

In cooperation with the Texas Natural Resource Conservation Commission  
under the authorization of the Texas Clean Rivers Act

## Chemical Quality of Sediment Cores from the Laguna Madre, Laguna Atascosa, and Arroyo Colorado, Texas

Many contaminants introduced into the environment by human activities are hydrophobic, meaning they are relatively insoluble in water and, thus, are associated primarily with sediments. These contaminants include the organochlorine pesticides DDT and chlordane, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) from industrial facilities and urban areas, and heavy metals such as arsenic, lead, mercury, and zinc. Understanding the occurrence of these contaminants in the environment requires sampling the sediments where the contaminants might be detected.

This fact sheet presents the results of a study to determine concentrations and temporal trends in contaminants in surficial sediments in water bodies near the mouth of the Arroyo Colorado at Laguna Madre in South Texas (fig. 1). Sediment cores were collected at three sampling sites (fig. 1): the south end of the main brackish-water lagoon in Laguna Atascosa National Wildlife

Refuge (site LAT), the old channel of the Arroyo Colorado about 1 kilometer (km) northeast of where the Harlingen Ship Channel connects the arroyo to the Intracoastal Waterway (site LAC), and Laguna Madre about 3 km south of where the ship channel and the Intracoastal Waterway meet (site LMD). Selected sediment samples from these cores were analyzed for cesium-137 ( $^{137}\text{Cs}$ ), lead-210 ( $^{210}\text{Pb}$ ), organochlorine pesticides, PCBs, PAHs, and major and trace elements.

This study was a collaborative effort between the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program (Leahy and others, 1990) and the Texas Natural Resource Conservation Commission (TNRCC) under the authorization of the Texas Clean Rivers Act. A similar collaborative study of sediment cores identified trends in the three main Rio Grande reservoirs: Elephant Butte, Amistad International, and Falcon International Reservoirs (Van Metre and others, 1996).

### Setting

The study area is near the mouth of the Arroyo Colorado near Laguna Madre in South Texas (fig. 1). The Arroyo Colorado is a distributary of the Rio Grande that flows across a broad, flat, coastal plain generally known as the lower Rio Grande Valley. The Rio Grande delta contains many old river channels known locally as "resacas." The economy of the area is largely agricultural, but manufacturing, food processing, and tourism are also major economic activities.

### Field and Laboratory Methods

Bottom sediment cores were collected using a gravity corer (4 meters (m) long and 6.3 centimeters (cm) diameter), a hand corer (1 m long and 6.3 cm diameter), and a box corer (15 by 15 by 20 cm). Gravity cores were collected at site LAC from a custom-built pontoon boat, and cores were collected in shallow water at sites LAT and LMD by pushing core liners into the sediments by hand. Box cores were collected at all three sites.

One core from each site was split lengthwise and described visually. Other cores were extruded vertically and slices removed for analysis of chemical constituents.  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  were analyzed by high-resolution gamma spectrometry (American Society for Testing and Materials, 1995). Major and trace element concentrations were determined in concentrated-acid digests using inductivity coupled plasma-atomic emission spectrometry; 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). Concentrations of organochlorine compounds and PAHs were analyzed in

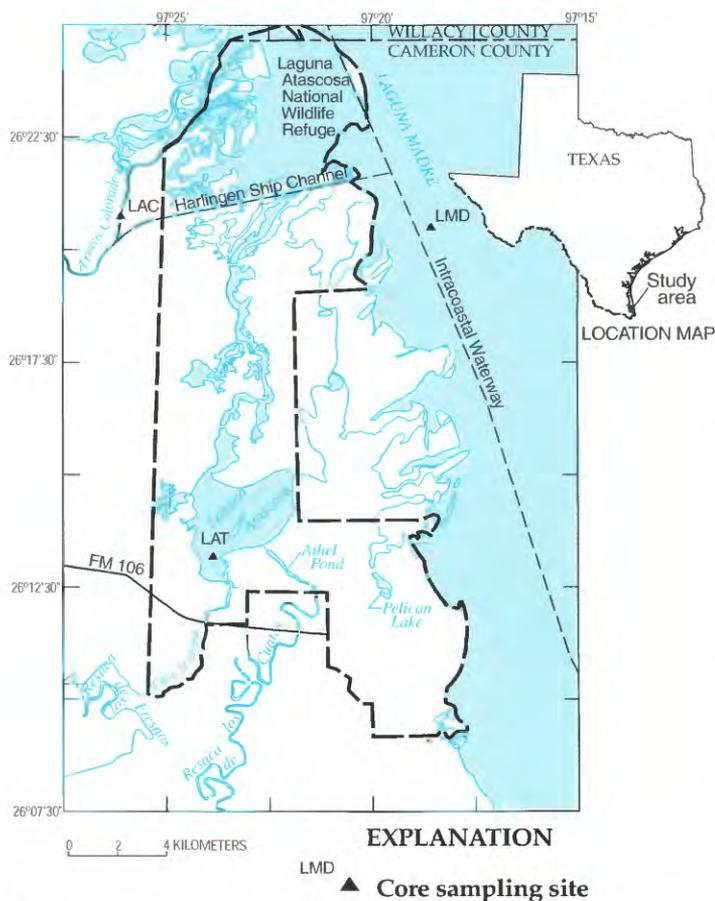


Figure 1. Location of study area and core sampling sites.

organic-solvent extracts using a dual capillary-column gas chromatograph with dual electron-capture detectors (Foreman and others, 1995; E.T. Furlong, U.S. Geological Survey, written commun., 1996). Methods of sample collection and analyses are similar to those used by the NAWQA Program in lakes and reservoirs (Van Metre and Callender, 1997; Van Metre and others, 1997).

## Age-Dating

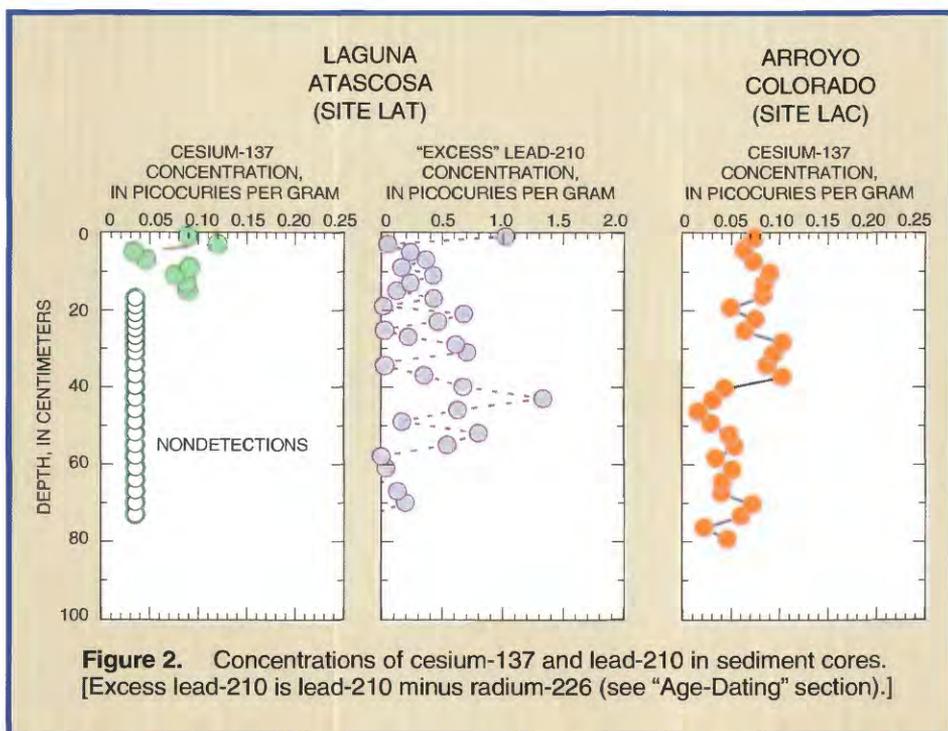
Sediment coring to identify trends is done in aquatic settings where sediments accumulate over time and where physical mixing and chemical alteration of the sediments after deposition are minimal. One prerequisite to identifying trends in contaminants in a core is to age-date the core. The most common approaches for age-dating recent (about 100 years or less) sediments is to measure  $^{137}\text{Cs}$  and (or)  $^{210}\text{Pb}$  in the core samples.  $^{137}\text{Cs}$  is a radionuclide released to the global environment by atmospheric testing of nuclear weapons. Age-dating using the naturally occurring  $^{210}\text{Pb}$  is based on the fact that  $^{210}\text{Pb}$  is separated from radium-226 ( $^{226}\text{Ra}$ ) in the uranium-238 decay series by a noble gas, radon ( $^{222}\text{Rn}$ ). As  $^{226}\text{Ra}$  in soils and rocks decays,  $^{222}\text{Rn}$  is formed, and some of it escapes to the atmosphere.  $^{222}\text{Rn}$  decays within a few days to form  $^{210}\text{Pb}$ , which as a metal, typically attaches to fine particles and falls to the earth. Surficial soils, therefore, have more  $^{210}\text{Pb}$  than would be expected from the decay of  $^{226}\text{Ra}$  contained in them.  $^{210}\text{Pb}$  decays with a half-life of about 22 years, so the “excess”  $^{210}\text{Pb}$  in surficial soils gradually decays after those soils (or sediments) are buried. This excess  $^{210}\text{Pb}$  provides an indication of the age (since exposure at the surface) of buried sediments.

Both  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  were measured in the LAT core, and  $^{137}\text{Cs}$  was measured in the LAC core (fig. 2). Down-core profiles of  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  do not show the characteristics of stable deposition over time indicated by many other lake and reservoir cores (Van Metre and others, 1998). Concentrations of  $^{137}\text{Cs}$  are small, but detectable, to the bottom of the LAC core and small,

but variable, in the top 16 cm of the LAT core. Neither core shows a definite  $^{137}\text{Cs}$  peak indicating sediments deposited during about 1963–64 to coincide with nuclear weapons testing, as expected. Excess  $^{210}\text{Pb}$  in the LAT core shows an unusual distribution with the largest concentrations deeper in the core (fig. 2). These profiles indicate three possibilities: (1) major post-depositional disturbance of sediments, perhaps by hurricanes or other storms; (2) very rapid sedimentation combined with highly variable inputs of older,  $^{137}\text{Cs}$ - and excess  $^{210}\text{Pb}$ -free sediments, perhaps influenced by dredging; and (or) (3) substantial, nonuniform loss of  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  by leaching. The first two possibilities are considered more likely to result in the observed profiles than the third possibility. Regardless of the causes, these cores cannot be reliably age-dated on the basis of available information. Possibly the only sediment-age related information indicated by the radionuclides is that on the basis of  $^{137}\text{Cs}$  and excess  $^{210}\text{Pb}$  at depth, some of the sediment in these cores is of recent origin.

## Organic Compounds

Three types of organic compounds were analyzed in the cores—organochlorine pesticides, PCBs, and PAHs. Except for a concentration of 40 micrograms per kilogram ( $\mu\text{g}/\text{kg}$ ) of DDE (fig. 3), a common breakdown product of DDT, concentrations of organic compounds were small in the three cores. Organochlorine pesticides and PCBs were not detected in the LMD core; DDE was the only organochlorine pesticide detected in the LAT and LAC cores. Very small concentrations of several common PAHs were detected—for example, the most commonly detected PAH in aquatic sediments, fluoranthene, was less than  $5 \mu\text{g}/\text{kg}$  in all cores. By comparison, fluoranthene concentrations were 262 and  $1,320 \mu\text{g}/\text{kg}$  in recent sediments in White Rock Lake in Dallas, Tex., and Town Lake in Austin, Tex., respectively. The small concentrations of organic compounds indicate the lack of anthropogenic effects on sediment chemistry in the area and also could



Gravity cores are collected by lowering the coring tool from the 15-foot aluminum A-frame on a custom-built pontoon boat.

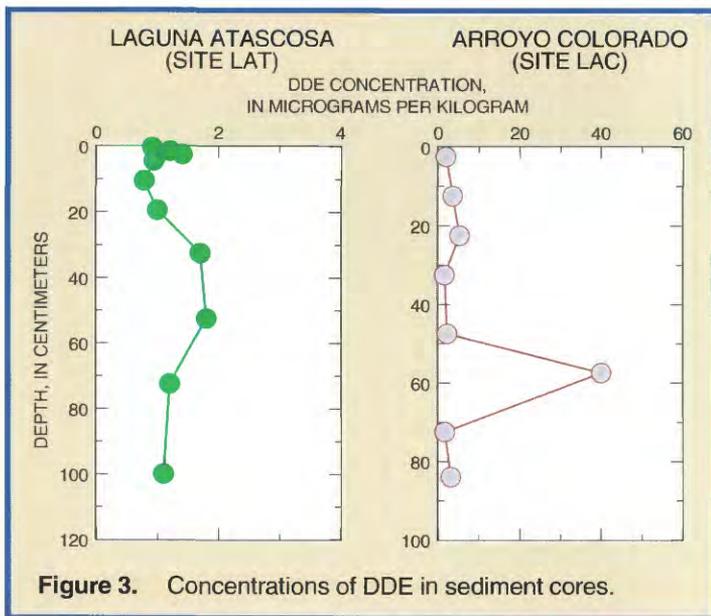


Figure 3. Concentrations of DDE in sediment cores.

indicate substantial sediment dilution by older, uncontaminated sediments, as also suggested by the radionuclide analyses.

### Metals

Unlike the radionuclides and organic compounds, several metals show vertical variations in the LAT and LMD cores (fig. 4). Metals were not analyzed in the LAC core. Because age-dating of the cores was not conclusive, it is not known whether these vertical variations represent temporal changes in inputs of these metals.

Concentrations of arsenic in the LAT and LMD cores and chromium concentrations in the LAT core are larger in near-surface sediments than in deeper sediments (fig. 4). In contrast, chromium, copper (not shown), lead, nickel (not shown), and zinc concentrations in the LMD core are smaller in near-surface sediments. Mercury was not detected in either core at the minimum reporting level of 0.04 microgram per gram ( $\mu\text{g/g}$ ). Concentrations of all these metals were relatively small compared to concentrations in some urban lakes—for example, lead concentrations in White Rock Lake ranged from 18 to 90  $\mu\text{g/g}$  (Van Metre and Callender, 1997). Concentrations also were similar or smaller than concentrations in Falcon International Reservoir on the Rio Grande, where lead ranged from 10 to 23  $\mu\text{g/g}$  (Van Metre and others, 1996).

### Implications for Aquatic Life

Sediment-quality guidelines published by three agencies are listed in table 1 along with median and maximum concentrations for each of the sediment cores and for a sediment core from Falcon International Reservoir (Van Metre and others, 1996). The guidelines are not enforceable standards; however, they do provide a basis to further evaluate the sediment data. The U.S. Environmental Protection Agency (1996) and Environment Canada (1995) guidelines 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 smaller value is referred to as the threshold effects level (TEL) and represents the concentration below which adverse effects are rarely expected to occur. The larger value, referred to as the probable effects level (PEL), is the concentration above which adverse effects are predicted to occur frequently (Environment Canada, 1995; U.S. Environmental Protection Agency, 1996). The TNRCC screening level is the 85th percentile for concentrations from historical estuary sediment samples and is not effects based.

The PELs were not exceeded by either the median or the maximum concentrations of organic compounds and metals in the LAT and LMD cores. Median concentrations of organic compounds and metals in all sediment cores were less than the TELs except for DDE in the LAC core and chromium in the LMD core, both of which exceeded the Environment Canada TEL but not the U.S. Environmental Protection Agency TEL (table 1). Median concentrations also were less than the TNRCC guidelines except for one DDE concentration (LAC) and two chromium concentrations (LAT and LMD). Maximum concentrations of organic compounds and metals in all sediment cores were less than the TELs

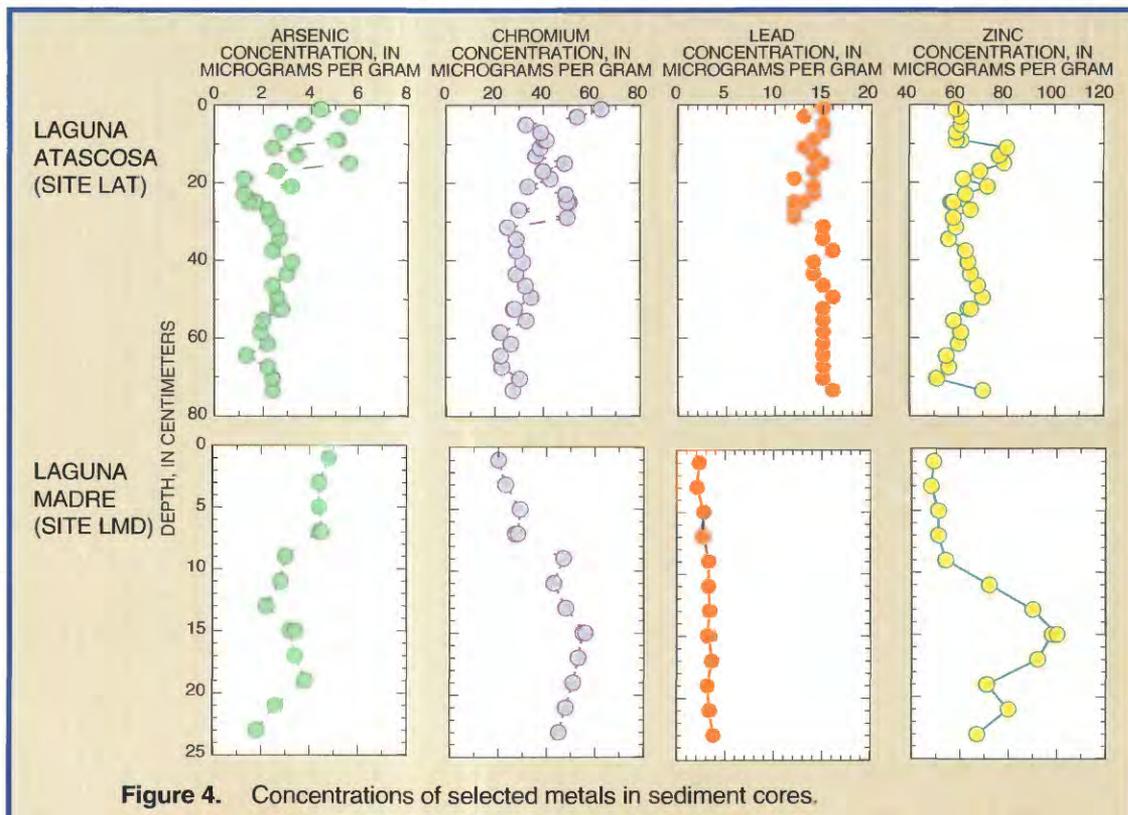


Figure 4. Concentrations of selected metals in sediment cores.

**Table 1.** Sediment-quality guidelines and median and maximum concentrations of organic compounds and metals in sediment cores[ $\mu\text{g}/\text{kg}$ , micrograms per kilogram;  $\mu\text{g}/\text{g}$ , micrograms per gram; --, not applicable or not analyzed; <, less than]

Agency or core sampling site	Effects level	DDE ( $\mu\text{g}/\text{kg}$ )	PCB ( $\mu\text{g}/\text{kg}$ )	Arsenic ( $\mu\text{g}/\text{g}$ )	Chromium ( $\mu\text{g}/\text{g}$ )	Copper ( $\mu\text{g}/\text{g}$ )	Lead ( $\mu\text{g}/\text{g}$ )	Mercury ( $\mu\text{g}/\text{g}$ )	Nickel ( $\mu\text{g}/\text{g}$ )	Zinc ( $\mu\text{g}/\text{g}$ )
<b>Sediment-quality guidelines</b>										
U.S. Environmental Protection Agency, 1996	Threshold	15	22	8.2	81	34	46.7	0.15	20.9	150
	Probable	52	189	70	370	270	218	.71	51.6	410
Environment Canada, 1995	Threshold	1.42	34	5.9	37.3	35.7	35.0	.17	18.0	123
	Probable	6.75	277	17.0	90.0	197	91.3	.49	35.9	315
Texas Natural Resource Conservation Commission <sup>1</sup>	Statewide 85th percentile	1.5	10	6.2	29	26	30	.29	18	120
<b>Median (maximum) concentrations</b>										
Laguna Atascosa (LAT)	--	1.1 (1.8)	<15 (<15)	2.6 (5.6)	33 (64)	4.0 (4.6)	15 (16)	<.04 (<.04)	11.9 (14.0)	61 (80)
Arroyo Colorado (LAC)	--	2.5 (40)	<15 (<15)	--	--	--	--	--	--	--
Laguna Madre (LMD)	--	<.5 (<.5)	<15 (<15)	3.3 (4.8)	44 (56)	10 (16.4)	3.2 (3.8)	<.04 (<.04)	12.2 (20.1)	60 (100)
Falcon International Reservoir <sup>2</sup>	--	6.0 (14)	<1 (<1)	12 (25)	36 (51)	14.5 (19.0)	15 (23)	--	19.0 (24.0)	85 (100)

<sup>1</sup> Guidelines are for estuaries.<sup>2</sup> Van Metre and others, 1996.

except for DDE in the LAC core, which exceeded both TELs; and DDE and chromium in the LAT core and chromium and nickel in the LMD core, each of which exceeded the Environment Canada TEL. The maximum DDE concentration in the LAC core was the only concentration that exceeded the Environment Canada PEL. This anomalously large concentration was measured about 60 cm below the sediment surface (fig. 3) and therefore, is of little immediate concern to biota.

The organic compound and metals concentrations in the sediment cores are similar to, or less than, concentrations measured in a core from Falcon International Reservoir in 1995. On the basis of the sediment-quality guidelines and the comparisons to other sediments, sediments from the Laguna Atascosa, Arroyo Colorado, and Laguna Madre sites are relatively uncontaminated by organochlorine pesticides, PCBs, PAHs, and heavy metals.

## References

- American Society for Testing and Materials, 1995, Standard practice for alpha-particle spectrometry of water: American Society for Testing and Materials, v. 11.02, ASTM D3084-95.
- Environment Canada, 1995, Interim sediment quality guidelines: Ottawa, Ontario, Ecosystem Conservation Directorate, Evaluation and Implementation Branch, 63 p.
- Foreman, W.T., Connor, B.F., Furlong, E.T., Vaught, D.G., Merten, L.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of organochlorine pesticides and polychlorinated biphenyls in bottom sediment by dual capillary-column gas chromatography with electron-capture detection: U.S. Geological Survey Open-File Report 94-140, 78 p.
- Leahy, P.P., Rosenshein, J.S., and Knopman, D.S., 1990, Implementation plan for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 90-174: 10 p.
- Lichte, F.E., Golightly, D.W., and Lamothe, P.J., 1987, Inductively coupled plasma atomic emission spectrometry, in Baedecker, P.A., ed., Methods for geochemical analysis: U.S. Geological Survey Bulletin 1770, p. B1-B10.

- U.S. Environmental Protection Agency, 1996, (Draft) National sediment contaminant point-source inventory—Analysis of facility release data: Washington, D.C., Office of Water, Office of Science and Technology, EPA-823-D-96-001, 148 p.
- Van Metre, P.C., and Callender, Edward, 1997, Water-quality trends in White Rock Creek Basin from 1912-94 identified using sediment cores from White Rock Lake Reservoir, Dallas, Texas: *Journal of Paleolimnology*, v. 17, p. 239-249.
- Van Metre, P.C., Callender, Edward, and Fuller, C.C., 1997, Historical trends in organochlorine compounds in river basins identified using sediment cores from reservoirs: *Environmental Science and Technology*, v. 31, no. 8, p. 2,339-2,344.
- Van Metre, P.C., Mahler, B.J., and Callender, Edward, 1996, Water-quality trends in the Rio Grande/Río Bravo Basin using sediment cores from reservoirs: U.S. Geological Survey Fact Sheet FS-221-96, 8 p.
- Van Metre, P.C., Wilson, J.T., Callender, Edward, and Fuller, C.C., 1998, Similar rates of decrease of persistent, hydrophobic, and particle-reactive contaminants in riverine systems: *Environmental Science and Technology*, v. 32, p. 3,312-3,317.

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