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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

UNDATED

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Review of Six Documents Regarding Monitoring of Pesticides in Northwestern Ohio Rivers

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In February 1984, Region V of the U.S. Environmental Protection Agency sent six documents regarding monitoring of pesticides in northwestern Ohio river basins to the Exposure Assessment Branch for review.

The monitoring data on currently used pesticides were collected by Dr. David B. Baker, Director of Water Quality Laboratory, Heidelberg College, Tiffin, Ohio, for the years 1981, 1982 and 1983.

The monitoring programs were funded partly by: (1) U.S. Army Corps of Engineers; (2) U.S. Environmental Protection Agency (Great Lakes National Program Office, Region V, and ERL/ORD, Athens); (3) National Oceanic and Atmospheric Administration; (4) Defiance County (Ohio) Soil and Water Conservation District; (5) Ciba Geigy Corporation, (6) Monsanto Agricultural Products Company; and (7) Proctor and Gamble Company.

The monitoring reports are reviewed individually as follows:

(1) Title: The Concentrations and Transport of Pesticides in Northwestern Ohio Rivers - 1981.

Summary: This report was submitted in partial fulfillment of Contract DA-CW-49-81-C-0028 from U.S. Army Corps of Engineers, Buffalo, New York. This study was conducted to determine the

(1)

occurrence and transport of currently used pesticides in northwestern Ohio rivers. In 1981, water samples were collected at 12 U.S.G.S. stream gauging stations in northwestern Ohio rivers of the Honey Creek watershed. An automatic sampler (an ISCO model 2100 or 1680 sequential sampler) was used at the gauging stations to collect water samples and a grab sampling program was operated during large storm events. The Honey Creek watershed was chosen because the land use pattern there consists of 83% cropland, 1% pasture, 10% woodland, and 6% other. Tap water from the municipal water supply at Tiffin, Ohio (which withdraws its water directly from the Sandusky River), was also collected.

In northwestern Ohio, 1981 was a wet year due to four large rainfalls. Unusually large runoff events occurred during these rainfall events. Comparison of the pesticide chemographs with the hydrographs for June storm days suggests that, during the first storm, surface runoff of water was the major route for pesticide transport from fields to the sampling stations. In subsequent storms, tile flow seems to account for more of the pesticide movement than does surface runoff. The maximum stream concentrations found for each pesticide tested are: atrazine, 87 ug/l; desethyl atrazine, 8.3 mg/l; desisopropyl atrazine, 3.0 mg/l; simazine, 7.4 mg/l, metribuzin, 23 mg/l; alachlor, 105 ug/l; metolachlor, 140 ug/l; butylate, 0.49 ug/l; phorate, 0.24 ug/l; terbufos, 0.54 ug/l; fonofos, 1.0 ug/l; and carbofuran, 45 ug/l.

Tap water from the city of Tiffin, Ohio, contained similar levels of pesticides to that found in the stream gauge sampling stations at approximately the same times. The runoff of nutrients and sediments was also measured in the monitoring program.

(2) Title: Pesticide Monitoring Notes 1982

Summary: This report was a brief summary of the results obtained in the pesticide monitoring program in progress during 1982. In this study, automatic samplers (ISCO model 2100) were used to collect water samples at the Defiance, Maumee (Bowling Green), Sandusky (Fremont), and Honey Creek (Melmore) stations; and a grab sampling program was used at the River Raisin near Monroe, Michigan, and on the Cuyahoga River at Independence, Ohio. The soil types, land use patterns, and crops grown are similar in all these watersheds (Maumee, Sandusky, Defiance and Honey Creek). Nineteen currently-used pesticides were measured in each location. Table 3 of that report, attached hereto, summarizes the peak concentrations of each pesticide in 6 river basins (Maumee, Sandusky, Raisin, Melmore, Defiance, Cuyahoga).

The dates on which peak concentrations occurred are also shown. The drainage area in square miles and the number of samples analyzed are listed for each station. Comparisons of chemographs

of 7 pesticides and the associated hydrographs for the Honey Creek Station at Melmore and for the Sandusky River Station at Fremont were made; the report indicated that similar data were available for four other stations. The highest concentrations were found during the first runoff event after the planting season (in late May for most of the stations).

A small number of tap water samples from the Tiffin, Ohio, water supply were analyzed and the pesticides concentrations were found to be very similar to the river water concentrations. The Tiffin, Bowling Green, and Fremont sites all withdraw water directly from northwestern Ohio rivers.

The 1982 pesticide concentrations were only slightly lower than those found in 1981 in spite of the fact that 1982 was a "dry year" in comparison to 1981, a "wet year." In 1981, large runoff events occurred in early June due to strong storm events and large rainfalls. It was observed that chlorpyrifos concentrations in Sandusky Bay often reached 1.5 ug/l which could be an acutely toxic level to local fish species.

(3) Title: Herbicide Contamination in Municipal Water Supplies of Northwestern Ohio

Summary: Six herbicides (atrazine, alachlor, metolachlor, linuron, cyanazine, and simazine) were analyzed in the finished tap waters at three municipal water treatment plants (Tiffin, Fremont, Bowling Green) and in the two rivers (the Sandusky River which supplies the Tiffin and Fremont water treatment plants and the Maumee River which supplies the Bowling Green water treatment plant) which serve as a source for raw water. This monitoring study was conducted in the period from May 15 to August 1, 1983, since this time period encompasses the maximum herbicide concentrations in the northwestern Ohio rivers (Sandusky and Maumee). The herbicide concentrations in the finished tap waters at the Tiffin and Bowling Green plants were similar to the concentrations in the raw river waters (Sandusky and Maumee). For detailed information, see Table 2 of that report, attached hereto. The use of an activated carbon filter greatly reduced the concentrations of soluble herbicides.

In 1983 relatively low concentrations of herbicides were found due to the late occurrence of rainfall of sufficient size to induce runoff events as compared with previous years, and because the acreage of corn was lower by 30% due to the PIK (payment-in-kind) program, thus resulting in fewer treated areas. The herbicide concentrations found in northwestern Ohio rivers were much higher than the concentrations reported as of 1977 in other municipal water supplies in the United States. (For details, see Table 4 of that report attached hereto.)

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(4) Title: Fluvial Transport and Processing of Sediments and Nutrients in Large Agricultural River Basins.

Summary: This report summarizes in detail a number of studies conducted on the transport of nutrients and sediments at 12 U.S. Geological Survey stream gauge stations in northwestern Ohio. The studies were conducted from 1975 to 1979. The report included information on: (1) watershed size (ranged from 171 km^2 to 16,395 km^2), (2) land use patterns, (3) soil structure and type; (4) methods of collecting river transport data, and (5) loadings of nutrients and sediments.

The data from these studies were used for (1) The Lake Erie Wastewater Management Study; (2) regional water quality management programs; (3) evaluating and/or calibrating several water quality models developed by ERL Athens/EPA; and (4) development of a generalized river transport model.

The data show many patterns of nutrient and sediment transport in these river systems and should be useful in evaluating the effectiveness of conservation tillage in controlling agricultural non-point source pollution. The author (Dr. Baker) stated that conservation tillage is very effective in reducing erosion and phosphorous loading but may increase the concentrations of soluble herbicides and nitrates in rivers and lakes.

(5) Title: Studies of Sediment, Nutrient and Pesticide Loading in Selected Lake Erie and Lake Ontario Tributaries

Part IV
Pesticide Concentrations and Loading in Selected Lake Erie Tributaries - 1982

Summary: This report discusses the effects of conservation tillage on pesticide runoff in the Lake Erie Basin. In 1982, pesticide transport was analyzed at U.S.G.S. gauging stations on the River Raisin in Michigan; on the Maumee, Sandusky and Cuyahoga Rivers in Ohio; and at conservation tillage demonstration project areas in the Honey Creek and Lost Creek watersheds. Seventeen currently used pesticides and two major metabolites were measured in the water of these sampling stations. The concentrations of these pesticides as described in Table 6 of that report, are the same data described in Table 3 of the report, "Pesticide Monitoring Notes 1982", reviewed in this memorandum.

The pesticide unit area load in g/ha in 1982 for five major herbicides in three northwestern Ohio watersheds (Honey Creek, Sandusky and Maumee) are shown in the attached Table 7 of that report. The herbicide loads were 5 to 10 times smaller than the corresponding loads observed at the Honey Creek Stations during the heavy storm in June 1981. Comparison of herbicide loads in 1981 and in 1982 at the Honey Creek Station are shown in Table 9 of that report (attached).

(6) Title: Studies of Sediment, Nutrient and Pesticide Loading in Selected Lake Erie and Lake Ontario Tributaries

Part V
Sediment and Nutrient Loading Summary

Summary: This report concludes that these studies have produced a comprehensive and consistent data base for the calculation of tributary loads (Raisin, MI; Maumee, OH; Honey Creek, OH; Sandusky, OH; Cuyahoga, NY; Genesee, NY; Oswego, NY; Black, NY) to Lake Erie and Ontario for the year 1982. The unit area nutrient and sediment loadings from these rivers differ from one another and reflect a combination of differences in both land use and land resources. The "event response" (for events such as storms and large rainfalls) character of northwestern Ohio rivers is clearly evident in the data. The calculation of tributary loadings to the lower lakes is currently in progress and reports will be forthcoming.

Comments on the Six Documents Reviewed

A. Quality Assurance

1) Quality control for the pesticide analytical methodology was in place in all six studies.

2) Sampling methodology was presented for all studies.

3) The percent recoveries of all pesticides from natural water samples were determined.

4) Quality control studies were conducted on nutrient and sediment measurements.

B. Usefulness of Data

1) The pesticide monitoring data contained in these documents will be useful in determining runoff of pesticides for the measured years and in projecting runoff of pesticides in future years for northwestern Ohio Rivers and the Great Lakes (Erie, Ontario) using meteorological models.

2) Environmental concentrations are available for measured pesticides for the period studied in the rivers and/or tributaries of these Great Lakes (Erie and Ontario).

3) Effect of conservation tillage on runoff of pesticides during storm events and large rainfall events can be evaluated for the study years (1981, 1982, etc.).

C. Limitation of These Studies

1) Estimated Environmental Concentrations (EEC's) cannot be calculated or projected for farmlands in other watersheds or tributaries. Region V wishes to study at least 26 tributaries (rivers) where lands are used primarily for agricultural crops (e.g., 12, OH; 2, IN; 1, PA; 4, NY; 2, MI; 10, WI (Telecon with M. Gewirtch of Region V, EPA.)

2) A precise, reliable projection model for weather events (large rainfall, storm, hurricane, etc.) will be needed to obtain meaningful EEC's for any pesticides used in Region V in future years.

3) Estimated Environmental Concentrations (EEC's) for smaller water bodies, such as ponds adjacent to or within the farmlands, cannot be obtained from these pesticide monitoring data.

Recommendations

1) The data from pesticide monitoring studies conducted as part of the Great Lakes Program by Region V of EPA should be included in "STORET" data base.

2) EAB/OPP should investigate further the Region V efforts and related state efforts on monitoring pesticides in tributaries adjacent to farmlands.

3) EAB/OPP should investigate pesticide monitoring programs in other regions and possibly provide technical assistance on experimental design, analytical methodology, and data handling.

4) Regional monitoring studies such as these should be incorporated into the "National Pesticide Monitoring Plan."

5) EEB/OPP should receive this data in order to evaluate the chronic effects of the concentrations of pesticides on aquatic biota (fish, invertebrates, and microorganisms) from runoff events.

6) The pesticide concentrations in tap water should be considered in evaluating the toxicological significance of chronic human dietary exposure and dermal exposure via bathing and showering.

Table 3 Peak pesticide concentrations observed during the April - August sampling period in 1982

	Maumee (6,313 mi^2) 50 Samples		Sandusky (1,251 mi^2) 50 Samples		Raisin (1,042 mi^2) 25 Samples		Melmore (149 mi^2) 63 Samples		Defiance (4.3 mi^2) 48 Samples		Cuyahoga (707 mi^2) 22 Samples	
	Ug/L	Date	Ug/L	Date	UG/L	Date	Ug/L	Date	Ug/L	Date	Ug/L	Date
Linuron	2.32	06/02	3.51	05/26	2.79	05/28	13.1	05/25	5.66	06/21	7.68	06/14
EPTC	.187	06/02	.168	05/29	.103	05/29	.82	05/25	.837	05/28	2.84	05/11
Butylate	.160	06/02	.184	05/28	.094	06/02	.213	05/24	.248	07/11	.051	06/28
Ethoprop	.243	06/02	.129	07/29	.031	07/17	1.13	05/17	.112	05/22	.314	05/11
DIA	2.79	07/15	1.98	05/28	.635	06/02	4.65	05/25	5.81	07/11	3.62	06/07
DEA	1.37	07/13	2.57	07/08	.569	05/30	3.31	05/24	2.97	07/11	.43	05/24
Treflan	.056	08/06	.097	06/03	.041	06/02	.093	06/03	.316	07/11	.240	07/19
Phorate	.009	06/02	.019	05/28	.011	06/05	.022	05/28	.020	06/07	.019	05/11
Simazine	2.85	06/13	2.52	07/06	4.95	08/07	3.60	06/29	3.3	07/11	10.7	08/09
Atrazine	9.5	05/28	18.8	05/28	9.26	05/30	48.4	05/25	38.9	05/22	1.5	05/24
Terbufos	.158	07/15	.104	07/08	.127	07/03	.124	07/08	.09	07/13	.058	06/14
Fonofos	.026	05/30	.050	05/30	.205	05/28	.024	05/26	.08	05/28	.00	---
Diazinon	.023	05/27	.016	06/30	.010	07/17	.008	06/29	.013	06/28	.083	08/09
Cyanazine	4.26	05/30	3.82	05/26	4.29	05/29	1.49	05/25	10.1	05/22	6.62	05/03
Metribuzine	3.35	05/30	8.20	05/25	1.72	05/30	8.24	05/25	5.4	05/23	.284	07/19
Alachlor	9.27	05/28	18.19	05/29	8.16	05/29	6.96	05/25	18.5	05/22	.60	07/19
Metolachlor	10.1	05/28	40.6	05/25	3.30	05/28	90.8	05/28	12.7	05/29	.733	08/02
Chlorpyrifos	1.04	06/02	1.98	05/28	1.42	05/30	2.69	05/29	4.43	05/29	.147	05/24
Penoxalin	.37	06/11	.343	05/31	.448	06/01	.65	05/27	2.48	05/28	.793	07/19

Table 2. Average herbicide concentrations during the period from May 28 to July 27, 1983 at the river stations and in finished tap water.

Herbicide	Sandusky River ug/l	Tiffin Tap Water ug/l	Fremont Tap Water ug/l	Maumee River ug/l	B.G. Tap Water ug/l
Simazine	0.26	0.30	0.077	0.44	0.19
Atrazine	3.55	3.31	0.90	3.38	2.13
Alachlor	1.24	1.08	0.22	3.11	1.87
Metolachlor	5.63	5.72	0.81	3.71	2.00
Cyanazine	0.74	0.75	0.29	1.36	0.85
Metribuzin	0.99	0.02	0.03	1.77	0.03
DEA*	0.70	0.60	0.24	0.63	0.32
DIA**	0.49	0.53	0.24	0.45	0.33
No. of Samples in period	(23)	(18)	(15)	(23)	(16)

*desethylatrazine
**deisopropylatrazine

from: Herbicide Contamination in Municipal Water Supplies of Northwestern Ohio.

Table 4. Comparison of peak herbicide concentrations in tap water of Tiffin, Fremont, and Bowling Green, Ohio for 1983 with previous measurements in Tiffin and maximum values reported in the United States as of 1977.

	Tiffin Tap Water 1983 ug/l	Fremont Tap Water 1983 ug/l	Bowling Green Tap Water 1983 ug/l	Tiffin Tap Water 1980-82 ug/l	Max. Obs. Conc. 1977* ug/l
Simazine	0.63	0.13	.35	1.90	detected
Atrazine	7.64	1.22	5.20	30.0	5.1
Alachlor	2.73	0.47	5.91	14.3	2.9
Metolachlor	13.65	1.33	4.75	24.2	no data
Linuron	0.61	—	0.39	—	no data
Cyanazine	1.49	0.39	1.92	2.40	detected

*Taken from National Research Council, 1977, Drinking Water and Health.

from: Herbicide Contamination in Municipal Water Supplies of Northwestern Ohio.

Table 7. Pesticide loads and unit area loads for the period between May 1, 1982 and July 31, 1982 at three Northwestern Ohio stream gauging stations.

Pesticide	Total Loads, Kg			Unit Area Loads, g/ha		
	Honey Cr.	Sand. R.	Maumee R.	Honey Cr.	Sand. R.	Maumee R.
Metolachlor	241	1750	2920	6.24	5.39	1.78
Atrazine	223	1600	4240	5.78	4.94	2.58
Alachlor	89.2	1290	2820	2.31	3.98	1.72
Metribuzin	27.5	518	1370	0.713	1.60	0.839
Cyanazine	24.7	226	1590	0.640	0.696	0.970
Simazine	19.7	179	1280	0.510	0.551	0.779
Linuron	62.4	264	571	1.62	0.816	0.348
DEA	29.4	168	490	0.762	0.518	0.299
DIA	52.0	130	629	1.35	0.400	0.383
Chlorpyrifos	9.47	135	226	0.245	0.417	0.138
Penoxalin	2.38	19.3	95.4	0.061	0.060	0.058
Butylate	0.70	12.3	22.9	0.018	0.038	0.014
Ethoprop	1.06	3.76	34.7	0.027	0.012	0.021
Terbufos	0.98	4.59	33.9	0.025	0.014	0.021
Fonofos	0.04	1.97	16.4	0.001	0.006	0.010
Trifluralin	0.80	2.76	0.6	0.021	0.008	0.000
EPTC	0.73	9.85	12.6	0.019	0.030	0.008
Phorate	0.15	0.96	10.6	0.004	0.003	0.006
Diazinon	0.26	0.20	1.8	0.007	0.001	0.001

from: Studies of sediment, nutrient and pesticide loading in selected Lake Erie and Lake Ontario Tributaries

Part IV

Pesticide Concentrations and Loading in Selected Lake Erie tributaries - 1982

Table 9. A comparison of herbicide loads, herbicide concentrations, and water discharge during the first two runoff events of 1981 and 1982 at the Honey Creek, Melmore Station.

	June 2 - June 21, 1981		May 23 - June 13, 1982	
	Load Kg	Time Wt. Conc. Ug/L	Load	Time Wt. Conc. Ug/L
Atrazine	1295	22.2	116.2	13.9
Alachlor	903	13.9	59.4	7.6
Metolachlor	1106	17.8	185.8	14.2
Metribuzin	153	2.92	19.9	2.12
Discharge	$15.2 \times 10^6 m^3$		$4.4 \times 10^6 m^3$	

from: Studies of sediment, nutrient and pesticide loading in selected Lake Erie and Lake Ontario tributaries

Part IV

Pesticide Concentrations and Loading in Selected Lake Erie Tributaries - 1982

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OF NORTHWESTERN OHIO

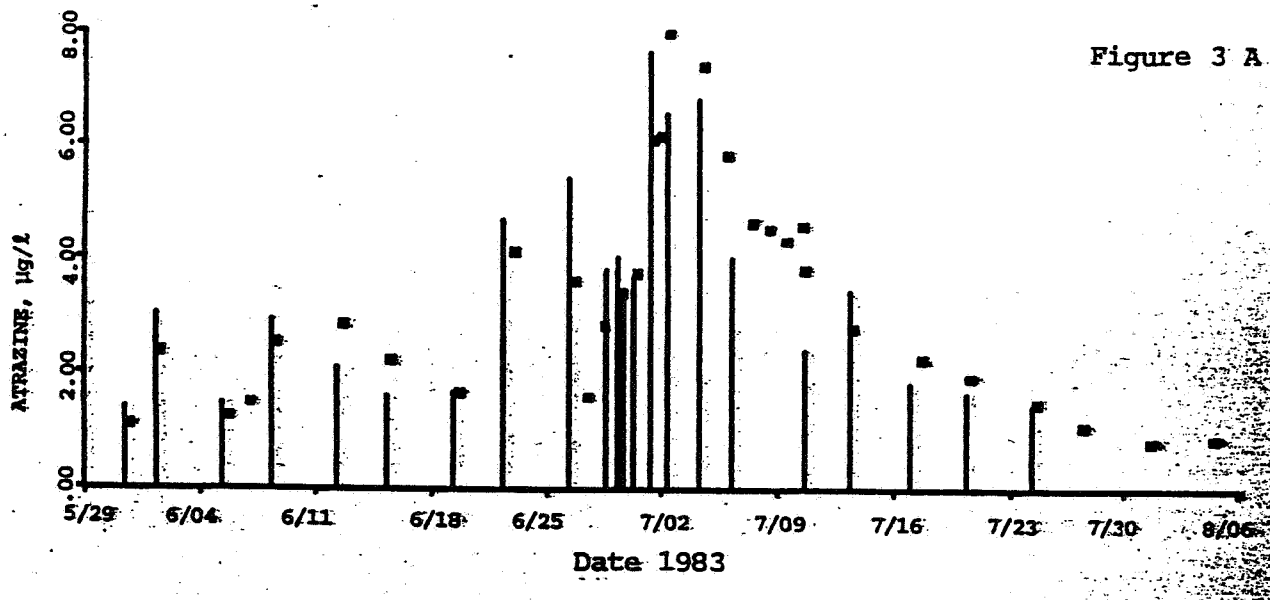

Figure 3 A

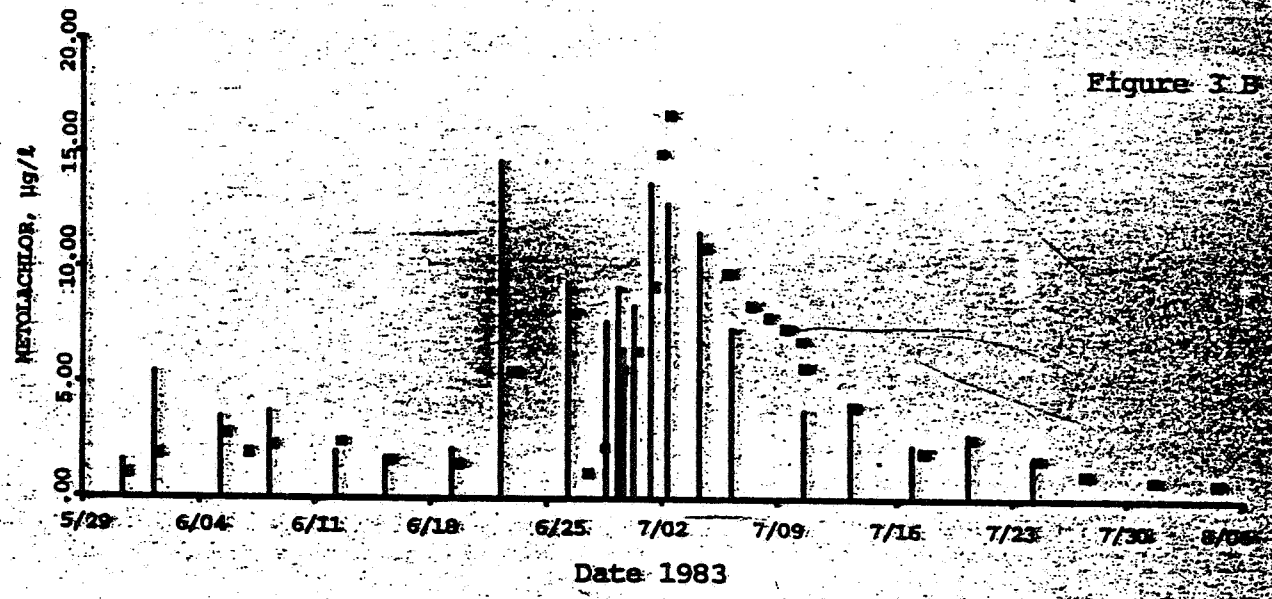

Figure 3 B

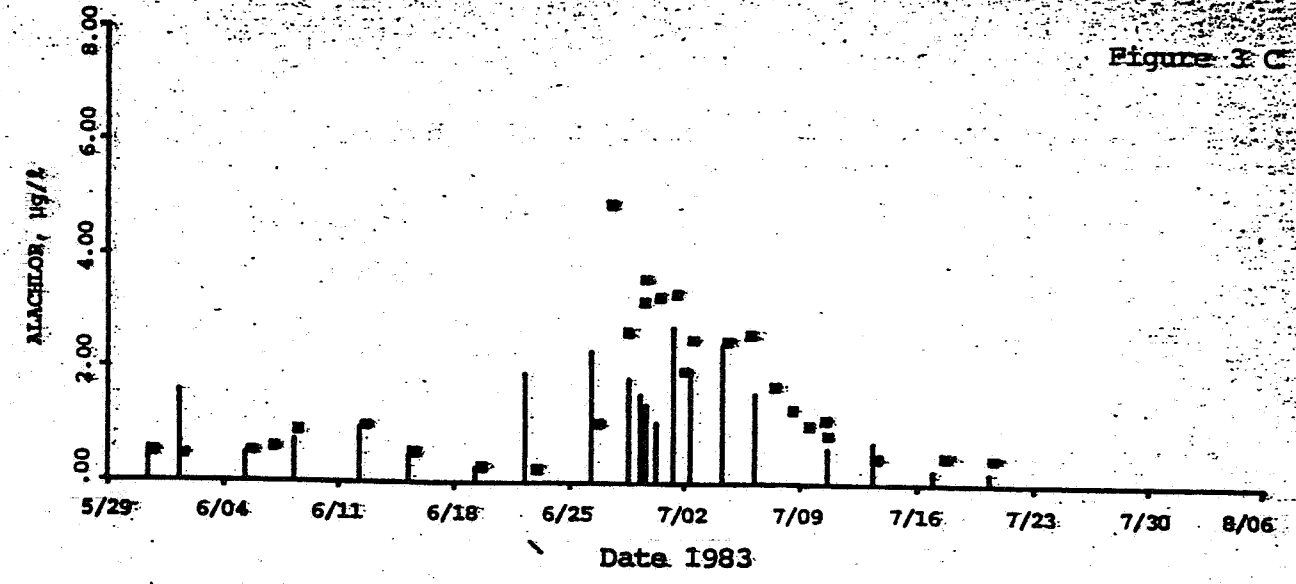

Figure 3 C

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