U.S. Fish and Wildlife Service
Region 2
Contaminants Program

CONTAMINANTS INVESTIGATION OF THE SAN ANTONIO RIVER OF TEXAS 1995

by

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Abstract

In 1992, the U.S. Fish and Wildlife Service conducted a contaminants investigation on fish collected from the San Antonio and Guadalupe Rivers in southeast Texas. Results indicated polychlorinated biphenyl (PCB) contamination near Floresville, Wilson Co., Texas on the San Antonio River. A follow-up study near Floresville was conducted in 1995 to locate the source of contamination, and to test the usefulness of semi-permeable membrane devices (SPMDs) for detecting contaminants in riverine systems. Replicate SPMDs were deployed for approximately 30-days at ten sites. Longnose gar (*Lepisosteus osseus*) were collected from four sites. Data from the SPMDs indicated greater concentrations of some of the PCB congeners at two of the sites but the variability was too great between replicates to draw valid conclusions. Longnose gar from three of the four sites contained PCB concentrations that exceeded the Food and Drug Administration Action Level of 2.0 µg/g total PCBs. Copper, chromium, mercury, and DDE in whole body fish were also found to be elevated.

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Introduction

The San Antonio River in Texas originates in the city of San Antonio and flows about 238 miles to the Gulf of Mexico. After converging with the Guadalupe River a few miles from the Gulf of Mexico, the combined rivers discharge into Guadalupe Bay, a minor bay in the San Antonio Bay System. The San Antonio River Basin includes four major tributaries: Medina River, Leon Creek, Cibolo Creek, and Salado Creek, which, along with other minor tributaries, drain the 10,826 km^2 (4,180 sq. mile) basin.

In 1992, the U.S. Fish and Wildlife Service (USFWS) conducted a contaminants investigation in the San Antonio River from the confluence of the Medina River, 12 miles south of the city of San Antonio, Bexar Co., to the Hwy 77 bridge, approximately 12 miles above the confluence of the Guadalupe River in Victoria Co. (Lee and Schultz 1994) . Results of that study indicated that total polychlorinated biphenyls (PCBs) at the site near Floresville, Wilson Co., Texas were tenfold higher in fish tissue than the National Contaminants Biomonitoring Program (NCBP) geometric mean of 0.39 µg/g (wet weight) (Schmitt et. al. 1990). In 1995, this study was conducted with a two-fold purpose: 1) to attempt to locate the source of PCB contamination identified in the 1992 study, and 2) to test the usefulness of semi-permeable membrane devices (SPMDs) for detecting contaminants in riverine environments.

Study Area

The Upper San Antonio River lies largely within the Gulf Coastal Plain, an area of low elevation and little topographic relief that is characterized by unconsolidated mud and sand substrate, thick, organic soils, and an abundance of shrub and grassland vegetation. The climate is subtropical and semi-arid with normal mean temperatures ranging from 10.4° C in January to 29.3° C in July. Summer weather patterns are dominated by systems originating in the Gulf of Mexico and are characterized by southeasterly winds, warm temperatures and high humidity. Continental weather systems predominating during the winter months bring northerly winds, cooler temperatures, and less humid conditions.

The majority of the land use along the San Antonio River is rural, both farmland and ranchland. The San Antonio River is subject to drainage from urban and agricultural stormwater runoff, point source discharges from industry and municipalities, as well as runoff from illegal dumps that occur directly onto portions of the river bank or within the drainage area. The Texas Natural Resource Conservation Commission's (TNRCC) segment 1911 of the San Antonio River extends from the headwaters in the city of San Antonio, Bexar Co. to Falls City, Karnes Co., a distance of about 85 miles (135 km) (TNRCC 1996). TNRCC's designated uses are contact recreation and high aquatic life use. There are 4 domestic, 12 industrial and 3 agricultural permitted outfalls in segment 1911, for a total discharge of 968 million gallons/day. The segment is classified as water quality limited due to water quality standards violations (TNRCC 1996). In the Floresville area, there are five hazardous waste sites: AT&T Long Lines (permit

#TX980598957), Benny Cope Oil Co. (permit #TXD00782821), PSL SVCS (permit #TX988075602), Sun Exploration and Production Co. (permit #TXD000838235), and Texaloy Foundry Co. (permit #TX981915168). There are two Toxic Release Inventory (TRI) sites: Fibrcon Inc. (permit #TXD988043493) and Texaloy Foundry Co. (permit #TX981915168) which are also hazardous waste sites. In addition, there are two wastewater discharges: City of Floresville (permit #TX0056227) and Koch Refining Co. (permit #TX0110744) (USEPA 1999). A twelve-mile portion of the Upper San Antonio River near the city of San Antonio is on the 1998 List of Impaired and Threatened Water Bodies (Clean Water Act §303(d) List) for exceeding the criterion for bacteria levels (TNRCC 1998). Levels in bed sediments in excess of TNRCC's 85th percentile screening level have been detected for cadmium, copper, and lead in the some sections of the upper half of segment 1911, and silver in the lower half of segment 1911 (TNRCC 1996).

Methods

The San Antonio River sites were located above and below the community of Floresville at creeks, and agricultural, domestic, and industrial runoff ditches (Figure 1). Two semi-permeable membranes, designated as A and B were placed in a stainless-steel deployment device at each of ten sites on the river. Dates and Geographic Positioning System (GPS) coordinates for the sites are given in Table 1. Semi-permeable membrane devices (SPMDs) were developed by Huckins et al. (1990) at the U.S. Geological Survey - Biological Resources Division as a tool to simulate bioaccumulation of hydrophobic contaminants for evaluation by in-situ bioassays. This device consists of a gram of triolein encased in a strip of low density nonporous polyethylene tubing. The SPMDs were purchased from Environmental Sampling Technologies[1] (EST) in St. Joseph, Missouri, and deployed according to protocols developed by the EST. Membranes arrive from the lab threaded on "spider carriers" and sealed in a can. In the field, spider carriers are removed from the can and placed inside a stainless-steel, mesh cage. Each deployment device (cage) was secured from an overhanging tree branch and suspended approximately 0.7 to1 m (3 ft.) below the surface of the water by a stainless steel cable. Trip blanks, consisting of an SPMD in a sealed container, were used to verify that results were due to the uptake of aquatic contaminants as opposed to exposure to air during the actual deployment. During both deployment and recovery, each trip blank container was opened, exposing the SPMD to the air. Exposure times for the trip blanks ranged from 1 min, 30 sec to 7 min, 50 sec. Recorded water temperatures ranged from 27.2 - 29.5 ^{0}C. SPMDs were checked twice during the approximate 30-day deployment period, and any sediment that may have accumulated was respectively cleared from the cage by gently shaking under water.

Streambed sediments were also collected at each site downstream from a creek or drainage ditch.

[1]Sole source of SPMDs at the time of this study.

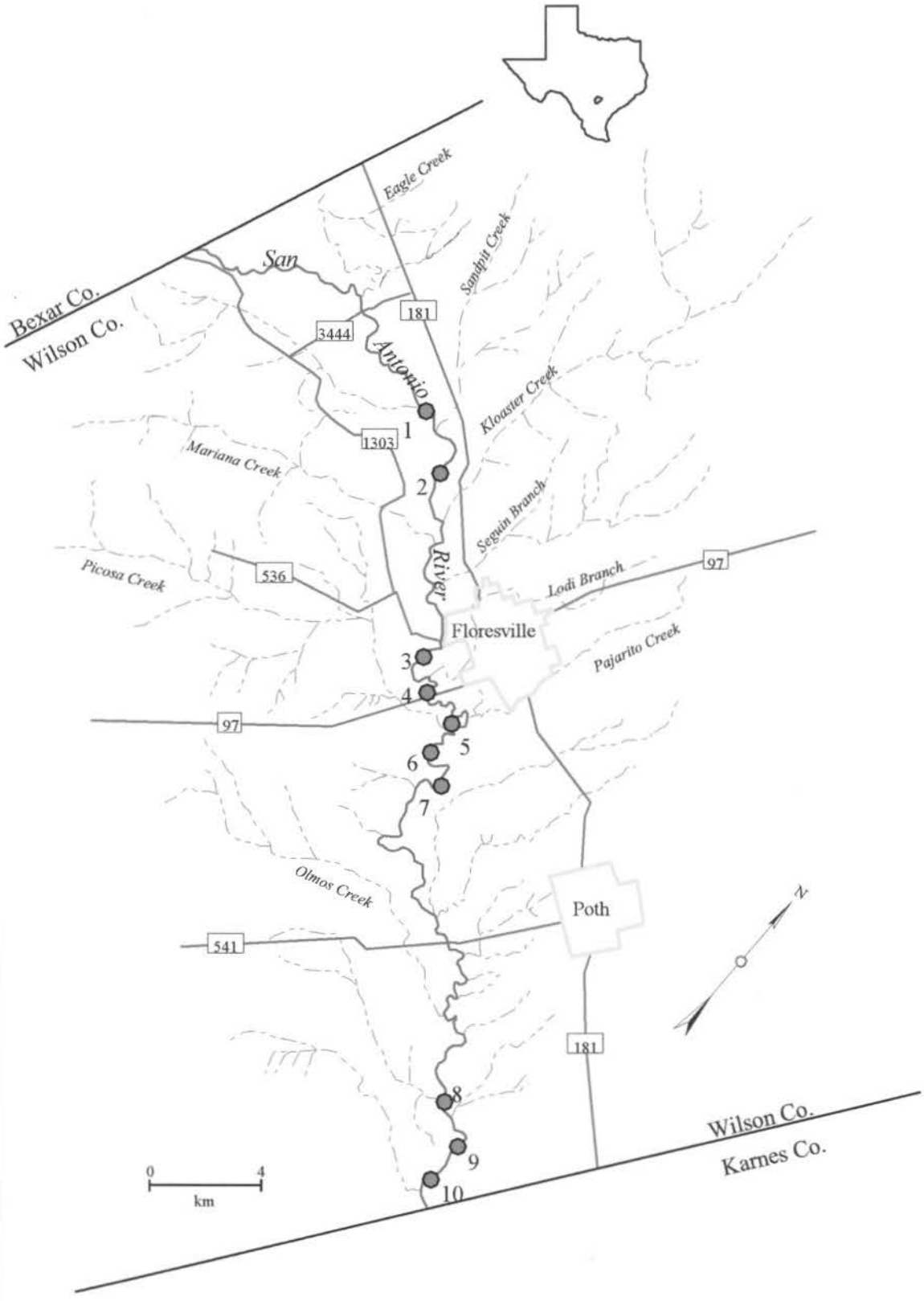

Figure 1. Data collection sites on the San Antonio River, 1995.

A stainless steel pan and spoon were used to collect subsamples of the top 10 cm (4 in.) of sediment. Subsamples were composited and an aliquot was placed into a chemically-cleaned jar. Longnose gar (*Lepisosteus osseus*) were collected from four sites (#1, #3, #7, #10) using gill nets, weighed and measured, and wrapped in foil. Clams (*Corbicula* sp.) were found at only two (site #1 and #2) of the four sites in which fish were collected; at these sites they were collected by hand and wrapped in foil. Upon returning to the lab, clams were pried open using a clean scalpel and placed directly into chemically-cleaned jars; excess liquid was decanted. All samples were kept on wet ice in the field and then frozen in a commercial freezer (-20^0 C) prior to shipping to an analytical lab.

Organochlorine analyses of fish composites, SPMDs, and *Corbicula* sp. included hexachlorobenzene (HCB), alpha benzene hexachloride (BHC), alpha chlordane, beta BHC, cis-nonachlor, delta BHC, dieldrin, endrin, gamma BHC, gamma chlordane, heptachlor epoxide, mirex, o,p' DDD, o,p' DDE, o,p' DDT, p,p' DDD, p,p' DDE, p,p' DDT, oxychlordane, toxaphene, trans-nonachlor, total PCBs, and PCB congeners 105, 114, 118/106, 126, 128, 138, 156, 157, 158, 166, 167, 169, 170, 189, and 77. SPMDs were sent to Environmental Sampling Technologies (EST) in St. Joseph, Missouri where the membranes were removed from the spider carriers, rinsed with tap water, and all algae, bacteria, and other material was cleaned from the surface of the membrane with a clean brush. The membrane was rinsed in a solution of hexane and 1N hydrochloric acid, rinsed again with tap water and then acetone. Each membrane was submersed in a jar filled with 125-ml of hexane, using a watch glass, if necessary, to hold the membrane down. Jars were covered with hexane-rinsed aluminum foil and a lid, and incubated at 18^0C for 24 hours. The dialysate was poured into a second labeled jar and the original jar was filled with an equal amount of hexane. Both jars were allowed to incubate at 18^0C for another 8 hours. The membrane was discarded and the dialysate was concentrated down to1 ml in a Kuderna-Danish flask in a hot water bath and then concentrated further with nitrogen gas. The ampulized samples were then sent to Mississippi State University Chemical Laboratory for organic analyses. All trip blanks were dialyzed, but only those from sites #1, 5, and 10 were analyzed. The remaining seven trip blanks were ampulized and retained frozen, if needed.

Fish composites and sediments were analyzed for the following inorganic elements: aluminum, arsenic, boron, barium, beryllium, cadmium, chromium, copper, iron, mercury, magnesium, manganese, molybdenum, nickel, lead, selenium, strontium, vanadium, and zinc. Samples were analyzed at Research Triangle Institute in Research Triangle Park, NC. Arsenic and selenium concentrations were determined using atomic absorption spectroscopy hydride generation. Mercury concentrations were determined by cold vapor atomic absorption. All other element concentrations were determined using inductively coupled plasma spectroscopy. Laboratory quality assurance and quality control (QA/QC) was monitored by the USFWS Patuxent Analytical Control Facility. All element concentrations are reported on a µg/g dry weight basis. An assigned value of one-half the detection limit was substituted for the "not detected" values to facilitate calculations where at least 50% of the samples were above detection.

Table 1. Dates and GPS coordinates for semi-permeable membrane device (SPMD) deployment and retrieval in the San Antonio River, TX.

Site	GPS coordinates	SPMD Deployment Date	SPMD Retrieval Date
#1	29°N 12.096; 98°W 14.175	25 July 1995	25 August 1995
#2	29°N 11.680; 98°W 13.080	27 July 1995	25 August 1995
#3	29°N 07.063; 98°W 10.981	28 July 1995	24 August 1995
#4	29°N 06.897; 98°W 10.514	28 July 1995	24 August 1995
#5	29°N 06.695; 98°W 10.134	28 July 1995	24 August 1995
#6	29°N 06.650; 98°W 09.970	28 July 1995	24 August 1995
#7	29°N 06.559; 98°W 10.514	28 July 1995	24 August 1995
#8	28°N 59.680; 98°W 05.980	04 August 1995	08 September 1995
#9	28°N 57.670; 98°W 05.520	04 August 1995	07 September 1995
#10	28°N 57.280; 98°W 04.800	04 August 1995	07 September 1995

Results and Discussion

Metals in fish

Thirteen of the nineteen metals were detected in one or more of the whole fish composite samples (Table 3). Arsenic, beryllium, cadmium, lead, molybdenum, and vanadium were below detection levels in all fish composites. Detection limits are given in Table 2. Elements of most concern to wildlife are discussed below.

Copper

Copper is an essential element but an excess of copper may be harmful to aquatic species. It is one of the most common contaminants found in urban runoff. Other anthropogenic sources include pipe corrosion, industrial effluents and aerial fallout, and sewage treatment plant effluents (EPA 1980a). In 1984, the NCBP average freshwater fish concentration was 2.60 µg/g dw and the 85th percentile was 4 µg/g dw (Schmitt and Brumbaugh 1990). At a downstream San Antonio River site (NCBP #113 - McFaddin), longnose gar contained 1.6 µg/g dw (Schmitt and Brumbaugh 1990). In the 1992 study, longnose gar at the Floresville site (#3) had a

Table 2. Detection limits for sediment, biota, and SPMD samples collected from the San Antonio River.

Metals	Detection Limit (µg/g dry wt.) Sediment	Detection Limit (µg/g dry wt.) Biota	Organochlorines	Detection limit (µg/g weight wt.) Biota, SPMD
Aluminum	100.0	10	HCB	.01
Arsenic	.5	1.0	PCB congeners	.0001
Boron	5.0	2.0	Total PCBs	.05
Barium	3.0	1.0	alpha BHC	.01
Beryllium	.2	.2	alpha chlordane	.01
Cadmium	.2	.2	beta BHC	.01
Chromium	5.0	1.0	cis-nonachlor	.01
Copper	5.0	1.0	delta BHC	.01
Iron	100.0	19.0	dieldrin	.01
Mercury	.1	.2	endrin	.01
Magnesium	100.0	19.0	gamma BHC	.01
Manganese	4.0	.8	gamma chlordane	.01
Molybdenum	5.0	1.0	heptachlor epoxide	.01
Nickel	5.0	1.0	mirex	.01
Lead	5.0	2.0	o,p'-DDD, DDE, DDT	.01
Selenium	.5	1.0	oxychlordane	.01
Strontium	2.0	.4	p,p'-DDD, DDE, DDT	.01
Vanadium	5.0	1.0	toxaphene	.05
Zinc	5.0	2.0	trans-nonachlor	.01

Table 3. Trace elements in fish and sediments from the upper San Antonio River, 1995.

		Trace element concentration , µg/g dry weight																	
Site	**Sample**	**Al**	**As**	**B**	**Ba**	**Be**	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Mg**	**Mn**	**Ni**	**Pb**	**Se**	**Sr**	**V**	**Zn**
01	sediment	5154	2.77	11.5	48.8	0.37	0.31	17.7	9.1	9798	ND	2686	208.1	8.3	21.8	ND	121.4	11.9	46.9
02	sediment	3562	2.0	8.45	38.9	0.32	0.27	11.3	6.5	8184	ND	2117	176.8	6.5	15.6	ND	100.7	7.9	37.0
03	sediment	4523	2.25	10.6	39.9	0.43	0.30	12.0	7.0	9053	ND	2164	179.3	7.2	14.0	ND	91.0	10.0	35.9
04	sediment	4631	2.32	10.5	38.5	0.34	0.23	11.4	6.5	8730	ND	2172	174.1	6.3	12.3	ND	89.4	9.3	34.6
05	sediment	3818	1.94	9.15	36.5	0.29	0.21	10.0	5.7	8003	ND	2118	179	5.9	12.5	ND	88.5	8.8	31.5
06	sediment	3815	1.84	8.23	31.2	0.27	ND	8.6	ND	7442	ND	1644	144.2	5.2	9.4	ND	69.3	8.3	23.5
07	sediment	3587	1.96	7.19	34.3	0.27	ND	8.7	ND	7402	ND	1889	163.4	5.3	10.9	ND	81.6	7.9	27.3
08	sediment	5098	3.99	12.6	44.9	0.40	0.41	11.1	6.7	10690	ND	2727	224.5	8.8	23.6	ND	106.3	11.0	52.6
09	sediment	7158	3.79	14.7	59.9	0.49	0.34	11.9	7.6	11660	ND	2915	218.8	8.7	15.2	ND	106.3	12.5	41.4
10	sediment	6258	3.13	14.0	53.3	0.54	0.42	11.6	8.0	11370	ND	2789	210.8	8.7	16.5	ND	110.4	12.0	43.1
01	longnose gar	58.54	ND	2.4	4.6	ND	ND	12.4	4.2	337.4	0.828	10980	8.6	2.7	ND	ND	218	ND	92.9
03	longnose gar	88.37	ND	2.1	5.2	ND	ND	19.9	1.7	222.2	1.511	10280	9.5	4.7	ND	1.8	248.6	ND	98.9
07	longnose gar	47.07	ND	3.77	4.6	ND	ND	9.8	2.0	175.2	0.488	11560	9.0	2.6	ND	1.6	235	ND	88.2
10	longnose gar	119.4	ND	ND	4.2	ND	ND	9.7	2.4	193.2	0.472	5455	5.8	2.9	ND	1.1	96.19	ND	60.2

concentration of 1.1 µg/g dw, and the highest concentration was detected in an alligator gar at McFaddin (2.4 µg/g dw) (Lee and Schultz 1994). Concentrations in whole body fish in the 1995 study ranged from 1.7- 4.2 µg/g dw. The highest concentration was at site #1 which exceeded the NCBP 85th percentile, indicating possible local contamination. However, the threshold of concern for adverse affects in rainbow trout *(Salmo gairdneri)* is in the range of 9.8-13.3 µg/g dw in whole body fish (Julshamn et al. 1988), so while there may be copper contamination present, it may not be sufficiently elevated to harm fish.

Chromium

Chromium is a USEPA priority pollutant and is most toxic in its hexavalent form. At high concentrations it is a mutagen, teratogen and carcinogen. Organs and tissues of fish and wildlife that contain 4.0 mg total Cr/kg dry weight are considered evidence of chromium contamination although the significance of tissue concentration is not clear (Eisler 1986). The major sources of chromium in the atmosphere are chromium alloy and metal producing industries, while electroplating and metal finishing industries, and domestic treatment plants, are the major sources that contribute to aquatic environments (Eisler 1986). Generally, elevated levels of chromium in biological samples have paralleled increased industrial uses, especially those associated with plating and foundry applications, chemical manufacturing, and corrosion inhibition (Taylor and Parr 1978).

Based on the results of three USFWS river basin studies in the southwest, the Rio Grande (Irwin 1989), the San Juan River (O'Brien 1987) and the Lower Gila River (Kepner 1986), Irwin (1988) concluded that chromium levels above 0.8 µg/g ww in fish and wildlife tissues should be considered elevated. The highest concentrations in whole body mosquitofish (9.7 µg/g ww) in the Trinity River were detected downstream of Dallas, Texas (Irwin 1988). In a Lower Rio Grande Valley irrigation study, the highest level of chromium was 3.4 µg/g ww in *Tilapia* sp. (Wells et al. 1988). In this study, chromium concentrations ranged from 9.7 µg/g dw (3.1 µg/g ww) at site #10 to 19.9 µg/g dw (7.3 µg/g ww) at site #3. In the 1992 study, the highest concentration was 8.0 µg/g dw in longnose gar from Floresville on the San Antonio River, less than half of the highest concentration from this current study. Based on these results, chromium is elevated in this reach of the river, and should be taken into account during development of TMDLs, discharge permit renewals and when any new permits with chromium limits are issued.

Mercury

Mercury is the heavy metal most toxic to fish (Eisler 1987) and is listed by USEPA as a priority pollutant. Mercury bioconcentrates and biomagnifies through the food chain causing various cytochemical and histopathological effects (Eisler 1987) in addition to being extremely embryotoxic and teratogenic (Sorenson 1991). The majority of mercury in fish is methylmercury (Sorenson 1991). Fish do not readily excrete methylmercury and may store it in axial muscle, a tissue less sensitive to the toxic effects, as a means of detoxification (Weiner and Spry 1996). Generally, axial muscle concentrations of 6-20 µg/g ww are associated with toxicity. In whole body brook trout, probable toxic effects were observed at 5 µg/g ww but no effects were observed at 3 µg/g ww (Weiner and Spry 1996). The neurotoxicity of methylmercury may cause

behavioral effects at much lower levels than these. The most sensitive life stage in fish populations is the developing embryos which are impacted at mercury concentrations 1-10% that of adults (Weiner and Spry 1996).

Mercury concentrations in whole body gar samples from this study ranged from 0.47 µg/g dw (0.15 µg/g ww) at site #10 to 1.5 µg/g (0.55 µg/g ww) at site #3. All four samples were below levels believed to adversely affect adult fish, the FDA action level of 1.0 µg/g ww for human consumption, and the level (1.1 µg/g ww) for protection of mammalian predators (Eisler 1987). Levels found in this study were consistent with concentrations in the 1992 gar from Floresville (Lee and Schultz 1994). However, all four samples were well above the predator protection level of 0.1 µg/g ww for avian predators (Eisler 1987).

Selenium

The difference between normal background levels of selenium and toxic concentrations is quite narrow, and since selenium bioaccumulates, even slight increases may adversely affect aquatic organisms (Lemly 1996). In whole body fish, 4 µg/g dw is considered the toxic effects threshold with effects to reproductivity, organs and tissues beginning at 4-16 µg/g dw (Lemly 1996). The concentrations detected (max.1.8 µg/g dw) in gar in this study were well below that level.

Zinc

Zinc concentrations ranged from 60.2-98.9 µg/g dw (19.1-36.2 µg/g ww). Three sites,#1, 3, and 7, were at or slightly above the NCBP national average of 88 µg/g dw (Schmitt and Brumbaugh1990). Results from the 1992 San Antonio River study ranged from 18-25 µg/g ww in gar and was highest in Floresville (site #3). Based on these data, zinc does not appear to of concern here.

Metals in sediment

Sixteen of nineteen elements were present in sediment samples. Three elements- molybdenum, mercury and selenium- were below detection in all samples. Detection limits are given in Table 2 and residue data are given in Table 3.

Sediment residue levels were compared to recent sediment quality guidelines and to the Texas Natural Resource Conservation Commission (TNRCC) 85th percentile for freshwater streams (Table 4). Smith et al. (1996) used a weight-of-evidence approach to develop biological effects-based sediment quality guidelines (SQGs) for Canada. MacDonald et al. (1996) developed similar SQGs for coastal Florida. The threshold effects level represents an estimate of the concentration of the chemical below which effects only rarely occur whereas the probable effects represents a concentration above which adverse effects frequently occur.

Although SQGs formulated by MacDonald et al. (1996) are for marine sediments, USDOI (1998) considers them to be applicable to freshwater sediments until further guidelines are available. Residues of arsenic, cadmium, chromium, copper, lead, nickel, and zinc in this study were well below the threshold effects levels for adverse biological effects.

Table 4. Comparison of residue levels detected in sediment samples from the San Antonio River (1995) to sediment quality guidelines and TNRCC screening values. All values are in µg/g dry weight.

Element	San Antonio River at Floresville	Florida SQGs[4] TELs[5] (Marine)	Canadian SQGs TELs- PELs[6] (Freshwater)	TNRCC Sediment 85th % Screening Values[7] (Freshwater Stream)
Arsenic	2.5[1] (1.8-4.0)[2] 10[3]	7.24	5.90-17.0	6.9
Cadmium	.24 (<.2-0.42) 8	0.68	0.596-3.53	1.0
Chromium	11.2 (8.6-17.7) 10	52.3	37.3-90.0	20.0
Copper	5.7 (<5.0-9.1) 8	18.7	35.7-197	19.2
Lead	14.6 (9.4-23.6) 10	30.2	35.0-91.3	40.0
Nickel	7.0 (5.2-8.7) 10	15.9	18.0-35.9	15.0
Zinc	36.4 (23.5-52.6) 10	124	123-315	83.0

[1]Geometric mean
[2]The minimum and maximum detected values (min-max)
[3]The number of samples exceeding the detection limit
[4]Sediment quality guidelines
[5]TEL, threshold effect level (McDonald et al. 1996)
[6]TEL-PEL, threshold effect level-probable effect level (Smith et al. 1996)
[7]TNRCC 1996

Organics in Biota

Organochlorine pesticides and congener-specific PCB concentrations in fish were below detection for HCB, PCB 77, alpha BHC, alpha chlordane, beta BHC, delta BHC, endrin, gamma BHC, heptachlor epoxide, mirex, o,p' DDD, o,p' DDE, o,p' DDT, oxychlordane, and toxaphene.

Table 5 lists the results for any concentrations above the detection level in fish and *Corbicula* .

Table 5. Organochlorine pesticides and PCBs in longnose gar (*Lepisosteus osseus*) and *Corbicula* collected in the San Antonio River near Floresville, 1995

	Gar Site #1	Gar Site #3	Gar Site #7	Gar Site #10	*Corbicula*	*Corbicula*
% moisture	65.5	64.5	68.5	70.0	87.5	91.5
% lipid	4.78	3.93	4.32	7.48	1.09	.683
Weight (range) *(g)* Length (range) *(mm)*	340-1219 525-810	652-2183 620-1020	652-822 600-740	539-737 505-640		
cis-nonachlor	0.019	0.024	0.019	0.013	ND	ND
trans-nonachlor	0.048	0.061	0.048	0.027	ND	ND
dieldrin	0.010	ND*	ND	0.010	ND	ND
gamma chlordane	0.014	0.015	0.015	0.010	ND	ND
p,p'-DDD	0.088	0.099	0.095	0.046	ND	ND
p,p'-DDE	0.50	1.20	0.55	0.17	0.014	ND
p,p'-DDT	0.020	0.017	0.021	ND	ND	ND
PCB 105	0.019	0.052	0.018	0.0049	0.0008	0.0005
PCB 114	0.0012	0.0064	0.0011	0.0029	ND	ND
PCB 118/106	0.042	0.082	0.040	0.011	0.0022	0.0012
PCB 126	0.0002	ND	0.0002	ND	ND	ND
PCB 128	0.022	0.048	0.021	0.0067	0.001	0.0006
PCB 138	0.062	0.089	0.059	0.037	0.009	0.0047
PCB 156	0.013	0.044	0.012	0.036	0.0004	0.0001
PCB 157	0.0031	0.015	0.003	0.001	0.0001	ND
PCB 158	0.016	0.037	0.015	0.0039	0.0006	0.0003
PCB 166	0.0009	0.0017	0.0004	ND	0.0001	0.0003
PCB 167	0.0069	0.032	0.0067	0.0021	0.0005	0.0002
PCB 169	ND	ND	0.0001	ND	ND	ND
PCB 170	0.035	0.059	0.033	0.016	0.0006	0.0001
PCB 189	0.0017	0.009	0.0016	0.0005	ND	ND
Total PCB	2.3	7.4	2.0	0.68	0.08	<0.05

*ND no detect
PCB #77 all below detect

PCBs

PCB's are a group of 209 synthetic halogenated aromatic hydrocarbons. They were used in the electrical industry as insulating or cooling agents in transformers and capacitors. Environmental contamination resulted from several sources including leaks from closed systems, landfills, equipment dumps, industrial and municipal discharges, and atmospheric deposition (Eisler and Belisle 1996). Significant quantities are still in use; 780 x 10^3 t of PCB are present in older electrical equipment, in landfills and dumps or in storage (Tanabe 1988). Since production was banned in 1979, environmental concentrations of PCBs have decreased considerably yet continue to be a hazard to wildlife. PCBs are bioaccumulators with a high lipophilicity and low biodegradability. Once released into the environment, PCBs bind tightly to sediments and soils in lakes, estuaries, and rivers, and remain available for at least 8-15 years (Swain 1983). Differences in toxic and biologic responses of PCB congeners are due to the number and substitution of chlorine on the biphenyl rings. Specific congeners which are substituted on both para and at least two meta positions (PCB 77, PCB169, and PCB126) are the most biochemically active as well as the most toxic (Voogt et al. 1990).

In fish tissues, 14 of the15 PCB congeners tested were detected (Table 5). Concentrations of PCB congeners were generally low but concentrations were highest for almost all congeners at site #3. The most toxic congeners (PCB 77, PCB169, and PCB126) were either below detection or concentrations were the lowest of all the congeners analyzed. Total PCB ranged from 0.6 to 7.4 µg/g wet wt. The highest total PCB concentration in whole body fish tissue (7.4 µg/g) was at site #3 and sites #1 and #7 were at or above the FDA critical action limit for human consumption (2.0 µg/g fresh weight). Nationwide maximum concentrations in whole body freshwater fish decreased from 70.6 µg/g in 1976-77 to 6.7 µg/g in 1984 (Schmitt et al. 1990), so the highest level from this study (7.4 µg/g) exceeded the 1984 maximum nationwide. This particular sample was partially scavenged in the gill nets, with most of the internal organs missing, which probably means the concentration is inflated but it is still indicative of contamination. Only twelve of the 112 NCBP stations sampled nationwide in 1984 were above 2.0 µg/g and those were highest in the industrialized regions of northeast (Schmitt et al. 1990).

There is some discrepancy in the literature concerning the toxicity of PCBs to fish. When parent fish were exposed to 0.14 ug Aroclor 1254/l for 28 days, sheepshead minnow (*Cyprinodon variegatus*) embryos containing 7 mg Aroclor 1254/kg fresh weight had low survival (USEPA 1980b). Rainbow trout eggs containing 0.33 mg Aroclor 1254/kg fresh weight had reduced hatch and numerous posthatch larval deformities (Niimi 1983). Sublethal exposure may include decreased growth, liver disorders, and low reproductive success with levels as low as 0.4 µg/g causing reproductive toxicity in some fish (USEPA 1980b). However, a recent literature review by Niimi (1996) indicates that fish may accumulate >50-100 mg/kg before chronic or adverse reproductive, cytological, or biochemical changes occur.

DDT

Three out of four of the fish samples contained DDT concentrations of 0.02 µg/g. DDE was present in all four fish samples and one mussel sample and ranged from 0.014 to 1.2 µg/g. The highest concentration was again detected at site #3 and although the highest concentration is unlikely to adversely affect fish, sensitive fish-eating birds (such as raptors) in the area may be reproductively impaired.

Organics in Semi-Permeable Membrane Devices

SPMDs were analyzed for the PCB congeners 105, 114, 118/106, 126, 128, 138, 156, 157, 158, 166, 167, 169, 170, 189, and 77, as well as total PCBs, HCB, alpha BHC, alpha chlordane, beta BHC, cis-nonachlor, delta BHC, dieldrin, endrin, gamma BHC, gamma chlordane, heptachlor epoxide, mirex, o,p' DDD, o,p' DDE, o,p' DDT, p,p' DDD, p,p' DDE, p,p' DDT, oxychlordane, toxaphene, and trans-nonachlor. Concentrations in all SPMDs were below detection limits for HCB, alpha BHC, alpha chlordane, beta BHC, cis-nonachlor, delta BHC, endrin, gamma BHC, mirex, o,p' DDD, o,p' DDE, o,p' DDT, oxychlordane, p,p' DDT, and toxaphene. All but three PCB congeners (PCB 126, 189, 77) were above detection.

Gamma chlordane was below detect for all sites except site #1, #6, and #7 and ranged from .01-.016 µg/g per SPMD. Heptachlor epoxide was detected at sites #1-7 and ranged from 0.01-0.015 µg/g per SPMD. The homolog p,p' DDD, detected at sites #1, #3, #6, and #7, ranged from 0.01-0.02 µg/g per SPMD; p,p' DDE was detected in one or more membranes at sites #1, #7, #8, and #10 and ranged from 0.01-.024 µg/g per SPMD. Trans-nonachlor was detected only at site # 7 with concentrations of 0.014 and 0.015 µg/g per SPMD. Dieldrin was detected in each SPMD at all ten sites and ranged from 0.013-0.035 µg/g per SPMD.

Figures 2-8 indicate that the highest concentrations of PCBs are occurring at site #2 and site #5 or upstream of these two sites. Summing the PCB congeners as shown in Figure 9 leads to much the same conclusion. However, analytical results for the SPMDs showed much more variability than expected between the two membranes (A and B), deployed side-by-side at each site, making interpretation difficult. Biofouling may explain ±50 % of the variability but does not explain larger differences between replicates (J. Huckins, pers. comm.) such as the 2300% variability seen in PCB 128. With such a large variability it is difficult to place confidence in the results obtained from the SPMDs other than that PCBs were detected in the dissolved phase.

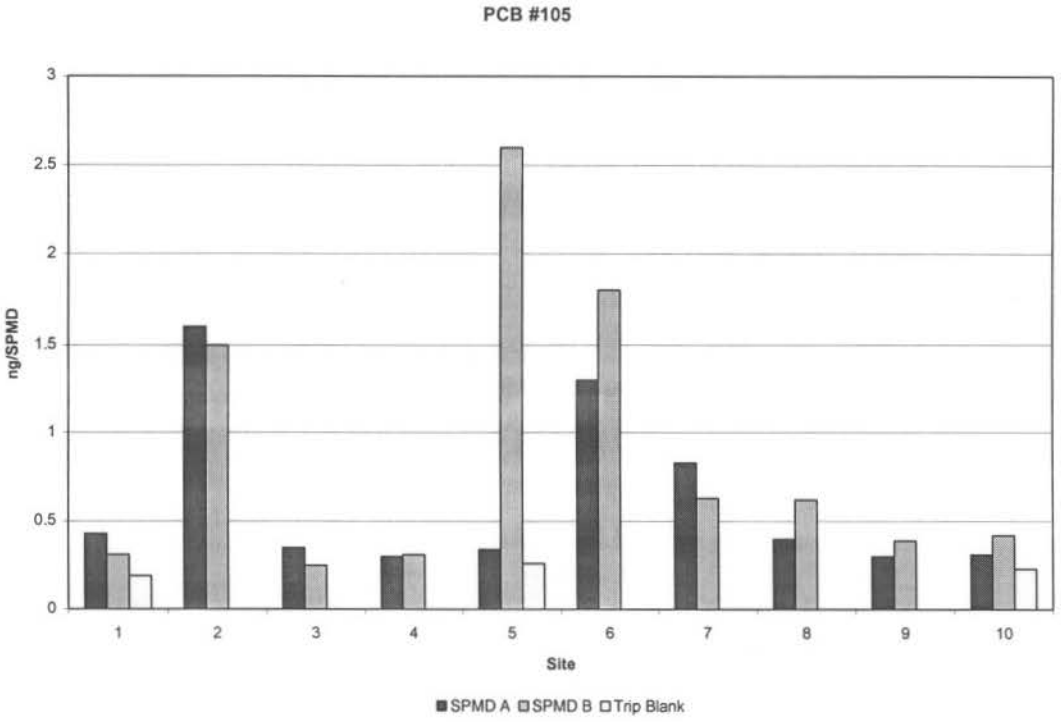

Figure 2. PCB #105 concentrations in SPMDs deployed in the San Antonio River, 1995.

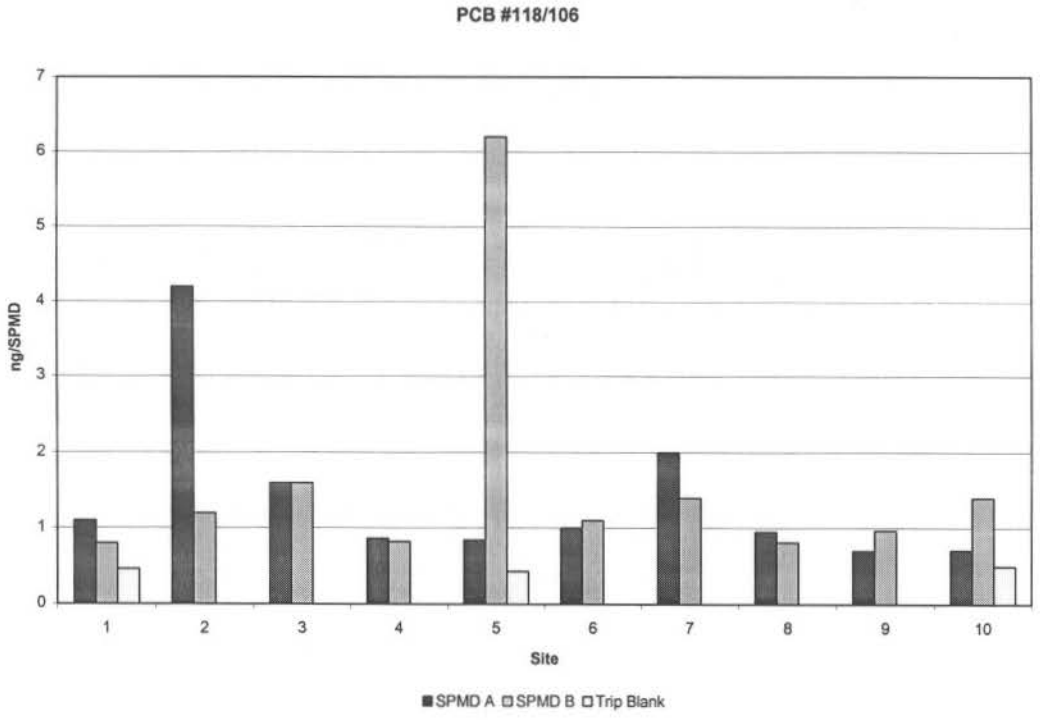

Figure 3. PCB #118/106 concentrations in SPMDs deployed in the San Antonio River, 1995.

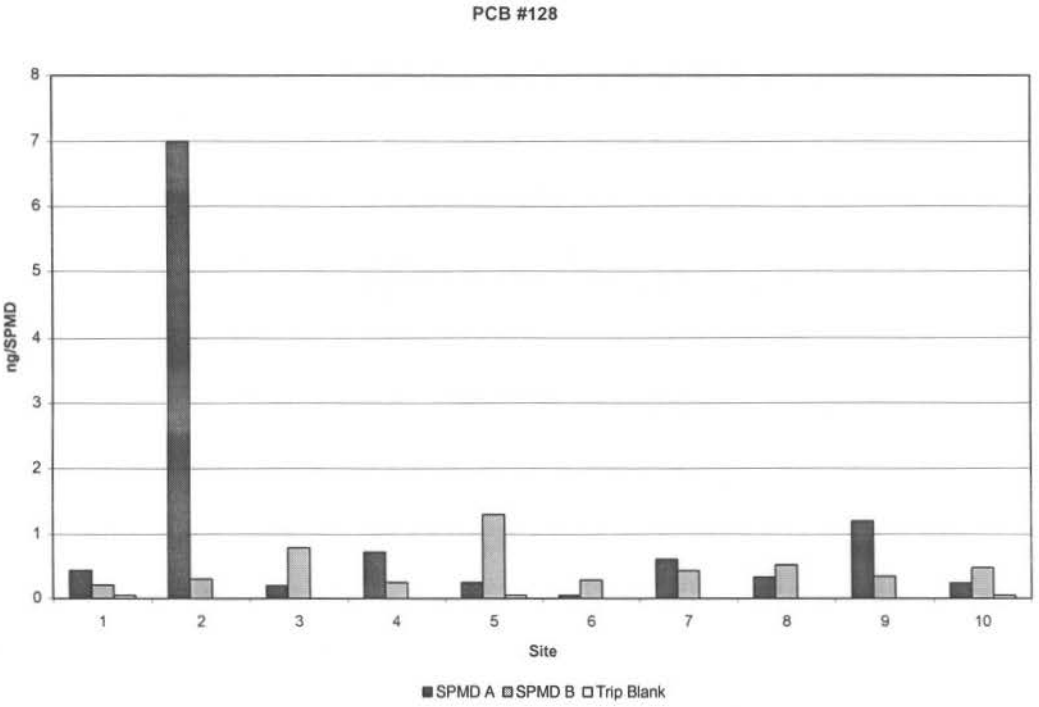

Figure 4. PCB #128 concentrations in SPMDs deployed in the San Antonio River, 1995.

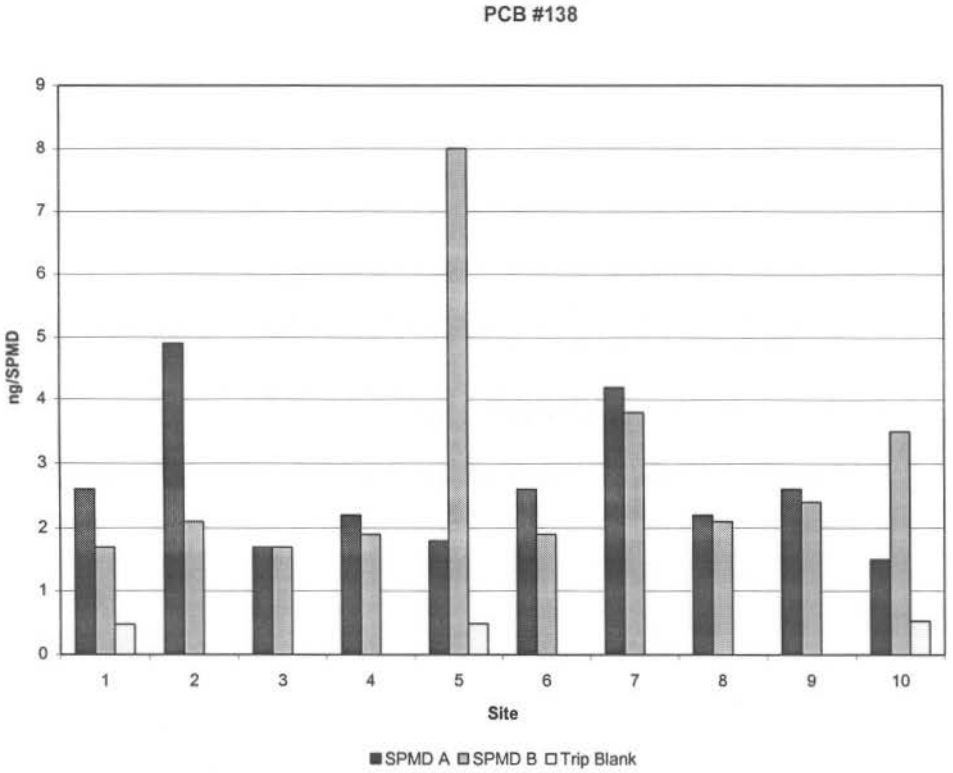

Figure 5. PCB #138 concentrations in SPMDs deployed in the San Antonio River, 1995.

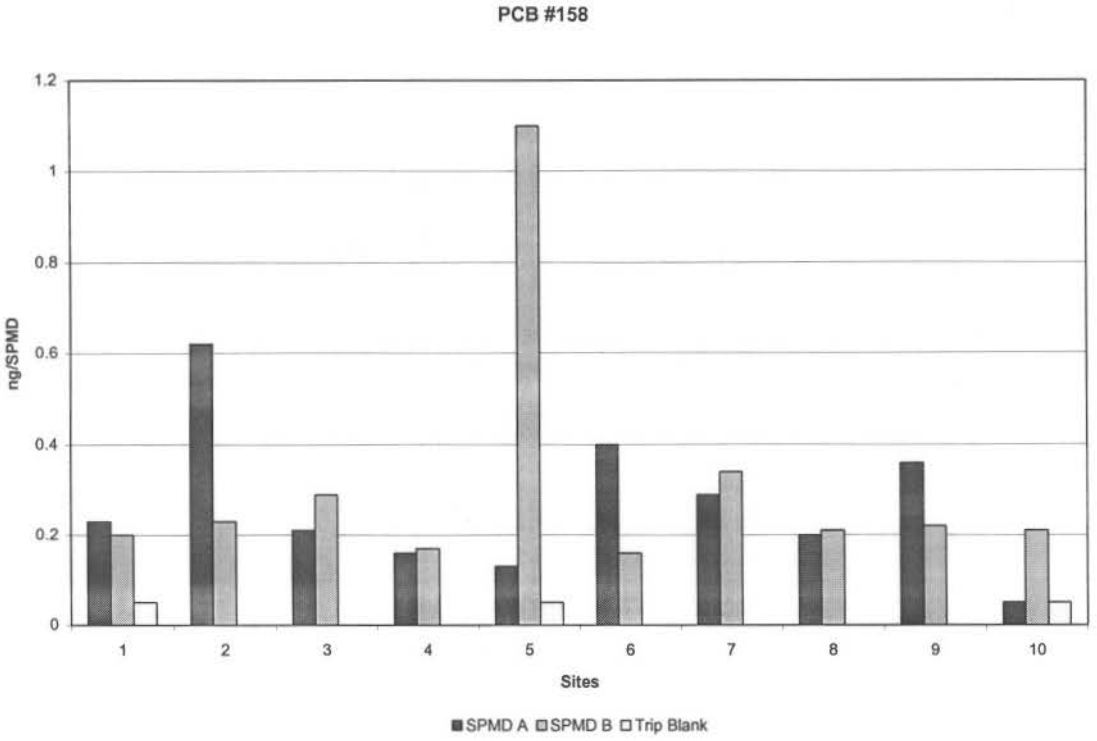

Figure 6. PCB #158 concentrations in SPMDs deployed in the San Antonio River, 1995.

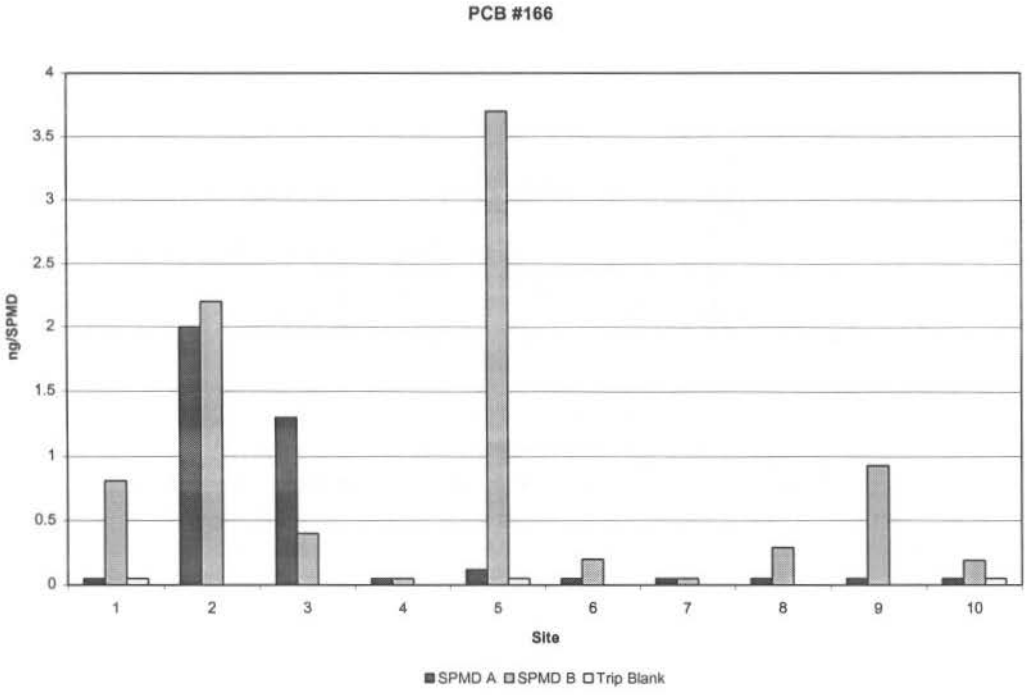

Figure 7. PCB #166 concentrations in SPMDs deployed in the San Antonio River, 1995.

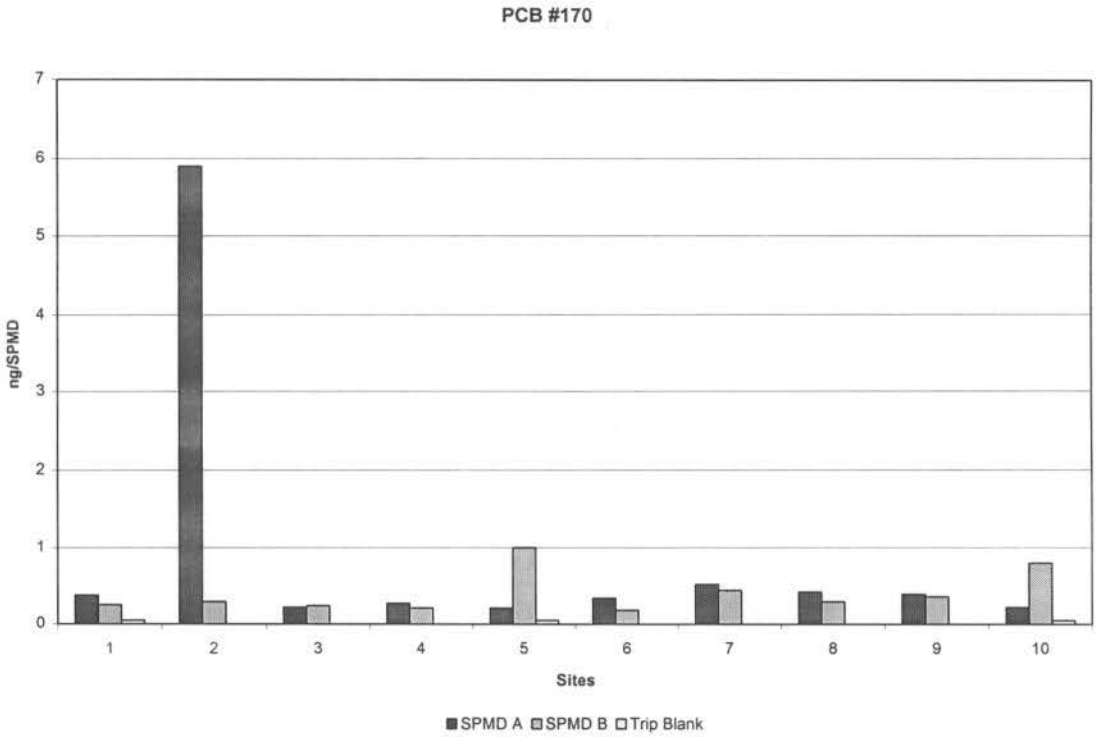

Figure 8. PCB #170 concentrations in SPMDs deployed in the San Antonio River, 1995.

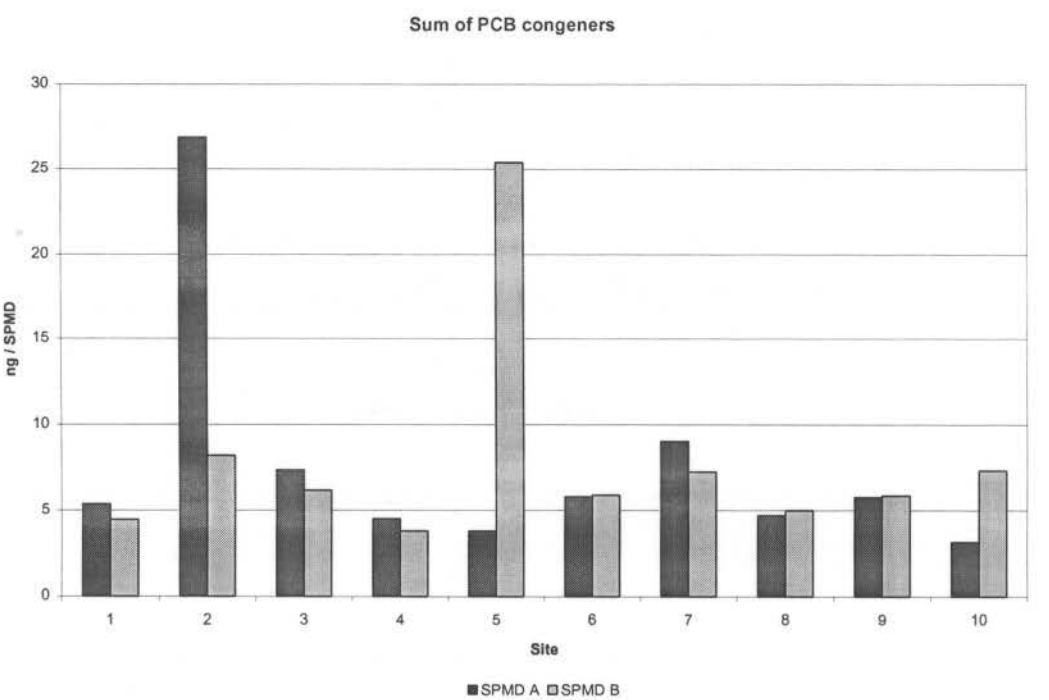

Figure 9. Sum of PCB congener concentrations in SPMDs deployed in the San Antonio River, 1995.

Conclusions and Recommendations

Copper in whole body longnose gar ranged from 1.7- 4.2 µg/g dw; the highest concentration was at site #1 and exceeds the NCBP 85th percentile. Chromium, mercury, PCBs, and p,p' DDE in whole body fish were all highest at site #3. Chromium in fish (19.9 µg/g dw) was twice as high as the 1992 study (Lee and Schultz 1994) and mercury concentrations were well above the avian predator protection level of 0.1 µg/g ww at all sites. The highest concentration of p,p' DDE (1.2 µg/g ww) may be elevated enough to affect reproduction in sensitive fish-eating birds (such as raptors) in the area.

Longnose gar (*Lepisosteus osseus*) collected from the San Antonio River near the Hwy 97 bridge had elevated levels of PCBs in 1992 (Lee and Schultz 1995). Gar from the same area (site #3) had PCB concentrations twice as high in 1995. SPMDs indicated a higher level of contamination at site #2 and #5 although there is too much variability between replicates to draw valid conclusions. However, there is enough evidence to indicate the presence of PCB contamination, although it may be quite localized. Possible sources could include a landfill, junkyard, or historical spill. SPMDs sample the dissolved phase of hydrophobic organochlorines so residual contaminants in bed sediments may be a source. Results of this study and potential for human health concerns over PCB levels have been communicated to the Texas Department of Health. They collected fish in 1998 between the Hwy 37 bridge and the Hwy 97 bridge, but did not find concentrations of PCBs at high enough levels to warrant a fish advisory (M. Ordner, pers. comm.).

The majority of the contamination appears to be coming from sites nearest Floresville and may be fairly localized. Monitoring should be continued especially near drainages into the San Antonio River above Hwy 97. Efforts should also be made to ensure that sources are not continuing and enforce permit limitations. In some areas, large trees have been removed from the edge of the bank to cultivate more land, consequently promoting erosion. During the previous study, hundreds of thousands of tires were observed below the confluence of the San Antonio and Medina Rivers. The banks of the river are used for disposing of garbage. A public education program is needed to curb these practices and convey the importance of this river to the ecosystem. In this area, an easy, inexpensive alternative to dispose of waste of any kind in a designated landfill should be made available. The costs to clean up illegal dumps and the long term damage is much higher. If not halted, the condition of the river will only continue to degrade as the human population in the watershed increases.

Several difficulties were encountered in implementing this investigation. Fluctuations in water level were a constant threat. Between visits, drops in water level were noticeable due to withdrawal for irrigation. Fortunately, during this study only one SPMD was slightly exposed but the sampling membranes remained well below the water line and it was easily re-adjusted. There were also several tropical storms that threatened the coast, and more than a nominal amount of rain would have swept away the SPMDs. In that respect, SPMDs have limitations; too little flow may not allow for adequate uptake and too much flow can cause a complete loss of

equipment and data.

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