the Butte-Slough-Near-Meridian gage and the Tisdale Bypass estimates. Additional inputs from smaller streams such as Gilsizer Slough and Wadsworth Canal are not included.

The DWR gaging station at Bryte was decommissioned after this study began, requiring the use of data from the Verona USGS gaging station, 18 miles up river from the Bryte sampling location. The Verona site captures all major input to the Sacramento River above the sampling site but it does not account for the outflow through the Sacramento Weir, approximately 1 mile above the Bryte sampling site. There was water flowing through this weir from the Sacramento River into the Yolo Bypass during most of this study. All precipitation and discharge data were taken from provisional, National Weather Service, Department of Forestry and DWR information and is subject to revision. This information will be used to follow annual changes in chemical concentrations with respect to fluctuations in flow and will also be useful for modeling efforts, should they be undertaken.

Pesticide Analysis and Toxicity Testing

Chemical Analvses

Pesticide analyses of water samples were performed by the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry and consisted of organophosphate and carbamate screens and diazinon analysis (Table 1). Briefly, the organophosphate samples were extracted with methylene chloride. The extract was passed through sodium sulfate to remove residual water and was then evaporated to dryness on a rotary evaporator and brought to a 1 mL final volume. The extract was then analyzed using gas chromatography (GC) and flame photometric detection (FPD). Carbamate samples were also extracted with methylene chloride. The extract was evaporated to a concentrate of 3-5 mL on a rotary evaporator. Sodium sulfate was added to remove residual water. The extract was then reduced to dryness, brought to a final volume of 0.2 mL with methanol, and separated by high performance liquid chromatography (HPLC). The eluant was derivatized with OPA by post column reaction and detected with a florescence detector. Comprehensive chemical analytical methods are provided in appendix A. Method validation results are presented in appendix B.

Quality control (QC) was conducted in accordance with Standard Operating Procedure QAQC001.00 (DPR, 1996). Data generated during method validation (Appendix B) were used to assess all subsequent results. Specifically, the data were used to establish warning and control limits. A warning limit was the mean ±2s, where the mean was the average percent recovery found in the method validation and s, the standard deviation. A control limit was the mean ±3s. Continuing QC samples consisted of water samples spiked with an analyte at a given concentration, extracted and analyzed with each extraction set. An extraction set consisted of 1 to 12 field samples depending on how many samples were received in the laboratory for processing at one time. During the course of the study, continuing QC samples were compared to the warning and control limits. If the continuing QC sample exceeded the warning limit, the chemist was notified. If the control limit was exceeded, corrective measures were taken in the lab to bring conditions back under control. Only field samples below the lower control limit for continuing QC were noted in the report.

In addition to a continuing QC program, approximately 10 percent of the total number of primary analyses were submitted with the field samples as blind spikes and rinse blanks of the splitting equipment. A blind spike was a surface water sample that was spiked by one chemist and submitted to another chemist who did not know the concentration of analyte for analysis. Rinse blanks were prepared by pouring deionized water over and through the equipment used in sample collection and preparation after a typical cleaning procedure. The resultant rinse water was then collected in 1-L amber bottles and submitted for chemical analysis as a normal field sample to check for any potential contamination.

Toxicity Tests

Acute toxicity testing was conducted by the DFG ATL following current U.S. Environmental Protection Agency (U.S.EPA) procedures using the cladoceran *Ceriodaphnia dubia* (U.S.EPA, 1993). Acute toxicity was determined using a 96-hour, static-renewal bioassay in undiluted sample water. Chronic toxicity was determined using a static renewal 7-day bioassay of undiluted sample water with C. ***dubia*** and followed current U.S.EPA guidelines (U.S.EPA, 1994). Test organisms used in chronic testing were placed in sample water on day one of testing, with test water replenished on days three and five. All acute and chronic tests commenced and renewal water was used within 36 hours of sample collection. Data were reported as percent survival for both acute and chronic tests and the average number of offspring per surviving adult for the chronic tests.

Quality control for the acute toxicity monitoring portion of this study consisted of submission of a split sample for each sample collected from the Sutter Bypass site to the DFG Aquatic Toxicity Laboratory for acute toxicity testing. Acute toxicity samples were labeled only with a sample number and were submitted along with samples from the companion San Joaquin River study. The resultant data will help DPR scientists better understand and characterize intra-laboratory precision of acute toxicity tests performed on ambient water samples.

RESULTS AND DISCUSSION

The results of this monitoring program consist of the following sections: environmental measurements, pesticide use, pesticide detections and toxicity, transport, and aquatic toxicity. Basic environmental parameters were measured on site and examined in a historical context. Pesticide loads (concentration x discharge volume) were estimated for those pesticides detected to establish a dormant spray season baseline. During a typical winter season, many growers would begin to apply dormant spray insecticides in mid December and continue through early March. The following results include data collected during an unusually wet season which included extensive flooding during the first half of the winter followed by an abnormally dry second half. Any interpretation of the results by the reader should take into account that conditions during the monitoring period were not necessarily characteristic of a typical winter spray season.

Environmental Measurements

Sutter Bypass

Water temperature at the Sutter Bypass sites ranged from 9.6 to 12.1° C, DO ranged from 8.2 to 10.6 mg/L and EC ranged from 95 to 359 µS/cm with the highest readings for each occurring in the December background samples at Karnak (Figure 3). pH values ranged from 7.0 to 8.5. All of these measurements are within parameters established by the U.S. EPA (1987) and CVRWQCB (1994) for cold waters.

Alkalinity ranged from 56 to 278 mg/L and hardness ranged from 50 to 162 mg/L (Figure 3). There are no established acute water quality objectives or criteria for these parameters. Ammonia levels remained below the detection limit of 50 µg/L for all samples.

Precipitation and discharge were high for the period from late December through the end of January (Figure 4). Figure 4 presents precipitation data averaged for two stations in the Sacramento Valley and discharge for the Sacramento River and the Sutter Bypass. Rainfall for the period of December 20, 1996 to January 19, 1997 was 7.0 inches with an additional 6.4 inches falling from January 20 to March 7, 1997. Due to flooding, all flow data presented in Figure 5 are approximate as all inputs and diversions were not gaged, many gages were not accurately calibrated for such extreme flows, and data is preliminary and thus subject to revision (personal communication: Steven Graham, DWR Surface Water Unit). The discharge at Butte-Slough-near-Meridian ranged from 205 cfs to a peak of 136,000 cfs in early January. The flow through the Tisdale Bypass was estimated at 19,000 cfs at this same time. The combined flow of 155,000 cfs exceeded the discharge through the Sacramento River at Verona by 70% due to the diversion of a large portion of the Sacramento River, Sutter Bypass and Feather River flows into the Yolo Bypass. In addition to many ungaged inputs, another unknown factor was caused by a large levee break in late January, along the Sutter Bypass near Wadsworth Canal. This break diverted some of the flow from the bypass back to the town of Meridian, seven miles upstream.

Sacramento River

Data for pH, DO, temperature, EC, alkalinity and hardness for the Sacramento River at Bryte site are presented in Figure 5. Ammonia levels remained below the detection limit of 50 µg/L for all samples. pH values ranged from 6.9 to 8.5. Water temperature ranged from 8.8 to 10.9° C, DO ranged from 8.6 to 11 mg/L and EC ranged from 60 to 176 µS/cm. All of these measurements are within parameters established by the U.S. EPA (1987) and CVRWQCB (1994).

The discharge at Verona for the 1996-97 dormant spray period ranged from 10,600 to 90,200 cfs. Total discharge for the 1996-97 dormant spray period was 140% greater than the discharge in the 1994-95 and 1995-96 dormant spray seasons. As a further comparison, the 1996-97 dormant spray period discharge was 360% of the 1993-94 levels, which was a below average water year.

Pesticide Use

The Sacramento Valley is an area of extensive agriculture with roughly 4 million pounds of fungicides, herbicides, and insecticides used during the typical dormant spray period in the six county region (DPR 1993-95). The organophosphates diazinon and methidathion are the primary insecticides used on dormant nut and stone fruit trees to control pests. Applications made during January and February of 1995 and 1996 amounted to 77,000 pounds of diazinon and 49,000 pounds of methidathion (DPR 1995-96[2]). Applications of diazinon and methidathion during the same period of 1997[2] were 52,500 and 35,700 pounds, respectively, which was a 32% decrease in use of diazinon and a 27% decrease in the use of methidathion over the previous two years. As dormant sprays are preferably applied by ground rigs in clear weather, this marked decrease in use was attributable to intense rainfall, ground saturation, and subsequent flooding. These conditions prohibited growers from entering their orchards to manage overwintering pests. The geographical component of the spatial distribution of these chemicals remains consistent over the years as they are predominantly applied to orchard crops (Figures 6 - 9).

Pesticide Detections and Toxicity

Sutter Bypass

Diazinon was detected in seven of the 16 samples collected in the Sutter Bypass (Table 3). Diazinon was detected in the Sutter Bypass at Kirkville Road on January 27 and 29 at 0.086 and 0.063 µg/L, respectively. Methidathion was also detected on January 27 at 0.071 µg/L. Diazinon was again detected in the Sutter Bypass at Karnak in five consecutive samples collected between February 17 and March 4 at levels ranging from 0.040 to 0.056 µg/L.

The percent survival of the C. ***dubia*** test animals ranged from 85% to 100% in the acute toxicity samples while the corresponding controls ranged from 90% to 100% survival. There was no significant acute toxicity in any of the samples. The lowest percent survival did not correspond with any pesticide detections. Raw data for the acute bioassays performed by DFG-ATL are presented in Appendix C. The February 3 sample was inadvertently terminated after 48 hours by

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[2] 1996 and 1997 pesticide use information is derived from preliminary draft data from DPR.

DFG-ATL. No toxicity in the sample had been observed at this time. This sample was one of the two split samples provided to CVRWQCB for acute toxicity testing and pesticide analysis. The CVRWQCB results for the February 3 sample were 95% survival and diazinon concentrations of 0.019 µg/L. The bioassay and analysis results of the CVRWQCB split of the February 24 sample were 95% survival and diazinon concentrations of 0.040 µg/L. This was roughly the same diazinon concentration reported by CDFA. Low levels of simazine and metalochlor were observed in both CVRWQCB split samples. Raw results of the CVRWQCB splits are presented in Appendix D.

Sacramento River

Diazinon was detected in four of 24 samples collected from the Sacramento River at Bryte. These detections occurred from January 24 through February 1 and ranged in concentration from 0.061 to 0.065 µg/L (Table 3). In addition, methidathion was detected in the January 27 sample collected at Bryte at 0.056 µg/L.

There was no chronic toxicity reported in any of the samples. No chronic toxicity sample or control had less than 90% survival. All chronic toxicity samples had between 15.4 and 34.9 offspring and controls had between 14.8 and 27.2 offspring average per adult at the end of the 7 day test. All controls met the minimum U.S. EPA method requirement of an average of 15 offspring per surviving adult female.

Note: There are two separate numbers used to calculate the numbers of offspring in the EPA test. For comparison and statistical evaluation, the number of offspring is calculated based on the total offspring produced divided by the number of adult females starting the test. For test validity, only the offspring of surviving adult females in the control are counted and then divided by the number of surviving adult females at the end of the test. For these tests there were always ten adult female C. ***dubia*** starting the test but often less than ten animals survived until the end of the test producing two different numbers for reproductive rates.

Reproduction rates were higher in the sample than in the control in seven of the eight chronic samples tested. On average, the sample fecundity was 25% higher than the corresponding control. Previous studies have noted that ***Ceriodaphnia*** reproduction is commonly greater in ambient water that in diluted mineral water controls, due to nutritional benefits present in the sample water (Stewart, 1996). Stewart suggests that filtering the sample may reduce reproduction by as much as 10%. Raw data for the chronic bioassays performed by DFG-ATL are presented in Appendix E.

Diazinon was detected in 11 of 40 samples from all sites at levels not exceeding 0.086 µg/L. No numeric objectives or criteria for diazinon have been established by the CVRWQCB or U.S. EPA for the protection of aquatic life. The DFG has suggested that "freshwater aquatic organisms should not be affected unacceptably if the one-hour average concentration does not exceed 0.08 µg/L ..."(Menconi and Cox, 1994). Only one sample, collected on January 27 from the Sutter Bypass site, exceeded this suggested level. This sample also contained methidathion for which no numeric criteria for the protection of freshwater aquatic life has been established. Mortality did not exceed 5% in either of the acute tests conducted on this sample. Diazinon and methidathion were also detected in the Sacramento River sample collected on the same date and diazion was detected in each of the replacement water samples for that week. No significant toxicity was observed and reproduction rates were the highest observed for this study.

The diazinon detections that were observed could be broken into two distinct pulses, one in late January and one in late February. The initial diazinon detections appear related to storm event runoff. There had been 4 days of significant rain prior to the first detection at Bryte on January 24 and rain continued for another 4 days. No corresponding sample was taken that day from the Sutter Bypass. Sacramento River discharge was high and increasing during this time. This discharge remained high through most of February due to high reservoir releases. Sutter Bypass discharge increased drastically and continued rising until January 29. There were four consecutive diazinon detections spanning 8 days in the Sacramento River and two detections spanning 3 days at the Sutter Bypass site. A previous study (MacCoy et al., 1995) has observed diazinon pulses on the Sacramento River lasting up to 27 days with concentrations above our reporting limit of 0.04 µg/L. The maximum concentrations detected by USGS during this pulse was 0.39 µg/L. During 1997, 52,000 pounds of diazinon were applied in the watershed during January and February. Only sporadic rain fell from January 3 to the 19 when half of this diazinon was applied and no detections were made in the January 20 or January 22 samples. Only after several days of rain had resulted in substantial runoff, as indicated by the rising discharge, were detections made. Due to the differing sampling schedules between the two sites, it cannot be determined if diazinon was present in the Sutter Bypass on the dates preceding and following the two detections there. The detection of methidathion at both sites on January 27 and the similarity of the water quality parameters around this time indicate that the water at the two sites may have been substantially the same.

The second set of diazinon detections in the Sutter Bypass were not associated with any rain events and occurred at a time of decreasing discharge in the bypass with no flow through the Tisdale Bypass. These detections spanned a 15-day period and demonstrated a slowly declining low level of contamination from 0.056 to 0.040 µg/L. These detections began in conjunction with the move of the sampling site from Kirkville Road to Karnak. It is assumed that the waters at both sites were substantially the same but concurrent sampling from both sites was not conducted to confirm this. The changes in environmental parameters from the February 12 to the 17 (Figure 3) may indicate a change in water sources between the two sites or may reflect changes due to declining water levels in the Sutter Bypass and cessation of flow through the Tisdale Bypass.

The 30% reduction in diazinon applications was likely the result of orchards remaining flooded or very wet until the dormant season had passed. This assumption may also provide an explanation for the low levels of diazinon detected in the bypass. There were 16,000 pounds of diazinon applied in February, some of which may have been applied to wet orchards. Diazinon could then be carried offsite by water which continued to drain from the orchard. However, an alternate hypothesis might be related to the earlier flooding of pesticide storage facilities. A flooded diazinon container or other runoff from one of these facilities could also have leaked pesticide into the watershed without the need for rain runoff.

Quality Control

Results from the CDFA laboratory's continuing QC are presented in Appendix F and blind spike results are presented in Appendix G. Since samples from both the Sacramento (Study 154) and San Joaquin (Study 155) studies were analyzed at the same time, the tables for all QC results contain data from both studies. Table entries in Appendix F with asterisks indicate that the spike analyzed with the extraction set fell below the lower control limit and the resultant concentration may have been under estimated. Table entries in Appendix G with asterisks indicate that the blind spike sample recovery was below the lower control limit.

Pesticide Mass Transport

Mass loading calculations are helpful in estimating instantaneous, daily, storm event and seasonal loads of pesticides. Pesticide loads were calculated by multiplying the daily mean discharge volume at the sampling site times the instantaneous pesticide concentration of individual samples from that site. The integrated load over the period of observation is the total mass of the detected pesticide transported past the monitoring site. These loading calculations have a high degree of uncertainty due to the necessity to estimate discharges through the Sutter Bypass and the unavailability of discharge data for the Yolo Bypass. Several assumptions were made in arriving at these figures. First, that the concentrations observed were representative of the stream being sampled and could also be used to represent up to a 24-hour period of flow. Second, that the concentrations increased and decreased linearly in order to bridge periods where no samples were taken with estimated data. The day preceding or following a detection was estimated to be half the detected level if nothing was detected in the next sample period. Thus the four diazinon detections on the Sacramento River in late January are considered to represent a 10-day pulse with concentrations of approximately 0.03 µg/L on the first and last day and approximately 0.06 µg/L for the middle 8 days.

The estimated mass of diazinon transported through the Sutter Bypass was 127 lbs. Ninety-seven percent of this mass was accounted for in the 5-day period from January 26 to 30. The mass transported during the late January period was 123 lbs which represents 0.3% of the total diazinon applied in the six county region during January (36,000 lbs) according to 1997 draft pesticide use data. There were 2,900 lbs of diazinon applied in Sutter County during February, 1997. Assuming that Sutter County is the primary source of diazinon during low flow periods, a mass of 4 lbs would represent 1.4% of the total diazinon applied.

Diazinon loading in the Sacramento River for January 23 to February 1 was 202 lbs. During flooded conditions, as were observed during January and February, the Sutter Bypass cannot fully be considered a tributary of the Sacramento River which flows past Bryte. Discharge through the bypass alone can exceed that in the Sacramento River at Verona. The lower Sacramento River channel carries off only a portion of the flows from the upper Sacramento River, the Sutter Bypass, and the Feather River. The remainder is carried south through the Yolo Bypass. Due to the geographical layout of this confluence, the primary source of water entering the lower Sacramento River channel during floods is from the Feather River.

Methidathion mass loading was calculated from a single detection on January 27 at each site. Methidathion loading in the Sutter Bypass and Sacramento River was 58 and 42 lbs respectively. The reduced loading in the Sacramento River as compared to the Sutter Bypass is once again due to diversion of water into the Yolo Bypass at this time.

CONCLUSIONS

During the winter of 1996-97, the waters of the Sutter Bypass and Sacramento River at Bryte were found to be non-toxic to the water flea ***Ceriodaphnia dubia.*** Water quality and pesticide concentrations were influenced by a very high flows in the region. Discharge in the watershed during January and February was much higher than previous years due to heavy rains and rapid snow melt. The high river levels resulted in broken levees and flooding which, combined with the heavy rains, reduced dormant spray insecticide use in the Sacramento River watershed. Both of these factors contributed to lower concentrations of the two major dormant spray insecticides, diazinon and methidathion, than have been detected in previous studies. Mass loading would be understated because pesticide laden runoff was diluted yielding concentrations below our ability to detect them.

The toxicity of water samples provides the principle indicator of compliance regardless of the pesticide concentration level. However, since toxicity tests lack causal specificity, DPR in cooperation with the CVRWQCB and DFG, prepared quantitative response limits (QRLs) for chlorpyrifos, diazinon, and methidathion. QRLs help DPR determine whether pesticide concentrations reach levels attributable to aquatic toxicity. QRLs neither present an enforceable standard nor supersede the CVRWQCB's narrative toxicity standard. Most importantly, QRLs provide a benchmark to gauge whether the concentrations of dormant spray pesticides correspond to verified aquatic toxicity. The proposed QRL values for acute and chronic exposures are as follows: chlorpyrifos--0.04 and 0.02 µg/L, diazinon--0.08 and 0.04 µg/L, and methidathion--1.1 and 0.83 µg/L, respectively.

Diazinon was the most frequently detected insecticide and it was also the most heavily used. Methidathion was detected only once at both the acute and chronic monitoring sites. Methidathion usage, in pounds of active ingredient, was 68% of the diazinon totals. No other pesticides were detected. Only 6% as much phosmet, the next highest used insecticide included in our analysis, was applied as compared to diazinon.

High flows blurred the typical tributary to main stem relationship which prevented the determination the sources of pesticides detected. During flood conditions, water in the lower Sacramento River watershed is rerouted through a number of bypass systems such that water from the upper Sacramento River flows through the Sutter Bypass and a portion of the combined Sacramento River, Sutter Bypass and Feather River flows into the Yolo Bypass. Additionally, some of the areas flooded included pesticide storage facilities which add a further unaccountable factor.

In conclusion, the data presented here are useful for comparison to other flood years and determining if a problem exists. However, the conditions unique to each flood season prevent the absolute correlation of any two flood years without meticulous attention to those unique conditions.

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Table 1. California Department of Food and Agriculture, Center for Analytical Chemistry organophosphate and carbamate pesticide screens for the Sacramento River toxicity monitoring study.

Organophosphate Pesticides in Surface Water by GC **Method: GC/FPD**		**N-Methyl Carbamate in Surface Water by HPLC** **Method: HPLC/Post Column-fluorescence**	
Compound	**Reporting Limit (µg/L)**	**Compound**	**Reporting Limit (µg/L)**
Chlorpyrifos	0.04	Carbaryl	0.05
Diazinon’	0.04	Carbofuran	0.05
Dimethoate (Cygon)	0.05		
Fonofos	0.05		
Malathion	0.05		
Methidathion	0.05		
Methyl parathion	0.05		
Phosmet	0.05		

[1] Diazinon was analyzed from a separate, unpreserved, split sample. Other chemical samples were preserved with 3N HCl to a pH of 3-3.5 to retard analyte degradation.

Table 2. Historical applications of diazinon and methidathion (pounds active ingredient) during January and February in Butte, Colusa, Glenn, Sutter, Tehama and Yuba Counties.

	YEAR			
	1994	**1995**	**1996[1]**	**1997[1]**
Diazinon	71,467	77,076	77,379	52,520
Methidathion	48,171	48,840	49,170	35,765

[1]. Data for 1996 and 1997 are preliminary and subject to revision when the database is reviewed.

Table 3. Results of Sacramento River Watershed Toxicity Study, Winter 1996-97. Only results for diazinon and methidathion are shown since no other pesticides in the organophosphate and carbamate pesticide screens were detected.

Table 3

	SACRAMENTO RIVER AT BRYTE				SUTTER BYPASS				
Sampling Date	Methidathion (µg/L)	Diazinon (µg/L)	Chronic Toxicity Percent Survival[1]	Chronic Toxicity Offspring /animal[1]	Site	Methidathion (µg/L)	Diazinon (µg/L)	Acute Toxicity A Percent Survival[1]	Acute Toxicity B Percent Survival[1]
12/2/96	nd[2]	nd	-		Karnak	nd	nd	95/100	100/100
12/4/96	nd	nd			Karnak	nd	nd	100/100	100/100
12/6/96	nd	nd	90/90	15.4/16.8					
1/20/97	nd	nd			Sac. Ave.	nd	nd	100/100	85/100
1/22/97	nd	nd			Sac. Ave.	nd	nd	100/100	100/100
1/24/97	nd	0.061	90/100	22.5/18.9					
1/27/97	0.056	0.061	-		Sac. Ave	0.071	0.086	100/95	95/95
1/29/97	nd	0.065	-		Sac. Ave	nd	0.063	90/100	90/100
1/31/97	nd	0.064	90/100	34.9/27.2					
2/3/97	nd	nd	-		Sac. Ave	nd	nd	--/--[3]	--/--[3]
2/5/97	nd	nd	-		Sac. Ave	nd	nd	100/90	100/90
2/7/97	nd	nd	100/90	25.2/14.8					
2/10/97	nd	nd	-		Sac. Ave	nd	nd	100/100	100/100
2/12/97	nd	nd	-		Sac. Ave	nd	nd	100/100	100/100
2/14/97	nd	nd	100/90	25.5/14.8					
2/17/97	nd	nd			Karnak	nd	0.056	100/100	100/100
2/19/97	nd	nd			Karnak	nd	0.052	100/90	100/90
2/21/97	nd	nd	90/100	27.9/24.5					
2/24/97	nd	nd	-		Karnak	nd	0.047	100/95	100/95
2/26/97	nd	nd	-		Karnak	nd	0.041	95/95	100/95
2/28/97	nd	nd	90/100	24.9/21.8					
3/3/97	nd	nd	-		Karnak	nd	0.040	100/100	90/100
3/5/97	nd	nd			Karnak	nd	nd	100/100	95/100
3/7/97	nd	nd	100/100	25.5/25.1					

Notes:

[1] Two numbers are reported for all toxicity tests. The first number is the result from the sample, the second is the result from the corresponding control. Chronic toxicity water was replaced twice each week using new sample water . The numbers reported for percent survival refers to the survival at the end of the test. Offspring per animal is the total number of offspring produced during the test divided by the number of animals starting the test (10).

[2] nd = none detected at the reporting limit for that chemical.

[3] The February 3 acute toxicity tests were accidentally terminated after 48 hours with 100% survival in all samples and controls. New 96-hour tests could not be run on the sample within the 72-hour maximum time limit from collection to test initiation, as required by U.S. EPA.

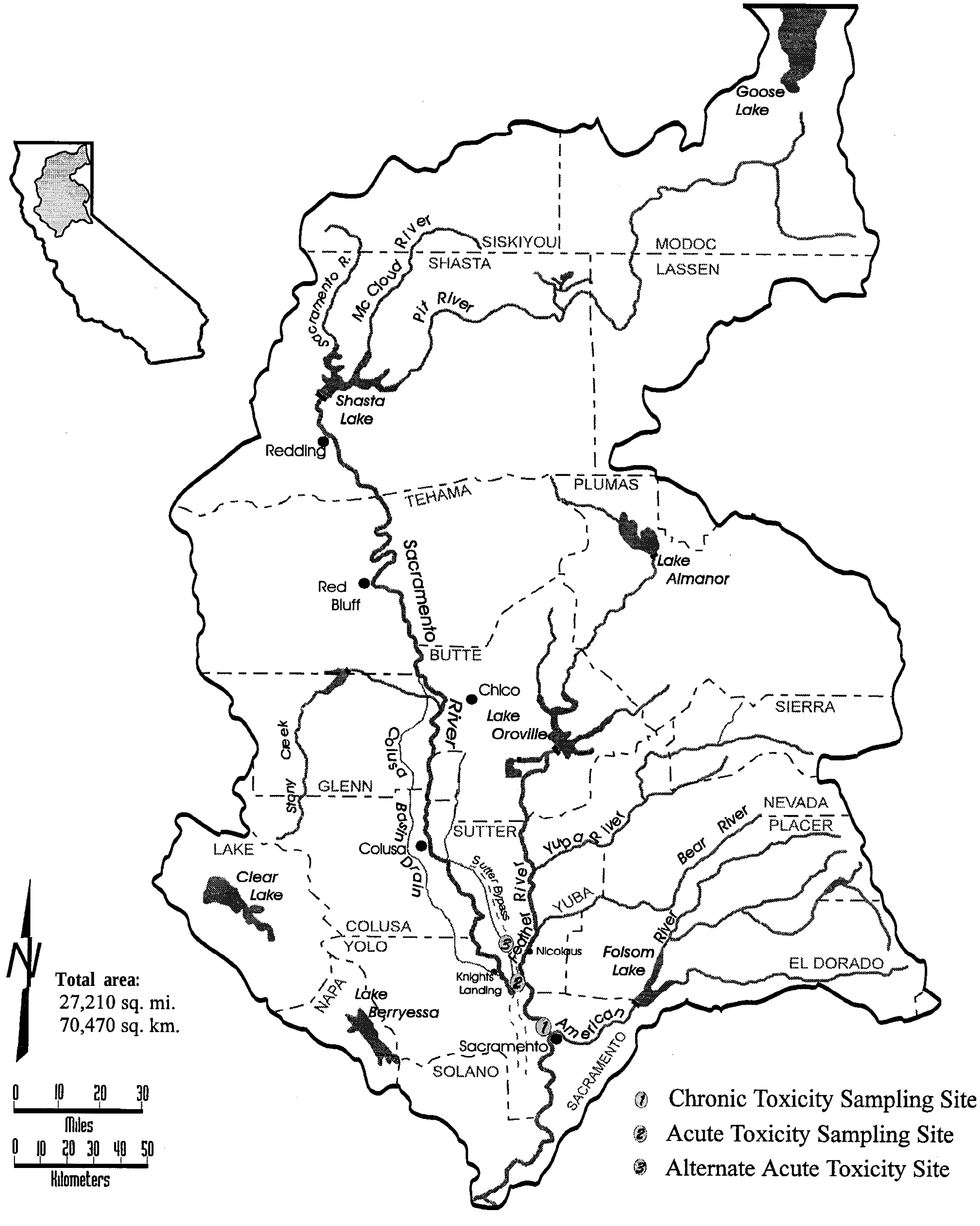


Figure 1. Map of the Sacramento River Hydrologic Basin

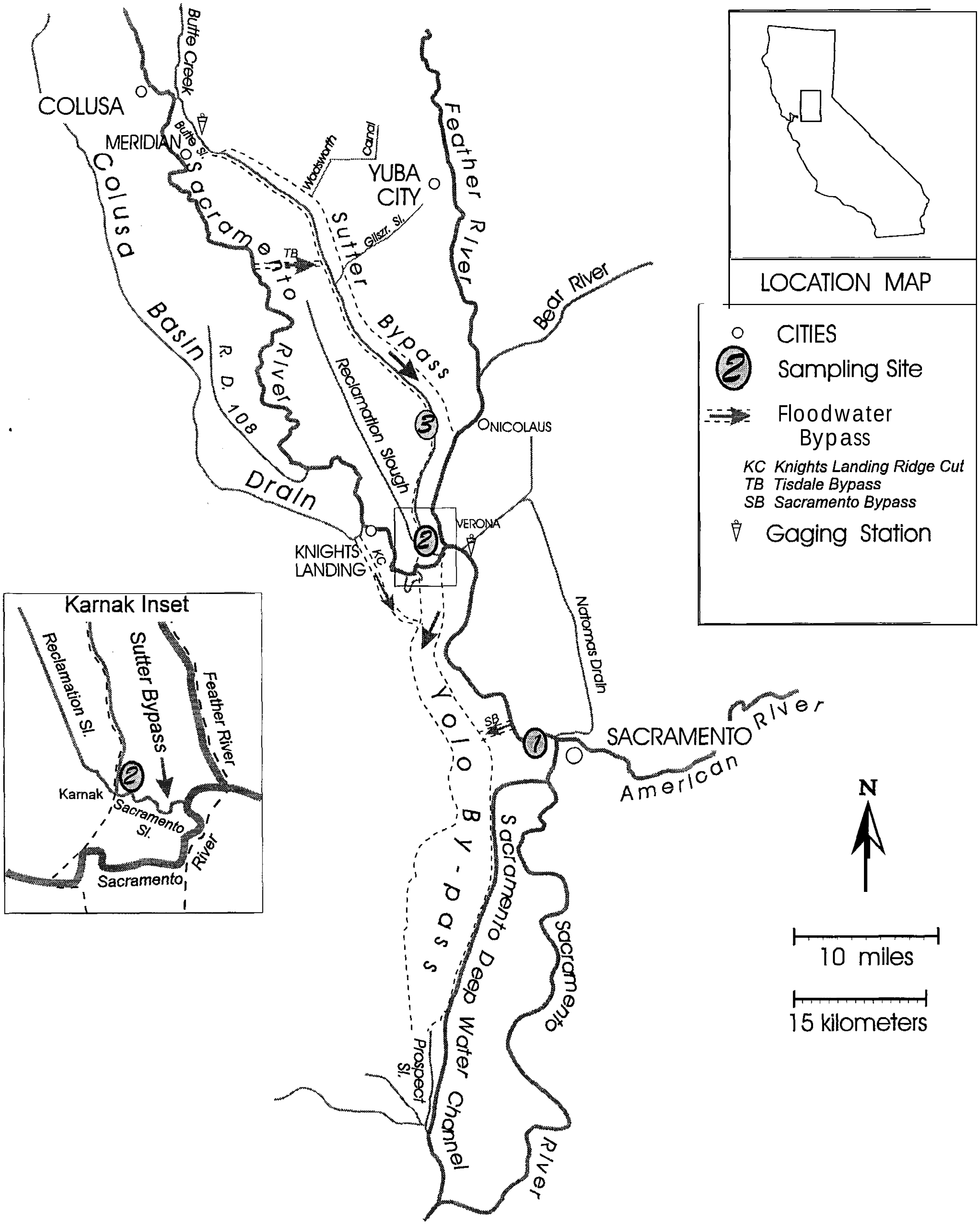
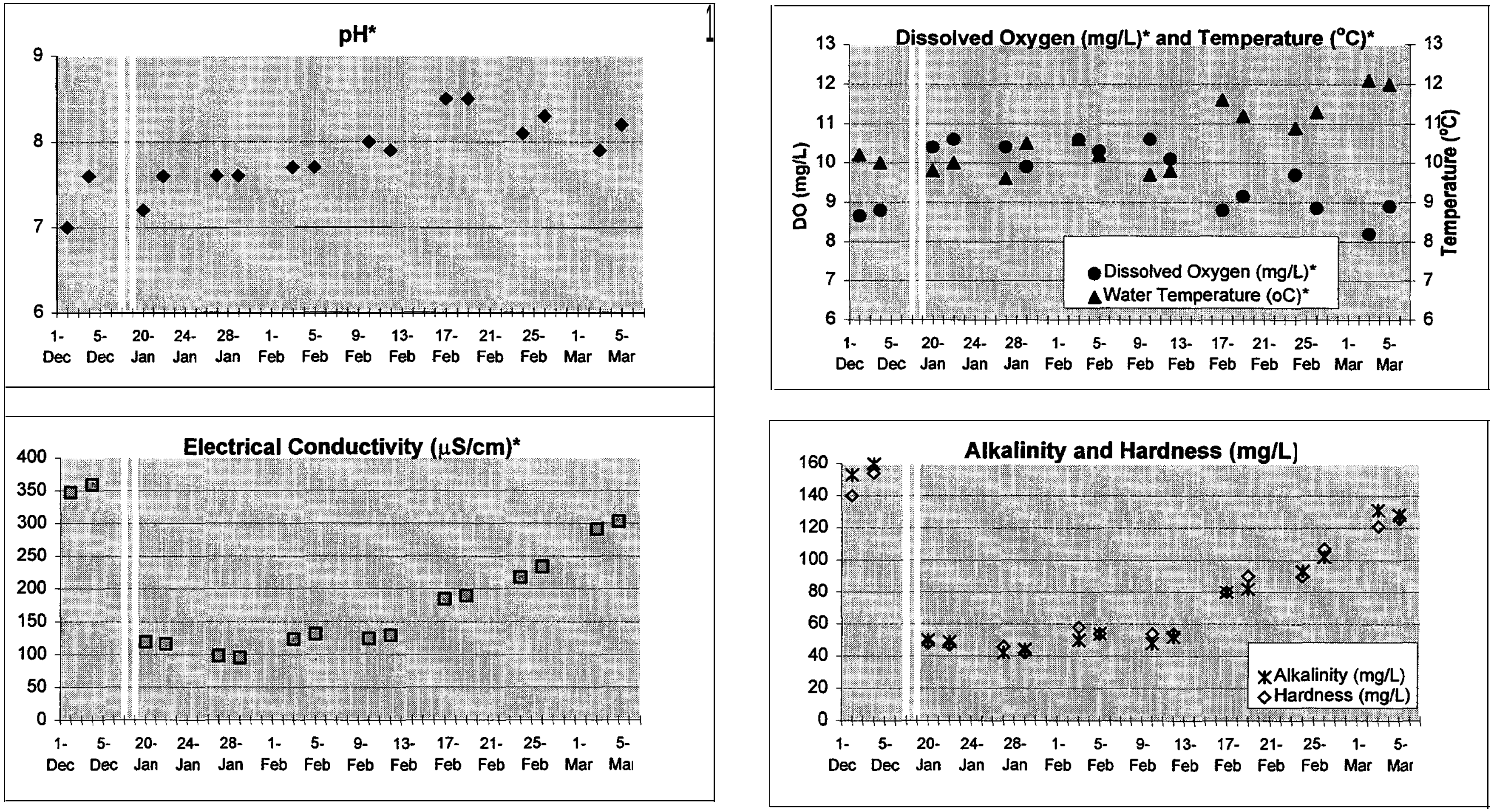


Figure 2: Sampling sites in the Sacramento River watershed.
Site 1= West Sacramento water intake at Bryte , Sacramento River Chronic Toxicity Site,
Site 2= Sutter Bypass at Karnak Pumping Station, Acute Toxicity Site.
Site 3= Sutter Bypass at Sacramento Avenue, Alternate Acute Toxicity Site.

ENVIRONMENTAL DATA FOR THE SUTTER BYPASS SITES, WINTER 1996-97


pH*

Dissolved Oxygen (mg/L)* and Temperature (°C)*

Electrical Conductivity (μS/cm)*

Alkalinity and Hardness (mg/L)

Figure 3. Environmental measurements for the Sutter Bypass taken either at the Karnak or the Kirkville Road sites. Data collected at Karnak from December 2-6, 1996 and February 17 to March 5. Data taken at Sacramento Avenue from January 20 to February 12, 1997. Double bar denotes a break in sampling between background and dormant season samples. * Denotes measurements made on site.

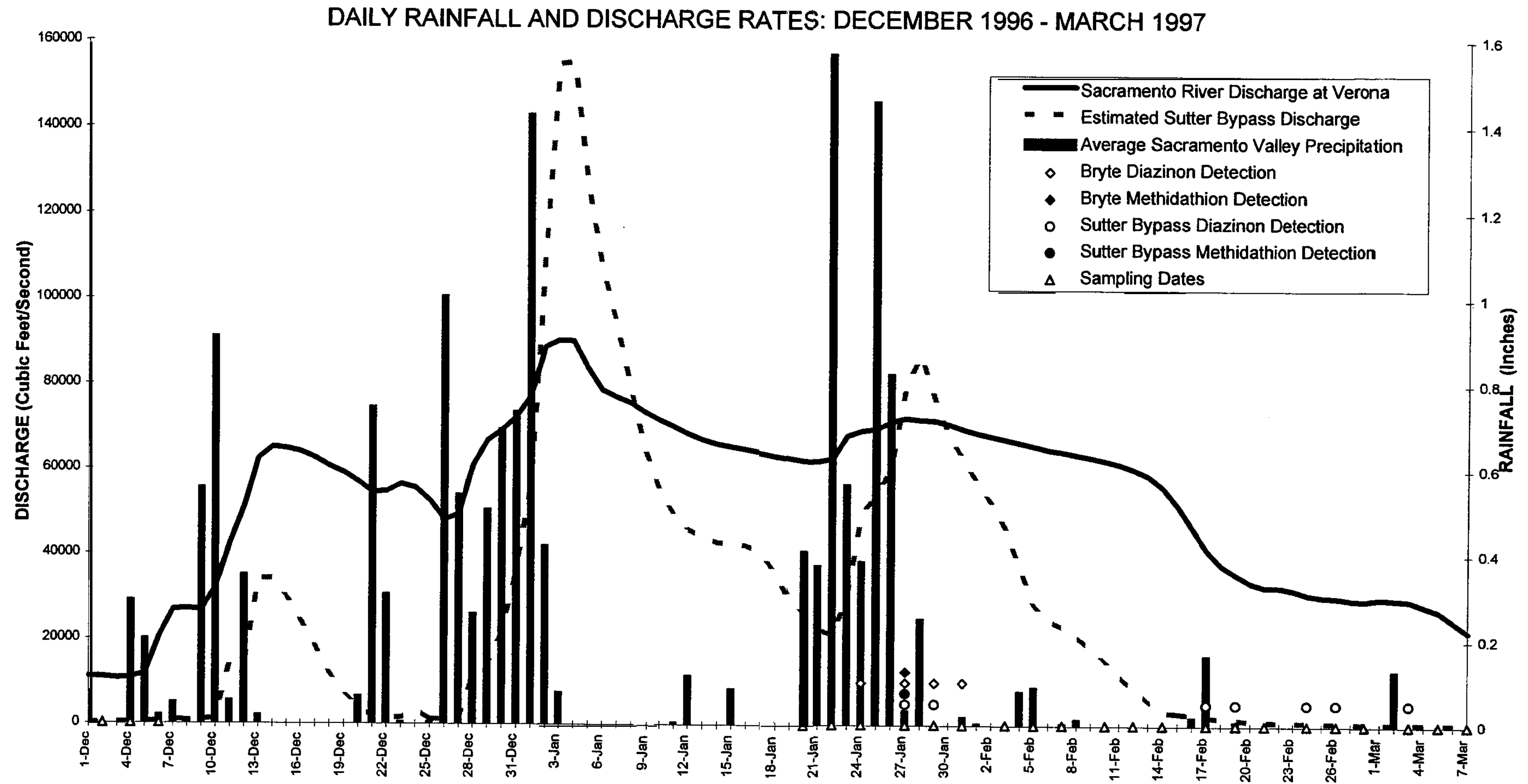


Figure 4. Daily rainfall and flow rates (discharge) for the Sacramento River and the Sutter Bypass from December 1, 1996 through March 7, 1997. Rainfall data is an average of two stations in the Sacramento River Basin: Sacramento Post Office and Chico weather stations. Sacramento River discharge was measured at Verona. Sutter Bypass discharge was estimated by adding measurements from the Butte Slough near Meridian gage and approximated flows for Tisdale Bypass based on discharge measurements at the Wilkins Slough DWR station. The Sutter Bypass (Acute Toxicity) site was not sampled on Fridays. Rainfall and discharge data is provisional and is subject to revision.

ENVIRONMENTAL DATA FOR THE SACRAMENTO RIVER AT BRYTE, WINTER 1996-97

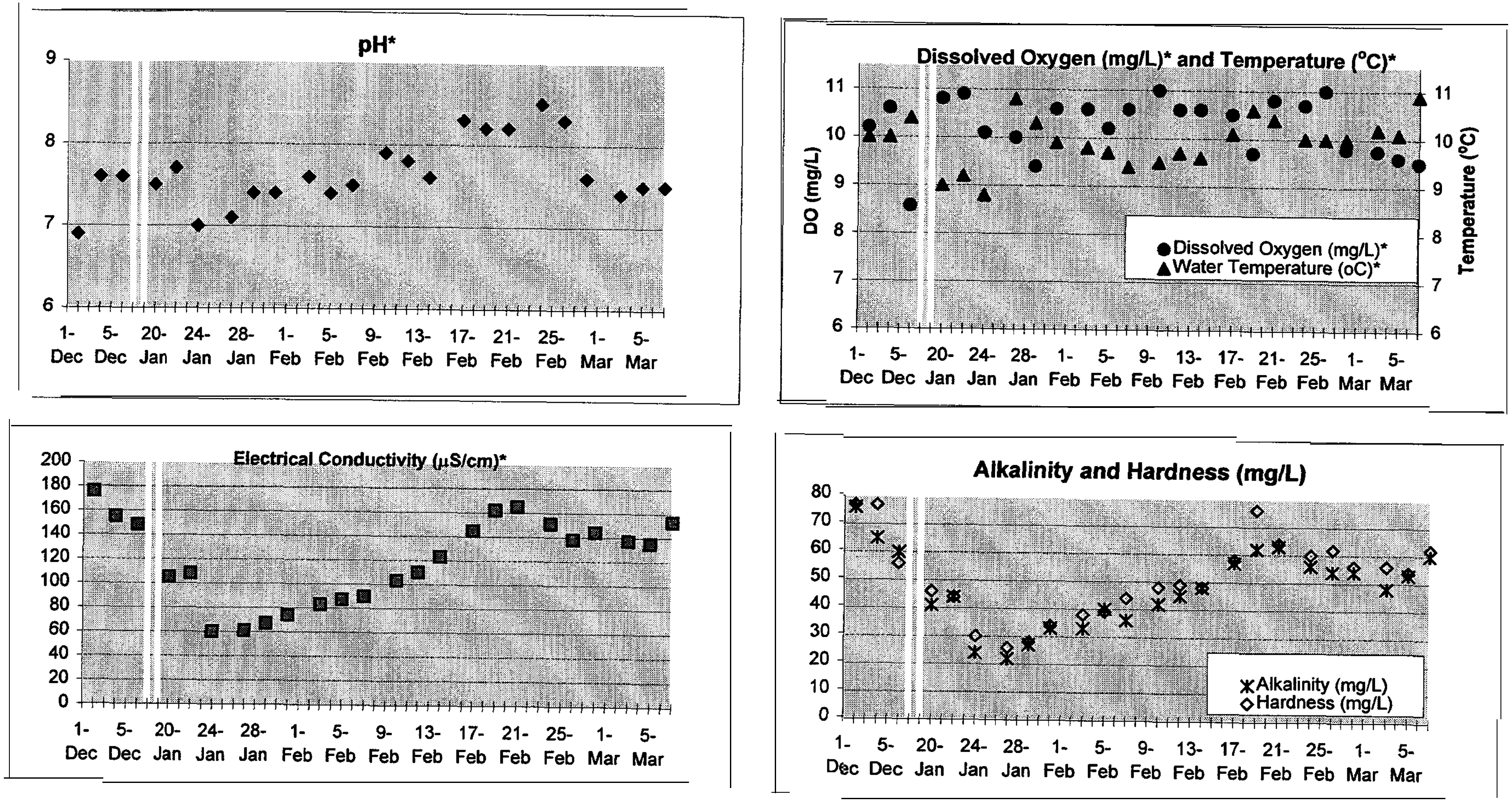


Figure 5. Environmental measurements for the Sacramento River at the Bryte Water Intake Tower. Data collected from December 2-6, 1996 and January 20-March 7, 1997. Measurements were collected three times per week during the stated period. *Denotes measurements made on site. Double bar denotes a break in sampling between the background and dormant season samples.

Figure 6: Diazinon use in the Sacramento River Watershed during January, and February, 1995

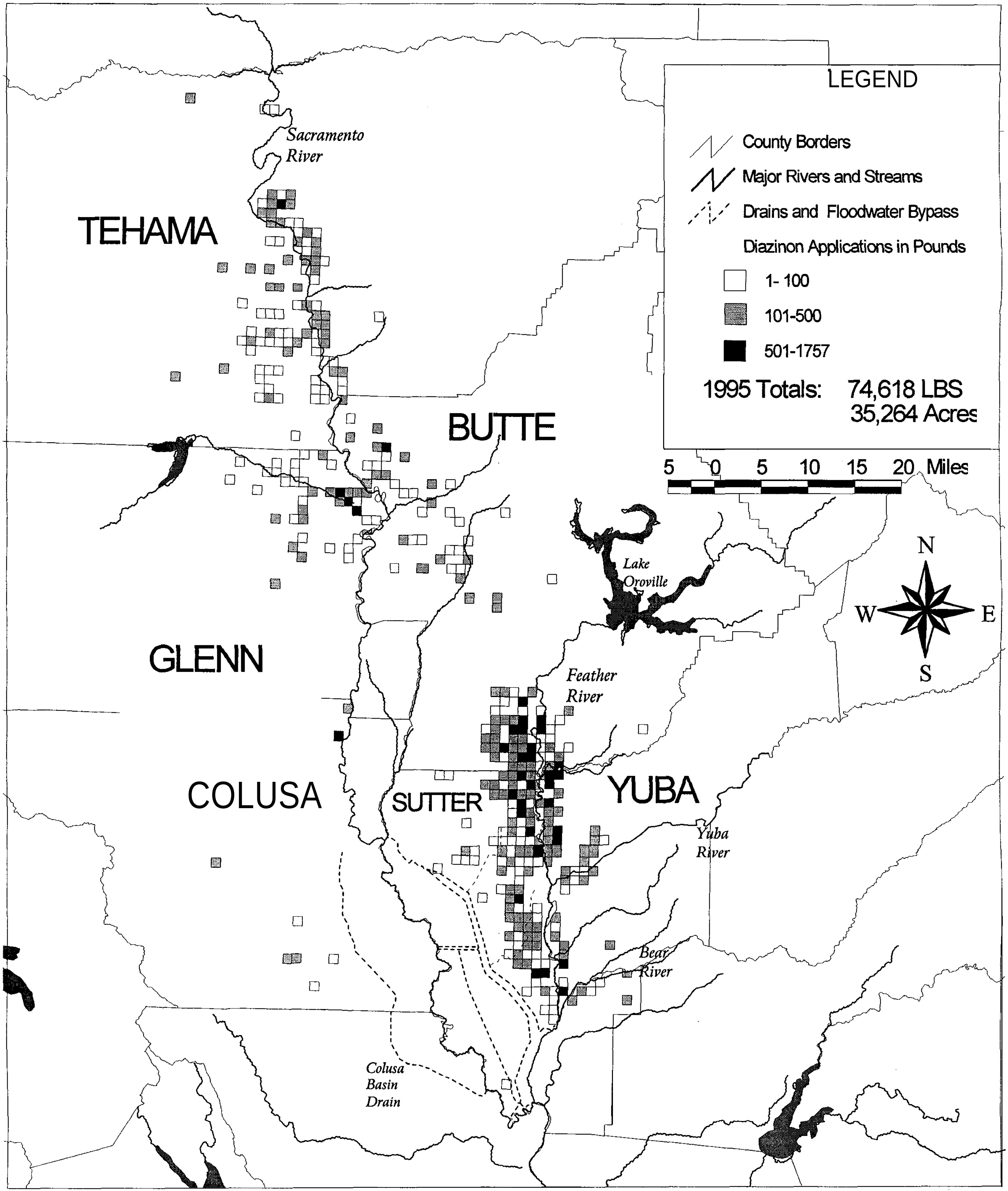


Figure 7: Methidathion use per section in the Sacramento River Watershed during January and February, 1995

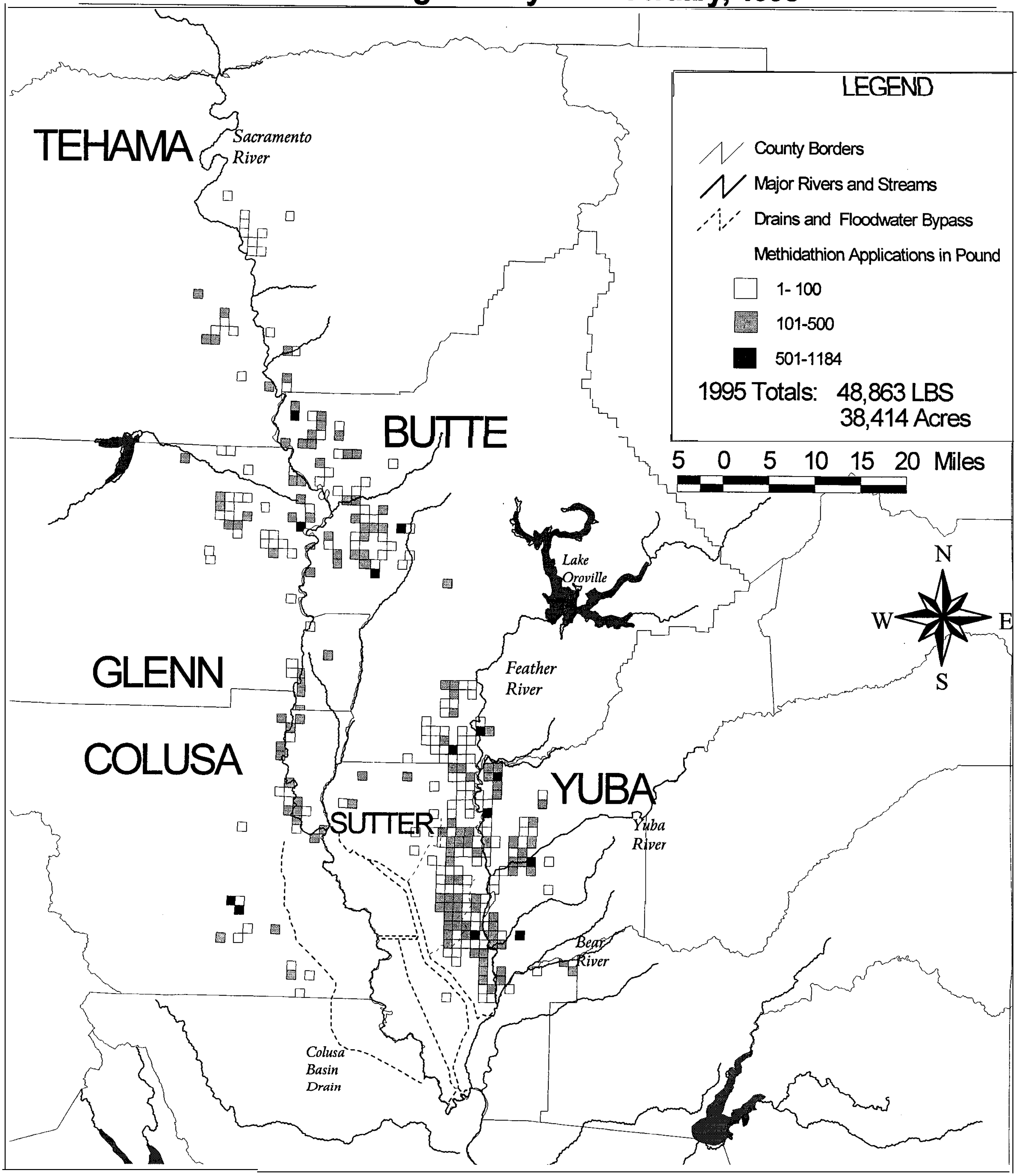


Figure 8: Diazinon use per section in the Sacramento River Watershed during January and February, 1997

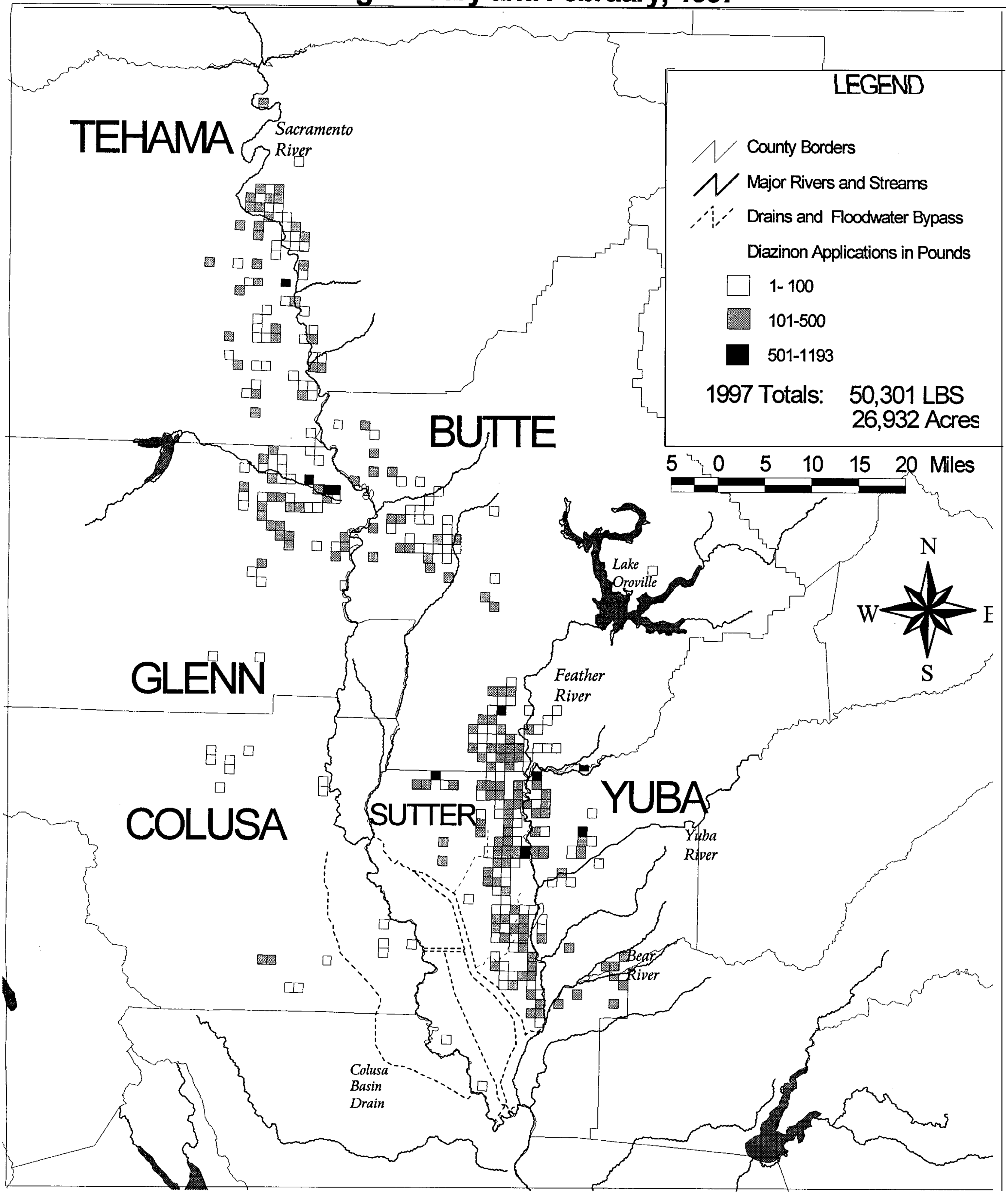


Figure 9: Methidathion use per section in the Sacramento River Watershed during January and February, 1997