ORGANOCHLORINE, TRACE ELEMENT, AND PETROLEUM HYDROCARBON CONTAMINANTS INVESTIGATION OF THE LOWER RIO GRANDE VALLEY, TEXAS, 1985-1986

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INTRODUCTION

The U.S. Fish and Wildlife Service (Service) has been actively involved in the monitoring of contaminants in the Lower Rio Grande Valley of Texas for more than 20 years. In 1967, a fish sampling station (Station 16) was established on the Rio Grande near Mission as part of the National Contaminant Biomonitoring Program. Every two or three years, composite samples of representative predator and bottom feeding fish species have been collected at this station to monitor levels of organochlorine pesticides and trace elements. Since the inception of the contaminant monitoring program, Station 16 has consistently registered some of the higher levels of DDT, DDE, and toxaphene recorded in the United States. Even though the registration of DDT was canceled in 1972, elevated levels of the parent compound, and particularly of its metabolite DDE, have persisted in fish and wildlife.

The obvious persistence of DDT and toxaphene prompted the Service to expand its sampling program in the Lower Rio Grande Valley. In 1976, 1978, and 1979, Service biologists collected fish from the Arroyo Colorado, a primary waterway that traverses the Valley from Mission to the Laguna Madre adjacent to the Laguna Atascosa National Wildlife Refuge (White et al. 1983). Alarmingly high levels of DDE and toxaphene were detected in virtually every sample from McAllen to the Port of Harlingen near Rio Hondo. DDE values as high as 31.5 ppm (wet weight) were detected in a whole fish composite sample of channel catfish (scientific names are presented in Appendix A, Table A-1) captured in the Llano Grande, a relatively wide and shallow portion of the Arroyo Colorado located south of Weslaco. Toxaphene levels as high as 31.5 ppm (wet weight) were detected in a whole fish composite sample of blue catfish collected near the Port of Harlingen. In response to these findings, advisories were posted along the Arroyo Colorado warning fishermen of high organochlorine levels in fish.

White et al. (1983) also reported elevated levels of DDE in birds collected from several locations in the Lower Rio Grande Valley: near Llano Grande, the mouth of the Arroyo Colorado, and the mouth of the Raymondville Drain. DDE residues in laughing gulls ranged from 5 to 71 ppm, 5 to 41 ppm, and 2 to 82 ppm (wet weight) in these areas respectively. Ring-billed gulls, Franklin's gulls, pied-billed grebes, Forster's terns, great-tailed grackles, and red-winged blackbirds collected in the vicinity of Llano Grande contained DDE residues ranging from 2 to 37 ppm (wet weight). Toxaphene levels in birds were low throughout the region, ranging from nondetectable levels to 3 ppm (wet weight).

Several other studies to document the fate and effects of contaminants have been conducted in the Lower Rio Grande Valley of Texas. Not surprisingly, most of these studies have focused on the organochlorine pesticides DDT, DDE, DDD, and toxaphene. Marion (1976) investigated organochlorine levels in plain chachalacas from several areas in the Lower Rio Grande Valley. The author concluded that these birds accumulated lower residue levels than most birds associated with heavily treated lands and attributed this to the plain chachalacas' preference for native fruits rather than sprayed crops. Mean pesticide residues for p, p'-DDT and p, p'-DDE (whole tissue wet-weight basis) ranged from 0.03-5.46 ppm to 0.07-4.25 ppm, respectively. The author

also found no significant difference in shell thickness in plain chachalaca eggs collected during this study compared with eggshells collected in southern Texas before 1900.

Andreason (1985) reported that mosquitofish from the Lower Rio Grande Valley developed a genetic resistance to toxaphene. He found that mosquitofish collected from this area were 122 times more resistant to toxaphene than control fish. The author emphasized the ecological consequences of this phenomenon, especially in terms of biomagnification by predatory species and the death or adverse impacts that may result as a consequence of ingesting resistant prey.

Ahr (1973) documented the persistence of pollutants, primarily DDT, in sediments from the Laguna Atascosa National Wildlife Refuge. Core samples were collected from the major drain (Resaca de los Fresnos) entering the Laguna Atascosa and the Cayo Atascosa. He found DDT to be most abundant near the surface, ranging as high as approximately 16 ppb from the drain site, approximately 10 ppb in a site near the mouth of the Arroyo Colorado, and approximately 5 ppb in the surface sediments from a site on the Cayo Atascosa. DDT was found in relatively high concentrations in sediments deeper than 100 cm. This relocation was attributed to burrowing and mixing by crabs, worms, and other organisms. The author used tissue data to demonstrate progressive exponential increases in DDT residues as higher trophic levels were encountered.

In light of the documented contaminants problems, the Corpus Christi Ecological Services Field Office initiated a two-phase study to determine the extent of the contamination. The initial phase involved the collection of sediment samples throughout the Valley for analysis of trace elements, organochlorines, and polycyclic aromatic hydrocarbons. The second phase involved the collection of fish, birds, oysters, blue crabs and aquatic vegetation for similar analyses. This report presents the findings of this two-phase study.

METHODS AND MATERIALS

Sediment

Sediment was collected at 95 sites throughout the Lower Rio Grande Valley in July and August 1985. Several factors were considered for selection of site locations: 1) sites that have been used as regular sampling sites by federal, state, local, or private organizations, 2) sites with known or suspected contamination; 3) important federal refuge tracts and state wildlife management areas; and 4) primary irrigation and flood control drainage systems. Figure 1 shows the locations of sediment sites and Appendix B, Table B-1 lists the site descriptions.

Samples were placed in quart glass jars with teflon lid liners. Jars and lid liners were chemically cleaned with acid and organic solvents according to EPA procedures (EPA 1982a).

Samples were collected with a stainless steel Ekman dredge or a stainless steel ponar dredge. A stainless steel scoop was used at sites with exposed sediments. A dredge sample from each site was placed in a deep stainless steel pan and the top 15 cm of sediment were removed and transferred to the jars. All sampling equipment was cleaned between each use and additionally the equipment was given hexane solvent rinses at the beginning of each day and several times throughout the day. Samples were frozen as soon as possible after collection and kept frozen until analyzed at contract laboratories.

Sediment was analyzed for 23 trace elements (Table 1) at the Environmental Trace Substance Research Center in Columbia, Missouri. Inductively coupled plasma emission spectroscopy was used to determine all of the elements except arsenic, selenium, and mercury. Arsenic and selenium were determined by hydride generation with atomic absorption. Cold vapor reduction was used for mercury analysis. Blanks, duplicates, spiked samples, and standards were used for quality control and quality assurance and was monitored by the Service's Patuxent Analytical Control Facility (Patuxent).

Organic analysis of sediment was performed at the Mississippi State University's Hand Chemical Laboratory, Starkville, Mississippi. Aromatic hydrocarbons and organochlorines (Table 1) were determined using gas chromatography with mass spectrophotometry for confirmations. Quality control was monitored by Patuxent. Aromatics were analyzed in 15 of the 95 samples and organochlorines were analyzed in all samples. Nominal detection limits in sediment for organics and trace elements analyzed for this study are presented in Table 2.

Biota

Softshell turtles, fish, blue crab, oysters, seagrasses, cotton rats, and birds were collected at 64 sites throughout the Lower Rio Grande Valley in July and August, 1986. Appendix B, Table B-2 lists the species and site

See Table/Figure

(SEE ORIGINAL)

Figure 1. Location of study area and sediment and biota sample sites.

Table 1. Compounds and elements analyzed in sediment and biota from the Lower Rio Grande Valley of Texas, 1985-1986.

ALKANES[sup]1	ORGANOCHLORINESý	ELEMENTS[sup]3
n - DODECANE (n-C12)[sup]4	OXYCHLORDANE	ALUMINUM(AL)
n - TRIDECANE (n-C13)	c - CHLORDANE	ANTIMONY(SB) *
n - TETRADECANE (n-C14)	t - CHLORDANE	ARSENIC (AS)
OCTYLCYCLOHEXANE (n-C14)	c - NONACHLOR	BARIUM(BA)
n - PENTADECANE (n-C15)	t - NONACHLOR	BERYLLIUM(BE)
NONYLCYCLOHEXANE	HEPTACHLOR	BORON (B)
n - HEXADECANE (n-C16)	HEPTACHLOR EPOXIDE	CADMIUM(CD)
n - HEPTADECANE (n-C17)	METHOXYCHLOR	CHROMIUM(CR)
PRISTANE	o,p' - DDE	COPPER (CU)
n - OCTADECANE (n-C18)	o,p' - DDD	IRON (FE)
PHYTANE	o,p' - DDT	LEAD(PB)
n - NONADECANE (n-C19)	p,p' - DDE	MAGNESIUM(MG)
n - EICOSANE (n-C20)	p,p' - DDD	MANGANESE (MN)
n - HENEICOSANE (n-C21)	p,p' - DDT	MERCURY(HG)
ENDRIN	MOLYBDENUM (MO)	
DIELDRIN	NICKEL (NI)	
ALDRIN	SELENIUM (SE)	
alpha-BHC	SILVER (AG)	
beta-BHC	STRONTIUM (SR)	
gamma-BHC	THALLIUM (TL)	
delta-BHC	TIN(SN) *	
AROMATIC[sup]5	HEXACHLOROBENZENE	VANADIUM (V)
HYDROCARBONS	ENDOSULFAN I	ZINC(ZN)
ENDOSULFAN II		
NAPHTHALENE	ENDOSULFAN SULFATE	* - SEDIMENT
FLUORENE	MIREX	ONLY
PHENANTHRENE	DCPA	
ANTHRACENE	DICOFOL	
FLUORANTHRENE	TETRADIFON	
PYRENE	AROCHLOR 1221	
1,2 - BENZANTHRACENE	AROCHLOR 1016	
CHRYSENE	AROCHLOR 1232	
BENZO(b)FLUORANTHRENE	AROCHLOR 1242	
BENZO(k)FLUORANTHRENE	AROCHLOR 1248	
BENZO(e)PYRENE	AROCHLOR 1254	
BENZO(a)PYRENE	AROCHLOR 1260	
1,2,5,6-DIBENZANTHRAC	AROCHLOR 1262	
TOTAL PCB'S		
BENZO (g,h,i)PERYLENE	TOXAPHENE	

[sup]1 ALKANES - BIOTA ONLY
ý ORGANOCHLORINES - BIOTA AND SEDIMENT
[sup]3 ELEMENTS - BIOTA AND SEDIMENT
[sup]4 CARBON NUMBER IN THE COMPOUND
[sup]5 AROMATICS - BIOTA AND SEDIMENT

Table 2. Nominal detection limits of analytical methods used in the analysis of sediment and biota samples collected from the Lower Rio Grande Valley, Texas, 1985-1986.

BIOTA CHEMICAL	SEDIMENT UG/G(WET WT)	UG/G(DRY WT)
SE	0.5	0.2
HG	0.5	0.05
AS	0.5	0.2
AG	0.2	0.3
AL	1.0	10.0
B	5.0	1.0
BA	0.1	0.1
BE	0.1	0.1
CD	0.1	0.2
CR	0.1	1.0
CU	0.1	1.0
FE	1.0	3.0
MG	1.0	0.2
MN	1.0	0.1
MO	0.1	2.0
NI	0.1	2.0
PB	0.2	3.0
SB	---[sup]1	3.0
SN	1.0	2.0
SR	0.1	0.1
TL	0.3	7.0
V	0.1	1.0
ZN	1.0	1.0
ALKANES	0.03	---
ORGANOCHLORINES	0.01	0.01
TOXAPHENE	0.25	0.05
PCB's	0.25	0.05
PETROLEUM AROMATIC HYDROCARBONS	0.03	0.01

[sup]1 ---- NOT ANALIZED

locations. Preliminary site selection was based upon the same factors listed above for sediment although some sites were added or removed due to availability of target species.

Softshell turtles were collected using 12" X 24" X 24" crab traps set with the top above or just below the surface of the water. Fish were collected by electroshocking, gill nets, and minnow traps. Oysters were gathered by hand as were seagrasses and chara. Cotton rats were live trapped using Sherman mammal traps. Black-necked stilts were taken with a shotgun using steel-shot. A single white pelican was salvaged by U.S. Fish and Wildlife

Service refuge personnel earlier in the year. Turtle, crab, cotton rat, black-necked stilt, and most fish samples were composites of 5 individuals (whole body). Tilapia, sheepshead minnow, sailfin molly, and gizzard shad samples consisted of 10-50 individuals.

Upon collection, all fish, bird, cotton rat, turtle, and blue crab samples were wrapped in aluminum foil and kept on ice until frozen. Seagrass samples were placed in two 32 oz. whirl-pak bags per site. Samples were then frozen until preparation for analysis. Oyster tissue was placed in chemically cleaned quart jars (as above), kept on ice and later frozen. Approximately one pint of oyster tissue was collected per site. The claws of blue crabs were removed and analyses included the exoskeleton. There was only enough sheepshead minnow tissue available at site 6 to analyze for organics, arsenic, selenium, and mercury.

All analyses for biota sites 1-15 were performed at the Patuxent Wildlife Research Center. Aromatic hydrocarbons and organochlorines were determined using gas chromatography with mass spectrophotometry for confirmation. Trace elements were determined using inductively coupled plasma emission spectroscopy. Hydride generation with atomic absorption was used for arsenic and selenium determination and cold vapor reduction was used for mercury.

All other samples were analyzed using the same methods as above (except where noted below), but were done at contract laboratories. Analyses for trace elements were performed at the Trace Substance Research Center in Columbia, Missouri. Preconcentration methods were used to enhance detection limits for cadmium, copper, molybdenum, nickel, lead, thallium, vanadium, and zinc. Organics analyses were performed at Weyerhaeuser Analytical and Testing Services in Takoma, Washington. The Patuxent Analytical Control Facility monitored quality control at these laboratories. Nominal detection limits for the chemicals and elements that were analyzed in biota for this study are given in Table 2.

Data Analysis

Minimum and maximum values were determined for all organochlorine, trace element, and petroleum hydrocarbon concentrations found above detection limits. Geometric means were determined in those instances where more than 50% of the samples were above detection limits. In those cases where geometric means were calculated, one-half the detection limit was used for those samples below detection limit. The numerical log of each value was

taken and then the mean of the logs was calculated. The antilog of the mean was then taken to convert the value back to the arithmetic scale.

All fish data was combined so that it could be compared to National Contaminant Biomonitoring Program summary data (Schmitt et al. 1981, Schmitt et al. 1983, Schmitt et al. 1985). Because this study was intended as a reconnaisance investigation of contaminants in various matrices, residues in fish are not presented by species or trophic level. Geometric means were not determined for bird and oyster data because of the small sample size.

RESULTS

Organochlorines

Fifteen organochlorine compounds (plus one PCB compound) were found above the detection limits in all samples analyzed. However, only nine of these contaminants were detected in greater than 10 percent of all samples. Table 3 presents the geometric means and ranges of these 9 organochlorines. (Appendix C, Tables C-1 through C-6, provides summaries of all organochlorines).

Five organochlorines were detected in sediment samples. DDE, a metabolite of DDT, was the most pervasive contaminant found in sediments, occurring in 70 of 95 samples. DDE was the only residue detected in enough sediment samples to determine a geometric mean. DDE ranged from 0.01 to 6.00 ppm with a geometric mean of 0.02 ppm. The parent material, DDT, was detected in only one sample at 0.89 ppm. DDD, which is another metabolite of DDT, was detected in only 3 samples at concentrations near the detection limit. Dieldrin and toxaphene were detected in 4 and 3 samples, respectively. Toxaphene residues were relatively high, ranging from 1.10 to 20.00 ppm.

All nine of the most common organochlorines were detected in fish tissue. The family of DDT compounds was detected most frequently; DDE occurred in all samples, DDD in 76 percent of the samples, and DDT in 42 percent of the samples. The concentrations of DDE were the highest of any organochlorine in fish, ranging from 0.02 to 9.90 ppm, with a geometric mean of 0.55 ppm. Toxaphene, which was detected in 12 samples, was found at concentration levels of 0.98 to 5.10 ppm.

The softshell turtles proved to be an excellent indicator of pesticide contamination. This is likely because they are a top predator in aquatic environments and relatively long-lived (Garrett and Barker 1987). All but one of the 15 organochlorines, hexachlorobenzene, were detected in turtle tissues of the nine most frequently detected organochlorines, eight were found in more than 50 percent of the samples. DDE was detected in all 27 samples, DDD was detected in 22 and dieldrin was found in 19 samples. The geometric mean of DDE was 2.38 ppm, with a range of 0.02 to 11.30 ppm. Although toxaphene was found in only seven samples, a maximum concentration of 7.10 ppm was detected in one sample.

The white pelican carcass, which was found at the Pharr Settling Basin, contained detectable levels of eight among the nine most common organochlorines. The DDE residue of 46.10 ppm was the highest concentration detected in any organism from this study. The endrin and dieldrin residues of 0.29 ppm and 0.80 ppm were also the highest concentrations found in biota samples. In contrast, the black-necked stilt composite contained just three residues above the detection limit, all DDT family compounds. DDE was found at 3.30 ppm, DDD at 0.02 ppm and DDT at 0.04 ppm.

See Table/Figure

Table 3. Geometric means and ranges (ppm) of the most frequently detached organochlorines in sediment (dry weight) and biota (wet weight) from the Lower Rio Grande Valley, 1985-1986.

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Six of the more common organochlorines were detected in the cotton rats. DDE was detected in all samples at low concentrations ranging from 0.01 to 0.10 ppm, with a geometric mean of 0.02 ppm. All other residues were found above detection in either one or two samples at low concentrations.

Five organochlorines were detected in blue crabs. DDE was again the most frequently detected residue. It was found in all 12 samples and ranged from 0.01 ppm to 1.10 ppm, with a geometric mean of 0.08 ppm. DDD was found in three samples at concentrations from 0.01 ppm to 0.03 ppm. Other residues were detected at low concentrations in single samples.

Trace Elements

Twenty one of 23 trace elements were found above the detection limit in sediment. Silver and tin were the only elements not found above detection in any of the samples. In biota, all 21 trace elements analyzed for were found above detection in at least one environmental component. Silver was found above detection in blue crabs only. Table 4 summarizes the geometric means and ranges of selected trace elements considered to be of greatest concern to fish, wildlife and ecosystems health. Summaries of all trace elements in sediment and biota are presented in Appendix D (Tables D-1 through D-7).

Of the selected trace elements, arsenic, chromium, copper, nickel, lead, and zinc were all found above detection in 97 percent of sediment samples. Cadmium was found above detection in only 44 samples. In order to gain a general understanding of where the concentration levels of these elements lie, they can be compared with the baseline concentrations in soils of the western U.S. (Table 4). The geometric mean of all selected trace element concentrations in sediment, except selenium, are below those in soils of the western U.S. The geometric mean of selenium at 0.28 ppm, is only slightly higher than the geometric mean in soils (0.23 ppm).

Trace element concentrations in biota samples were fairly similar, with some noticeable exceptions. The geometric mean of arsenic concentrations was much higher in blue crabs than in other animal tissue, although concentrations in some fish tissues (sea catfish) were also relatively high. The concentrations of arsenic in softshell turtles were much lower than those in other animals. The geometric means and maximum of copper concentrations were much higher for the tissues of two marine organisms (blue crab and oyster) than for the other animal tissues. Concentrations of zinc in oysters were much higher than those in other animal tissues. In fact, the geometric mean of zinc in oysters is at least 20 times higher than that for other organisms.

Petroleum Hydrocarbons

Fourteen selected aliphatic hydrocarbons were analyzed for in biota samples and selected aromatic hydrocarbons were analyzed for in sediments. Aliphatic hydrocarbons, or alkanes, were analyzed for in spiny softshell turtles, fish, blue crabs, oysters, cotton rats, and birds. However, cost prohibited analysis of all turtle, fish, and blue crab samples. Analysis of

See Table/Figure

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Table 4. Geometric means and ranges (ppm) of selected trace elements in sediment (dry weight) and biota (wet weight) from the Lower Rio Grande Valley, 1985-1986.

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sediments for aromatic hydrocarbons was limited to 15 samples.

Aliphatic hydrocarbon compounds were found above detection most frequently in spiny softshell turtles, fish, blue crabs, and cotton rats (Table 5). Only two alkanes, n-pentadecane and n-heptadecane, were found above detection in the two oyster samples. N-pentadecane was detected at 0.07 ppm (wet weight) in one oyster sample and 0.05 ppm in the second; n-heptadecane was detected at 0.07 ppm and 0.05 ppm. Of the two bird samples, alkanes were found above detection only in the American white pelican; n-heptadecane was detected at 0.11 ppm and phytane at 0.03 ppm.

All 14 alkanes were found above detection in fish and softshell turtle samples. Seven alkanes were found in blue crab and cotton rat samples. N-pentadecane, n-hexadecane, n-heptadecane, phytane and n-nonadecane were the alkanes found most frequently above detection in fish. N-tridecane, n-pentadecene, n-hexadecane, n-heptadecane and heneicosane were the alkanes found most frequently above detection in softshell turtles.

The highest alkane residues were detected in fish. Three samples of gizzard shad had concentrations of n-heptadecane of 64.70 ppm, 49.9 ppm, and 31.5 ppm. The value of 64.70 ppm n-heptadecane was the highest alkane concentration detected in all biota samples. The geometric mean for n-heptadecane in fish was 1.01 ppm, the highest geometric mean for alkane residues in fish samples. The geometric mean for n-heptadecane was also the highest for softshell turtle samples at 0.34 ppm. The maximum value for n-tridecane (1.64 ppm) was the highest alkane concentration detected in softshell turtle samples. Alkane concentrations were generally much lower in blue crabs and cotton rats. The highest alkane residue in blue-crab samples was phytane at 0.75 ppm, and 0.23 ppm heneicosane was the alkane residue detected at highest levels in cotton rats.

Fourteen of 15 polycyclic aromatic hydrocarbons (PAH's) were detected in sediments (Table 6). PAH's were detected in only 5 of 15 sediment samples. Two samples stand out in terms of the numbers of PAH's that were detected (sites 46 and 50). Site 46, collected at Resaca Lozano Banco near the Brownsville Unit of the Lower Rio Grande Valley National Wildlife Refuge, had detectable levels of all 14 PAH's. The sample from site 50, located at the Turning Basin of the Brownsville Ship Channel, had the highest concentration of 13 PAH's. The other three sites had few PAH residues above detection.

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Table 5. Geometric mean and ranges (ppm wet weight) of aliphatic hydrocarbons (alkanes) in biota from the Lower Rio Grande Valley, 1985-1986.

Softshell		Cotton		
Fish	Turtle	Blue Crab	Rat	
Chemical	n=10	n=20	n=8	n=11
n - Dodecane	---1	---		
(0.03)ý	(0.05)	BDL[sup]4	BDL	
1[sup]3	1			
n - Tridecane	---	0.10		---
(.03)	(0.03-1.64)	BDL	(0.03-0.09)	
3	18		5	
n - Tetradecane	0.03	---		
(0.03-0.05)	(0.03-0.10)	BDL	BDL	
6	5			
Octylcyclohexane		---		
BDL	(0.03-0.16)	BDL	BDL	
3				
n - Pentadecane	0.47	0.17	---	0.05
(0.04-5.90)	(0.07-0.50)	(0.03-0.05)	(0.03-0.18)	
10	20	3	10	
Nonylcyclohexane	---	---		
(0.04)	(0.03-0.11)	BDL	BDL	
1	2			
n - Hexadecane	0.11	0.03	---	---
(0.03-0.93)	(0.03-0.19)	(0.03)	(0.05)	
9	14	1	1	
n - Heptadecane	1.01	0.34	0.04	0.03
(0.04-64.70)	(0.07-1.07)	(0.03-0.15)	(0.03-0.05)	
9	20	5	9	
Pristane	---	---	---	
(0.03-0.40)	(0.03-0.46)	(0.04-0.06)	BDL	
4	6	2		
n - Octadecane	0.17	---		0.04
(0.05-0.41)	(0.03-0.18)	BDL	(0.03-0.09)	
6	6		9	

Phytane 0.05 0.08 ---
(0.03-0.23) (0.04-0.19) (0.04-0.75) BDL
7 11 3

n - Nonadecane 0.05 --- --- 0.04
(0.03-0.25) (0.03-0.14) (0.03) (0.03-0.13)
7 9 1

n - Eicosane --- ---
(0.03-0.04) (0.03-0.10) BDL BDL
4 5

Heneicosane 0.05 0.11 --- 0.10
(0.03-0.23) (0.03-1.20) (0.09-0.13) (0.04-0.23)
5 20 2 11

[sup]1 Geometric means (Geometric mean calculated only for those with > 50% detection).
ý Range in parenthesis
[sup]3 Number of samples above detection
[sup]4 BDL - Below detection limit
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Table 6. Polycyclic Aromatic Hydrocarbons in Sediment From The Lower Rio Grande Valley of Texas, 1985-1986. (PPM Dry Weight)[sup]1

Sediment Sample Site

Chemical	42	46	50	66	71
Naphthalene	BDLý	BDL	BDL	BDL	BDL
Fluorene	BDL	0.02	BDL	BDL	BDL
Phenanthrene	BDL	0.01	0.02	0.01	0.01
Anthracene	BDL	0.03	0.23	BDL	BDL
Fluoranthrene	0.01	0.09	1.80	BDL	BDL
Pyrene	0.01	0.03	3.00	BDL	BDL
1,2 - Benzanthracene	BDL	0.04	1.00	BDL	BDL
Chrysene	BDL	0.05	1.50	BDL	BDL
Benzo(b)Fluoranthrene	0.01	0.08	6.50	BDL	0.10
Benzo(k)Fluoranthrene	BDL	0.01	0.86	BDL	BDL

Benzo(e)Pyrene	0.01	0.09	0.87	BDL	BDL
Benzo(a)Pyrene	0.01	0.15	1.50	BDL	BDL
1,2,5,6-Dibenzanthracene	BDL	0.07	0.84	BDL	BDL
Benzo (g,h,i)Perylene	0.02	0.27	2.70	BDL	BDL

[sup]1 Sites analized for PAH's but none detected
1,51,55,60,63,64,65,68,72, and 80

ý BDL - Below detection limit
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DISCUSSION

Organochlorines

The detection of 15 different organochlorine insecticides in a variety of environmental compartments is indicative of the widespread agricultural development in the Lower Rio Grande Valley and of the persistence of these pesticides. Most of these organochlorines have been banned, have restricted uses, or are currently being phased out (Table 7). Several of these have been restricted from use on most crops for many years, yet they still persist in soil and animal tissues. Several compounds (c-chlordane, t-chlordane, c-nonachlor, heptachlor epoxide, hexachlorobenzene, endosulfan sulfate and PCB) were detected at very low concentrations and in less than 10 percent of all samples. These residues are not at levels considered to be biologically significant and will not be discussed.

In the study by White et al. (1983), conducted eight to ten years prior to this study, freshwater fish from the Arroyo Colorado were discovered to be highly contaminated with DDE and toxaphene. In 1980-1981, the National Contaminant Biomonitoring Program also found elevated DDE and toxaphene residues in fish from the lower Rio Grande (Schmitt et al. 1985). Comparison of the concentrations in fish tissue from this study with national baseline geometric means (Table 8) demonstrates this same pattern of elevated DDE and toxaphene residues. All 33 fish samples from this study exceeded the national geometric mean of 0.20 ppm for DDE. When detected, toxaphene was significantly greater than the national geometric mean of 0.27 ppm, and the minimum toxaphene concentration (0.98 ppm) was 3.6 times the national mean. The remaining organochlorines exceeded the national geometric means in relatively few samples.

The National Academy of Sciences and National Academy of Engineers (1972) established a level of 1.0 ug/g (ppm) of total DDT (including DDE and DDD, based on whole body, wet weight, residues) as the recommended level for protection of aquatic life. Ten fish samples and 21 softshell turtle samples exceeded this level. The geometric mean of 0.55 ppm DDE in all fish tissue samples, however, is below the established ppm level. The geometric mean of DDE residues in softshell turtles (2.38 ppm) exceeded the recommended level. The biological significance of these residues in turtles is unknown (Hall 1980, Albers et al. 1986).

Due to the potential for biomagnification, the levels in fish also have significance for fish-eating birds. DDE concentrations of 3 ppm in the diet of some birds may result in eggs that are 12 to 14 percent thinner than normal (McLane and Hall 1972, Lincer 1975). Lincer (1975) determined that a diet containing 1 ppm DDE for 2 to 3 months prior to nesting would result in eggshells that are 7 percent thinner. Eggshell thinning that exceeds 15 percent is generally considered serious and may be associated with population decline (Risebrough et al. 1970, Anderson and Hickey 1972). Therefore, the data from this study indicates that the DDE levels in fish have likely caused some degree of eggshell thinning for some fish-eating

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Table 7. Regulatory status in the United States of some organochlorines commonly detected in the Lower Rio Grande Valley.[sup]1

Chemical	Status
DDT	Cancelled except for limited use related to human health - 1972.
Toxaphene	Cancelled - 1982. Use of existing stock allowed through 1986.
Aldrin	Cancelled except for limited use- 1984.
Dieldrin	Cancelled except for limited use- 1984.
Chlordane	Cancelled except for limited use - 1980. Cancelled for termite control 1987, use of existing stock allowed.
Heptachlor	Uses restricted - 1980; total phase out starting 1983.

[sup]1 Adopted from Fleming et al. 1983.

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Table 8. Geometric mean or ranges (ppm wet weight) of the most frequently detected organochlorines in fish from the Lower Rio Grande Valley, 1985-1986, compared to national geometric means (ppm wet weight) for the National Pesticides Monitoring Program, 1930-1981 (Schmitt et al. 1985).

No. of Samples
National Geometric   Range or Geometric Exceeding National
Mean. 1980-81   Mean[sup]1   Meaný

p,p'DDE	0.20	0.55	33
p,p'DDD	0.07	0.03	4
p,p'DDT	0.05	0.01-0.07	3
Toxaphene	0.27	0.98-5.10	12
Endrin	<0.01	0.01	2
Dieldrin	0.04	0.01-0.08	1
Oxychlordane	0.01	0.01-0.02	2
t-nonachlor	0.04	0.02-0.05	1
Methoxychlor	<0.01	0.01-0.05	2

[sup]1 Geometric means were only calculated when residues were detected in greater than 50 percent of the samples (p,p'DDE and p,p'DDD).

ý The total sample number for fish was 33.
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birds. But the degree of thinning is not expected to be at levels associated with population declines. These levels could be a problem for migratory birds which winter in areas of higher contamination and return to the Lower Rio Grande Valley to nest.

The DDE concentration detected in the American white pelican carcass (46.1 ppm wet weight) is relatively high. Knopf and Street (1974) determined that American white pelican eggs containing DDE at 13.62 ppm (wet weight) were significantly thinner than pre-DDT era eggs. However, because of the migratory nature of this species and the fact that only one sample was analyzed, few conclusions can be made regarding the implications for the study area. Black-necked stilts, which are nesting birds in the study area, had much lower DDE residues, at 3.30 ppm. White et al. (1980) found similar DDE concentrations in shorebirds in the vicinity of Corpus Christi, Texas, and considered these levels to be relatively low.

Toxaphene is rapidly metabolized by mammals and birds and does not constitute a major threat to these animals (Eisler and Jacknow 1985). Toxaphene is, however, a serious threat to marine and freshwater organisms, especially fish. Residues at concentrations of 0.4 to 0.6 ppm in the bodies of freshwater fish were associated with reductions in growth, reduced fecundity and abnormal bone growth (Mayer and Mehrle 1977). Although the maximum residues detected in fish in this study (5.10 ppm) were much lower than the maximum of 31.5 ppm found eight to ten years ago by White et al. (1983) in the Arroyo Colorado, they are still above the levels considered harmful to fish. Andreason (1985) discovered that mosquitofish from the Lower Rio Grande Valley had developed genetic resistance to toxaphene.

Further investigation would be necessary to determine if a similar resistance to toxaphene has developed in other species or whether these elevated toxaphene residues are impacting fish populations.

Of the other frequently detected organochlorines, only endrin and dieldrin were detected at levels above 0.1 ppm. The National Academy of Science and National Academy of Engineers (1972) recommend that 0.1 ppm endrin and dieldrin should not be exceeded (singly or together) for the protection of aquatic life. Ten spiny softshell turtles exceeded this recommended level. It is not known how these residues may be affecting these turtles.

Four locations had some of the highest DDE and toxaphene residues in turtles and/or fish: 1) Llano Grande on the Arroyo Colorado, 2) Laguna Atascosa and Cayo Atascosa before it flows into the Laguna Atascosa, 3) the Rio Grande above Anzalduas Dam (National Contaminant Biomonitoring Station 16), and 4) the Resaca de los Cuates. The highest DDE and toxaphene residues in fish were from the Llano Grande. The highest DDE residues in turtles were from the Arroyo Colorado at Farm-to-Market Road 1015, directly south of Mission, Texas. Relatively high DDE concentrations were also found in turtles collected from the North Floodway, Hidalgo/Willacy County Drain, and the Raymondville Drain. These findings are not surprising in light of previous studies which have found elevated levels of DDT, DDE, and toxaphene in the Arroyo Colorado (Childress 1966, Tidswell and McCasland 1972, White et al. 1983) and the Rio Grande above Anzalduas Dam (Schmitt et al. 1981, Schmitt et al. 1983, Schmitt et al. 1985). It is important to note that of the four

See Table/Figure

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(SEE ORIGINAL)

Figure 2. DDE and toxaphene residue trends in gizzard shad from Station 16 of the National Contaminant Biomonitoring Program

locations with higher residue levels, three are bodies of water that have been impounded. Kepner (1986) also found elevated organochlorine residues in fish and turtles from impounded bodies of water in Arizona and noted that these areas may act as contaminant sinks.

The trends of DDE and toxaphene residues in the Lower Rio Grande Valley over the past two decades can be examined by comparing residues in gizzard shad from station 16 of the National Contaminants Biomonitoring Program (Figure 2). Except for 1973 and 1974 (when only single composites of gizzard shad were available), there is a steady decline in DDE residues from 1970 to 1986. The 1986 DDE value, from this study, is a decrease of nearly one-half that from 1984. The slight rise of DDE residues in 1978 may be a result of the use of dicofol as an acaricide on citrus and cotton crops. Dicofol has been found to contain DDT as an impurity at levels up to 9 percent (Clark et al. 1983).

The trend of toxaphene is not as encouraging. Toxaphene residues appear to be stable or slightly increasing since 1976. Toxaphene came into heavy use on cotton crops after the 1972 ban on DDT. Most uses of toxaphene were cancel led by the Environmental Protection Agency in 1982 (EPA 1982b). Use of existing available stocks was allowed through 1986. It is likely that the stable or increasing toxaphene residues through 1986 are a result of the use of remaining stocks. Future sampling at Station 16 for the National Contaminant Biomonitoring Program should help confirm this.

Trace Elements

Unlike the organochlorine contaminants, trace elements are intrinsic in nature. In fact, many are essential micronutrients (copper, chromium, iron, manganese, nickel, molybdenum, selenium, and zinc) and thus are important for functioning of plants and animals (Leland and Kuwabara 1985). Above certain levels, however, these trace elements can have toxic effects.

Arsenic

Arsenic was found above detection in all animal tissues. The geometric mean of arsenic for all fish samples (0.21 ppm) exceeded the geometric mean from the 1980-81 National Contaminants Biomonitoring program (0.14 ppm) (Lowe et al. 1985). This is misleading, however, since the geometric mean presented in Table 3 includes eight samples of sea catfish. Marine biota have the ability to accumulate arsenic from seawater and food and typically have higher arsenic concentrations than freshwater organisms (Maher 1985). Six of the highest arsenic concentrations were in sea catfish. The geometric mean using only the freshwater fish is 0.11 ppm, which is below the national baseline. The highest residue in freshwater fish was 1.19 ppm in a sheepshead minnow sample. Both the geometric mean and maximum for freshwater fish are below the lowest residue level (1.35 ppm) known to reduce growth and survival in freshwater fish (NRCC 1978). The concentrations in the sea catfish are all within the 2 to 5 ppm range considered typical of marine fish tissues (Eisler 1988a).

The arsenic levels in softshell turtles (0.03 to 0.06 ppm) were much lower than the concentrations found in freshwater fish, which are a large part of the turtle diet. This supports the findings of Spehar et al. (1980) that arsenic does not biomagnify up the food chain but tends to accumulate at lower trophic levels. The arsenic levels in softshell turtles found in this study are very similar to the levels in softshell turtles collected from the upper Trinity River, Texas (0.025 to 0.060 ppm) (Irwin 1988).

The concentrations in black-necked stilts, blue crab and oysters were all at levels considered to be within normal ranges and below levels of concern for those organisms (White et al. 1980, Hall et al. 1978, NOAA 1987).

Cadmium

Cadmium is generally considered a nonessential trace element (Eisler 1985a). It is potentially toxic to most fish and wildlife at sufficient concentrations and freshwater organisms are especially sensitive. In general, concentrations exceeding 2.0 ppm whole body, fresh weight, in vertebrate animals is considered evidence of probable cadmium contamination (Eisler 1985a).

Levels of concern were not found in this study. Less than half of the sediment and fish samples contained concentrations above detection, and cadmium was not found above detection in the black-necked stilt sample. The maximum concentration in a fish sample (0.031 ppm) is near the baseline geometric mean of 0.03 ppm for fish (Lowe et al. 1985). The slightly higher levels in blue crabs and oysters is indicative of the higher levels found in marine organisms (Eisler 1985a).

Chromium

Chromium is known to have both lethal and sublethal effects on fish and wildlife. However, the significance of tissue residues is imperfectly understood. Current evidence suggests that tissue levels in excess of 4.0 ppm dry weight are indicative of chromium contamination (Eisler 1986).

Nearly all biota samples from this study were below the 4.0 ppm (dry weight) level. Three fish samples, however, did exceed this level. One tilapia composite sample from the upper end of Resaca de los Cuates contained 14.0 ppm chromium (whole body, dry weight), one gizzard shad composite from Pintail Lake at Santa Ana National Wildlife Refuge contained 7.7 ppm (whole body, dry weight), and the concentration of one carp composite collected from Falcon Reservoir was 4.8 ppm (whole body, dry weight). It is difficult to explain these unusually high concentrations of chromium since sediment and other biota samples from those same locations had lower concentrations. Wells et al. (1988) did detect elevated chromium levels in some water samples from the Lower Rio Grande Valley. Except for these three fish samples, chromium levels were generally at lower concentrations. The geometric mean for all fish samples on a dry weight basis was 0.95 ppm. Further investigation would be necessary to determine the reason for these three elevated levels.

Copper

Copper is an essential element for both plant. and animals. At sufficient concentrations copper may also be toxic to a variety of fish and wildlife (EPA 1980). Breteler (1984) placed copper as one of the major threats to ecosystem health relative to other heavy metals.

The 1980-81 national baseline geometric mean for fish (Lowe et al. 1985) is 0.68 ppm (wet weight) and the 85th percentile for the same data is 0.90 ppm. The geometric mean for fish from this study (0.45 ppm) was below the baseline geometric mean, but six fish samples exceeded both the baseline geometric mean and 85th percentile. Three of these samples contained concentrations of copper (between 2.40-5.09 ppm, wet weight) that were in the same range as copper concentrations in fish from the Santa Catarina River, Nuevo Leon, Mexico (Villarreal-Trevino et al. 1986). This river was considered polluted from industrial and municipal discharges. Current information is lacking on the relationship between whole body residues and biological effects.

Copper concentrations were highest in blue crab and oysters samples. These levels are not considered elevated for these marine organisms. Experimental evidence indicates that decapod crustaceans, such as blue crabs, are able to regulate internal copper concentration and avoid toxic levels (Rainbow 1985). The copper concentrations in the oysters were below the median copper concentration for oysters collected for the 1986 National Status and Trends Program (NOAA 1987).

Mercury

Mercury concentrations in biota are of special concern because mercury can bioconcentrate in organisms and biomagnify through food chains, impacting fish, wildlife and man (Eisler 1987a). Mercury does occur naturally, but it has no known biological function.

Mercury levels in all biota samples were below levels of concern for these organisms. The highest concentrations were detected in sea catfish. Mercury was detected at 0.431 and 0.424 ppm (wet weight, whole body) in two samples of sea catfish. This is below the level of 0.5 ppm generally accepted as a level for unpolluted environments (Abernathy and Culmbie 1977) and below the FDA's 1.0 ppm action level for edible portions.

Nickel

Apparently because of its low toxicity to humans, there is a lack of residue data on nickel for comparisons. In addition, nickel does not accumulate in aquatic organisms (Phillips and Russo 1978).

Comparison of sediment concentrations to the baseline for soils of the western U.S. (Wilson 1986) indicates that nickel is relatively low in sediments of the Lower Rio Grande Valley. Nickel concentrations in all biota samples were also low. The Panel on Nickel (1975) considered levels below 0.75 ppm nickel to be normal for aquatic organisms; this level was exceeded by only one sample of gizzard shad.

Lead

Lead is both a nonessential and nonbeneficial element. Lead is toxic in most of its chemical forms and can bioaccumulate causing sublethal effects to hematopoietic, vascular, nervous, renal and reproductive systems (Eisler 1988b)

The geometric mean of 10.7 ppm lead in sediments is an indication that sediments of the study area are relatively uncontaminated. Harrison (1987) determined that the background lead level of soils in the vicinity of Corpus Christi, Texas, was 13.0 ppm. The maximum concentration in sediment of 240 ppm lead was found in Brownsville Resaca within the city limits of Brownsville. The lead levels in Brownsville Resaca are similar to the mean levels (250 ppm) that Harrison found in soils near the edges of roadways in Corpus Christi, Texas, and attributed to automobile emissions. Brownsville Resaca is in the vicinity of several roadways. This level in sediment is comparable to sites with moderate contamination (Eisler 1988b), however a direct cause and effect relationship between lead concentrations in sediment and impacts to aquatic organisms has not been made.

Lead levels in biota were generally below levels of concern. Only nine fish samples contained lead levels above detection, ranging from 0.02-1.01 ppm. These levels are much lower than those from a known contaminated river in Mexico, where lead concentrations in fish ranged from 2.0 ppm to 6.5 ppm (wet weight) (Villareal-Trevino 1986). The lead concentration in the one black-necked stilt whole body composite was above the levels found in black-necked stilt livers by White and Cromartie (1985). Lead levels in waterfowl livers ranging between 6 ppm and 20 ppm (wet weight) or greater were considered diagnostic of acute intoxication by Longcore et al. (1974). The significance of the lead levels in black-necked stilts found in this study is unknown.

Selenium

Selenium is an essential trace element. Impacts to animals may result from both selenium deficiency and selenium poisoning (Eisler, 1985b). Potential effects of high levels of selenium range from physical malformations during embryonic development to sterility and death (Lemly and Smith 1987).

The levels of selenium detected in sediments of the Lower Rio Grande Valley are relatively low and probably are indicative of the natural selenium content of soils. The maximum concentration detected was 0.66 ppm (dry weight), with a geometric mean of 0.28 ppm. Lemly and Smith (1987) state that soils rarely contain greater than 2 ppm selenium (dry weight).

Residue levels in all biota samples were below levels considered to be harmful. Baumann and May (1984) considered that selenium levels of 2 ppm (wet weight) or more in fish tissue may be indicative of concentrations that could cause toxic effects. All concentration in fish from this study were well below this level (maximum for this study was 0.95ppm). The selenium concentration in black-necked stilts (0.47 ppm) compares with the levels found in duck breast tissue (0.19 - 0.65 ppm) from an uncontaminated area in California (Ohlendorf et al. 1986). The highest concentration was detected in blue crab samples (maximum of 1.07 ppm; geometric mean 0.42 ppm). These levels are typical of selenium concentrations in marine invertebrates which are usually less than 2 ppm on a wet weight basis (Eisler 1985b).

Zinc

Zinc is another essential micronutrient which at sufficient concentrations can result in lethal or sublethal effects. Marine fish and oysters have been noted for accumulating higher levels relative to freshwater organisms (Phillips and Russo 1978, Duke 1967). Oysters in this study contained the highest concentration of zinc (geometric mean of 253.2 ppm wet weight). In fish, the highest zinc concentrations were detected in sea catfish. The geometric mean for zinc in sea catfish was 50.1 ppm (range = 0.5-146.7 ppm wet weight) compared to a geometric mean of 8.3 ppm (range = 0.5-51.0 ppm wet weight) for all freshwater fish. Comparison of the geometric mean and range of freshwater fish with that for the national baseline indicates that zinc levels are relatively low in these fish. The national baseline geometric mean for 1980-81 for zinc was 23.82 ppm (wet weight) and the 85th percentile was 40.09 ppm (Lowe et al. 1985).

The levels in oysters can be compared with levels reported in the National Status and Trends Program for 73 oyster sampling stations along the Gulf and Atlantic coasts (NOAA 1987). The zinc concentrations in oysters from this study are below the median levels in the National Status and Trends Program.

Based on sediment samples, one location had noticeably elevated zinc levels. The Turning Basin of the Brownsville Ship Channel had zinc levels in sediment three times higher than any other sampling location (439.0 ppm dry weight). The Texas Water Commission has attributed this in part to ship dismantling operations and an ore loading facility located near the Turning Basin (Bowles 1983).

Petroleum Hydrocarbons

Aliphatic hydrocarbons (alkanes) are a major component of petroleum products (Sandmeyer 1981). Armstrong et al. (1979) listed several alkanes found in crude oil at separator platforms in Trinity Bay, Texas. This included several of the selected alkanes investigated in this study. These selected alkanes are also components of kerosene, jet and turbo fuels, and lubricating oils (Sandmeyer 1981).

Several alkanes (the odd-numbered carbon n-alkanes) are also produced biogenically by algae and phytoplankton (Coates et al. 1986, D. Scalen, pers. comm.). The alkane n-heneicosane (C21) and higher odd-numbered carbon n-alkanes are produced by terrestrial plants (Shaw et al. 1986).

A determination of the contribution from petroleum and biogenic sources is possible only on a relative basis. A predominance of odd-numbered carbon n-alkanes suggests a biogenic source (Sanders et al. 1980). In petroleum hydrocarbon, there is no distinct preference for odd or even-numbered carbon n-alkanes, and the occurrence of phytane suggests a petroleum hydrocarbon source since it is rarely found in biogenic material (National Academy of Science 1985).

Using these guidelines it appears that both petroleum hydrocarbon and biogenic sources contributed to the concentrations found in this study. The odd-numbered carbon n-alkanes were detected in more samples and at greater concentrations than the even-numbered carbon n-alkanes, suggesting that biogenic production was the major contributor of aliphatic hydrocarbons. This supposition is further supported by the fact that the alkane detected at highest levels was n-heptadecane in gizzard shad. N-heptadecane is one of the odd-numbered carbon n-alkanes produced by algae and phytoplankton, and the gizzard shad is a filter feeder that consumes both phytoplankton and algae.

Information is currently lacking on the relationship between alkane tissue residues and biological effects. Sandmeyer (1981) reviewed the toxicology of alkanes and states that the liquid alkanes are moderately toxic. The lowest toxic dose for pristane fed to mice was 9600 mg/kg (ppm). Miller et al. (1982) examined the toxicity of crude oil components fed to young herring gulls and found that aliphatics had no obvious effect while the aromatic component reduced gull rates of weight gain.

Although current information suggests aliphatic hydrocarbons are of relatively low toxicity compared to the PAH's, they may be important in determining the extent of exposure to petroleum hydrocarbons. Data from this study demonstrates that fish, in particular, may accumulate considerable concentrations in their tissues.

A large information base is developing for the PAH's. This is largely due to their toxicity and the fact that several are among the most potent carcinogens known to exist (Eisler 1987b). Like the aliphatic hydrocarbons, PAH's may also be biogenically produced by microorganisms, algae and macrophytes. A variety of other sources contribute to aromatics in the environment. In aquatic environments, petroleum spillage is the major source of PAH's; other sources are atmospheric deposition (emissions from the burning of fossil fuels, refuse burning, grass fires), wastewater discharges and land surface runoff (Eisler 1987b).

Two sites stand out as having several PAH's above detection. The Turning Basin of the Brownsville Ship Channel had the highest levels. This is probably related to the spillage of a variety of petroleum products and the former practice of discharging ballast wastes directly into the ship channel. The second site is Resaca Lozano Banco, an old oxbow of the Rio Grande, near downtown Brownsville. All but one of the PAH's analyzed for were detected at this site, but the concentrations were much lower than those found in the ship channel. Atmospheric deposition of automobile emissions is probably a major source of PAH's at this site. The data indicates that, except for the two sites mentioned,polycyclic aromatic hydrocarbon levels are generally low or below detection. The levels of PAH's in sediment at Resaca Lozano Banco and the Turning Basin are comparable to sites that exhibit low to moderate contamination (Alden and Butt 1986).

SUMMARY

Organochlorine, trace element, and petroleum hydrocarbon contaminants were examined in sediment and biota from the Lower Rio Grande Valley, Texas. The study was designed to monitor organochlorine contaminants and provide baseline information on trace elements and petroleum hydrocarbons.

The detection of 15 different organochlorine insecticides in a variety of environmental compartments is indicative of the widespread agricultural development in the valley and of the persistence of the pesticides. DDE and toxaphene residues, in particular, were elevated compared to national baseline data. This continues a trend which has been documented in previous

studies. The maximum levels of DDE and toxaphene in fish are much lower than the levels found by White et al. (1983) in a study conducted 8 to 10 years prior to this study.

The data indicates that DDE levels are gradually declining. The geometric mean in fish was below the 1.0 ppm level recommended for the protection of aquatic life. Several fish samples still exceeded this level, though. The levels of DDE in spiny softshell turtles, which are highly piscivorous, exceeded the 1.0 ppm levels. The biological significance of these residues in turtles is unknown. The DDE levels in fish are sufficient to cause some degree of eggshell thinning in fish-eating birds, but are not expected to cause bird population declines.

Toxaphene was detected in fish at levels that have been associated with reduced growth, reduced fecundity and abnormal bone growth. Examining several years of data from station 16 of the National Contaminants Biomonitoring Program indicated that toxaphene residues have not declined like those of DDE. This may be due to the cancellation of toxaphene by EPA which allowed for the use of existing stocks through 1986.

Four locations had some of the highest DDE and toxaphene residues in turtles and fish: 1) Llano Grande on the Arroyo Colorado, 2) Laguna Atascosa and Cayo Atascosa before it flows into Laguna Atascosa, 3) the Rio Grande above Anzalduas Dam, and 4) the Resaca de los Cuates. Three of these four locations are bodies of water that have been impounded.

Trace elements were generally low in biota, but some fish samples had elevated chromium and copper levels. Three fish samples exceeded the tissue level of 4.0 ppm dry weight which is considered to be an indication of chromium contamination, and six fish samples exceeded the national baseline 85th percentile for copper.

Aliphatic hydrocarbons (alkanes) were found above detection most frequently in spiny softshell turtles, fish, blue crabs, and cotton rats. The highest alkane residues were detected in fish. Both petroleum hydrocarbon and biogenic sources contributed to the concentrations found in this study. The data indicates that biogenic sources were the major contributors of aliphatic hydrocarbons.
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Polycyclic aromatic hydrocarbons (PAH's) were found in five sediment samples. Two samples contained several PAH's. The sample with the highest levels was from the Turning Basin of the Brownsville Ship Channel. The second highest level sample was from an oxbow within the city limits of Brownsville. The levels of PAH's in sediment are comparable to areas that are considered slightly to moderately contaminated.
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RECOMMENDATIONS

Organochlorines, DDE and toxaphene in particular, remain elevated in the Lower Rio Grande Valley. The data indicates that DDE levels are steadily declining. Data from station 16 indicates that toxaphene levels have not declined. This could be a result of the cancellation of toxaphene, which allowed the utilization of remaining stocks through 1986. Another possibility is that toxaphene use is continuing in Mexico. Pesticide use across the border in Mexico can impact resources in the Lower Rio Grande Valley, since waters draining these lands flow into the Rio Grande and are then used to irrigate U.S. crops. Therefore, it is recommended that a study be conducted to investigate organochlorine and other pesticide use in agricultural areas of the Rio Grande in Mexico.

Continued contaminants monitoring of the Lower Rio Grande Valley is essential if the Service is to ascertain the quality of habitats for resident and migratory wildlife. Because the Service administers three wildlife refuges in the Lower Rio Grande Valley it is important to monitor contaminants on a valley-wide basis. Laguna Atascosa National wildlife Refuge, for example, receives irrigation drainage from a broad portion of the Valley. Irrigation drainwater has been identified by the Department of Interior as a potential source of contaminants for wildlife refuges. Also, the Rio Grande Valley National Wildlife Refuge has numerous tracts of land, many of which are encircled by agricultural land, throughout the Lower Rio Grande Valley.

Any such monitoring program should continue to examine organochlorines, trace elements and petroleum hydrocarbons. In addition to these analyses, the Service should also incorporate some form of biomonitoring or bioassay techniques. This will be extremely important if it is to assess the threat of "new age" agricultural pesticides. For example, organophosphates, carbamates, and synthetic pyrethroids are commonly used in the Lower Rio Grande Valley, but tissue analysis for these chemicals is a poor indicator of exposure.

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APPENDIX A

COMMON AND SCIENTIFIC NAMES OF SPECIES REFERENCED IN THE TEXT

Table A-1. Scientific and common names of species sampled in 1985-1986 contaminants study of Lower Rio Grande Valley.

	Common Name	Scientific Name
Aquatic Vegetation	Chara (musk grass)	Chara sp.
	Shoal grass	Halodule wrightii
	Manatee grass	Syrinaodium filiforme
Marine Invertebrates	Blue crab	Callinectes sapidus
	Eastern oyster	Crassostrea virginica
Reptiles	Texas spiny softshell turtle	Trionyx spiniferus emorvi
Mammals	Hispid cotton rat	Sigmodon hispidus

Fish	Freshwater drum	Aplodinotus arunniens
Sea catfish	Arius felis	
Sheepshead minnow	Cyprinodon varieaatus	
Common carp	Cyprinus carpio	
Gizzard shad	Dorosoma cepedianum	
Gulf killifish	Fundulus grandis	
Mosquitofish	Gambusia affinis	
Blue catfish	Ictalurus furcatus	
Channel catfish	Ictalurus Dunctatus	
Alligator gar	Lepisosteus spatula	
Largemouth bass	Microuterus salmoides	
Striped bass hybrid	Morone chrysops x	
Morone saxatilis		
Sailfin molly	Poecilia latipinna	
Tilapia	Tilapia sp.	
Birds	Red-winged blackbird	Agelaius phoeniceus
Black-necked stilt	Himantopus mexicanus	
Herring gull	Larus argentatus	
Laughing gull	Larus atricilla	
Ring-billed gull	Larus delawarensis	
Franklin's gull	Larus pipixcan	
Plain chachalaca	Ortalis vetula	
American white pelican	Pelecanus erythrorhynchos	
Pied-billed grebe	Podilymbus podiceps	
Great-tailed grackle	Quiscalus mexicanus	
Forster's tern	Sterna forsteri	

APPENDIX B

SAMPLE SITE DESCRIPTIONS

Table B-1. Sediment site locations in the Lower Rio Grande Valley, Texas, 1985-1986.

Site No.	Description of Site
1-S	Rio Grande above Falcon Dam
2-S	Drain @ FM 493 south of junction with Highway 107, Deepened for Hidalgo/Willacy Drain "Big Ditch" in 1986.
3-S	Rio Grande above confluence of Rio Saladito, upstream of Fronton, Tx.
4-S	Rio Grande below confluence of Rio Saladito
5-5	Rio Grande above confluence of Rio San

Juan, 300 feet upstream of pump station, west of Rio Grande City, Tx.

6-5	Rio Grande below confluence of Rio San Juan
7-S	Los Olmos Creek @ Hwy 83, Rio Grande City, Tx.
8-S	La Grulla Unit - Ramirez tract LRGV-NWR
9-S	Drain @ FM 1925, south of Lake Edinburg
10-S	North Floodway ù Hwy 107, east of Edcouch, Tx.
11-S	Abrams Unit LRGV-NWR-resaca near Abram, Tx.
12-S	Bentsen State Park (TPWD) - transect across resaca
13-S	Palmview Unit LRGV-NWR - drainage ditch, south of Palmview, Tx.
14-S	DDT Plant - irrigation supply canal east of old DDT plant in Mission, Tx.

Table B-1. Sediment site locations in the Lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Description of Site
15-S	Main Floodway @ Fm 1016, south of Mission, Tx.
16-S	Madero Unit LRGV-NWR - south of Madero, Tx.
17-S	Rio Grande - Anzalduas Dam, mid channel, 300 feet above dam
18-S	Gabrielson Unit LRGV-NWR - tract downstream of Anzalduas Dam
19-S	Drain @ Fm 493, 1-1/2 miles north of Main Floodway, south of Donna, Tx.
20-S	Main Floodway @ Hwy 115, south of McAllen, Tx.
21-S	Banker Floodway (Hackney Lake Inlet)

Hwy 115, south of Main Floodway

22-S	Spiller Pond (Dry) - Lake Tropicana, Hidalgo Bend tract LRGV-NWR,
23-S	Pharr Settling Basin LRGV-NWR - south east of Hidalgo, Tx.
24-S	Sonny Miller Resaca - LaChapena Banco # 99, Hidalgo Bend tract LRGV-NWR
25-S	Vella Woods LRGV-NWR - southeast of Hidalgo, Tx.
26-S ABCD	Santa Ana NWR - Pintail Lake (impoundment # 2)
26-S EFGH	Santa Ana NWR-west border, east side of tour loop road, pipe draining field adjacent to refuge
26-5 IJKL	Santa Ana NWR - Cattail Pond at well outlet

Table B-1. Sediment site locations in the Lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Description of Site
27-S	Main Floodway @ FM 907, south of Alamo, Tx.
28-S	Krenmueller Pond, San Juan del Rio Banco #40 east of Santa Ana NWR
29-S	Main Floodway @ FM 493, south of Donna, Tx.
30-5	McManus Unit (TPWD) - Southeast of junction of FM 493 and Hwy 281, just north of Bancos 105 and 106
31-S	La Coma Unit LRGV-NWR - dry resaca downstream of Retamal Dam
32-S	Llano Grande (Arroyo Colorado) @ FM 1015, south of Weslaco, Tx.
33-S	Arroyo Colorado @ FM 491, south of Mercedes, Tx.
34-S	North Floodway @ FM 491, north of Mercedes, Tx.

35-5 Thompson Road (soil) LRGV-NWR - 2 miles S.E. of Santa Rosa, Tx. on Thompson Road

36-5 North Floodway @ FM 506, north of Santa Rosa, Tx.

37-S Arroyo Colorado @ FM 506, south of La Feria, Tx.

38-S Mercedes Settling Basin @ Hwy 281, southeast of Mercedes, Tx.

39-S Santa Maria Unit LRGV-NWR - southwest of Santa Maria, Tx.

40S Arroyo Colorado @ Hwy 77 south exit to FM 1479, Harlingen, Tx.

Table B-1. Sediment site locations in the Lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Description of Site
41-S	Tucker - Di Shazo Unit (TPWD) drainage ditch, center of area bordered by FM 509, FM 800, FM 2520, and FM 675
42-S	Arroyo Colorado - above railroad bridge upstream of Port Harlingen
43-S	North Floodway @ FM 1420, south of Santa Monica, Tx.
44-S	Garza - Cavozos Unit LRGV-NWR - dry resaca, west of San Pedro, Tx. south of Hwy 281 junction with FM 1732
45-S	Brownsville Resaca (developed) @ Boca Chica Blvd. 3300 feet east of junction with FN 415 (Central Blvd.)
46-S	Brownsville Unit LRGV-NWR - resaca Lozano Banco, east of USDA research center on Gorgas Dr.
47-S	Voshell Unit (TPWD) - resaca at 5-curve on FM 511, south of Brownsville airport
48-S	Bascaje de Ia Palma Unit LRGV-NWR - resaca south of Palm Grove School
49-S	Southmost Ranch - resaca behind main

house

50-S Brownsville Ship Channel - Turning Basin, west end

51-S Brownsville Ship Channel - Boca Chica Turning Basin at buoy marker 35

52-S Rio Grande - near mouth just around first bend

53-S South Bay - one mile from Brownsville Ship Channel through South Bay Pass

Table B-1. Sediment site locations in the Lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Description of Site
54-S	Bahia Grande (dry) @ FM 1792, 300 feet north of road, southwest of Port Isabel
55-S	Laguna Madre - between old and new causeways to South Padre Island at Port Isabel, Tx. southwest corner
56-S	Brazos - Santiago Pass - bay on south side of pass
57-S	Laguna Madre - 300 feet offshore from drain pipe south of Laguna Vista, Tx.
58-S	Laguna Atascosa NWR - Stover Cove (Laguna Madre), west of Gabrielson Island
59-S	Laguna Atascosa NWR - Cayo Atascosa at FM 106
60-S	Laguna Atascosa NWR - Laguna Atascosa, composite of 5 grabs on east/west transect passing north tip of Needle Island
61-S	Laguna Atascosa NWR - Laguna del Cayo Atascosa crossing # 1
62-S	Laguna Atascosa NWR - Laguna del Cayo Atascosa crossing #2
63-S	Laguna Atascosa NWR - Harlingen Ship Channel at dredged harbor upstream of mouth of Cayo Atascosa

64-S Arroyo Colorado - old outlet 1000 feet in from Harlingen Ship Channel

65-S Laguna Madre - bay area off GIWW west of buoy marker 299

66-S Raymondville Drain @ FM 2209, north of San Perlita, Tx.

67-S Hidalgo/Willacy County Drainage Project ("Big Ditch") 1.5 miles east of Hwy 77, south of FN 498

Table B-1. Sediment site locations in the Lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Description of Site
68-S	Laguna Madre - backwater bay off GIWW between buoy markers 313A and 315
69-S	Pothole (dry) - west side of Hwy 77 south of Sebastian, Tx.south side of dike, north of "Dirty Cotton Co."
70-S	Raymondville Drain @ junction of Bus. Hwy 77 and FM 1761
71-S	La Sal Vieja - southwest side of east lake
72-S	Payne Unit LRGV-NWR - La Sal Vieja, west side of west lake
73-S ABCD	Rudman Unit LRGV-NWR-saltwater pond north central area of tract
73-S EFGH	Rudman Unit LRGV-NWR-impounded area both sides of north border road
74-S	Pothole - west side of Hwy 77 at Lyford, Tx. northeast area of pothole
75-S	Pothole - west side of Hwy 77 south of Sebastian, Tx. north side of dike, north of "Dirty Cotton Co."1 pooled area
76-S	Monte Alto Reservoir - pedestrian bridge near shelter in park
77-S	Raymondville Drain @ FM 493 - west of Monte Alto, Tx.

78-S Drain @ FM 1015, North of Edcouch, Tx.

79-S Drain @ Hwy 281, 1/4 mile east of highway, east of Lake Edinburg

80-S Schalaeben Unit LRGV-NWR - pond at old well site, southeast of Sal del Ray

Table B-1. Sediment site locations in the Lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Description of Site
81-S	Cottam Unit (LRGV-NWR) - southeast of Granjeno, Tx.
82-S	Brownsville Resaca (undeveloped) @ Boca Chica Blvd. 1400 feet east of FM 415 (Central Blvd.)
83-S	Laguna Atascosa NWR - Resaca de los Cuates, southmost dike at water meter site, north side of dike
84-S	Resaca de los Cuates @ Hwy 100, north side of third crossing traveling east, east of Russelltown, Tx.
85-S	Raymondville Drain @ Rwy 186, west of Port Mansfield, Tx.
86-S	Hidalgo/Willacy County Drainage Project ("Big Ditch") - @FM 1420 near Willamar, Tx.
87-S	Laguna Atascosa NWR-Pelican Lake at tour road
88-S	Laguna Atascosa NWR - Drain at FM 106, 1/2 mile east of Cayo Atascosa
89-S	Laguna Madre - Bay north of Rattlesnake Island and east of Horse Island
90-S	Resaca de los Cuates @ FM 3069 at crossing closest to FM 510, northeast of Los Fresnos, Tx.
91-S	Drainage Ditch @ FM 1847, 2 miles south of Los Fresnos. Tx.
92-S	Baird Unit (TPWD) - south of Donna, Tx.

east of FM 493

Abbreviations:
LRGV-NWR - Lower Rio Grande Valley, National Wildlife Refuge
TPWD - Texas Parks and Wildlife Department
GIWW - Gulf Intracoastal Waterway

Table B-2. Biota site locations in the Lower Rio Grande Valley, Texas, 1985-1986.

Site No.	Species	Description of Site
1-B	Turtle, Carp, Largemouth Bass Striped Bass Hybrid, Gizzard Shad	Rio Grande at Falcon Dam
2-B	Channel Catfish, Carp, Gizzard Shad, Turtle	Rio Grande at Anzalduas Dam
3-B	Turtle, Gizzard Shad	Arroyo Colorado at Llano Grande (FM 1015)
4-B	None Collected	Arroyo Colorado at Rio Hondo
5-B	Blue Crab, Sea Catfish Gizzard Shad	Arroyo Colorado at Mouth of Old Channel
6-B	Turtle, Sheepshead Minnow, Tilapia	Resaca de los Cuates west of Hwy 77
7-B	Turtle	Resaca de los Fresnos west of Hwy 77
8-B	Gulf Killifish, Sheepshead Minnow, Turtle	Resaca de los Cuates at FM 106-LA-NWR
9-B	Blue Crab, Turtle, Blue Catfish Alligator Gar	Resaca de los Fresnos at Caya Atascosa-LA-NWR
10-B	Blue Catfish, Black-Necked Stilt, Cotton Rat, Freshwater Drum, Carp, Chara	Laguna Atascosa-LA-NWR
11-B	Blue Crab	Caya Atascosa at Crossing # l-LA-NWR
12-B	None Collected	Caya Atascosa at Crossing #2-LA-NWR
13-B	Sea Catfish, Blue Crab	Harlingen Ship Channel- Delta

14-B	None Collected	Athel Pond-LA-NWR
15-B	None Collected	Pelican Lake-LA-NWR

Table B-2. Biota site locations in the Lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Species	Description of Site
16-B	Blue Crab, Sea Catfish	Lower Laguna Madre-Port Mansfield, Tx.
17-B	Blue Crab, Sea Catfish	Lower Laguna Madre-Mouth of Raymondville Drain
18-B	Blue Crab, Shoalgrass	Lower Laguna Madre-Mouth of "Big Ditch"
19-B	None Collected	bower Laguna Madre-Mouth of North Floodway
20-B	Sea Catfish, Manateegrass Blue Crab	Lower Laguna Madre-Laguna Vista, Tx.
21-B	Sea Catfish, Blue Crab, Oyster Manateegrass	Lower Laguna Madre-Port Isabel, Tx.
22-B	Oyster, Manateegrass, Blue Crab Sea Catfish	Lower Laguna Madre at South Bay
23-B	Turtle	Santa Ana NWR- Pintail Lake
24-B	Cotton Rat	Santa Ana NWR-West border
25-B	Cotton Rat	Santa Ana NWR-East border
26-B	Cotton Rat	Vella Woods - LRGV-NWR
27-B	Cotton Rat	Gabrielson Unit -LRGV-NWR
28-B	Cotton Rat	Santa Maria Unit - LRGV-NWR

Table B-2. Biota site locations in the Lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Species	Description of Site
29-B	None Collected	Boscaje de la Palma
30-B	Cotton Rat	Payne Unit-LRGV-NWR
31-B	None Collected	La Sal Vieja

32-B	None Collected	Los Olmos Creek at Hwy 83
33-B	Cotton Rat	Bentsen State Park-TPWD
34-B	Cotton Rat	McManus Unit-TPWD
35-B	Cotton Rat	Baird Unit-TPWD
36-B	None Collected	Tucker Unit-TPWD
37-B	Turtle	Monte Alto Reservoir
38-B	Cotton Rat	Thompson Unit-LRGV-NWR
39-B	None Collected	La Grulla Unit LRGV-NWR
40-B	Turtle	Raymondville Drain Near Bus. Highway 77
41-B	Turtle	Hidalgo/ Willacy Drain ("Big Ditch") east of Hwy. 77
42-B	Blue Crab, Sea Catfish	Brownsville Ship Channel
43-B	Turtle	Pharr Settling Basin - LRGV-NWR
44-B	White Pelican	Pharr Settling Basin
45-B	Turtle	Carmen Blvd. Resaca-LRGV-NWR
46-B	Turtle	North Floodway at Hwy. 107
47-B	Turtle	Arroyo Colorado at FM 491

Table B-2. Biota site locations in the lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Species	Description of Site
48-B	Turtle	Hidalgo/Willacy Drain ("Big Ditch") at FM 493
49-B	Turtle	Drain at Hwy. 281 North, east of Lake Edinburg
50-B	Turtle	Raymondville Drain at FM 493
51-B	Turtle	Main Floodway at FM 1016 south of Mission, Tx.
52-B	Turtle	Drain at FM 1925 South of Lake

Edinburg

53-B Turtle Canal within North Floodway, west of FM 49

54-B Turtle Main Floodway at FM 115, south of McAllen, Tx.

55-B Turtle Banker Floodway (Hackney Lake Inlet) at FM 115, south of Main Floodway

56-B Turtle North Floodway at FM 1420

57-B Turtle Fort Brown Resaca at Southmost College, Brownsville, Tx.

58-B Turtle Resaca de los Cuates at FM 3069 point closest to FM 510

59-B Turtle Drain at FM 1847 south of Los Fresnos, Tx.

60-B Sailfin Molly Drain entering Laguna Atascosa - NWR at FM 106

Table B-2. Biota site locations in the Lower Rio Grande Valley, Texas, 1985-1986. (Continued)

Site No.	Species	Description of Site
61-B	Gizzard Shad	Pintail Lake (2) Santa Ana - NWR
62-B	Sheepshead Minnow	Willow Lake (4) Santa Ana - NWR
63-B	Gizzard Shad	Large Pintail Lake (3) Santa Ana -NWR
64-B	Gizzard Shad	Pintail Lake (1) Santa Ana - NWR

Abbreviations:
LA-NWR - Laguna Atascosa National Wildlife Refuge
LRGV-NWR - Lower Rio Grande Valley National Wildlife Refuge
TPWD - Texas Parks and Wildlife Department

APPENDIX C

ORGANOCHLORINE SUMMARY

Table C-1. Geometric mean, minimum and maximum values (ppm dry weight) for organochlorines in sediment from the Lower Rio Grande Valley, Texas. 1985-1986. (N=95)

CHEMICAL	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
p,p' DDE	0.01	6.00	0.02	70
p,p' DDD	0.01	0.02	----	3
p,p' DDT	BDLý	0.89	----	1
TOXAPHENE	1.10	20.00	----	3
DIELDRIN	0.01	0.15	----	4

[sup]1 Geometric mean not determined when < 50% detection
ý BDL - Below detection limit

Table C-2. Geometric mean, minimum and maximum (ppm wet weight) for organochlorines in fish from the Lower Rio Grande Valley, Texas, 1985-1986. (N=33)

CHEMICAL	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
CHLORDANE	0.01	0.02	---	3
c - CHLORDANE	BDLý	0.02	---	1
t - CHLORDANE	BDL	BDL	---	0
c - NONACHLOR	BDL	0.01	---	1
t - NONACHLOR	0.02	0.05	---	4
HEPTACHLOR EPOXIDE	BDL	BDL	---	0
METHOXYCHLOR	0.01	0.05	---	2
p,p' DDE	0.02	9.90	0.55	33
p,p' DDD	0.01	0.18	0.02	25
p,p' DDT	0.01	0.07	---	14
ENDRIN	0.01	0.01	---	2
DIELDRIN	0.01	0.08	---	6
HEXACHLOROBENZENE	BDL	BDL	---	0

ENDOSULFAN SULPHATE	BDL	BDL	---	0
TOXAPHENE	0.98	5.10	---	12
PCB's	0.10	0.11	---	8

[sup]1 Geometric mean not determined when < 50% detection
ý BDL - Below detection limit
Table C-3. Geometric mean, minimum and maximum values (ppm wet weight) for organochlorines in spiny softshell turtles from the Lower Rio Grande Valley, Texas, 1985-1986. (N=27)

CHEMICAL	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
OXYCHLORDANE	0.01	0.14	0.01	15
c - CHLORDANE	0.01	0.10	---	11
t - CHLORDANE	0.01	0.06	---	12
c - NONACHLOR	0.01	0.07	---	13
t - NONACHLOR	0.01	0.36	0.02	15
HEPTACHLOR EPOXIDE	0.01	0.30	---	12
METHOXYCHLOR	0.01	0.06	0.01	14
p,p' DDE	0.02	11.30	2.38	27
p,p' DDD	0.01	0.28	0.02	22
p,p DDT	0.01	0.05	0.01	14
ENDRIN	0.02	0.14	0.01	16
DIELDRIN	0.03	0.51	0.04	19
HEXACHLOROBENZENE	BDLý	BDL	---	0
ENDOSULFAN SULPHATE	0.01	0.03	---	12
TOXAPHENE	0.25	7.10	---	7
PCB's	BDL	0.15	---	1

[sup]1 Geometric mean not determined when < 50% detection.
ý BDL - Below detection limit
C-4. Organochlorine residues (ppm wet weight) in birds from the Lower Rio

Grande Valley, Texas, 1985-1986.

BLACK-NECKED	WHITE	
CHEMICAL	STILT	PELICAN
OXYCHLORDANE	BDL[sup]1	0.06
c - CHLORDANE	BDL	0.09
t - CHLORDANE	BDL	BDL
c - NONACHLOR	BDL	0.11
t - NONACHLOR	BDL	0.08
HEPTACHLOR EPOXIDE	BDL	0.07
METHOXYCHLOR	BDL	0.04
p,p' DDE	3.30	46.10
p,p' DDD	0.02	0.24
p,p' DDT	0.04	0.08
ENDRIN	BDL	0.29
DIELDRIN	BDL	0.80
HEXACHLOROBENZEN	BDL	0.01
ENDOSULFAN SULPHATE	BDL	0.01
TOXAPHENE	BDL	BDL
PCB's	BDL	BDL

[sup]1 BDL - Below detection limit

Table C-5. Geometric mean, minimum and maximum values (ppm wet weight) for organochlorines in cotton rats from the Lower Rio Grande Valley, Texas, 1985-1986. (N=11)

# SAMPLES				
CHEMICAL	MINIMUM	MAXIMUM	GEO MEAN[sup]1	DETECTED
OXYCHLORDANE	BDLý	BDL	---	0
c - CHLORDANE	BDL	BDL	---	0
t - CHLORDANE	BDL	0.02	---	1

c - NONACHLOR	BDL	0.01	---	1
t - NONACHLOR	BDL	0.01	---	1
HEPTACHLOR EPOXIDE	BDL	BDL	---	0
NETHOXYCHL0R	0.01	0.02	---	2
p,p' DDE	0.01	0.10	0.02	11
p,p' DDD	BDL	BDL	---	0
p,p' DDT	BDL	0.01	---	1
ENDRIN	BDL	0.03	---	1
DIELDRIN	BDL	0.01	---	1
HEXACHLOROBENZENE	BDL	0.01	---	1
ENDOSULFAN SULPHATE	BDL	BDL	---	0
TOXAPHENE	BDL	BDL	---	0
PCB's	BDL	BDL	---	0

[sup]1 Geometric mean not determined when < 50% detection
ý BDL - Below detection limit

Table C-6   Geometric mean, minimum and maximum values (ppm wet weight) for organochlorines in blue crab from the Lower Rio Grande Valley, Texas, 1985-1986. (N=12)

CHEMICAL	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
OXYCHLORDANE	BDLý	0.02	---	1
c - CHLORDANE	BDL	BDL	---	0
t - CHLORDANE	BDL	BDL	---	0
c - NONACHLOR	BDL	BDL	---	0
t - NONACHLOR	BDL	BDL	---	0
HEPTACHLOR EPOXIDE	BDL	BDL	---	0
METHOXYCHLOR	BDL	0.050	---	1
p,p' DDE	0.01	1.10	0.08	12
p,p' DDD	0.01	0.03	---	3

p,p' DDT	BDL	BDL	---	0
ENDRIN	BDL	BDL	---	0
DIELDRIN	BDL	0.01	---	1
HEXACHLOROBENZENE	BDL	BDL	---	0
ENDOSULFAN SULPHATE	BDL	BDL	---	0
TOXAPHENE	BDL	BDL	-- -	0
PCB's	BDL	BDL	---	0

[sup]1 - Geometric mean not determined when < 50% detection.
ý - BDL - Below detection level

APPENDIX D

TRACE ELEMENT SUMMARY

Table D-1. Geometric mean, minimum and maximum (ppm dry weight) for trace elements in sediment from the Lower Rio Grande Valley, Texas, 1985-1986. (N=95)

CHEMICAL	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
SE	0.20	0.66	0.28	59
HG	0.05	0.50	0.04	48
AS	0.1	15.0	2.6	95
AG	BDLý	BDL	---	0
AL	351	20200	7762	95
B	1.0	110.0	1.5	51
BA	3.1	564.0	100.0	95
BE	0.02	1.10	0.51	94
CD	0.2	2.0	---	44
CR	3.0	32.0	8.7	94
CU	2.2	72.8	8.3	95
FE	352	18300	8128	95
MG	185	12700	4169	95

MN	37	7280	316	95
MO	2.0	2.0	---	2
NI	2.2	16.0	7.9	94
PB	3.0	240.0	10.7	92
SB	3.0	5.0	---	32
SN	BDL	BDL	---	0
SR	9.0	1140	224	95
TL	BDL	10.0	---	1

Table D-1. Geometric mean, minimum and maximum (ppm dry weight) for trace elements in sediment from the Lower Rio Grande Valley, Texas, 1985-1986. (N=95) (Continued)

CHEMICAL	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
V	0.4	31.3	7.6	95
ZN	1.6	439.0	34.7	95

[sup]1 - Geometric mean not determined when < 50% detection
ý - BDL - Below detection limit

Table D-2ù Geometric mean, minimum and maximum values (ppm wet weight) for trace elements in fish from the Lower Rio Grande Valley, Texas, 1985-1936. (N=32)

	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
SE	0.12	0.95	0.41	33[sup]3
HG	0.038	0.431	0.062	22[sup]3
AS	0.04	4.72	0.21	30[sup]3
AG	BDLý	BDL	----	0
AL	2.3	1164.8	15.7	32
B	1.0	6.3	----	15
BA	0.10	13.10	0.95	32
BE	0.01	0.05	----	4

CD	0.003	0.031	----	9
CR	0.07	3.40	0.19	21
CU	0.12	5.09	0.45	30
FE	3.9	777.4	25.8	31
MG	152.7	631.4	210.9	30
MN	1.1	33.2	2.8	25
MO	0.16	0.39	----	3
NI	0.02	1.25	----	11
PB	0.02	1.01	----	9
SN	1.0	61.0	2.2	17[sup]4
SR	15.0	168.1	48.6	32
V	0.08	2.89	0.160	20
ZN	0.5	146.7	16.9	32

[sup]1 - Geometric mean not determined when < 50% detection
ý - BDL - Below detection limit
[sup]3 - N = 33
[sup]4 - N = 22

Table D-3. Geometric mean, minimum and maximum values (ppm wet weight) for trace elements in spiny softshell turtles from the Lower Rio Grande Valley, Texas, 1985-1986. (N = 27)

	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
SE	0.14	0.68	0.26	26
HG	0.022	0.202	0.062	26
AS	0.03	0.06	----	12
AG	BDLý	BDL	----	0
AL	8.6	270.7	38.3	27
B	0.5	4.6	1.2	17
BA	0.57	9.83	2.88	27
BE	BDL	0.01	----	1

CD	0.008	0.050	0.019	19
CR	0.19	1.26	0.34	22
CU	0.16	1.86	0.64	27
FE	8.0	420.0	56.9	26
MG	170.0	464.6	346.7	27
MN	1.1	676.3	4.8	26
MO	BDL	BDL	----	0
NI	0.07	0.63	0.16	21
PB	0.09	0.59	0.16	19
SN	1.5	8.5	3.6	7/7
SR	17.0	233.5	84.1	27
V	0.07	0.55	0.15	20
ZN	9.8	33.1	22.7	27

[sup]1 - Geometric mean not determined when < 50% detection
ý - BDL - Below detection limit

Table D-4. Trace elements (ppm wet weight) in birds from the Lower Rio Grande Valley, Texas, 1985-1986.

	BLACK-NECKED STILT	WHITE PELICAN
SE	0.47	0.43
HG	0.27	0.12
AS	0.16	0.10
AG	---1	BDLý
AL	8.7	11.4
B	.7	1.6
BA	1.20	1.22
BE	BDL	0.01
CD	BDL	0.024
CR	0.14	0.46

CU	1.40	2.57
FE	36.0	97.5
MG	220.0	304.8
MN	1.1	1.0
MO	ND	0.05
NI	ND	0.13
PB	0.93	ND
SN	5.3	---
SR	19.0	24.0
V	BDL	0.05
ZN	17.0	32.5

[sup]1 - Not Analyzed
ý - BDL - Below detection limit

Table D-5. Geometric mean, minimum and maximum values (ppm wet weight) for trace elements in cotton rats from the Lower Rio Grande Valley, Texas, 1985-1986. (N=11)

	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
SE	0.20	0.44	0.31	11
HG	0.002	0.006	0.003	11
AS	0.03	0.10	---	4
AG	BDLý	BDL	---	0
AL	39.3	194.3	94.8	11
B	0.5	1.8	0.7	9
BA	1.69	3.85	2.43	11
BE	BDL	0.01	---	1
CD	0.009	0.039	0.012	10
CR	0.25	1.37	0.37	11
CU	1.38	1.95	1.63	11

FE	59.5	106.0	84.3	11
MG	365.6	495.8	417.8	11
MN	1.9	5.3	3.0	11
MO	0.09	0.19	0.13	11
NI	0.17	0.60	0.28	11
PB	0.05	0.06	---	2
SN	---	---	---	---
SR	9.0	17.4	11.8	11
V	0.06	0.19	0.10	11
ZN	18.4	26.5	23.1	11

[sup]1 - Geometric mean not determined when < 50% detection
ý - BDL - Below detection limit

Table D-6. Geometric mean, minimum and maximum values (ppm wet weight) trace elements in blue crab from the Lower Rio Grande Valley, Texas, 1985-1986. (N=12)

	MINIMUM	MAXIMUM	GEO MEAN[sup]1	# SAMPLES DETECTED
SE	0.20	1.07	0.42	12
HG	0.028	0.086	0.050	12
AS	0.19	6.51	1.57	12
AG	0.1	0.24	0.08	4/7
AL	2.9	148.8	50.5	12
B	3.0	9.7	4.6	12
BA	0.10	28.86	4.40	12
BE	0.01	0.05	---	2
CD	0.045	0.358	0.09	7
CR	0.12	0.33	0.13	8
CU	0.45	25.25	6.15	11

FE	25.0	122.0	34.0	11
MG	290.0	2324.4	558.5	11
MN	15.0	62.7	22.6	11
MO	0.25	0.37	---	2
NI	0.08	0.21	0.09	7/10
PB	0.07	0.35	---	4
SN	3.5	6.3	4.9	5/5
SR	25.0	701.1	299.2	12
V	0.12	0.38	0.12	8
ZN	0.5	27.6	12.7	12

[sup]1 - Geometric mean not determined when < 50% detection

Table D-7. Trace elements (ppm wet weight) in oysters from the Lower Rio Grande Valley, Texas, 1985-1986.

	SITE 21	SITE 22
SE	0.33	0.28
HG	0.022	0.036
AS	2.18	4.40
AG	BDL[sup]1	BDL
AL	67.5	103.4
B	3.8	4.0
BA	0.51	1.61
BE	BDL	BDL
CD	0.273	0.460
CR	0.29	0.20
CU	9.99	23.00
FE	66.2	85.2
MG	835.4	902.0

MN	4.6	5.0
MO	0.02	0.04
NI	0.17	0.15
PB	0.17	0.12
SN	---ý	--
SR	20.6	15.1
V	0.24	0.26
ZN	225.7	284.0

[sup]1 - BDL - Below detection limit
ý - Not analyzed