Residual 2,4-D Levels In The St. Johns River, Florida[1]

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ABSTRACT

The U.S. Army Corps of Engineers (USACE), Jacksonville District, conducted preliminary studies on the St. Johns River, Florida in order to determine residual levels of (2,4-Dichlorophenoxy)acetic acid (2,4-D) in flowing waters and in commercial shellfish populations. During waterhyacinth (*Eichhornia crassipes* (Mart.) Solms.) chemical control operations, water samples and blue crabs (*Callinectes sapidus* Rathbun) were collected at nine and four locations, respectively, along the river course. Levels of 2,4-D observed were well below established tolerance limits and exhibited no apparent accumulation from the amount of 2,4-D applied during routine waterhyacinth control operations in flowing waters.

INTRODUCTION

The St. Johns River originates in an extensive marsh near Vero Beach, Florida (Figure 1) and flows northward approximately 312 miles (502 km) through a series of lakes to Jacksonville and then eastward to the Atlantic Ocean. The topographic drainage area of the river is 9,430 mi^2 (24,424 km^2) of which the flood plain contains an open water area of more than 300 mi^2 (777 km^2) during seasonal low water periods.[2]

The Jacksonville District along with various State and local agencies conducts waterhyacinth control operations throughout the St. Johns River Basin, using the most economical and efficient method of control available which

[1]Supported in part by Contract No. DACW39-74-C-0068 with the U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, Mississippi.

[2]Anderson, Warren and Goolsby, D.A. 1973. Flow and Chemical Characteristics of the St. Johns River at Jacksonville, Florida U. S. Geological Survey Open File Report 73008, 105 pp.

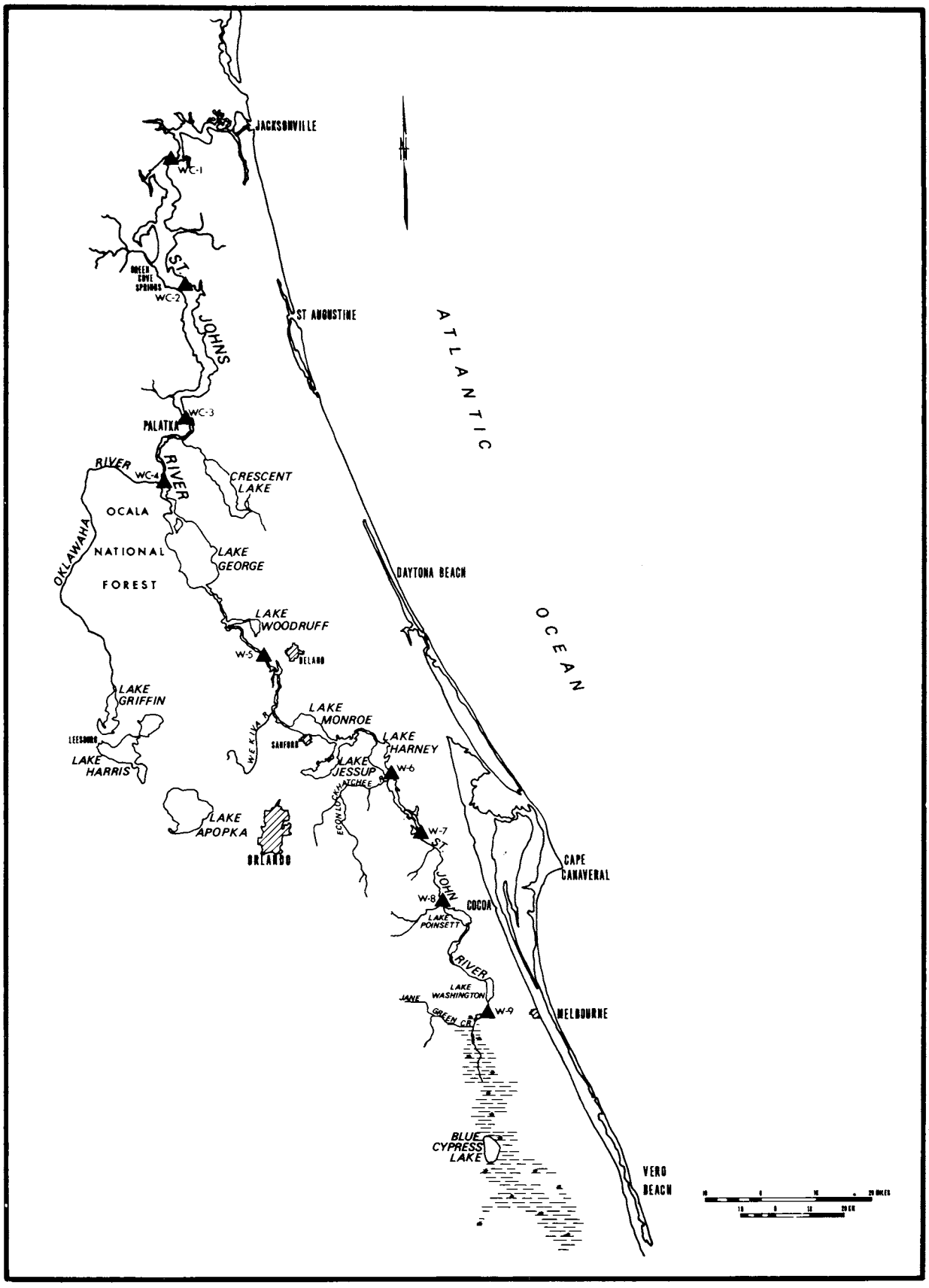

Figure 1. 2,4-D Residue sampling stations, St. Johns River, Florida.

is chemical spray treatment with the dimethylamine salt of 2,4-D.

Prior to the registration of 2,4-D for use in flowing and potable waters by the Environmental Protection Agency (EPA), public concern was expressed over environmental effects resulting from its use in the St. Johns River. As a result, on 4 December 1973, the EPA directed the USACE to discontinue the use of any product containing 2,4-D which was not specifically labeled for use in flowing waters. All waterhyacinth control operations in the St. Johns River ceased since none of the available 2,4-D products were specifically registered by EPA for use in flowing waters. In the absence of control operations, plant populations increased to problem proportions. In order to preclude major economic and environmental damage attributable to massive hyacinth infestations the Corps requested a specific exemption from EPA so that control efforts could resume. EPA granted such an exemption on 2 May 1974 and control operations began shortly thereafter subject to the following conditions:

a. No spraying was to be done on the river after 1 November of each year for the purpose of protecting migrating manatees.

b. The USACE would notify agricultural interests along sections of the river to be treated and caution them not to use the river water for irrigation purposes for a period of 5 weeks after treatment.

c. No applications of 2,4-D were to be made south of Lake Washington (Figure 1) which is a source of potable water, since no tolerance limit for the herbicide had been established for potable waters.

d. The USACE would continue to compile data necessary to obtain registration for the use of 2,4-D in moving and potable waters.

The USACE noted that past experience in waterhyacinth control indicated that general restrictions such as a., b., and c. above were not conducive to effective and ecologically sound control of waterhyacinths. Until a compromise was developed, the USACE abided by conditions set forth by EPA.

In order to comply with condition d., above and to assist in the establishment of tolerance limits for residues of 2,4-D in or on raw agricultural commodities, fish and shellfish, and in potable water, the USACE continued to gather data on toxicity, persistence, mobility and use patterns of the chemical.

This short term study reported here was initiated in order to evaluate the residual 2,4-D levels in naturally flowing waters expected to occur during normal, large-scale waterhyacinth control operations and to monitor 2,4-D residues in commercially available shellfish taken from the treated waters. Numerous other studies have been conducted such as the biodegradation of 2,4-D (3), the accumulation of the chemical by aquatic organisms under controlled conditions[3, 4] (2,4) and monitoring 2,4-D under operational conditions in lake, ponds, and potable water[5, 6] also footnote 5, 6.

METHODS AND MATERIALS

Water samples were collected at nine locations (Figure 1) by personnel from the Environmental Quality Section of the Jacksonville District, USACE. Samples were collected with a 4.9-liter PVC sampler, transferred to 0.9-liter glass bottles with teflon caps, placed on ice at approximately 25 F, and shipped to the U.S. Geological Survey Laboratory in Doraville, Georgia for 2,4-D analysis. The analytical method used was the ASTM multiresidue ethyl-ether extraction technique for chlorinated phenoxy acids. At the time of sample collection, various physio-chemical measurements were made with an in situ electronic water quality monitor which was field calibrated daily. The data collected included dissolved oxygen, temperature, specific conductance, and pH (Table 1). Additional water samples were returned to the Jacksonville Office for suspended solids and turbidity measurements (1).

Blue crabs were purchased from local commercial shellfishermen. Only those crabs obtained from dealers who operated their traps in the sections of the St. Johns River near the sampling stations noted in Figure 1 were used. It is recognized that this method of obtaining sample specimens does not lend itself to strict experimental control, however, it does provide information on residual 2,4-D concentration in blue crabs available to the public through commercial outlets in areas affected by spray operations.

The crabs were frozen and shipped to Syracuse Research Corporation, Inc., for analysis. The edible portion of six crabs collected from a single location was removed, composited and homogenized. Duplicate samples, each weighing 0.03 to 0.04 lb (15-20 g) were withdrawn for analysis using a multiresidue extraction technique for chlorinated phenoxy acid herbicides as described by Schultz (4) and Yip (7).

The dimethylamine salt of 2,4-D was applied by airboat at a rate of 2 lb acid equivalent (ae) per acre (2.24 kg/ha) or by aircraft at a rate of 4.0 lb ae per acre (4.48 kg/ha). A log of daily operations was maintained so that the number of acres sprayed and gallons of chemical applied could be accounted for. Quantities of 2,4-D applied in any one river section for a given month ranged from zero to

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[3]Davis, Frank S. 1974. Toxicology, Persistence, and Mobility of Phenoxy Herbicides in the Environment. In *Aquatic - Use Patterns* for 2,4-Dimethylamine and Integrated Control. U.S. Army Corps of Engineers Waterways Experiment Station. Technical Report 7, E1-E16.

[4]Duke, Thomas 1971. Technical Report on the Effects of 2,4-D on Estuarine Organisms. Environmental Protection Agency, Gulf Breeze Laboratory, Sabine Island, Gulf Breeze, Florida.

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[6]Zeiger, C. F. 1974. Hyacinth Control in Shell Creek Reservoir, Punta Gorda, Florida. In Aquatic - Use Patterns for 2,4-Dimethylamine and Integrated Control. U.S. Army Corps of Engineers Waterways Experiment Station. Technical Report 7, G1-G23.

TABLE 1. WATER QUALITY DATA COLLECTED DURING RESIDUAL 2,4-D SAMPLING IN THE ST. JOHNS RIVER, FL.

Station[a]	Date	Temperature (C)	Specific conductance (μMHOS/cm)	Dissolved oxygen (ppm)	pH	Suspended Solids (ppm)	Turbidity (JTU)
	7-23-75	28.0	290	1.7	6.4	—	0.5
W-9	8-25-75	29.0	185	2.1	6.2	—	0.6
Hwy 192	9-30-75	25.5	140	2.0	6.1	1.6	0.5
	10-20-75	23.5	185	1.1	6.6	0.8	0.7
	1-28-76	19.0	460	8.4	7.4	—	0.7
	7-23-75	27.8	1220	6.6	7.4	—	1.8
W-8	8-25-75	28.5	410	5.7	7.0	—	2.2
Hwy 520	9-30-75	25.0	330	5.7	6.8	5.4	0.8
	10-20-75	23.0	390	6.2	7.1	2.4	0.8
	1-27-76	19.5	520	9.4	7.4	—	3.8
	7-23-75	29.0	1450	6.1	6.8	—	2.8
W-7	8-25-75	29.0	850	2.5	6.5	—	2.6
Hwy 50	9-30-75	26.0	620	4.0	6.6	5.2	0.8
	10-20-75	22.0	520	4.5	6.7	4.8	0.6
	1-27-76	19.0	730	8.7	7.4	—	3.2
	7-23-75	29.7	1025	5.3	6.3	—	4.3
W-6	8-25-75	28.5	495	4.1	6.4	—	2.9
Hwy 46	9-30-75	26.0	460	8.4	6.1	7.0	2.5
	10-20-75	24.5	700	6.9	7.1	3.8	1.7
	1-27-76	17.5	1100	9.5	7.8	—	4.9
	7-23-75	29.6	1300	7.9	7.8	—	5.4
W-5	8-25-75	29.0	90	7.3	7.0	—	3.5
DeLand	9-30-75	26.0	730	4.7	6.9	4.4	1.5
	10-20-75	24.5	710	4.9	7.1	11.2	2.8
	1-27-76	17.5	790	10.8	8.1	—	3.2
	7-23-75	29.5	1250	10.3	8.8	—	6.5
WC-4	8-25-75	27.5	120	7.1	8.6	—	5.2
Welaka	9-30-75	25.5	770	5.4	7.2	9.0	2.4
	10-20-75	24.0	1100	7.7	8.2	15.0	3.8
	1-27-76	16.5	950	10.4	7.9	—	4.2
	7-23-75	29.0	930	9.2	8.3	—	3.5
WC-3	8-25-75	29.0	890	6.2	7.4	—	3.0
Palatka	9-30-75	25.5	900	7.0	5.4	6.2	2.6
	10-20-75	24.0	1100	6.4	7.5	8.0	2.9
	1-27-76	15.5	620	10.4	8.0	—	3.8
	7-23-75	27.1	912	8.1	7.9	—	1.8
WC-2	8-25-75	28.2	230	6.8	7.6	—	4.6
Green	9-30-75	25.0	870	7.3	7.6	3.3	1.0
Cove Springs	10-20-75	22.5	900	7.6	7.8	10.4	2.8
	1-27-76	13.5	600	10.8	7.9	—	1.9
	7-23-75	27.1	1330	7.1	7.6	—	8.3
WC-1	8-25-75	29.0	767	3.3	7.2	—	18.0
Jacksonville	9-30-75	25.5	730	5.3	7.5	11.3	4.5
	10-20-75	23.5	850	7.0	7.0	16.4	5.4
	1-27-76	13.0	3600	10.8	7.8	—	4.2

[a]Station locations refer to Figure 1.

820 gallons (Figure 2). Quantities applied in any one section for a given day ranged from zero to 340 gallons (Figure 3).

RESULTS AND DISCUSSION

A total of 45 water samples were analyzed for 2,4-D residuals. The 2,4-D concentrations detected ranged from nondetectable levels to 1.30 ppb (Table 2).[7] These values are within the values previously reported for 2,4-D in natural aquatic ecosystems (5,6) and are well below the 0.10 mg per liter (ppm) tolerance limit established for 2,4-D in potable waters.[8] The concentrations of 2,4-D detected are compared with the volumes (gallons) of 2,4-D applied monthly and daily in the given river sections in Figures 2 and 3, respectively. No apparent correlation exists between quantities of 2,4-D applied and the amount of 2,4-D detected in the water. There was no apparent build-up of 2,4-D in downstream areas, and the ambient water quality data (Table 1) are within the normal seasonal ranges expected for these locations.[9, 10]

[7]Sikka, Harish C. 1975. Progress Report for the U.S. Army Corps of Engineers Waterways Experiment Station Contract DACW39-74-C-0068.

[8]21 CFR 123.100, 16 December 1975. Tolerances for Pesticides in Foods, Administered by the Environmental Protection Agency.

[9]Department of the Army, Jacksonville District, Corps of Engineers. 1975. Water Quality Report, Upper St. Johns River Basin.

[10]United States Department of the Interior, Geological Survey. 1970-1974. Water Resources Data for Florida. Part 2, Water Quality Records.

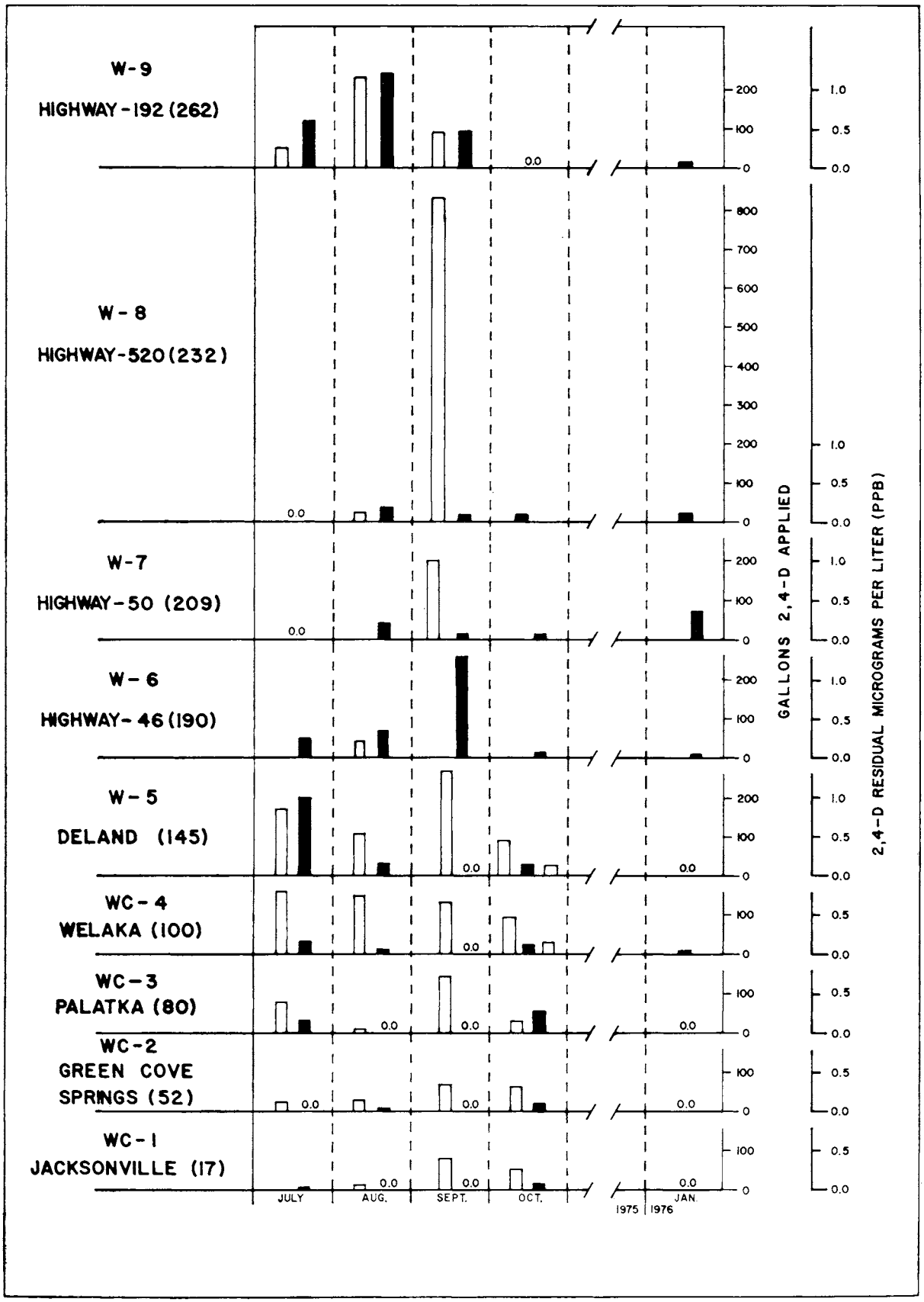

Figure 2. Comparison of 2,4-D residual in water and the number of gallons of 2,4-D applied monthly in the St. Johns River, Florida. Open bars represent cumulative gallons of 2,4-D, closed bars represent 2,4-D residual in ppb, and ( ) represents the distance upstream from mouth in river miles.

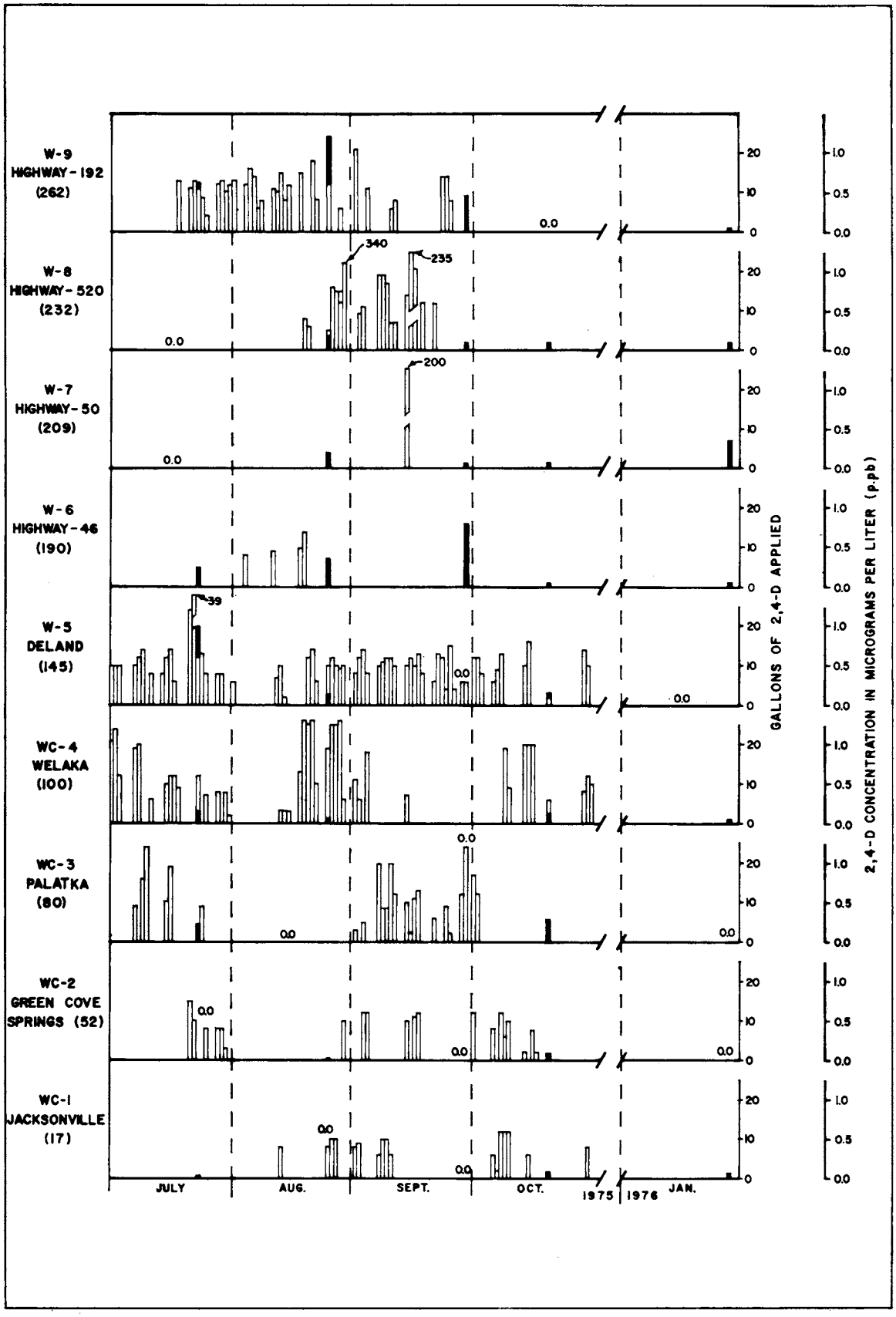

Figure 3. Comparison of 2,4-D residual in water and the number of gallons of 2,4-D applied daily in the St. Johns River, Florida. Open bars represent number of gallons of 2,4-D applied, closed bars represent 2,4-D residual in ppb, and ( ) represents distance from mouth in river miles.

TABLE 2. RESIDUES (PPB) OF 2,4-D IN WATER AND BLUE CRABS IN THE ST. JOHNS RIVER, FL.

Station[a]	Date	Water	Blue crabs
	7-22-75	0.61	NA[b]
W-9	8-25-75	1.20	NA
Hwy 192	10- 1-75	0.45	NA
	10-20-75	0.00	NA
	1-28-76	0.04	NA
	7-22-75	0.00	NA
W-8	8-25-75	0.18	NA
Hwy 520	10- 1-75	0.08	NA
	10-20-75	0.08	NA
	1-27-76	0.10	NA
	7-22-75	0.00	NA
W-7	8-25-75	0.20	NA
Hwy 50	10- 1-75	0.06	NA
	10-20-75	0.07	NA
	1-27-76	0.35	NA
	7-22-75	0.25	NA
W-6	8-25-75	0.36	NA
Hwy 46	10- 1-75	1.30	NA
	10-20-75	0.04	NA
	1-27-76	0.04	NA
	7-22-75	1.00	NA
W-5	8-25-75	0.15	NA
DeLand	10- 1-75	0.00	NA
	10-20-75	0.15	NA
	1-27-76	0.00	NA
	5- 1-75	ND[c]	47.80
WC-4	7-22-75	0.15	0.00
Welaka	8-25-75	0.05	0.00
	10- 1-75	0.00	0.00
	10-20-75	0.11	0.00
	1-27-76	0.05	0.00
	5- 1-75	ND	65.10
WC-3	7-22-75	0.18	0.00
Palatka	8-25-75	0.00	0.00
	10- 1-75	0.00	0.00
	10-20-75	0.28	0.00
	1-27-76	0.00	NA
	5- 1-75	ND	53.40
WC-2	7-22-75	0.00	0.00
Green Cove Spgs	8-25-75	0.02	0.00
	10- 1-75	0.00	0.00
	10-20-75	0.09	0.00
	1-27-76	0.00	NA
	5- 1-75	ND	61.00
WC-1	7-22-75	0.02	0.00
Jacksonville	8-25-75	0.00	0.00
	9-30-75	0.00	0.00
	10-20-75	0.08	0.00
	1-27-76	0.06	0.00
Guano Wildlife Preserve	5-14-75	ND	62.6

[a] Station locations refer to Figure 1.
[b] NA—Not Applicable—Blue crabs not available at these locations
[c] ND—No Data Available

No waterhyacinth control operations were conducted in the mainstream of the river by the agencies involved in waterhyacinth control operations between 31 October 1975 and 31 January 1976 (Figures 2 and 3) due to the expiration of the EPA exemption. However, 2,4-D levels ranged from nondetectable levels to 0.35 ppb, indicating possible runoff from agricultural applications or waterhyacinth control operations in private drainage districts adjacent to the river.

A total of 23 composite crab samples were analyzed for residual 2,4-D levels. Four of these samples were collected in May 1975, prior to the actual initiation of the study in order to determine if 2,4-D was detectable in commercially available blue crabs captured in the St. Johns River. Levels of 2,4-D in the May 1975 samples ranged from 47.8 to 65.1 ppb (Table 2). These values are within ranges previously reported for blue crabs (6) and well below the established tolerance limit for 2,4-D of 1.0 ppm in or on fish and shellfish.[11] However, it is not certain that the compound which was identified as 2,4-D in the May 1975 samples was in fact 2,4-D and not some other interfering compound. Two factors account for this uncertainty; (a) the detection of 62.6 ppb of 2,4-D in the crabs collected at Guano Wildlife Preserve, an isolated watershed located east of the St. Johns River Basin, which has not received any treatment with 2,4-D and (b) 2,4-D was not detected in any of the other 19 crab samples analyzed which were from areas receiving treatment.

The results presented herein demonstrate that the use pattern of 2,4-D necessitated by large scale waterhyacinth control operations in flowing waters, does not result in the accumulation of levels of the herbicide in excess of the established tolerance limits for 2,4-D in commercially available blue crabs or potable water supplies.

ACKNOWLEDGMENTS

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[11] 40 CFR 180.142 9 December 1975. Tolerances and exemptions from tolerances for pesticide chemicals in or on raw agricultural commodities.