PCB Florida

Polychlorinated Biphenyls and Chlorinated Pesticides in Soils of the Everglades National Park and Adjacent Agricultural Areas

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■ Soil samples collected from the eastern Everglades National Park and adjacent farmlands were analyzed for certain chlorinated pesticides and polychlorinated biphenyls (PCBs). The results indicate that although concentrations of PCBs, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), and chlordane are high at the agricultural sites, little contamination of parklands has occurred. Pesticide concentrations decrease by two orders of magnitude (to unit parts per billion levels) within 2 km of the agricultural sites sampled. Individual contributions of four Aroclors (1242, 1248, 1254, and 1260), calculated using pattern recognition techniques, suggest that plastic sheeting used in agricultural fields is a local source of PCBs. A comparison of the results to those from other environments reveals that PCB and DDT concentrations found within the Park (<1.0–33 and <1.0–22 ppb, respectively) are as low as any site in North America.

The Everglades National Park in South Florida is a unique, delicately balanced ecosystem. Within the last 30 years, lands adjacent to the southeastern boundary of the park have been extensively rock plowed and drained for farming. This agricultural activity has grown and currently accounts for a significant portion of the United States winter vegetable crop. The encroachment of man upon this wilderness has resulted in the introduction of industrial chemicals and pesticides, which threaten the environmental quality of pristine lands to the west. The National Park Service, in an effort to minimize contamination of parklands, obtained an indefinite moratorium on farming in an area known as "Hole-in-the Donut", located within the boundaries of the park. The moratorium was the result of a study which found elevated levels of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), DDT metabolites, and dieldrin in soils and biota south of "Hole-in-the-Donut" (*1*). A monitoring program conducted by the U.S.G.S. has found increased levels of DDT and DDT metabolites in submerged soils collected from nearby Taylor Slough (*2*). Although domestic use of DDT was banned in 1972, the quantities used and the persistence of DDT degradation products continue to make these compounds environmentally hazardous. Other chlorinated pesticides, such as chlordane and toxaphene, are still applied to various crops. Chronic inputs of these pesticides to the park via irrigation runoff or careless application could have a disastrous effect on wildlife, especially the diverse avian population (*3–5*).

In addition to pesticides, industrial chemicals which may be affecting this region include polychlorinated biphenyls (PCBs), of which the toxicity and persistence have been widely researched (*6–10*). PCBs have been used as plasticizers in a variety of commercial plastics (*11*), and are suspected present in plastic sheeting used by farmers to aid seed germination (*1*). The sheeting (or mulching) also reduces the frequency of irrigation by preventing evaporation, and substantially improves crop yields. Following use, it is routinely burned and plowed into the soil, thereby releasing any PCBs present in the plastic matrix into the atmosphere. Once airborne, these compounds can be transported by wind into the adjacent parklands.

Because of the environmental and legal implications involved in determining whether the Everglades National Park is being contaminated by these anthropogenic pollutants, a study was undertaken to analyze soil samples from a southeastern section of the park, as well as samples of plastic sheeting obtained from local sources. The study area encompassed Taylor Slough, a major conduit of freshwater into the park, and adjacent agricultural lands. This paper presents the results of this study.

Experimental

Sampling. Samples were collected at sites along the southeastern boundary of the park as shown in Figure 1. The sampling grid was closely spaced in order to detect any horizontal gradients of agricultural chemicals in the area. Sites included both active (A1 and A2) and fallow (A3) agricultural lands, recently farmed lands (1, 3, 4, and 6), and locations in Taylor Slough and south and west of Context Road. All sampling was done in May 1976 in order to facilitate collection, as many of the locations sampled within the park are covered with water during the summer and early fall.

Surface soil samples were collected using a Teflon scoop to remove approximately the upper 2 cm of soil. Nonrepresentative surface debris (leaves, roots, etc.) was removed prior to collection. Samples were placed in cleaned glass jars and sealed with Teflon-lined caps. Upon return to the laboratory, all samples were immediately frozen. They were subsequently freeze-dried and stored frozen for later analysis.

Analysis. A weighed portion of the freeze-dried soil was extracted with hexane in a Soxhlet apparatus for 24 h. Saponification of random samples to determine extraction efficiency showed this procedure to be greater than 80% efficient for chlorinated hydrocarbons. However, this efficiency can vary with the chemical composition of the soil.

An aliquot of the hexane extract was concentrated to near dryness using a rotary evaporator and transferred onto a column of Florisil deactivated with 3% water. The column was

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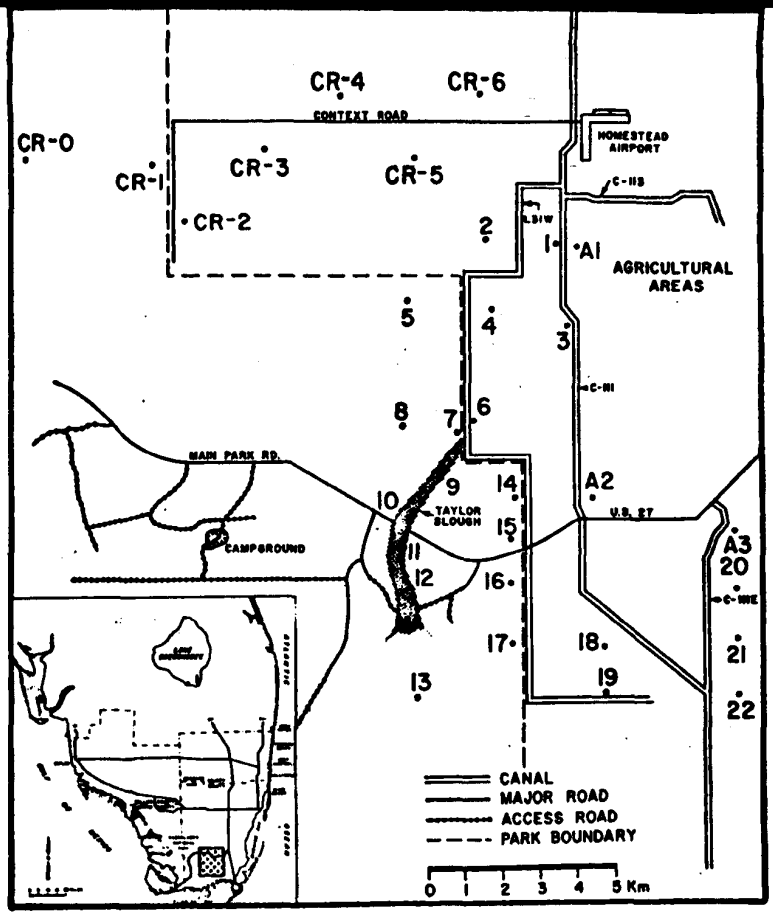

Figure 1. Location of sampling sites along the southeastern boundary of the Everglades National Park

eluted sequentially with hexane, 6% diethyl ether/hexane (v/v), and 50% diethyl ether/hexane (v/v). The 6 and 50% ether/hexane fractions were concentrated in preparation for analysis by gas chromatography. In order to separate PCBs from DDT and DDT metabolites, the hexane fraction was rechromatographed on 3% deactivated silicic acid (*12, 13*). The column was eluted with hexane followed by benzene. These fractions were similarly concentrated for gas chromatographic analysis. The separation scheme is detailed in Figure 2. Recovery of standard mixtures averaged 80–90%. No corrections for recovery were applied to the results. PCBs were extracted with hexane from plastic sheeting following treatment with boiling sulfuric acid. The hexane extract was analyzed using the procedure described above.

Chlorinated hydrocarbons were chromatographed and quantitated using a Tracor 550 gas chromatograph equipped with a ^{63}Ni electron-capture detector. Peak areas were measured by a Hewlett-Packard 3380A recording integrator. Three different column packings were used: glass columns (2 m × 2 mm i.d.) packed with 5% OV-210 on 100/120 mesh Supelcoport were used primarily for quantitation of pesticides while columns packed with 1.5% SP-2250/1.95% SP-2401 and 4% SE-30/6% QF-1, both on 100/120 mesh Supelcoport, were used for PCB analysis.

Pesticide concentrations were calculated using external standard techniques. Total DDT and total chlordane values were reported as the sum of DDTs (*p,p'*-DDT, *o,p'*-DDT), DDT metabolites (*p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, *o,p'*-DDD), and the γ and α isomers of chlordane, respectively. Total pesticide concentrations less than 1.0 ppb were not reported.

PCB concentrations were also calculated using external

Table I. Chlorinated Hydrocarbon Concentrations in Soil Samples from the Everglades National Park and Adjacent Areas (ng/g Dry Weight)

Sites	Total Chlordane	Total DDT	Total PCB	% Aroclor 1242/1248	% Aroclor 1254/1260
Agricultural					
A1 (active)[a]	68	230	43	63	37
A2 (active)[a]	195	761	39	46	54
A3 (fallow)[a]	1.4	11	36	69	31
1 (winter only)[b]	<1.0	<1.0	23	91	9
3 (winter only)[b]	<1.0	<1.0	18	72	28
4 (winter only)[b]	<1.0	<1.0	11	91	9
6 (winter only)[b]	<1.0	<1.0	<0.1	--	--
Peninsula					
West-southwest					
2	<1.0	<1.0	18	78	22
5[c]	<1.0	<1.0	24	92	8
9[c]	<1.0	<1.0	11	91	9
13[c]	1.4	1.7	1.7	76	24
14[c]	1.5	<1.0	12	92	8
15[c]	3.1	1.2	2.9	76	24
16[c]	<1.0	<1.0	5.0	84	16
17[c]	<1.0	<1.0	0.9	0	100
South					
18	1.3	<1.0	0.4	0	100
19	<1.0	<1.0	<0.1	--	--
20	4.8	2.4	12	0	100
21	<1.0	2.7	2.7	0	100
22	2.0	3.0	2.7	0	100
Taylor Slough					
7[c]	2.1	1.2	12	50	50
8[c]	1.6	22	<0.1	--	--
10[c]	2.8	6.7	2.1	0	100
11[c]	2.7	7.6	11	0	100
12[c]	1.1	1.7	11	18	82
Context Road					
CR-0[c]	<1.0	<1.0	33	54	46
CR-1[c]	1.6	<1.0	11	82	18
CR-2	<1.0	2.0	2.0	50	50
CR-3	<1.0	<1.0	5.0	92	8
CR-4	3.4	7.1	17	35	65
CR-5	<1.0	<1.0	5.7	50	50
CR-6	<1.0	<1.0	5.1	59	41

[a] Actively farmed since early 1960s. [b] Farming began approximately 1973. [c] Sites within the boundary of the park.

standards; however, individual contributions of four Aroclors (1242, 1248, 1254, and 1260), which accounted for the majority of domestic use from 1957 to 1971 (*14*), were calculated using a computerized pattern recognition program (*15*). Pattern matchings of PCBs isolated from soils are reported as percent Aroclor 1242/1248 and Aroclor 1254/1260. These percentages represent approximate pattern matchings and are not quantitative estimates of the PCB composition of each sample. The detection limit was 0.1 ppb. Since PCB pattern recognition programs had not been widely applied to environmental samples, it was difficult to assess whether this technique could be useful in determining sources and transport pathways of these compounds. West et al. (*16*) have used an identical program to characterize sources of sewage material in New York Bight sediments with limited success.

Results and Discussion

Pesticides. Chlordane, DDT, and DDT metabolites were the principal pesticides detected. Residues of other chlorinated and organophosphate pesticides examined in this study were present at only three sites (A1, A2, and 20). The results are summarized in Tables I and II. Agricultural sites A1 and A2 were highest in total DDT and total chlordane. Detailed application histories of these fields were not available; however, the DDT metabolite *p,p'*-DDE accounted for a major portion of total DDT, indicating a lack of recent use. The detection of aldrin and dieldrin at site A2 indicates a recent application, as aldrin is quickly oxidized to dieldrin in soils (*17*). Low levels of total chlordane and total DDT at agricultural sites 1, 3, 4, and 6 can be explained by the fact that these are very recently farmed areas (ca. 1973) and, thus, have received little application of these compounds. In addition, these fields are cultivated only in the winter and left fallow the remainder of the year. This is in contrast to active agricultural sites A1 and A2, which are farmed most of the year. Lower levels of these compounds at the fallow agricultural site (A3) suggest it has been inactive for some time.

Nearly all sites proximate to the agricultural lands contained pesticide concentrations below the detection limits of the analysis (Tables I and II). Concentrations of total DDT drop from 761 ppb (site A2) to <1.0–1.2 ppb (sites 14 and 15, respectively) over a distance of slightly more than 2 km. The same is true of chlordane which falls from 190 to 1.5–3.1 ppb at the same sites. This drastic decrease in concentration suggests that little horizontal movement of pesticides has occurred. The highest concentrations of total DDT and total chlordane within the park are found in Taylor Slough. Elevated pesticide concentrations in the Slough would be indicative of a major pathway for these compounds into the park, i.e., transported by the sheetwater flow either adsorbed on particulate matter or in the dissolved phase. Although higher than in the surrounding areas, the extremely low levels de-

Table II. Occurrence of Other Pesticides in Soil Samples from the Everglades National Park and Adjacent Areas

pesticide	result
lindane	none detected at any site
heptachlor epoxide	none detected at any site
dieldrin	concentrations greater than 1.0 ppb detected at three sites: 20, 2.0 ppb; A1, 16 ppb; A2, 238 ppb
aldrin	detected at one site: A2, 11 ppb
endrin	none detected at any site
toxaphene	none detected at any site[a]
parathion/malathion	none detected at any site[b]

[a] Toxaphene is a complex mixture of chlorinated compounds and may be difficult to detect in the presence of other chlorinated pesticides. [b] Low levels of organophosphate pesticides cannot be adequately determined using an electron capture detector.

Table III. Individual Aroclor Distributions in Plastic Sheeting and the Sampling Grid (Percent of Total)

	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
plastic sheeting	34	30	17	19
sampling grid	31	29	18	22

tected indicate that these are not significant processes. It appears that agricultural activity adjacent to the park is responsible for only low-level contamination of parklands through Taylor Slough. Because of the importance of Taylor Slough to wildlife in the Everglades, however, pollutant levels in this area should be carefully monitored.

The low levels detected at these sites are surprising considering their proximity to active agricultural fields. Factors which could account for these low concentrations include the following:

(a) The application of fertilizers, pesticides, etc., is confined to the fields with little accidental application to surrounding areas.

(b) Canals C-111 and L31W that separate the agricultural lands from parklands are receiving most of the irrigation and rainwater runoff.

(c) Many soil samples contained relatively large amounts of organic matter. Humic substances, the major organic component of soils and sediments, have been shown to adsorb *p,p'*-DDT (*18*) and other hydrophobic organic compounds (*19, 20*). The amounts of chlorinated hydrocarbons bound in this manner, and, thus, not extractable by organic solvent, could be significant. However, the availability of humic bound chlorinated hydrocarbons to biological systems has not been documented.

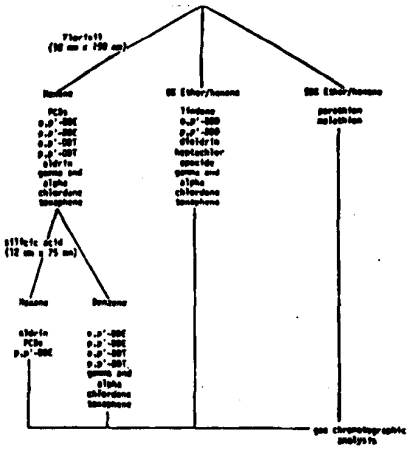

Figure 2. Separation scheme for chlorinated hydrocarbon analysis of soil samples

(d) The high rate of evaporation and intense heat in the dry season could account for loss of even moderately volatile or unstable components.

Further investigation is necessary to determine which of these factors, if any, is prevalent.

PCBs. Agricultural sites A1 and A2 are highest in total PCB, but concentrations are an order of magnitude less than the chlorinated pesticides (Table I). This is expected, as thousands of pounds of the pesticide DDT were used annually in South Florida (*21*), whereas plastic sheeting, the suspected source of PCBs, is a relatively new item in agriculture. Concentrations at these sites are only slightly greater than at other sites in the grid. PCBs apparently are not accumulated preferentially in farmland soils. A westerly decrease in concentration is also observed for PCBs, but is more gradual than that of the pesticides. In some areas, such as the transect through sites 3–4–5 and CR-5–CR-3–CR-1–CR-0, levels initially decrease and then increase away from the agricultural lands (Figure 1 and Table I). These increases may reflect alternate point sources of PCBs or physical differences in accumulative tendencies among the different soils. The widespread distribution of PCBs throughout the grid implies that

Table IV. PCB and DDT Concentrations in Various Soils and Marine Sediments throughout North America and the North Atlantic

environment[a]	total PCB, ng/g	total DDT, ng/g	source
(se) Monsanto production facility, Ill.	150–2.1 × 10⁶		25
(se) agricultural lands, western Canada		760–4010	26
(se) New York Bight	0.5–1460	<0.1–120	16
(se) Mississippi Delta	0.2–35	0.2–9.3	27
(se) Irish Sea	<2–16	<0.2–1.6	28
(se) North Atlantic abyssal plain	0.2–2.8	0.5	29
(se) Firth of Clyde	10–2900		30
(se) Chesapeake Bay	11–1200	<1.0–273	31
(se) Santa Barbara Basin	103	178[b]	32
(se) Everglades National Park	<1.0–33	<1.0–22	this study

[a] As *p,p'*-DDE + *p,p'*-DDD. [b] se = marine sediment; so = soil.

dispersal of these compounds is not limited by physical boundaries such as canals or sloughs.

Two separate analyses of plastic sheeting for PCBs averaged 273 ppb. Although the sale of PCBs was voluntarily limited to closed systems after 1970, it is probable that materials containing PCBs were marketed and sold after this date. The levels detected in the sheeting, however, are indicative of contamination during the manufacture rather than deliberate formulation. In spite of these trace levels, the individual Aroclor distribution in plastic sheeting closely resembles the Aroclor distribution in the sampling grid; i.e., if PCBs isolated from all samples were combined, the pattern would be similar to that of plastic sheeting (Table III). These data suggest that plastic sheeting is the source material in this area. The individual Aroclor distribution in soil samples supports this assertion. A pattern similar to a mixture of Aroclor 1242 and 1248 is found almost exclusively west-southwest of the farmlands and, to a lesser degree, in the Context Road area, while Aroclors 1254 and 1260 predominate south of the farmlands and in Taylor Slough. In addition, the average PCB concentrations in the areas where Aroclor 1242/1248 predominate are nearly twice the concentrations where Aroclor 1254/1260 predominate (Table I). One explanation for these unequal distributions is the different volatilities of individual chlorobiphenyls. The major chlorobiphenyls in Aroclor 1242/1248, which have vapor pressures an order of magnitude greater than those of Aroclor 1254/1260 (*22, 23*), would be more easily volatilized during burning and, thus, more susceptible to aerial transport. The east-southeast winds which prevail during most of the year (*24*) would account for the observed distribution and the westerly concentration decrease. Differences in average PCB concentrations can be explained by the fact that PCBs in plastic sheeting consist of nearly twice as much Aroclor 1242/1248 as Aroclor 1254/1260 (Table III). The predominance of Aroclor 1254/1260 in Taylor Slough implies that transport of these chlorobiphenyls occurs by an alternate mechanism, probably adsorption on particulate matter, which is deposited and resuspended in the slough. Sampling of atmospheric particulates and volatiles, especially during the burning of plastic sheeting, should determine the validity of this atmospheric transport mechanism.

The data presented above suggest that volatile PCBs are being mobilized by the burning of plastic sheeting and transported by the prevailing winds. Thus, the levels detected in the park are probably the result of low level inputs occurring during the burning of contaminated sheeting. However, based on the magnitude of these levels, this input accounts for little contamination of parklands. A comparison of the data in this study to other areas (Table IV) shows that PCB and DDT levels found within the park are as low as at any site sampled in North America. Comparisons of this type can be misleading due to differing analytical techniques, but it is surprising to find lower levels of these compounds in the park, a region especially susceptible to direct inputs, than in coastal depositional environments which receive indirect inputs (via sedimenting particulate matter, sludge dumping, etc.). Although data presented herein indicate that the area is pristine with respect to chlorinated hydrocarbons, levels of other pollutants, such as phthalate esters and polycyclic aromatic hydrocarbons, as well as other insecticides and herbicides, should be determined in order to more accurately assess man's impact on this fragile environment.

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