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Four Total Maximum Daily Loads for Legacy Pollutants in the Arroyo Colorado Above Tidal and the Donna Reservoir and Canal System

For Segments 2202 and 2202A

Prepared by the:
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TEXAS NATURAL RESOURCE CONSERVATION COMMISSION

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Introduction

Section 303(d) of the Clean Water Act requires all states to identify waters that do not meet, or are not expected to meet, applicable water quality standards. For each listed water body that does not meet a standard, states must develop a total maximum daily load (TMDL) for each pollutant that has been identified as contributing to the impairment of water quality in that water body. The Texas Natural Resource Conservation Commission (TNRCC) is responsible for ensuring that TMDLs are developed for impaired surface waters in Texas.

In simple terms, a TMDL is a quantitative plan that determines the amount of a particular pollutant that a water body can receive and still meet its applicable water quality standards. In other words, TMDLs are the best possible estimates of the assimilative capacity of the water body for a pollutant under consideration. A TMDL is commonly expressed as a load, with units of mass per time period, but may also be expressed in other ways. TMDLs must also estimate how much the pollutant load needs to be reduced from current levels in order to achieve water quality standards.

The Total Maximum Daily Load Program, a major component of Texas' statewide watershed management approach, addresses impaired or threatened streams, reservoirs, lakes, bays, and estuaries (water bodies) in or bordering the state of Texas. The primary objective of the TMDL Program is to restore and maintain the beneficial uses (such as drinking water, recreation, support of aquatic life, or fishing) of impaired or threatened water bodies.

Section 303(d) of the Clean Water Act and the U.S. Environmental Protection Agency's (EPA) implementing regulations (40 Code of Federal Regulations, Section 130) describe the statutory and regulatory requirements for acceptable TMDLs. The TNRCC guidance document, *Developing Total Maximum Daily Load Projects in Texas* (GI-250, 1999), further refines the process for Texas. This TMDL document has been prepared in accordance with these guidelines, and is composed of the following six elements:

- Problem Definition
- Endpoint Identification
- Source Analysis
- Linkage Between Endpoint and Sources

- Margin of Safety
- Pollutant Load Allocation

This TMDL document was prepared by:

- Region 4 of the Field Operations Division of the Office of Compliance and Enforcement of the Texas Natural Resource Conservation Commission, and
- the TMDL Team in the Strategic Assessment Division of the Office of Environmental Policy, Analysis, and Assessment of the Texas Natural Resource Conservation Commission.

It was adopted by the Texas Natural Resource Conservation Commission on January 17, 2001. Upon adoption, the TMDL became part of the state Water Quality Management Plan. The Texas Natural Resource Conservation Commission will use this document in reviewing and making determinations on applications for storm water permits and in its nonpoint source pollution abatement programs.

Background Information

These TMDLs address contamination of fish tissue by several legacy pollutants in water bodies in the Lower Rio Grande Valley of south Texas:

- portions of the Arroyo Colorado above tidal, and
- Donna Reservoir and Canal, an unclassified system in Hidalgo County.

Legacy pollutant is a collective term used to describe substances whose use has been banned or severely restricted by the U.S. Environmental Protection Agency (EPA). Because of their slow rate of decomposition, these substances frequently remain at elevated levels in the environment for many years after their widespread use has ended. No additional loading of legacy pollutants is allowed or expected due to the EPA restrictions. Gradual declines in environmental legacy pollutant concentrations occur as a result of natural attenuation processes.

EPA guidance (*Draft Guidance for Water Quality-Based Decisions: The TMDL Process, Second Edition*, EPA 841-D-99-001, 1999a) on the development of TMDLs offers flexibility in addressing particular situations and unusual circumstances, allowing States the discretion to adopt different approaches where appropriate. The guidance states that the allowable pollutant load "must be expressed in a manner ... that represents attainment and maintenance of water quality standards." The guidance allows for the use of a surrogate target for situations where "no .... quantifiable pollutant load can be used to .... express the TMDL."

In preparing these TMDLs for legacy pollutants, the TNRCC has modified the typical loading allocation approach of a TMDL, which limits the amount of a pollutant that can be added to an impaired water body. Because these legacy pollutants are already restricted, and no significant additional loading is expected, these TMDLs do not specifically attempt to quantify allowable loads for these contaminants. The ultimate goal of these TMDLs is the reduction of fish tissue

contaminant concentrations to levels that constitute an acceptable risk to consumers, allowing TDH to remove the bans on fish consumption and the beneficial use to be restored to these water bodies.

Problem Definition

The water bodies covered by this TMDL document were included on the State of Texas 1998, 1999, and 2000 §303(d) lists (see corresponding *State of Texas Clean Water Act Section 303(d) List and Schedule of Development of Total Maximum Daily Loads*, SFR-58) as a result of the issuance of fish consumption advisories and bans by the Texas Department of Health (TDH). The TDH actions were taken following determinations of unacceptable human health risk due to elevated concentrations of one or more legacy pollutants in fish tissue (Table 1).

Table 1. Lower Rio Grande Valley water bodies on the State of Texas 303(d) list due to concentrations of legacy pollutants in fish tissue that have resulted in the issuance of a fish consumption advisory or ban by the Texas Department of Health.

Segment Number	Segment Name (Portion Covered by TDH Fish Consumption Ban or Advisory)	Fish Tissue Contaminants on the 303(d) List	TDH Action
2202	Arroyo Colorado Above Tidal (Arroyo Colorado upstream of the Port of Harlingen, including Llano Grande Lake and the main floodway)	Chlordane Toxaphene DDE	Consumption advisories issued in 06/1993 and 11/1993*
2202A	Donna Reservoir and Canal (entire reservoir and main canal)	PCBs	Consumption ban issued in 04/1994

*Updates to 1980 consumption advisory issued for portions of the Arroyo Colorado.

The impacted water bodies lie within Hidalgo and Cameron Counties, in the Nueces–Rio Grande Coastal Basin, which lies on the coastal plain between the Nueces River and the Rio Grande in the Lower Rio Grande Valley of south Texas (Figure 1):

- Segment 2202 (Arroyo Colorado above Tidal) extends from a point 100 meters downstream of Cemetery Road south of the Port of Harlingen in east-central Cameron County, upstream to Farm-to-Market (FM) Road 2062 near the City of Mission in south-central Hidalgo County. The segment includes the Main Floodway and Llano Grande Lake, but does not include the North Floodway.
- Donna Reservoir (Segment 2202A) is a 400-acre impoundment located southwest of the City of Donna in southeast Hidalgo County, within the Arroyo Colorado watershed. Water for the Donna Reservoir is pumped from the Rio Grande, through a seven mile elevated earthen Main Canal, to the reservoir.

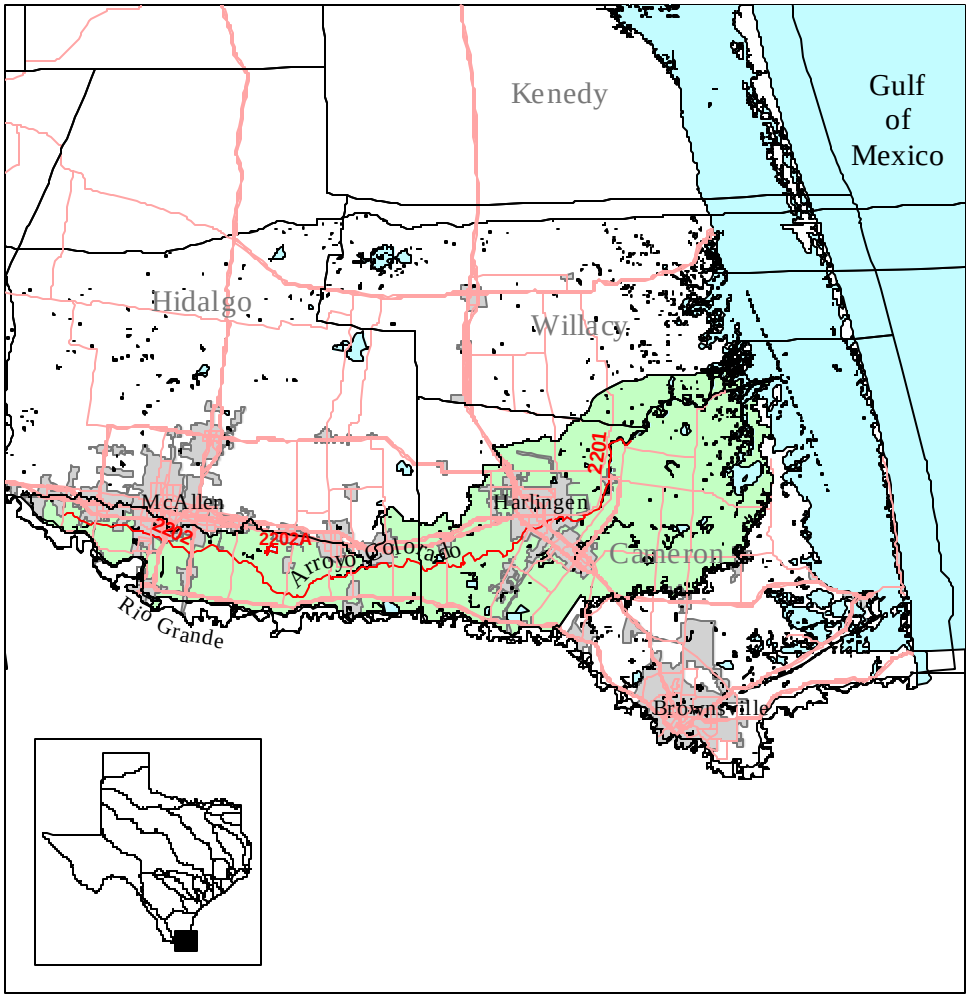

Figure 1. Study Area in the Lower Rio Grande Valley.

The Arroyo Colorado system is the major drainage for Cameron, Hidalgo, and Willacy Counties. The Arroyo consists of two major channels that drain a 2344 square mile watershed (TWC 1990). The Main Floodway extends from the headwaters near the City of Mission in southwest Hidalgo County, to Llano Grande Lake southwest of the City of Mercedes in southeast Hidalgo County. Llano Grande Lake is a long, shallow depression that acts as a large settling basin, collecting much of the upstream sediment load.

The main channel of the Arroyo Colorado continues downstream from Llano Grande Lake, across southern and central Cameron County to the Port of Harlingen (UTPanAm 1995). The tidal portion of the main Arroyo Colorado (Segment 2201) flows northeast from the Port of Harlingen, and discharges into the Laguna Madre. The main floodway and channel portion of the Arroyo Colorado, from the headwaters to the Laguna Madre, drain a 675 square mile watershed (TNRCC 2000).

The North Floodway splits from the Main Floodway of the Arroyo Colorado at the upper end of Llano Grande Lake. The vast majority of Willacy County drains to the North Floodway, as does a significant portion of northern and eastern Hidalgo County and a small portion of northwestern Cameron County. During flood conditions (flow >1400 cubic feet per second), approximately 60 percent of the flow in the Arroyo is diverted into the North Floodway (see TWC 1990).

Aquatic Life Advisories 5 and 6 were issued on 24 June and 17 November 1993, respectively, advising persons "... not to consume any species of fish ..." from the Arroyo Colorado upstream from the Port of Harlingen, including Llano Grande Lake and the Main Floodway, due to elevated levels of chlordane, DDE, and toxaphene in fish tissue (TDH 1997). These advisories were updates to a 1980 advisory issued for portions of the Arroyo Colorado. The North Floodway is not covered by the consumption advisories.

The Arroyo Colorado lies in an extensive agricultural belt, where numerous crops are grown year-round, and where heavy pesticide applications are frequent (White *et al.* 1983). More than 90 percent of Hidalgo County, and more than 80 percent of Cameron County, are farm and ranch land (Garza 1999; Garza and Long 1999). The Arroyo Colorado watershed contains approximately 290,000 acres of irrigated cropland in these two counties. Primary agricultural crops include cotton, corn, grain, sorghum, sugercane, citrus, and a variety of vegetables (TAES 2000).

Significant urbanization began in areas adjacent to the Arroyo Colorado in the late 1980s, particularly in the western and central portions of the watershed. The population in Hidalgo County more than doubled, while that of Cameron County nearly doubled, between 1970 and 1990 (Chapman *et al.* 1998). Perennial flow in the Arroyo begins at the City of Mission wastewater treatment plant (WWTP) discharge, and is sustained primarily by municipal WWTP discharges, with the seasonal addition of irrigation return flows and urban runoff (Davis 1989; Chapman *et al.* 1998). There are currently 34 active wastewater discharge permits associated with the Arroyo Colorado (31 domestic WWTPs and three industrial outfalls), with a total permitted flow of approximately 55 million gallons per day. Flood water overflows from the Rio Grande can be diverted into the Main Floodway south of the City of Pharr. This diversion occurs infrequently, during extreme flood events.

Donna Reservoir (Segment 2202A) is a 400-acre impoundment located 0.5 mile southwest of the City of Donna in southeast Hidalgo County, within the Arroyo Colorado watershed. Water for the reservoir is pumped from the Rio Grande (Segment 2302) at a point approximately one mile downstream from the Reynosa, Tamaulipas, Mexico WWTP outfall (Webster *et al.* 1998). Fish can be pumped into the canal, but cannot return to the Rio Grande. The water flows through a seven mile elevated earthen Main Canal, passing under the Arroyo Colorado via a concrete siphon. The only apparent hydrologic connections between the Donna system and the Arroyo Colorado are shallow groundwaters and possible leakage into and out of the siphon (Webster *et al.* 1998, 1999).

The Donna Reservoir is partially divided into eastern and western portions by FM 1423 (Valley View Road), which acts as a causeway. The reservoir is used for water supply and irrigation storage by the City of Donna and surrounding areas. The area around the reservoir and canal is primarily irrigated crops and pastureland, with scattered residences (Webster *et al.* 1998). Area roads provide easy access for fishing along 80 percent of the canal and reservoir shoreline. Residents of nearby colonias and other low-income areas use local fish as a supplement to their diets. Aquatic Life Order No. 9 was issued on 4 February 1994, prohibiting persons "... from possessing any species of fish ..." from Donna Reservoir and its interconnecting canal system due to elevated levels of PCBs in fish tissue (TDH 1997).

The fish consumption use of a water body is not supported when TDH has issued a fish consumption ban or advisory. The fish consumption restrictions on the water bodies addressed here are the result of contamination by one or more organochlorine insecticides, degradation products of organochlorine insecticides, and polychlorinated biphenyls (PCBs).

Organochlorine insecticides and PCBs were widely used in the U.S. prior to EPA restriction, and are common environmental contaminants (Moore and Ramamoorthy 1984; Schmitt *et al.* 1985, 1990; Smith *et al.* 1988; USGS 2000). These substances are a frequent cause of fish consumption advisories in the U.S. (EPA 1999b,c,d), and elevated concentrations of some of these contaminants are frequently found in game fish tissue (Kuehl *et al.* 1994). Fish consumption can be a primary route of human exposure to these contaminants (Schwartz *et al.* 1983; Humphrey 1987; Fiore *et al.* 1989), which can cause a variety of adverse health effects (Swain 1988; Longnecker *et al.* 1997).

Endpoint Identification

The ultimate goal of these TMDLs is the reduction of fish tissue contaminant concentrations to levels that constitute an acceptable risk to fish consumers, allowing TDH to remove the bans on fish consumption. The allowable load of contaminant is based on fish tissue concentrations.

EPA (1997a) provides guidance for assessing contaminant data for risk assessment. This guidance and TDH assumptions were used to develop target values for tissue contaminant levels that result in an acceptable risk level. EPA (1997a) presents equations for calculating the maximum allowable fish consumption rate given consumer body weight, contaminant concentration, an acceptable cancer risk level, and the contaminant risk values for carcinogenic and noncarcinogenic risk. A cancer potency value (q_1*) is the risk value for carcinogens. The oral reference dose (RfD) is the risk value used to protect against chronic exposure by noncarcinogens.

The consumption rate and consumer body weight were set at the TDH constants of 30 grams of fish per day (0.03 kg/d) for a 70-kg adult, and at 15 grams of fish per day (0.015 kg/d) for a 15- and 35-kg child, both over a 30-year time period. TDH uses an acceptable cancer risk level of 1×10^{-4}, adjusted to 2.33×10^{-4} to account for the use of the 30-year time period.

Cancer potency and chronic RfD values (Table 2) were obtained from EPA (1997a) and the EPA IRIS database.

Equations in EPA (1997a) were solved to calculate the maximum allowable concentration of contaminant in tissue (1) at a given cancer risk level, and (2) based on the noncarcinogenic health effects of a contaminant:

(1) $C_m = (ARL)(BW) / (C_{lim})(q_1^*)$

(2) $C_m = (RfD)(BW) / (C_{lim})$

where

C_m = maximum allowable concentration of contaminant in tissue (mg/kg)
ARL = acceptable cancer risk level = 2.33×10^{-4}
BW = consumer body weight (kg)
C_{lim} = allowable fish consumption rate (kg/d)
q_1^* = cancer slope factor for given contaminant (see Table 2)
RfD = oral reference dose for given contaminant (see Table 2).

Substituting adult and child consumption rates and body weights used by TDH, the maximum tissue contaminant concentrations that can be consumed within an acceptable level of risk were calculated (see Table 2).

Table 2. Maximum fish tissue concentrations (mg/kg) for individual contaminants that can be ingested by consumers of given body weights, within the acceptable cancer risk level (ARL) used by TDH, and without causing adverse noncarcinogenic health effects. Carcinogenic (q_1^*) and noncarcinogenic (RfD) risk values were obtained from EPA (1997a) and EPA IRIS database.

	Carcinogenic Risk ARL = 2.33×10^{-4}			**Noncarcinogenic Risk**		
	Maximum Fish Tissue Concentration (mg/kg)					
		Consumer Body Wt.			**Consumer Body WT.**	
Contaminant	**q_1^***	**15-kg**	**35-kg / 70-kg**	**RfD**	**15-kg**	**35-kg/70-kg**
Total Chlordane	0.35	0.67	1.55	5×10^{-4}	0.5	1.17
Total DDT[1]	0.34	0.68	1.6	5×10^{-4}	0.5	1.17
DDD	0.24	0.97	2.3	na	na	na
DDE	0.34	0.68	0.68	na	na	na
Toxaphene	1.1	0.2	0.5	3.6×10^{-4}	0.36	0.84
Total PCBs	2.0	0.12	0.27	2×10^{-5}	0.02	0.05

[1]Sum of 4,4'- and 2,4'- isomers of DDT, DDE, and DDD (EPA 1997a).
na = Separate RfDs not available for DDE and DDD.

The calculated contaminant concentrations are valid targets only for each contaminant individually. The PCB target can be used for the Donna Reservoir and Canal because the TDH risk assessment identified PCBs as the risk factor. The target concentration that will achieve an acceptable noncarcinogenic risk is less than that needed for an acceptable carcinogenic risk. The target concentration for a 15-kg child is less than that of a 35-kg child and 70-kg adult (see Table 2). The noncarcinogenic value for a 15-kg child is therefore most protective, and this value (0.02 mg/kg) becomes the endpoint target for PCBs in the Donna Reservoir and Canal (Table 3).

The situation is different in the Arroyo Colorado, where multiple contaminants were determined to be contributing to risk. TDH assumes that risk is additive when more than one contaminant is present at sufficient levels. The additive risk of all contaminants cannot exceed either the cancer risk level or a noncarcinogenic hazard index. When multiple contaminants are present, the concentration of one or more must be reduced so that the additive carcinogenic risk does not exceed 2.33×10^{-4}. The endpoint target for carcinogenic risk in this case is an additive risk that is no greater than the acceptable cancer risk level (Table 3).

Table 3. Most protective endpoint target for fish tissue contamination in each §303(d) list water body that will allow removal of the TDH fish consumption ban.

Segment	Primary Endpoint Target
Arroyo Colorado (2202)	additive cancer risk $\leq 2.33 \times 10^{-4}$ cumulative noncarcinogenic hazard index ≤ 1
Donna Reservoir and Canal (2202A)	≤ 0.05 mg/kg PCB in fish tissue for adults ≤ 0.02 mg/kg PCB in fish tissue for children
All Water bodies	Removal of fish consumption bans

The noncarcinogenic hazard index is the sum of the hazard ratios of each individual contaminant, and must be no greater than one for noncarcinogenic risk to be acceptable. The hazard ratio of a contaminant is the ratio of the actual noncarcinogenic exposure level to the oral reference dose (RfD). When multiple contaminants are present, the concentration of one or more must be reduced so that the additive hazard index does not exceed one. The endpoint target for noncarcinogenic risk is a hazard index that is no greater than one (Table 3).

The calculated target values are valid only under the assumed conditions. TDH has the authority and jurisdiction for the decision to issue or remove fish consumption bans. Subsequent risk assessments by TDH may result in no change to a ban, removal of the ban, or a shift to an advisory for certain groups at greater risk. The ultimate endpoint goal for the affected water bodies is the protection of all groups and complete removal of the fish consumption bans.

Source Analysis

Production and use of legacy pollutants has been banned or severely restricted by the EPA. Because of their past heavy and widespread use, strong affinities for sorption to sediment organic matter and tissue, and slow rates of decomposition, these substances and/or their degradation products frequently remain at elevated levels in the environment for many years after widespread use has ended (Moore and Ramamoorthy 1984; Smith *et al.* 1988; Jones and de Voogt 1999; USGS 2000).

- Chlordane was introduced in 1948, and was used extensively as a broad spectrum insecticide to control soil insects on agricultural crops, as a home lawn and garden insecticide, as a fumigating agent, and for termite control (EPA 1980a; Dick 1982; Dearth and Hites 1991). EPA suspended use of chlordane on food crops in 1978, and phased out other above-ground uses over the following five years (EPA 1997b; Mattina *et al.* 1999). All uses except underground application for termite control were banned in 1983 (Mattina *et al.* 1999). Manufacture and domestic sales were halted in 1987, and use of existing stores was allowed until April 1988 when sale and use were terminated (Dearth and Hites 1991; EPA 1997b; Mattina *et al.* 1999).
- DDE is the major degradation product of DDT and DDD, and is among the most widely occurring pesticide residues (Schmitt *et al.* 1990; Kuehl *et al.* 1994). DDT was initially used in World War II for control of disease-carrying insects, and was used extensively as a broad spectrum insecticide for the control of almost all agricultural and disease-carrying insects (EPA 1980b; NPTN 1999). It was used extensively in the 1950s and 1960s for mosquito control in urban areas. DDD is a metabolite of DDT, and was itself manufactured as a pesticide for several years. Most uses of DDT, and all uses of DDD, were banned by EPA in December 1972 (EPA 1980b).
- Toxaphene was introduced in 1948, and used primarily in the southern U.S. to control agricultural insects. It was used predominately on cotton, but also on grains, alfalfa, fruit, and vegetables. Toxaphene was also used to control insect pests on livestock, and as a piscicide (Andreasen 1985; ATSDR 1997). Toxaphene replaced DDT in many agricultural uses after the 1972 ban on DDT use, particularly in the south (Harner *et al.* 1999), and was the most heavily used insecticide in the U.S. during the 1970s (EPA 1999c). Most uses of toxaphene were canceled in 1982, and all uses were banned in 1990 (ATSDR 1997; EPA 1999c).
- Polychlorinated biphenyls (PCBs) are a group of synthetic organic chemicals containing 209 possible individual compounds, which vary in chemical and physical properties, toxicity, environmental persistence, and degree of bioaccumulation (EPA 1980c, 1999b). PCBs were manufactured as mixtures of different congeners, and generally sold under the trade name Aroclor. PCBs were most widely used as coolants and lubricants in transformers, capacitors, and other electrical equipment. In 1976 the Toxic Substances Control Act banned, with limited exceptions, the

manufacture, processing, distribution in commerce, and use of PCBs (EPA 1994). TSCA also required the EPA to promulgate regulations for proper use, cleanup, and disposal. TSCA and subsequent EPA rules did not require PCB-containing materials to be removed from service, and many are still in use (EPA 1999b). A substantial portion of the PCBs manufactured before 1977 remain in service, although these are being phased out as equipment is replaced or decontaminated.

Organochlorine insecticides have entered aquatic systems as a result of direct application to a water body, drift from aerial spraying, urban and agricultural runoff, spills, industrial and municipal wastewater discharges, and erosion of contaminated soils (Dick 1982; Smith *et al.* 1988; Van Metre *et al.* 1998). PCBs can enter the environment via spills and leaks from sites where they are used, improper disposal methods, and leaching from landfills (Tanabe 1988). Studies that have examined the relationship between land use and contamination by legacy pollutants suggest that problems can originate from both urban and agricultural land uses (White *et al.* 1983; Stamer *et al.* 1985; Arruda *et al.* 1987; Smith *et al.* 1988; Ulery and Brown 1995; Pereira *et al.* 1996; Moring 1997; Mattina *et al.* 1999; Black *et al.* 2000), although determination of a specific source can be very difficult (Tate and Heiny 1996; Munn and Gruber 1997; Webster *et al.* 1998).

Arroyo Colorado

The Arroyo Colorado watershed is an intensively farmed area (TAES 2000). Agricultural chemicals are used year-round in the lower Rio Grande Valley, and the extensive drainage network in the area routes considerable amounts of agricultural runoff into the Arroyo Colorado. The use of pesticides on surrounding cropland probably accounts for a substantial portion of the fish tissue residues in the Arroyo Colorado, as all three pesticides of concern were used extensively for control of agricultural insects. Davis (1989) concluded that overall occurrences of toxic chemicals in the Arroyo Colorado watershed were mainly attributable to agricultural nonpoint sources. DDT was banned prior to any appreciable urbanization in the area. Toxaphene subsequently replaced DDT in many agricultural uses, particularly for control of cotton insects. Surveys conducted prior to any significant urbanization in the area found fish to be highly contaminated with DDE and toxaphene (White *et al.* 1983). The use of toxaphene, especially on cotton fields, was observed at the time of that study. Elevated DDE and toxaphene levels in Llano Grande Lake fish may reflect the tendency of the lake to act as a settling basin, resulting in the accumulation of pesticide-laden suspended solids from upstream areas.

Runoff was mostly associated with agricultural land uses until 20-30 years ago, when urbanization and associated population increase began to occur in the region (Chapman *et al.* 1998). Erosion as a result of more recent urban development along the Arroyo Colorado may have contributed contaminants attached to the previously agricultural source soils. Municipal WWTP discharges also may have contributed pesticides to the Arroyo. Studies conducted in 1981-82 (see Davis 1984) found pesticide levels to be higher in discharges from WWTPs that received washings from fruit and vegetable processing plants.

Urban and rural residents may have continued using existing stocks of chlordane until the late 1980s, since it was in use longer than some of the other legacy insecticides. Arruda *et al.* (1987) reported anecdotal evidence of significant home and garden use of chlordane after the 1983 EPA ban on that particular use. Van Metre and Callender (1997) found the chlordane peak in sediment cores from White Rock Lake in Dallas to have occurred around 1990, reflecting relatively recent urban use. Because much of the more extensive urbanization along the Arroyo occurred after the chlordane ban, urban runoff may not have been as significant a contributor of chlordane as in more heavily urbanized areas.

Three Superfund sites contaminated with pesticides are located within the Arroyo Colorado watershed (see <http://www.tnrcc.state.tx.us/permitting/remed/superfund/>), and may have been sources of contaminants (White *et al.* 1983; Davis 1984). All three sites were placed on the first Texas Superfund registry on16 January 1987. Two of the sites are in the City of Mission, near the Arroyo headwaters, while the third is near the downstream end of the segment in the City of Harlingen:

- The Munoz Borrow Pits site is located 0.1 mile south of U.S. Highway 83, on the east side of State Highway 1016 in Mission. During the late 1950s, the property owner accepted several dump truck loads of soil contaminated with pesticides, including DDT. The contaminated soil was excavated and removed for off-site disposal in mid-1997, and the site was removed from the Superfund registry in September 1998.
- The Hayes-Sammons Warehouse site is located on Miller Avenue and East Eighth Street in downtown Mission. Two warehouses were used from 1945-1968 for the storage of commercial-grade pesticides. Soil contaminants at the site included DDT. Demolition and off-site disposal of the warehouses, excavation and off-site disposal of approximately 1700 cubic yards of contaminated soil, and backfilling and grading of the excavated areas occurred in June-October 1998. A remedial action report was approved by TNRCC in April 1999, and the site was proposed for deletion from the Superfund registry. Following a public hearing, TNRCC announced in March 2000 that additional soil testing would be performed. Follow-up activity is underway.
- The Niagara Chemical site is located west of the intersection of Commerce Street and Adams Avenue near downtown Harlingen. A two-acre site was used from 1946-1962 to formulate dry and liquid pesticides. Formulation ceased in 1962, and liquid formulation equipment was removed. All remaining equipment was removed in 1968. The buildings were razed in 1970, leaving only concrete slabs. Pesticide contamination of groundwater and soil was detected at the site. A final Administrative Order was issued in December 1996 requiring excavation, removal, and off-site disposal of contaminated soils and materials, followed by ten years of groundwater monitoring to confirm natural attenuation. The remedial action was performed in August 1997 through April 1998. Groundwater monitoring began in June 1998 and is ongoing.

Donna Reservoir and Canal

Webster *et al.* (1998, 1999) conducted extensive investigations into the PCB contamination in the Donna Reservoir and Canal, but were unable to locate a specific source. No visible oil contamination was observed in the vicinity of the Donna intake pumps, and there were no detectable PCBs in sludges collected from a below-ground equipment sump at the pump site, or in sediment samples collected within 20 meters of the pumps (Webster *et al.* 1998). PCB oils were used as carriers for hydrophobic pesticides prior to 1978, but agricultural runoff is considered an unlikely source because the Donna Canal is elevated above ground level, and because much of the land around the reservoir is pasture rather than cropland (Webster *et al.* 1998).

Two closed municipal landfills and numerous unauthorized dump sites are present in the area around the reservoir and canal. Indiscriminate dumping of municipal, agricultural, commercial, construction, and some industrial waste is rather common in the area (Webster *et al.* 1999). Illegal dumping was observed at numerous sites around the reservoir, but not in the immediate vicinity of the canal where PCB contamination appears greatest. No PCBs were detected in sediment samples from a shallow groundwater seep on the reservoir bank, just down-gradient from a sizeable unauthorized disposal site on the northwest side of the reservoir (Webster *et al.* 1998). Results of sediment sampling along the leachate line of shallow groundwater seeping from the closed Alamo landfill, located 0.25 mile upgradient from the reservoir and canal, appear to effectively eliminate that site as the PCB source (Webster *et al.* 1999). No PCBs were detected in shallow groundwater samples from a monitoring well at the closed Donna Landfill, which is located approximately 0.5 mile downgradient from the reservoir and canal (Webster *et al.* 1998).

In a joint investigation with the TNRCC , the U.S. Geological Survey (USGS) has also investigated the source of the PCB contamination in the Donna Reservoir and Canal (*USGS Final Progress Memoranda dated December 2000*). Suspended sediment samples were collected in the canal near the Donna intake pumps, upstream and downstream from the siphon, and in the Arroyo Colorado approximately 50 meters downstream from the siphon in February 1999. No PCBs were detected (<0.014 and <0.032 mg/kg detection limits) at those locations.

Results of subsequent sampling have yielded significant detections of PCBs in suspended sediment at specific sampling points in the canal, with a decreasing trend in concentration in a downstream direction from the highest detectable PCB value. Four suspended sediment samples were collected in the canal in July 1999, between the siphon and Donna Reservoir. PCBs (Aroclor 1254) were detected at all four locations, with the largest concentration (0.102 mg/l) at the most upstream location, just downstream from the 90-degree bend in the canal.

Sediment cores were also collected in July 1999 from the east and west portions of the reservoir. Very low concentrations were detected (0.004 - 0.007 mg/kg in the top 15-cm of the west core, and <0.005 mg/kg in the east core). No evidence of a historical release of PCBs to the reservoir was found.

Additional suspended sediment sampling was conducted in January 2000 in an attempt to further bracket the possible PCB source. Samples were collected at 60-meter intervals between the siphon discharge and FM 1423 in an effort to further isolate the PCB source. Those results have narrowed the location of a probable source of PCBs to a 35-m long stretch on the right bank of Donna Canal just downstream the siphon outlet. However, a relatively high detection of PCBs detected upstream of 90° Bend in July 2000, suggests that a second PCB source may be located between the downstream end of the syphon and the upstream end of 90° Bend. Additional sampling will be required to confirm the exact location(s) of potential source(s).

Linkage Between Endpoint and Sources

The time required for the reduction of legacy pollutant tissue concentrations to endpoint levels is a function of their persistence and fate in the environment. Organochlorine insecticides and PCBs are extremely hydrophobic, and their affinity for sorption to soil and sediment, along with their tendency to partition into the lipid of aquatic organisms, determine their transport, fate, and distribution (Smith *et al.* 1988).

Numerous studies have documented the long-term persistence of organochlorine pesticides and their degradation products in soil. Pesticide residue concentrations in soils can span several orders of magnitude, and are a reflection of application history and loss rates (Lichtenstein *et al.* 1971; Harner *et al.* 1999). Heavily used pesticides will be present in higher concentrations years later. Degradation rates of organochlorine residues are highly variable, and soil half-lives of as much as 20 to 35 years have been reported (Nash and Woolson 1967; Dimond and Owen 1996; Mattina *et al.* 1999).

The primary method of transport of legacy pollutants into aquatic systems is by erosion of soil and attached contaminants (Munn and Gruber 1997). Sedimentation has been observed to be a major cause of legacy pollutant loss from the water column, particularly in lakes (Hamelink and Waybrant 1976; Schnoor 1981; Bierman and Swain 1982). Aquatic sediments act as a reservoir for hydrophobic pesticides and PCBs (Moore and Ramamoorthy 1984). Contaminants may be present in sediment at concentrations that are orders of magnitude higher than in the water column, where they are typically very low or undetectable (see Smith *et al.* 1988).

These contaminants degrade slowly, and may be present for long periods of time (Oliver *et al.* 1989; EPA 1999b). Van Metre *et al*. (1998) analyzed sediment core samples from 11 reservoirs, including White Rock Lake in Dallas, and determined mean sediment half-lives of 7.7 to 17 years for chlordane, 13 $\pm$ 5.8 years for total DDT, and 9.5 $\pm$ 2.2 years for PCBs. Field and laboratory studies of contaminated sediments have found that the greatest amount of PCB dechlorination occurs during a relatively short and rapid initial phase after contaminant input, but then slows or effectively ceases (Rhee *et al.* 1993; Sokol *et al.* 1998).

Sediments may act as long-term sources of contamination through desorption of contaminants, and as a result of the resuspension of sediment particles by disturbances (Oliver *et al.* 1989; Baker *et al.* 1991; Zaranko *et al.* 1997; Maher *et al.* 1999). Sediment-associated contaminants can be a long-term source of chronic toxicity to organisms that live or feed in contact with the sediments, and provide a source for the introduction of contaminants into the food web (Reynoldson 1987; Farrington 1991; Larsson 1986).

Organochlorine insecticides and PCBs are highly lipophilic and rapidly accumulate in the tissue of aquatic organisms. Contaminant concentrations are found in fish tissue at levels considerably higher than that of the water column and sediments (Smith *et al.* 1988; Rinella *et al.* 1993; EPA 1997a, 1999b). Fish tissue contaminant concentrations can vary within the same water body (Stow *et al*. 1995; Lamon and Stow 1999), and among different fish species, size classes within a fish species, and various tissues within a fish (Swackhamer and Hites 1988; EPA 1997a).

A large number of factors have been found to influence contaminant uptake, accumulation, and elimination in fish and other aquatic organisms. Characteristics of fish species and their environments are very important to uptake and elimination processes (Swackhamer and Hites 1988). Fish characteristics include lipid content, age, length, weight, diet and feeding habits, reproductive status, contaminant transfer from females to young, growth dilution, metabolism, and other species-specific physiological factors. Environmental factors include contaminant levels in food items, trophic position and length of the food chain, habitat use and movement, seasonal variation in contaminant availability, water column contaminant concentration, and sediment contaminant concentration and bioavailability. The relative importance of these factors is much debated, and research has found the effects of many of them to be interrelated (Smith *et al*. 1988; Farrington 1991; Pritchard 1993; Jones and de Voogt 1999; Gobas and Morrison 2000; Sijm *et al*. 2000).

Characteristics of the contaminants also affect their tissue concentrations. These factors include differences in isomer and residue bioavailability, equilibrium time, and susceptibility to uptake, biotransformation, and elimination. Schmitt *et al.* (1985) found that changes in tissue concentrations over time vary with differences in chlordane and PCB isomers. Significant differences have been found in the accumulation rates of different PCB congeners, and in the degree of accumulation within different fish body tissues (Gruger *et al*. 1975; van der Oost *et al*. 1988; Zhou and Wong 2000).

The time necessary for a contaminant to reach equilibrium in tissue is variable, hard to determine, and generally very long. Stable organic compounds with low aqueous solubility, such as many legacy pollutants, generally exhibit the longest equilibrium times. Time to equilibrium is also a function of fish size, with larger fish accumulating contaminants at a slower rate (Smith *et al.* 1988).

Once equilibrium is reached, the time necessary for a contaminant to be eliminated from tissue is also long, often on the order of years, and variable, generally increasing with the

hydrophobicity and lipophilicity of the compound (Larsson 1986). Contaminant elimination may occur through respiration, metabolism, egestion, growth dilution, and transfer to eggs or young (Sharpe and Mackay 2000). Elimination rates can also be affected by the form of the contaminant (Niimi and Oliver 1983; Sijm *et al.* 1992; de Boer *et al.* 1994; Delorme *et al.* 1999; Vetter and Maruya 2000), especially in the case of PCBs. Half-lives for DDT, DDE, and PCBs in lake trout have been estimated at 9 to 10 years (see Borgmann and Whittle 1992; Van Metre *et al.* 1998). Delorme *et al.* (1999) suggest that hydrophobic contaminants may not remobilize from fish tissue unless severe nutritional stress occurs.

In addition to generally excluding the effects of contaminated sediment and food, most studies of contaminant uptake and elimination are relatively short-term laboratory experiments (de Boer *et al.* 1994; Sijm *et al.* 2000). Long-term field studies have generally found that elimination rates are considerably longer than in those measured in laboratory studies (de Boer *et al.* 1994; Delorme *et al.* 1999). The interval between bioconcentration and elimination may be too short in laboratory studies to allow equilibrium within all tissues, allowing elimination to proceed much faster than in a field situation. Published uptake and elimination rates derived from laboratory studies may not reflect field conditions, limiting their use for the prediction of contaminant behavior (Swackhamer and Hites 1988; de Boer *et al.* 1994).

Arroyo Colorado

Fish tissue data have been collected at several locations in the Arroyo Colorado since the late 1970s, most often in the upper and lower end of Llano Grande Lake and at the downstream end of the segment near the Port of Harlingen. Species collections most often included one or more of the bottom-feeding common carp, smallmouth buffalo, blue catfish, and channel catfish, although a wide variety of game and nongame fish have been collected at various times. Most of the earlier (1970s and early 1980s) tissue analyses were conducted on whole fish (Dick 1982; White *et al.* 1983; Davis 1984, 1989). Residues of one or more pesticides were generally very high in these samples (up to 31.5 mg/kg for toxaphene and DDE).

The range and mean of contaminant levels for each sample date and location in Segment 2202 were examined for available fish fillet data, to see if any trends were apparent in tissue concentrations (Table 4). Fish fillet tissue data is available for eight years of the 1980-1998 time period in Llano Grande Lake, and for nine years at the Port of Harlingen. The range of pesticide concentrations in fish from a given sample is often wide. In many cases, several fish had very low concentrations while others contained elevated levels. The mean was often influenced by elevated concentrations in one or two fish. Erratic concentrations at the Port of Harlingen may be a result of fish moving in and out of the site from downstream areas. Samples collected at this location included a wider variety of fish than the upstream locations, including marine and estuarine species.

Toxaphene exhibits the clearest decreasing trend in tissue concentration. Toxaphene levels have been less than the detection limit in all fish collected since 1987 in Llano Grande Lake, and since 1986 near the Port of Harlingen. Toxaphene was also less than the detection limit in all fish collected southeast of the City of Donna in 1998.

Chlordane concentrations were somewhat erratic in Llano Grande Lake through the 1980s, which is not unexpected given the continuing use of chlordane through much of that decade. The greatest mean and maximum chlordane concentrations were measured in 1987 in both Llano Grande Lake and the Port of Harlingen. Manufacture and domestic sale of chlordane ceased in 1987, and all remaining uses were banned as of April 1988. Tissue chlordane concentrations have subsequently declined in both locations (Table 4).

DDE concentrations have been the most erratic and the most resistant to decrease. This is not entirely unexpected given the widespread use of DDT and the resulting common occurrence of DDE as a pesticide residue (Schmitt *et al.* 1990; Kuehl *et al.* 1994). Mora (1996) found that DDE remained elevated in the eggs of four species of waterbirds nesting in Lower Laguna Madre, which receives drainage from the Arroyo Colorado, but noted that the levels were much lower than those measured in the 1970s and early 1980s. This suggests that there has been progress in reducing environmental DDE concentrations in the area.

Table 4. Mean and range of contaminant fish tissue (fillet) concentrations through time in Segment 2202. N = number of samples (individual fish and composites). nd = less than detection limit.

			Chlordane (mg/kg)		**DDE (mg/kg)**		**Toxaphene (mg/kg)**	
Sample Location	**Date**	**N**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**
southeast of Donna	11/1998	9	0.203	0.015 - 0.610	1.26	0.074 - 3.3	nd	nd
Llano Grande Lake	07/1980	8	0.054	nd - 0.110	3.38	0.052 - 6.90	1.7	nd - 4.8
	07/1981	14	0.096	nd - 0.748	2.22	0.077 - 8.91	1.14	nd - 5.9
	05/1983	12	0.039	nd - 0.157	1.47	0.013 - 5.10	0.94	nd - 5.0
	08/1985	10	0.292	nd - 0.930	1.63	0.13 - 4.7	1.16	nd - 4.1
	07/1987	15	0.353	nd - 1.4	1.42	0.02 - 5.1	nd	nd
	06/1989	7	0.158	nd - 0.530	1.45	0.120 - 4.0	nd	nd
	06/1993	6	nd	nd	0.76	0.03 - 2.2	nd	nd
	11/1998	11	0.092	nd - 0.420	0.66	0.044 - 4.2	nd	nd
Port of Harlingen	07/1980	7	0.102	0.014 - 0.220	2.06	0.17 - 7.9	2.98	0.22 - 9.1
	03-07/1981	12	0.15	nd - 0.874	1.21	nd - 4.92	1.25	nd - 3.49
	05/1983	8	0.027	nd - 0.048	1.05	0.052 - 2.3	1.08	nd - 2.44
	08/1984	12	nd	nd	0.903	0.051 - 1.74	nd	nd
	06/1985	10	0.115	nd - 0.500	1.34	0.040 - 3.33	0.214	nd - 1.04

	03/1986	6	nd	nd	0.097	nd - 0.301	nd	nd
	07/1987	7	0.544	nd - 1.4	2.14	0.02 - 5.1	nd	nd
	05/1989	12	0.068	nd - 0.200	0.423	nd - 1.17	nd	nd
	10/1998	12	0.118	0.027 - 0.470	0.786	0.13 - 3.0	nd	nd

Sources of Data:

Davis (1984, 1989)
TDH - Fish Tissue Sampling Data 1970-1997
Texas Department of Health - unpublished data

Donna Reservoir and Canal

Fish tissue data was collected in the Donna system in 1993, 1994, and 1997. The mean and range of PCB levels for each sample date and location were examined using available fish fillet data, to see if any trends were apparent in tissue PCB concentrations (Table 5). Values for individual fish and composites from the canal were often variable. The eight carp in collected in the canal in 1997 had PCB concentrations ranging from less than the detection limit to 20 mg/kg. Reservoir tissue concentrations were less variable.

PCB levels were greatest in the main canal, from just south of the Arroyo Colorado through the bend north of US 281; however, concentrations were lower in 1997 relative to 1993-94. There was a large decrease in mean and maximum PCB concentrations in the reservoir between 1993 and 1994, and the mean was less than the detection limit in 1997.

Table 5. Mean and range of PCB fish tissue (fillet) concentrations through time in the Donna Reservoir and Main Canal (Segment 2202A). All PCB measurements greater than the detection limit were Aroclor 1254. N = number of samples (individual fish and composites). nd = less than detection limit.

Sample Location	Date	N	PCB Mean (mg/kg)	PCB Range (mg/kg)
Main Canal, 0.25 mile north of Rio Grande pump station	03/1994	5	nd	nd
Main Canal, just south of Arroyo Colorado	01/1994	5	3.8	nd - 8.8
Main Canal, at 90-degree bend north of US 281	05/1993	4	5.0	1.4 - 9.3
Main Canal, at 90-degree bend north of US 281	01/1994	5	5.8	0.34 - 24
Main Canal, 3.5 miles north of Rio Grande pump station	03/1994	4	nd	nd
Main Canal	07/1997	8	2.7	nd - 20
Donna Reservoir	05/1993	6	1.6	nd - 9.6
Donna Reservoir	01/1994	10	0.026	nd - 0.08

Donna Reservoir	07/1997	2	nd	nd

Sources of data:

TDH - Fish Tissue Sampling Data 1970-1997

Webster *et al*. (1998)

Texas Department of Health - unpublished data

Margin of Safety

The margin of safety is required in a TMDL in order to account for any uncertainty about the pollutant load and its association with water quality. The margin of safety may be an explicit component that leaves a portion of the assimilative capacity of a water body unallocated, or an implicit component established through the use of conservative analytical assumptions (EPA 1999a).

These TMDLs use an implicit margin of safety. EPA (1997a) guidance on the assessment of contaminant data for use in fish advisories contains an extensive discussion of the assumptions and uncertainties present in the calculation of fish consumption limits. Conservative assumptions and calculations are used throughout the guidance to provide a margin of safety for the various uncertainties. Strict criteria exist concerning the types of studies and the data required to support assumptions and calculations. Numeric adjustments are made for the extrapolation of study results from animals or humans to the general population, and to provide a conservative upper bound on cancer risk values and a conservative RfD for noncarcinogens. Adjustments are designed to provide a safe margin between observed toxicity and potential toxicity in a sensitive human.

EPA assumes no safe threshold for exposure to carcinogens. Any exposure is assumed to pose some cancer risk. Noncarcinogenic effects occur with chronic exposure over a significant period of time. The oral reference dose (RfD) is defined in EPA (1997a) as “an estimate (with uncertainty perhaps spanning an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.” Calculated RfDs reflect the assumption that, for noncarcinogens, a threshold exists below which exposure does not cause adverse health effects. RfD calculations use modifying and uncertainty factors to account for variables such as the variability of responses in human populations, differences in responses between animal study species and humans, and gaps in available data. The RfD is calculated so there is little probability of an adverse health effect due to chronic exposure to concentrations below the RfD (EPA 1997a).

The flexibility provided by having numerous combinations of contaminants and concentration reductions that can produce acceptable carcinogenic and noncarcinogenic risk when multiple contaminants are present provides an inherent margin of safety that the goal of acceptable risk will be met. Use of the most protective target concentration for single contaminants provides additional assurance that protection from both carcinogenic and noncarcinogenic effects will be

achieved. Because the goal of this TMDL is removal of fish consumption bans through reduction of the consumption risk, the margin of safety inherent in the EPA guidance, combined with the conservative use of endpoint targets, will provide an adequate margin of safety for the protection of human health. The decline of tissue contaminant concentrations to within an acceptable level of risk will allow TDH to remove the fish consumption bans, which will effectively restore the fish consumption use to these water bodies.

Pollutant Load Allocation

Restrictions on the use of legacy pollutants generally have resulted in a slow but steady decline in environmental residues (Smith *et al.* 1988). Contaminant levels in lake sediment cores have shown good agreement with production and usage histories of the parent compounds, with peak concentrations appearing at the times of peak use (Ricci *et al.* 1983; Oliver *et al.* 1989; Van Meter and Callender 1997; Van Metre *et al.* 1998). Higher concentrations generally appeared deeper in the cores, indicating that input and accumulation were decreasing with time. Although residues continue to persist in deeper parts of the cores, burial by more recently deposited sediments may result in effective removal of the contaminants from bioavailability to aquatic life (Ricci *et al.* 1983).

Decreases in fish and human tissue concentrations of organochlorine insecticides and PCBs have been observed where no major additional inputs are occurring (see Moore and Ramamoorthy 1984; Brown *et al.* 1985; Hovinga *et al.* 1992; Bremle and Larsson 1998). Reviews of tissue data collected from a variety of water bodies in northern Europe between 1967 and 1995 have found a significant decrease in organochlorine concentrations over time (Skåre *et al.* 1985; Bignert *et al.* 1998). Fish tissue concentrations of total DDT, chlordane, and toxaphene have declined across the U.S. since uses of these substances were discontinued (Schmitt *et al.* 1985, 1990; USGS 2000). The DDE component of total DDT has increased as a result of continued degradation. Declining tissue DDT, toxaphene, and PCB concentrations have been reported in various locations and fish species in the Great Lakes (Glassmeyer *et al.* 1997; Scheider *et al.* 1998). Less consistent trends in tissue PCB levels may be a reflection of the congener-specific nature of PCB metabolism and degradation. In addition, strong oscillations in PCB levels influenced by food web interactions can be superimposed on a gradual decline (see Borgmann and Whittle 1992).

Continuing decreases in environmental legacy pollutant levels are expected, although the necessary time frame is subject to debate. Within the context of these TMDLs, legacy pollutants are considered background sources that reflect the site-specific application history and loss rates of the subject area. Continuing sources of pollutant loadings occur from nonpoint source runoff , leaching, or erosion of the various sinks that may exist within the watersheds. No authorized point source discharges of these pollutants are allowed by law. Therefore, any contribution from point source discharges would be the result of illegal disposal of these contaminants by customers of the treatment systems.

Available evidence indicates that fish tissue toxaphene concentrations have declined to generally nondetectable levels, and that chlordane concentrations are declining, in the Arroyo Colorado. PCB concentrations have generally declined in the Donna Reservoir and Canal. DDE concentrations in Arroyo Colorado fish have been erratic, and have not yet shown an obvious decline. Continuing natural attenuation of these contaminants is expected due to ongoing degradation and metabolism, burial of contaminated sediment through natural sedimentation in Donna Reservoir and Llano Grande Lake, and through scouring and redistribution of sediments in Arroyo Colorado and Donna Canal. Remediation and elimination of the PCB source contributing to the Donna Canal will be undertaken when delineation of the exact location is complete.

Natural attenuation is generally a preferred option for the elimination of legacy pollutants from aquatic systems. More drastic alternatives, such as sediment removal by dredging, can result in considerable habitat disturbance and destruction. Sediments resuspended during dredging further expose aquatic life to contaminants and the potential for additional uptake, cause abrasive damage to gills and sensory organs of fish and invertebrates, and interfere with fish prey selection (O'Brien 1990; Waters 1995). Alternatives such as dredging or eradication of contaminated fish communities and restocking (O'Meara *et al.* 2000) are generally better justified at sites heavily contaminated by point source discharges and major spills.

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