U.S. Department of the Interior
U.S. Geological Survey

Water-Quality Trends in the Rio Grande/Río Bravo Basin Using Sediment Cores from Reservoirs

At Elephant Butte Reservoir ...

PCB and total DDT concentrations increase in sediments deposited in the 1950s, peak in sediments deposited in the 1960s, then decrease in sediments deposited to the present.

Trends in uranium were not detected, however, some "excess" uranium relative to thorium occurs in sediments deposited after about 1970, possibly a subtle effect of uranium mining.

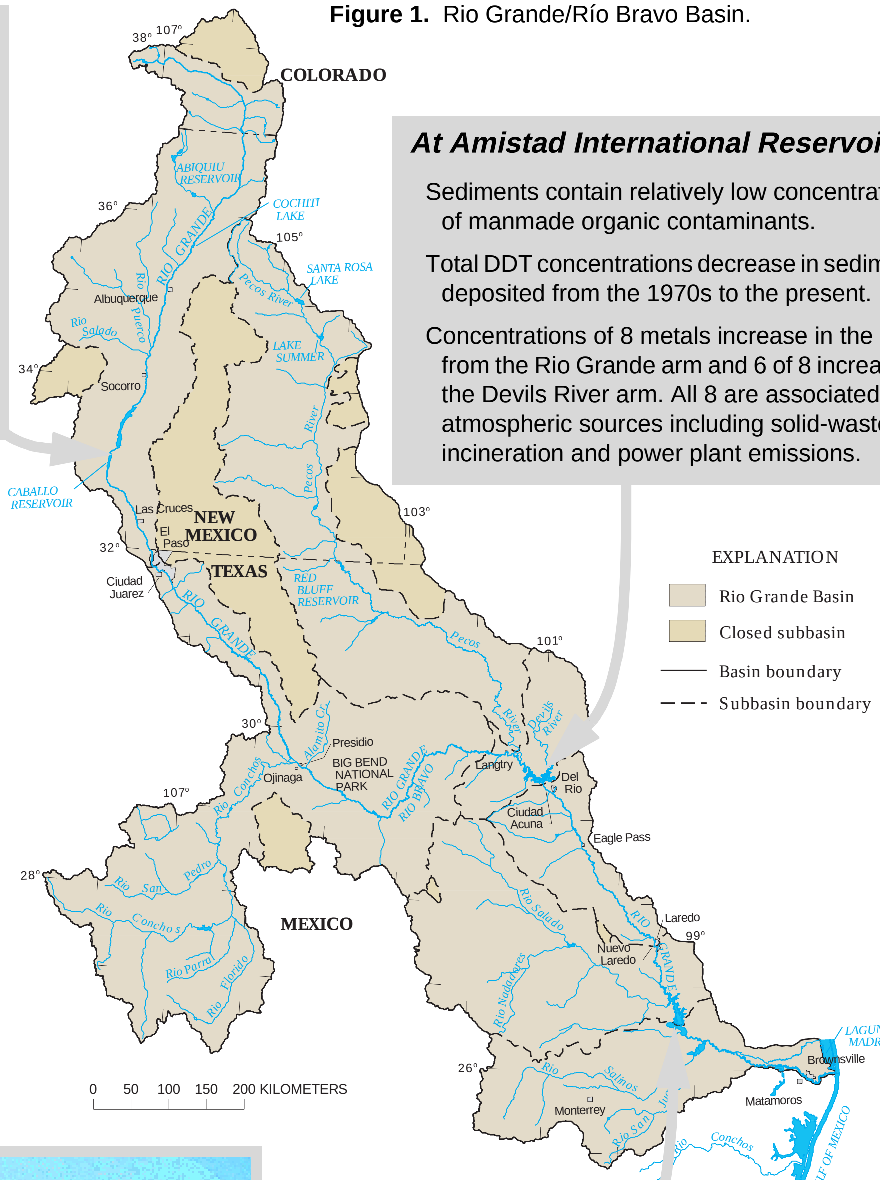

Figure 1. Rio Grande/Río Bravo Basin.

At Amistad International Reservoir ...

Sediments contain relatively low concentrations of manmade organic contaminants.

Total DDT concentrations decrease in sediments deposited from the 1970s to the present.

Concentrations of 8 metals increase in the core from the Rio Grande arm and 6 of 8 increase in the Devils River arm. All 8 are associated with atmospheric sources including solid-waste incineration and power plant emissions.

At Falcon International Reservoir ...

Sedimentation rate decreases by approximately 75 percent after the construction of Amistad International Reservoir upstream.

Total DDT concentrations peak in sediments deposited in the 1960s, decrease rapidly in sediments deposited soon after the U.S. ban on use in 1972, then remain stable in sediments deposited to the present, indicating continuing sources of DDT in the middle Rio Grande Basin.

Rio Grande above Amistad International Reservoir.

Trends

Water-quality trends reflect the relation between water quality and human activities, chronicling changes in concentrations of environmental contaminants, introduction of new contaminants, and successful efforts in environmental pollution remediation. Historical data available for analyzing trends often have severe limitations, from questionable accuracy to unknown sampling and analytic methodologies. Where data are unavailable or have such limitations, water-quality trends sometimes can be reconstructed using sediment cores from lakes and reservoirs (Eisenreich and others, 1989; Van Metre and Callender, 1996, 1997).

The purpose of this fact sheet is to summarize the findings of a study to assess historical changes in surface-water quality in the Rio Grande Basin (known as the Río Bravo Basin in Mexico) by analyzing changes in sediment chemistry in cores from three reservoirs: Elephant Butte Reservoir, Amistad International Reservoir, and Falcon International Reservoir (fig. 1). Sediments that erode from the land surface are transported by tributaries into the Rio Grande/Río Bravo. Metals and some persistent pesticides and industrial organic compounds sorb to these sediments, which eventually accumulate at the bottom of the reservoirs or are transported to the Gulf of Mexico. Although use of reservoir cores has limitations—for example, the cores do not record trends in non-persistent compounds—in many cases the data provide a partial historical record of water quality.

In 1991, the U.S. Geological Survey (USGS) began full implementation of the National Water-Quality Assessment (NAWQA) Program (Leahy and others, 1990). Also in 1991, the State of Texas established the Clean Rivers Program (CRP) administered by the Texas Natural Resource Conservation Commission (TNRCC). The coring study reported here was a collaborative effort between the NAWQA Program and the CRP Rio Grande Border Environmental Assessment Team, with additional funding support from the El Paso County Water Improvement District No. 1.

Setting

The Rio Grande/Río Bravo originates in the Rocky Mountains of Colorado, flows south through New Mexico, and then defines the Texas-Mexico border from El Paso/Ciudad Juárez to the Gulf of Mexico. The population of the Rio Grande/Río Bravo Basin is concentrated in several rapidly growing urban areas: 1 million in the Colorado-New Mexico part of the basin, 1 million in the Texas part, and 8 million in Mexico. Most of the U.S. part of the basin is rangeland, with smaller amounts of agriculture, forests, and urban areas (Texas Natural Resource Conservation Commission, 1994a). An important feature of the border region since the mid-1960s is the growth of *maquiladoras*, industrial plants set up in Mexico to process or assemble goods for a foreign country using material supplied by that country (Texas Natural Resource Conservation Commission, 1994a). Approximately one-half of the more than 600 *maquiladoras* located in the Rio Grande/Río Bravo Basin are in Ciudad Juárez.

Elephant Butte Reservoir, built in 1916, is the oldest major reservoir in the basin and is located in south-central New Mexico 200 kilometers (km) north of El Paso, Tex., and downstream from Santa Fe and Albuquerque, N. Mex. (fig. 1). It has a drainage area of 83,100 square kilometers (km^2) and a storage capacity of 2,550 million cubic meters (m^3) (2,070,000 acre-feet (acre-ft)).

Amistad International Reservoir, located on the Texas-Mexico border, was impounded in 1969. It dams both the Rio Grande/Río Bravo and the Devils River. It has a drainage area of 403,000 km^2 and a conservation storage capacity of 4,170 million m^3 (3,380,000 acre-ft). Flow in the Rio Grande/Río Bravo from El Paso/Ciudad Juárez to Presidio/Ojinaga is intermittent and consists largely of stormwater runoff, treated wastewater from El Paso, and irrigation return flows. The Río Conchos, which enters the Rio Grande/Río Bravo near Presidio/Ojinaga, provides more than 75 percent of the flow in the Rio Grande/Río Bravo through the Big Bend area (Texas Natural Resource Conservation Commission, 1994a). Sediment cores for this study were taken from both the Rio Grande/Río Bravo and the Devils River arms of the reservoir.

Falcon International Reservoir, impounded in 1954, is 480 km downstream from Amistad International Reservoir and 440 km upstream from the Gulf of Mexico. Falcon has a drainage area of 525,000 km^2 and a storage capacity of 3,290 million m^3 (2,670,000 acre-ft). Its effective contributing drainage area for sediment was reduced by 77 percent (from 525,000 to 122,000 km^2) by construction of Amistad in 1969.

Field and Laboratory Methods

Cores of bottom sediment were collected using a Benthos gravity corer, a Benthos piston corer (both are 4 meters (m) long and 6.3 centimeters (cm) in diameter), and a Wildco box corer (15 by 20 cm). The corers were deployed from a custom-built pontoon boat. Replicate cores were collected from a site in the downstream end of each reservoir. Additional cores were collected in Amistad Reservoir from a site on the Devils River arm.

At each coring location, one core was split lengthwise and described visually. Other cores were extruded vertically and slices removed for analysis of cesium-137 (^{137}Cs), major, minor, and trace elements, and organochlorine compounds. ^{137}Cs was analyzed by high-resolution gamma spectrometry; elemental concentrations were determined on concentrated-acid digests using atomic emission spectrometry-inductivity coupled plasma; concentrations of chromium, lead, and zinc were determined on concentrated-acid digests using graphite furnace atomic adsorption; concentrations of mercury were determined by cold-vapor atomic adsorption (Lichte and others, 1987). Uranium and thorium isotopes were determined by alpha spectrometry on acid digests (American Society for Testing and Materials, 1995). Concentrations of organochlorine compounds were analyzed in organic solvent extracts using a dual column capillary gas chromatograph with dual electron capture detectors (Wershaw and others, 1987).

Sediment Characteristics and Age-Dating

Cores from all three reservoirs show a noticeable contrast at the interface of pre-reservoir and reservoir sediments. Pre-reservoir sediments contain some sand and root hairs and are drier and firmer than reservoir sediments. Reservoir sediments in cores from Falcon and Amistad International Reservoirs are uniform, fine-textured, olive-gray to olive-green silt and clay with a high water content. Reservoir sediments in the Elephant Butte Reservoir core have layers of silts and clays with numerous interbedded layers (1 to 2 cm thick) containing fine sand.

Sediment cores were age-dated by correlating sample depth with ^{137}Cs content, a radioactive isotope with a half-life of 30.1 years. A by-product of nuclear weapons testing, ^{137}Cs first occurred at appreciable concentrations in the atmosphere in 1952, reached a peak concentration in 1963, and decreased to almost zero by the mid-1970s (fig. 2). The ^{137}Cs concentration in sediment, to which ^{137}Cs sorbs, is a useful age-dating tool. The pre-reservoir land surface is assigned the date of the reservoir's construction, the deepest occurrence of ^{137}Cs in a core is assigned a date of 1952, the maximum concentration is assigned a date of 1964, and the top of the core is assigned the sampling date. Barring major hydrologic changes, such as construction of another reservoir upstream, sedimentation rates are assumed to be constant during time intervals between these dates.

Elephant Butte Reservoir was constructed in 1916, yet the presence of ^{137}Cs in the deepest part of the core indicates that the oldest reservoir sediments cored are from the early 1950s (fig. 2). ^{137}Cs strongly sorbs to clays; hence, the ^{137}Cs profile normalized to clay (fig. 2) is used to indicate a ^{137}Cs peak at 133 cm down core. Cores were collected about 500 m east of the pre-reservoir stream channel because reservoir sediments in the channel were about 10 m thick, exceeding the length of the gravity corer. The site cored was exposed (dry) during the severe drought of the early 1950s. The ^{137}Cs record and historical water levels indicate that sediments deposited at the coring site before 1952 were eroded during and after the drought but that the site has since been continuously depositional at a rate of 3.3 grams per centimeter squared per year ((g/cm^2)/yr) or about 3.8 centimeters per year (cm/yr).

Amistad International Reservoir was filled in 1969, post-dating the ^{137}Cs peak. As at Elephant Butte, cores were collected away from the pre-reservoir stream channel because of the thickness of channel sediments. Sedimentation rates of 1.1 and 2.7 (g/cm^2)/yr (1.2 and 3.8 cm/yr) were computed for the Rio Grande/Río Bravo and Devils River arm cores, respectively, based on the thickness of sediments from the pre-reservoir surface to the top of the cores. Sedimentation rates in both these cores are much lower than in the pre-reservoir stream channels: International Boundary & Water Commission sedimentation surveys indicate approximately 12 m of sediment was deposited in the Rio Grande/Río Bravo channel in the lower part of Amistad from 1969 to 1994, an average rate of about 45 cm/yr. This is an extremely high sedimentation rate compared to other U.S. reservoirs (Callender and Robbins, 1993; Van Metre and Callender, 1996, 1997).

Falcon International Reservoir was filled in 1954. ^{137}Cs concentrations peak at a core depth of 57 cm (fig. 2), corresponding to a date of 1964 and a sedimentation rate of 3.46 (g/cm^2)/yr (4.7 cm/yr) for 1954–64. We assume this sedimentation rate continued until the construction of Amistad Reservoir in 1969 (core depth of 30 cm). The accumulation of the remaining 30 cm of reservoir sediment reflects a sedimentation rate of 0.57 (g/cm^2)/yr, (1.1 cm/yr) for 1969–95. The effect of the construction of an upstream reservoir is to decrease the sedimentation rate, "compressing" the depth-to-time relation of the upper part of the core.

Elephant Butte Reservoir Trends

Two groups of organic compounds were detected in most Elephant Butte Reservoir core samples: polychlorinated biphenyls (PCBs) and the DDT metabolites (breakdown products) DDE and DDD (fig. 3). These compounds are widely distributed in the environment and frequently detected in reservoir and lake sediments (Eisenreich and others, 1989; Van Metre and Callender, 1996, 1997).

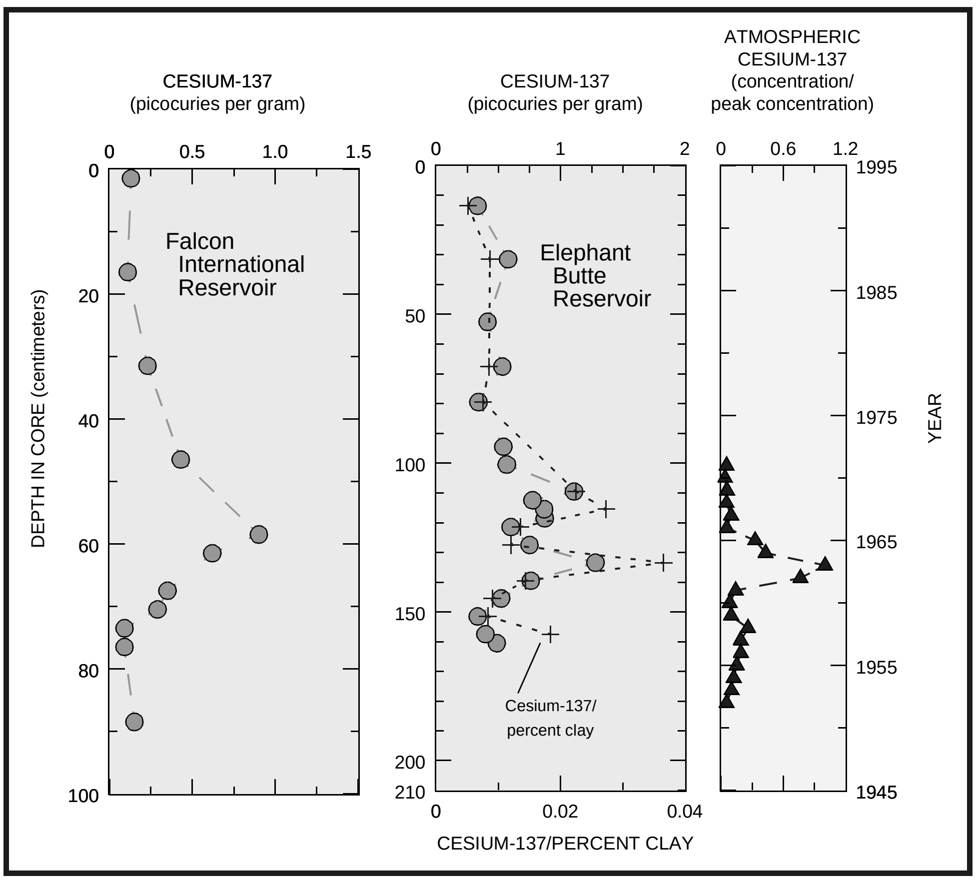

Figure 2. Cesium-137 in cores from Elephant Butte and Falcon International Reservoirs and in the atmosphere.

Trends in PCB concentrations in sediments at Elephant Butte Reservoir reflect the restriction and eventual ban on the use of these compounds. PCBs were first synthesized in 1929 and were widely used as plasticizers, hydraulic lubricants, and dielectric fluids in electrical transformers and capacitors. Annual sales of PCBs in the United States peaked in 1970 and then declined by one-half by 1973. In 1979 all new uses of PCBs were banned. PCBs were detected in 8 of 10 samples from the Elephant Butte Reservoir core (fig. 3). Concentrations increase rapidly in sediments deposited during the 1960s, peak at 4.7 micrograms per kilogram (μg/kg) in sediments deposited in about 1970, then decline with non-detections (at 1.0 μg/kg) in two of the samples deposited since 1980.

Total DDT (T-DDT = DDT + DDE + DDD) in the Elephant Butte core similarly reflects the success of the ban on this chemical. DDT use in the United States peaked in the early 1960s, declined during the late 1960s, and ceased with the ban in 1972. T-DDT concentrations in Elephant Butte reach a maximum of about 10.5 μg/kg in sediments deposited in the late 1960s, then decrease exponentially, indicating the gradual removal of residual T-DDT from the watershed.

The Rio Puerco joins the Rio Grande 90 km upstream from Elephant Butte Reservoir, and its basin of 17,900 km^2 represents about 22 percent of the reservoir's drainage area (fig. 1). The Rio Puerco carries an extremely large sediment load and is estimated to contribute 60 percent of the sediment entering the reservoir (Gorbach, 1996). The headwaters of the Rio Puerco are in the Grants Mineral Belt of northwest New Mexico, an area that accounted for more than 40 percent of the uranium mined in the United States during 1966–77. Large-scale uranium mine discharges in the headwaters of the Rio Puerco occurred from 1957 until the mid-1980s (Gallaher and Cary, 1986), releasing uranium and other trace elements and radionuclides. Effects on water quality have been documented tens to hundreds of kilometers downstream from the mines (Gallaher and Cary, 1986; Van Metre and others, 1996).

Uranium and thorium isotopes were measured in the Elephant Butte core. Neither shows a significant trend in sediments deposited since the 1950s (fig. 3) indicating substantial enrichment

of uranium in sediments has not occurred. Another data analysis technique is available to test for more subtle effects of uranium mining, uranium to thorium isotopic ratios (Van Metre and others, 1996). Over geologic time, uranium-238 (^{238}U), uranium-234 (^{234}U), and thorium-230 (^{230}Th) in rocks come to secular equilibrium (activity ratios equal 1.0). As one radionuclide decays, the next radionuclide down the series is formed and in turn decays. As a result, after a long period of time all the nuclides in the series attain approximately the same activity. Van Metre and others (1996) showed that sediments in and near the channel of the Puerco River (sister stream to the Rio Puerco but draining to the west) that were subjected to mine-dewatering releases contained "excess" ^{238}U and ^{234}U relative to ^{230}Th. The excess indicated sorption of dissolved uranium in mine effluents

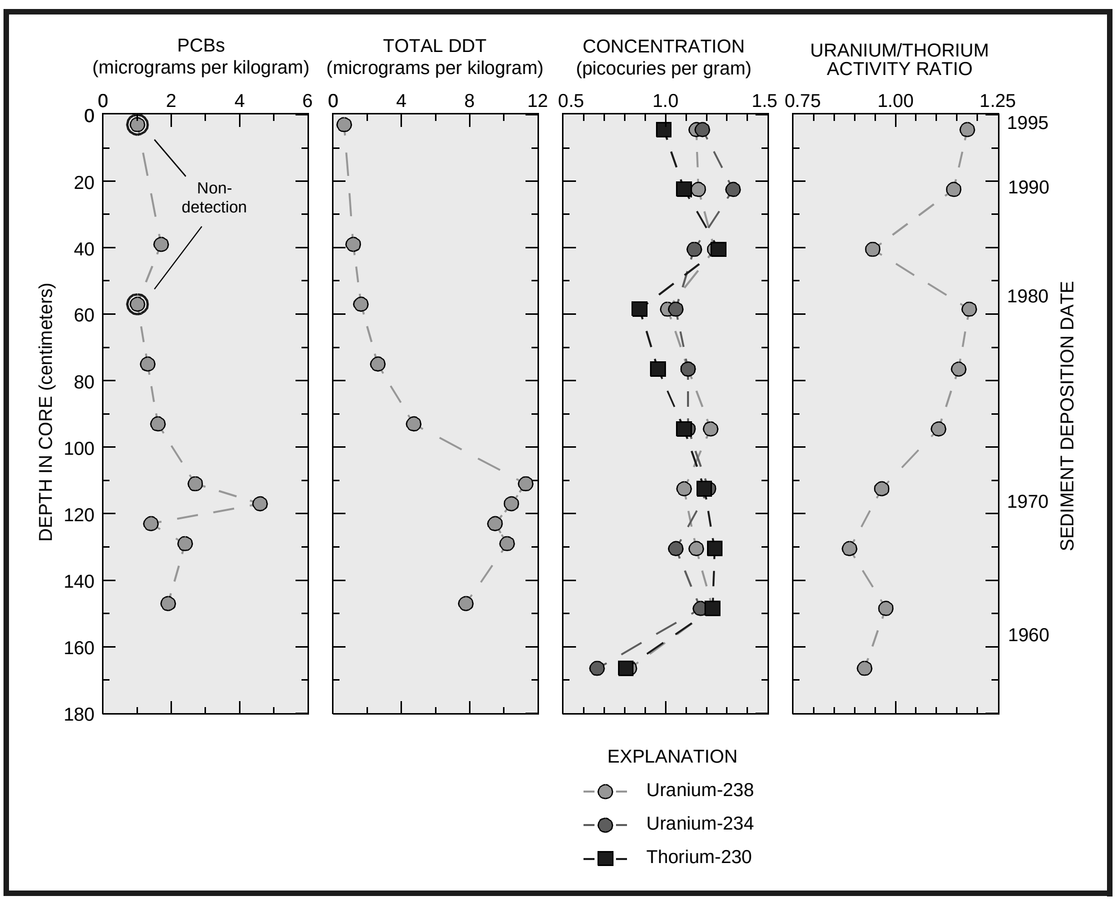

Figure 3. Trends in PCBs, total DDT, and uranium/thorium activity ratios in Elephant Butte Reservoir cores.

onto sediments, leading to relative enrichment of ^{238}U and ^{234}U when compared to the chemically less-mobile ^{230}Th.

Uranium/thorium activity ratios (calculated as $[(^{238}U + ^{234}U)/2]/^{230}Th$) in a sample of pre-reservoir soil and in three samples deposited prior to the early 1970s are from 0.89 to 0.98 (fig. 3). The median uranium/thorium ratio in six samples deposited after the early 1970s is 1.15, indicating enrichment of uranium relative to thorium. Core geochronology indicates that there is an appreciable (more than 10-year) time lag between the onset of uranium mining releases in the Rio Puerco and the occurrence of excess uranium in sediment in the lower part of Elephant Butte Reservoir.

Amistad International Reservoir Trends

Sediments from the Rio Grande/Río Bravo and the Devils River arms of Amistad International Reservoir reflect different land uses. The drainage basin for the Rio Grande/Río Bravo arm includes El Paso/Ciudad Juárez, a major industrial center for Texas and Mexico, although the river is frequently dry between El Paso and the Río Conchos. The Río Conchos contributes the bulk of the flow in the Rio Grande/Río Bravo through Big Bend National Park to Amistad Reservoir. In contrast, the drainage basin for the Devils River arm is largely undeveloped with a population density of 0.81 people/km^2.

The only organochlorine compounds detected in cores from Amistad Reservoir are the DDT metabolites DDD and DDE, and these are detected at low concentrations. Lack of detection of most organochlorines and relatively low concentrations of DDT metabolites indicate minimal human impact on sediment quality in Amistad. This might be attributable to the remarkably high sedimentation rates in Amistad International Reservoir, which effectively dilute the load of anthropogenic constituents associated with sediments. Temporal patterns of T-DDT in the Rio Grande/Río Bravo arm of Amistad are similar to temporal patterns found in other U.S. reservoirs and in Elephant Butte Reservoir with a maximum concentration of 5.6 µg/kg in the early 1970s decreasing to 1.8 µg/kg in the most recently deposited sample. The most notable characteristic of these trends is the decrease in concentrations in response to the banning of DDT in the United States in 1972.

Trends in 8 metals are shown on figure 4. All 8 of these metals are associated with fossil fuel combustion (especially coal) and solid waste incineration (Shendrikar and Ensor, 1986; Vogg and others, 1986). All 8 had statistically significant increasing trends (Spearman's rank correlation at 95-percent confidence level) in the Rio Grande arm, and 6 of the 8 increased on the Devils River arm. Concentrations of mercury and nickel both more than doubled. The only decreasing trend was for lead on the Devils River arm, a trend that is common in the United States since unleaded gasoline was introduced in the 1970s.

At least two factors could contribute to increasing trends in Amistad:

1. Increases in fluvial inputs (increasing concentrations of metals in suspended sediments transported from point and nonpoint sources upstream) from the Rio Grande and, to a lesser extent, the Devils River; and
2. Increasing atmospheric fallout of metals over Amistad and its watershed.

The two contributing factors are not mutually exclusive. For example, atmospheric fallout over the watershed can become fluvial input to a downstream reservoir.

The relatively smaller trends in the Devils River arm core could result from the larger sedimentation rate at the coring site; it was about 3 times greater than the rate in the Rio Grande arm core (for atmospherically derived contaminants, enrichment is inversely related to sedimentation rate); and (or) increases in atmospheric fallout of contaminants could be greater to the west of Amistad (over the Rio Grande watershed) than to the north (over the Devils River watershed).

Falcon International Reservoir Trends

The only consistently detected organochlorine compounds in Falcon International Reservoir are DDT and its metabolites. Maximum T-DDT concentrations in the Falcon International Reservoir core are in sediments deposited in the early 1960s, consistent with Elephant Butte Reservoir, White Rock Lake in Dallas, Tex. (Van Metre and Callender, 1997), and natural lakes (Eisenreich and others, 1989). T-DDT concentrations decrease rapidly in sediments deposited after the ban on DDT use in the United States; yet concentrations in sediments deposited since the early 1970s are approximately constant at about 5 µg/kg (fig. 5). Stable concentrations since the early 1970s indicate continuing input of T-DDT, albeit at smaller levels than those that occurred during its permitted use in the United States. Limited use of DDT in Mexico was not banned as of 1990 (United Nations Economic Commission for Latin America and the Caribbean, 1990). At Amistad Reservoir, in contrast, T-DDT concentrations show a decreasing trend since the 1970s. Differences in trends in the two reservoirs could be due to differing land uses in Mexico in the two basins, or to differences in the proportion of each basin that is in Mexico (fig. 1).

Dilution of sediment-borne contaminants is a factor in Falcon International Reservoir, as at Amistad and Elephant Butte Reservoirs, as demonstrated by data from the "1994 Binational Study Regarding the Presence of Toxic Substances in the Rio Grande/Río Bravo and its Tributaries Along the Boundary Portion Between the United States and Mexico" (Texas Natural Resource Conservation Commission, 1994b). In the survey, riverbed sediment samples were collected on the main stem of the Rio Grande and on three urban tributaries in the Laredo area upstream of Falcon International Reservoir. Chlordane, widely used in urban areas as recently as 1990, was detected in the tributaries at concentrations of 59, 172, and 185 µg/kg, yet was not detected at a reporting level of 3.0 µg/kg in the Rio Grande/Río Bravo downstream from Laredo. Using a simple mass-balance approach, this implies that sediment input to the Rio Grande/Río Bravo from these tributaries was diluted by a factor of about 100 or more.

Major-element concentrations in Falcon International Reservoir sediments changed in response to construction of Amistad

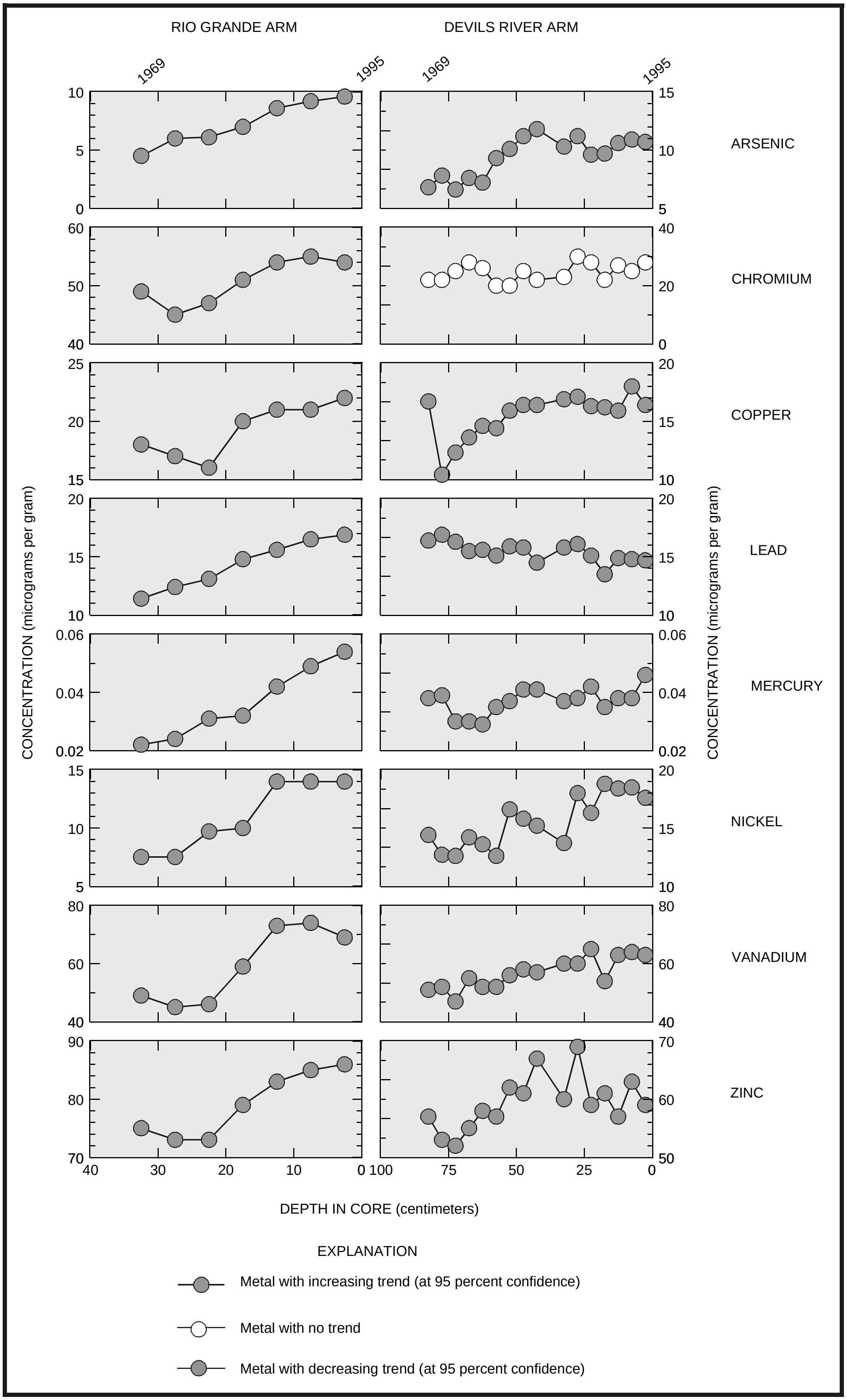

Figure 4. Trends in eight metals in Amistad International Reservoir cores.

Table 1. Sediment-quality guidelines

[µg/g, microgram per gram; µg/kg, microgram per kilogram; USEPA, U.S. Environmental Protection Agency; TNRCC, Texas Natural Resource Conservation Commission]

Agency	Effect level	Arsenic (µg/g)	Chromium (µg/g)	Copper (µg/g)	Lead (µg/g)	Mercury (µg/g)	Nickel (µg/g)	Zinc (µg/g)	Total DDT (µg/kg)	PCB (µg/kg)
USEPA (1996)	THRESHOLD	8.2	81	34	46.7	0.15	20.9	150	15	22
	PROBABLE	70	370	270	218	.71	51.6	410	52	189
Environment Canada (1995)	THRESHOLD	5.9	37.3	35.7	35.0	.17	18.0	123	7.0	34
	PROBABLE	17.0	90.0	197	91.3	.49	35.9	315	44.5	277
TNRCC	STATEWIDE 85th PERCENTILE	19	34	34	60	.12	27	116	3.0	10

International Reservoir upstream in 1969, as indicated by trends in aluminum (fig. 5), but did not show other systematic trends. Concentrations of major elements appear to vary less after the construction of Amistad, possibly because Falcon International Reservoir now receives sediments from a smaller, less geologically diverse area.

Implications of Trends in Metals, Total DDT, and PCBs

For Aquatic Life—Sediment-quality guidelines published by three agencies are listed in table 1. The guidelines are not enforceable standards; however, they do provide a basis for further evaluating the sediment data for the Rio Grande reservoirs. The first two guidelines listed are based on numerous studies relating contaminant concentrations to measures of biological effects. The guidelines separate concentrations into those that are "rarely," "occasionally," and "frequently" associated with biological effects. The lower value, which is referred to as the threshold effect level, represents the concentration below which adverse effects are rarely expected to occur. The higher value, referred to as the probable effect level, is the concentration above which adverse effects are predicted to occur frequently (Environment Canada, 1995). The TNRCC screening level is the 85th-percentile value of historical reservoir sediment samples and is not effects based.

Concentrations of arsenic, chromium, and nickel exceed either the threshold effect level or the TNRCC guideline in some samples from Amistad International Reservoir. The largest exceedances are for arsenic in both arms and for chromium in the Rio Grande arm of the reservoir. Concentrations of copper, lead, mercury, and zinc in all Amistad samples are below the threshold levels and the TNRCC guidelines, indicating no immediate cause for concern. Increasing trends do, however, raise several questions including: What is the source of these trends, will they continue to increase, and are the concentrations at these two coring locations representative of other parts of the reservoir.

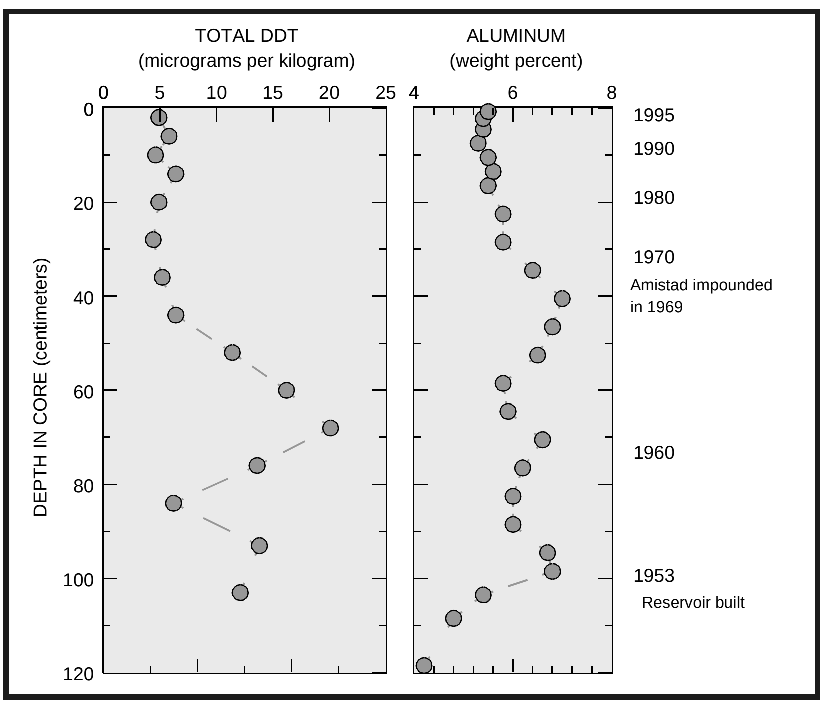

Figure 5. Trends in total DDT and aluminum in Falcon International Reservoir cores.

Concentrations of T-DDT in samples from all three reservoirs exceed the TNRCC guideline and, in selected samples, exceed the Environment Canada threshold effect level. Maximum T-DDT in Falcon also exceeds the U.S. Environmental Protection Agency threshold effect level. Based on these guidelines, T-DDT concentrations in recent Falcon sediments of about 5 µg/kg might be of limited concern for the protection of aquatic life.

Guidelines for PCBs are not exceeded in samples from any of the three reservoirs.

For Public Health—The primary public health concern posed by these metals, T-DDT, and PCBs in lakes is accumulation in fish, an issue that is not considered in setting the above aquatic-life guidelines. Therefore, no direct assessment can be made of possible public health concerns related to fish consumption using these sediment data.

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