DDT IN THE SALINAS VALLEY

A Special Report on the Probable Source of Technical Grade DDT Found in the Blanco Drain Near Salinas, California

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TABLE OF CONTENTS

		TABLE OF CONTENTS	Page
	ACKN	IOWLEDGEMENT	2
ı.	INTR	RODUCTION	7
II.	SUMM	MARY	9
III.	FIND	DINGS	10
IV.	CONC	CLUSIONS	11
٧.	BACK	KGROUND	14
VI.	MATE	ERIALS AND METHODS	19
	Α.	Field Operations	19
		 Phase 1 Study Stations Phase 2 Study Stations Biological Sampling 	19 19 19
	В.	Sample Collections	19
	c.	Laboratory Operations	22
VII.	RES	ULTS	25
	Α.	Phase 1 Study	25
		 Soil Sediment Suspended Sediment 	25 25 25
	в.	Phase 2 Study	31
		 Soils Sediment Biological Analysis 	31 31 31
VIII	. DIS	SCUSSION	36
	Α.	Presence of o,-p'-DDT	36
	В.	Soil Samples	36
	C.	Sediment Samples	40
	D.	Station 30	46

	E. Environmental Effects	46
IX.	RECOMMENDATION	48
х.	REFERENCES	49

LIST OF FIGURES	Page
Figure 1 Breakdown of DDT	8
Figure 2 Schematic Map of TSM DDT Data from the Salinas Area	17
Figure 3 Blanco Drain DDT Study Phase 1 Stations and Cooperative Study Stations	20
Figure 4 Blanco Drain DDT Study Phase 2 Stations	21
Figure 5 Schematic Diagram of 1984 Blanco Drain DDT Study Phase 1 Sediment Analyses	29
Figure 6a Frequency Distribution of Percent Technical DDT in Blanco Drain Soils	41
Figure 6b Frequency Distribution of Percent Technical DDT in Blanco Drain Sediments	41
Figure 7a Frequency Distribution of Percent DDD in Blanco Drain Soil	42
Figure 7b Frequency Distribution of Percent DDD in Blanco Drain Sediment	42
Figure 8a Frequency Distribution of Percent DDE in Blanco Drain Sediment	43
Figure 8b Frequency Distribution of Percent DDE in Blanco Drain Soil	43
Figure 9 Distribution of Sediment Types in Blanco Drain	47

LIST OF TABLES		Page
Table 1 1983 TSM Data; DDT vs. Four Cri	teria	16
Table 2a Phase 1 Study: DDT Compounds i Drain, June 25, 1984. (Risebro	n S oil Adjacent to Blanco ough, 1984)	26
Table 2b Phase 1 Study: DDT Compounds i June 12, 1984. Department of E	in Blanco Drain Sediment, Food and Agriculture Analyses.	27
Table 2c Phase 1 Study: DDT Compounds in June 12, 1984. Department of E	in Blanco Drain Sediment, Fish and Game Analyses.	28
Table 2d Phase 1 Study: DDT Compounds in the Blanco Drain, June 26,	in Water Particulates 1984. (Risebrough)	30
Table 3a Phase 2 Study: DDT Compounds is Sediment, October 23, 1984. (1	in Blanco Drain Soil and DFA Analyses)	32
Table 3b Phase 2 Study: DDT Compounds : Sediment, October 23, 1984. (1	in Blanco Drain Soil and DFG Calibration Analyses)	33
Table 3c Special Analysis of Selected B	lanco Drain Soils.	34
Table 3d pH of Selected Blanco Drain So:	ils	35
Table 3e DDT Compounds in Corbicula Plan	nted in Blanco Drain.	35
Table 3f DDT Compounds in Suckers Collection Salinas River and Blanco Drain	cted by 1984 TSM in the	37
Table 4 Blanco Drain DDT Summary		39
Table 5 Classification of Blanco Drain	Sediment Samples	45

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INTRODUCTION

The sale and use of DDT, once thought to be the ultimate pesticide, was banned by the U. S. Environmental Protection Agency in 1972 after it was found to be responsible for the rapid decline of several predator species in the environment and questions were raised concerning potential effects on human health. California had curbed the sale and use of DDT two years earlier in December 1970.

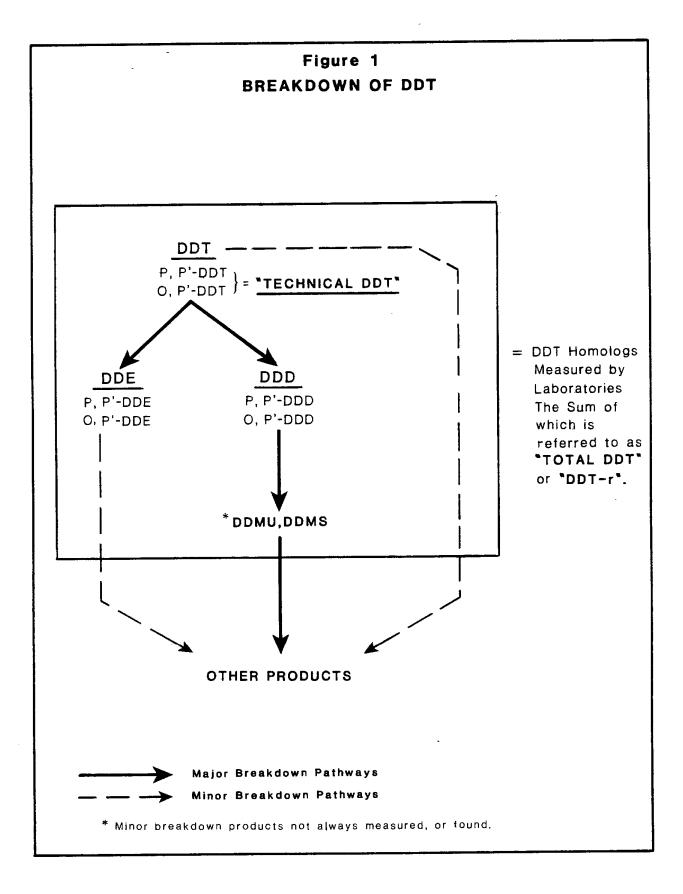
The special characteristics that made DDT such a persistent and deadly pesticide are also the characteristics that still make it a potent environmental hazard. DDT, or dichloro-diphenyl trichloroethane, is a white amorphous powder that is nearly insoluble in water, but readily soluble in organic solvents. It has a low volatility and is not easily decomposed by sunlight. When DDT does break down, it is converted initially to DDD or DDE. Usually, DDE is the major initial breakdown product. However, in sediments, DDD can also be a significant component. These products--DDD and DDE--are also toxic and very persistent in the environment. DDE is the chemical linked to the thinning of eggshells in birds and was responsible for the reproductive failures of the Brown Pelican along the California coast.

DDT and its related products are found virtually everywhere on earth. Its high solubility in (non-polar) organic mixtures such as oils or fats causes it to have a high affinity for living organisms; once ingested by an organism, DDT or its metabolites are not quickly lost, so they tend to accumulate. As predator eats prey, DDT is passed upwards in the food chain in higher and higher concentrations.

Although use of DDT was banned in California in 1970, it is still found in high concentrations in fish from several California rivers and lakes. For example, in 1983 DDT was found at levels exceeding National Academy of Sciences (NAS) guidelines for predator protection in fish from seven rivers and streams, including the Old Salinas River, the Salinas River at Blanco Drain, Harbor Park Lake, San Joaquin River at Vernalis, Alamo River, New River, and San Diego Creek.

As in previous years, speculation as to the possible sources of DDT included old residues, continued illegal use, leaky waste dumps, or contamination from use of a related pesticide, Kelthane (dicofol). In an attempt to identify the possible sources of DDT, monitoring staff began to look more closely at DDT isomers and breakdown products rather than simply at the total concentration of DDT.

The term "Total DDT", as used in this report, refers to the sum of the individual concentrations of DDT and its closely related breakdown products, DDD and DDE. Some laboratories (e.g., Department of Fish and Game) also measure two minor breakdown products, DDMU and DDMS, found in small amounts. When found, these are also included in Total DDT (Figure 1). Each of these



chemicals actually occurs in two closely related forms, or isomers. Most of a given chemical is found in the "para-para" form (e.g., p,p'-DDT, p,p'-DDD, p,p'-DDD). However, often the "ortho-para" forms are also present (e.g., o,p'-DDT, o,p'-DDD, o,p'-DDE). The original formulation of DDT, as applied to crops, is referred to as "Technical DDT" and is a mixture of roughly 80 percent p,p'-DDT and 20 percent o,p'-DDT. When DDT breaks down, the relative amounts of DDD and DDE that are formed depend on environmental conditions. Over time, DDD will break down to other products (e.g., DDMU and DDMS) and eventually disappear from the environment. DDE is much more stable and remains in the environment for a long time.

SUMMARY

DDT has been found in moderate to high concentrations in the Salinas River and lower Moss Landing watershed for many years. In 1984, staff from the State Water Resources Control Board (State Board) devised some simple criteria designed to indicate how closely the Total DDT resembled Technical DDT as compared to its breakdown products, DDD and DDE.

Upon analysis, staff found that fish from the Salinas area were among those that had unusually high fractions of Technical or "fresh" DDT. In particular, both fish and sediment samples from the Salinas River clearly indicated that one source of this material was the Blanco Drain which empties into the Salinas River. At the time, we considered any measurement greater than 10 percent Technical DDT (DDT only) as compared to Total DDT (DDT + DDD + DDE) as high and worthy of further investigation. Approximately 25 percent of the Total DDT found in sediments and fish from the mouth of the Blanco Drain was Technical DDT. This value was about as high as had been found in the Toxic Substances Monitoring Program.

These results provided the impetus for a special study in the Blanco Drain to determine the probable source of the DDT found at the mouth of the Drain. That study, coordinated by the State Board, involved the cooperation and resources of several local and state agencies including the Monterey County Agricultural Commissioner, the County of Monterey, the Central Coast Regional Water Quality Control Board, the California Department of Fish and Game (DFG), the California Department of Food and Agriculture (DFA), and the Moss Landing Marine Laboratory.

The study was conducted in two phases. Phase 1 was intended to characterize the Blanco Drain. Fifteen sediment samples were collected by staff and five composite soil samples were collected by Dr. Robert Risebrough in cooperation with State Board staff. The results were striking. Both the soils and sediments of Blanco Drain contained up to 5 parts per million (ppm) Total DDT and up to 70 percent Technical DDT. The percent Technical DDT was the highest ever measured in the TSM program. In addition, the sediment data indicated that the highest values were confined to a few stations, possible "hot spots" along the Drain.

One isomer of DDT, o-p'-DDT, was believed by scientists to be fairly unstable and was expected to break down more rapidly than the p-p' isomer in the aquatic environment. Dr. Risebrough found that in the soils contiguous to the Blanco Drain the o-p' isomer was, if anything, breaking down <u>less</u> rapidly than the p-p' isomer and stated that the DDT was likely not fresh, simply well preserved. (Risebrough, 1985).

After considering the preliminary results, Phase 2 of the study was initiated. The purposes of the second phase study were to verify the Phase 1 results and to isolate and identify possible sources of DDT to the Blanco Drain from adjacent fields. In the second phase survey, sediment was collected from 23 locations while soil was collected from 13 locations.

FINDINGS

Soils

- Soils from fields adjoining the east leg of Blanco Drain contain up to 5,000 ppb (5 ppm) Total DDT and average 3,100 ppb (3.1 ppm) DDT while soils from fields adjoining the west leg of the Drain contain up to 3,000 ppb (3 ppm) DDT and average 1,800 ppb (1.8 ppm) DDT.
 - With the exception of one sampling station, soils from fields adjoining all parts of the Drain contain a nearly uniform 66 to 80 percent Technical DDT (average 72 percent).
- o With the exception of the same sampling station, soils from fields adjoining all parts of the Drain contain a uniform 1.4 to 5.6 percent DDD (average 3.5 percent).
- o DDT and DDD from the exceptional station more closely resemble the DDT and DDD found in the sediments in the Drain itself, and there is some indication that the soils at that station were derived from sediment moved when the Drain was physically relocated at that location.
- o Most of the soil samples also contain 15 to 20+ percent o-p'-DDT as a percentage of Technical DDT (average 17 percent). This is very similar to the original formulation of Technical DDT.

Sediments

o Bottom sediments in the east leg of the Drain had levels of Total DDT ranging from 800 ppb (0.8 ppm) to 6,200 ppb (6.2 ppm). The average concentration was 2,200 ppb (2.2 ppm). Sediments in the west leg of the Drain had levels of Total DDT ranging from 200 ppb (0.2 ppm) to 1,700 ppb (1.7 ppm). The average was 800 ppb (0.8ppm). These levels are 200 to 400 times the levels measured in the Salinas River above the outfall of Blanco Drain.

Breakdown of DDT

- o DDT slowly breaks down in the Drain sediments; by the time it reaches the Salinas River, it has broken down to about 20 percent Technical DDT, 35 percent DDD, and the remainder DDE. The major breakdown products, DDD and DDE are as undesirable in the environment as the parent compound.
- o The persistence of DDT in the soils could not be determined by this study, but it is probably very persistent. Earlier studies conducted in the Salinas/Elkhorn Slough area reported lesser amounts of Total DDT in soils than found in this study. Further study is needed to determine how persistent DDT is in Salinas soils.
- o Salinas area agricultural soils contain a "reservoir" of DDT, which is being released to the aquatic environment (drains, canals, rivers, bays, etc.) through soil erosion due to agricultural practices and rainfall runoff events. Considering the mixing of DDT into the soil column and normal soil erosion rates, it is probable that this release of DDT into the Salinas River will continue well into the 21st Century.

Possible Transport Mechanisms

- o Fields on the east end of the Drain are literally plowed over the edge and into the Drain. Sediments in the east end of the Drain contain the unmistakable fingerprint of soil-based DDD and Technical DDT. In the lower portions of the Drain, where berms exist, DDD and DDT ratios are more characteristic of sediment. Staff are convinced that the observed practice of plowing over the edge of the Drain is a major source of DDT to the Drain. Other erosion events may also contribute to the DDT found in the Drain.
- o Corbicula (clams) planted by State Mussel Watch in the Blanco Drain contained the highest concentrations of Total DDT (and other chemicals) ever seen in California: 3,800 ppb (3.8 ppm, wet weight). This indicates that much of the transport of DDT is via very fine suspended materials through and out of the Drain.

DDT on Food Crops

o DFA regularly tests vegetables in the Salinas area and has reported finding no (or extremely little) DDT in unwashed vegetables. This has generally been true ever since the use of DDT was discontinued in 1972. This strongly indicates that there has been no continued use of DDT in the Salinas area for agricultural purposes.

Corrective Measures

o Positive steps taken to reduce or eliminate soil erosion could result in major reductions in the amounts of DDT input to the aquatic environment, with increased water quality/aquatic life benefits. If these steps are

not found to be sufficient, the Central Coast Regional Water Quality Control Board may need to consider other measures, as appropriate.

Effectiveness of DDT Fingerprinting

o Careful comparison of percent Technical DDT and o,p'-DDT as a percent of Technical DDT appears to be effective in finding sources of recently mobilized DDT in rivers and other waterways. Percent Technical DDT and percent DDD have proven to be excellent tools for tracing soil-sourced introduction of DDT into the aquatic environment.

Implications of Statewide Problem

There are no known extraordinary environmental or physical conditions in the Salinas area which would cause soil-based DDT to behave differently than in other areas of the State. A recent study by DFA indicates that DDT is being preserved in soils all over California (Mischke, et al., 1985). Therefore, the Blanco Drain should not be considered a unique situation. The legacy of DDT use in California will probably be with us for some time.

BACKGROUND

Technical DDT is normally a mixture of about 75-80 percent p,p'- DDT (parapara DDT, the principal insecticidal ingredient) and 15 to 20 percent o,p'- DDT (ortho-para DDT), with the remainder being impurities such as DDE. For purposes of monitoring, the ratio of p,p'-DDT to o,p'-DDT is assumed to be four-to-one (80:20). The o,p' isomer of DDT has been generally regarded as unstable and was expected to quickly disappear once exposed to the elements. The relative presence or absence of o,p'-DDT in the environment has sometimes been used as an indicator of the relative age of DDT found in the environment.

Both isomers of Technical DDT are subject to breakdown and loss via several pathways once they are applied to crops and soils. These include:

- o chemical conversion to other products such as DDD or DDE.
- o metabolic conversion to DDD or DDE by organisms such as bacteria.
- o transport from the area by wind or water erosion of soil particles or DDT particles.
- o transport from the area by evaporation to the atmosphere or solution in water.

When we discuss the degradation of DDT we are referring to the end product of any or all of these processes.

Degradation of DDT to DDD and DDE is a relatively slow process that depends on many environmental variables. In soils, the variables may include soil type, organic content, available moisture, pH, temperature, and the presence of flooding. Many studies conducted in the 1960's and 1970's indicated that the time for half of the DDT in soils to be degraded (half-life) ranged from three to fourteen years. (Yale, 1973; Lichtenstein, et al., 1971; Menzic, 1972).

Degradation of DDT to DDE and DDE in aquatic systems also depends on many variables such as the presence of oxygen and the pH. The half-life in sediment has been reported reported to range from 3 months to 12 years (Wolfe et al., 1976). DDT, nearly insoluble in water, attaches itself strongly to sediment particles.

Degradation of DDT to DDD and DDE in organisms such as fish is relatively rapid compared to that in soil or sediment. Estimates range from two months in Atlantic Salmon (Addison et al., 1976) to one month in the Carp family (Grezenda et al., 1970).

DDT breaks down to one of two homologs, DDD or DDE, both of which are harmful to organisms. The major breakdown product is usually DDE. DDE is much more persistent than DDT both in the environment and in living creatures. For example, the half-life of p,p-DDE in rainbow trout from the Great Lakes has been estimated to be nearly a year. (Hesselberg and Nicholson, 1981). The

half-life of DDE in some ocean fish may be decades (E. Dellanino, pers. comm.).

Based on these general principles, staff from the State Water Board devised four criteria to indicate the relative "freshness" of DDT in the environment (G. Bowes and D. Cohen, pers. comm.).

The four criteria are:

Criterion 1: p,p'-DDT comprises at least 15 percent of all the p,p' isomers in Total DDT.

Criterion 2: o,p'+p,p'-DDT (Technical DDT) comprises at least 10 percent of the Total DDT homologs measured.

Criterion 3: o,p'-DDT comprises at least 8 percent of o,p'+p,p'-DDT
(Technical DDT).

Criterion 4: Total DDT measured in fish is greater than 1,000 ppb (1 ppm wet weight).

Criteria 1 and 2 are actually very similar in what they measure: the percent of <u>Total</u> DDT that is Technical DDT (vs. DDD or DDE). Criterion 3 is a measure of how close the ratio of DDT isomers matches the original 80 percent:20 percent mixture. The fourth criterion is the same as the NAS guideline for protection of predator species.

These criteria were not intended to measure the actual age of Technical DDT, but to provide threshold criteria to identify locations with the highest relative amounts of Technical DDT, as compared to more "typical" locations, based on our experience. As a practical matter, the second and third criteria have proven to be the more useful of the four.

Table 1 provides a summary of 1983 TSM DDT data versus the four criteria. Fish from two stations, the San Joaquin River at Vernalis and the Salinas River near Blanco Drain, exceeded all four tests, indicating the possibility that the DDT might somehow have been "fresher" than DDT from other parts of the State. In addition, the Salinas area had several other sampling stations that were used to pinpoint one source of the DDT to the river.

Figure 2 is a schematic map of 1983 DDT data from the Salinas area. It displays both sediment and tissue data collected in 1983. Both fish and sediment samples taken along the Salinas River indicated a large increase in the percent of "Technical DDT" (Criterion 2) at the outfall of the Blanco Drain. The levels of Total DDT taper off downstream of the Drain. However, the "percent Technical DDT" measure stays about the same as illustrated in the figure. Note that, generally, the percent o,p'-DDT in fish is about the same as in the sediments. However, in most cases, the concentration of Total DDT in fish is several times greater than that in the sediments from the same station.

TABLE 1

1983 TSM DATA DDT VS. FOUR CRITERIA

NO. OF CRITERION 1 CRITERION 2 CRITERION 3 CRITERION 4 CRITERIA EXCEEDED EXCEEDED EXCEEDED STATION 2 X Pajaro R. 2 Salinas R. (mouth) X X 2 L. Tembladero Sl. Х Х X Х 3 Old Salinas R. X X 4 X X Х Salinas/Blanco Drain 2 X " " Road X Carpinteria Marsh 11 11 Ventura R. 2 Los Angeles R. Х X 11 11 11 X 1 Harbor Park Lake 11 11 11 11 11 11 X 1 San Gabriel R. 25 17 17 1 Hansen Dam Lake Χ 11 11 11 X Sacramento R. (Hood) 11 11 11 Feather R. L. American R. 11 11 11 11 11 11 1 X Х 1 Sutter Bypass X 2 X 11 11 4 S. Joaquin R. (Vernalis) X X Х X 2 n n n X Stanislaus R. 11 11 Tuolumne R. X 1 11 11 Lower Merced 11 11 East Walker R. 11 11 11 X X 2 Alamo R. 11 11 X 2 X X 1 New R. 17 17 San Diego Cr. X X Х 3 Santa Ana R. (Prado Dam) Lake Elsinore San Diego R. X 1 Otay R.

SALINAS RIVER BLANCO RD. SCALE, ppb (%03) 86 (%91) 51 1000 FIGURE 2, SCHEMATIC MAP OF 1983 TSM DDT DATA FROM THE SALINAS AREA 100 TOTAL TECHNICAL GRADE DDT DRAIN TOTAL DDT, DDE, & DDD ppb wet weight (fish) ppb dry weight (sediment) SALINAS RIVER BLANCO DRAIN 1877 310.7 (36%) (30%) KEY SEDIMENT (ppp) BLANCO FISH (ppb) (52%) 250 SALINAS RIVER 103.1 (28%) HWY 1 LOWER TEMBLADERO SLOUGH OLD SALINAS RIVER 171 (10%) **5** 20.7 (36%) SALINAS RIVER LAGOON 257 (7%) (%92) 621 * Whole body lish 248.7 2504 / -17-

These indications of a possible identifiable source of "fresh" or "recently mobilized" DDT in the Salinas area were the impetus for the Central Coast Regional Water Quality Control Board and the Monterey County Agricultural Commissioner to request a special study of the Blanco Drain sediments. The purpose of the study was to isolate and characterize the sources of "recently mobilized" DDT in the Blanco Drain.

MATERIALS AND METHODS

Field Operations:

Phase 1 Study Stations

The field portion of the Phase 1 study of the Blanco Drain was conducted on June 12, 1984, as part of the regular Toxic Substances Monitoring (TSM) Program. Sediment samples were collected from 15 locations along the Blanco Drain and from two stations in the Salinas River (Figure 3). Fish were collected in and near the Drain as part of the Toxic Substances Monitoring Program and bagged freshwater clams were planted at several stations along the Drain by State Mussel Watch personnel.

A cooperative Phase 1 study of soils was conducted on June 25, 1984, by Dr. Robert Risebrough from the Bodega Marine Laboratory and Dr. Gerald Bowes from the State Board. They collected composite samples of soils from fields adjacent to the Blanco Drain. They divided the Drain's length into five sampling zones and collected ten soil subsamples from fields adjacent to each zone. Soil subsamples from each zone were mixed together to construct composite samples (Figure 4). Four samples of suspended sediment were also collected from the Drain waters.

Phase 2 Study Stations

The Phase 2 samples were collected on October 23, 1984. Sediment was collected at twenty-three locations along the Drain. Composite soil samples were collected from four of the five zones defined in the Phase 1 study. In addition, ten individual soil samples were taken for analysis (Figure 4).

Biological Sampling

Seven bags of corbicula (freshwater clams) were planted by the State Mussel Watch in Blanco Drain in the Summer of 1984. The corbicula died at four stations for undetermined reasons. However, corbicula were recovered and analyzed from three locations in the lower reaches of Blanco Drain. One station was west of the pump station corresponding to Phase 2 Station 25 (Phase 1 station 4). The second was east of the pump station, corresponding to Phase 2 station 34 (Phase 1 Station 5). The third was between the pump station and the Salinas River (Figure 4).

Fish were collected as a regular part of TSM activities in the Salinas River at two locations: near Blanco Road and just below Blanco Drain. One sample of fish was also collected from the lower portion of the Drain that feeds into the Salinas River (Figure 4).

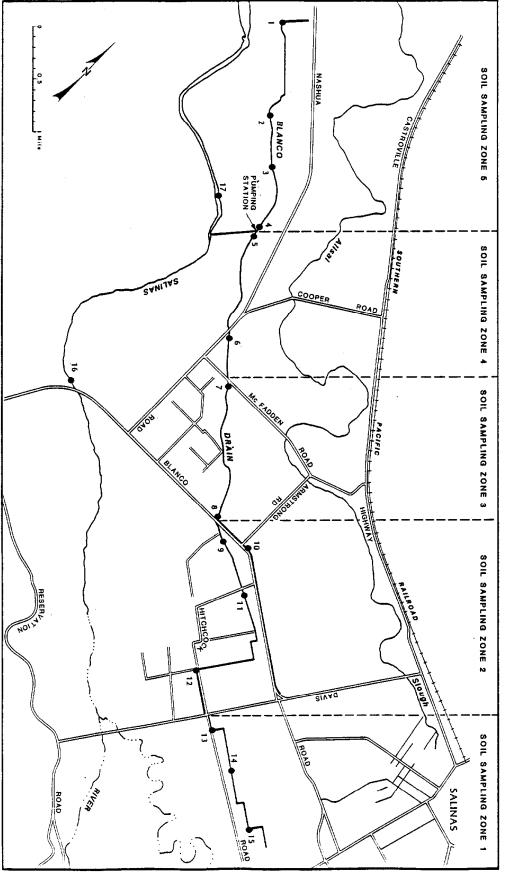


Figure 3. BLANCO DRAIN DDT PHASE 1 SAMPLING STATIONS

■ 10,11 SOIL ZONE COMPOSITES SOIL SAMPLING ZONE 1 SALINAS Figure 4. BLANCO DRAIN DDT STUDY PHASE 2 SAMPLING STATIONS AND COOPERATIVE STUDY STATIONS ■ 24,25 SOIL ZONE COMPOSITES SOIL SAMPLING ZONE 2 # 31, 32 SOIL ZONE COMPOSITES SOIL SAMPLING ZONE 3 PACIFIC DRAIN SOIL SAMPLING ZONE 4 OAOR 434000 SOUTHERN 34,35,A SMW (State Mussel Watch Corbicula) A TSM (Taxle Substance Monitoring Program Fish) OTHER (Cooperative Study) COOPERATIVE STUDY STATION MEDIA 33,34, suspended solids 35,A PUMPING STATION -SAMPLING MEDIA # 40, 41 SOIL ZONE COMPOSITES A SEDIMENT SOIL SAMPLING ZONE 5 BLANCO NASHUA

-21-

Sample Collections

Soil and sediment samples were collected in new or acid-cleaned pint glass jars. Sediment was collected from the top 1 inch of the sediment layer by gently scooping along the bottom of the drain with the jar. Care was taken to minimize disturbing the surrounding sediment. Soil was collected in a similar manner, except that no attempt was made to differentiate the top layer as the fields are plowed regularly. The sample jars were covered with heavy duty aluminum foil and then sealed with screw-top lids. All samples were immediately placed on ice for transport.

Sediment samples were collected from as near to the center-line of the Drain as possible. If fine sediments were not present along the center-line of the Drain, samples were collected from areas with fine sediments. In sections of the Drain not totally submersed, sediments were taken from wet areas. Care was taken to exclude any soil that might have been recently introduced to the Drain.

Individual soil samples were collected in adjacent fields near the Drain. Composite soil samples were collected from at least ten different locations in fields adjacent to the Drain. The locations were chosen at random on both sides of the Drain. All soil from composite samples was placed in a stainless steel pail and mechanically mixed before taking subsamples for transport.

Laboratory Operations:

Soil and sediment samples were kept on ice until divided at the DFG Game Water Pollution Control Laboratory in Rancho Cordova. Duplicate soil and sediment samples were first mixed together in a blender before being redivided for analysis. Soil and sediment samples were then forwarded to the Department of Food and Agriculture.

Analysis of Soil and Sediment Samples:

In both phases, about 15 percent of the samples were split with the DFG Water Pollution Control Laboratory in Rancho Cordova, California, for the purposes of quality assurance. The majority of the soil and sediment samples from both phases of the study were analyzed by the Department of Food and Agriculture at its Meadowview Road Laboratory. Replicate samples were analyzed by both laboratories for purposes of internal quality control.

Quality control samples were analyzed at the DFG Water Pollution Control Laboratory. Digestion techniques and instrumentation for the detection of organic compounds in sediment were identical to those described in the TSM Program.

Sediment samples were decanted to remove the water layer and mixed to give as homogeneous a sample as possible. A 20 gram portion of sample was taken for synthetic organic analysis, and a 5 gram sample was taken for moisture determination. The 20 gram portion of sample was blended with acetone:hexane

(1:1) and vacuum filtered. The water layer was extracted with 15 percent methylene chloride/hexane. The hexane layers were combined, washed twice with water, and dried with sodium sulfate. The dry extract was then cleaned up with Florisil. Sulfur was removed with acid-rinsed copper turnings which were added to the Florisil—cleaned extracts. The samples were then analyzed by gas chromatography.

Samples were stored at cool temperatures until analysis. Techniques used by DFA for analysis of the Phase 1 samples varied slightly from those used by the DFG laboratory. The percent water in the samples was not determined, and the samples were reported on a wet weight basis. Analysis of the Phase 2 samples paralleled the method used by the DFG laboratory. The percent water in the Phase 2 samples was determined, and the samples were reported on a wet weight basis.

Soil and Suspended Solids

Phase 1 soil samples collected by Drs. Risebrough and Bowes were analyzed at the Bodega Marine Laboratory. Approximately 100 grams of each soil sample were mixed with anhydrous sodium sulfate, then ground with mortar and pestle, and soxhlet-extracted with methylene chloride. Copper filings, activated by rinsing with dilute HCl, were added to reduce the sulfur content of the extract.

Filters containing suspended solids were torn into small pieces and soxhlet-extracted successively with acetone and hexane. Acetone was subsequently removed by the addition of water.

Extracts were analysed with a Carlo-Erba 4160 gas chromatograph, equipped with a 30 m fused silica SE-30 capillary column and a Carlo Erba electron capture detector. Injection was on-column, under the following conditions: 45 C for 3 minutes, 10 C/minute to 140 C, 4 C/minute to 290 C.

Several extracts were also analysed with a Carlo Erba 2350 gas chromatograph with a 30 m DB-5 fused silica capillary column in order to confirm the identification of the several compounds reported.

Seven soil samples from the Phase 2 study were sent to A-1 Analytical Laboratory in Salinas, California, for analysis of total organic carbon, volatile solids, and for particle size analysis.

Phase 1 soil samples analyzed by DFA did not include a measure of the soil moisture and so had to be expressed on a "wet weight" basis rather than the standard dry-weight basis. The DFA dry weight measures reported here are estimates based on DFG measures of moisture in their samples. For sample split with DFG the percent moisture measured by DFG was assumed. For all other samples, the mean value of all the split samples was used. After this conversion, the DFA analytical results are quite close to those reported by DFG. The ratio of various isomers used in our criteria is not affected by this conversion.

Similarly, the Risebrough soil samples were "air dried" before analysis. Since the handling of the Risebrough soil samples was very different from the other samples, no attempt was made to estimate true dry weight measures. The Risebrough soil analyses are therefore reported on an "air dried" basis. As with the DFA samples, the ratio of the isomers remains unaffected.

Analysis of Fish and Clam Tissue

Procedures used in preparation, extraction, and analysis of DDT in fish tissues are described in the 1983 Toxic Substances Monitoring Report (Agee, 1985). Procedures used in preparation, extraction, and analysis of DDT in clam tissue are described in the 1983-84 State Mussel Watch Report (Hayes and Phillips, 1985).

RESULTS

Phase 1 Study

Soil

Phase 1 soil analyses are summarized in Table 2a. Blanco soil samples in Phase 1 had 61 to 71 percent (average 67 percent) Technical DDT as a fraction of Total DDT. Ortho-para (o,p'-) DDT as a fraction of Technical DDT (Criterion 3) ranged from 22 to 29 percent (average 26 percent). Data from these samples indicated that relatively large amounts of DDT could still be found in Salinas soils and that a large fraction remained as Technical DDT. The fraction of o,p'-DDT was similar to the original 20% fraction in freshly applied Technical DDT. At that point there were several possible explanations including the possibility that o,p'-DDT might not be breaking down any faster than p,p'-DDT or that there had been some recent use of DDT.

Sediment

Phase 1 sediment analyses are summarized in Tables 2b and 2c and illustrated in Figure 5. Total DDT in Blanco Drain sediment ranged from 145 ppb to 3,984 ppb. Technical DDT as a percent of Total DDT ranged from 13 to 69 percent. Several stations near the east end of the Drain seemed to be comparatively "hot". In particular, Stations 9, 10, 13 and 14 showed much higher levels of DDT than adjacent stations. Stations with higher levels of DDT generally also contained higher percentages of Technical DDT, as compared to the other stations. Phase 2 was designed in part to determine the source of these apparent hot spots.

DDT concentrations in sediment samples taken in the Salinas River above and below the outlet of the Blanco Drain were consistent with earlier findings that indicated the Blanco Drain as a source of DDT. Both the Total DDT and the percent Technical DDT increased at the downstream station as compared to the upstream station.

Suspended Sediment

DDT concentrations in suspended sediment samples collected and analyzed by Risebrough reflected ratios of isomers similar to those found in the sediment (Table 2d). A discussion of this will follow in the discussion of Phase 2 samples.

Table 2a

Phase 1 Study: DDT Compounds in Soils adjacent to Blanco Drain,
June 25, 1984. (Risebrough, 1984)

Soil					 	
Sampling Zone#	p,p'-DDT	o,p'-DDT	p,p'-DDE**	o,p'-DDD	p,p'-DDD	Total DDT
	Nanogr	ams/Gram (pa	rts per billi	on) Sampled	l Weight	
1	900	360	680	44	81	2,065
2	1,200	440	820	48	93	2,601
3	1,200	340	470	36	140	2,186
ħ	1,500	450	730	28	180	2,888
5	550	200	220	29	68	1,067

^{*} cf. Figure 2

^{**} No o,p'-DDE was detected by Risebrough.

Table 2b

Phase 1 Study: DDT Compounds in Blanco Drain Sediment,
June 12, 1984. Department of Food and Agriculture Analyses

Station	o,p'-DDT	p,p'-DDT	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	Total
No.#	Nanograms/Gran		(parts per billion)		estimated	dry weigh	t ———
1	N.D.	36	N.D.	59	N.D.	50	145
2	21	59	15	151	38	120	403
3	N.D.	29	N.D.	116	N.D.	74	218
14	29	93	29	209	80	226	666
5	80	219	24	230	66	203	822
6	67	296	6	494	63	210	1,136
7	34	120	17	265	65	187	687
8	15	59	6	307	40	149	575
9	275	1,460	19	655	36	137	2,581
10	353	1,419	30	759	49	77	2,687
11	13	95	13	309	53	212	693
12	86	433	25	405	53	233	1,235
13	590	2,144	57	878	109	206	3,984
14	443	1,804	57	821	63	109	3,297
15	168	712	13	437	40	82	1,451

[#] cf. Figure 2
N.D. = Not Detected

Table 2c

Phase 1 Study: DDT Compounds in Blanco Drain Sediment,
June 12, 1984. (Fish and Game Analyses)

Station No.	o,p'- DDT	p,p'- DDT	o,p'- DDE	p,p'- DDE	o,p'- DDD	p,p'-	DDMS p,p'	DDMU P,P'	Total
	N	anograms	/Gram (parts p	er bill:	ion) dry	weight	; 	
4	19	130	15	400	74	360	N.D.	23	1,021
5	23	150	10	360	48	240	N.D.	15	846
10	280	1,600	20	,200	20	66	N.D.	9.7	3,196

^{*} cf. Figure 3

Detection Limit = 1 ppb

N.D. = Not Detected

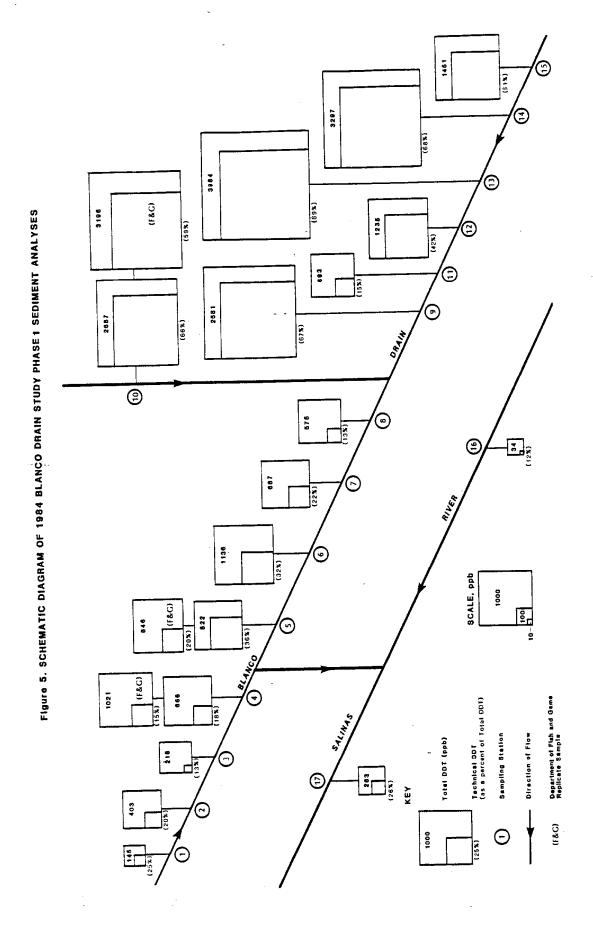


Table 2d

Phase 1 Study: DDT Compounds in Water-Borne Particulates in the Blanco Drain, June 26, 1984.

(Risebrough)

Sampling Area*	Near Phase 1 Sediment Station No.	Volume (Liters)	p,p'- DDT	o,p'-	- p,p'- DDE	o,p'-	- p,p'	- Total DDT
		Na	anogram	s/Liter	r (parts	per tr	illion)
Blanco Drain Between Pump Station and Salinas River	-	114	0.27	0.14	0.65	0.070	0.31	1.44
Blanco Drain 100 Meters West of Pump Station	14	76	10	3.7	9•7	N.D.	4.5	27.9
Blanco Drain East of Pump Station	5	19	87	28	160	50	270	595
Blanco Drain at Cooper Road	6	57	8.9	3.2	23	7.0	21	63.1

^{*} cf. Figure 3 N.D. = Not Detected

Phase 2 Study

Soils

Phase 2 soil analyses are summarized in Tables 3a and 3b. Total DDT in Phase 2 soil samples varied from 1,400 to 5,000 ppb. Total DDT in soils adjacent to the west leg of the Drain ranged from 1,400 to 3,200 ppb (average 1,800 ppb). DDT in soils adjacent to the east leg of Blanco Drain ranged from 1,400 ppb to 5,000 ppb (average 3,100 ppb). Total DDT in the zone composite samples taken in Phase 2 cannot be compared directly to Phase 1 samples because of the different units ("air dried" weight in Phase 1 vs. dry weight in Phase 2). However, they reflect the same relative amounts of DDT from one zone to the next as the Phase 1 soil samples. Comparisons of ratios such as percent Technical DDT remain valid.

Table 3c is a summary of special analyses performed on six soil samples and one sediment sample. The analyses were performed to determine if differences in soil DDT could be linked to differences in the soils. Although there were some small differences between the soil samples, there was no obvious correlation between the measured parameters and soil DDT, percent Technical DDT, or percent DDD as a percent of Technical DDT.

Table 3d is a summary of pH measured by DFA in eight soil samples. There was little variation in the measured pH and no correlation between pH and any of the DDT measures.

Sediment Analyses

Sediment analyses from Phase 2 are also summarized in Tables 3a and 3b. Unlike the soil samples, the sediment samples were more variable in all measurements. Total DDT in sediment samples varied from values about equal to those found in soils down to less than 1 ppm. Sediments in the east leg of the Drain ranged from 6,200 ppb to 400 ppb (average 2,200 ppb). Sediments in the west leg of the Drain ranged from 200 to 1,700 ppb (average 800 ppb).

Biological Analyses

Corbicula (clams) planted by the State Board's State Mussel Watch program were recovered and analyzed from three stations in the lower reaches of the Blanco Drain. The results of the study are presented in Table 3e. The measurements are reported on a wet weight basis. All of the measurements are very high compared to other samples collected by State Mussel Watch. The 3,800 ppb measurement at the "pump station east" site is the highest ever found in a shellfish by the State Mussel Watch. As DDT and its by-products are lipid soluble, the lipid-based measure of 754,000 ppb is even more noteworthy.

In general, the percent Technical DDT was similar to that found in the sediment (Table 2c) (15.6 to 38 percent) as was the percent ortho-para DDT (10.6 to 30.7 percent). However, there was little correlation among corbicula, sediment, and suspended sediment percentage measures at specific stations. This lack of exact correlation is not surprising considering the fact that these were three different media and considering the inherent

Table 3a

Phase 2 Study: DDT Compounds in Blanco Drain Soil and Sediment,
October 23, 1984. (DFA Analyses)

Phase 2 Sample No.	Soil*	o,p'- DDT	p,p'- DDT	o,p'- DDE	p,p'- DDE	o,p'- DDD	p,p'-	Total
		Nanog	rams/Gram	(parts	per billi	on, dry	weight)	
1		184	853	20	582	55	162	1,856
2	_	427	1,561	24	742	45	38	2,837
3 4	S	698	2,578	61	1,388	123	157	5,005
		807 47	3,752	51	1,252	204	114	6,180
5 6	s	338	137 1,607	76 32	754 689	105 46	329 52	1,448
7	5	181	604	11	444	27	40	2,764 1,307
8		344	1,806	15	477	23	28	2,693
9		68	156	20	342	60	237	885
10	S	411	1,551	37	736	49	37	2,821
11	S	330	1,507	30	463	41	56	2,427
12		395	1,965	26	529	38	150	3,103
13		333	447	24	539	51	329	1,723
14 15		117	656 168	11	238	51 50	196	1,269
15 16		31 33	148	14 20	274 355	50 56	225	762
17	S	33 481	2,304	16	355 836	56 30	253 46	865 3 , 713
18	D	171	1,064	16	539	42	158	1,990
19		272	1,463	20	704	86	488	3,033
20	S	345	2,571	13	634	21	28	3,612
21	S	184	851	13	375	18	16	1,457
22		437	1,475	201	386	1,312	2,453	6,264
23		17	100	4	143	16	75 - 6	355
24 25	s s	504	2,450	27	964	39	36	4,020
26	ಎ	576 335	2,271 1,265	53 17	1,134 291	73 20	67 85	4,174
27	S	571	1,554	38	1,016	29 35	85 28	2,022 3,242
28		199	663	13	483	38	96	1,492
29	S	308	996	16	581	25	26	1,952
30	S	66	343	25	377	154	422	3,387
31	S	551	2,884	39	971	74	100	4,619
32	S	321	1,680	20	672	20	29	2,742
33		343	1,632	50	485	209	351	3,070
34 35		91 140	297	45 20	807	130	598	1,968
35 36		149 11	597 70	39	356 161	196	340	1,677
30 37		27	70 59	14 15	161 63	38 20	123 34	417
38	S	264	995	20	250	35	34 44	218 1,608
39	S	198	867	14	249	36	35	1,399
40	Š	295	1,454	22	463	38	45	2,317
	S	396	-		·		• •	

^{*} cf. Figure 2, ** S = soil, all others sediment.

Phase 2 Study: DDT Compounds in Blanco Drain Soils and Sediment,
October 23, 1984. (DFG Intercalibration Analyses)

Phase 2 Sample No.	o,p'- DDT	p,p'-	o,p'- DDE	p,p'- DDE	o,p'- DDD	p,p'- DDD	p,p'- DDMU	Total
	Na	nograms/G	ram (par	ts per b	illion) (dry weigh	nt 	
(5D)	30	94	14	290	74	240	34	796
(6D)	270	1,000	19	300	30	70	12	1,701
(10D)	430	1,300	27	560	42	98	28	2,485
(11D)	320	1,400	27	520	40	82	30	2,419
(24D)	290	980	23	500	26	56	4.5	1,879.5
(30D)	77	300	11	250	72	240	20	969
(31D)	380	1,500	20	580	49	86	6.6	2,621.6
(40D)	260	1,000	14	350	30	49	20	1,723

D = Duplicate sample number.

Table 3c Analysis of Selected Blanco Drain Soils and Sediments

Analysi	s		Pha	se 2 Sampl	e Numbers		
	6	5 (Sediment)	10/11	25	30	31/32	41
TOC * 1850 (mg/kg)		1840	2700	2190	2130	1080	1990
VS ** 9.6 (mg/kg)		7.7	7.1	6.0	7.0	6.6	6.4
U.S. Se Size (m			Part	icle Size (percent			
18	_	_	.1372	.0663	_	.1086	•1591
25	. 1575	.2239	•9175	.3966	.0713	.2402	•3355
35	•3311	.4244	.6777	.7206	•2190	• 1542	.3484
60	.4369	.5669	1.5242	1.0761	.7919	.6247	1.0274
80	.2700	.6068	.6891	1.5207	•7258	1.3229	.7123
120	1.7875	.7230	.7113	2.5925	1.9525	5.3285	.8633
170	15.5636	5.3723	•5940	6.0523	11.3174	13.9820	4.3540
200	22.7825	16.5939	9.8734	20.1693	21.9605	19.3418	20.6710
Bottom	56.7542	74.4241	83.9067	66.1513	61.1497	58.0764	69.8651

^{*} Total Organic Carbon
** Volatile Solids

Table 3d

pH of Selected Blanco Drain Soils

Phase 2 Sample No.	3	6	17	20	21	27	38	39
рН#	7.71	7.70	7.79	7.10	7.41	7.81	7.74	7.74

^{*} Saturated Paste Method, DFA Analysis

Table 3e

DDT Compounds in Corbicula planted in Blanco Drain

Phase 1 Station No.	o,p'- DDT	p,p'- DDT	o,p'- DDE	p,p'- DDE	o,p'- DDD	p,p'- DDD	p,p- DDMU	Total DDT					
Nanograms/Gram (parts per billion) wet weight													
ц	42	94	8	375	66	275	8	868					
5	146	467	42	1,971	234	876	33	3,769					
A	166	728	14	853	94	478	18	2,351					

variability of all samples in the Drain. Even the sediment samples taken at these locations varied between Phase 1 and Phase 2. The general agreement of DDT concentration, and the high concentrations of DDT found in the corbicula samples indicates that much of the DDT transported in and through the Drain is associated with fine suspended particulate matter in the Drain.

Fish were collected in the Salinas River above and below the outlet of Blanco Drain and in the lower part of the Drain as part of regular TSM activities (Table 3f). The analyses confirmed the now familiar pattern found near the Drain. Fish collected from reaches of the Salinas River above Blanco Drain contained very little DDT (36 ppb). The amounts were too small to make reliable estimates of percent Technical DDT. Fish taken just below the outfall of Blanco Drain in the Salinas River contained about 500 ppb DDT. Approximately 20 percent of this was Technical DDT.

Fish collected in the lower reaches of the Drain itself contained approximately 1,000 ppb Total DDT, 25 percent of which was Technical DDT. The NAS guideline for protection of predator species is 1,000 ppb. These and earlier data indicate that nearly all of the DDT in fish collected in the Salinas River below Blanco Drain comes from Blanco Drain itself.

DISCUSSION

Presence of o,p'-DDT

The presence of o,p'-DDT in soils adjacent to Blanco Drain at levels exceeding 20 percent of Technical DDT came as something of a surprise to researchers familiar with the breakdown of DDT in aquatic systems (Risebrough, 1984). Upon reflection, the reason that it has not been observed in many papers may be because often it has not been measured. The reasons for this may be related to the difficulty of measuring an otherwise minor component of Technical DDT particularly when using older technology (packed column). However, finding o,p'-DDT in soils is not unique. Lichtenstein et al. (1971) reported similar results in a 15-year study of the breakdown of DDT.

The assumption that o,p'-DDT would somehow drop from 20 percent of Technical DDT to zero in a short time in soil turns out to be incorrect. Even so, the usefulness of using o,p'-DDT as a fingerprint of recently mobilized DDT remains. We rarely find o,p'-DDT in fish at levels exceeding 8 percent of Technical DDT. The times that we do are invariably associated with elevated measures of Total DDT or Technical DDT (cf. Table 1). As such, it provides supportive evidence in identifying those locations in which Technical DDT is currently being introduced into the aquatic environment.

Soil

Total DDT measured in soil did not reveal any obvious pattern in either Phase 1 or Phase 2. Soils adjacent to the west leg of the Blanco Drain (Zone 5) contained somewhat less DDT (average 1,800 ppb) than soils adjacent to the east leg of the Drain (average 3,100 ppb), but no individual soil sample

Table 3f

DDT Compounds in Suckers Collected by
1984 Toxic Substances Monitoring Program (TSM)
in the Salinas River and in Blanco Drain

								
Station		o,p'- DDT	p,p†- DDT rams/Gram	o,p'- DDE	DDE	DDD	DDD	Total DDT
Salinas River/ Blanco Road		ND	10	ND	26	ND	ND	36
17 77		ND	11	ND	25	ND	ND	36
Salinas River/ below Blanco D		ND	88	ND	240	24	120	472
11 11	11	18	120	ND	320	30	160	648
Blanco Drain Station A		32	220	ND	470	36	220	978
79 TI		27	220	ND	390	40	240	917

^{*} Detection Limit = 5 ppb, all others = 10 ppb.

appeared to have unusually more or less Total DDT than the others. One surprising development, however, was the high level of uniformity found in the measures of percent Technical DDT and percent DDD.

Table 4 is a summary of all of the soil and sediment analyses performed in this study including Phase 1 and Phase 2 analyses by both DFA and DFG, as well as the Risebrough soil analyses. The measures listed for each sample include the Total DDT, the percent Technical DDT, and the percent DDD.

All of the Phase 2 soil samples (except Sample No. 30) had between 65 and 81 percent (average 72 percent) Technical DDT. This near uniformity was in contrast to sediments which ranged from 19 to 80 percent Technical DDT. Also, all of the Phase 2 soil samples except Sample No. 30 had between 1.4 and 5.6 percent DDD (average 3.5 percent). By contrast, DDD in sediment samples ranged from 1.9 to 60 percent.

The high level of uniformity originally led to speculation that the uniform measures of Technical DDT and DDD represented a very uniform breakdown of DDT in the area, something to which one could "set one's clock". This view of things inherently includes the assumption that the timing of DDT use was about the same from one year to the next, so that, in 1972 when DDT use was discontinued, all of the fields had nearly the same percent Technical DDT even at that time. Although this may be true, there is a second possible explanation for the uniformity.

Closer inspection of data from other studies such as Lichtenstein et al. (1971) showed that Total DDT could be dissipating from fields while the various homologues such as Technical DDT remained in a near constant proportion of the total remaining DDT over several years.

A study conducted by the U. S. Food and Drug Administration (USFDA) in 1981 included some measures of soil DDT in and around the Blanco Drain. Percent Technical DDT in that study fell directly into 60 to 80 percent range found in this study, again demonstrating that the percentages of DDT may not have measurably changed in the intervening years. It is quite possible that while Total DDT dissipating there is in a near equilibrium maintained between the main chemical species. In the case of Blanco Drain soils, this theoretical equilibrium favors about 70 percent DDT and 3.5 percent DDD. Such an equilibrium could be governed by both chemical processes and certain transport processes such as differential vaporization of the products.

To our knowledge, the breakdown of DDT in soils has never been expressed in exactly this way; however, it goes a long way to explain the almost "unnatural" uniformity found there and does not conflict with the general pattern of DDT breakdown described in other papers. This theory will have to await further testing for verification. However, the fact that DDD and DDT are so uniform in soils adjacent to Blanco Drain (whether in equilibrium or not) makes it possible to fingerprint samples that are of recent soil origin.

TABLE 4 BLANCO DRAIN DOT SUMMARY (ppb, dry weight)

			Phase 2 (10-23-84)			Phase 1 (6-12-84)			Bowes - Riseborough		
10-23-84 Sta. #	6-12-84 Sta. #	Type	! ! Total ! DDT	% Tech. DDT	2 000	! ! Total ! DDT**	% Tech. DDT	XDDD	! ! Total ! DDT***	% Tech DDT	X DDD
1 2	15 14	SED SED	1856 2837	55.9 70.1	11.7	(1451) (3297)	60.6 68.1	8.4 5.2			
3 4 5	13	SOIL SED SED	5005 6180 1448	65.5 73.8 12.7	5.6 5.1 30.0	(3984)	68.6	7.9			
5 D 6	-	SED SOIL	796 2764	15.6 70.4	39.4 3.5						٠
6 D	-	SOIL	1701	74.7	5.9						
7 8	•	SED SED	1307 2693	60.1 79.8	5.1 1.9	•					
9	•	SED	885	25.5	33.6	-			2015	ZONE 1 *	
#1* 10 #1 10 D	-	SOIL	2821 2485	69.5 71.2	3.0 5.9	•	-		2065	61.0	6.1
#1 10 D #1 11	-	SOIL SOIL	2427	75.7	4.0	•					
#1 11 D	-	SOIL	2419	71.1	5.0	•					
12	12	SED	3103	76.1	6.1 22.1	(1235)	42.0	23.2			
13 14	-	SED SED	1723 1269	45.3 60.9	19.4	-					
15	•	SED	762	26.1	36.1	•					
16	•	SED	865	20.9	35.7	-					
17	•	SOIL	3713	75.0	2.0 10.1						
18 19	11	SED SED	1990 3033	62.1 57.2	18.9	(693)	15.6	38.2			
20	•	SOIL	3612	80.7	1.4	•					
21	•	SOIL	1457	71.0	2.3	•					
22	8	SED	6264	30.5	60.0	(575)	12.9	32.9		D	
23 #2 24	9	SED SOIL	355 4020	33.0 73.5	25.6 1.9	(2581)	67.2 -	6.7	2601	<u>ZONE</u> 2 63.1	5.4
#2 24 D	•	SOIL	1880	67.6	4.4	-					
# 2 2 5	-	SOIL	1875	68.2	3.4	•					
26	10	SED	2022	79.1	5.6	(2687) 3195	65.9 58.8	4.7 5.5			
- 2 7	10 D	SED SOIL	- 3242	65.5	1.9	2172	,6.0	3.5			
28	-	SED	1492	57.8	9.0	•					
29	•	SOIL	1952	66.8	2.6	-					
30	-	SOIL	1387	29.5 38.9	41.5 3 2.2	•				ZONE 3	
30 D #3 31	•	SOIL SOIL	96 9 4619	74.4	3.8	-	•	-	218 6	70.4	8.1
#3 31 D	•	SOIL	2622	71.7	5.1	•					
#3 32	•	SOIL	2742	73.0	1.8			7/ 7			
-	7	SED			18.2	(687) (1136)	25.3 32.0	3 6.7 24.0			
33	6 5	SED SED	3070 1968	64.3 19.7	37.0	(822)	36.4	32.7			
34	5 D	SED	•			846	20.4	34.0	2888	<u>ZONE</u> 4 67.5	7.2
•	•	SOIL	•	•	•	•					
3 5	4	SED	1677	44.5	32.0	(666) 1021	18.3 14.6	45.9 42.5			
	4 D 3	SED SED	•			(218)	13.3	33.9			
3 6	2	SED	417	19.4	38.6	(403) (145)	19.9 24.8	39.2 34.5			
37	1	SED	218	39.4	24.8	(143)	L4.0	2715			
38	-	SOIL	1608	78.3	4.9 5.1	:				ZONE 5	
39 #5 40	-	SOIL SOIL	1399 2317	76.1 75.5	3.6	•	•	•	1067	70.3	9.1
#5 40 D	-	SOIL	1723	73.1	4.6	-					
#5 41	•	SOIL	3201	73.5	4.6	-					

^{*} Soil Zone D = Duplicate analysis by DFG ** Figures in parentheses are estimates of dry weight measures. *** Does not include o-p'DDE. Air-dry measures.

Sediment

As mentioned earlier, percent Technical DDT and percent DDD measured in sediment ranged from those values found in soil to values much greater or smaller. An examination of the frequency distribution of the measures of percent Technical DDT, DDD and DDE for both soils and sediment is shown in Figures 6a, 6b, 7a, 7b, 8a, and 8b. Although they are constructed only from the data reported by the DFA laboratory to eliminate inter-laboratory variance, inclusion of the DFG analyses or the Risebrough analyses would not change any of the following results. Sediment samples from both Phase 1 and Phase 2 are included together in the histograms. This was done because the two samples are independent in time, if not in space. Also, even though they are not completely independent spatially, many of the samples from individual stations were very different between Phase 1 and Phase 2 and so did not necessarily represent a replicate measurement.

Field replicates were averaged and used as a single entry in constructing the histograms. Figure 6a illustrates the uniformity of percent Technical DDT found in the soils near Blanco Drain. The single exception (Sample 30) is noted on the figure.

In Figure 6b, percent DDT in sediment follows a bimodal distribution. One peak falls directly beneath the soil peak at 60 to 80 percent Technical DDT. The second peak centers on approximately 20 percent DDT and ranges from approximately 10 to 45 percent.

Figures 7a and 7b illustrate the frequency distribution of percent DDD in soil and sediment samples. With the exception of Station 30, all of the soil samples fall in a single histogram bar. The frequency distribution of percent DDD in sediment contains two distinct peaks. Again, one peak lies beneath the soil peaks (0 to 10 percent DDD), and the second centers at about 35 percent, ranging from 20 to 60 percent DDD.

The amount of DDD in the second peak is consistent with our experience in the TSM program in measuring DDD in sediments. Other researchers, such as Parr et al. (1970), and Beland, et al. (1974) indicate that DDT breakdown under anaerobic conditions found in sediment typically favors the production of DDD.

Although the Blanco Drain does not have uniformly anaerobic conditions in sediment, similar processes are apparently going on there. It appears that soil containing approximately 70 percent Technical DDT and 3.5 percent DDD is introduced into the Drain where different breakdown processes shift the balance to 10 to 30 percent Technical DDT and 30 to 40 percent DDD.

Figures 8a and 8b illustrate the frequency distribution of DDE in soil and sediment. The frequency distribution of DDE in sediment is not bimodal like DDT and DDD but does cover a broader range of values than DDE in the soil. Soil DDE ranged from 10 to 40 percent, while sediment DDE ranged from 0 to 60 percent.

If it is true that sediment samples that fall under the "soil peak" of a given measure are actually recently mobilized soil that has not had time to shift to

Figure 6a. FREQUENCY DISTRIBUTION OF PERCENT TECHNICAL DDT IN BLANCO DRAIN SOILS

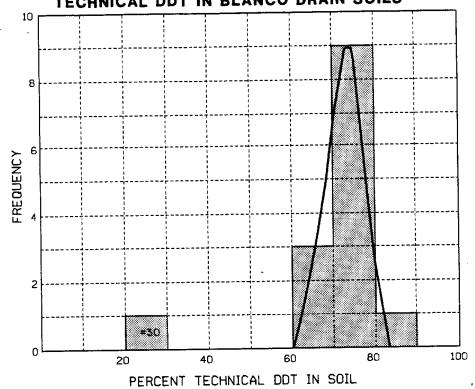


Figure 6b. FREQUENCY DISTRIBUTION OF PERCENT TECHNICAL DDT IN BLANCO DRAIN SEDIMENTS

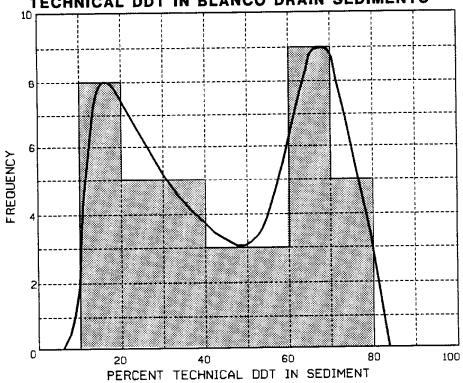


Figure 7a. FREQUENCY DISTRIBUTION OF PERCENT DDD IN BLANCO DRAIN SOILS

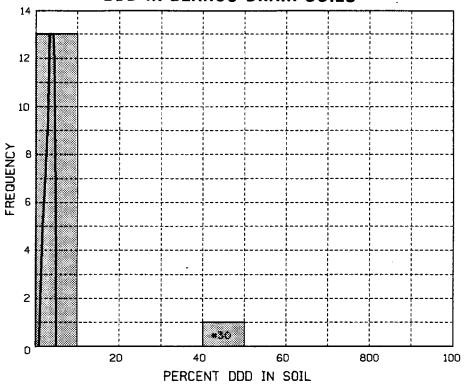


Figure 7b. FREQUENCY DISTRIBUTION OF PERCENT DDD IN BLANCO DRAIN SEDIMENTS

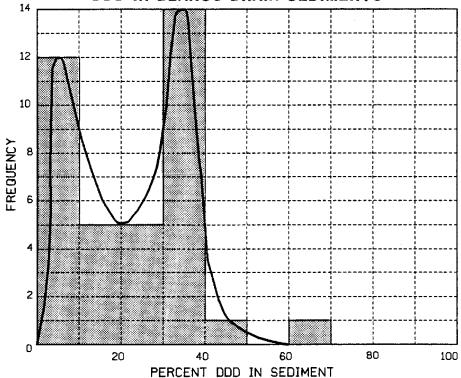


Figure 8a. FREQUENCY DISTRIBUTION OF PERCENT DDE IN BLANCO DRAIN SOILS

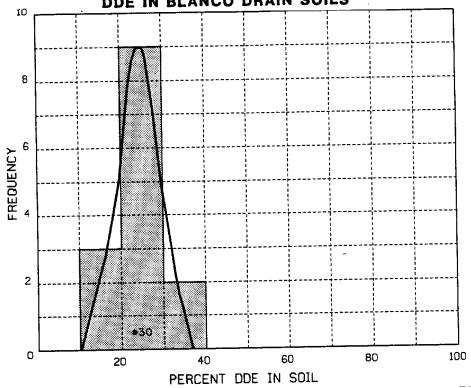
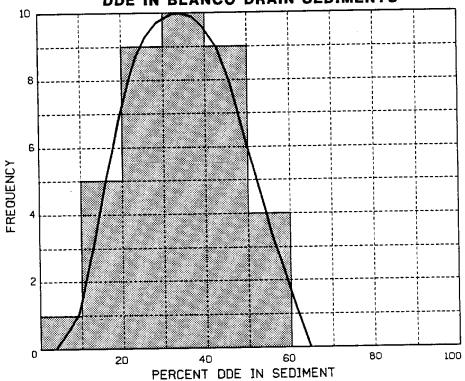


Figure 8b. FREQUENCY DISTRIBUTION OF PERCENT DDE IN BLANCO DRAIN SEDIMENTS



sediment-like DDT ratios, then one should expect a certain amount of consistency in the measures. Three measures of that consistency should follow:

- a. Sediment samples found in the "soil peaks" illustrated in both Figures 6b and 7b should all be from the same station.
- b. Sediment samples found in the "sediment peaks" illustrated in both Figures 6b and 7b should also be from the same stations.
- c. The location of the soil-like stations should be consistent with general field observations of erosion or mechanical movement of soil into the Drain.

The first two tests are summarized in Table 5. The criteria used are as follows:

- o Soil-like analyses are defined as having more than 60 percent Technical DDT and less than 10 percent DDD.
- o Sediment-like analyses are defined as having less than 45 percent Technical DDT and more than 20 percent DDD.
- Analyses not falling entirely into either the soil-like or the sediment-like categories are shown in the transition category.

Table 5 illustrates very clearly the high degree of uniformity found in the Blanco Drain sediment samples. Very few samples show any overlap between soil-like and sediment-like characteristics. Although not shown on Table 5, most of the stations can also be divided into the same soil-like versus sediment-like categories using the percent DDE measure. However, there is enough overlap to make the DDE measures less reliable.

Five sediment stations from Phase 1 fall into the soil-like category. These stations are the very stations identified as possible Phase 1 "hot spots". The "hot spots" identified in Phase 1 are likely recently mobilized soil.

Seven Phase 2 sediment stations also fall into the soil-like category. Three of these, numbers 2, 4, and 26, correspond to Phase 1 Stations 14, 13, and 10. Phase 2 station 1, corresponding to Phase 1 Station 15, is listed as a transition station but is nearly a soil-like station like its Phase 1 counterpart. The percent DDD measure exceeded the 10 percent criterion by only 1.1 percent at Station 1. Phase 2 Station 23 shows a definite change from Phase 1 Station 9, falling completely into the sediment category compared to the soil-like characteristics measured in Phase 1.

It is not just the soil-like analyses that show consistency between the two sampling phases. Stations with sediment-like characteristics also show a great deal of consistency between Phase 1 and Phase 2. Only Phase 2 Station 33 fell into the transition category, as compared to its counterpart, Phase 1 Station 6, in the sediment category.

Table 5 CLASSIFICATION OF BLANCO DRAIN SEDIMENT SAMPLES

STUDY PHASE/ STATION	SOIL CRI	TERIA	SEDIMENT	CRITERIA	TRANSITION	CLASS	
	TECH DDT ≥60%	DDD ≤IO%	TECH DDT ≤45%	DDD ≥20%	TECH 45% < DDT < 60%	10% < DDD < 20%	CLASS
1/9	•	•					
1/10	•	•			ļ		
1/13	•	•					Ì
1/14	•	•					
1/15	•	•			 	<u> </u>	6011
2/2	A					 	SOIL
2/4	A	A		<u></u>			
2/7	A			<u> </u>			
2/8	A				<u> </u>		ł
2/12	A			<u> </u>	ļ	 	-
2/18	A	10.1%				 	Ì
2/26	A	A					
1/1			0	0	 		Ì
1/2			0	0	 		
1/3			0	0	- 	 	
1/4			0	0			1
1/5			0	0			
1/6			0	0		 	
1/7			0	0	- 	 	
1/8			0	0			
1/11	l		0	0			
1/12		<u> </u>	0	0			SEDIMENT
2/5			Δ	Δ	_		LIKE
2/9				Δ			'
2/13			45.3%	Δ			
2/15		<u> </u>	<u> </u>	<u> </u>			
2/16		<u> </u>	<u> </u>	Δ			
2/22			<u> </u>	<u>^</u>		<u> </u>	
2/23				<u> </u>			1
2/30 *							1
2/34			Δ	<u> </u>		 	1
2/35			<u> </u>				1
2/36			<u> </u>	Δ	_		
2/37		<u> </u>	Δ	<u> </u>	Δ	Δ	
2/1				 		- 	1
2/14	Δ			Δ_	-	Δ	
2/19				_	<u>Λ</u>		TRANSITION
2/28		Δ				▲ 18.2	1
2/33	Δ						†

^{*} STATION #30 IS A SOIL SAMPLE. ALL OTHER SOIL SAMPLES ARE NOT SHOWN

O PHASE I SEDIMENTS

Δ PHASE II SEDIMENTS

[☐] SOILS

Figure 9 is the now familiar map of the Blanco Drain with symbols mapping out where each soil/sediment-type was found in the Drain. The circles represent Phase 2 analyses; the squares represent Phase 1 analyses. A filled symbol represents "soil-like" analyses, an empty symbol represents "true-sediment" analyses and half-filled symbols represent "transition" analyses.

The pattern is very clear. All of the "soil-like" analyses, and all but one of the "transition" analyses are mapped east of Station 8, the confluence of the Blanco Drain with its major tributary at Blanco Road. These reaches of the Drain correspond exactly to the reaches where erosion and mechanical movement of soil into the Drain were observed.

The variability between Phase 1 and Phase 2 analyses taken at the same locations only serves to demonstrate the dynamic nature of the sediments in the Drain, particularly at this end of the Drain. The conversion of soil-like DDT to sediment-like DDT probably takes place in a relatively short time (perhaps only a few months) and would depend on how recently soil had entered the Drain, conditions of flooding, movement of sediment, and other factors. In the remaining portions of the Drain, only one station was ranked in the "transition" category, indicating that erosion may be occasionally found even here.

Station 30

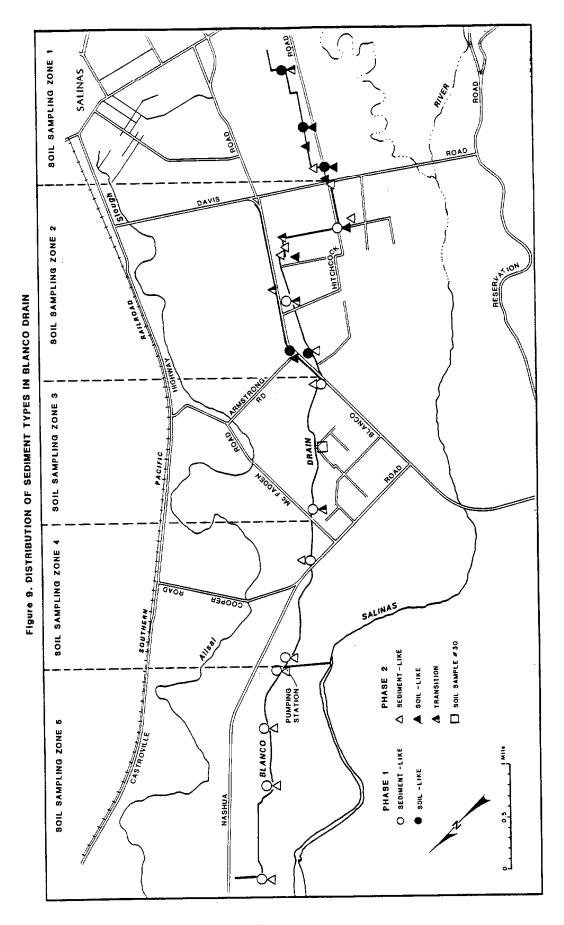
Station 30, a soil sample, was included in all of the tests to differentiate soil and sediment analyses (Table 5) to demonstrate that the sample falls directly in the sediment classification. Station 30 is located in a part of the Drain that had been relocated a few years earlier and is most probably sediment that was moved onto the field in the process. This one exception only goes to prove the role of being able to fingerprint soil and sediment in Blanco Drain.

Environmental Effects

Much of this report has been concerned with the sources and fate of Technical DDT in the Blanco Drain. One usually associates DDT or DDE with environmental problems. Of course, conversion of these chemicals to other products does not necessarily remove the environmental threat. Many of the breakdown products are just as undesirable in the environment as DDT. If indeed these products are more stable than Technical DDT, the problem could remain in soils for a very long time.

The situation in Blanco Drain is certainly not unique to the Blanco Drain. Many, if not most, of the agricultural lands in the Salinas area have similar amounts of DDT in the soils. A report by DFA (Mischke, et al., 1985) indicates that the scope of this phenomenon may indeed be statewide.

While there is no pretense in this report to predict the environmental fate of the Blanco Drain sediments, some general observations are offered here. It is likely that most of the DDT introduced into the Salinas River from the Blanco Drain is associated with erosion and mechanical movement of soil particles associated with working the soil near the edge of the Drain. Much of the DDT



is probably introduced into the Salinas River during storm events and is carried to the sea where its fate is unknown. However, as late as 1979 the USFDA found that 40 percent of "Thorny Heads" and 5 percent of the Black Cod caught in Monterey Bay exceeded the 5.0 ppm FDA tolerance limit for DDT for protection of human health. That year over 17,000 lbs of fish were destroyed and the Thorny Head market dried up (E. Dellanina, 1979). Other species sampled more recently have not had as much DDT in their tissues; however, no study of Thorny Heads has been conducted since 1979.

It is the feeling of some USFDA officials that the body burden of DDT in fish like Thorny Heads may reflect both past and current exposure and that older fish may have higher levels of DDT than younger fish (E. Dellanina, pers. comm.). Other researchers (Risebrough, pers. comm.) disagree with this view. However, if this <u>is</u> true, it may be possible to design a study of selected fish species in Monterey Bay and to correlate the cumulative exposure with the age of the fish, thereby giving a measure of the relative impact of current DDT inputs into the ocean.

According to the recent Department of Food and Agriculture Report (Mischke et al., 1985), little, if any, DDT or its homologues is getting into the human food chain via fruits and vegetables. Potential impact on other food chains via insects or rodents is not addressed by that report or this report.

Recommendation

Whereas there is no known economical method of removing DDT from soils, the best method of protecting the aquatic environment probably is to limit the amount of DDT-laden soil entering the Drain. Regular periodic movement of soil into the Drain by farm machinery is probably the largest source of DDT to the Drain. Best management practices would require that a buffer zone (such as a berm) be established between the Drain and adjacent fields. If constructed properly, the loss of productive land would be small but would serve to curtail the majority of DDT currently entering the Drain. The success of these procedures could be monitored using the DDT and DDD measures used in this report.

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