

In cooperation with the Texas Natural Resource Conservation Commission

Introduction

In 1991, the Texas Natural Resource Conservation Commission (TNRCC) was mandated by the Texas Clean Rivers Act (Senate Bill 818) to assess water quality of rivers in Texas. Recent efforts to collect information for the assessment of water quality in the Rio Grande/Río Bravo Basin have involved Federal agencies on both sides of the 1,248-mile U.S.-Mexico border—U.S. Environmental Protection Agency, U.S. Geological Survey (USGS), Secretaria de Desarrollo Social (Secretary for Social Development, Mexico), National Water Commission of Mexico, and International Boundary and Water Commission—as well as State and local agencies in a spirit of international cooperation. Substantial efforts have been made to gather data needed to determine the quality of water and ecological status of the Rio Grande/Río Bravo, especially at sites along the border (fig. 1). The purpose of this report is to assess selected historical data of trace elements and organic compounds in riverbed sediments of the Rio Grande/Río Bravo, and of the Pecos River and the Arroyo Colorado in Texas.



Rio Grande/Río Bravo Basin in West Texas.

Why Analyze for Trace Elements and Organic Compounds in Riverbed Sediments?

Sediments in rivers usually come from erodible materials in a watershed, primarily soils and weathering rocks. During storms these sediments wash into tributary channels and into the main channel of a river. As flow velocity and turbulence decrease following a storm, suspended particles settle, accumulating along the riverbed near the sediment sources in slow-moving waters. Reservoirs on a river system further decrease flow velocity and turbulence and accumulate the sediment transported by runoff from upstream watersheds. In the river channel where sediments accumulate, the top layer of sediment represents recent transport and deposition of erodible materials from tributary watersheds. Some transport of sediment will continue under base-flow conditions, but the transported sediment typically is finer grained; and less sediment is transported than under stormflow conditions.

In a natural setting, the sources of trace elements in riverbed sediments are geologic materials and atmospheric deposition. In the Rio Grande/Río Bravo Basin in Texas, the primary geologic materials are sedimentary rocks of Cretaceous, Tertiary, and Quaternary age (fig. 2) consisting principally of limestone and dolostone with sand, sandstone,

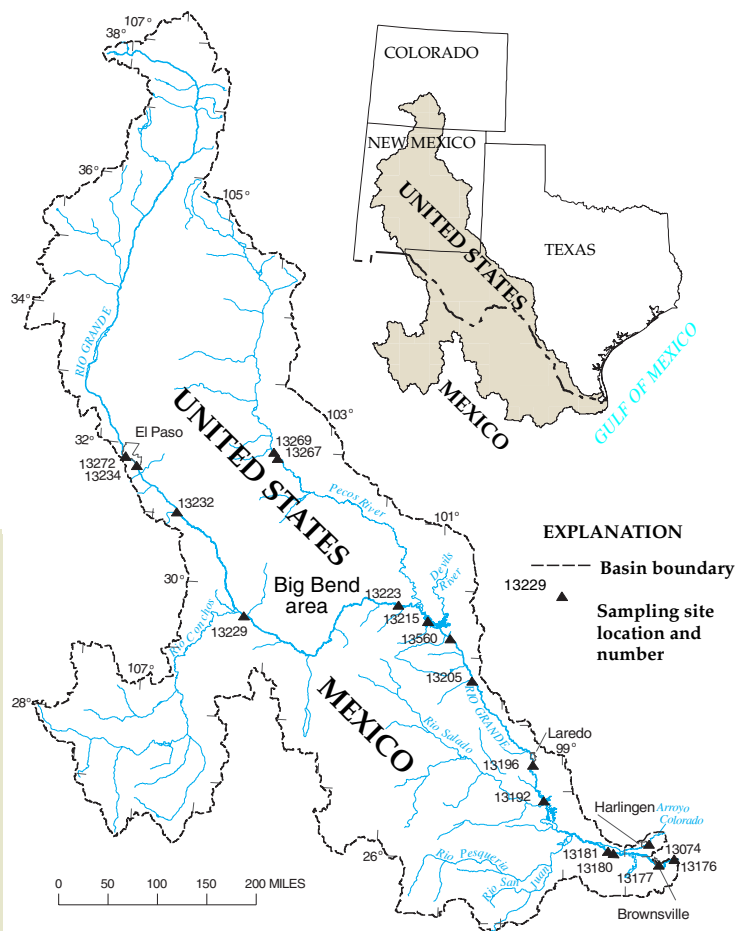


Figure 1. Rio Grande/Río Bravo Basin, United States and Mexico, showing major streams and riverbed-sediment sampling sites.

clay, and shale locally. Exposed bedrock and atmospheric deposition from volcanos are natural sources of trace elements in riverbed sediments. Concentrations of trace elements from these natural sources should remain relatively constant over decades and even for centuries.

Human activities can cause release of trace elements and synthetic organic compounds to the atmosphere or to stormwater runoff in a watershed. Many of these constituents are more concentrated in sediments than in the water column. Mining and disposal of tailings, followed by weathering of tailings, and stormwater transport of trace element-laden sediment from mined areas, can produce pulses of high concentrations of some trace elements in riverbed sediments. Cinnabar (mercury ore) was mined in the Big Bend area of Texas from the late 1800s to as recently as the late 1960s. The occurrence of concentrations of synthetic organic compounds in riverbed sediments is a more recent phenomenon resulting from development and other human activities and cannot be related to geologic sources.

Many trace elements and organic compounds are toxic to humans and aquatic life. These constituents could originate from point or nonpoint sources in a watershed, or might be deposited in the watershed from atmospheric sources outside the watershed. Under some chemical

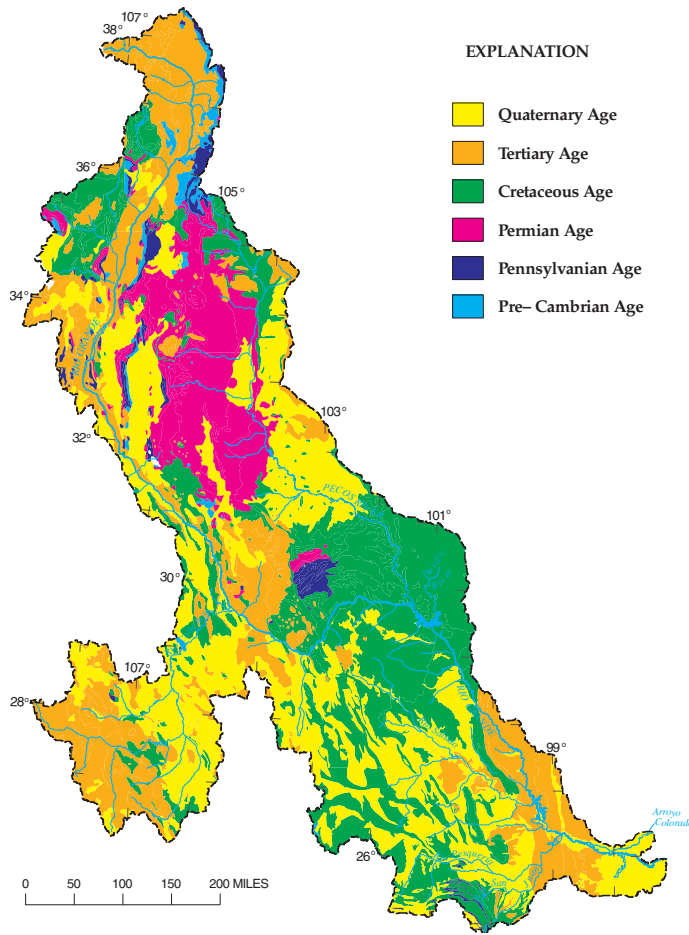


Figure 2. Surface geology of the Rio Grande/Río Bravo Basin.

conditions, many trace elements will attach or "sorb" to available inorganic materials such as clays or mineral coatings rather than remaining dissolved in the water. Similarly, many organic compounds (especially high molecular-weight chlorinated hydrocarbon compounds) attach to particles of natural organic matter or to inorganic particles coated with organic matter rather than remaining dissolved in the water. Sediments laden with various trace elements and organic compounds from a source watershed are transported in runoff and streamflow and deposited on the river bottom. Screening levels for trace elements and organic compounds detected in sediments of Texas waterbodies have been established by the TNRCC. The screening level for each substance is the 85th-percentile concentration (85 percent of the concentrations are less than this value) computed from the 1983–92 TNRCC statewide Surface Water Quality Monitoring data base of waterbody sediment analyses (Steve Twidwell, Texas Natural Resource Conservation Commission, written commun., 1997).

What Historical Trace Element and Organic Compound Data Are Available and How Can They Be Interpreted?

Samples of riverbed sediments of the Rio Grande/Río Bravo Basin for this study were collected and analyzed for trace elements and organic compounds from the early 1970s through 1994. Chemical data for riverbed sediments from the international watershed gathered during investigations in the United States are accessible through the STORET water-quality data base of the U.S. Environmental Protection Agency. Samples analyzed for trace element concentrations are available for about 50 sites in Texas; samples analyzed for concentrations of organic compounds are available for as many as 59 sites.

Sampling has been sporadic. Only a few sites in the entire basin have been sampled annually and have relatively complete analyses. On the basis of data availability, 19 sites were selected for study. All 19 of the sites were selected to show the ranges in concentration of 4 trace elements (arsenic, lead, mercury, and selenium); 17 of the 19 sites were selected for analysis of spatial and temporal trends in concentrations of 12 trace elements. Sufficient data are available to show the ranges in concentration of 8 organic compounds detected at 16 sites; organic compound data are insufficient for analysis of temporal trends, with the exceptions of bis(2-ethylhexyl)phthalate, chlordane, and PCBs at one site on the Arroyo Colorado. Collectively among all sites with organic compound analyses, 140 compounds were analyzed.

The ranges in concentration and summary statistics (25th percentile, median, and 75th percentile) of trace elements and organic compounds are shown by boxplots grouped by site from El Paso to the Gulf of Mexico. Spatial trends in concentrations of trace elements and organic compounds—that is, significant increases or decreases in concentrations along the Rio Grande/Río Bravo from El Paso to the Gulf of Mexico—were determined by a statistical test (Kendall's tau (Helsel and Hirsch, 1992, p. 212)) for the significance (at the 90-percent confidence level) of the correlation between concentrations and downstream order of 17 sampling sites. Temporal trends in concentrations—that is, significant increases or decreases in concentrations with time at each of the 17 Rio Grande/Río Bravo sites—were similarly determined on the basis of the significance (at the 90-percent confidence level) of the correlation between concentrations and chronological order of sampling. No trend analyses were done on sites with fewer than seven analyses.

What Do the Historical Trace Element and Organic Compound Data Show?

Trace Elements

Historical median arsenic concentrations exceed the TNRCC screening level in the Big Bend area downstream of the Río Conchos (site 13229) and at Amistad International Reservoir (site 13215) (fig. 3A). Arsenic concentrations in sediments are greatest from the Río Conchos to Amistad International Reservoir. Arsenic concentrations in sediments show an increasing trend in downstream direction (table 1). Arsenic concentrations increase with time at the three most upstream sites in and near El Paso (sites 13272, 13234, and 13232), which historically have relatively low arsenic concentrations. Although median arsenic concentrations are relatively high at site 13229, concentrations with time at the site show a decreasing trend. Concentrations in Falcon International Reservoir also show a decreasing trend (site 13192).

Historical median lead concentrations are well below the screening level at all sites (fig. 3B). Lead concentrations in riverbed sediments show a decreasing trend in downstream direction (table 1). Lead concentrations increase with time upstream of the Big Bend area (site 13232) and at Laredo (site 13196) and either decrease or have no discernible trend at the other sampling sites.

Historical median mercury concentrations are below the screening level for all sites (fig. 3C). However, recent (about 1994) TNRCC analyses for mercury in riverbed sediments show concentrations above the screening level at 14 of the 19 Rio Grande/Río Bravo sites (13272, 13234, 13232, 13229, 13223, 13269, 13267, 13215, 13560, 13196, 13192, 13180, 13074, and 13177). Mercury concentrations show an increasing trend in downstream direction (table 1). Mercury concentrations increase with time at the 2 Pecos River sites and at 7 sites on the Rio Grande/Río Bravo (sites 13272, 13223, 13215, 13205, 13196, 13180, and 13177). Of the 12 trace elements analyzed for trends, only mercury has no decreasing trend in concentrations with time at any of the 17 sites.

Historical median selenium concentrations exceed the screening level at the 2 Pecos River sites and the 2 Rio Grande/Río Bravo sites downstream of Amistad International Reservoir and upstream of Laredo

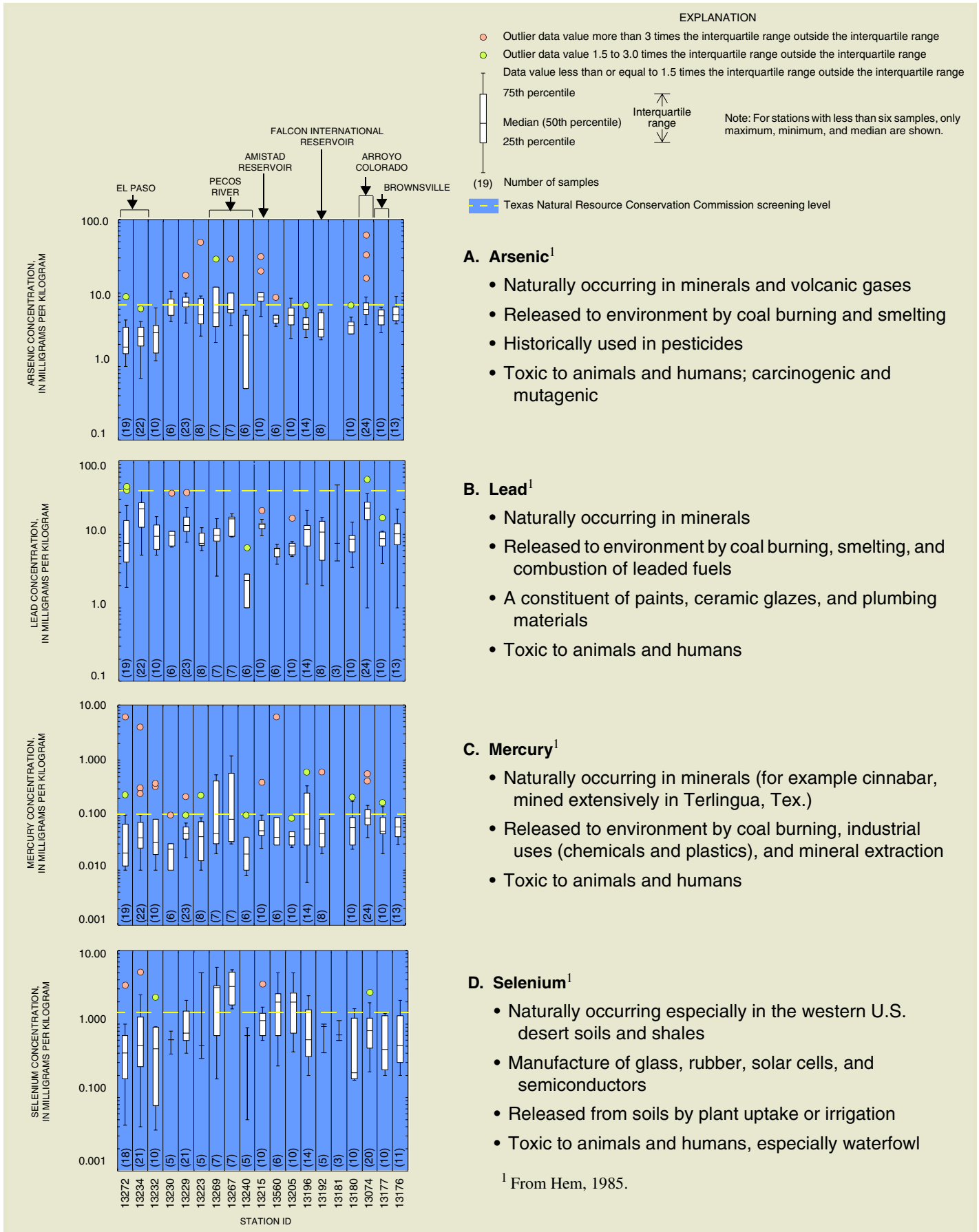


Figure 3. Concentrations of selected trace elements in riverbed sediments of the Rio Grande/Río Bravo, Pecos River, and Arroyo Colorado.

Table 1. Spatial and temporal trends of trace elements and selected organic compounds in riverbed sediments in the Rio Grande/Río Bravo Basin

[Number of detections shown if insufficient for temporal trend analysis; -- indicates no detections]

Site Name	Texas Natural Resource Conservation Commission site no. (downstream order)	Trace elements											Organic compounds																
		Arsenic	Barium	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Selenium	Silver	Zinc	bis(2-Ethylhexyl)phthalate	Chlordane	Chloroform	Cresol	Methylene chloride	PCBs	p,p'-DDE	Toluene								
		Spatial trends																											
		Temporal trends																											
El Paso	13272	Red	Red	Light blue	Red	Light blue	Light blue	Red	Red	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	1	1	--	1	--	--	3
	13234	Red	Light blue	Light blue	Red	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	1	--	3	4	2	--	--	3
	13232	Red	Light blue	Light blue	Red	Light blue	Light blue	Red	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	2	--	3	3	1	--	--	2
	13229	Green	Light blue	Light blue	Green	Green	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	--	1	--	1	3	2	1
	13223	Light blue	1	Light blue	Light blue	Light blue	Light blue	Red	Green	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	--	--	--	1	--	--	--
Pecos River	13269	Light blue	4	Light blue	Light blue	Light blue	Light blue	Red	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	--	--	--	--	--	--	--
	13267	Light blue	4	Light blue	Light blue	Light blue	Light blue	Red	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	--	--	--	--	1	--	--
Amistad International Reservoir	13215	Light blue	--	Light blue	Green	Light blue	Light blue	Red	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	--	--	--	--	--	2	--
	13560	Light blue	6	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	--	1	1	2	--	--	2
	13205	Light blue	Red	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	1	--	--	--	1	--	--	1
Laredo	13196	Light blue	Green	Red	Red	Red	Light blue	Red	Red	Green	Green	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	3	--	3	1	1	--	--	3
Falcon International Reservoir	13192	Green	4	1	Green	Green	Green	Light blue	Green	Green	Green	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	--	1	--	1	1	--	1
	13181	Light blue	--	2	1	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	1	--	--	--	3	2	--
	13180	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	--	1	--	1	--	--	1
Arroyo Colorado (Harlingen)	13074	Light blue	Green	Light blue	Green	Green	Red	Green	Green	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Green	--	--	--	Light blue	6	4
	13177	Light blue	Light blue	Green	Light blue	Light blue	Light blue	Red	Red	Green	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	--	1	--	1	--	--	--
	13176	Light blue	Light blue	Red	Light blue	Green	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	Light blue	--	1	1	--	1	1	2	1

(sites 13560 and 13205) (fig. 3D). Although intermediate increases and decreases can be observed in the selenium data, there is no downstream trend for the reach from El Paso to the Gulf of Mexico. Selenium concentrations show increasing trends with time at two sites, Amistad International Reservoir (site 13215) and at the mouth of the Rio Grande/Río Bravo (site 13176); other sites have decreasing trends or no trend.

The remaining eight trace elements analyzed for trends are near or below screening levels at most sites except for copper at the two El Paso sites (13272 and 13234) and the Arroyo Colorado site (13074) near Harlingen; and manganese at the El Paso, Laredo (13196), and Arroyo Colorado sites. Analyses show increasing trends in downstream direction in barium concentrations; and decreasing trends in downstream direction in cadmium and copper concentrations. Of all trace elements analyzed for, the largest number of trace elements with increasing temporal trends are at sites in and near El Paso (13272, 13234, and 13232) and at Laredo (13196); and the largest number of trace elements with decreasing temporal trends are at Falcon International Reservoir (13192).

Organic Compounds

Of the 140 organic compounds for which available samples were analyzed, 16 compounds were detected at least once (table 2). Of the 16 compounds detected at least once, 8 compounds (bis(2-ethylhexyl)phthalate, chlordane, chloroform, cresol, methylene chloride, PCBs, p,p'-DDE, and toluene) were found at 16 of the 17 sites (fig. 4). Of the 8 organic compounds, 7 compounds (bis(2-ethylhexyl)phthalate, chloroform, cresol, methylene chloride, PCBs, p,p'-DDE, and toluene) have sufficient data to test for trends in downstream direction. None of the seven compounds show a downstream trend in concentration (table 1).

Bis(2-ethylhexyl)phthalate, chlordane, and PCBs at the site near Harlingen on the Arroyo Colorado (13074) are the only organic compounds with sufficient data to test for temporal trends. Chlordane concentrations show a decreasing trend with time at the site; bis(2-ethylhexyl)phthalate and PCBs show no trends with time.

Table 2. Number of sites sampled, detections, and nondetections of organic compounds in the Rio Grande/Rio Bravo Basin

Organic compound	No. of sites	Detections	Nondetections	Organic compound	No. of sites	Detections	Nondetections
Acenaphthylene	25	0	99	2-Chlorophenol	24	0	99
Acrylonitrile	25	0	86	2-Nitrophenol	24	0	99
Anthracene	21	0	94	di (n-octyl) Phthalate	24	0	99
Benzo(b)fluoranthene	25	0	100	2,4-Dichlorophenol	24	1	96
Benzene	25	0	96	2,4,-Dimethylphenol	24	0	98
Benzo(k)fluoranthene	25	0	100	2,4-Dinitrotoluene	24	0	99
Benzo(a)pyrene	25	0	99	2,4-Dinitrophenol	24	0	99
beta Benzene hexachloride	25	0	6	2,4,6-Trichlorophenol	24	0	97
bis(Chloromethyl)ether	5	0	6	2,6-Dinitrotoluene	24	0	98
delta Benzene hexachloride	6	0	6	3,3-Dichlorobenzidine	24	0	99
bis(2-Chloroethyl)ether	6	0	99	4-Bromophenyl phenyl ether	24	0	97
bis(2-Chloroethoxy)methane	25	0	100	4-Chlorophenyl phenyl ether	24	0	99
bis(2-Chloroisopropyl)ether	25	0	100	4-Nitrophenol	24	0	99
Bromoform	25	0	96	Phenol (C ₆ H ₅ OH)	24	0	99
n-butyl Benzyl phthalate	25	0	100	trans-1,3-Dichloropropene	23	0	92
Carbon tetrachloride	25	0	97	cis-1,3-Dichloropropene	23	0	93
Chlorobenzene	25	2	94	PCP (pentachlorophenol)	45	0	176
Chlorodibromomethane	25	0	96	Chlordane nonachlor, trans isomer	28	0	63
Chloroethane	25	1	94	alpha Benzene hexachloride	46	0	161
Chloroform	25	16	90	bis(2-Ethylhexyl)phthalate	40	15	142
Chrysene	25	0	100	di (n-butyl) Phthalate	39	4	150
Dichlorobromomethane	24	0	93	Pentachlorobenzene	20	0	63
Dichlorodifluoromethane	6	0	6	Benzidine	23	0	92
Diethyl phthalate	25	0	100	Polychlorinated naphthalenes	4	0	6
Dimethyl phthalate	25	0	96	p,p'-DDT	32	1	66
1,2-Diphenylhydrazine	24	0	91	o,p'-DDT	28	0	63
Endosulfan sulfate	28	0	119	p,p'-DDD	32	0	68
Endosulfan, beta	6	0	6	o,p'-DDD	28	0	62
Endosulfan, alpha	6	0	6	p,p'-DDE	32	24	44
Endrin aldehyde	6	0	6	o,p'-DDE	28	0	63
Ethylbenzene	25	1	95	Chlordane	59	23	271
Fluoranthene	25	0	100	Endosulfan	22	0	94
Fluorene	25	0	99	Heptachlor epoxide	60	0	294
Hexachlorocyclopentadiene	25	0	99	Methoxychlor	60	0	299
Hexachloroethane	25	0	100	PCB-1221	25	0	90
Indeno (1,2,3-cd) pyrene	25	0	100	PCB-1232	25	0	90
Isophorone	25	0	100	PCB-1242	25	0	90
Methylene chloride	25	18	78	PCB-1248	25	0	90
N-Nitrosodi-n-propylamine	25	0	100	Arochlor 1254	25	0	90
N-Nitrosodiphenylamine	25	0	100	PCB-1260	25	0	90
Methyl bromide	6	0	6	PCB-1016	25	0	90
Methyl chloride	6	0	6	PCBs	55	29	197
N-Nitrosodimethylamine	24	0	92	Guthion	23	0	78
Naphthalene	25	0	100	Methyl parathion	42	0	173
Nitrobenzene	25	0	100	Atrazine	5	0	5
Parachlorometa cresol	22	0	75	Hexachlorobenzene	45	0	171
Phenanthrene	21	0	94	Hexachlorobutadiene	24	0	99
Pyrene dry	25	0	100	2,4-D	45	0	178
Tetrachloroethylene	24	2	92	2,4,5-T	42	0	173
Toluene	25	26	81	Silvex	51	0	200
Trichloroethylene	24	0	92	Lindane	60	0	304
Vinyl chloride	25	0	95	Xylene	24	0	95
1,1-Dichloroethane	24	0	95	Hexachlorophene	19	0	56
Trichlorofluoromethane	6	0	6	N-Nitrosodi-n-butylamine	19	0	56
1,1-Dichloroethylene	23	0	87	Styrene	5	0	5
1,1,1-Trichloroethane	24	0	94	2,4,5-Trichlorophenol	20	0	66
1,1,2-Trichloroethane	24	0	94	Mirex	23	0	68
1,1,2,2-Tetrachloroethane	24	1	92	Dursban	23	0	80
Benzo(g,h,i)perylene 1,1,2-benzoperylene	24	0	99	Sevin	15	0	27
Benzo(a)anthracene 1,2-benzanthracene	24	0	99	Anthracene and phenanthrene	5	0	5
1,2-Dichloroethane	24	0	95	Demeton	15	0	37
1,2-Dichlorobenzene	24	0	99	Bromomethane	21	0	90
1,2-Dichloropropane	24	0	94	1,2-Dibromoethane	21	0	77
trans-1,2-Dichloroethene	22	0	88	Cresol	20	9	73
1,2,4-Trichlorobenzene	24	0	96	N-Nitrosodiethylamine	19	0	56
1,2,5,6-Dibenzanthracene	24	0	99	Pyridine	19	0	58
1,3-Dichlorobenzene	24	0	99	1,2,4,5-Tetrachlorobenzene	19	0	56
1,4-Dichlorobenzene	24	0	99	Chloromethane	21	0	89
2-Chloroethyl vinyl ether	21	0	89	Chlorfenvinphos	5	0	5
2-Chloronaphthalene	24	0	99	Chlorothalonil	5	0	5

Detections

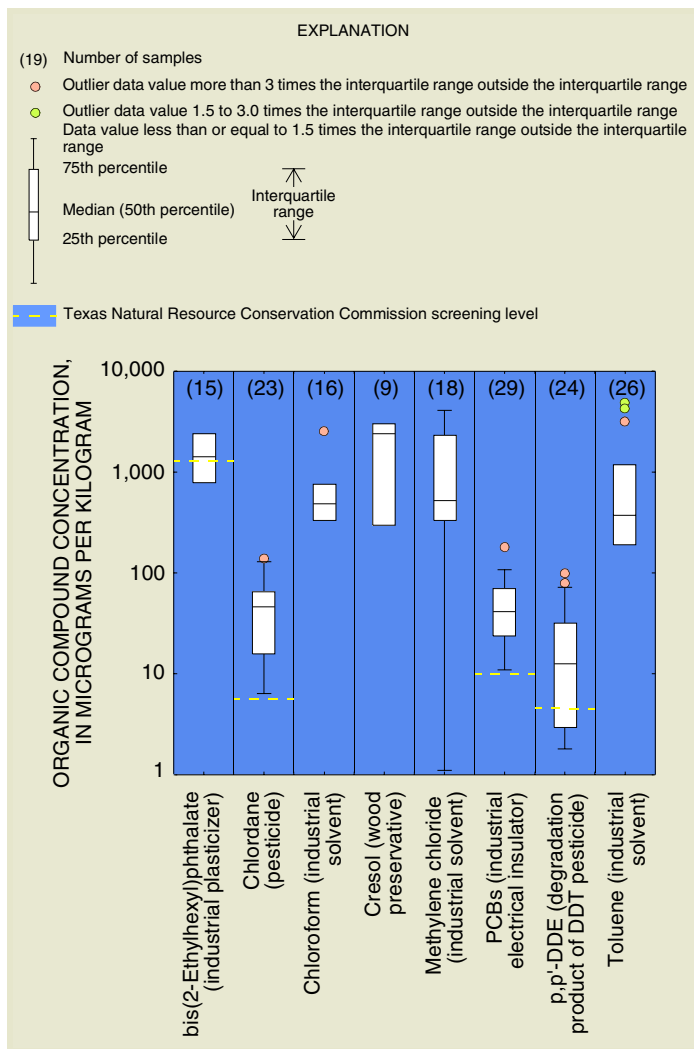


Figure 4. Concentrations of selected organic compounds in riverbed sediments of the Rio Grande/Río Bravo and Arroyo Colorado.

What Do These Results Indicate?

Based on the data for riverbed sediments in the Rio Grande/Río Bravo Basin, trace elements are more commonly detected than organic compounds. Geologic sources of trace elements that could account for background concentrations of trace elements cannot be readily identified because the amounts from sources associated with human activities in the basin are unknown. Increasing temporal trends in more trace elements in the vicinity of El Paso and Laredo than in other reaches of the rivers for which samples are available indicate that sources of trace elements possibly are related to human activities within the respective watersheds. Although historical median mercury concentrations are below the TNRCC screening level, recent sample concentrations above the screening level, increasing temporal trends at more than one-half the sites, and no decreasing temporal trends at any site could indicate that either mercury sources are widespread in the basin or the source of mercury is non point, possibly atmospheric. Regional-scale increases in mercury concentrations in the northeastern and north-central United States during the past 100 years have been documented using lake-sediment cores and attributed to atmospheric pollution (Swain and others, 1992).

Organic compounds are not prevalent in riverbed sediments, but the presence of those detected probably warrants continued monitoring.

The generally greater occurrence of organic compounds near El Paso, Laredo, and Harlingen indicates the likelihood of urban sources.

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