

In 1991, the Texas Natural Resource Conservation Commission was mandated by the Texas Clean Rivers Act (Senate Bill 818) to assess the quality of streams in Texas. Despite the knowledge that selected organic compounds, particularly the organochlorine pesticide DDT and its degradation products DDD and DDE, occur in streambed sediments of the Rio Grande and in Amistad International and Falcon International Reservoir bottom sediments, little is known about the occurrence and concentrations of the organic compounds as water-borne contaminants in the Rio Grande. During 1997, the U.S. Geological Survey (USGS), in cooperation with the Texas Natural Resource Conservation Commission under the authorization of the Texas Clean Rivers Act, used semipermeable membrane devices (SPMDs) to detect concentrations of organic compounds at six sites on the Rio Grande. The objectives of this report are to (1) assess the occurrence and estimate the water concentrations of selected dissolved organic compounds using SPMDs in the main stem of the Rio Grande; and (2) compare findings from SPMDs with findings from water samples collected as part of the International Boundary and Water Commission Binational Toxics Study (International Boundary and Water Commission, 1994) and with analytical results from samples collected at a USGS National Stream Quality Accounting Network (NASQAN) site on the Rio Grande.

Organic compounds such as DDT and various PCBs and PAHs frequently have been detected in streambed sediments in the Rio Grande Basin. The greater occurrence of organic compounds in streambed sediments near El Paso, Laredo, and Harlingen, Tex., might indicate an urban source for some of these compounds (Lee and Wilson, 1997). Concentrations of DDT and its degradation products DDD and DDE in sediments deposited in Amistad International and Falcon International Reservoirs show decreasing trends over time (Van Metre and others, 1997). DDT concentrations in sediment deposited in Falcon International Reservoir decreased soon after the 1972 ban on DDT in the United States by the U.S. Environmental Protection Agency (EPA), but concentrations have remained stable in sediments deposited from the post-1972 decrease to the present, indicating a continuing source of DDT in the Rio Grande Basin upstream of Falcon Reservoir.

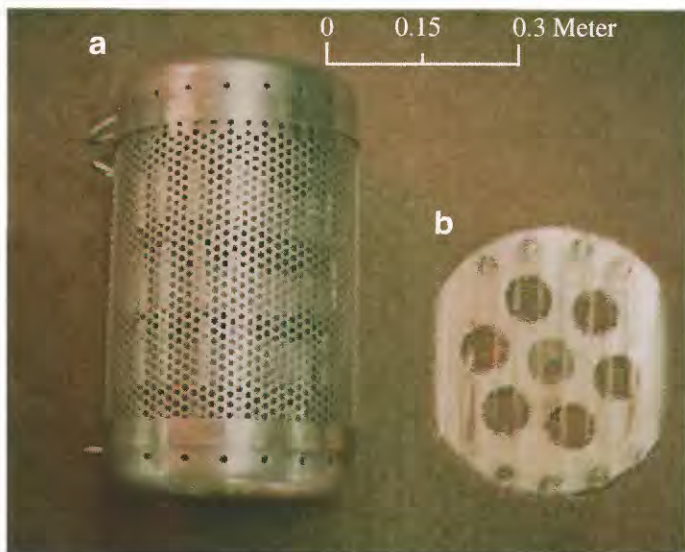
Many organic compounds that are thought to be in the waters of streams and reservoirs are difficult to detect because they occur in such small concentrations. In addition, many compounds, like DDT and chlordane, are highly water insoluble (hydrophobic), but highly lipid soluble (lipophilic), and as such, are some of the more bioavailable organic compounds in aquatic systems. Aquatic organisms can absorb bioavailable organic compounds through the ingestion of food or by diffusion from the surrounding water across a semipermeable membrane. Semipermeable membranes form respiratory structures such as the gills of fish and respiratory surfaces or membranes of many aquatic invertebrates.

Aquatic monitoring and assessment of hydrophobic organic compounds typically emphasize the collection and analysis of surficial bed sediments and the tissues of aquatic organisms rather than samples from the overlying water column (Crawford and Luoma, 1993; Schmitt and others, 1990). The principal instream source of these compounds might be from streambed sediment because of the hydrophobic and adsorptive qualities of the compounds. Traditional methods of water-sample collection and analysis generally are inadequate for assessing occurrence and estimating concentrations of hydrophobic organic compounds. Traditional water-sampling methods generally involve a single grab or a representative composite sample that is taken during a few seconds or minutes. Such samples provide only a "snapshot" of the constituents of interest during the short sampling time, not a longer "time exposure" of the constituents that might be needed to detect dissolved hydrophobic organic compounds. In addition, the small volumes of traditional water samples contribute to making the probability small that hydrophobic compounds will be detected.

The SPMD and its Application in the Rio Grande

The SPMD is a relatively new technology (Huckins and others, 1993) that can be used as an integrative, time-weighted sampler of dissolved hydrophobic organic compounds. An SPMD typically consists of a long strip of low-density polyethylene tubing filled with a thin film of a purified lipid such as triolein. The long tubing and thin lipid film provide a large surface-area-to-volume ratio that is similar to a biological membrane such as a fish gill. When placed in water, SPMDs can concentrate dissolved hydrophobic organic compounds above ambient concentrations. Therefore, SPMDs can be used as a tool for assessing the occurrence of dissolved hydrophobic organic compounds in water and for calculating a time-weighted estimate of the average water concentration over the period that the SPMD is in use in a stream.

SPMDs were placed at six sites (fig. 1; table 1) on the Rio Grande from just downstream of the confluence of the Río Conchos and Rio Grande to just downstream of Brownsville, Tex. Each site was selected to be within or just downstream of an urban area because point discharges and runoff from urban areas likely would influence water quality. All SPMDs were placed in late July and early August 1997, except the SPMD downstream of Brownsville, which was placed in October 1997. SPMDs were placed during late summer low-flow conditions for accessibility and to ensure optimal water temperatures for uptake of organic compounds by the SPMD. Five SPMDs were placed at each site in a stainless steel canister. A submersible temperature data logger



(a) SPMD deployment device and (b) SPMD spooled onto a mount that is inserted into the deployment device.

Table 1. SPMD sites on the Rio Grande from downstream of Presidio, Texas, to downstream of Brownsville, Texas

[km, kilometer]

Site (fig. 1)	Description
1 Rio Grande downstream of Presidio	14.4 km downstream from Río Conchos confluence near Presidio/Ojinaga, at river km 1,528.5
2 Rio Grande downstream of Del Rio	7.24 km downstream from Del Rio/Ciudad Acuna International Bridge, at river km 896.8
3 Rio Grande upstream of Eagle Pass	Near power plant 7.8 km upstream from Eagle Pass/Piedras Negras International Bridge (U.S. 57), at river km 862.7
4 Rio Grande downstream of Laredo	At pipeline crossing 13.2 km downstream from Laredo/Nuevo Laredo International Bridge (U.S. 81), at river km 567.6
5 Rio Grande downstream of Hidalgo	At Hidalgo/Reynosa International Bridge (U.S. 281), at river km 256.7
6 Rio Grande downstream of Brownsville	0.3 km downstream from El Jardin pumping plant and 11.2 km downstream from Brownsville/Matamoros International Bridge (U.S. 77), at river km 78.3

was attached to each SPMD canister to monitor water temperature during the period of use. Average water temperature over the period of use is used to calculate an estimated water concentration. A set of SPMD trip blanks (SPMDs free of analytes) was exposed to the atmosphere at each site during SPMD placement and recovery to account for any atmospheric contamination. The SPMDs were in use from 30 days at Brownsville to 38 days at the site upstream of Eagle Pass. All of the SPMDs from each site were composited for analysis of organic compounds.

The recovered SPMDs were sent to Environmental Sampling Technologies (EST) in St. Joseph, Mo., for initial processing,

and the resulting extracts were sent by EST to the USGS National Water-Quality Laboratory in Arvada, Colo., for the analysis of organochlorine pesticides and PCBs, soluble pesticides, and semivolatile organic compounds (SVOCs) (Moring and Rose, 1997).

Pesticides Detected in SPMDs

Seven organochlorine pesticides were detected in SPMDs. The DDT degradation product *p,p'*-DDE was detected in SPMDs at four of the six sites (fig. 2). The common occurrence of DDE in streams and reservoirs is an indication of the continued decomposition of the banned parent compound DDT (Schmitt and others, 1990). Dieldrin was detected at two sites. Like DDT, dieldrin is an organochlorine pesticide that still commonly is found in the aquatic environment despite a ban on its use by the EPA in 1987. Pentachloroanisole was detected in SPMDs at two sites. *Gamma*-HCH, *trans*-chlordane, *trans*-nonachlor, and *p,p'*-DDD were each detected at one site. All of the organochlorine pesticides detected in the SPMD extracts were banned or restricted by the EPA from use in the United States in the 1970s or 1980s. Frequent detections of these compounds, and the recent issuance of health advisories for edible fish tissues contaminated with these organochlorine pesticides (Texas Department of Health, 1997), are an indication of the persistence of these compounds in the aquatic environment.

Chlorpyrifos, an organophosphorus insecticide that is easily solubilized in the lipid of the SPMD, was detected at all sites.

Five other pesticides that are more water soluble and less lipid soluble than the organochlorine pesticides were detected. Dacthal was detected at five sites, diazinon at two sites, trifluralin, metribuzin, and pendimethalin each at one site. The more water/less lipid soluble pesticides would not be expected to be concentrated in the SPMDs as much as the organochlorine pesticides.

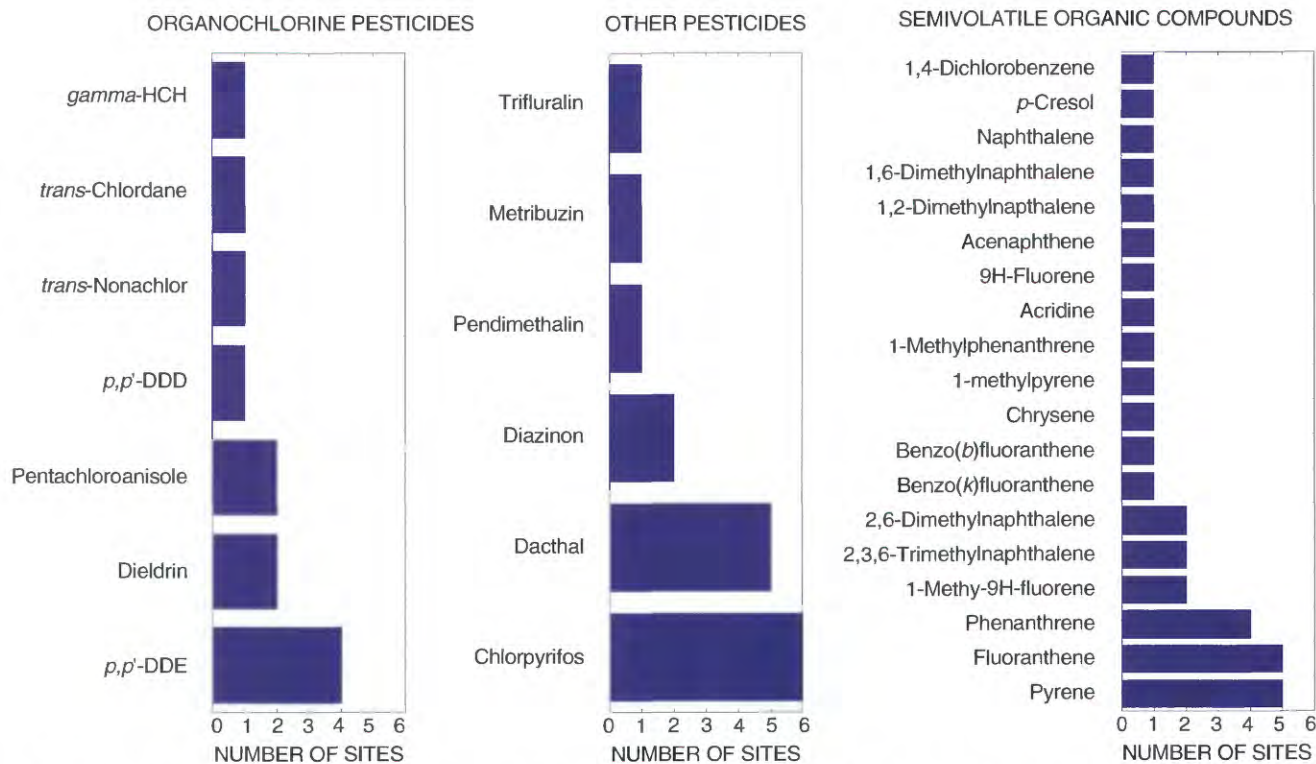


Figure 2. Pesticides and semivolatile organic compounds detected in SPMDs at six sites on the Rio Grande.

Semivolatile Organic Compounds Detected in SPMDs

Nineteen SVOCs were detected in the SPMDs at one or more of the six sites (fig. 2). Eight of the SVOCs detected—naphthalene, acenaphthene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, phenanthrene, fluoranthene, and pyrene—have been listed by the Agency for Toxic Substances and Disease Registry (1997) as priority hazardous substances. Fluoranthene and pyrene were detected at five sites, phenanthrene at four sites, and the remaining priority hazardous substances were detected at one site each.

Concentrations of Selected Organic Compounds in SPMDs

Because the number of days the SPMDs were in use at each site varied, concentrations of the organic compounds detected in the SPMDs were normalized by dividing the concentration of each compound by the number of days the SPMD was in use at each site and multiplying the quotient by 100 to allow comparison of concentrations among sites. More organochlorine pesticides were detected at larger concentrations in the SPMDs at the site downstream of Brownsville than at the other sites (fig. 3). In general, more pesticides were detected at larger concentrations downstream of the larger metropolitan areas (Laredo and Brownsville) than at the other sites. In general, larger normalized concentrations of the more water-soluble pesticides (trifluralin, metribuzin, pendimethalin, diazinon, and dacthal) and priority hazardous substances were detected in SPMDs at the three sites downstream of Laredo. Chlorpyrifos, the only pesticide detected at all sites, had the largest normalized concentration at the site downstream of Laredo and the smallest normalized concentration at the site downstream of Hidalgo. The site upstream of Eagle Pass had the least number of detections of all compounds.

Estimated Concentrations of Selected Organic Compounds in Water

Huckins and others (1993) developed a linear model to estimate the water concentrations of selected organochlorine pesticides and SVOCs concentrated in SPMDs. Sampling rates, in liters per day, for individual compounds were developed from flow-through SPMD calibration studies. Number of days in use, average water temperature, concentration of the compound in the SPMD, and a coefficient to account for algal growth on the surface of the SPMD membrane (that has been shown to impede the absorption of compounds across the SPMD membrane) are factors used in the calculation of an estimated water concentration.

Estimated water concentrations of all pesticides detected ranged from a minimum of 0.018 nanogram per liter (ng/L) for *p,p'*-DDD at the Hidalgo site to a maximum of about 0.13 ng/L for dieldrin, also at the Hidalgo site (fig. 4). Estimated water concentrations of pentachloroanisole, 0.089 ng/L, and *p,p'*-DDE, 0.099 ng/L, were largest at the site downstream of Brownsville. The only organochlorine pesticide concentrated in the SPMDs at any of the three sites upstream of Laredo was *p,p'*-DDE; the second-largest estimated concentration of *p,p'*-DDE, 0.047 ng/L, was from the site downstream of Presidio, downstream of the confluence of the Río Conchos and Río Grande.



Río Grande near Presidio, Texas.

Estimated water concentrations for the selected SVOCs ranged from a minimum of 0.02 ng/L for benzo(*k*)fluoranthene at the site downstream of Brownsville to a maximum of 1.35 ng/L for naphthalene at the same site. Estimated water concentrations were largest at the site downstream of Brownsville. Unlike the other SPMD placement sites on the Río Grande, the site downstream of Brownsville is immediately (within 0.4 kilometer) downstream of a wastewater treatment plant outfall.

Comparison With Previous Findings

During 1992 and 1993, water samples were collected at 45 stations in the Río Grande Basin from El Paso to south of Brownsville as part of a binational water-quality study done by the United States and Mexico (International Boundary and Water Commission, 1994). During the binational study, only one water sample collected at the site downstream of Brownsville was analyzed for a suite of constituents that included pesticides and priority hazardous substances. Pesticides and priority hazardous substances were not detected in that sample (table 2). Analytical reporting levels used in the binational study for these compounds were appreciably larger than the estimated water concentrations from the SPMD at the site. The priority hazardous substances naphthalene, acenaphthene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, fluoranthene, and pyrene were detected in the SPMDs of this study but were not detected in the water sample of the binational study.

Water samples are routinely collected for the analysis of many pesticides at NASQAN stations throughout the United States (Hooper and others, 1997). One NASQAN station is located just upstream of the Brownsville site of this study. During 1996–97, six water samples were collected at the Brownsville NASQAN station. Five pesticides that were analyzed for in the SPMD samples of this study also were analyzed for in the NASQAN samples (table 2). Dacthal and chlorpyrifos were detected in both the NASQAN and SPMD samples; *gamma*-HCH, *p,p'*-DDE, and dieldrin were detected only in the SPMDs. The lack of detections for most pesticides in NASQAN samples at this station would be expected because of the small (nanogram per liter) estimated water concentrations from the SPMD samples.

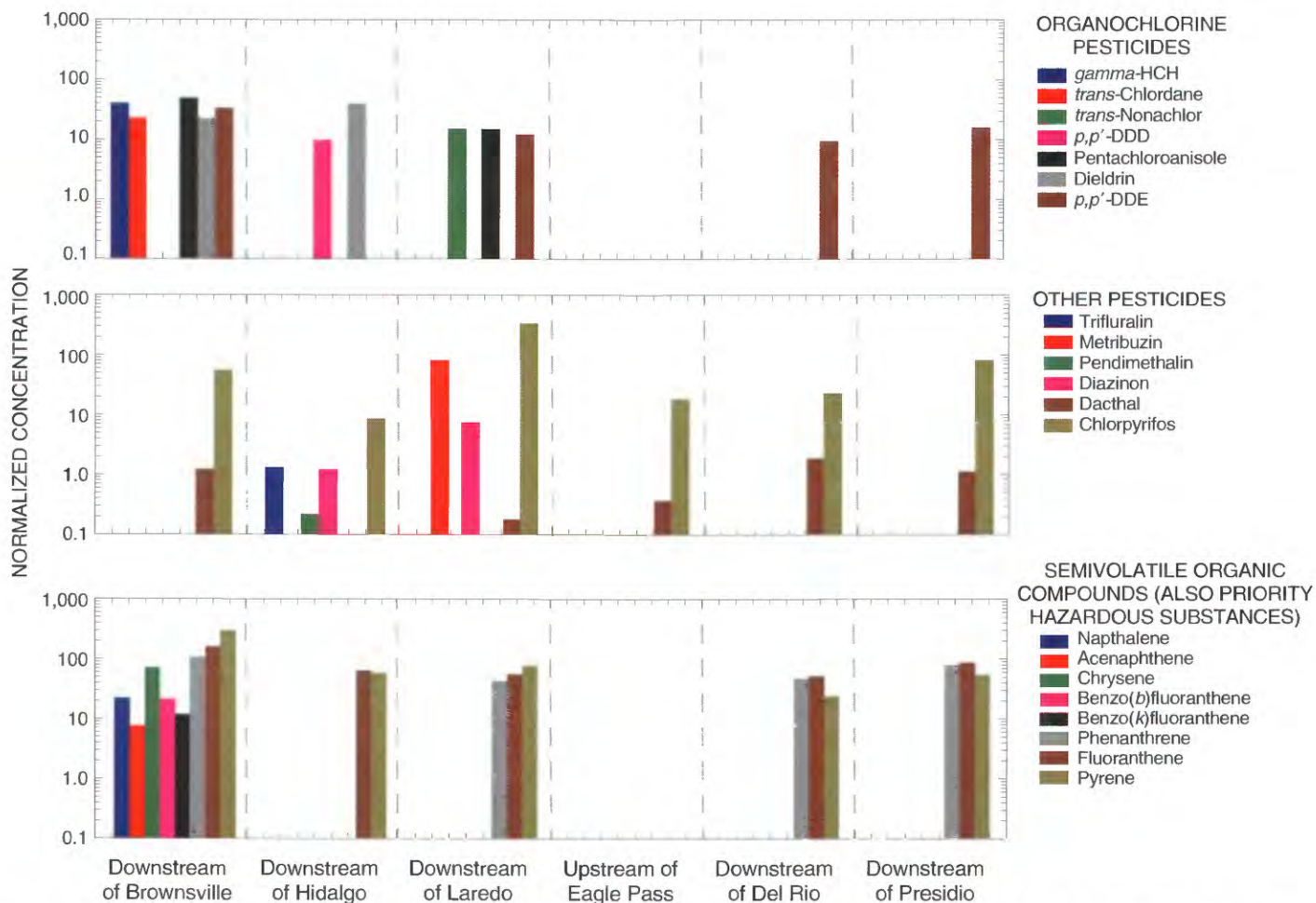


Figure 3. Normalized concentrations of pesticides and semivolatile organic compounds detected in SPMDs at six sites on the Rio Grande.

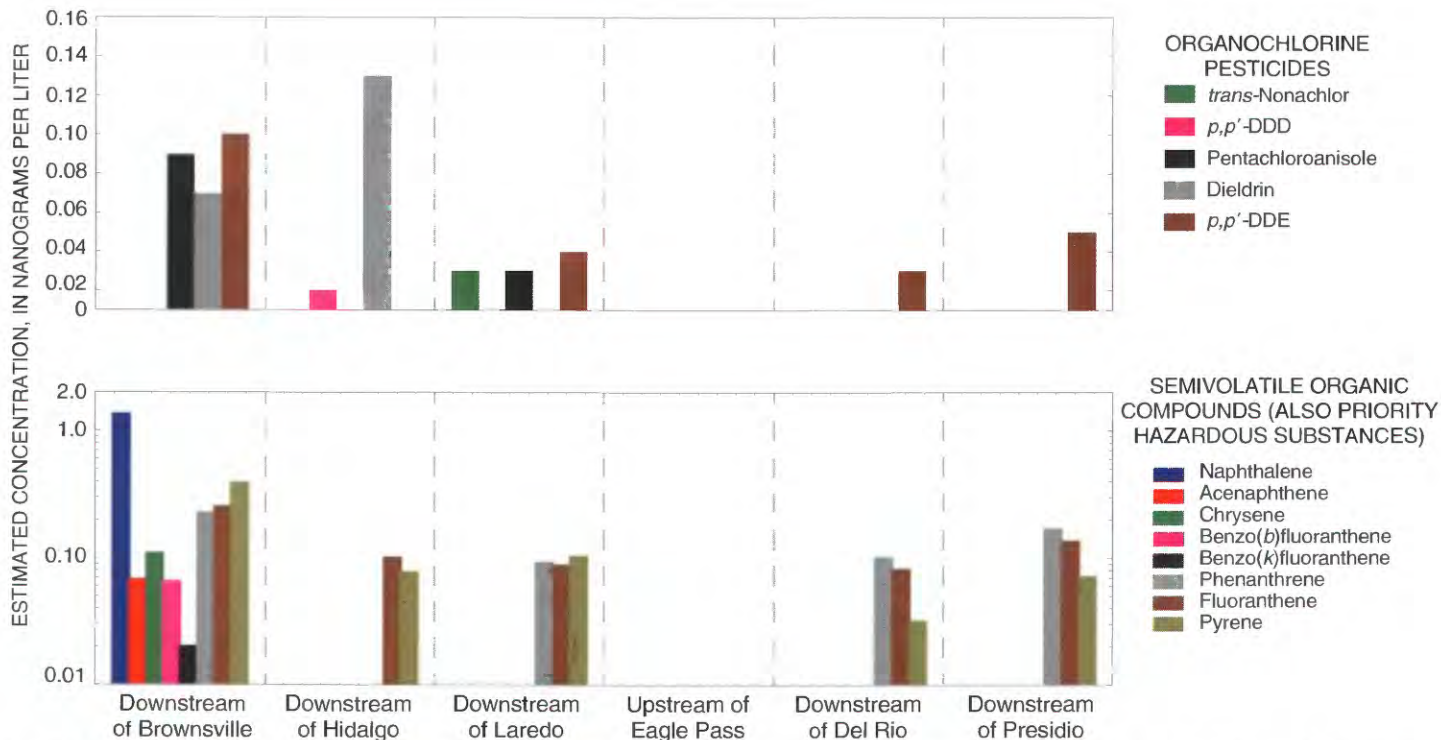


Figure 4. Estimated water concentrations of selected pesticides and semivolatile organic compounds at six sites on the Rio Grande.

Table 2. Findings from the analysis of organic compounds in the Rio Grande downstream of Brownsville from two previous studies and this study

[ng/L, nanograms per liter; SPMD, semipermeable membrane device; *, pesticide; <, less than; NA, not available; **, priority hazardous substance]

Compound	Binational study ¹		National Stream Quality Accounting Network (NASQAN)			This study	
	Detected in water	Reporting level (ng/L)	Percent detections in water	Reporting level (ng/L)	Median water concentration (ng/L)	Detected in SPMD	Estimated water concentration from SPMD (ng/L)
<i>gamma</i> -HCH*	No	30.0	0	<4.0	NA	Yes	NA
<i>p,p'</i> -DDE*	No	100	0	<6.0	NA	Yes	0.10
Dieldrin*	No	100	0	<1.0	NA	Yes	.07
Dacthal*	No	NA	36	<2.0	3.5	Yes	NA
Chlorpyrifos*	No	600	14	<4.0	9.0	Yes	NA
Naphthalene**	No	2,000	NA	NA	NA	Yes	1.35
Acenaphthene**	No	5,700	NA	NA	NA	Yes	.07
Chrysene**	No	5,700	NA	NA	NA	Yes	.10
Benzo(<i>b</i>)fluoranthene**	No	5,700	NA	NA	NA	Yes	.06
Benzo(<i>k</i>)fluoranthene**	No	5,700	NA	NA	NA	Yes	.02
Fluoranthene**	No	5,700	NA	NA	NA	Yes	.25
Pyrene**	No	5,700	NA	NA	NA	Yes	.39

¹ International Boundary and Water Commission, 1994.

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