# Chlorinated Hydrocarbon Pesticides in Major River Basins, 1957-65

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CINCE 1957, water quality data, including I data on trace organic contaminants, have been collected periodically through a system of operated cooperatively sampling stations located on the major rivers and Great Lakes (1). During the ensuing 8 years about 6,000 samples were collected, with the carbon adsorption method (CAM) (2), at more than 100 stations. Initially, the extracts from these samples were examined with the best methods then available. The concentration values for the substances extracted from the carbon by chloroform and by alcohol have been reported routinely (3-8). A variety of chemicals has been identified in these extracts. The dried extracts have been stored for future reference.

Concurrently, improvements in sampling (9, 10) and analytical technology (2) for one type of organic contaminant, chlorinated hydrocarbon pesticides, have been substantial. Thus, recently, when widespread public awareness of the adverse effect of pesticide pollution developed, it was possible to retrieve and analyze

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This report presents and discusses the results of the 1965 synoptic survey as they relate to the 1964 data ( $\mathscr{B}$ ), and summarizes and comments on the historical occurrence of pesticides in a selection of surface water CAM samples taken during 1957-65.

### Sampling

All sampling was conducted through the coordinated and cooperative efforts of Federal, State, local, and private agencies which jointly operate an existing system of water pollution surveillance stations in each river basin.

The stations selected for sampling in the 1965 synoptic survey closely paralleled those chosen for the 1964 effort, which attempted minimum coverage of the several hydrological basins with emphasis on areas of known pesticide usage. September was selected for the sampling, as previously, to coincide generally with the postapplication, low-flow period.

Also, 600 earlier CAM samples were selected

#### Table 1. Synoptic survey of chlorinated hydrocarbon pesticides, U.S. river basins, September 1965

	Concentration in micrograms per liter												
Location <sup>1</sup>	Dieldrin	Endrin	DDT	DDE	DDD	Aldrin	Heptachlor	Heptachlor epoxide	BHC				
Northeast Basin													
Connecticut River: Enfield Dam. Conn. (82)	ND	ND	ND	ND	ND	ND	ND	ND	Р				
Northfield, Mass. (11)	P	ND ND	ND ND	ND ND	ND	ND	ND	ND	NÔ				
Wilder, Vt. (103)	ND ND	ND ND	ND ND	ND ND	ND P	ND ND	ND ND	ND ND	ND ND				
Lake Erie: Buffalo, N.Y. (14)	ND	ND	ND	ND	ND	ND	ND	0.002	ND				
Connecticut River: Enfield Dam, Conn. (82) Northfield, Mass. (11) Wilder, Vt. (108) Hudson River: Poughkeepsie, N.Y. (18) Lake Erie: Buffalo, N.Y. (14) Merrimack River: Lowell, Mass. (19) St. Lawrence River: Massena, N.Y. (63)	0.068 ND	ND ND	ND ND	ND ND	0.007 .010	ND ND	P 0.031	ND .017	ND ND				
North Atlantic Basin													
Delaware River	010	0.010	ND	ND	010	• ND	NTD	ND	ND				
Trenton, N.J. (100) Martins Creek, Pa. (61)	.018 ND	0.018 ND	ND ND	ND ND	.018 ND	ND ND	ND .025	ND P	ND ND				
Potomac River:													
Washington, D.C. (130)	.003	ND ND	ND ND	ND ND	.007 ND	ND ND	ND P	. 003 P	ND ND				
Great Falls, Md. (40) Schuylkill River: Philadelphia, Pa. (74) Shenandoah River: Berryville, Va. (87)	.014	ND	ND	ND	ND	ND	ND	P	ND				
Shenandoah River: Berryville, Va. (87)	ND	ND	ND	ND	ND	ND	ND	ND	ND				
Susquehanna River:	. 002	ND	ND	ND	ND	ND	ND	ND	ND				
Conowingo, Md. (75) Sayre, Pa. (76)	P	ND	NĎ	ND	ND	NĎ	ND	NĎ	ND				
Southeast Basin													
Apalachicola River: Chattahoochee, Fla. (57)	. 016	ND ND	ND 0.017	ND ND	ND . 012	ND ND	ND ND	ND ND	ND ND				
Chattahoochee River: Lanett, Ala. (120) Escambia River: Century, Fla. (62)	ND	ND	. 017	ND	ND ND	ND	ND	ND	ND				
Escambia River: Century, Fla. (62) Roanoke River: John H. Kerr Reservoir and		ND		ND					ND				
Dam, Va. (91) Savannah River:	ND	ND	ND	ND	ND	ND	ND	ND	ND				
Port Wentworth, Ga. (47)	. 022	ND	. 016	ND	. 006	ND	Р	ND	ND				
Port Wentworth, Ga. (47) North Augusta, S.C. (48) Tombigbee River: Columbus, Miss. (95)	.051	ND .015	ND ND	ND ND	ND ND	ND ND	ND ND	ND P	ND ND				
								1					
Tennessee River Basin Clinch River: above Kingston, Tenn. (106)	007	.015	Р	ND	ND	ND	ND	ND	ND				
Tennessee River		-	_										
Bridgeport, Ala. (77) Lenoir City, Tenn. (107)	. ND	ND	.015 ND	ND ND	ND ND	ND ND	ND .020	ND P	ND ND				
Lenoir City, Tehn. (107)	. 028	. 009	ND	ND	ND	ND	. 020	I I	ND				
Ohio River Basin	ND	ND	.004	ND	ND	ND	ND	ND	ND				
Allegheny River: Pittsburgh, Pa. (79) Kanawha River: Winfield, Dam, W. Va. (68) Monongahela River: Pittsburgh, Pa. (83)	.045	ND P	ND	ND	ND	ND ND	P	ND	ND				
Monongahela River: Pittsburgh, Pa. (83)	. 005	. 014	.016	ND	ND	ND	ND	ND	P				
Ohio River:	. 028	ND	. 023	ND	. 003	ND	ND	. 002	0.002				
Evansville, Ind. (36)	. 002	ND	ND	ND	ND	ND	ND	ND	ND				
Cincinnati, Ohio (37)	. 006	ND	ND P	ND ND	ND P	ND ND	.024 P	ND . 020	ND ND				
Cairo, III. (35) Evansville, Ind. (36) Cincinnati, Ohio (37) above Addison, Ohio (17) Wabash River: New Harmony, Ind. (105)	. 007 ND	ND ND	. 012	ND	ND	ND	. 009	.012	ND				
Lake Erie Basin													
Maumee River: Toledo, Ohio (127)	. 024	ND	ND	ND	ND	ND	ND	ND	ND				
Upper Mississippi River Basin Illinois River: Peoria, Ill. (67)	ND	ND	Р	ND	ND	ND	Р	ND	ND				
Mississinni River		ND	r		ND ND		, r	ND					
Cape Girardeau, Mo. (23)	ND	ND	ND	ND	ND	ND	ND	ND	ND				
East St. Louis, Ill. (24) Burlington, Iowa (25)	005	ND ND	P ND	ND ND	ND ND	ND ND	ND P	ND P	ND ND				
		ND	ND	ND	ND	ND	.048	. 067	ND				
Lock and Dam 3 below St. Paul, Minn. (27)_	- P	ND	ND	ND	ND	ND	ND ND		ND ND				
Lock and Dam 3 below St. Paul, Minn. (27)- Rainy River: Baudette, Minn. (96)- Red River (North): Grand Forks, N. Dak. (69)-	- ND 007	ND . 009	ND . 034	ND P	ND ND	ND ND	ND . 155	ND . 020	. 004				
Western Great Lakes Basin								_					
Detroit River: Detroit Mich (15)	018 - ND	ND ND	ND ND	.008 ND	ND ND	ND ND	.015 ND	P ND	ND ND				
St. Clair River: Port Huron, Mich. (64) Lake Michigan: Milwaukee, Wis. (65)	. 003	ND	ND	ND	ND	ND	ND	ND	ND				
Lake Superior: Duluth, Minn. (16)	_ ND	ND	ND	ND	ND	ND	ND	ND	ND				

<sup>1</sup>Numbers in parentheses are those assigned to the sampling stations by the Federal Water Pollution Control Administration, Water Pollution Surveillance System.

NOTES: All but the following samples were collected Sept. 22, 1965: Rio Grande at Alamosa, Colo., Sept. 20; Bear River at Preston, Idaho, Sept. 21; Apalachicola River at Chattahoochee, Fla., Sept. 23; Ohio River at Evansville, Ind., Sept. 23; Big Horn River at Hardin, Mont., Sept 23; Rio Grande at Laredo, Tex., Sept. 23; Connecticut River at Wilder, Vt., Sept. 23; Lake Erie at Buffalo, N.Y., Sept. 23; Schuylkill River at Philadelphia, Pa., Sept. 23; Lake Superior at Duluth, Minn., Sept. 24; Waikele Stream, Hawaii, Sept. 24. ND—indicates none detected. P—indicates presumptive. Data are reported as presumptive in instances where the results of chromatography were highly indicative but did not meet all requirements for positive identification and quantification.

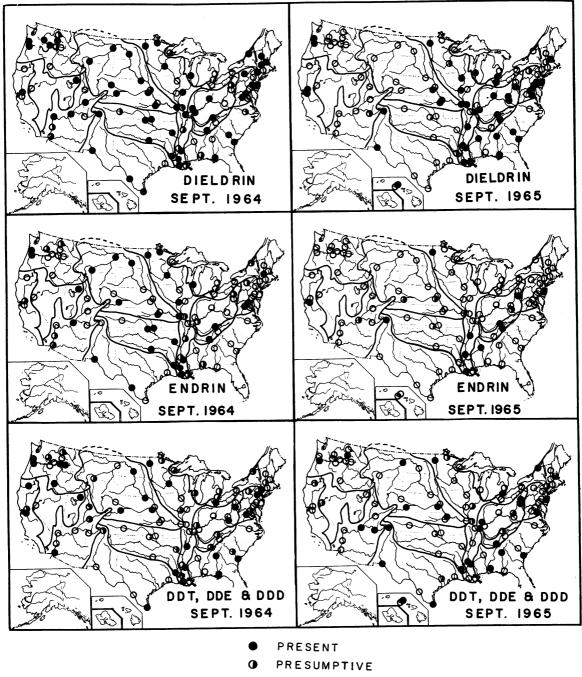
# Table 1. Synoptic survey of chlorinated hydrocarbon pesticides, U.S. river basins, September 1965—Continued

	Concentration in micrograms per liter												
Location 1	Dieldrin	Endrin	DDT	DDE	DDD	Aldrin	Heptachlor	Heptachlor epoxide	внс				
Missouri River Basin													
Big Horn River: Hardin, Mont. (104) Kansas River: DeSoto, Kans. (128) Missouri River:		ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND				
St. Louis, Mo. (28)	. 004	P	ND	ND	ND	ND	0.020	0.007	ND				
Kansas City, Kans. (29) Omaha, Nebr. (31)	023 ND	ND ND	0.016 ND	ND ND	0.011 ND	ND ND	.008 ND	.014 ND	ND ND				
Yankton, S. Dak. (32)	_ ND	ND	ND	ND	ND	ND	ND	ND	ND				
Bismarck, N. Dak. (33)	- ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND				
North Platte River: above Henry, Nebr. (94) Platte River: above Plattsmouth, Nebr. (86)	. 010	P	. 039	P	. 010	ND	ND	.002	ND				
South Platte River: Julesburg, Colo. (92) Yellowstone River: near Sidney, Mont. (55)	_ ND	P ND	. 023 . 002	ND 0.002	ND .005	ND ND	ND ND	ND P	ND ND				
Southwest River Busin Arkansas River:													
Little Rock, Ark. (131) near Ponca City, Okla. (1)	ND	ND	ND	ND	ND	ND	ND	ND	ND				
near Ponca City, Okla. (1)		ND	ND	ND	ND	ND	ND	ND	ND				
Coolidge, Kans. (2) Red River (South)	- ND	ND	ND	ND	ND	ND	ND	ND	ND				
Alexandria, La. (42)		ND	ND	ND	. 008	ND	ND	ND	ND				
Denison, Tex. (44) Verdigris River: Nowata, Okla. (109)	- ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND P				
Lower Mississippi River Basin Atchafalaya River: Morgan City, La. (132)	. 013	C. 019	ND	ND	ND	ND	. 010	ND	ND				
Mississippi River: New Orleans, La. (20)	. 005	ND	ND	ND	ND	ND	ND	ND	ND				
Vicksburg, Miss. (21)	. 004	ND	. 017	ND	ND	ND	ND	ND	ND				
Delta, I.a. (54)	004 018	. 008 . 116	. 019 ND	ND ND	ND ND	ND ND	ND ND	ND .020	ND ND				
Colorado River Basin Colorado River:													
Yuma, Arig. (3)	ND	ND	ND	ND	ND	ND	ND	ND	ND				
above Parker Dam, ArizCalif. (4)	- ND	ND	ND	ND	ND	ND	ND	ND	ND				
near Boulder City, Nev. (5) Page, Ariz. (60)	ND ND	ND P	ND .058	ND ND	ND ND	ND ND	ND P	ND P	ND ND				
Loma, Colo. (6)	. ND	ND	ND	ND	ND	ND	ND	ND	ND				
Green River: Dutch John, Utah (121) San Juan River: Shiprock, N. Mex. (93)	- ND - P	ND ND	ND . 125	ND . 009	ND ND	ND ND	ND . 012	ND ND	ND ND				
Western Gulf Basin Brazos River: Arcola, Tex. (SC5)	ND	ND	ND	ND	Р	ND	ND	ND	ND				
Rio Grande:													
Brownsville, Tex. (71) Laredo, Tex. (45)	ND ND	ND ND	ND ND	ND ND	.026 ND	ND ND	.035 ND	P ND	ND ND				
El Paso, Tex. (46)	. 003	ND	.012	ND	ND	ND	ND	ND	ND				
below Alamosa, Colo. (72)	029	. 014	.149	ND	ND	ND	Р Р	ND	ND				
Sabine River: near Ruliff, Tex. (73) Paciác Northwest Basin	ND	ND	ND	ND	ND	ND	P	Р	ND				
Clearwater River: Lewiston, Idaho (97)	. ND	ND	ND	ND	ND	ND	ND	ND	ND				
Clatskanie, Oreg. (7)	. 003	ND	ŃD	ND	ND	ND	ND	ND	ND				
McNary Dam, Oreg. (81) Pasco, Wash. (9)	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND				
Pend Oreille River: Albeni Falls Dam, Idaho		ND	ND	ND	AD.	ND							
(113)	. ND	ND	ND	ND	ND	ND	ND	ND	ND				
Snake River: Ice Harbor Dam, Wash. (115)	. ND	ND	ND	ND	ND	ND	ND	ND	ND				
Wawawai, Wash. (49)	ND	ND	ND	ND	ND	ND	ND	ND	ND				
Payette, Idaho (102) Spokane River: Post Falls Dam, Idaho (114)	- ND - ND	ND ND	ND .037	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND				
Yakima River: Richland, Wash. (89)	.005 ND	ND ND	ND ND	ND ND	.013 ND	ND ND	ND ND	ND .002	ND ND				
California Basin													
Klamath River: Dear Keno, Oreg. (78)	_ ND 011	ND ND	ND ND	ND ND	P ND	ND ND	ND .020	ND .019	ND ND				
Sacramento River: Greens Landing, Calif. (116) San Joaquin River: near Vernalis, Calif. (122)	. 005	. 005	ND	ND	ND	ND	ND	ND	ND				
Great Basia Bear River: Preston, Idabo (125) Truckee River: Farad, CalifNev. border (88)	ND ND	ND ND	ND P	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND				
Hewaii Waikele Stream (SC15)		ND	ND	ND	. 006	ND	ND	ND	ND				
Kiikii Stream (SC16)		ND	ND	ND	ND	ND	ND	ND	ND				

for analysis, based on the results of the 1964 synoptic survey or in response to requests for information in areas experiencing fish kills assumed to be associated with pesticide pollution. Particular emphasis was given to analyzing CAM extracts from June or July samples to include periods early in the growing season.

Carbon adsorption systems. Two types of

Figure 1. Occurrence of chlorinated hydrocarbon pesticides in major U.S. river basins, synoptic surveys of 1964 and 1965



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carbon adsorption systems have been employed. The first type (2) passes the water over a cylindrical cartridge containing coarse and fine carbon at a rate of 0.5 gallon per minute (gpm). Sample volumes are 1,000 or 5,000 gallons. A settling tank or sand strainer is usually necessary to prevent suspended matter from clogging the cartridge. The second, more recent, type (2, 12) employs a cartridge filled with only fine carbon through which the sample is passed at 100 milliliters per minute (approximately 1/32 gpm). The sample volume is 1,000 liters (approximately 250 gallons). No removal of suspended material is necessary. It is recognized that quantitative adsorption on, and desorption from, carbon of all organic substances does not always occur. Thus, positive values for substances measured are minimum values. Moreover, in the use of the 0.5-gpm system, the exclusion of the suspended material may have eliminated some organic compounds adsorbed on the sediment.

Grab sampling. Two 1-quart grab samples

were requested for September 22, 1965, from each of the 99 points listed in table 1. Samples were collected in glass jars fitted with screwtype caps lined with Teflon (2).

### **Analytical Procedures**

Carbon adsorption systems. Carbon adsorption extracts, except as noted, were analyzed according to the methods previously compiled (2, 11). These methods will detect dieldrin, endrin, DDT, DDE, DDD, aldrin, heptachlor, heptachlor epoxide, and BHC.

Samples were extracted with chloroform followed by ethanol according to the standard procedures. The carbon chloroform extracts were subjected to a silica gel column cleanup. The aromatic fraction thus obtained was subjected to thin-layer chromatography (13) and electron capture as well as microcoulometric titration gas chromatography.

The electron-capture detector is specific for all electronegative compounds. The microcoulometric titrator is specific for halogens.

Basin	Dieldrin	Endrin	DDT	DDE	DDD 1	Aldrin	Heptachlor	Heptachlor epoxide 1	внс
Northeast:		_		-				<i>(</i> 1)	
1964 1965	72 29	29 0	14 0	<b>43</b> 0	<sup>(1)</sup> 43	14 0	0 29	<sup>(1)</sup> 29	14
North Atlantic: 1964	62	38	38	38	12	0	25	(1)	12
1965 Southeast:	75	12	0	0	25	0	25	50	(
1964 1965	72 72	14 14	43 43	29 0	<sup>(1)</sup> 29	0	<b>43</b> 14	<sup>(1)</sup> 14	0
Dhio, Lake Erie, and Tennessee: 1964	55	36	50	33	(1)	8	17	( <sup>1)</sup>	
1965 Upper Mississippi:	75	33	58	0	17	0	42		17
1964 1965	88 62	62 12	50 38	<b>50</b> 12	(1) 0	12 0	12 50	<sup>(1)</sup> 38	12
Western Great Lakes: 1964	50	25	50	50 25	(')	25	25 25	( <sup>1</sup> ) 25	9
1965 Missouri:	50	0							
1964 1965	91 36	54 27	27 <b>36</b>	45 18	(1) 27	9 0	18 18	<sup>(1)</sup> 36	
Southwest-Lower Mississippi: 1964	100	100	42 18	42	(י)	0	25	(1)	5
1965 Colorado:	55	27		0	-	0	18	<b>9</b>	
1964 1965	72 14	<b>43</b> 14	43 29	29 14	<b>(</b> <sup>1</sup> )	29 0	14 29	<sup>(1)</sup> 14	
Western Gulf: 1964	80	40	40	40	(1)	20	0	(1)	ç
1965 Pacific Northwest:	33	17	33	0	33	0	50	33	
1964 1965	70 18	40 0	70 9	40 0	( <sup>1</sup> ) 9	10 0	10 0	<sup>(1)</sup> 9	Ċ
California-Great Basin: 1964		40	80	40	(1)	20	0	<sup>(1)</sup>	9
1965 Hawaii: 1965	40 50	20 0	20 0	<b>0</b> 0	20 50	0	20 0	20 0	
Total:	74		44	39	(1)	10	17	(1)	
1964 1965	47	46 16	44 25	<b>39</b> 5	(*)	0	24	() 25	1

 Table 2. Percent of grab samples showing positive or presumptive evidence of chlorinated hydrocarbon pesticides in 1964 and 1965 synoptic surveys

<sup>1</sup> 1964 analyses were at a lower level of sensitivity and not comparable with 1965 results.

# Table 3. Occurrence of positive and presumptive pesticide determinations in carbon adsorption method samples and in grab samples collected during 1964 and 1965 synoptic surveys

	1	- T		1		1						1		1	-	1		1	
		Di	eldrin	E	ndrin	D	DT	I	DE	D	DD	A	ldrin	Нер	tachlor		tachlor oxide	F	внс
Water year	Number samples	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)
Northeast Basin																			
CAM samples: 1958	67	5 4 3 5 6 7 5 5 2	0.004 .011 .011 .009 .005 .023 .010 >.071 .068	1 0 1 1 0 0 2 0	0. C01 P . 001 . 025	3 1 0 0 0 1 1 0	0.004 P 	2 1 3 2 0 1 3 3 0	0.004 P .006 P <.001 .002 .004	5 1 3 4 2 4 0 3	0.006 .003 .003 .003 .006 .P .010	0 0 1 0 1 0 1 0	<0.001 P P	0 0 0 0 0 0 0 0 0 2		0 0 0 0 0 1 0 2	0.001	1 0 1 1 0 1 0 1	P  P C. 003 P P
North Atlantic Basin CAM samples:																			
1958	2 1 7 5 10 9 5 8 8	2 1 7 5 8 9 5 5 6	<. 001 P . 026 . 010 . 035 . 033 . 010 >. 040 . 018	1 0 1 0 1 1 2 3 1	P P P P P P S. 094 .018	1 0 2 1 2 4 4 3 0	P .006 .001 .003 .070 .002 .026	2 0 4 2 3 4 4 3 0	<. 001 . 002 . 001 . 002 . 012 . 002 . 002	1 5 1 7 5 4 1 2	. 001 . 002 . 022 . 003 . 011 . 080 . 004 . 083 . 018	0 0 1 1 0 0 0	P P	1 0 0 0 0 0 2 2	P   P . C25	2 0 1 2 0 2 1 0 4	.007 .001 <.001 .008 <.001 .003	1 2 0 0 1 1 0	P P P P
Southeast Basin																			
CAM samples: 1958 1959. 1960 1961 1962 1963 1964 Grab samples: 1964 1965	2 1 6 3 14 10 7 7	2 1 6 3 13 9 5 5	. 002 . 010 . 011 . 013 . 020 . 056 . 035 >. 118 . 100	1 0 1 0 1 1 1 1	<. 001 . 001 P . 001 P . 015	1 2 1 1 8 5 3 3	P . 002 . 002 . 001 . 011 . 005 . 020 . 017	2 1 3 1 6 6 2 0	0.002 <.001 0.001 <.001 <.001 0.001 0.002 0.004	2 1 5 3 2 10 8 0 2	. 031 . 002 . 008 . 005 . 007 . 006 . 008	0 0 1 1 3 1 0 0	P P P .002 P	0 0 0 0 0 0 3 1	  P P	0 0 0 0 0 0 0 0	   P	0 1 3 2 0 1 0 0 0 0	P .022 P 
Ohio, Tennessee, and Lake Erie Basins		_												_	_				
CAM samples: 1958 1960 1961 1962 1962 1963 1964 Grab samples: 1964 1965	4 4 3 6 5 11 18 12 12	3 4 3 6 4 9 17 6 9	. 020 . 055 . 021 . 004 . 008 . 006 . 005 . 015 . 045	0 0 0 2 4 7 4 4	P .012 P .015 .014	0 0 0 2 4 6 7	       	0 0 0 2 9 4 0	. 004	0 2 1 2 2 14 0 2	. 002 P P . 006	0 0 0 0 1 1	 P P	0 0 0 0 0 2 5	  P .024	0 0 0 0 0 0 0 0 0		0 0 1 1 0 0 0 0 0 2	 . 002 P 
Upper Mississippi								-		_									
River Basin           CAM samples:           1958	4 2 4 7 2 15 130 8 8 8 8	0 2 4 5 2 14 36 8 7 4	.004 <.001 .010 <.001 .067 .007 .002 .008 .024	0 1 1 1 9 0 5 1	. 013 P . 001 . 007 . 004 . 023 . 009	0 0 1 0 1 3 1 4 3	<. 001 P <. 001 P . 072 . 034	0 2 0 0 7 2 4 1	<. 001 . 002 P . 011 P	0 0 1 2 0 2 8 0 0 0	P .002 .001 <.001	0 0 0 0 5 1 1 C	 P P P	0 0 0 0 0 0 0 1 4	  P . 155	0 0 1 0 0 0 0 0 0 0 0 3	P   . 067	0 0 0 0 2 0 0 1	 P 
Western Great Lakes Basin           CA M samples:           1958	1 3 3 4	0 2 3 3	<.001 .002 <.001	0 0 0 0		0 0 0 1	. 001	0 1 1 1	P P . 004	0 1 1 1	<.001 .001 <.001	0 0 0 1	 P	0 0 0 0		0 0 0 0		0 0 0 0	

Notes: Additional samples analyzed for dieldrin and endrin only: 1 12, 2 2, 3 48, 4 1, 5 62, 6 1.

P-indicates presumptive.

# Table 3. Occurrence of positive and presumptive pesticide determinations in earbon adsorption method samples and in grab samples collected during 1964 and 1965 synoptic surveys—Continued

		Di	aldrin	E	drin	D	DT	D	DE	D	DD	А	ldrin	Нер	tachlor	Нер ер	tachlor oxide	F	внс
Water year	Number samples	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen-
1962 1963 1964	<b>3</b> 2 7	2 0 5	0.001 <.001	0 0 2	<.001	0 1 3	 P P	1 0 2	P P	2 0 4	0.004 P	0000		003	 P	0 0		0 0 0	
1964 rab samples: 1964 1965	4	22	. 007 . 018	10	. 006	2 0		2 1	P 0.008	0		1 0	P	1	P 0.015	0	P	0	
fissouri River Basin AM samples: 1958 1959 1960 1961	4 6 6	344	.005 .005 .002	1 0 2	P .004	0 0		0 0 0	  P	000		000000000000000000000000000000000000000		0 0 0 0		0 0 1 0	 P	1 0 0	<b>Q</b> . 
1962 1963 1964	7 8 8 14	5 7 7 10	.008 .008 .006 .008	2 4 1 4	P .003 P .001	0 1 1 3	P <.001 <.001	1 2 1 4	.003 P <.001	1 4 9	.001 .004 .002 .002	0 1 3	<.001 P	000000000000000000000000000000000000000		0 1 0 0	0. 002	1 2 1 1	<.
rab samples: 1964 1965	11 11	10 4	. 023 . 023	6 3	. 026 P	3 4	. 024 . 039	5 2	. 018 . 002	0 3	.011	1 0	P	2 2	P .020	0 4	. 014	0 0	
uthwest Basin M samples: 1958	1	1	. 002	0		0		0		1	<. 001	0		0		0		0	
1959 1960 1961	0 0 0																		
1962 1963 1964	1 6 18	1 5 7	.001 .001 .002	0 6 6	. 007	0 3 6	P . 005	0 4 6	P . 001-	0 5 8	.011	0 1 1	. 006	0 0 0		0 0 0		0 0 0	
ab samples: 1964 1965	6 6	6 1	.008 P	5 0	. 014	2 0	. 031	1 0	P	0 1	. 008	0 0		1 0	P	0 0		0 1	
eer Mississippi tieer Busin M samples: 1958 1959	34	3 4 3 5	. 001	3	. 004	1 2	P P	1 2	PP	02	. 001	0		0		C		0	
1960 1961 1962 1963 1964	3 6 3 12 327	3 12 72	. 002 . 022 . 015 . 058 . 122	3 2 3 12 74	.064 .029 .160 .214 .150	1 4 1 1 12	P P P .010	1 3 0 0 11	P P 	0 2 1 1 8	P .001 P P P	0 0 0 4	 P	0 0 0 0 0		C 1 0 0 1	Р  Р	1 0 0 5	
1965 ab samples: 1964 1965	433 6 5	31 6	.008	22 6 3	. 015 . 025 . 116	9 3 2	. 019 . 047 . 019	11 4 0	. 011 . 007	24 0 0	. 012	3 0 0	P	2 2 1	.002 P .010	11 0 1	. 001	5 1 0	
orade River Busin M samples: 1958	0	5	. 018	3	. 110	2	. 019	v		v		U		•	. 010	•			
1959 1960 1961	0 1 0	1	. 001	0		0		0		1	. 001	0		0		0		0	
1962 1963	1 0	0		0		0		0		0	·····	0		0		0		0	
1964 ab samples: 1964 1965	2 7 7	0 5 1	. 008 P	0 3 1	. 012 P	0 3 2	. 021 . 125	0 2 1	. 004	1 0 0	P	0 2 0	. 085	0 1 2	P . 012	0 1	P	0	
stern Gulf Basin M samples: 1958		4	. 012	1	. 006	3	. 052	3	. 004	4	. 009	0		0		0		1	
1969 1969 1961 1961 1962 1963 1964	4 3 5 4 10 7	12 4 3 3 6 6	. 012 . 005 . 002 . 008 . 001 . 005 . 001	1 1 3 4 3 5	.005 .001 .002 .008 .009 .011 .004	3123273	. 052 . 007 . 032 . 010 . 007 . 144 . 009	3233244	. 004 . 002 P . 002 . 002 . 004 . 004	1334473	. 009 . 004 . 006 . 012 . 009 . 019 . 010	0 1 0 0 0	P	0 0 0 0 0		0 1 0 0 0	P	0 1 1 1 2 0	
ab samples: 1964 1965	1 5 6	4	.001 .032 .029	5 2 1	.001 .067 .014	22	.009 .025 .149	20	P	0 2	. 010	1 0	Р	03	. 035	0 2	P	00	

Table 3-Continued on p. 146.

# Table 3. Occurrence of positive and presumptive pesticide determinations in carbon adsorption method samples and in grab samples collected during 1964 and 1965 synoptic surveys—Continued

		Die	eldrin	En	ıdrin	D	DT	D	DE	D	DD	A	ldrin	Hep	tachlor	Hep ep	tachlor oxide	В	нс
Water year	Number samples	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)	Number positive	Maximum concen- tration (µg./1.)
Pacific Northwest Basin           CAM samples:           1959           1960           1961           1962           1964           1965	3 4 1 7 5 12 13 10 11	2 4 1 6 3 7 12 7 2	<. 001 . 002 . 001 . 002 . 002 . 002 . 003 . 003 . 015 . 005	0 0 0 1 0 0 1 1 <b>4</b> 0	P P 0.019	1 2 0 1 1 5 4 7 1	0.005 .008 .004 .003 .004 <.001 .034 .037	1 3 0 3 2 3 5 4 0	P 0.001 .002 .001 .002 <.001 .005	1 2 0 3 3 4 10 0 1	<. 001 . 003 . 003 . 001 . 003 . 002 . 013	1 0 0 0 1 1 0	P 0.003 	0 0 0 0 0 0 0 0 0 1 0	, , P	0 0 0 0 0 0 0 0 1	0.002		
California, Hawaii, and Great Basin 1958	0	0 0 6 4 3 3	. 005 . 001 . 006 . 018	0 0 1 1 2 1	. 001 P . 009 . 005	0 3 5 3 4 1	. 007 . 007 . 009 . 066 P	0 2 3 3 2 0	. 002 . 001 . 002 . 011	0 3 5 5 0 2	. 001 . 006 . 010 . 008	0 0 0 0 1 0	  P	0 0 0 0 1	0. 020	0 0 0 0 0 1	. 019	0 1 1 0 0 0	0. 011
1958 1959 1960 1961 1962 1963 1964	43 56 57 117 <sup>5</sup> 156 <sup>6</sup> 41	25 24 36 46 42 95 188 39 71 47	. 020 . 055 . 026 . 022 . 035 . 067 . 122 . 008 >. 118 . 100	8 5 9 10 16 39 108 22 44 16	. 008 . 013 . 064 . 029 . 160 . 214 . 150 . 019 >. 094 . 116	10 6 8 11 11 38 51 10 43 25	0.052 0.08 0.32 0.007 0.144 0.009 0.019 0.087 0.149	11 12 17 16 13 30 64 13 37 5	. 004 . 002 . 006 . 004 . 003 . 012 . 004 . 011 . 015 . 009	14 11 17 4 30 45 86 24 1 17	. 031 . 004 . 022 . 012 . 011 . 080 . 011 . 012 . 083 . 026	1 2 0 1 6 16 4 10 0	P .003 P <.001 P .002 .006 P .085	1 0 0 0 3 2 16 24	P  P . 002 P . 155	$     \begin{array}{c}       2 \\       0 \\       4 \\       3 \\       1 \\       2 \\       3 \\       11 \\       0 \\       25 \\       \end{array} $	. 007 . 001 <. 001 . 002 . 008 . 001 . 001 . 007	4 1 8 6 5 5 10 5 2 5	. 003 P . 022 P . 011 . 006 P P . 004

Aluminum columns 4 feet long,  $\frac{1}{4}$ -inch outside diameter, packed with 5 percent Dow Corning 200 silicone grease on 60- to 80-mesh acid-washed Chromosorb P were employed in both gas chromatographic instruments.

The procedure provides corroborative identification in that each of the nine pesticides (a) is adsorbed on carbon, (b) is desorbed with chloroform, (c) is benzene soluble, (d) moves on thinlayer chromatography in the same fashion as a given standard, (e) is eluted from the electroncapture gas chromatograph at the same retention time as, and having the same peak geometry as, a given standard, (f) is identical to the same standard when chromatographed with the microcoulometric titration gas chromatograph in terms of its retention time, peak geometry, and degree of chlorination, and (g) produces an infrared spectrum which in many cases supports the identifications made by chromatography.

Repetitive injections of reference standards of aldrin into the electron-capture gas chromatograph gave a precision of about  $\pm 1$  percent throughout the 0.0001 µg. to 0.010 µg. range. The microcoulometric titration gas chromatograph has a precision of  $\pm 12.6$  percent at the 0.002 µg. level and  $\pm 4.0$  percent at the 0.100 µg. level. This provided for practical lower limits of sensitivity of 0.001 µg. per liter for aldrin, BHC, DDE, DDD, dieldrin, endrin, heptachlor, and heptachlor epoxide and of 0.002 µg. per liter for DDT in the CAM samples.

Water grab samples. Analytical procedures were similar to those used for the 1964 survey

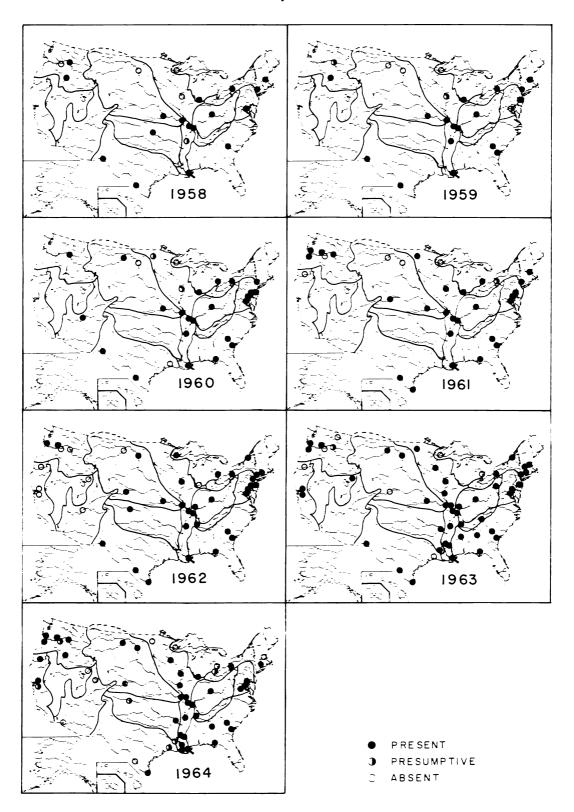


Figure 2. Historical occurrence of dieldrin in major U.S. river basins, selected CAM samples from water years 1958–64

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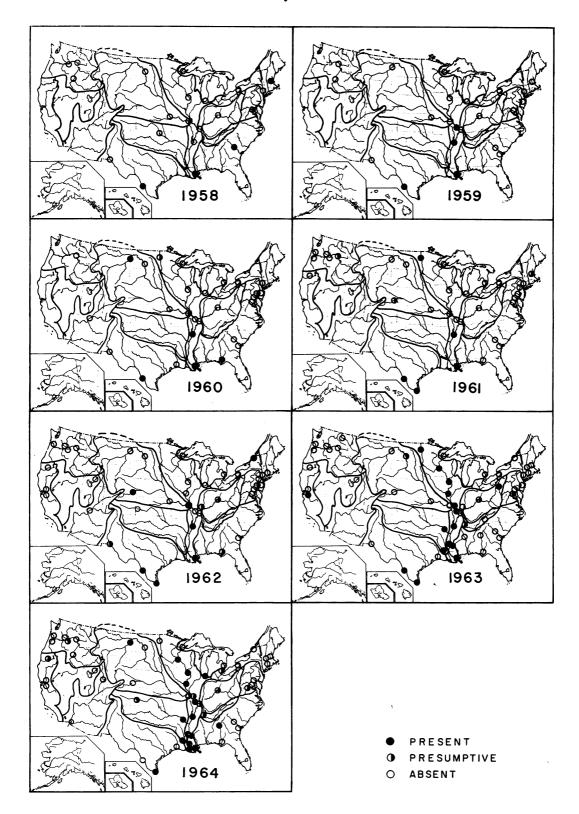


Figure 3. Historical occurrence of endrin in major U.S. river basins, selected CAM samples from water years 1958-64

(11) and included liquid-liquid extraction, thinlayer chromatography, and gas chromatography. All grab samples were extracted with a mixture of hexane-benzene (9:1) by a semiautomatic extraction procedure which provides for recoveries ranging from 77 to 95 percent (14). Extracts of the water grab samples were subjected to thin-layer chromatography (13)and electron capture as well as microcoulometric titration gas chromatography.

The practical limits of sensitivity for the grab samples was  $0.002 \ \mu g$ . per liter for all nine pesticides. No corrections were made for recovery efficiencies for either the semiautomatic extraction or for the thin-layer chromatography in which recoveries of 75 to 104 percent obtain.

## **R**esults and Discussion

The results of the 1965 synoptic survey of pesticides at 99 stations in major river basins of the conterminous United States and Hawaii are listed in table 1. A qualitative comparison of these data with those gathered in 1964, shown in figure 1, indicates a reduction in the incidence of dieldrin in 1965, particularly in the western States. Endrin occurred less in all river basins except the lower Mississippi basin, and the incidence of DDT and its congeners remained essentially unchanged.

The frequency of occurrence of the nine pesticides in September 1964 and 1965 are shown in table 2. The comparison of the 1964 data with the 1965 data for heptachlor epoxide, aldrin, and the DDT group must be cautious because procedural improvements restrict unqualified comparison.

The results of both synoptic surveys as well as the data obtained from a selection of stored CAM samples collected since 1958 are summarized in table 3. Data are arranged by water years in which the reporting period is October 1 through September 30. We anticipate that detailed results will be published in a statistical review and compilation of data from the Federal Water Pollution Control Administration's surveillance system. The results are summarized here to provide a general background for the following discussion.

A comparison of results from 251 analyses

from samples collected near the end of the water year with 274 samples from the rest of the year did not reveal any consistent difference in pesticide levels. The synoptic survey data are thus considered reasonably representative of the year.

A 7-year illustrative summary of the occurrence of dieldrin, endrin, and the DDT group is shown in figures 2-4. Obviously, dieldrin has dominated the pesticide picture throughout the period of record (fig. 2). This is also consistent with the results of the two synoptic surveys. Figure 3 shows endrin appearing occasionally in early CAM samples. This was followed by sharp increases in incidence in 1962 and 1963, with maximum occurrence in 1964. The reduction in endrin found in the synoptic survey of 1965 was reflected in CAM samples from the Mississippi River; this is discussed later in greater detail. A moderate increase in the occurrence of DDT and congeners over the years is indicated in figure 4.

The frequency of occurrence, by river basin, of the dominant pesticides is summarized in figure 5. The bar graphs for the "combined" data support the observations just presented, as do data from the individual river basins. In some of these basins, however, rather wide year-toyear variations are indicated, possibly because of the limited number of samples analyzed thus far.

Concentrations of pesticides found during the two synoptic surveys and in the stored extracts are generally extremely low and fall in the parts-per-trillion range. Occasionally, however, levels approach those which are reportedly toxic to fish (15-17). The 10 stations showing the highest concentrations in the 1965 synoptic survey are listed in table 4. Table 5 presents comparable data for 1958-65 from CAM samples. Both tables indicate a tendency for a particular station to show higher levels of more than one pesticide; this is also evident in the 1964 synoptic survey data (11).

The recurrent fish kills on the lower Mississippi River which took place during fall and winter months and the identification of endrin as the cause of the 1963-64 kill have been widely reported (18).

A major technical assistance project to define

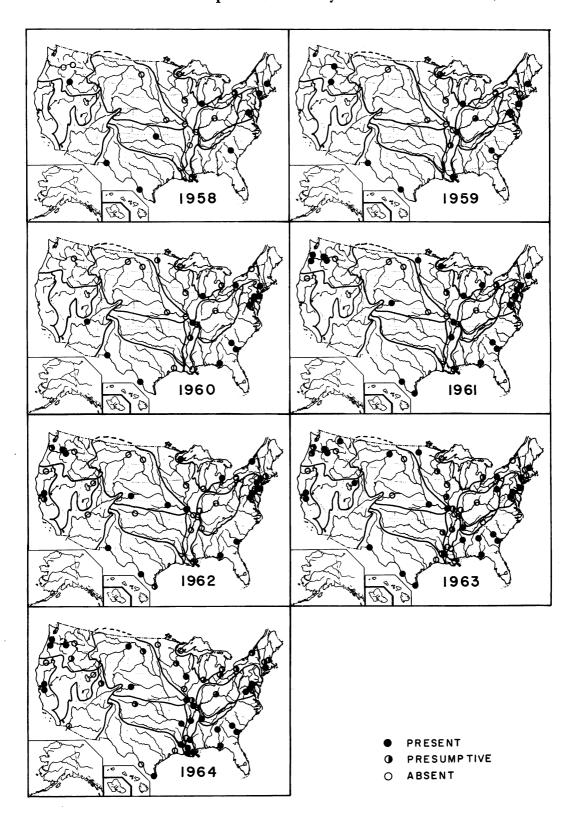


Figure 4. Historical occurrence of DDT, DDE, and DDD in major U.S. river basins, selected CAM samples from water years 1958-64

	Dieldrin	Endrin	DDT	DDE	DDD
Basins				_	-
Northeast	50	<b>.</b>	<b>L</b>		
North Atlantic					
Southeast					
Ohio River, Tennesee River, and Lake Erie			6		<u> </u>
Western Great Lakes	50 -				
Missouri River					
Southwest	- 100 -	h	ď		
Upper Mississippi River	50 50 100 t 50 0 100 100 100 100 100 100 100				
Lower Mississippi River	50 - 0		aller		
Western Gulf					
Colorado River, California and Great Basin		-	ш	<b></b>	
Pacific Northwest				dma	
Combined		1965 1963 1963 1965	1959 1963 1963 –	1959 1963 1963 -	1959 1963 1963 1965
			Water year		

Figure 5. Percent occurrence	e of selected	pesticides in	CAM sample	s, 1958–64
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Table 4. Levels of chlorinated hydrocarbon pesticides, by order of decreasing concentrations, for about 10 synoptic sampling stations at which the highest levels were observed, September 1965<sup>1</sup>

River and location	Con- cen- tra- tion (µg. per l.)	River and location	Con- cen- tra- tion $(\mu g.$ per l.)
Dieldrin		777	
		DDD Rio Grande: Browns-	
Tombigbee: Columbus, Miss	0.100	ville Ter	0.026
Merrimack: Lowell,		Delaware: Trenton, N.J Willamette: Portland,	. 018
Mass Savannah: North	. 068	Oreg Missouri: Kansas City,	. 013
Augusta, S.C. Kanawha: Winfield Dam, W. Va	. 051	Kang	.011
Dam, W. Va Rio Grande: Alamosa,	.045	St. Lawrence: Massena, N.Y	. 010
Colo	. 029	Platte: Plattsmouth,	
Tennessee: Lenoir City, Tenn	. 028	Waikele Stream:	. 010
Ohio: Cairo, Ill	. 028	Waipahu, Hawaii Red (South): Alexan-	. 008
Mississippi: Dubuque, Iowa	. 024	dria, La	. 008
Missouri: Kansas City, Kans	. 023	Merrimack: Lowell, Mass	. 007
Savannah: Port Went-	. 022	Potomac: Washington, D.C.	. 007
worth, Ga	. 022	1	
Endrin		Heptachlor	
Mississippi: West Memphis, Ark Atchafalaya: Morgan	116	Red (North): Grand Forks, N. Dak Mississippi: Dubuque,	. 155
Atchafalaya: Morgan	. 116	Mississippi: Dubuque, Iowa	. 048
City, La Delaware: Trenton, N.J.	. 019	Rio Grande: Browns-	
Tombigbee: Columbus, Miss		ville, Tex. St. Lawrence, Massena,	. 035
Clinch: Kingston, Tenn	. 015	N.Y Delaware: Martins	. 031
Rio Grande: Alamosa, Colo	. 014	Creek, Pa Ohio: Cincinnati, Ohio	. 025
Monongahela: Pitts- burgh, Pa	. 014	Missouri: St. Louis, Mo	. 024
Tennessee: Lenoir City,		Tennessee: Lenoir City,	. 020
Tenn Red (North): Grand	. 009	Sacramento: Greens Landing, Calif Detroit: Detroit, Mich	. 020
Red (North): Grand Forks, N. Dak Mississippi: Delta, La	. 009	Detroit: Detroit, Mich	. 020
	.000	Heptachlor epoxide	
DDT		Mississippi: Dubuque,	
Rio Grande: Alamosa, Colo	. 149	Red (North): Grand	. 067
San Juan: Shiprock.		Forks, N. Dak	. 020
N. Mex. Colorado: Page, Ariz	. 125	Ohio: Addison, Ohio Mississippi: West	
Platte: Plattsmouth, Nebr	. 039	Memphis, Ark Sacramento: Greens Landing, Calif	. 020
Snokana, Post Falls		Landing, Calif	. 019
Dam, Idaho Bed (North): Grand Forks, N. Døk Ohio: Cairo, Ill South Platte: Julesburg,	. 037	N.Y.	. 017
Forks, N. Dak	. 034	Missouri: Kansas City, Kans	. 014
South Platte: Julesburg,		Wabash: New Har- mony, Ind	. 012
Colo Mississippi: Delta, La Mississippi: Vicksburg,	. 023	mony, Ind Missouri: St. Louis, Mo Petomae: Washington,	. 007
Mississippi: Vicksburg, Miss. <sup>2</sup>	. 017	D.C.	. 003
		BHC	
DDE		Red (North): Grand	
San Juan: Shiprock, N. Mex	. 009	Forks, N. Dak	. 004
Detroit: Detroit. Mich Yellowstone: Sidney,	. 008	Ohio: Cairo, Ill. Verdigris: Nowata, Okla	P
Mont.	. 002	Connecticut: Enfield	1
Platte: Plattsmouth, Nebr	P	Dam, Conn Monongahela: Pitts-	. P
Rainy: Baudette, Minn_ Other stations	. P 0	burgh, Pa	. P

<sup>1</sup> No aldrin detected.
 <sup>2</sup> Same concentration found in Chattahoochee River at Lanett, Ala., and Mississippi River at Vicksburg, Miss.

NOTE: P-indicates presumptive.

Table 5. Levels of chlorinated hydocarbon pesticides, by order of decreasing concentrations for about 10 CAM stations at which the highest levels were observed, water years 1958-65

River and location	Con- cen- tra- tion	River and location	Con- cen- tra- tion
	(µg. per l.)		(µg. per 1.)
Dieldrin		DDD	
Mississippi: West Mem-		Delaware: Philadelphia,	
phis, Ark	0.122	Pa Savannah: North Au-	0.080
Savannah: North Au- gusta, S.C Ohio: Cincinnati, Ohio.	. 056	gusta, S.C	. 031
Ohio: Cincinnati, Ohio Schuylkill: Philadelphia,	. 055	Rio Grande: Brownsville, Tex	. 019
Pa	. 035	El Paso, Tex Mississippi: New Roads,	. 012
Mississippi: New Or- leans, La	. 034	La.	. 012
Delaware: Philadelphia, Pa	. 033	Red (South): Alexan- dria, La	. 011
Apalachicola: Chatta-		San Joaquin: Vernalis,	
hooche, Fla Mississippi: Vicksburg,	. 024	Calif Rio Grande: Laredo,	. 010
Miss Mississippi: Delta, La	. 023 . 022	Tex. Apalachicola: Chatta-	. 009
Savannah: Port Went-		hoochee, Fla	. 008
worth. Ga. <sup>1</sup>	. 016	Sacramento: Green's Landing, Calif. <sup>3</sup>	. 006
Endrin		Aldrin	
Mississippi: West Memphis, Ark.	.214	Red (South): Alexan-	
New Orleans, La Vicksburg, Miss	. 160 . 072	dria, La. Snake: Wawawai, Wash.	.006 .003
Delta, La	. 044	Chattahoochee: Lanett,	
Connecticut: Enfield Dam, Conn	. 023	Ala Savannah: North Au-	. 002
Atchafalaya: Morgan	. 015	gusta, S.C Merrimack: Lowell,	<. 001
City, La Mississippi: Cape Gir-		Mass	<. 001
ardeau, Mo Allegheny: Pittsburgh,	. 013	Yakima: Richland, Wash	<. 001
Pa Rio Grande: Browns-	. 012	Yellowstone: Sidney, Mont	<. 001
ville, Tex. Mississippi: New Roads,	. 011	19 stations in various	
La	. 010	river basins	P
DDT		Heptachlor Atchafalaya: Morgan	
Rio Grande:		City La	. 002
Brownsville, Tex Laredo, Tex	.144 .052	Mississippi: West Mem- phis, Ark	Р
Laredo, Tex El Paso, Tex	. 032 . 023	Potomac: Great Falls, Md	Р
Ohio: Cairo, Ill Mississippi: New Or-		Detroit: Detroit, Mich	P
leans, La	. 019	Other stations	0
Delaware: Philadelphia,	015	Heptachlor <sup>*</sup> epoxide Mississippi: West Mem-	
Pa Chattahoochee: Lanett,	. 015	nhie Ark	. 020
Ala Tennessee: Pickwick	. 011	Missouri: St. Louis, Mo. Mississippi: New Orle-	. 002
Tennessee: Pickwick Landing, Tenn Mississippi: Vicksburg,	. 011	ans, La St. Lawrence: Massena,	. 001
M1SS	. 010	N.Y	. 001
Sacramento: Green's Landing, Calif. <sup>2</sup>	. 009	Potomac: Great Falls, Md	<.001
DDE		6 stations in various river basins	P
Delaware: Philadelphia,		BHC	· ·
Pa Mississippi: Vicksburg,	. 012	Apalachicola: Chatta-	
Miss	. 011	hoochee, Fla	. 022
Hudson: Poughkeepsie, N.Y	. 006	Sacramento: Green's Landing, Calif	. 011
South Platte: Julesburg, Colo	. 005	Red (North): Grand Forks, N. Dak	. 004
Mississippi: New Orle-		St. Lawrence: Massena,	. 003
Rio Grande:		N.Y. Missouri: Kansas City,	
Brownsville, Tex Laredo, Tex	. 004	Kans Ohio: Cairo, Ill	.003
Lake Superior: Duluth,	. 004	Ohio: Cairo, Ill Savannah: North Au- gusta, S.C.	<. 001
Minn 12 stations in various		15 stations in various	1
river basins	. 002	river basins	P
<sup>1</sup> Same concentration in	Merrima	ck River at Lowell, Mass.	

 Same concentration in Merrimack River at Lowell, Mass.
 Same concentration in Tombigbee River at Columbus, Miss.
 Same concentration in Tennessee River at Pickwick Landing Dam, Tenn.

NOTE: P-indicates presumptive.

the sources, transport mechanisms, biological concentration, and uptake factors, as well as related hydrologic features is now underway (19). In support of this investigation, a large

LAKE ITASCA MICHIGAN SOTA ALSO TA R IBUQUE URLINGTON z SALLINOIS < KANSA ٥ RAFTON MISSOURI z DESOTO KANSAS < ξ 0 OPT SMITH 154.5 WEST uthe × OUACHITA 0 ARKAN BASTROP BOSSIER CITY Ō VISIAN NECHES ALEXANDRIA W. ORLEANS

### Figure 6. Mississippi River and Delta area

Dots indicate water pollution surveillance stations.

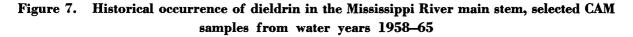
number of CAM samples taken since 1958 have been analyzed for pesticides. The locations of water pollution surveillance stations in the Mississippi River and Delta area are shown in figure 6. The dots indicate stations for which data are summarized in figures 7 and 8.

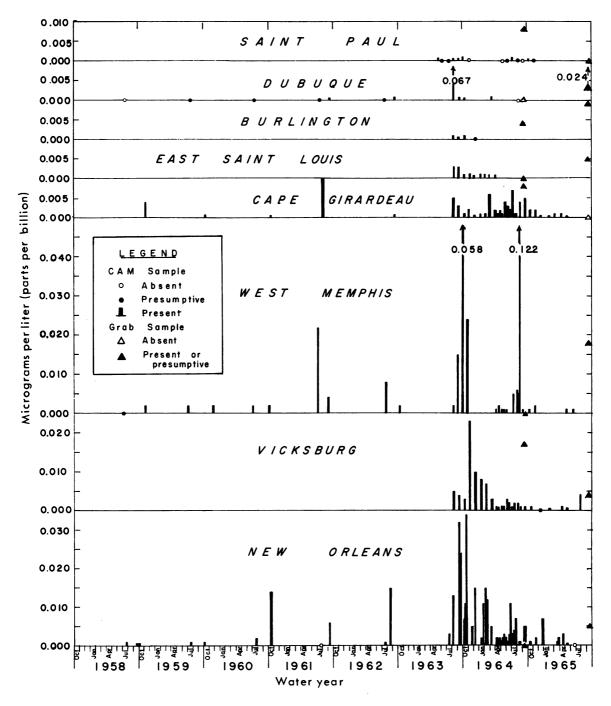
Concentrations of dieldrin from selected CAM samples are presented in figure 7. Widths of bars on the graph represent continuous sampling periods. Results from the 1964 and 1965 synoptic surveys have also been included. Levels of  $0.005 \ \mu$ g. per liter or greater have occurred fairly frequently since October 1961. Higher levels were found in the lower Mississippi from summer 1963 through spring 1964, with only occasional highs thereafter. The figure also shows that higher levels of dieldrin were found in two samples from Dubuque, at widely separated times, indicating pulses presumably related to local pesticide applications.

The concentration of endrin in the Mississippi River is shown in figure 8. The occurrence of high concentrations at and below West Memphis is even more striking than that for dieldrin, particularly when the fivefold difference in vertical scales of the two figures is considered. Concentrations of endrin have shown a general decrease since about spring 1964, although a single sample from West Memphis during the 1965 synoptic survey approached earlier maximums. No major fish kills have been reported on the lower Mississippi River during fall or winter of 1964-65 or 1965-66.

The concentration of a pesticide in solution and adsorbed on solids in water is most probably a function of the amount reaching the water, the volume of water available for dilution, and the degradability of the pesticide. Concentrations of persistent or difficultly degradable pesticides in drainage basins where these pesticides are used regularly should be reasonably constant. Concentrations of readily degradable pesticides, on the other hand, could be expected to vary widely depending on the period available for degradation.

A comparison of the 10 highest values for each pesticide obtained in (a) the 1964 survey (11), (b) the 1965 survey (table 4), and (c) the historical CAM data (table 5) indicates that the results of CAM sampling and grab sampling have given noticeably similar results for the more stable pesticides, dieldrin, endrin, DDT, DDE, and DDD. On the other hand, higher levels of heptachlor and its epoxide and of aldrin in the grab samples suggest that these compounds are much less persistent. It is not possible, however, to separate degradation of these pesticides in the environment from degradation in either the carbon column or subsequently in the storage vial. The BHC data do





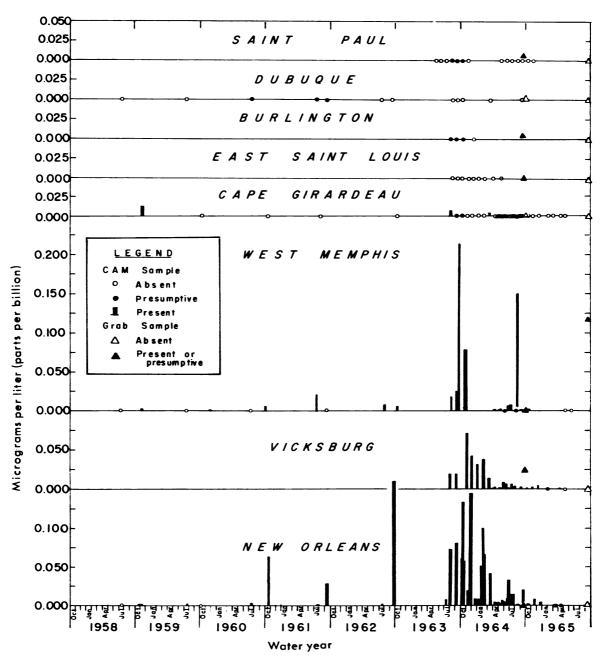
not fit either category, presumably because of a sampling artifact. This material was found comparatively rarely.

# **Summary and Conclusions**

The results of the synoptic pesticide surveys of 1964 and 1965 and the examination of stored carbon adsorption extracts for water years 1958 through 1965 reveal that dieldrin has dominated pesticide occurrences in all river basins since 1958.

Endrin occurrence reached a maximum, particularly in the lower Mississippi River in the fall of 1963 (the first quarter of water year 1964). Since then, endrin levels have decreased. Major fish kills in the lower Mississippi, which

Figure 8. Historical occurrence of endrin in the Mississippi River main stem, CAM samples from water years 1958-65



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had previously occurred during the late fall months, were not reported in 1964 or 1965.

DDT and its congeners have been fairly common since 1958. There has been a slightly increasing trend in these occurrences.

There is a noticeable agreement in data from grab samples and CAM samples in both frequency of occurrence and concentrations of chlorinated hydrocarbon pesticides. This suggests that occasional synoptic surveys may be adequate to characterize pesticide levels on a broad scale in those places where there are no dominant sources of pollution. In areas such as the lower Mississippi River, however, the variability of both dieldrin and endrin clearly requires a greater sampling frequency, possibly including continuous sampling backup with the CAM method. This is consistent with earlier studies (20) which show that, as a dominant source of pollution is approached, more frequent sampling is necessary.

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