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Four Total Maximum Daily Loads for Two Volatile Organic Compounds in Clear Creek

For Segments 1101 and 1102

Prepared by the:
Strategic Assessment Division, TMDL Team

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 unit of time, but may be expressed in other ways also. 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.

The ultimate goal of these TMDLs is the reduction of fish tissue contaminant concentrations to levels that constitute an acceptable risk to consumers, allowing the Texas Department of Health to remove the bans on fish consumption and the beneficial use to be restored to these 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), further refines the process for Texas. Following all these guidelines, this TMDL document has been prepared and is composed of six elements which are summarized in the following sections:

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

- Margin of Safety
- Pollutant Load Allocation

This TMDL document was prepared by 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 June 14, 2002. Upon adoption, the TMDL became part of the state Water Quality Management Plan. The Texas Natural Resource Conservation Commission will use this document as a regulatory tool for managing and abating contamination from 1,2-dichloroethane and 1,1,2-trichloroethane in the Clear Creek watershed.

Background Information

These TMDLs address the contamination of fish tissue by the volatile organic chemicals 1,2-dichloroethane and 1,1,2-trichloroethane in portions of two classified Segments of Clear Creek in Harris, Galveston, Fort Bend, and Brazoria Counties in southeast Texas.

Problem Definition

Clear Creek was included on the State of Texas 1998 and 1999 §303(d) lists as a result of the issuance of a fish consumption advisory by the Texas Department of Health (TDH) on November 18, 1993. TDH advised against consuming fish from Clear Creek upstream and west of State Highway 3. The fish consumption advisory was issued following determinations of unacceptable human health risk due to elevated tissue concentrations of chlordane and volatile organic chemicals including 1,2-dichloroethane, 1,1,2-trichloro-ethane, and carbon disulfide. The impacted portions of Clear Creek and their watersheds lie within Harris, Galveston, Fort Bend, and Brazoria counties in the San Jacinto-Brazos Coastal Basin (see Figure 1).

- Segment 1102 (Clear Creek Above Tidal) extends from Rouen Road in Fort Bend County to a point 100 meters upstream of FM 528 in Galveston/Harris County, where it meets Segment 1101. The fish consumption advisory applies to the entire 47 kilometer length of Segment 1102.

- Segment 1101 (Clear Creek Tidal) extends downstream from 100 meters upstream of FM 528 to its confluence with Clear Lake 2.0 miles downstream of El Camino Real in Galveston/Harris County. The fish consumption advisory applies to the upper 15 kilometers of Segment 1101, to State Highway 3 in Webster.

Chlordane is addressed in separate TMDLs. These TMDLs address the volatile organic chemicals 1,2-dichloroethane and 1,1,2-trichloroethane.

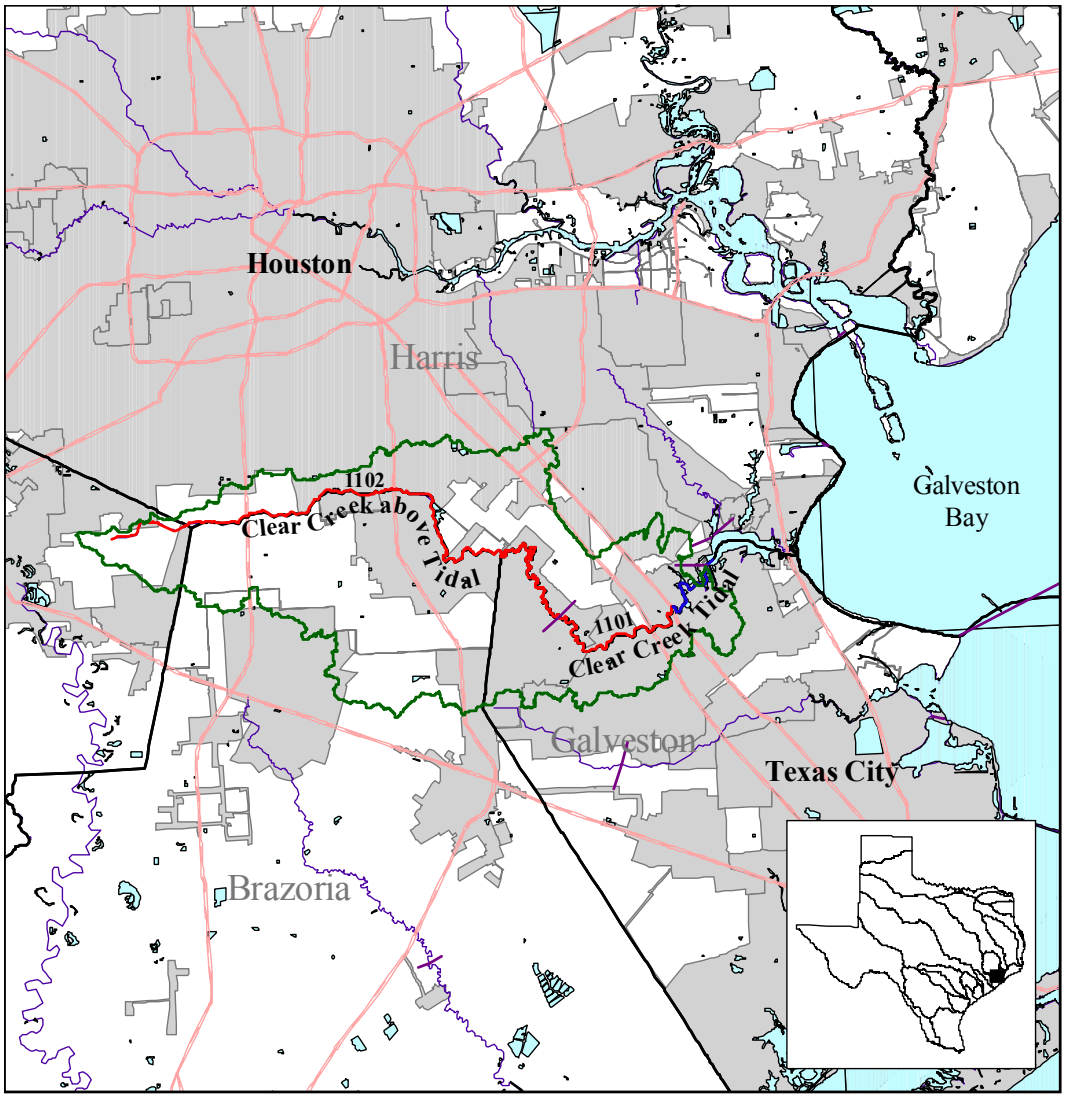

Figure 1. Study Area–Clear Creek Watershed

1,2-Dichloroethane (CASRN 107-06-2) is a volatile organic chemical used primarily in chemical manufacturing and as a solvent for a variety of products and processes. It does not concentrate in fish tissue to a great degree. When released to water, it is expected to volatilize to air with a half-life of several hours to days. Photolysis, hydrolysis, bio-degradation, and sorption to sediments are not significant loss processes from water. Risk assessments that resulted in the fish consumption bans in these waters were made on the basis of a risk of cancer. No information exists to indicate human non-carcinogenic risks through food consumption, and a reference dose for this chemical has not been established.

1,1,2-Trichloroethane (CASRN 79-00-5) is a volatile organic chemical used primarily in chemical manufacturing and as a solvent for a variety of products and processes. It does not concentrate in fish tissue to a great degree. When released to water, it is expected to volatilize to air with a half-life of several hours to days. Photolysis, hydrolysis, bio-degradation, and sorption to sediments are not significant loss processes from water.

Risk assessments that resulted in the fish consumption bans in these waters were made on the basis of a risk of cancer. Exposure to high levels of 1,1,2-trichloroethane may also lead to non-carcinogenic damage to livers and kidneys, but concentrations in Clear Creek fish tissue were far below these levels.

Carbon disulfide (CASRN 75-15-0) is a volatile organic chemical used primarily in the production of rayon, cellulose, agricultural fumigants, and rubber chemicals. It is also used as a solvent. It is produced through chemical manufacturing, but also naturally by microorganisms in the degradation of organic matter (EPA 749-F-94-008a). When released to water, it is expected to volatilize to air with a half-life of only one to three hours. Photolysis, hydrolysis, biodegradation, and sorption to sediments are not significant loss processes from water. Exposure to high levels of carbon disulfide may lead to neurological damage and other non-cancer effects, but concentrations in Clear Creek fish tissue were far below these levels. Carbon disulfide does not appear to be a carcinogen.

In their 1993 risk assessment for Clear Creek, TDH mentioned that carbon disulfide "... has also been noted as a possible degradation product of fish tissue undergoing laboratory analysis." Carbon disulfide has been detected in only one of over three hundred water samples collected in Mud Gully and Clear Creek since 1993, and that at a concentration near the analytical detection limit. There are no known sources of carbon disulfide to Clear Creek. With a very low bioconcentration factor, it is very unlikely that carbon disulfide accumulated substantially in Clear Creek fish tissue. TNRCC does not deem it necessary or appropriate to establish a TMDL for carbon disulfide in Clear Creek. It is apparent that carbon disulfide measured in fish tissue samples was an artifact of tissue degradation during laboratory analysis. Therefore the original basis for listing this water body for carbon disulfide is no longer valid and TNRCC will propose to remove this pollutant from the next 303(d) list.

Endpoint Identification

The ultimate goal of these TMDLs is the reduction of concentrations of 1,2-dichloroethane and 1,1,2-trichloroethane in fish tissue to levels that constitute an acceptable risk to fish consumers, allowing TDH to remove the fish consumption advisory. Other existing uses, such as prevention of toxicity to aquatic life, must also be protected. Both Segments of Clear Creek are designated a "high" aquatic life use in Texas Surface Water Quality Standards (30 TAC §307). The endpoints of these TMDLs are based on water quality criteria calculated according to Texas Surface Water Quality Standards to be protective of human health and aquatic life. These criteria are then converted to maximum daily loads based on the critical low flow.

Texas Surface Water Quality Standards state that numerical chronic criteria for toxic materials to protect aquatic life do not apply below the seven-day, two-year (7Q2) low flow, and specific human health criteria to prevent contamination of fish to ensure safety for human consumption do not apply below the harmonic mean flow (30 TAC §307.8). Thus, the 7Q2 flow will be used with aquatic life criteria in the calculation of maximum loads, and the harmonic mean flow will be used with human health criteria.

The harmonic mean flow for segment 1102, calculated from historical U.S. Geological Survey daily streamflow records, is 2.0 ft^3/s, or $4.9x10^6$ liters/day (30 TAC §307.10). The 7Q2 flow for segment 1102 is 0.5 ft^3/s, or $1.2x10^6$ liters/day. Segment 1101 is tidally influenced; therefore a critical flow is not meaningful. In calculating allowable loads for segment 1101, the minimum flows for segment 1102 were used in order to be sufficiently protective.

1,2-Dichloroethane

Texas Surface Water Quality Standards specify water quality criteria for 1,2-dichloroethane to prevent contamination of fish to ensure that they are safe for human consumption. The saltwater criterion (49.3 µg/L) is applicable to Segment 1101, while the freshwater criterion (73.9 µg/L) is applicable to Segment 1102.

Numerical criteria for protection of aquatic life from 1,2-dichloroethane are not specifically listed in Texas Water Quality Standards. Instead, they are calculated according to procedures specified in 30 TAC §307.6(c)(7). For toxic materials that do not bioaccumulate, the chronic criterion is calculated as 1/10th of the concentration that is lethal to the most sensitive aquatic species. The ECOTOXicology database is a source that provides chemical-specific toxicity values for aquatic life, terrestrial plants, and terrestrial wildlife. ECOTOX integrates three toxicology effects databases: AQUIRE (aquatic life), PHYTOTOX (terrestrial plants), and TERRETOX (terrestrial wildlife). These databases were created by the U.S. EPA, Office of Research and Development (ORD), and the National Health and Environmental Effects Research Laboratory. The ECOTOX database indicates that the lethal concentration to freshwater organisms such as the water flea has been measured to be 320,000 µg/L. Thus, the freshwater criterion is calculated to be 32,000 µg/L of 1,2-dichloroethane. In saltwater, a lethal concentration of 113,000 µg/L has been measured to the Opossum Shrimp. Thus, the saltwater criterion is calculated to be 11,300 µg/L.

1,1,2-Trichloroethane

Specific numerical water quality criteria for protection of human health or aquatic life are not listed for 1,1,2-trichloroethane in Texas Surface Water Quality Standards. 30 TAC §307.6(d)(8) specifies that for toxic materials of concern for which specific human health criteria are not listed, a cancer risk of 10^{-5} (1 in 100,000) shall be applied to the most recent numerical criteria adopted by the EPA and published in the *Federal Register*. EPA recommended a criterion of 42 µg/L for 1,1,2-trichloroethane to protect human health from consumption of fish using a cancer risk of 10^{-6}, or 1 in 1,000,000 (63 FR 67548). After adjusting the cancer risk factor, the appropriate criterion for 1,1,2-trichloroethane to prevent contamination of fish to ensure that they are safe for human consumption is 420 µg/L in saltwater or freshwater.

Criteria for protection of aquatic life from 1,1,2-trichloroethane were calculated according to procedures specified in 30 TAC §307.6(c)(7). For toxic materials that bioaccumulate, the chronic criterion is calculated as 1/100th of the concentration that is lethal to the most sensitive aquatic species. The ECOTOX database indicates that the lethal concentration to water fleas has been measured to be 30,200 µg/L. Thus, the freshwater criterion is

calculated to be 302 µg/L of 1,1,2-trichloroethane. In saltwater, a concentration of 43,000 µg/L has been measured which causes lethality to grass shrimp. Thus, the saltwater criterion is calculated to be 430 µg/L.

Endpoint targets to protect the designated uses of Clear Creek are summarized as follows:

Segment	Primary Endpoint (Concentrations)
Clear Creek Tidal (1101)	≤ 49.3 µg/L 1,2-dichloroethane in water (HH) ≤ 11,300 µg/L 1,2-dichloroethane in water (AL) ≤ 420 µg/L 1,1,2-trichloroethane in water (HH) ≤ 430 µg/L 1,1,2-trichloroethane in water (AL)
Clear Creek Above Tidal (1102)	≤ 73.9 µg/L 1,2-dichloroethane in water (HH) ≤ 32,000 µg/L 1,2-dichloroethane in water (AL) ≤ 420 µg/L 1,1,2-trichloroethane in water (HH) ≤ 302 µg/L 1,1,2-trichloroethane in water (AL)

HH= human health; AL=aquatic life

The maximum allowable daily load to protect human health from fish consumption = maximum allowable concentration (µg/L) × harmonic mean flow (L/day) × ($1x10^{-6}$g/µg)

The maximum allowable daily load to protect aquatic life =
maximum allowable concentration (µg/L) × 7Q2 flow (L/day) × ($1x10^{-6}$g/µg)

The primary endpoint for these total maximum daily loads is the lesser of the allowable loads to protect human health or aquatic life.

Segment	Primary Endpoint (Loads)
Clear Creek Tidal (1101)	241 grams/day 1,2-dichloroethane in water (HH) 516 grams/day 1,1,2-trichloroethane in water (AL)
Clear Creek Above Tidal (1102)	362 grams/day 1,2-dichloroethane in water (HH) 362 grams/day 1,1,2-trichloroethane in water (AL)

HH=human health; AL=aquatic life

The TDH has the authority and jurisdiction for the decision to issue or remove fish consumption advisories and bans. Subsequent risk assessments by TDH may result in no change to an advisory, removal of the advisory, or a prohibition from taking of fish. The ultimate endpoint target for all water bodies is the protection of all groups and the complete removal of the fish consumption advisories.

Source Analysis

1,2-dichloroethane and 1,1,2-trichloroethane are associated primarily with chemical manufacturing. Twenty-six domestic sewage treatment plants and two industrial facilities are currently permitted to discharge wastewater to Clear Creek. These are not expected to

be significant sources of these compounds. Nonpoint sources of these compounds are expected to be minor also.

The Brio Refining, Inc. waste site is an abandoned refinery located on approximately fifty-eight acres along Mud Gully, a tributary to Clear Creek in Friendswood, Harris County.

The facility was operated from the late 1950s until 1982. Past operations at the site included copper catalyst regeneration, oil blending and refining, chemical by-product recycling, petroleum recovery, and hydrocarbon cracking. Chemical spills at this facility have entered Mud Gully and contaminated soils and groundwater. Additionally, raw and process chemical mixtures were stored on site in unlined pits which continued to contaminate groundwater after operations ceased at the facility. Investigations revealed that soils and shallow groundwaters were contaminated with high concentrations of 1,2-dichloroethane, 1,1,2-trichloroethane, vinyl chloride, fluorene, anthracene, phenanthrene, pyrene, and other hydrocarbons and copper.

Contaminated groundwater from the Brio Refining site discharged to Mud Gully, which flows into Clear Creek. In 1993, the concentrations of 1,2-dichloroethane and 1,1,2-trichloroethane in water of Mud Gully just downstream of Brio Refining averaged 587 µg/L and 680 µg/L, respectively. Just downstream in Clear Creek, the concentrations of 1,2-dichloroethane and 1,1,2-trichloroethane averaged 91 µg/L and 96 µg/L, respectively, at that time.

Groundwater from the Brio site is pumped, treated, and discharged to Mud Gully under a U.S. EPA Record of Decision amended in 1997 (EPA/541/R-97/122). This discharge and the direct migration of groundwater to Mud Gully are believed to be the only significant continuing sources of 1,2-dichloroethane and 1,1,2-trichloroethane to Clear Creek. The Record of Decision states that "recovered groundwater shall be treated to meet relevant standards within the receiving water."

Linkage Between Sources and Receiving Waters

In 1989, the Brio Refining, Inc. Site was added to the National Priorities List under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA). Several measures were taken to reduce the contamination of Mud Gully and Clear Creek. Approximately 100,000 gallons of highly contaminated sludges and solids, and over 40,000 gallons of dense non-aqueous phase liquids have been removed from the site. Over 18 million gallons of ground water have been treated.

Following these remedial measures, the concentrations of contaminants in Mud Gully and Clear Creek water declined by more than 97%. This demonstrates that the Brio Refining, Inc. site was the source for these contaminants in Clear Creek. Currently, 1,2-dichloro-ethane is seldom detected in either Mud Gully (Figure 2) or Clear Creek water (Figure 3).

1,1,2-Trichloroethane concentrations in Mud Gully (Figure 4) and Clear Creek (Figure 5) water are well below the water quality targets, averaging approximately 10 µg/L and 3 µg/L, respectively.

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. These TMDLs use an implicit margin of safety, which is established through the conservative assumptions in Texas Surface Water Quality Standards for protection of human health and aquatic life, as well as the use of the most protective endpoint targets. These steps will provide an adequate margin of safety for the protection of aquatic life, human health and restoration of the fish consumption use in these water bodies.

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 TMDL document establishes primary endpoints (loads) for 1,2-dichloroethane and 1,1,2-trichloroethane in units of grams/day for Clear Creek Tidal (Segment 1101) and Clear Creek Above Tidal (Segment 1102). The TMDL document also states that the facilities currently permitted to discharge wastewater to Clear Creek, as well as the nonpoint sources of the VOCs in the watershed, are expected to be minor contributors of VOCs to Clear Creek. Data is presented in this TMDL document that supports the assertion that the Brio Refining Superfund Site was the sole source of VOC contamination in Clear Creek. The "Pollutant Load Allocation" section of this TMDL document states clearly that "All allowable loading is allocated to remedial actions at the Brio Refining Site." Remedial actions at the Brio Refining Site were completed in July, 2001. The site is in a post-remediation monitoring phase that includes sample collections in Clear Creek. Currently, VOC concentrations in water in Clear Creek are well below the primary endpoint targets and are rarely above analytical detection limits.

Pollutant Load Allocation

The TMDLs described in this section will result in compliance with water quality standards. All allowable loading is allocated to remedial actions at the Brio Refining Site. Because concentrations of 1,2-dichloroethane and 1,1,2-trichloroethane are now below the water quality targets for protection of the fish consumption use, no further reduction in their concentrations is required by these TMDLs. Continuing natural attenuation of 1,2-dichloroethane and 1,1,2-trichloroethane is expected via volatilization from the creek to the atmosphere. Concentrations in fish tissue are expected to decline rapidly by metabolism and excretion following a decline in the concentrations in water. Thus, concentrations of these volatile organic compounds in fish tissue have likely declined (as they have in water) to safe levels.

Continued periodic monitoring will be required to confirm that concentrations of volatile organic compounds in Mud Gully and Clear Creek water do not exceed the water quality targets, and thus will be protective of the fish consumption use. Additional monitoring of

1,2-dichloroethane and 1,1,2-trichloroethane concentrations in fish tissue will be required to verify that fish are safe for consumption.

A U.S. EPA Record of Decision amended in 1997 (EPA/541/R-97/122) outlines several additional measures that will continue to reduce contamination of Clear Creek by the Brio Refining site. These include installing a sub-grade vertical barrier wall enclosing the site, capping the site with a liner and clay cover, and pumping and treating groundwater from fourteen recovery wells.

No allowance for future growth is explicitly incorporated into these TMDLs. As the remedial actions at the Brio Refining Site curtail discharges of 1,2-dichloroethane and 1,1,2-trichloroethane to Clear Creek, the allowable loading may be re-allocated.

Figure 2. 1,2-Dichloroethane in Mud Gully at Brio Refining Site (Station SW-1)

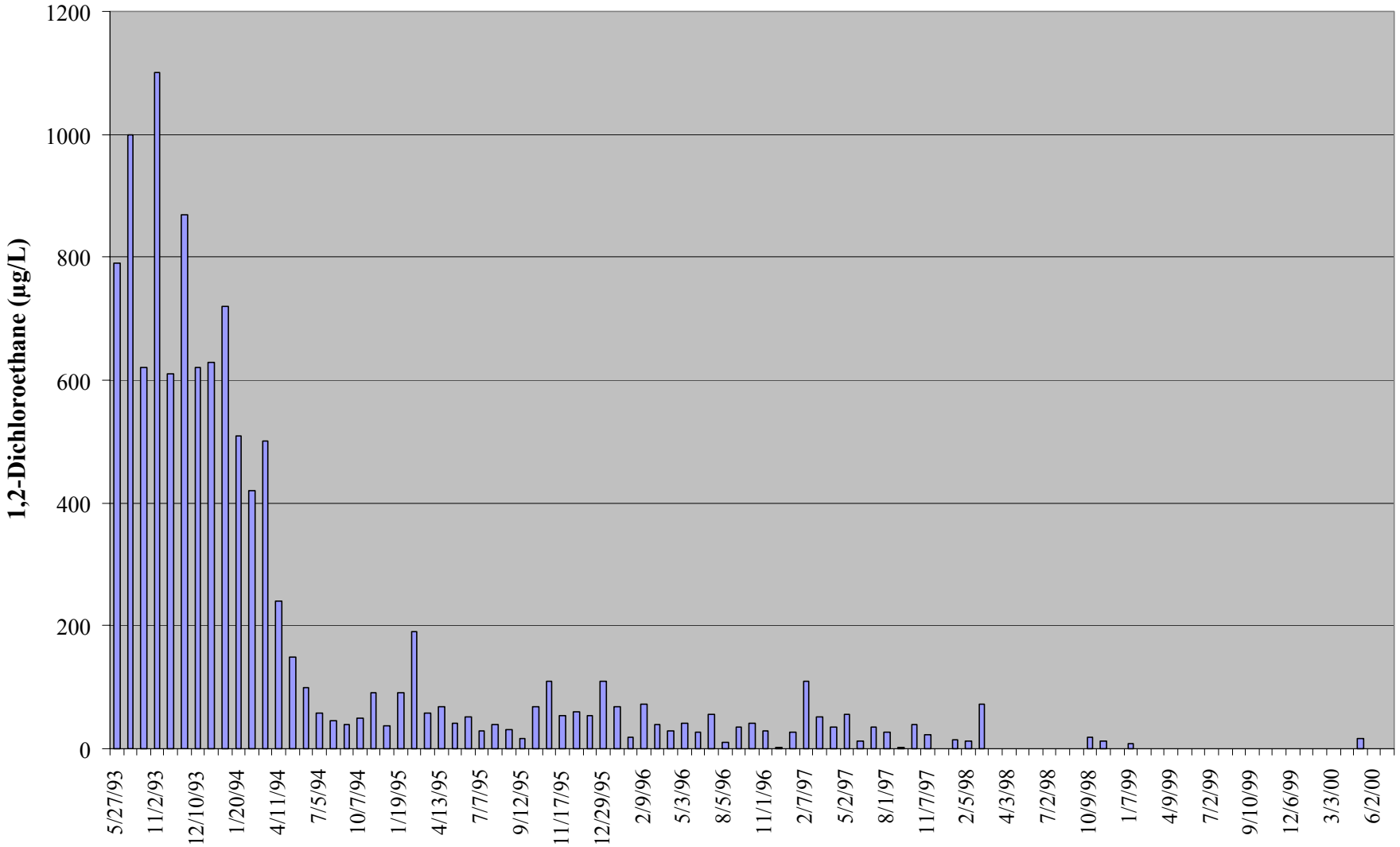

Figure 3. 1,2-Dichloroethane in Clear Creek below Mud Gully (Station SW-21)

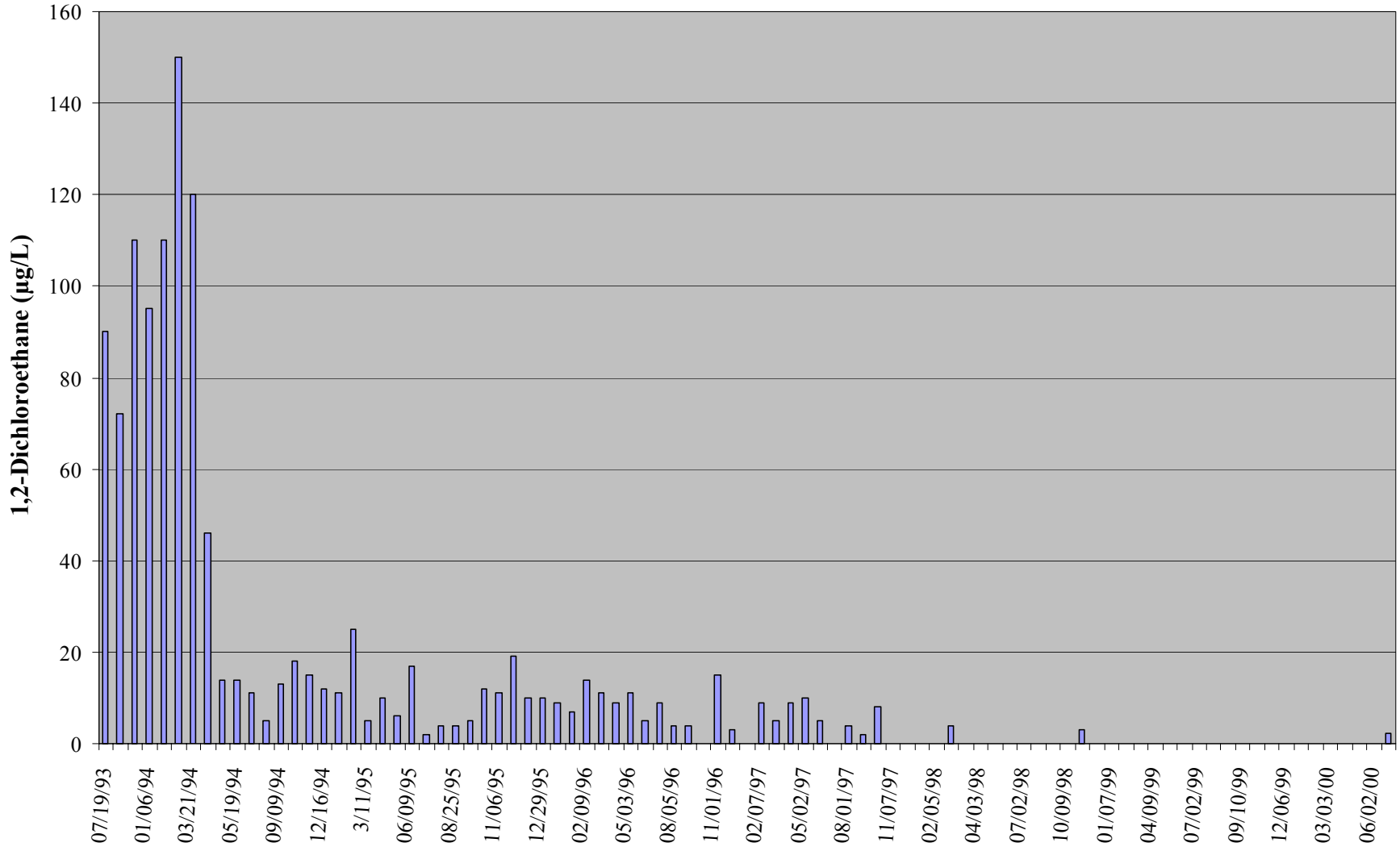

Figure 4. 1,1,2-Trichloroethane in Mud Gully at Brio Refining Site (Station SW-1)

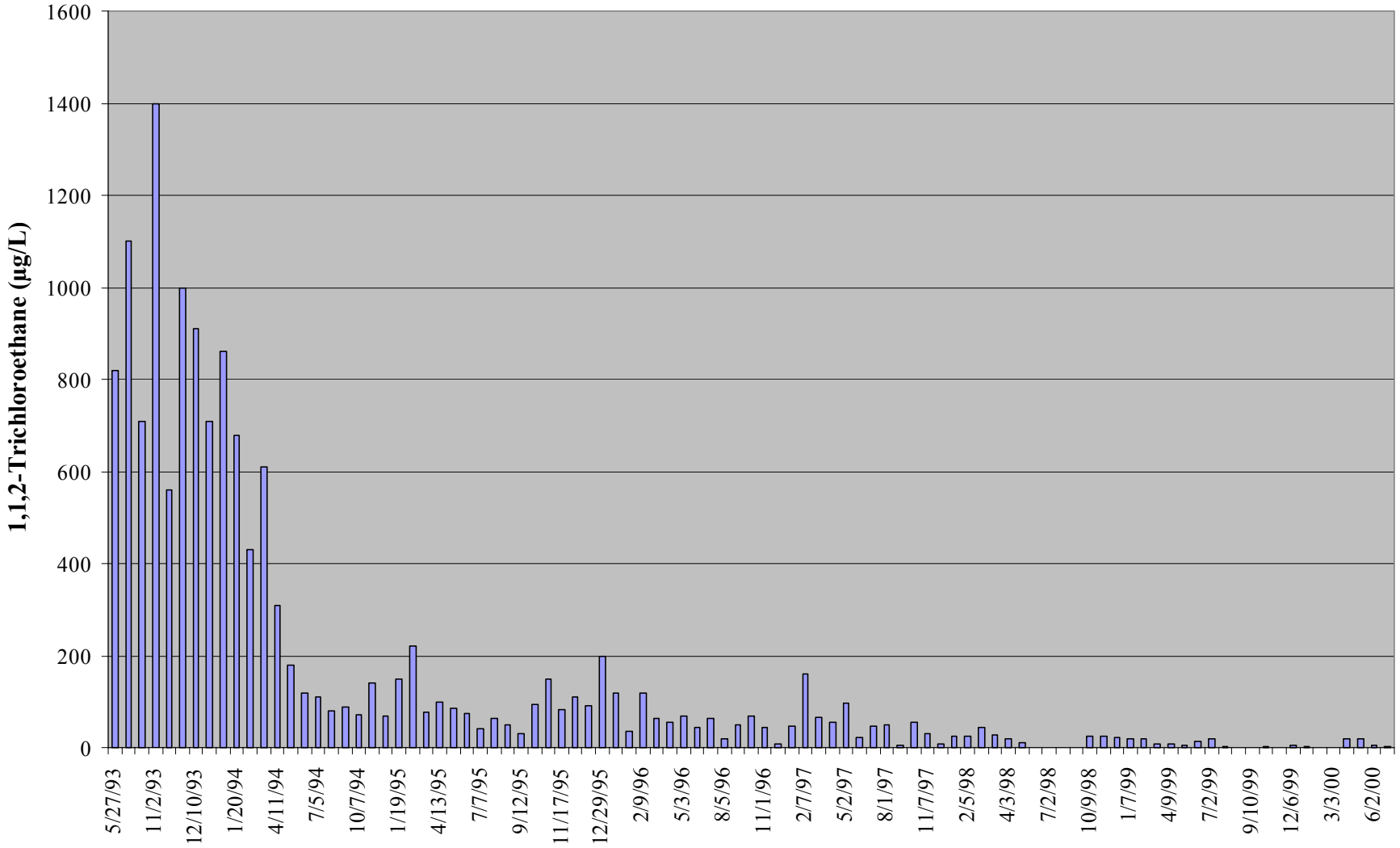

Figure 5. 1,1,2-Trichloroethane in Clear Creek below Mud Gully (Station SW-21)