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Organic Pollution of the Water in the Black Creek Vicinity, Biscayne National Park



United States Department of the Interior

National Park Service
Southeast Region

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ORGANIC POLLUTION OF THE WATER IN THE BLACK CREEK VICINITY,
BISCAYNE NATIONAL PARK

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NATIONAL PARK SERVICE - Southeast Region

Research/Resources Management Report SER-86

Produced under Contract No. CX5000-4-1096 for Biscayne National Park,
National Park Service, U.S. Department of the Interior

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75 Spring Street, S.W.
Atlanta, Georgia 30303

December 1987

UNITED STATES DEPARTMENT OF THE INTERIOR
NATIONAL PARK SERVICE



Corcoran, Eugene F., Melvin S. Brown and Ana D. Freay. 1987. Organic Pollution of the Water in the Black Creek Vicinity, Biscayne National Park. U.S. Department of the Interior, National Park Service, Research/Resources Management Report SER-86. Southeast Regional Office, Atlanta, Georgia. 19 pp.

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INTRODUCTION

In June 1980 the Biscayne National Park (BNP) extended its boundary northward to include Black Creek, an area which had been of ecological concern for several years. Prior to acquisition, many of the local commercial bait fishermen had complained of fish kills, and reduced catches; Metropolitan Dade County Department of Environmental Resources Management reported elevated water-column turbidity, ammonia and phosphate concentrations, and lower salinities as compared to other canals in lower Biscayne Bay and Card Sound; Corcoran et al. (1983 and 1984) reported high sediment concentrations of metals, chlorinated pesticides, and petroleum hydrocarbons. With the inclusion of the area in the BNP monitoring program and after several years of observation, park personnel also became concerned about the area due to consistently degraded water quality and what seemed to be a rapidly changing benthic community.

In September 1984 funding became available through the Southeast Region of the National Park Service to investigate the possible causes for several of the changes that were taking place in the Black Creek area. The objectives of the investigation were to document benthic community structure, and to determine if groundwater upwelling might be a source of nutrients and chlorinated pesticides. These tasks were accomplished by evaluating the overlying and sediment pore waters for insecticides, herbicides, polychlorinated biphenyls (PCBs), phthalic acid esters (PAEs), and common nutrient species; determination of their fluxes; a quantitative description of existing bottom biota; and the regrowth potential of seagrasses if herbivore activity was eliminated.

The determination of the common nutrient species in overlying and sediment pore waters, flux rates, description of the existing bottom community, and the regrowth of nonherbivorized seagrasses have been reported by Froelich (1985).

This report deals only with the insecticides, herbicides, PCBs, and PAEs that were detected in sediment pore waters.

STUDY AREA

The general study area is located in the southern portion of Biscayne Bay, latitude 25°32'N, longitude 80°19'W. The area reported to be most affected is located south of the Black Creek/Goulds Canal area between Moody and Military Canals. The canals in this area have salinity control structures which are operated by the South Florida Water Management District. The canals were constructed for and are presently being used for drainage of inland areas and as a source of water for agriculture. The canals drain areas of varying land use which include, but are not limited to, agriculture, sanitary landfills, a military airbase, residential communities, light industry, and undeveloped land.

Sampling Sites

A total of 18 sample stations was established for the collection of sediment pore water. The stations were arranged into six east-west transects of three stations each (Inner, Middle, and Outer). Nine of the stations were located within the area between Moody Canal, Fender point, and Military Canal. Two other study areas were chosen in what was believed to be unaffected areas. Three stations were located north of the impacted area (North Black Point) and the six remaining stations were located to the south between Florida City Canal and Turkey Point (North Turkey Point and South Turkey Point).

METHODS

The water sampling program was initiated and completed in November 1984. For a detailed discussion of the field methods used in collection of the water samples, and initial laboratory separation procedures see Froelich (1985).

The clean procedures and quality assurance guidelines discussed in Sherma (1976), and Plumb (1981) were followed for the synthetic organic analysis. Materials that were used were always glass, Teflon, or metal and were either solvent rinsed or burned at 500°C to remove all organic contaminants.

Sample Extraction - Synthetic Organics

The volume of each separated water sample was carefully measured upon receipt. All Sample volumes were small and varied considerably. Each sample was placed in a 125-ml separatory funnel and extracted with one-tenth its volume of 15% diethyl ether and hexane. This extraction was followed by a second extraction of 6% diethyl ether and hexane, and, finally, a third extraction was made with hexane only. This extraction procedure was introduced by Dr. David Young (U.S. Environmental Protection Agency, Hatfield Marine Science Center, Newport, Oregon 97365; personal communication) to avoid the use of the somewhat carcinogenic methylene chloride as a solvent.

The combined ether-hexane extracts were dried over anhydrous sodium sulfate, concentrated to about 0.5 ml in a micro Kuderna-Danish apparatus using a block heater, placed on a micro Florosil column, and separated into three fractions according to the procedure outlined by Watts (1980). Each fraction was then concentrated to 0.5 ml with a block heater under a stream of pure nitrogen. Using a Pasteur pipette, each fraction was, at last, transferred to a small vial to await the determination of the organochlorine pesticides, polychlorinated biphenyls, and phthalic acid esters by gas chromatography.

Gas Chromatographic Analysis

Two to ten microliters of the hexane extract was introduced into a TRACOR Model 222 gas chromatograph equipped with dual Ni-63 electron capture detectors and 185-cm by 0.2-cm glass columns packed with 1.5% SP2250, 1.95% SP2401, and 5% SP2401. Oven temperature was held at 200°C, injection temperature at 215°C,

detector temperature at 250°C and the carrier gas, nitrogen, was maintained at a flow rate of 45 ml·min⁻¹. The chromatograms were recorded on two Hewlett-Packard integrators that had been programmed to indicate the retention time, the area under each peak, and amounts of each compound. Standards from the U.S. Environmental Protection Agency repository (Health Effects Research Laboratory, Environmental Toxicology Division, Research Triangle Park, North Carolina 27711) were used to establish the calibration curves and to program the integrators. Each chromatogram was carefully examined and the concentration of each detected compound was calculated.

RESULTS

Four groups of compounds (insecticides, herbicides, PCBs, and PAEs) which included a total of 24 individual compounds were quantified (see Table 1). Thirteen of these compounds were detected in two groups: insecticides and PAEs. No herbicides or PCBs were detected in pore water or flux samples.

For reporting purposes, the o,p' and p,p'-DDT, -DDE, and -DDD compounds, although determined separately, were combined and are presented as total DDT, DDE, and DDD.

Pore Water

Fifty-three pore water samples were analyzed, only five of the samples were free of any contamination. Three of these samples were collected from the impacted area and two from the southern comparison area. The remaining 48 samples showed varying degrees of insecticides and PAE contamination (see Table 2). Concentrations were quite variable in the profiles although there does appear to be a general trend for concentrations to increase with depth. This was particularly evident for the PAEs.

Table 1. Synthetic chlorinated hydrocarbons and phthalic acid esters analyzed for in this study.

<u>INSECTICIDES</u>	<u>HERBICIDES</u>
Aldrin	2,4-D
p-p' DDE	2,4,5-T
o-p' DDE	Silvex
p-p' DDD	
o-p' DDD	<u>POLYCHLORINATED BIPHENYLS</u>
p-p' DDT	Aroclor 1016
o-p' DDT	Aroclor 1254
Dieldrin	Aroclor 1260
Endrin	
Endosulfan	<u>PHTHALIC ACID ESTERS</u>
Heptachlor Epoxide	Butylbenzyl
Heptachlor	Butylglycolbutyl
Methoxychlor	Di-butyl
Toxaphene	Di-ethylhexyl
	Di-ethyl
	Di-isobutyl
	Di-methyl

Table 2. Concentration profiles for the insecticides and phthalic acid esters detected in pore waters. Stations are listed in order of location from north to south within the study area. Insecticides are reported in ng/l and phthalic acid esters are in ug/l.

Station/ Location	Depth (cm)	Aldrin	DDE ^a	DDD ^b	DDT ^c	Dieldrin	Methoxy- chlor	Endo- sulfan	Heptachlor epoxide	Hepta- chlor	Endrin	BBP ^d	BBP ^d DEHP ^d
NORTHERN COMPARISON AREA													
North Black Point Inner	1	nd ^e	nd	nd	nd	29	nd	nd	34	116	nd	5	nd 38
	3	123	nd	594	1,577	1,597	nd	752	574	nd	1	nd	nd
	5	1,286	nd	nd	nd	1,063	nd	nd	nd	nd	nd	24	143 82
	9	4	nd	8,331	21,135	4,879	nd	5,185	nd	nd	nd	nd	nd
Middle	1	nd	nd	135	385	nd	nd	1,090	65	34	54	6	12 15
	3	nd	nd	236	695	nd	nd	4,017	119	155	nd	11	18 37
	7	nd	nd	1,409	3,044	1,544	nd	455	nd	nd	nd	32	33 78
	11	133	nd	486	1,122	228	nd	369	1,627	nd	nd	nd	nd 35
Outer	1	nd	nd	nd	nd	2,214	nd	nd	nd	nd	nd	22	98 36
	3	nd	nd	354	714	108	nd	187	69	nd	nd	9	23 38
	9	nd	nd	nd	nd	4,524	nd	nd	nd	nd	nd	15	102 28
	15	nd	1,183	286	nd	nd	nd	2,366	4,936	nd	1,158	182	358 280
IMPACTED AREA													
Moody Canal Inner	1	nd	nd	nd	nd	199	nd	nd	nd	nd	nd	22	12 60
	3	nd	nd	2	nd	68	nd	nd	56	29	nd	4	7 52
	9	123	152	nd	nd	nd	nd	nd	nd	nd	nd	10	85 98
Middle	1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	3	nd	nd	nd	nd	18	nd	nd	23	nd	nd	7	nd 36
	9	nd	nd	97	90	336	nd	nd	249	nd	nd	6	31 37
Outer	1	nd	854	nd	nd	nd	nd	nd	nd	144	nd	15	159 248
	3	nd	nd	nd	nd	nd	nd	nd	1,703	1,654	nd	15	95 53
	5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	13	4 34

Table 2. (cont'd)

Station/ Location	Depth (cm)	Aldrin	DDE ^a	DDD ^b	DDT ^c	Dieldrin	Methoxy- chlor	Endo- sulfan	Heptachlor epoxide	Hepta- chlor	Endrin	BBP ^d	BBP ^d	DEHP ^d
IMPACTED AREA (cont'd)														
Fender Point		Sample lost												
Inner														
Middle	1	9	nd	396	850	nd	nd	166	42	108	nd	10	nd	19
	3	nd	nd	243	934	99	nd	1,684	43	45	24	12	8	33
	7	nd	nd	758	2,807	415	nd	773	163	86	274	43	57	57
	10	nd	nd	334	832	263	nd	150	85	179	nd	27	43	60
Outer	1	Sample lost												
	3	Sample lost												
	11	232	nd	nd	440	nd	nd	nd	nd	nd	nd	36	98	112
	19	nd	nd	nd	508	1,838	nd	937	796	1,716	nd	17	126	36
Military Canal														
Inner	1	nd	3,256	1,702	6,114	nd	nd	1,861	924	487	1,052	70	38	62
	3	nd	nd	115	546	124	nd	501	591	166	40	18	25	28
	9	nd	nd	nd	1,476	945	nd	nd	1,831	1,770	nd	112	136	43
Middle	1	Sample lost												
	3	nd	nd	nd	382	64	nd	844	270	31	35	14	20	16
	7	nd	nd	nd	408	34	nd	1,096	238	52	26	11	10	16
Outer	1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	3	7	162	1,025	152	nd	nd	nd	nd	nd	nd	56	53	95
	11	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SOUTHERN COMPARISON AREA														
North Turkey Point														
Inner	1	nd	nd	nd	nd	11	nd	nd	nd	nd	nd	2	nd	30
	3	nd	63	nd	nd	nd	nd	nd	nd	nd	nd	32	16	202
	9	nd	nd	nd	nd	nd	nd	nd	59	nd	nd	57	30	331

Table 2. (cont'd)

Station/ Location	Depth (cm)	Aldrin	DDE ^a	DDD ^b	DDT ^c	Dieldrin	Methoxy- chlor	Endo- sulfan	Heptachlor epoxide	Hepta- chlor	Endrin	BBP ^d	BBP ^d DEHP ^d
SOUTHERN COMPARISON AREA (cont'd)													
North Turkey Point Middle	1	nd	94	nd	nd	nd	nd	nd	nd	nd	nd	12	11 121
	3	nd	nd	335	704	355	nd	124	118	nd	nd	24	5 36
	7	nd	nd	nd	nd	nd	nd	nd	6	nd	nd	14	nd 46
Outer	1	nd	nd	nd	nd	1,968	nd	2,308	nd	nd	nd	10	106 26
	3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	6	2 18
	19	nd	856	nd	nd	nd	nd	nd	1,676	nd	nd	24	134 236
South Turkey Point Inner	2	nd	nd	424	98	nd	nd	374	195	410	nd	41	54 112
	4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	6	nd	nd	nd	nd	1,820	nd	nd	nd	nd	nd	3	20 9
Middle	1	nd	nd	3,242	4,332	2,740	nd	nd	nd	nd	nd	5	11 32
	3	nd	nd	34	164	126	nd	nd	142	137	nd	14	6 64
	9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	23	nd 44
Outer	2	nd	nd	249	538	169	nd	420	402	61	nd	8	19 17
	4	nd	nd	981	nd	nd	nd	nd	nd	nd	nd	59	101 62
	8	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

^aDDE includes p-p'DDE and o-p'DDE^bDDD includes p-p'DDD and o-p'DDD^cDDT includes p-p' DDT and o-p'DDT^dPhthalic acid esters; BBP = butylbenzyl; DBP = Di-butyl; DEHP = Di-ethylhexyl^eNone detected

In summary, the three areas of investigation were characterized by mean numbers of compounds and mean concentrations per sample (see Table 3). Insecticide contamination indicated a corresponding increase in compounds per sample with concentration per sample, i.e., the greater the concentration the more compounds observed. The PAEs did not exhibit this trend. They indicated a different pattern with the number of compounds and concentrations inversely related, i.e., the greater the concentration the fewer the number of compounds observed. This reverse correlation was probably caused by the limited number of compounds detected (a total of three detected) and the fact that PAEs have become common in Biscayne Bay sediments (Corcoran et al. 1984).

In regard to insecticide contamination, the northern comparison site possesses the greatest degree of contamination, both in mean numbers of compounds per sample and mean concentrations. The northern site was followed by the impacted area and the southern comparison site. This ranking was supported partially by the mean PAE concentrations; the northern comparison site having the greatest concentration and the impacted site and southern comparison site being approximately equal.

Groundwater Flux

Froelich (1985), using salinity as the conservative tracer, stated that of the 17 groundwater flux samples, 10 indicated no change, three leaked ambient water, and four were observed where salinity decreased thereby indicating groundwater intrusion. These four samples were located at Military Canal (impacted area) and North Turkey Point (southern comparison site).

All of the 14 samples analyzed for insecticides and PAEs indicated losses of some of the detected compounds. Eight of the samples indicated increases in concentrations between initial and final values for some of the detected compounds (see Table 4). Comparison of these results with the salinity analyses discussed

Table 3. Summary of mean concentrations and compound frequencies by study area. Insecticide concentrations are expressed as ng/l and phthalic acid esters as ug/l.

Study Area	Sample Size	Insecticides		Phthalic Acid Esters	
		Compounds/ Sample	Concentration/ Sample	Compounds/ Sample	Concentration/ Sample
<u>NORTHERN COMPARISON AREA</u>					
(North Black Point)	12	4.1	6898	2.2	147
<u>IMPACTED AREA</u>					
(Moody Canal, Fender Point and Military Canal)	23	3.5	2276	2.6	121
<u>SOUTHERN COMPARISON AREA</u>					
(North and South Turkey point)	18	1.9	1430	2.5	124

Table 4. Insecticides and phthalic acid esters fluxes measured in dark glass chambers (3 liter volume; 511-cm² surface area) over approximately 24-hour periods. Insecticide concentrations are expressed as ng/l and phthalic acid esters as ug/l. Negative (-) values indicate a decrease in concentration, while a positive value indicates an increase in concentration between initial and final flux samples.

Station/ Location	Aldrin	DDE ^a	DDD ^b	DDT ^c	Dieldrin	Methoxy- chlor	Endo- sulfan	Heptachlor epoxide	Hepta- chlor	Endrin	BBP ^d	BBP ^d	DEHP ^d
NORTHERN COMPARISON AREA													
North Black Point Inner	nd ^e	nd	nd	-6	-5	nd	nd	-56	10	nd	3	2	24
Middle	nd	-8	-155	22	59	nd	nd	-14	29	-118	-7	11	6
IMPACTED AREA													
Moody Canal Inner	nd	nd	nd	nd	-8	nd	nd	-21	-37	nd	9	nd	13
Middle	nd	nd	nd	nd	-90	nd	nd	-69	nd	nd	-4	nd	-1
Outer	nd	nd	nd	nd	nd	nd	nd	-65	nd	nd	0	nd	-12
Fender Point Inner	Sample lost												
Middle	nd	nd	66	36	-71	nd	-70	-32	-27	nd	-7	-2	-24
Outer	nd	nd	8	90	-9	nd	58	162	-9	-96	1	-1	7
Military Canal Inner	Sample lost												
Middle	Sample lost												
Outer	nd	nd	44	112	-61	nd	-198	343	19	nd	1	2	-3

Table 4 (cont'd)

Station/ Location	Aldrin	DDE ^a	DDD ^b	DDT ^c	Dieldrin	Methoxy- chlor	Endo- sulfan	Heptachlor epoxide	Hepta- chlor	Endrin	BBP ^d	BBP ^d	DEHP ^d
<u>SOUTHERN COMPARISON AREA</u>													
North Black Point Inner	nd ^e	nd	nd	-27	48	nd	nd	-15	40	nd	4	nd	-8
Middle	-760	nd	-7,131	0	-3,657	-6,055	-9,455	99	47	-10,351	6	-130	38
Outer	-850	nd	nd	nd	-3,849	-7,883	nd	-2,997	-876	-11,006	6	14	31
Southern Turkey Point Inner	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Middle	nd	nd	nd	-1,334	-85	nd	nd	-573	-24	-10	-7	-11	-11
Outer	nd	nd	nd	-2,231	-91	nd	nd	-437	-25	nd	-12	-12	-13

^aDDE includes p-p'DDE and o-p'DDE^bDDD includes p-p'DDD and o-p'DDD^cDDT includes p-p'DDT and o-p'DDT^dPhthalic acid esters; BBP = Butylbenzyl; DBP = Di-butyl; DEHP = Di-ethylhexyl^eNone detected

above indicated no observable trends or correlations. Unfortunately, two of the four samples which indicated groundwater intrusion were lost during laboratory processing. The remaining two samples showed an increase in several compounds, although the increased concentrations were no different than those observed in other samples. In addition the compounds detected were the same as those in other samples.

DISCUSSION

Agriculture is important to the Florida economy, contributing \$4.4 billion in 1982 (Holden 1986). Citrus accounted for over \$1 billion in sales and vegetable, melon and strawberry crops accounted for just under \$1 billion. Pesticides are important to the production of these commodities. Dade County has extensive agriculture areas devoted to the production of vegetable crops and vast acres of coastal and freshwater wetlands which are a source of mosquitoes. Dade County has also been the entry point of numerous exotic pests e.g., the Mediterranean Fruit Fly. Historically pesticides have been used extensively in Dade County to control not only crop pests but also mosquitoes and introduced exotic pest species. In 1962, in excess of 10,000 pesticide preparations and formulations were registered with the Florida State Department of Agriculture (MacDonald 1965). All of these preparations which ranged in acute toxicity from relatively harmless to extremely toxic were available to the general public. According to MacDonald (1965) the most commonly used compounds in 1962 were malathion, dieldrin, DDT, chlordane, parathion, maned, tribasic copper sulfate, and aldrin.

Previous studies by Corcoran et al. (1983 and 1984) indicated the presence of insecticides, petroleum hydrocarbons, and other anthropogenic contaminants in sediments collected from the Black Creek area. These contaminants were also present in sediments collected from most of the canals which empty into Biscayne

Bay. These canals drain upland areas with dramatically different land use practices ranging from agriculture to intensive urban development. It is important to note that marine sediments, in many cases act as a chemical sink (Wurster 1969) for many very persistent organic compounds, their analyses provide integrated, long-term records of their introduction into the environment, but do not indicate the sources of the contamination or if those sources and pathways are still active.

The detection of insecticides and PAEs in the Black Creek area was not surprising since previous studies have confirmed their presence in the sediments. In addition, the extensive use of the drainage area of the creek for agricultural purposes would certainly provide a source. What is important to note is that these compounds were detected in the pore water indicating that they can become mobile and be introduced into the water column. This could occur by resuspension of the sediments (e.g., from storm events and prop-wash from boats) or the upwelling of groundwater through the sediments. As a result of the shallow depths in the study area the resuspension of sediments due to storm events and to a lesser degree prop-wash would appear to be viable pathways for insecticides to enter the water column and be transported to other areas of the bay or introduced into food chains.

The subsurface movement of groundwater from the terrestrial systems to the bay could not only serve as a mechanism for introduction of insecticides into the water column, but as an input pathway. The groundwater could transport contaminants from inland agricultural areas or landfill disposal sites. Although the results from this study, regarding the occurrence and magnitude of groundwater upwelling were inconclusive, the sediment pore waters did indicate contamination by insecticides and PAEs. The insecticides evaluated for include those which are highly persistent in the environment and which have been either banned or use restricted for many years (see Corcoran et al. 1984). Thus these pesticides have

been in the environment for many years and their presence would not, in most cases, indicate a recent input. The Dade County landfill, which is in close proximity to the study area, could be an existing source for these insecticides, although there is no evidence to support this.

Our analysis of pore water for chlorinated pesticides, PCBs, and PAEs supports the conclusions of Froelich (1985) that the area north of Black Creek, which had originally been designated as a comparison area, for the purpose of this study, was indeed more similar to the impacted site. She arrived at this conclusion through the analysis of type and distribution of benthic vegetation, and nutrient concentrations. Our results indicated that this area was degraded more than the impacted or southern comparison site (see Table 3). Mean sample concentrations in the northern comparison site were three times that at the impacted site and there were 0.6 more compounds per sample. This area had particularly high concentrations of DDD, DDT, Dieldrin, Endosulfan, and Heptachlor Epoxide. These compounds, although presently banned or use restricted in the United States, are all very effective, commonly used agriculture foliar or soil insecticides.

Future research should address whether a substantial input of anthropogenic contaminants is continuing, and by what pathway e.g., upland runoff, canal discharge, groundwater upwelling, or other mechanisms. If these inputs are occurring their source should be located, and actions should be taken to reduce, abate, or cleanse the input prior to it entering the BNP. For example, if the major pathway for contaminants is via the man-made canal system, an alternative would be to provide some natural cleansing by rerouting the discharge water through a coastal wetland. The present BNP water quality monitoring program should be continued, and if possible expanded to include, at least on a periodic basis, metals and organic compounds. It would be interesting to monitor the quality of the discharge water from the area after a major rain event to determine if substantial

enrichment occurs. Seasonal, low level aerial photography should be used to determine the condition and distribution of the benthic vegetation. If this is not possible, permanent study plots should be established for the determination of species composition and health. Side-scanning sonar imagery may be useful in determining the distribution of benthic vegetation, although this may not be practical in the shallow water areas.

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As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environment and cultural value of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

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