

**VARIATION OF ENDOSULFAN RESIDUES IN
WATER AND SEDIMENT TAKEN FROM THE
MOSS LANDING DRAINAGE OF
MONTEREY COUNTY**

by

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ABSTRACT

Data from previous studies conducted by the State Mussel Watch Program (SMW) implied increasing endosulfan residues in mollusks used as indicator organisms of chemical contamination in the Moss Landing Drainage area of Monterey County. As a first step in confirming a chronological trend, studies were conducted by the California Departments of Food and Agriculture (CDFA) and Fish and Game (CDFG) to determine within-site variability of endosulfan concentrations, and to estimate sample size necessary for future research. Personnel from the Environmental Hazards Assessment Program (EHAP) of CDFA collected sediment and water samples while personnel from the Pesticide Investigations Unit (PIU) of CDFG collected mollusk and fish samples at the same sites in a coordinated effort. This report contains results from the EHAP study.

Three sites previously monitored by SMW in Monterey County were selected for the collection of sediment and water samples. All samples were analyzed for endosulfan I, II and sulfate. Only 33, 33 and 25% of the sediment samples contained detectable residues of endosulfan I, II and sulfate, respectively. Endosulfan concentrations in sediment were not uniformly distributed in the Moss Landing Drainage area with residues occurring more frequently in agricultural areas, away from tidal action and dredging activities. Only 25% of the water samples contained detectable endosulfan residues in the form of endosulfan sulfate. However, it is conceivable that endosulfan residues exist in water (either dissolved or on suspended sediment) below the detection limit given the consistent find of residues in mollusks and fish in this area and the established bio-concentration factors for fish species. Minimum sample sizes of 22 and 11 for sediment and water, respectively, were estimated as necessary to calculate the true mean for a given site. Future study of temporal or spatial trends in endosulfan residues of this drainage area might best be concentrated on sediment and biological organisms since residues in water are mostly below the current detection limits.

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INTRODUCTION

Endosulfan is a chlorinated hydrocarbon insecticide that belongs to the chemical group of cyclodienes. The cyclodienes are produced from hexachlorocyclopentadiene or closely related compounds utilizing the Diels-Alder reaction (Brooks, 1979). In addition to being composed of chlorine, hydrogen and carbon, endosulfan is unique in that it also contains oxygen and sulfur. Technical grade endosulfan is a 7:3 mixture of two stereoisomers known as endosulfan I and II. The principal degradation product of environmental concern is endosulfan sulfate which is more stable in the environment and has toxicological properties comparable to the parent compounds. The non-sulfur containing endosulfan metabolites including endosulfan diol, endosulfan ethers and endosulfan lactones are about 10,000 times less toxic than the parent isomers and the sulfate (Ali et al., 1984).

Mechanisms of environmental dissipation include volatilization, photodecomposition, microbial metabolism, leaching, runoff and adsorption-desorption (Ali et al., 1984). Environmental dispersion of endosulfan appears to result primarily from volatilization and oxidation to endosulfan sulfate (Coleman and Dolinger, 1978). Endosulfan and the sulfate metabolite can have a soil half-life ranging from 120 days for endosulfan I (Van Dyk and Van Der Linde, 1976) to more than 800 days for endosulfan II and sulfate (Stewart and Cairns, 1974). As the endosulfan concentrations in these studies were reported in parts per million, it is possible that undetected residues persisted in the parts per billion range. Other factors such as soil temperature, soil moisture, and pH can greatly affect the degradation rate of endosulfan. In water, endosulfan is hydrolyzed to the diol. Hydrolysis half-life is very dependent on pH. At a pH of 5.5 the half-life

can be up to five months and at a pH of 8 the half-life is one day (Coleman and Dolinger, 1978).

Endosulfan does not appear to cause mutagenic, teratogenic, carcinogenic or adverse reproductive effects in studies using rats and mice (Goebel et al., 1982), however, adequate studies to support these initial findings have yet to be completed. Much of the research that has been completed on endosulfan is being reevaluated as most of the analysis was conducted only on endosulfan I. Newer studies, acknowledging the existing data gaps, are designed to include analysis for endosulfan II and sulfate.

The toxicity of endosulfan to aquatic organisms is well documented. Endosulfan is acutely toxic to marine and freshwater organisms. The LC50 values for endosulfan range from 0.17 to 4.4 ug/l and 0.09 to 3.45 ug/l in fresh water and salt water fish, respectively (Ali et al., 1984). Endosulfan was found to be the second most toxic compound to fish in an acute toxicity study of organochlorine and organophosphate insecticides (Ali et al., 1984). Endosulfan is widely used throughout the state as a broad spectrum insecticide. It is registered for use on over 60 crops in California. The greatest use is on tomatoes, alfalfa, artichokes, lettuce, celery and grapes. Monterey County has been in the top three counties with respect to endosulfan use in the state over the past five years.

The environmental quality of Monterey Bay and its estuaries has been monitored by the California State Mussel Watch Program (SMW) since 1977 using species of mussels and clams. The SMW is a statewide program administered by the State Water Resources Control Board and operated by the California Department of Fish and Game (DFG). As a result of this monitoring program, endosulfan was first sampled for and detected in the Moss Landing drainage area in the 1979-80 study

(Martin et al., 1980). Subsequent monitoring of the area has indicated possible increasing endosulfan residues in mussels. Statistically significant yearly and seasonal trends could not be established from SMW data because replicate sampling was not routinely conducted. To establish chronological trends of endosulfan residues, it is necessary to assess within-site variability and estimate appropriate sample sizes by collecting replicate samples. This study was conducted in coordination with the Pesticide Investigations Unit (PIU) of the DFG. Personnel from PIU collected replicate samples of mussels, clams and fish at three SMW sites to determine the chemical analytical and within-site variabilities of these organisms. Personnel from CDFA collected replicate samples of sediment and water at the same sites to determine within-site and chemical analytical variability in endosulfan concentrations in these media. Given within-site and chemical analytical variability, appropriate sample sizes could be estimated for future use in spatial and temporal comparison studies.

MATERIALS AND METHODS

Study Area

Three sites in Monterey County were selected for the collection of water and sediment samples. These sites were selected because they had been consistently monitored by SMW for the last 2-3 years and because they coincided with sampling locations used by PIU in their concurrent study (Figure 1). The sites were: 1) Old Salinas River at Sandholt Bridge (Figure 2); 2) Parson's Slough at its entry into Elkhorn Slough (Figure 2); and 3) Blanco Drain near the Salinas River (Figure 3). Site 1 (which corresponds to PIU's Old Salinas River site) was located approximately 900 m south of the Old Salinas River-Elkhorn Slough confluence. River sediment and water quality at this site typify the river's status just prior to its emptying into Monterey Bay after flowing through the extensive agricultural drainage area of the Salinas Valley. Site 2 (which corresponds to PIU's Elkhorn Slough site) was located on Parson's Slough approximately 300 m south of its entrance into Elkhorn Slough. The site was within the boundaries of the Elkhorn Slough National Estuarine Sanctuary and State Ecological Reserve. Site 3 (which corresponds to PIU's Blanco Drain site) was located just south of the pumping station that pumps water from northern and southern channels of Blanco Drain into the Salinas River. Agricultural lands bordered both sides of the drain at this sampling site. The primary function of Blanco Drain is transport of water runoff from surrounding farmland to the Salinas River. Sites 1 and 2 represented saltwater locations, site 3 was freshwater.

Sampling Design

Sediment and water samples were collected at site 1 along one upstream transect adjacent to the SMW sampling post. A downstream transect at site 1 could not be established due to an increase in water depth. Sediment and water samples were

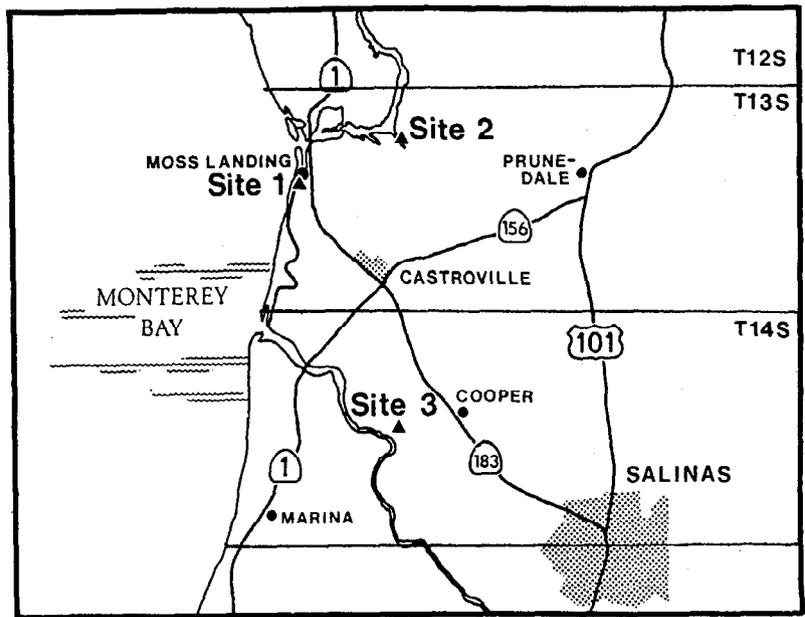


Figure 1. Overview of sampling area in Monterey County.

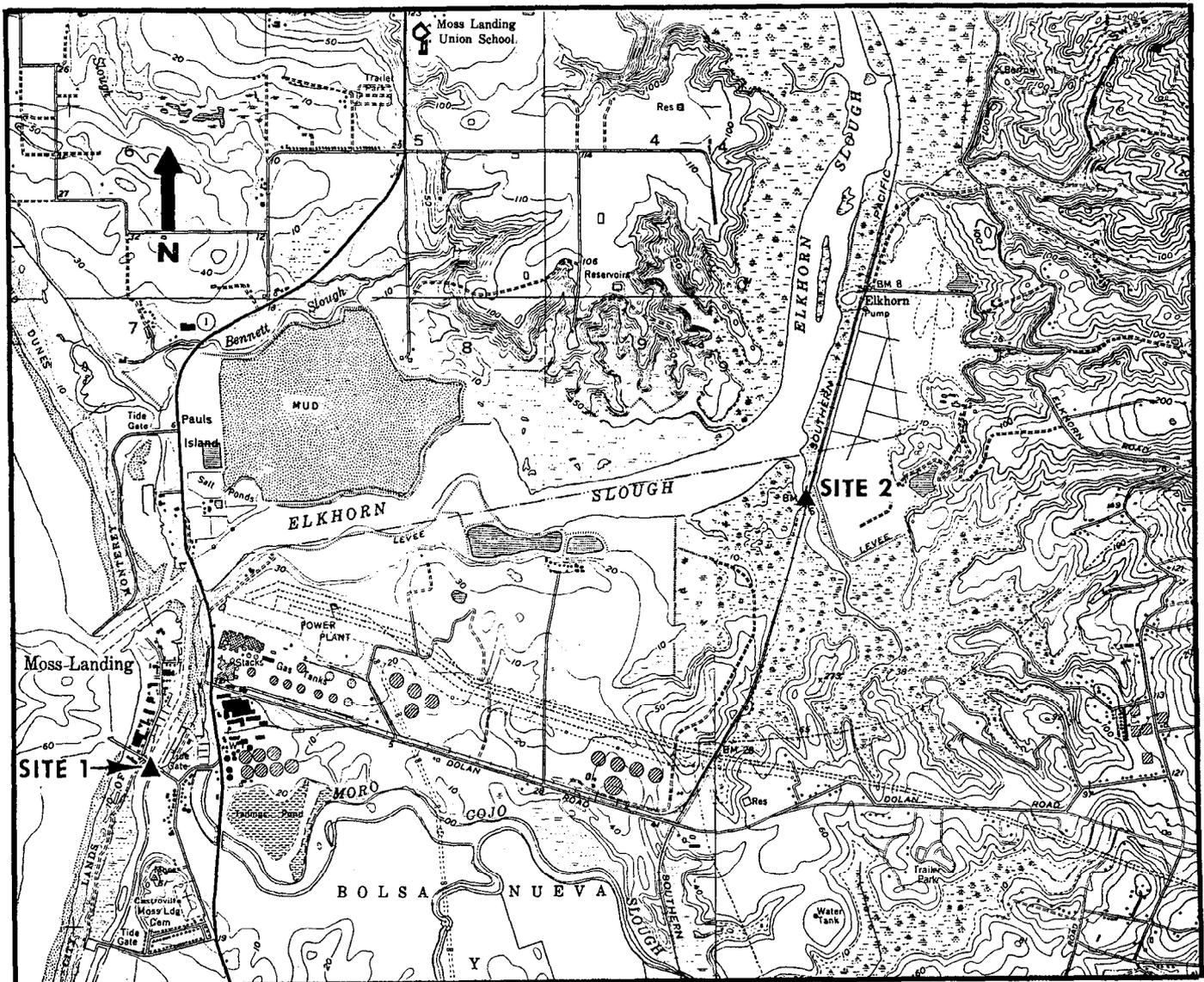


Figure 2. Sampling sites at Sandholt Bridge (Site 1) and Parson's Slough (Site 2) in Monterey County.

collected at sites 2 and 3 along two transects, one upstream and one downstream of the SMW sampling post within 12 m of each other and set perpendicular to water flow. Sediment and water samples were collected at sites 1 and 2 at six randomly selected points along each transect which were approximately 75 and 33 m wide, respectively. Because the width of site 3 was only about 10 m, samples were collected at three random points along each transect. Sediment and water samples were collected on October 26-27, 1985 to correspond with peak endosulfan applications.

Sediment Sampling

Sediment samples at sites 1 and 2 were collected at low tide when the current was at a minimum. Sediment samples at site 1 were collected using a Veihmeyer soil sampling tube having an inner diameter of 2.25 cm. The Veihmeyer tube was pushed into the sediment to a depth of 30 cm, the tube was removed and the top 0-15 cm of sediment core was kept for chemical analysis. At sites 2 and 3, samples were collected with a Wildco Instruments® (Model 2321-A10) sediment sampler because of soft substrate. The sampler length was 110 cm with the sampling barrel having an inner diameter of 4.60 cm. The sediment sampler was held above the surface of the water and released causing it to become embedded in the soft bottom. A rope attached to the top of the sampler was used to retrieve the sampler. The top 15 cm of the core was saved for chemical analysis.

All sediment samples were placed in one-quart jars and sealed with aluminum foil-lined lids. The samples were then placed on wet ice in a chest cooler and transported to the CDFA laboratory in Sacramento for analysis. Samples were stored at 4°C until analyzed.

As a quality control measure, additional sediment samples were collected, split and sent to two laboratories: CDFA, and Hoechst (AG) Aktiengesellschaft, Frankfurt, Federal Republic of Germany (the manufacturer of endosulfan). Split samples were produced at each site by mixing several randomly collected samples from the transects and equally dividing this mixture into four jars for chemical analysis. This same procedure was used at all sites except site 3 where enough sediment was collected to produce nine split samples. A total of six split samples were shipped to Hoechst (two samples from each site) in a foam freeze safe packed with dry ice according to manufacturer's instructions. However, four of the six sample jars were broken in shipment. The CDFA laboratories analyzed the nine remaining quality control samples.

Water Sampling

Water sampling at sites 1 and 2 were collected at low tide when the current was at a minimum. Water samples were collected in one-liter amber-glass bottles using a hand operated suction bulb that drew water into the bottle through a length of teflon tubing. Perforations were made at the end of the tube to allow for better water intake. A lead weight was attached to the end of the tubing to stabilize it in the current. The tubing was moved vertically through the water profile as the bottle was filling to obtain a depth integrated sample. When the bottle was full the suction device was removed, the bottle was topped off and sealed with a foil-lined cap. Each sample was stored and transported as described above.

As a quality control measure, additional water samples were collected, split and sent to CDFA and Hoechst laboratories for chemical analysis. Split water samples were collected at a random location along the transects at each site using the

suction apparatus with a one-gallon bottle. Water was then mixed in a clean stainless steel bucket and poured into four, one-liter amber glass bottles, sealed, transported and stored as above. At site 3 an additional five bottles were filled for a total of nine split samples for that site. The sample handling and shipping procedure for the split water samples was the same as for split sediment samples.

Statistical Analysis

The mean, standard deviation, and coefficient of variation were calculated for replicate sediment and water samples collected at each site. Sample size was estimated using the following equation taken from Cochran (1977):

$$N = (t)^2 (S^2) / (a\bar{x})^2$$

Where t is the tabled t value at a selected α level (0.05), S^2 is the estimated population variance, a is the accuracy needed in discerning the mean, and \bar{x} is the mean of the replicate samples. The value for a was 0.40 and 0.30 for sediment and water, respectively. These values were calculated from the analytical variability determined from spiked samples and variability estimated to exist in the environment (see Results: Quality Control).

Chemical Analysis

Water and sediment samples were analyzed for endosulfan I, II, and sulfate. Water samples were extracted with 100 ml analytical grade hexane in a separatory funnel. The extract was filtered through sodium sulfate, rotoevaporated to 3-5 ml, and brought down to final volume with nitrogen. Sediment samples were extracted with 250 ml of 50:50 analytical grade hexane:acetone and mechanically rolled for 2 hours. The extract was filtered through sodium sulfate, concentrated to 100 ml on the rotoevaporator, and transferred to a separatory

funnel. To separate out the acetone, 300 ml distilled water and 25 ml saturated sodium sulfate solution were added, and the funnel was shaken for 2 minutes. The water/acetone layer was drained to a clean beaker, the hexane layer to a second separatory funnel. The water/acetone layer was re-transferred to the first separatory funnel and re-extracted with 20 ml of 15% dichloromethane in hexane by shaking for 2 minutes. The water was then discarded and the extracts combined in the second separatory funnel, and washed twice with 100 ml distilled water each time by shaking for 30 seconds and discarding the water layer. The combined extract was rotoevaporated to a few ml, and brought to final volume under nitrogen. Where sample clean-up was necessary, the extract was transferred onto a florisil sep-pack, slowly eluted with ethyl acetate, and collected. Both water and sediment samples were analyzed with a Hewlett-Packard® Model 5880 gas chromatograph equipped with an electron capture detector and a 12 m X 0.20 mm I.D. high performance cross-linked fused silica capillary column. Column oven temperature was run isothermally at 200° C. Injector and detector temperatures were 225°C and 350°C, respectively, with injections made in the splitless mode. Confirmatory analyses were done on a Varian® Model 3700 gas chromatograph equipped with a Hall Detector (chlorine mode) and a 25 m X 0.2 mm I.D. 50:50 phenyl-methyl cross-linked methyl silicone capillary column (splitless mode). The oven temperature was programmed from 65°C (3 minute initial hold) to 230°C (final temperature held 11 minute) at a program rate of 40°C/minute. Injector and detector temperatures were 240°C and 250°C, respectively.

The quality assurance procedure for CDFA consisted of spiking, extracting, and analyzing 10 sediment and 10 water samples for endosulfan I, II and sulfate. Sediment samples were spiked at 2, 20 and 100 ppb. Water samples were spiked at .025, .100 and 1 ppb.

Chemical analytical procedures used by Hoechst are contained in Appendix I. Quality control procedures for Hoechst consisted of spiking two water samples at 10 and 50 ppb. Spikes of sediment samples were not reported by Hoechst.

RESULTS

Pesticide Use

The total pounds of endosulfan applied in Monterey County in 1984 and 1985 was 25,549 and 21,517 respectively.¹ September and October were consistently the peak months of endosulfan applications (Figure 4). This study was conducted within the watershed areas of Monterey County located in Townships 12, 13 and 14 South, Mt. Diablo Base (Figure 1). In 1984 and 1985, the study area represented about 91 and 82% respectively, of the county's endosulfan use. Over 98% of the endosulfan used in Monterey County during 1984 and 1985 was applied to artichokes, lettuce, strawberries, cabbage and celery (Table 1). Depending upon the crop, endosulfan can be applied up to three times in one growing season. Ground application is the most frequently used method of application, but aerial application is also used when the ground is wet or the crop is near harvest.

Quality Control

Recoveries from spiked sediment samples analyzed by CDFA averaged 72% for each endosulfan compound. Recoveries from spiked water samples analyzed by CDFA averaged 97% for each of the three compounds. The recoveries from spiked sediment samples were not reported by Hoechst, while water recovery values for endosulfan I, II and sulfate averaged 106, 99 and 94%, respectively.

Quality control data from the CDFA laboratory for sediment and water samples were within the range of acceptable analytical variance (Horwitz 1978). The coefficients of variation for percent recovery data ranged from 10 - 23% and 9-18% for sediment and water respectively. The coefficients of variation for stability (i.e., repeat GC injections of a single extract) ranged from 9-14% and

1. Total endosulfan applied calculated from pesticide use report information filed in Monterey County.

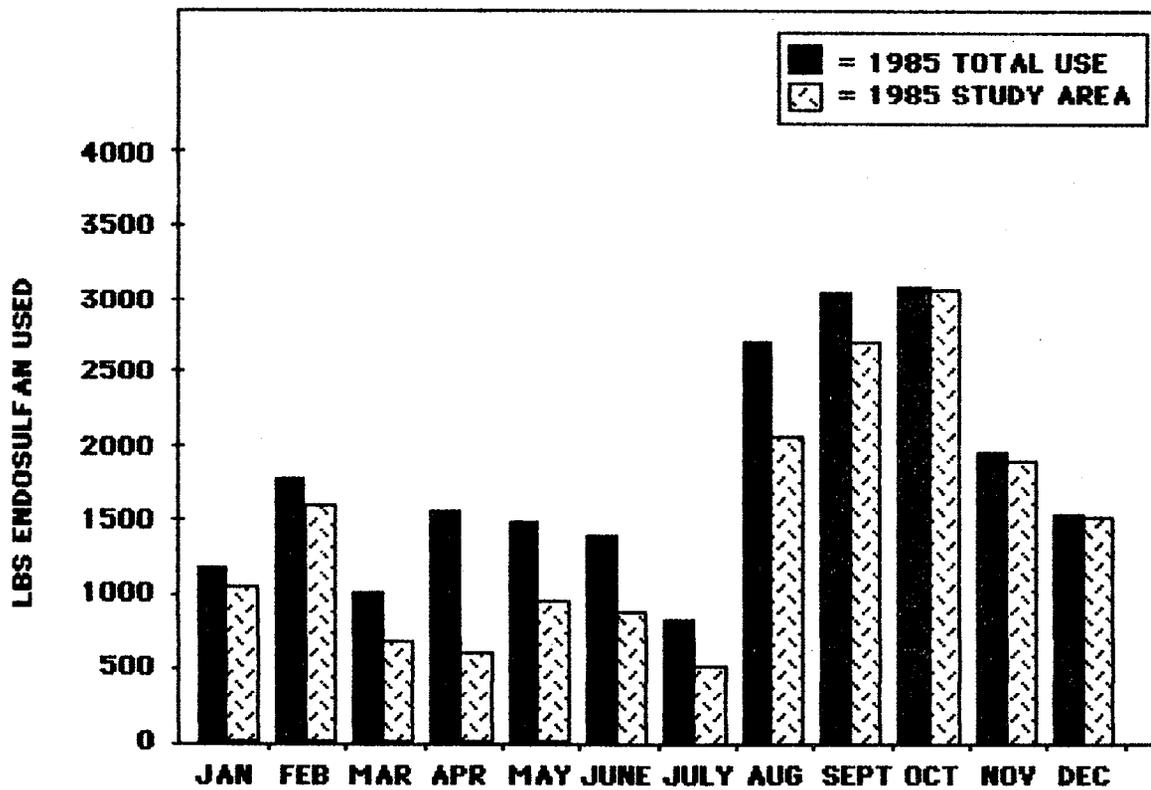
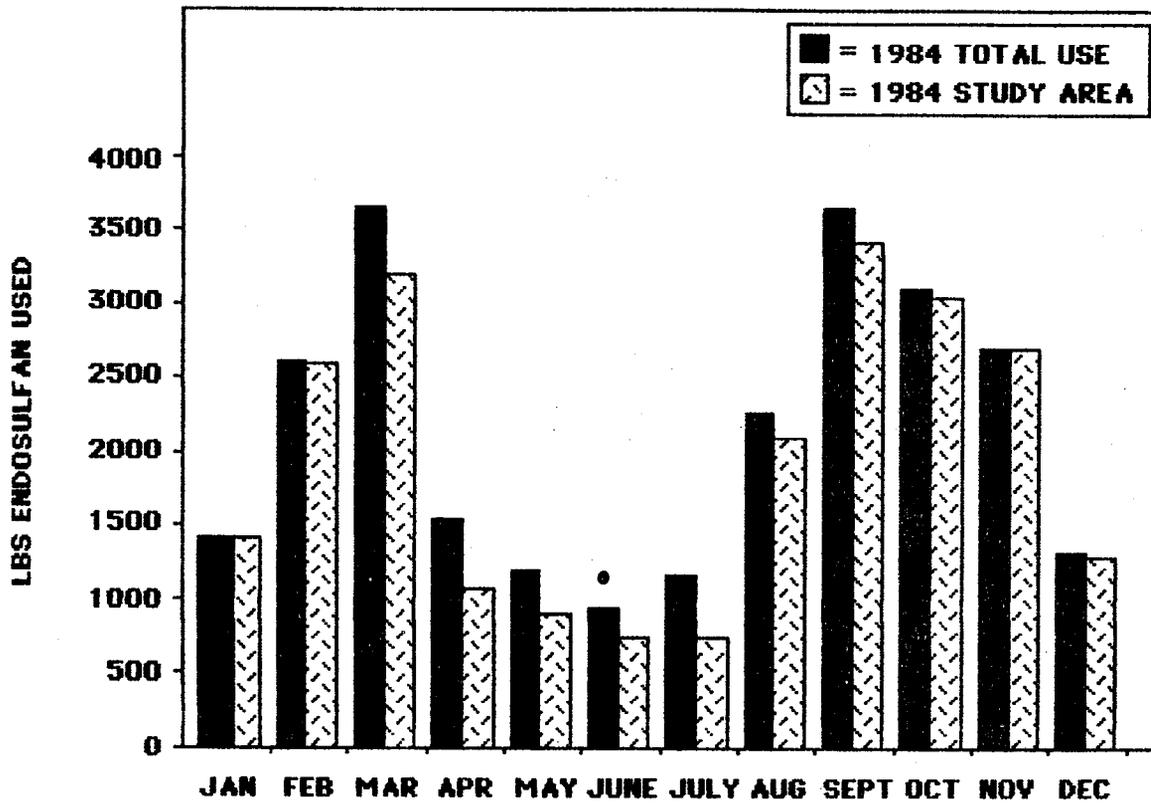


FIGURE 4. TOTAL AMOUNT OF ENDOSULFAN USED IN MONTEREY COUNTY COMPARED TO THE AMOUNT OF ENDOSULFAN USED IN THE STUDY AREA DURING 1984 AND 1985.

Table 1. Crops in study area receiving the largest amounts of endosulfan compared to the crops in entire county receiving largest amounts of endosulfan in 1984 and 1985.

1 9 8 4			
Study Area		Entire County	
<u>Crop</u>	<u>Lbs Endosulfan Used</u>	<u>Crop</u>	<u>Lbs Endosulfan Used</u>
Artichokes	22,086	Artichokes	22,116
Strawberries	613	Head lettuce	1,489
Head lettuce	289	Strawberries	1,210
Celery	159	Cabbage	296
Cauliflower	22	Celery	256
Top 5 total	<u>23,169</u>	Top 5 total	<u>25,367</u>
Total lbs endosulfan used		Total lbs endosulfan used	
	23,205		25,549
99.8% used on top 5 crops		99.3% used on top 5 crops	

1 9 8 5			
Study Area		Entire County	
<u>Crop</u>	<u>Lbs Endosulfan Used</u>	<u>Crop</u>	<u>Lbs Endosulfan Used</u>
Artichokes	16,256	Artichokes	16,341
Head lettuce	1,046	Head lettuce	3,578
Strawberries	161	Strawberries	858
Mustard	28	Cabbage	207
Collard	17	Bell peppers	204
Top 5 total	<u>17,508</u>	Top 5 total	<u>21,188</u>
Total lbs endosulfan used		Total lbs endosulfan used	
	17,536		21,517
99.8% used on top 5 crops		98.5% used on top 5 crops	

4-6% for sediment and water respectively. Results from sediment analyses were more variable than those for water due to the complexity of the matrix. Given the minimum variation in the laboratory results (as indicated by the recovery data), the minimum accuracy possible to describe a mean sediment or water concentration would be 23 or 18%, respectively. Using these minimum values, plus 15% for environmental variation, the calculation for sample size was made (see methods above for sample size calculation).

Results of split sediment samples analyzed by CDFA indicated a wide range in variability (Table 2 and Appendix II). The coefficients of variation ranged from 27 to 76%. Four of the six split sediment samples shipped to Hoechst were broken in transit. The two split samples analyzed were from site 2 and the coefficients of variation ranged from 6 to 19% for the compounds (Table 2 and Appendix II). Split sediment samples (from site 2) that were analyzed by CDFA were both negative while analyses performed by Hoechst were both positive. All split water samples were below the MDL (0.1 ppb and 2.0 ppb for CDFA and Hoechst, respectively) for endosulfan I and II in water (Table 2 and Appendix II). The CDFA laboratory detected endosulfan sulfate in 4 of the 9 split water samples ranging from 0.03 to 0.06 ppb (Appendix II) while Hoechst had an MDL of 2.0 ppb and therefore may not have detected endosulfan sulfate.

Due to the loss of sediment samples and the extremely low (or undetected) concentrations in water, the interlaboratory comparison could not be fully evaluated. Chemists from both laboratories agree that differences were minor. However, some discrepancies were indicated. Hoechst detected all three compounds in one set of sediment samples taken from Parson's Slough, whereas CDFA did not detect any residue. While this variation could have been related to

Table 2. Summary Statistics of Endosulfan Concentrations in Split Samples Collected From the Moss Landing Drainage.

Location	Laboratory	Endosulfan Form	Sample Size ^a	Mean ^b	Standard Deviation	Coefficient of Variation (%)
<u>SEDIMENT</u>						
Sandholt Bridge	CDFA	I	2	2.0	1.4	71
		II	2	3.0	1.4	47
		Sulfate	2	1.5	0.7	47
	Hoechst	I	2	N.A. ^c	-	-
		II	2	N.A.	-	-
		Sulfate	2	N.A.	-	-
Parson's Slough	CDFA	I	2	N.D. ^d	-	-
		II	2	N.D.	-	-
		Sulfate	2	N.D.	-	-
	Hoechst	I	2	3.8	0.35	9
		II	2	3.7	0.21	6
		Sulfate	2	2.2	0.42	19
Blanco Drain	CDFA	I	5	5.8	4.4	76
		II	5	4.8	1.3	27
		Sulfate	5	5.6	1.7	30
	Hoechst	I	2	N.A.	-	-
		II	2	N.A.	-	-
		Sulfate	2	N.A.	-	-
<u>WATER^e</u>						
Sandholt Bridge	CDFA	I	2	N.D.	-	-
		II	2	N.D.	-	-
		Sulfate	2	0.06	0	-
	Hoechst	I	2	N.D.	-	-
		II	2	N.D.	-	-
		Sulfate	2	N.D.	-	-
Blanco Drain	CDFA	I	5	N.D.	-	-
		II	5	N.D.	-	-
		Sulfate	5	0.02	0.01	50
	Hoechst	I	2	N.D.	-	-
		II	2	N.D.	-	-
		Sulfate	2	N.D.	-	-

a. The number of split samples.

b. Mean concentrations in ppb dry weight for sediment and ppb (ug/l) for water samples.

c. Not analyzed. Samples broken in transit.

d. None detected. The CDFA MDL for soil = 1.0 ppb. The CDFA MDL for water = 0.02 ppb and for Hoechst = 2.0 ppb.

e. All water samples collected from Parson's Slough were below the MDL for both laboratories.

incomplete mixing of the sediment sample prior to splitting, none of the other sediment samples collected from the Parson's Slough were positive. The difference might have been related to the different analytical procedures used by the two laboratories. Another possibility may have been misidentification or misinterpretation of the results. CDFA used a second detector and column for confirmation, while Hoechst did not use any confirmatory techniques. Some type of analytical confirmation is essential when analyzing residues at a concentrations this low. For water samples, comparisons probably would not have been possible even if all samples were positive. The Hoechst detection limit of 2.0 ppb was much higher than the 0.01 ppb CDFA detection limit. Since concentrations were less than 1.0 ppb in these split water samples, the Hoechst detection limit was not low enough to detect any of the endosulfan compounds.

Sediment

Of the total sediment samples collected to ascertain within-site variability, 33, 33 and 25% contained endosulfan I, II and sulfate residues, respectively (Appendix III). Analytical results for samples collected from sites 1 and 3 were 10 ppb or less for all three chemical forms. Samples collected from site 2 were all below the MDL (1.0 ppb). The current at site 2 was faster than at sites 1 and 3, probably providing scouring action of bottom sediments, and perhaps contributing to the results found at this site. When calculating means, samples below the MDL were considered to be 1.0 ppb and those means were expressed as less than the tabled values (Table 3). This convention is one of three alternatives generally used in the scientific literature. The other two alternatives include using one half the MDL or zero to compute summary statistics. The decision to use the MDL was made to minimize sample size estimates since replicate sampling can be very costly.

Samples collected from site 1 were more variable than those from site 3 (Table 3). Site 1 was located near a marina where the water depth was influenced by the tide. Large variations in concentrations might have been caused by the heterogeneous substrate encountered there, or by dredging that occurred frequently in the river channel and/or by tidal action. In contrast, site 3 had a uniform substrate, relatively undisturbed sediment layer, no tidal action, and subsequently lower coefficients of variation. To minimize variation and maximize concentrations, it is recommended that future sampling be conducted in regions of uniform substrate composition in areas of minimal tidal action, and in areas where sediments are likely to be deposited based on streamflow characteristics.

Endosulfan residues show a wide range of concentrations in sediment taken from agricultural drainage basins. Frank et al. (1979) found 0.1 to 2.3 and 0.3 to 5.5 ppb of endosulfan II and sulfate, respectively, in sediment taken from Georgian Bay of Lake Huron. Endosulfan I was not detected in any sample taken in that study. Sediment concentrations of endosulfan I and II combined ranged from 4 to 62 ppb in agricultural ditches in Southwestern Ontario while soil from an adjacent farm contained 640 ppb (Miles and Harris 1971). Bureau et al. (1981) also found endosulfan concentrations as high as 650 ppb in farm soil taken from Monterey County but did not find any in sediment in that area. Ali et al. (1984) reported that sediment concentrations of endosulfan I, II and sulfate in Monterey County ranged from none detected to 1.6, 40 and 110 ppb, respectively. These samples were collected on September 29, 1982, from sites different than those reported here. Concentrations in this study were comparable to those found in the published literature. From this study it can be concluded that the distribution of endosulfan in the sediment of the Moss Landing Drainage Basin is

not uniform, however, detectable residues exist, particularly close to agricultural areas.

Given the variability in sediment samples, it was estimated that about 22 to 62 samples should be collected at site 1, and 19 at site 3 (Table 3) to establish statistically significant chronological trends. Sample size at site 1 could be reduced if samples were collected either (1) from a uniform portion of the channel that is not dredged or (2) in a stratified-sampling design.

Water

Except for the low endosulfan sulfate residues found at site 1, all samples were below the MDL of 0.01 ppb (Table 4, Appendix IV). This result seems reasonable since endosulfan has a very low solubility in water (150, 60 and 220 ppb for endosulfan I, II and sulfate, respectively). Also, the dilution ratio in the drains and sloughs is expected to be large thereby decreasing the concentration of endosulfan found in water. However, water samples did contain suspended sediment particles, and with a relatively high adsorption constant (Spencer et al., 1985) these samples might be expected to contain endosulfan residues. An explanation may be that the pH of water samples favored endosulfan hydrolysis to the diol metabolite. At pH 8, the hydrolysis rate for endosulfan I and II has been estimated to be one day. However, pH of the water was not tested nor was the diol analyzed for, therefore it is not known if endosulfan hydrolyzed or was simply not present in detectable quantities. Gorbach et al. (1971) found endosulfan I, II and sulfate in agricultural canals connecting river and coastal waters at concentrations below 6 ppb. Other research indicates that concentrations as high as 104 ppb (endosulfan I plus II) have been found in irrigation run-off water (Spencer et al. 1985). Even though samples in this investigation were collected during peak use of endosulfan, samples never

Table 3. Summary Statistics of Endosulfan Concentrations in Sediment Samples Collected From the Moss Landing Drainage.

Location	Endosulfan Form	Sample Size	Mean ^a	Standard Deviation	Coefficient of Variation(%)	N ^b
Sandholt Bridge	I	6	<1.7	1.2	71	22
	II	6	<2.3	2.3	100	42
	Sulfate	6	<2.0	2.5	125	62
Parson's Slough	I	12	- ^c	-	-	-
	II	12	-	-	-	-
	Sulfate	12	-	-	-	-
Blanco Drain	I	6	<4.2	2.9	69	20
	II	6	<4.7	3.1	66	19
	Sulfate	6	<5.0	3.5	70	20

a. Mean concentrations in ppb, dry weight.

b. Estimated sample size (see Methods).

c. Endosulfan residues were not detected therefore no summary statistics were calculated.

Table 4. Summary Statistics of Endosulfan Concentrations in Water Samples Collected From the Moss Landing Drainage^a.

Location	Endosulfan Form	Sample Size	Mean ^b	Standard Deviation	Coefficient of Variation (%)	N ^c
Sandholt Bridge	Sulfate	6	0.014	0.005	36	11

a. Data not entered in this table were all less than the MDL of 0.01 ppb (see Appendix III).

b. Mean concentration in ppb.

c. Estimated sample size (see Methods).

contained residues of such magnitude. Epstein and Grant (1968) and Spencer et al. (1985) found that after two or three irrigations, run-off water concentrations dropped rapidly. The mass of endosulfan leaving a treated field in this medium is small in comparison with the total applied. These studies indicate that in general, the concentration of endosulfan in water of agricultural drainages and watersheds tends to be low or undetected unless timed to coincide with irrigation runoff.

DISCUSSION

In this investigation residues of endosulfan in sediment samples were near or below the detection limit (1.0 ppb). Tidal action, dredging and swift currents play an important role in sediment movement in this area and may have affected these results. Still, 50% of sediment samples collected at Sandholt Bridge contained endosulfan residues, in spite of tidal action and dredging at this site indicating the ubiquitous occurrence of this pesticide. In the Blanco Drain, 5 of 6 samples contained residues, as expected, due to drain proximity to areas of endosulfan use. All samples from the Parson's Slough were below detection limits presumably due to swift currents encountered there during sampling.

Endosulfan concentrations in water are probably also affected by tidal action and current speed. However, it is conceivable that endosulfan residues in water (either dissolved or on suspended sediment) actually exist in this drainage area at or below the detection limits (0.01 ppb). Results from the PIU investigation (Finlayson et al., 1986) and Schimmel et al. (1977) support this theory. A bioconcentration factor (BCF) for fish was estimated to be between 1000 and 2400 (Schimmel et al., 1977). With a total endosulfan exposure of 0.014 ppb (the mean concentration of endosulfan found in water at Sandholt Bridge), fish could contain 14 to 33 ppb (fresh weight) of endosulfan. Results from the PIU investigation indicated a maximum of 11 and 38 ppb (fresh weight) in hitch and sucker flesh, respectively (Finlayson et al., 1986) corresponding well with our calculations. The minimum concentration found by PIU in hitch flesh was 8 ppb (fresh weight), corresponding to 0.008 ppb in water, below our detection limit for endosulfan. Therefore, it is reasonable to assume that biological organisms may contain residues of endosulfan while residues in water go undetected. Unfortunately, a BCF for mussels and clams has not been estimated so similar calculations for these organisms can not be made. Given the limitation in

chemical detection, the usefulness of water sampling in conjunction with biological monitoring is questionable.

Results from this study suggest that if spatial or temporal variability in sediment or water samples is to be assessed, large sample sizes would be required. This approach would be costly and time-consuming. In addition, the utility of water sampling may be minimal given the current detection limits. However, sediment and water sampling serves a useful purpose for discerning the mechanisms of off-target movement. Since endosulfan is accumulated efficiently by biological organisms and is toxic to fish at very low concentrations, regulations must be refined to control small quantities of off-target movement. Future sampling might best be concentrated on soil, sediment, air and irrigation run-off to determine the major mechanisms of off-target movement. Once these mechanisms are identified, appropriate measures can be taken to prevent further environmental contamination.

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Appendix I.

Chemical Analytical Procedures Used by Hoechst for Analysis of Endosulfan I, II and Sulfate in Water and Sediment

1. Extraction

50 g of the analytical sample prepared under 5. are weighed into a 250 ml beaker and extracted 3 times with 80 ml acetone and simultaneous homogenization of the material with al Ultraturrax.

The acetone extracts are each filtered through a sintered glass filter and collected in a 500 ml separating funnel.

80 ml water and 20 g sodium chloride are now added to the acetone extracts, taking into account of the water contained in the analytical sample.

2. Isolation of the active ingredient

The solution obtained in 1. is mixed with 100 ml methylene chloride and shaken for 10 minutes. After phase separation the methylene chloride layer is dried over a sodium sulphate column.

The column effluent is evaporated almost to dryness on the rotary evaporator at 20° C and the residue dissolved in 3 ml cyclohexane/ethyl acetate (1+1, v+v). Any undissolved material is filtered off.

3. The eluate obtained in 2. is introduced quantitatively into the delivery loop of the gel column filled with BIO-BEAD. A mixture of cyclohexane and ethyl acetate in the ratio 1+1 (v+v) serves as the eluting agent. The corresponding elution fraction is concentrated on the rotary evaporator and simultaneously dissolved in isoctane (0.5-1 ml).

4. Purification on a silica gel column

The substance isolated according to 3. is transferred quantitatively on to a silica gel column (1 g silica gel deactivated with 1.5% water). Impurities are pre-eluted with 10 ml n-hexane.

The active ingredient is then eluted with 10 ml toluene. The eluate is concentrated on the rotary evaporator and dissolved in toluene. The active ingredient is then determined by gas chromatography.

5. Measurement by gas chromatography

A portion (T_4) of the solution of V_i from 4. is injected into the gas chromatograph. Injection is carried out directly on to the column. The injection volume should be 1-2 μ l.

6. Measurements by gas chromatography

Equipment and conditions

Apparatus	Carlo Erba, 2150
Column	Glass Column i.d. 2.5 mm, length 1.2 m
Column packing	3% OV-1 on Chromosorb, W-HP, 100-120 mesh

Column Temperature	190° C
Temperature of injection block	250° C
Detector	Electron capture detector with ^{63}Ni foil, s^{-1} , 275° C

Carrier gas	Argon-methane mixture, 45 ml/min
Attenuation	10 . 16
Recorder	1 mV, chart speed 75 cm/h
Injection volume	1-2 μl

Appendix II. Endosulfan Concentrations in Split Samples Collected From the Moss Landing Drainage.

Location	Laboratory	Split Sample Number	Endosulfan Concentration (ppb, dry weight)		
			I	II	Sulfate
<u>SEDIMENT</u>					
Sandholt	CDFA	1	1.0	2.0	2.0
Bridge	CDFA	2	3.0	4.0	N.D. ^a
	Hoechst	3	N.A. ^b	N.A.	N.A.
	Hoechst	4	N.A.	N.A.	N.A.
Parson's Slough	CDFA	1	N.D.	N.D.	N.D.
	CDFA	2	N.D.	N.D.	N.D.
	Hoechst	3	3.5	3.5	1.9
	Hoechst	4	4.0	3.8	2.5
Blanco Drain	CDFA	1	9.0	5.0	6.0
	CDFA	2	9.0	6.0	7.0
	CDFA	3	9.0	6.0	7.0
	CDFA	4	N.D.	3.0	3.0
	CDFA	5	N.D.	4.0	5.0
	Hoechst	6	N.A.	N.A.	N.A.
	Hoechst	7	N.A.	N.A.	N.A.
<u>WATER</u>					
			<u>Endosulfan Concentration (ppb)</u>		
Sandholt	CDFA	1	N.D. ^c	N.D.	0.06
Bridge	CDFA	2	N.D.	N.D.	0.06
	Hoechst	3	N.D.	N.D.	N.D.
	Hoechst	4	N.D.	N.D.	N.D.
Parson's Slough	CDFA	1	N.D.	N.D.	N.D.
	CDFA	2	N.D.	N.D.	N.D.
	Hoechst	3	N.D.	N.D.	N.D.
	Hoechst	4	N.D.	N.D.	N.D.
Blanco Drain	CDFA	1	N.D.	N.D.	N.D.
	CDFA	2	N.D.	N.D.	N.D.
	CDFA	3	N.D.	N.D.	N.D.
	CDFA	4	N.D.	N.D.	0.04
	CDFA	5	N.D.	N.D.	0.03
	Hoechst	6	N.D.	N.D.	N.D.
	Hoechst	7	N.D.	N.D.	N.D.

- a. None detected. The MDL for sediment samples analyzed by CDFA = 1.0 ppb.
 b. Not analyzed. Samples broken in transit.
 c. None detected. The MDL for water samples analyzed by CDFA = 0.01 and for Hoechst = 2.0 ppb.

Appendix III. Endosulfan Concentrations in Sediment Samples Collected from the Moss Landing Drainage.

Location	Sample Number	Endosulfan Concentration (ppb, dry weight)		
		I	II	Sulfate
Sandholt Bridge	1	1.0	2.0	N.D. ^a
	2	4.0	7.0	7.0
	3	N.D.	N.D.	N.D.
	4	N.D.	N.D.	N.D.
	5	N.D.	N.D.	N.D.
	6	2.0	2.0	N.D.
Parson's Slough	1	N.D.	N.D.	N.D.
	2	N.D.	N.D.	N.D.
	3	N.D.	N.D.	N.D.
	4	N.D.	N.D.	N.D.
	5	N.D.	N.D.	N.D.
	6	N.D.	N.D.	N.D.
	7	N.D.	N.D.	N.D.
	8	N.D.	N.D.	N.D.
	9	N.D.	N.D.	N.D.
	10	N.D.	N.D.	N.D.
	11	N.D.	N.D.	N.D.
	12	N.D.	N.D.	N.D.
Blanco Drain	1	6.0	6.0	6.0
	2	3.0	3.0	5.0
	3	6.0	10.0	10.0
	4	N.D.	N.D.	N.D.
	5	8.0	5.0	7.0
	6	1.0	3.0	1.0

a. None Detected. MDL = 1.0 ppb.

Appendix IV. Endosulfan Concentrations in Water Samples Collected From the Moss Landing Drainage.

Location	Sample Number	Endosulfan Concentration (ppb)		
		I	II	Sulfate
Sandholt Bridge	1	N.D. ^a	N.D.	0.01
	2	N.D.	N.D.	0.01
	3	N.D.	N.D.	0.01
	4	N.D.	N.D.	0.02
	5	N.D.	N.D.	0.02
	6	N.D.	N.D.	0.03
Parson's Slough	1	N.D.	N.D.	N.D.
	2	N.D.	N.D.	N.D.
	3	N.D.	N.D.	N.D.
	4	N.D.	N.D.	N.D.
	5	N.D.	N.D.	N.D.
	6	N.D.	N.D.	N.D.
	7	N.D.	N.D.	N.D.
	8	N.D.	N.D.	N.D.
	9	N.D.	N.D.	N.D.
	10	N.D.	N.D.	N.D.
	11	N.D.	N.D.	N.D.
	12	N.D.	N.D.	N.D.
Blanco Drain	1	N.D.	N.D.	N.D.
	2	N.D.	N.D.	N.D.
	3	N.D.	N.D.	N.D.
	4	N.D.	N.D.	N.D.
	5	N.D.	N.D.	N.D.
	6	N.D.	N.D.	N.D.

a. None Detected. MDL = 0.01 ppb.