

TOTAL MAXIMUM DAILY LOAD (TMDL) FOR ZINC IN THE RED CLAY CREEK NEW CASTLE COUNTY, DELAWARE

Technical Background and Basis Document

August 1, 1999

**State of Delaware
Department of Natural Resources and Environmental Control
Division of Water Resources
Watershed Assessment Section**



CONTENTS

LIST OF FIGURES	ii
LIST OF TABLES	iii
ACKNOWLEDGMENTS	iv
EXECUTIVE SUMMARY	v
1. INTRODUCTION	1
1.1 Purpose	1
1.2 Background	1
1.3 Report Organization	2
2. CHARACTERIZATION	3
2.1 Environmental Setting	3
2.2 Applicable Water Quality Standards	4
2.3 Assessment of Zinc Concentrations and Mass Loading in the Red Clay Creek	6
2.3.1 Routine Water Quality Monitoring Data	6
2.3.2 EPA Region III Superfund Investigation	17
2.3.3 University of Delaware Investigation of Red Clay Creek Zinc Contamination	21
2.3.4 U.S. Fish & Wildlife Service Study of Red Clay Creek Sediments	21
2.3.5 DNREC Surveys of Zinc in Red Clay Creek Sediments	22
2.3.5.1 March 1987 Synoptic Survey	22
2.3.5.2 Sediment Contamination Study of the Red Clay Creek Near Glenville, DE	23
2.3.6 DNREC Surveys of Zinc in Red Clay Creek Fish Tissue	24
2.4 Mass Loading of Zinc From NVF, Yorklyn	25
2.4.1 NPDES Outfall 002	25
2.4.2 Toxics Release Inventory Data	27
3. TOTAL MAXIMUM DAILY LOAD	30
4. NEXT STEPS	35
5. REFERENCES	37
APPENDIX A: Summary of Routine Ambient Monitoring Data for the Red Clay Creek	
APPENDIX B: Summary of Effluent Monitoring Data for NVF Discharge 002	
APPENDIX C: Estimate of Diffusive Flux of Zinc from Red Clay Creek Sediments	

LIST OF FIGURES

Figure 1.	Red Clay Creek Watershed, New Castle County, Delaware	8
Figure 2.	Box-and-Whisker Plot for Total Zinc Concentration, Red Clay Creek	10
Figure 3.	Box-and-Whisker Plot for Total Zinc at Ashland	11
Figure 4.	Total and Dissolved Zinc at Ashland	12
Figure 5.	Total Zinc and Acute Criterion at Ashland	13
Figure 6.	Total Zinc and Acute Criterion at Marshall’s Bridge	14
Figure 7.	Box-and-Whisker Plot for Total Zinc Mass Loading, Red Clay Creek	14
Figure 8.	Box-and-Whisker Plot for Total Zinc Mass Load at Ashland	16
Figure 9.	Total Zinc and Flow at Ashland	16
Figure 10.	Daily Average Zinc Mass Loading Versus Effluent Limit	26
Figure 11.	Daily Max Zinc Mass Loading Versus Effluent Limit	26

LIST OF TABLES

Table 1.	Routine Monitoring Stations in the Red Clay Creek	7
Table 2.	Exceedance Frequencies for Zinc Water Quality Criteria in Red Clay Creek	13
Table 3.	Surface Water Results, EPA Superfund Investigation at NVF, Yorklyn	18
Table 4.	Groundwater Results, EPA Superfund Investigation at NVF, Yorklyn	19
Table 5.	Sediment Results, EPA Superfund Investigation at NVF, Yorklyn	20
Table 6.	Selected Zinc Results Reported by the USFWS, Red Clay Creek Sediments	22
Table 7.	Zinc Results of March, 1987 DNREC Survey, Red Clay Creek Sediments	23
Table 8.	Effluent Limitations for Total Zinc Discharged from NVF Yorklyn Outfall 002	25
Table 9.	Toxics Release Inventory (TRI) Data for Zinc Released from NVF Yorklyn	28
Table 10.	Zinc TMDL for the Red Clay Creek, New Castle County, Delaware	34

ACKNOWLEDGMENTS

This report was prepared by Richard Greene, Watershed Assessment Section, Division of Water Resources, Delaware Department of Natural Resources and Environmental Control. David Wolanski, also from the Watershed Assessment Section, is acknowledged for GIS mapping support.

Several people and agencies provided data and information that were useful in the development of the zinc TMDL for the Red Clay Creek. The assistance and coordination of William Goman and Michael Boyer in providing results of surface water testing performed by the Pennsylvania Department of Environmental Protection at the Marshall's Bridge Road monitoring station in Chester County, Pennsylvania is acknowledged and appreciated. Field, laboratory, and support personnel from the DNREC's Environmental Laboratory Section are acknowledged for collecting, analyzing, and delivering water quality data for samples taken in the Delaware portion of the Red Clay Creek. The United States Geologic Survey is recognized for their role in providing high-quality stream flow data from several gaging stations along the Red Clay Creek. James Pizzuto and Thomas Church from the University of Delaware are cited for their research efforts, which served to elucidate the fate and transport of zinc in the Red Clay Creek. David Fees, Toxics Release Inventory Coordinator for the State of Delaware, is acknowledged for providing release data for the NVF facility which proved vital in understanding the zinc mass balance in the Red Clay Creek. Roy Parikh and John DeFriece from Delaware's NPDES program provided discharge monitoring data for NVF discharge 002. Cindy Rice Tibbet from the U.S. Fish & Wildlife Service is recognized for kindly providing data on the distribution of zinc contamination in the sediments of the Red Clay Creek. Finally, a special note of thanks is offered to Debra Carlson, On-Scene Coordinator for the U.S. EPA Removal Enforcement and Oil Section, for providing site-specific, multi-media contaminant data for the NVF, Yorklyn facility.

EXECUTIVE SUMMARY

The Red Clay Creek drains a small (53.3 mi²) and scenic watershed in southeastern Pennsylvania and northern Delaware. The waters of the Red Clay are used for a variety of purposes, including public and industrial water supply, irrigation, put-and-take trout fishing, and general aquatic life maintenance and propagation. Testing by the Delaware Department of Natural Resources and Environmental Control (DNREC) and others has shown that the concentration of zinc in the Red Clay Creek from Yorklyn, Delaware to the Creek mouth near Stanton, Delaware does not meet applicable water quality standards intended to protect aquatic life.

To begin to remedy this situation, the DNREC has developed a Total Maximum Daily Load (TMDL) for zinc in the Red Clay Creek. A TMDL specifies the maximum allowable mass loading of a pollutant (i.e., pounds per day) that can be delivered to a waterbody while still assuring that applicable water quality standards are met. A TMDL is composed of three components, including a Waste Load Allocation (WLA) for point source discharges, a Load Allocation (LA) for nonpoint sources, and a Margin of Safety (MOS) to account for uncertainties regarding the relationship between mass loading and resulting water quality. In simple terms, a TMDL attempts to match the strength, location, and timing of pollution sources within a watershed with the inherent ability of the receiving water to assimilate the pollutant without adverse impact.

The major source of zinc to the Red Clay Creek is the National Vulcanized Fiber (NVF) facility located in Yorklyn, Delaware. Zinc is released from this facility to the Red Clay Creek through a permitted NPDES discharge (outfall 002) as well as through contaminated groundwater discharge. The amount of zinc released from the permitted discharge is relatively small in comparison to the amount of zinc released from the site groundwater. The total amount of zinc released from this facility to the Creek is roughly 60 to 100 pounds per day. In contrast, the amount of zinc flowing in the Creek just above the Yorklyn facility averages 0.6 pounds per day.

The DNREC has determined that the greatest amount of zinc loading that the Red Clay Creek can accommodate during critical low flow conditions is 1.81 pounds of zinc per day. Loadings in excess of this amount would be expected to violate applicable water quality criteria. This 1.81 pounds of zinc per day, which is the TMDL for the Red Clay Creek, is allocated as shown in the table below.

Zinc TMDL for the Red Clay Creek, New Castle County, Delaware

TMDL (#/d)	WLA ₀₀₂ + LA _{g.w.} (#/d)	LA _{up} (#/d)	MOS (#/d)
1.81	1.20	0.60	0.01

In this table, WLA_{002} refers to the allowable zinc loading from NVF discharge 002 and $LA_{g.w.}$ refers to the zinc loading from the NVF site groundwater. For purpose of this TMDL, and because the zinc discharged from 002 is actually derived from contaminated site groundwater, WLA_{002} and $LA_{g.w.}$ have been combined to represent the total zinc loading from the NVF facility to the Creek. The remaining terms in the table include the zinc loading in the Creek just upstream from the NVF facility, (LA_{up}), and a margin of safety. Based upon the analyses contained in this report, the DNREC concludes with a reasonable degree of scientific certainty that water quality standards for zinc will be met in the Red Clay Creek once the mass loading requirements listed in the above table are reached. This TMDL covers the entire main stem of the Red Clay Creek from the PA/DE border to its confluence with the White Clay Creek in Stanton, Delaware.

The DNREC will provide public notice that it intends to adopt the zinc TMDL for the Red Clay Creek as a State regulation. This notice will appear within the August 1, 1999 Delaware Register of Regulations. The Register will also announce a public hearing to gather comments on the proposed TMDL regulation. That hearing will be held on Tuesday, September 7, 1999, between 7:00 and 8:00 p.m., at the New Castle office of the Division of Air and Waste Management, Delaware Department of Natural Resources and Environmental Control, 391 Lukens Drive, New Castle, Delaware. Oral and/or written comments can be provided concerning the proposed TMDL regulation at the time of the public hearing, or otherwise can be submitted in writing by 4:30 p.m., September 15, 1999. All comments should be directed to the attention of Mr. Rod Thompson, Hearing Officer, DNREC, 89 Kings Highway, Dover, DE, 19901; facsimile: (302) 739-6242.

Following the hearing and consideration of the comments received, the DNREC will move to adopt the TMDL regulation and submit it to the U.S. EPA for their review and approval, all prior to December 31, 1999. If the State of Delaware fails to establish this TMDL by December 31, 1999, the EPA must do so by December 31, 2000.

1. INTRODUCTION

1.1 Purpose

The purpose of this report is to document the technical basis of the Total Maximum Daily Load (TMDL) for zinc discharged to the Red Clay Creek in northern New Castle County, Delaware.

1.2 Background

Section 303(d) of the Federal Clean Water Act (CWA) and implementing regulations (40 CFR 130.7) require the establishment of Total Maximum Daily Loads (TMDLs) for water quality limited segments. A water quality limited segment is a waterbody or portion of a waterbody (e.g., a length of river, an area of an estuary, a pond or wetland, etc.) in which water quality does not meet applicable water quality standards, and/or is not expected to meet applicable water quality standards, even after the application of technology-based effluent limitations required by sections 301(b) and 306 of the Clean Water Act. The Delaware Department of Natural Resources and Environmental Control (DNREC) has identified the main stem of the Red Clay Creek as being water quality limited due to zinc concentrations in excess of applicable water quality standards (DNREC, 1996; DNREC, 1998a). Therefore, a TMDL is needed for this waterbody.

A TMDL specifies the maximum allowable mass loading of a pollutant (i.e., pounds per day) that can be delivered to a waterbody while still assuring that applicable water quality standards are met. A TMDL is composed of three components, including a Waste Load Allocation (WLA) for point source discharges, a Load Allocation (LA) for nonpoint sources, and a Margin of Safety (MOS) to account for uncertainties regarding the relationship between mass loading and resulting water quality. In simple terms, a TMDL attempts to match the strength, location, and timing of pollution sources within a watershed with the inherent ability of the receiving water to assimilate the pollutants without adverse impact.

There are five (5) basic requirements of Section 303(d) and its implementing regulation. These requirements include the following:

1. Identification of water quality limited segments still requiring TMDLs;
2. Establishing a priority ranking for the identified segments, including an identification of waters targeted for TMDL activities during the next two year period;
3. Developing TMDLs/WLAs/LAs in accordance with the priority ranking through monitoring, modeling, and data analysis;
4. Incorporating approved loadings into permits and other pollution control requirements; and
5. Providing opportunity for public participation during steps 1, 2, 3, and 4.

Federal regulations instruct the States to satisfy the first two requirements by submitting a list of water quality-limited segments along with their prioritization to the EPA for review and approval by April 1 of every even numbered year. This list and associated prioritization is commonly referred to as the State's CWA 303(d) List. If a State fails to satisfy this listing requirement, the Clean Water Act and implementing regulations instruct the EPA to develop the list. With regard to requirement 3 above, the Clean Water Act and implementing regulations direct the States to submit all TMDLs to the EPA for approval/disapproval. Again, the Act and regulations require the EPA to develop the TMDLs if the State fails to do so. Unlike the listing and prioritization steps, however, development and submission of TMDLs are not mandated to occur on a biennial schedule. Rather, Federal regulations contemplate that EPA and the State will jointly establish a schedule for the development and submission of TMDLs/WLAs/LAs. Such a schedule was developed by Delaware DNREC and the EPA in 1997 in conjunction with and in response to a citizens lawsuit concerning the administration of the TMDL program in Delaware (ALS *et. al.*, 1996). The joint schedule is memorialized in a Memorandum of Understanding between the Secretary of DNREC and the Regional Administration of the EPA (DNREC/EPA, 1997). Among the deadlines included in the schedule is a commitment by the DNREC to establish a TMDL for zinc in the Red Clay Creek by December 31, 1999. The Memorandum of Understanding provides the EPA with an additional year to establish the Red Clay Creek zinc TMDL in the event that DNREC fails to meet its deadline.

1.3 Report Organization

Following the background information provided in this chapter, Chapter 2 presents a detailed characterization of zinc concentrations and mass loadings in the Red Clay Creek. Chapter 3 then derives the zinc TMDL for the Red Clay Creek and documents the assumptions used in that derivation. Chapter 4 identifies the next steps in the TMDL process, including public participation and the development of an implementation plan which the DNREC refers to as a Pollution Control Strategy (PCS). And finally, Chapter 5 provides a listing of references used to support the TMDL. Appendices present raw and processed data tables and selected calculations.

2. CHARACTERIZATION

2.1 Environmental Setting

The Red Clay Creek watershed covers a total drainage area of 53.3 square miles in southeastern Pennsylvania and northern Delaware. Nearly two-thirds (~64 %) of the watershed is located in Pennsylvania. The mainstem of the Creek is fed by two branches (East and West), both of which are located in Pennsylvania. The two branches join roughly 3/4 of a mile above the Pennsylvania-Delaware state line near Marshall's Bridge Road. The mainstem enters Delaware just north of Yorklyn, Delaware and flows southward to its confluence with the White Clay Creek in Stanton, Delaware. The White Clay, in turn, empties into the tidal Christina River, which then flows toward the Delaware River near Wilmington, Delaware. The length of the Delaware portion of the Red Clay is slightly less than 15 miles.

The Red Clay Creek watershed lies within two physiographic provinces which are separated by a fall line that runs along an east, northeast transect approximately following Kirkwood Highway. All of the Pennsylvania portion of the watershed and most of the Delaware portion of the watershed are located in the Piedmont Province to the north of the fall line. The Piedmont is characterized by gently sloping uplands, traversed by relatively narrow valleys. Elevations in this portion of the watershed range from roughly 100 to 450 feet, with slopes of the Creek bed ranging from nearly level (0 - 3 percent) to very steep (greater than 25 %). This portion of the watershed is underlain primarily by felsic and mafic metamorphic schists and gneisses, along with a locally important formation of calcite marble known as the Cockeysville Formation. The lower portion of the Red Clay watershed lies within the Coastal Plain Province. This area is characterized by gently-rolling to flat terrain composed of unconsolidated sediments derived from erosion of the crystalline rocks of the Piedmont. Elevations in the Coastal Plain portion of the watershed are generally less than 100' and slopes of the Creek bottom are nearly level (0 - 3 percent) to occasionally moderate (8 - 15 percent). The very lower reach of the Red Clay Creek experiences tidal backwater from the lower White Clay Creek/Christina River/Delaware River. The Creek is nevertheless fresh for its entire length. The flows at Wooddale, Delaware, which capture roughly 88% of the drainage area of the entire watershed, have ranged from an instantaneous maximum of 5,010 cubic feet per second (cfs) in 1975 to an instantaneous minimum of 2.9 cfs in 1966, with a long term (1943 to 1998) median of 44 cfs, (James, *et. al.*, 1999).

Land use/land cover in the Delaware portion of the Red Clay watershed is a mix of forest, large residential estates, agriculture, and scattered subdivisions north of the fall line. Much of this area is considered to be highly scenic and relatively undisturbed. Below the fall line, land use is primarily higher density residential development and commercial establishments. Overall, land use is categorized as 40 % urban/residential, 29 % forest, 26 % agriculture, and 5 % other.

The waters of the Red Clay have been used for a variety of purposes, including public and industrial water supply, irrigation, put-and-take trout fishing, and general aquatic life maintenance

and propagation. A major historical use of the Red Clay was to power various types of mills that were located along the banks of the Creek, (Marler, E.H., 1987). Although virtually all of these mills are now gone, remnants are still visible in the form of numerous low head dams and mill races in the Piedmont portion of the watershed.

One mill in the Red Clay watershed that is still in operation is the National Vulcanized Fiber (NVF) facility in Yorklyn, Delaware. The facility, which has been operational since the early 1900s, manufactures specialty paper products from rags and other paper. The rags are first broken down in a solution of sodium hydroxide to produce cellulose fiber. The fiber is then formed into sheets which are bonded together (vulcanized) using zinc chloride as a catalyst. Finally, the vulcanized fiber is washed to remove excess zinc. The excess zinc removed with the wash water is concentrated and recycled for subsequent use. Prior to the early 1970s, this excess zinc was discharged directly to the Red Clay Creek. Today, NVF holds an NPDES permit that allows them to discharge a maximum of 1.98 pounds of zinc per day to the Red Clay Creek.

In addition to the NVF facility, there are 4 other permitted NPDES point source discharges in the Delaware portion of the Red Clay Creek watershed. None of these other facilities discharge zinc at levels that impact water quality in the Red Clay Creek.

2.2 Applicable Water Quality Standards

As noted previously, the DNREC identified the mainstem of the Red Clay Creek as being water quality limited due to zinc concentrations in excess of applicable water quality standards. This section provides a brief overview of water quality standards and also identifies and discusses the applicable water quality standards for zinc in the Red Clay Creek.

Water quality standards include a specification of the beneficial use or uses to be made of a water body (referred to as the water's designated uses) and the water quality criteria intended to protect the use or uses. The State of Delaware Surface Water Quality Standards (As Amended, February 26, 1993) lists the following designated uses for the Red Clay Creek: public, industrial, and agricultural water supply; primary and secondary contact recreation; fish, aquatic life and wildlife; and cold water fish (put-and-take), (DNREC, 1993). The DNREC's decision to list the Red Clay on its 303(d) list was based upon exceedances of Delaware's zinc criteria for the protection of aquatic life. Those criteria are listed below.

$$\text{Freshwater Acute Criterion (ug/L)} = e^{(0.8473[\ln(\text{hardness})] + 0.8604)}$$

$$\text{Freshwater Chronic Criterion (ug/L)} = e^{(0.8473[\ln(\text{hardness})] + 0.7614)}$$

The DNREC interprets these criteria on a "total" zinc basis (rather than "dissolved") and has developed the zinc TMDL for the Red Clay Creek on this basis accordingly. The acute criterion

is a 1-hour average concentration not to be exceeded more than once in any three year period, while the chronic criterion is a 4-day average concentration, also with a 3 year return period. Note that both of these criteria increase as a function of water hardness. For hardness values between 100 mg/L and 200 mg/L, these criteria range between approximately 100 ug/L to 200 ug/L.

The above criteria are based on “national” criteria developed by the EPA, (EPA, 1987). These criteria are intended to protect a broad assemblage of freshwater plants and animals from the short and longer term toxic effects of zinc. In the case of fish, a number of behavior and physiological effects are known to occur when test organisms are exposed to zinc, (Sorensen, 1991). Behavioral effects that have been reported include avoidance response, feeding rate changes, and changes in movement patterns. With respect to physiological effects, it has been reported that fish exposed to increased zinc levels exhibit increased ventilation rate and frequency of coughing and a concomitant decrease in oxygen utilization. Presumably, these inter-related respiratory effects are caused by excess zinc adsorption to gill membranes, which in turn decreases functional surface area for oxygen transfer and oxygen diffusion capacity. Additional information concerning the types of adverse effects that excess zinc can have on aquatic life and the associated effect levels is available through the EPA’s on-line database AQUIRE, (EPA, 1999).

Because the above criteria are expressed as a function of hardness, there is not a single numerical value for the acute criterion and a single numerical value for the chronic criterion that apply under all circumstances. Rather, to determine whether a particular ambient water sample contains a zinc concentration that exceeds one or both of the criteria, the hardness value for that sample must first be substituted into the criteria equations and then the resulting concentrations are compared to the total zinc concentration in that same sample. For purposes of developing the TMDL, however, it is necessary to select a “design” hardness value that accounts for the critical conditions in the stream. In accordance with Section 9.3(a)(i) of Delaware’s Surface Water Quality Standards, the selection of an appropriate hardness value is a site-specific determination that is determined on a case-by-case basis by DNREC. This issue will be addressed in a subsequent section of this report.

As noted previously, the acute and chronic criteria both increase as a function of hardness. In other words, the toxicity of zinc decreases as hardness increases. Although the exact reason this is so is still an area of active research, it has been postulated that calcium and magnesium, which are the major divalent cations that contribute to hardness, compete with zinc, which is also a divalent cation, for binding sites on biological surfaces. Because less zinc is able to come into contact with the organism, the true exposure actually experienced by the organism is reduced, which in turn translates into less severe effects. In addition to this competitive factor, harder water also tends to have higher ionic strength, which may act to electrostatically inhibit the sorption of zinc to binding sites on the biological surfaces. Both of these phenomena, and all other physical, chemical, and biological factors that tend to moderate or mitigate toxicity, collectively determine what is known as a pollutant’s “bioavailability.”

Although Delaware's water quality criteria for zinc are expressed on a "total" metal basis, and the TMDL for zinc in the Red Clay Creek has been developed based upon "total" zinc, DNREC nevertheless recognizes the importance of considering the bioavailable fraction of the metal in assessing the likelihood of adverse effects to aquatic life. Bioavailability is taken into account by converting the "total" metal criteria to a "dissolved" basis and then by comparing the resulting dissolved criteria to dissolved metal measurements for ambient water samples. The conversion of the total zinc criteria to a dissolved basis is done simply by multiplying the total criteria by total to dissolved conversion factors. To convert the acute zinc criterion (expressed on a total basis) to a dissolved basis, the total criterion is multiplied by 0.978. Similarly, to convert the chronic zinc criterion (expressed on a total basis) to a dissolved basis, the total criterion is multiplied by 0.986. These conversion factors were taken from values published by the EPA in 1995, (Stephan, 1995). Again, this approach was taken to supplement, not to supercede, the "total" metal approach taken to establish the zinc TMDL for the Red Clay Creek.

The final point to be made in this section is that the water quality criteria necessary to protect aquatic life from the toxic affects of zinc are significantly more stringent than concentrations that are associated with increased risk to humans. The author has previously estimated an informal guideline of 3 mg/L (i.e., 3000 ug/L) as protective of human health, (Greene, 1995). The aquatic life criteria (at typical hardness values) are more than an order of magnitude (i.e., >10x) more stringent than this informal human health guideline. The aquatic life criteria are the controlling criteria for the Red Clay Creek TMDL.

2.3 Assessment of Zinc Concentrations and Mass Loading in the Red Clay Creek

An initial step in the TMDL process is to compile and analyze information on the concentrations, flows, and mass loadings for the pollutant of concern, in this case, zinc. This section presents the concentration and mass loading information for zinc in the water column of the Red Clay Creek and also presented data concerning zinc levels observed in groundwater, sediment, and fish tissue of the Red Clay watershed. Loading and release data for the NVF Yorklyn facility will be presented separately in Section 2.4 of this report.

2.3.1 Routine Water Quality Monitoring Data

The Delaware DNREC and the Pennsylvania DEP perform routine water quality monitoring at 4 locations along the mainstem of the Red Clay Creek. These 4 stations are identified in Table 1 below and are also shown in Figure 1. Water samples are collected at these four stations on a monthly to quarterly basis and are analyzed for total zinc, dissolved zinc, hardness, pH, and temperature, along with several other parameters. Total and dissolved zinc are analyzed using EPA Method 200.7, inductively coupled plasma, atomic emission spectrometry (ICAP-AES).

Table 1. Routine Monitoring Station in the Red Clay Creek

Sampling Location	Station ID	River Miles Above (-) or Below (+) Yorklyn	Number of Data Points	Period of Record Considered
Marshall's Br. Rd., PA	WQN 150	-2.3	55	1/25/94 - 8/24/98
Ashland, DE	103041	+1.7	46	7/21/93 - 9/15/98
Wooddale, DE	103031	+9.0	47	7/21/93 - 9/15/98
Stanton, DE	103011	+13.1	40	3/14/94 - 9/15/98

Table 1 specifies the period of record considered for each station, the number of samples taken over the period, and the number of river miles above (-) or below (+) Yorklyn, Delaware. The number of river miles above or below Yorklyn has relevance because the primary source of zinc to the Red Clay Creek is located in Yorklyn. Although there are over two decades of data available for each of these 4 stations, this report only considers the last five years in order to focus on current conditions and because sampling dates and analytical methods were closely coordinated between Pennsylvania and Delaware during the period. A detailed summary of pre-1990s zinc data is available elsewhere, (Dobroski and Salamon, 1988).

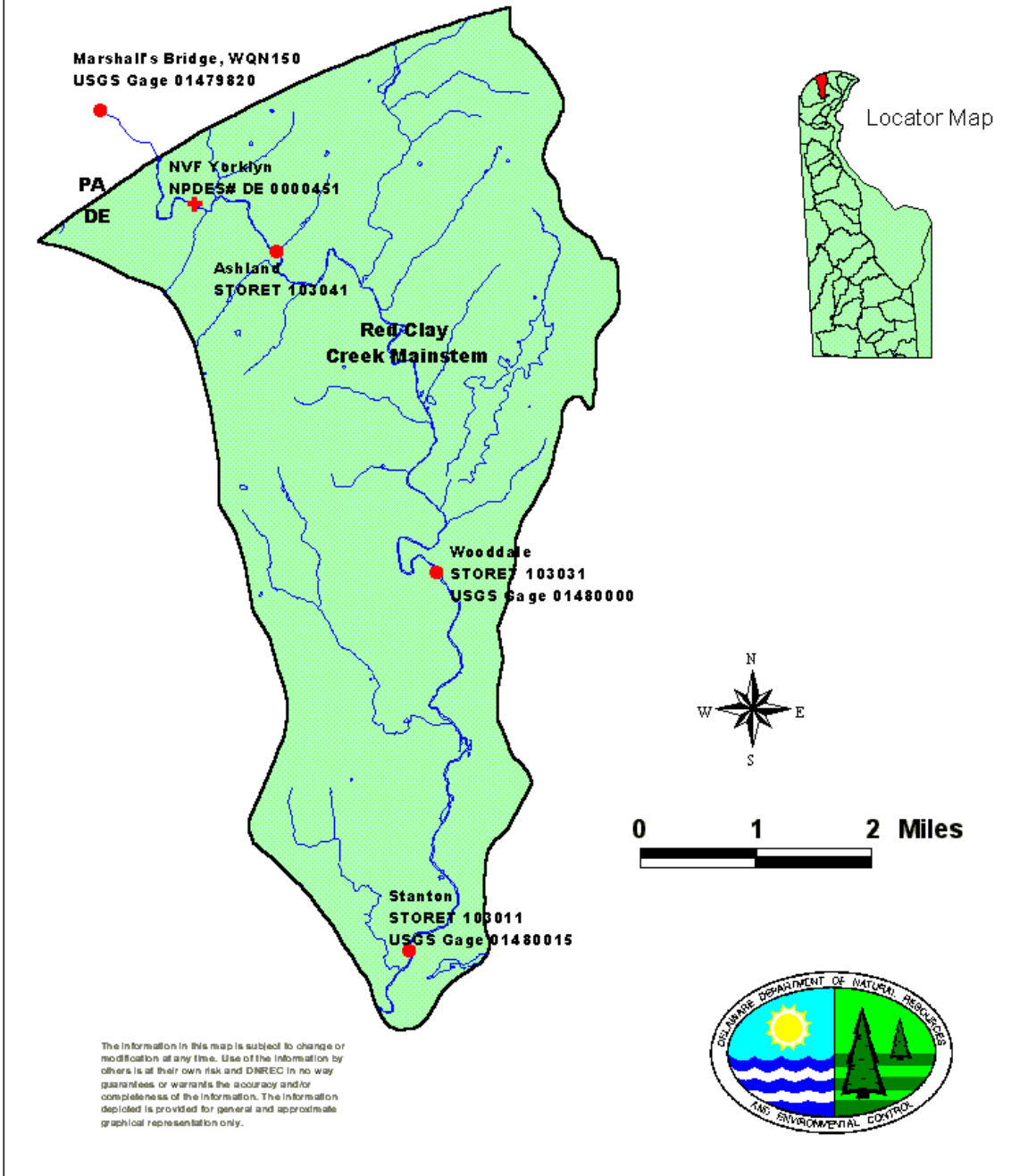
Appendix A of this report presents information on zinc concentration, streamflow, and zinc mass loading for the 4 stations listed in Table 1. For each station, 4 separate pages of printout are provided. The first page provides the sample date, streamflow, total zinc concentration, dissolved zinc concentration, the percentage of zinc in the dissolved form, the mass loading of total zinc, and the mass loading of dissolved zinc. The second page provides summary statistics for zinc concentration and mass loading for the full record considered as well as for individual water years, (i.e., October 1 through September 30). The third page lists the hardness reported for each day along with the computed acute and chronic criteria for zinc. And finally, the fourth page compares the measured zinc concentrations presented on the first page to the criteria listed on the third page.

Several explanatory notes are offered to clarify the data and information presented in Appendix A. First, flow values at the Marshall's Bridge, Wooddale, and Stanton locations were obtained directly from daily flow values reported by the USGS for those sites, (USGS, 1999). The gage numbers for those three locations are 01479820, 01480000, and 01480015, respectively. The flow values for Ashland were extrapolated from flows reported for the Marshall's Bridge gage, less 0.5 MGD that is permanently withdrawn from the Red Clay and discharged to the sewer system by the NVF facility. Specifically, flows at Ashland were estimated as follows:

$$\text{Flow at Ashland} = [\text{Flow at M.B.} \times (\text{Area above Ashland}/\text{Area above M.B.})] - \text{NVF withdrawal},$$

where the area above Marshall's Bridge is reported by the USGS to be 28.3 square miles. The additional drainage area between Marshall's Bridge and Ashland was determined to be 4.8

**Figure 1. Red Clay Creek Watershed
New Castle County, Delaware**



square miles through the use of a planimeter, making the total drainage area above Ashland 33.1 square miles.

The column headers “TZinc” and “DZinc” in Appendix A represent total zinc and dissolved zinc, respectively. The abbreviation “DQC” refers to “data qualifier code” in the column headers immediately following the total zinc and dissolved zinc concentrations. For example, the symbol “<” may appear in the DQC column, indicating that the laboratory did not detect zinc above the detection limit of the instrument. In those situation, ½ of the detection limit was substituted for the non-detected result in order to allow subsequent calculations with the concentration data.

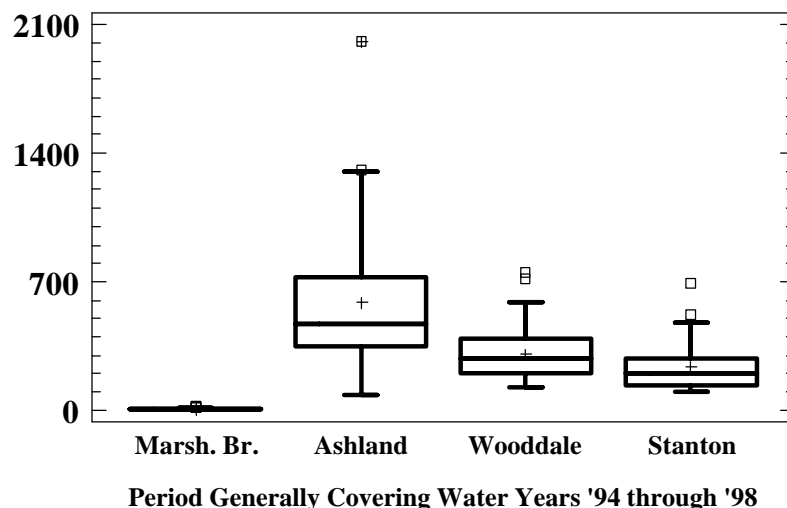
The column labeled “Mass Load Total Zinc” was calculated as the product of the total zinc concentration and the associated streamflow for that day. Similarly, “Mass Load Dissolved Zinc” was computed by multiplying the dissolved zinc concentration by streamflow.

Finally, “CMC_t” on the third of each group of 4 pages in Appendix A refers to the acute zinc criterion expressed on a total basis, and “CCC_t” refers to the chronic zinc criterion, also expressed on a total basis. Similarly, “CMC_d” refers to the acute criterion expressed on a dissolved basis, and “CCC_d” refers to the chronic criterion on a dissolved basis. The comparisons between the computed criteria and the sample results are shown on the fourth of each group of 4 pages and is expressed as the ratio of the sample result to the associated criterion. This ratio is identified as an “Ecorisk Index.” Indices greater than 1 signify that the concentration of zinc in the sample exceeded the corresponding criterion, while indices less than 1 mean that the sample did not exceed the criterion.

With the above explanatory notes in mind, a close examination of the data and information presented in Appendix A reveals the following key features regarding zinc in the Red Clay Creek:

- ▶ **Finding 1:** The concentrations of total and dissolved zinc at the Marshall’s Bridge station are very low, often registering non-detected results of 5 ug/L. The concentration of total and dissolved zinc at Ashland, Wooddale, and Stanton are, in comparison, quite high, ranging typically between 200 ug/L to 800 ug/L. Further, concentrations at Ashland have occasionally exceeded 1000 ug/L within the last 5 years and have even exceeded 2000 ug/L on one occasion (9/11/95). Figure 2 demonstrates the spread and central tendency of the total zinc concentrations at the 4 stations over the record considered .

Figure 2. Box-and-Whisker Plot for Total Zinc Concentration, Red Clay Creek (concentration in ug/L)

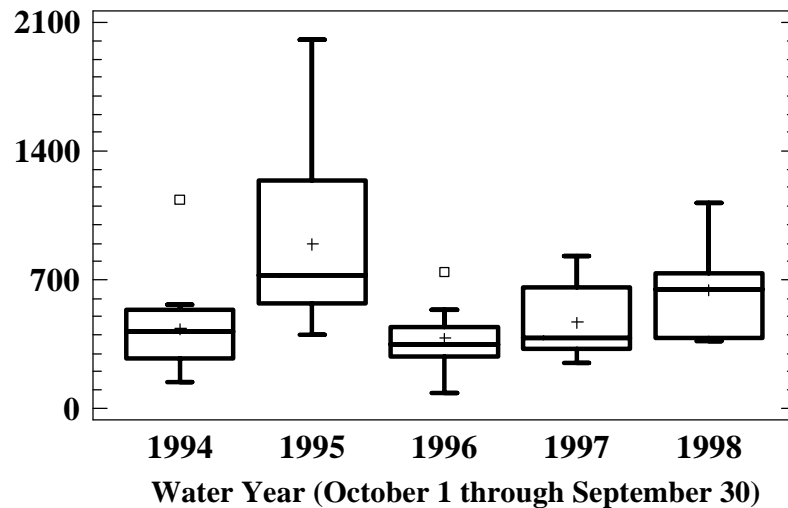


(Note about this figure: The horizontal line within the box represents the median and the “+” symbol represents the arithmetic average. The top of the box represents the upper quartile (75th percentile) of the data distribution and the bottom of the box represents the lower quartile (25th percentile) of the data distribution. The difference between the top of the box and the bottom of the box is known as the interquartile range over which the middle 50 percent of the data lies. The horizontal line at the top of the upper whisker is the largest data point within 1.5 times the upper quartile, which often corresponds to the maximum value. The horizontal line at the bottom of the lower whisker is the smallest point within 1.5 times the lower quartile, which often corresponds to the minimum value. Small squares beyond the whiskers are outliers or potential outliers).

From the above figure, and from Appendix A, note that the median total zinc concentration at Marshall’s Bridge, Ashland, Wooddale, and Stanton over the approximate 5 year period are 5.1 ug/L, 471 ug/L, 281 ug/L, and 203 ug/L, respectively. The median concentration at the upstream station is statistically less than the median for each of the 3 downstream stations, ($p = 0$, Kruskal-Wallis). Further, the median at Ashland is greater than the median at Wooddale, ($p = 9.5E-7$, Mann-Whitney), which in turn, is greater than the median at Stanton, ($p = 0.0015$, Mann-Whitney). In other words, there is a sharp increase in zinc concentration between Marshall’s Bridge and Ashland and a discernable decline from Ashland downstream to Stanton. The increase between Marshall’s Bridge and Ashland is attributed to the known source of zinc located in Yorklyn. The decline below Ashland is believed to be primarily due to dilution from clean baseflow and tributary inflow as the Creek flows towards its mouth. In addition, settling of particulate (adsorbed) zinc to the Creek bed and flood plain are also likely to account for some of this concentration drop-off. This point will be revisited in the discussion of mass loading to follow later in this report.

- **Finding 2:** There has been little change in the concentration of zinc in the Red Clay Creek over the last 5 years, with the exception of statistically higher concentrations during water year 1995, ($p = 0.0065$, Kruskal-Wallis). The lack of any major change with time is demonstrated in Figure 3 below which shows the annual variation of total zinc concentration at the Ashland station.

Figure 3. Box-and-Whisker Plot for Total Zinc at Ashland (concentrations in ug/L)



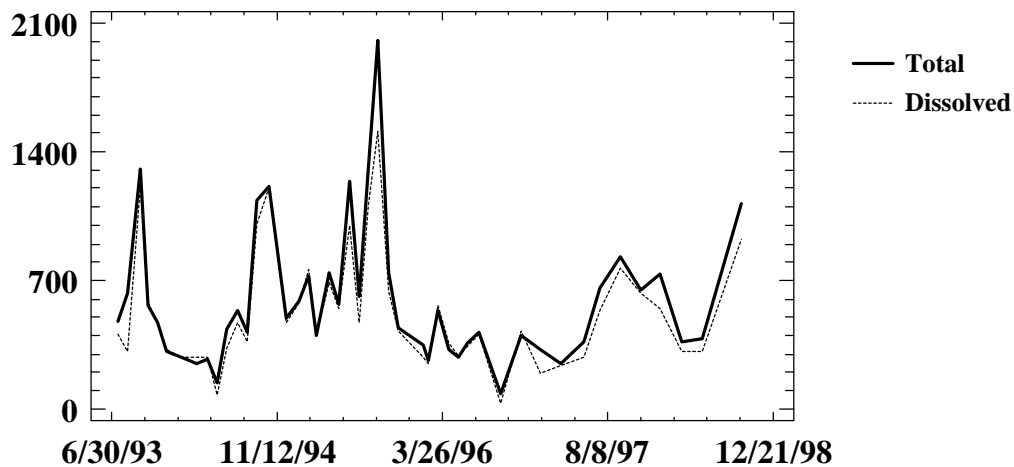
Note from the diagram (or from Appendix A) that the median total zinc concentration during water year 1995 was 729 ug/L, while the median during water year 1996 was approximately ½ that at 351 ug/L. Interestingly, the median annual flow in the Red Clay Creek during water year 1996, (57 cfs at Wooddale), was approximately twice that for water year 1995, (26 cfs, also at Wooddale). Therefore, zinc concentrations at Ashland tend to be higher when streamflows are lower, and vice versa. Viewed from a different perspective, this observation also suggests an ongoing waste discharge of more-or-less constant source strength that is moderated primarily by streamflow. The relationship between zinc concentration and streamflow will be explored more fully later in this section.

Since water year '96, the median zinc concentration at Ashland has nominally increased, most recently registering 647 ug/L during water year '98. Again, water year 1998 was drier than normal, registering a median annual flow of 33 cfs at Wooddale in comparison to a long-term median of 44 cfs. Although a complete record for water year 1999 is not yet available, it is predicted that the median zinc concentration will rival medians seen during water years 1995 and 1998 since low flow conditions experienced thus far in water year '99 are as severe or worse than those experienced during '95 and '98.

Although there has been no statistically significant decline in zinc concentrations over the last 5 years, it is important to note that a drop has occurred when viewed over a longer time frame. DNREC recently reported that there has been a statistically significant decline in zinc levels in the Red Clay Creek over the roughly 25 year period from 1971 through 1996, (DNREC, 1998b). With all of this information in hand, the picture that emerges is that zinc levels have come down over the long-term but have now leveled out and are subject to modest increases during dry periods and modest decreases during wet periods.

- ▶ **Finding 3:** The vast majority of zinc in the Red Clay Creek is in a dissolved state. Figure 4 below demonstrates this point through a plot of total and dissolved zinc at the Ashland monitoring station. The fraction of dissolved zinc at this station, computed as the geometric mean of dissolved to total zinc concentration pairs is 85.9 %. Similar

**Figure 4. Total and Dissolved Zinc at Ashland
(concentrations in ug/L)**



percentages apply to the other stations, especially for the downstream stations.

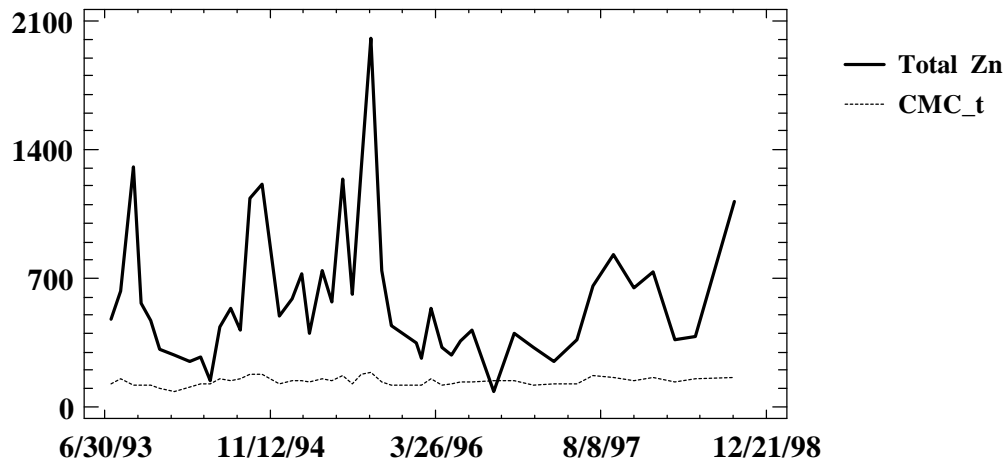
- ▶ **Finding 4:** The concentration of zinc at the Ashland and Wooddale stations virtually always exceed applicable water quality criteria. Although criteria exceedences are not as frequent at the Stanton station, exceedences are still very common. In contrast, no exceedences were observed for the upstream Marshall’s Bridge station. Table 2 below summarizes the exceedance frequencies for each of the 4 stations for acute and chronic criteria, on both a total and dissolved basis.

Table 2. Exceedance Frequencies for Zinc Water Quality Criteria in Red Clay Creek

Sampling Location	Number of Data Points	% of Samples > CMC _t	% of Samples > CCC _t	% of Samples > CMC _d	% of Samples > CCC _d
Marshall's Bridge, PA	55	0	0	0	0
Ashland, DE	46	97.8	97.8	95.6	95.6
Wooddale, DE	47	100	100	89.4	93.6
Stanton, DE	40	82.5	87.5	60	65

- ▶ **Finding 5:** Not only are the criteria exceeded frequently at the downstream stations, the magnitude of those exceedances are also quite large. This point is demonstrated in Figure 5 below, which plots the measured concentration of total zinc at Ashland versus the associated acute zinc criterion (which varies as a function of hardness).

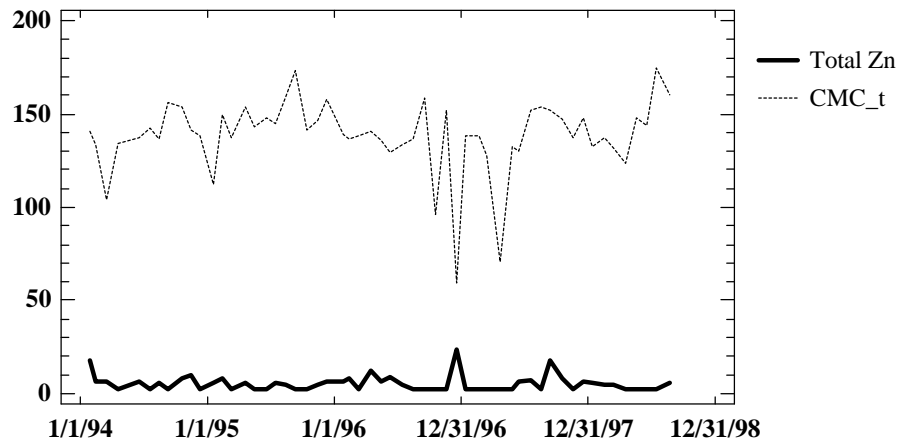
Figure 5. Total Zinc and Acute Criterion at Ashland (concentrations in ug/L)



On average, the concentration of total zinc at the Ashland station is four times (4x) the acute criterion (total basis) and 4.5x the chronic criterion (total basis). On a dissolved basis, the average magnitude of exceedance drops only slightly to ratios of 3.7 and 4 for dissolved acute and dissolved chronic criteria, respectively. Given that Ashland is located 1.7 miles downstream from the primary zinc source, the magnitude of exceedance would likely be even greater upstream from Ashland but below Yorklyn. There is evidence that will be discussed later which supports this contention.

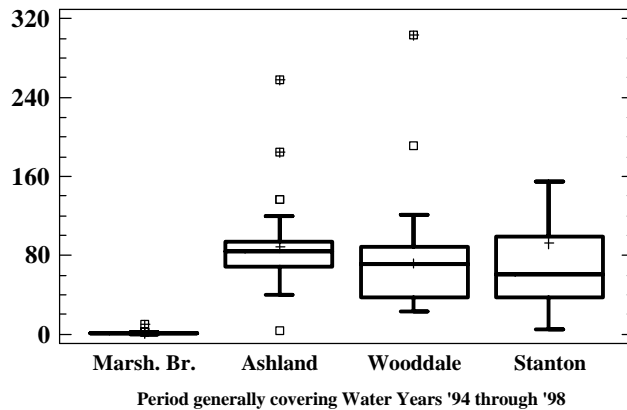
In contrast to the downstream stations, the concentrations of zinc at the upstream, Marshall's Bridge Road station, is typically 20 to 30 times less than water quality criteria. This is shown in Figure 6 below.

**Figure 6. Total Zinc and Acute Criterion at Marshall's Bridge
(concentrations in ug/L)**



Finding 6: When zinc concentrations are multiplied by streamflows, we see that the mass loading of total and dissolved zinc (upstream) at Marshall's Bridge is low, most often falling below 1 pound of zinc per day. In contrast, the mass loading of total and dissolved zinc at the 3 downstream stations is as much as two orders of magnitude greater, typically falling between 60 to 100 pounds per day. Figure 7 below shows the mass loading of total zinc at the four stations over the period considered.

**Figure 7. Box-and-Whisker Plot for Total Zinc Mass Loading, Red Clay Creek
(mass load in pounds per day)**

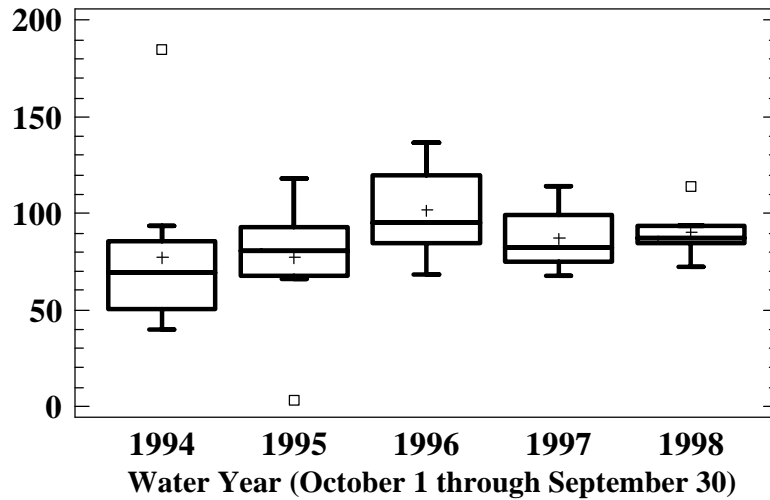


From this figure and from Appendix A, we see that the median mass loading of total zinc at Marshall's Bridge, Ashland, Wooddale, and Stanton over the period considered are 0.60, 84.85, 72.02, and 61.03 pounds per day, respectively. Therefore, there is more than a 100-fold increase in the mass loading of total zinc between the Marshall's Bridge and Ashland stations. As might be expected, the mass loading of zinc at the Marshall's Bridge station is statistically different (lower) than the mass loadings for the 3 downstream stations, ($p = 0$, Kruskal-Wallis). Further, the mass loading of total zinc at Ashland is statistically greater than the mass loading at Wooddale, ($p = 0.0041$, Mann-Whitney). However, the mass loading at Wooddale is not significantly greater than the loading at Stanton, ($p = 0.3274$). Although there is not a statistically significant drop in mass loading between Wooddale and Stanton, it is evident that there is nonetheless at least a nominal decline between these two stations, (i.e., 72 #/day to 61 #/day).

Because zinc is a conservative substance, the only loss process that can account for the decline in total zinc mass loading in the downstream direction is settling of particulate zinc from the water column. Baseflow and tributary dilution, although capable of reducing the concentration of zinc in the Creek, does not act to reduce mass loading. The fact that the decline in total zinc mass loading between Ashland and Stanton is only moderate is consistent with the data which shows that most of the zinc transported in the Red Clay is dissolved. The dissolved zinc moves along with the flow of the Creek and is not subject to immediate settling. Viewed from another perspective, there is very little particulate zinc normally in the water column available to settle out. This is not to say that a significant quantity of particulate zinc has not settled out of the water column over time. It has. Levels of zinc in the sediments of the Red Clay Creek, along with the implication to the TMDL, will be discussed in a later section of this report.

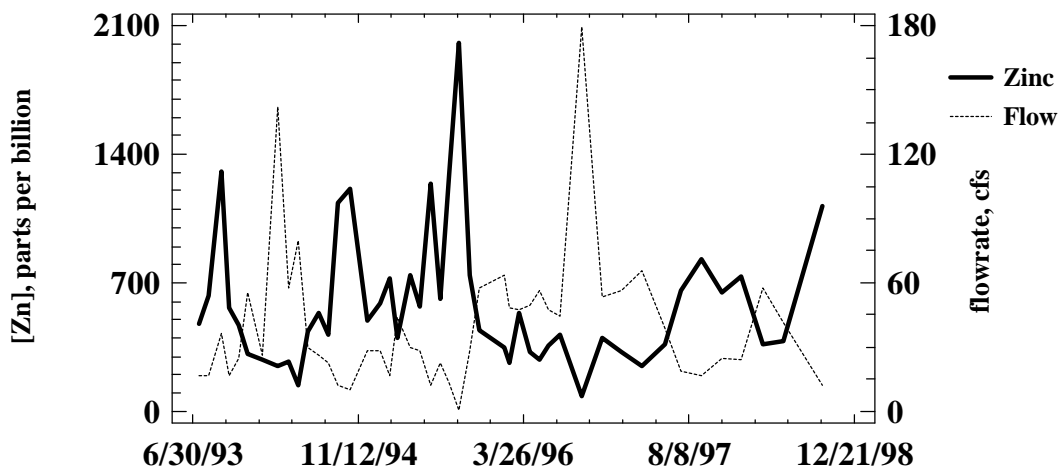
- ▶ **Finding 7:** Mass loading of zinc did not decline over the 5 year period considered in this analysis. This is shown in Figure 8, which plots the mass loading of total zinc at Ashland by water year. From the figure (and Appendix A), the medians are as follows, (by increasing water year): 69.02, 80.95, 95.62, 82.53, and 87.15 pounds per day. Although there is a 38.5% difference between the highest annual median (water year '96) and the lowest annual median (water year '94), none of the annual medians for Ashland for the years considered are statistically different at the 95% confidence level, ($p = 0.0754$, Kruskal-Wallis). Therefore, we see that the mass loading of zinc in the Red Clay remains fairly steady, despite the fact that zinc concentration increases and decreases in response to streamflow, as demonstrated earlier. Also as noted earlier, this observation strongly suggests a fairly constant waste source discharge to the Red Clay Creek.

Figure 8. Box-and-Whisker Plot for Total Zinc Mass Load at Ashland (mass load in pounds per day)



- **Finding 8:** Finally, it has been stated several times that there appears to be an inverse relationship between streamflow and zinc concentration at the downstream stations. Figure 9 below shows a time series plot for total zinc concentration and streamflow at the Ashland station which clearly demonstrates this point.

Figure 9. Total Zinc and Flow at Ashland



Formal regression analysis of the data pairs used to construct the above plot revealed a strong, statistically significant, inverse relationship between streamflow and zinc at the Ashland station. The relationship is best described by a reciprocal-Y function, (i.e., $Zn = 1/(0.00413228 + 0.0000514088 * Flow$, where Zn is in units of ug/L and Flow is in units of cubic feet per second). The p value for this relationship is less than 0.01, indicating that there is a statistically significant relationship between zinc and flow at the 99% confidence level. Further, the R-Squared statistic for the relationship is 75.5%, indicating that the vast majority of the variability observed for total zinc at the Ashland station is explained by flow. In contrast, streamflow and zinc concentrations were not related at the Marshall's Bridge Road station, ($p = 0.4049$ and $R^2 = 1.31\%$).

In addition to the relationships between zinc and flow, it is also important to consider any relationships between hardness and flow because both of these variables affect the design conditions, ("critical" conditions), for the TMDL. Regression analysis showed that there are relatively weak relationships between streamflow and hardness at both the Marshall's Bridge Road and Ashland stations when the full 5 year record was considered. However, when only low flows were considered, a moderately strong relationship emerged for the Marshall's Bridge Road station. Specifically, for flows of 12 cfs or less, (where 12 cfs represents the 10th percentile flow for the 5-year record), the relationship between flow and hardness at Marshall's Bridge became moderately strong (R^2 of 65%) and statistically significant ($p = 0.0288$). The relationship is as follows: $Hardness = 160.433 - 2.13374 * Flow$, where Hardness is in units of mg/L as $CaCO_3$ and Flow is in units of cubic feet per second (cfs) for flows of 12 cfs or less.

- ▶ As a final note in this section, the reader is reminded that all environmental measurements, including those for zinc, have some inherent uncertainties. However, the consistency from one sampling event to the next, coupled with the fact that analytical instrumentation has generally not been a limiting factor for the range of zinc concentrations under consideration, gives DNREC considerable confidence in the dataset described in this section. Detailed quality assurance/quality control (QA/QC) procedures were employed for the results presented in this section. The QA/QC results include, among other performance measures, percent recoveries of matrix spike samples and relative percent differences for duplicates. Those results are not presented in this report but can be provided upon request. With very few exceptions, data were all within acceptance criteria. The overall size and quality of the database discussed in this section of the report is thought to be good to excellent.

2.3.2 EPA Region III Superfund Investigation

Roy F. Weston, under contract to the U.S. EPA Region III Superfund Removal Branch, reported the results of surface water, groundwater, and sediment sampling conducted in May of 1997 as part of a multimedia assessment of contaminant release from the NVF Yorklyn facility, (EPA,

1997). The results of zinc analyses performed on the surface water samples are presented in the table below. Maps depicting the sample locations are available upon request.

Table 3. Surface Water Results, EPA Superfund Investigation at NVF, Yorklyn

Sample ID	Location	Zinc, (ug/L)
RCCW-5	Red Clay at Marshall's Bridge	9.7B
RCCW-2	Red Clay 20 yds downstream from Yorklyn Rd; Immediately upstream from NVF manufacturing operations	12.4B
RCCW-1	Red Clay immediately downstream from all NVF manufacturing operations, near #1 Mill	3500
RCCW-4	Red Clay approx. 850 feet downstream from NVF	399
RCCW-3	Red Clay downstream from NVF and immediately upstream from Ashland covered bridge	394
CSS-2	NVF cross stream upstream	23.7
CSS-1	NVF discharge 002, ten feet above discharge point	161

The first 5 rows in the table are presented in an upstream to downstream sequence rather than in numerical sequence. The two upstream results for zinc were 9.7B and 12.4B, where the "B" data qualifier code signifies that zinc was detected in the associated field blank. The low zinc concentrations for these 2 samples are consistent with results presented in the previous section for the Marshall's Bridge Road station. The zinc concentration in the closest downstream station from the NVF facility was 3,500 ug/L, a roughly 300-fold increase from the upstream stations. Further downstream from the facility, however, the zinc concentrations dropped back to approximately 400 ug/L, which is consistent with concentrations reported in the previous section for the Ashland station. Finally, the concentration of zinc in NVF's NPDES outfall 002 registered 161 ug/L, and that in the "cross stream" was 23.7 ug/L. The cross stream is a small tributary that runs parallel to Yorklyn Road and the Octoraro railroad tracks. It flows onto the NVF Yorklyn property, where it mixes with non-contact cooling water withdrawn from the Red Clay Creek. The cross stream plus the cooling water are then discharged to the Red Clay Creek through NVF outfall 002. The concentration of zinc in the discharge and in the cross stream are within the range of previously observed values.

The extremely high zinc concentration detected in the sample immediately downstream from the NVF facility is likely to be the result of sampling at a point where contaminated groundwater from

the facility enters the Red Clay but where that discharge had not had an opportunity to completely mix with the available flow of the Creek yet. This speculation is supported by groundwater data collected from several shallow monitoring wells that were sampled during the May 1997 multimedia investigation. The zinc concentrations reported for the groundwater samples are presented below. Again, maps showing the well locations are available upon request.

Table 4. Groundwater Results, EPA Superfund Investigation at NVF, Yorklyn

Sample ID	Location	Zn, (ug/L)
MW-3	Between zinc recovery unit and the Red Clay Creek, approx. 130' upstream from Yorklyn Rd.	11,700
MW-4	Between main paper mill and the Red Clay Creek, approx. 400' downstream from Yorklyn Rd.	24,000
MW-5	Between #1 Mill and the Red Clay Creek, approx. 950' downstream from Yorklyn Rd.	361,000
MW-2	Between #6 Fiber Mill and the cross stream, approx. 700' upstream of NVF outfall 002	57,800
MW-1	Near Building #25, approx. 600' from the Red Clay Creek, (Background)	6,240

The first three locations listed in the table (MW-3, MW-4, and MW-5) are presented in an upstream to downstream sequence. All three of these wells are located in close proximity (e.g., ~ 100' or less) to the Red Clay, while MW-2 and MW-1 are located 600 to 700 feet from the Creek. Note that the zinc concentrations in monitoring wells 2 through 5 are all elevated relative to monitoring well 1, (which was identified as the “background” well). Further, note that the concentration of zinc in monitoring well 5 was particularly elevated, (i.e., 361,000 ug/L). Interestingly, monitoring well 5 was the closest well to Red Clay Creek surface water sample RCCW-1, where the peak in-stream zinc concentration of 3,500 ug/L was reported.

In addition to the surface and groundwater results presented above, the EPA Superfund investigation also involved the collection of aquatic sediments from the Red Clay Creek and from the cross stream. Those results are presented below, again in an upstream to downstream sequence. Again, maps showing the exact locations of the sediment samples are available upon request.

Table 5. Sediment Results, EPA Superfund Investigation at NVF, Yorklyn

Sample ID	Location	Zn, (ug/g dry)
RCCS-8	Red Clay at Marshall's Bridge Road	87.2
RCCS-9	Duplicate of RCCS-8	62.4
RCCS-3	Red Clay 20 yds downstream from Yorklyn Rd; Immediately upstream from NVF manufacturing operations	38.8
RCCS-2	Red Clay approx. 400 - 500' downstream from Yorklyn Rd.	459
RCCS-1	Red Clay immediately downstream from all NVF manufacturing operations, near #1 Mill	3430
RCCS-7	Red Clay downstream from NVF, 730' upstream of dam near RR	219
RCCS-6	Red Clay downstream from NVF, 730' upstream of dam near RR	149
RCCS-5	Red Clay downstream from NVF, 200' downstream of dam near RR	254
RCCS-4	Red Clay downstream from NVF and immediately upstream from Ashland covered bridge	534
CSS-2	NVF cross stream upstream	104
CSS-1	NVF discharge 002, ten feet above discharge point	1590

As was the case for the surface water samples, the zinc concentration detected in the sediments of the Red Clay Creek downstream from the NVF facility were significantly higher than the zinc sediment concentrations upstream of the facility. Further, the peak sediment concentration (3430 ug/g) was detected immediately downstream from the NVF facility, (sample RCCS-1).

Based upon the results presented above, plus additional sampling performed in conjunction with the multi-media Superfund investigation, the NVF Company and the U.S. EPA Region III have executed a Consent Order to contain/prevent the migration of contamination at the Yorklyn facility, (EPA, 1998). On May 12, 1999, the EPA Region III approved NVF's Response Action Plan (NVF, 1999), thereby setting a removal action into motion.

2.3.3 University of Delaware Investigation of Red Clay Creek Zinc Contamination

Researchers from the University of Delaware conducted specialized testing of the Red Clay Creek between 1988 and 1990 to determine the fate of zinc trapped in the sediments of the Creek, (Pizzuto and Church, 1990). Their study focused primarily on an area between Yorklyn and Ashland where a low head dam serves to impound and slow downstream movement of water and sediment. That dam, which is the first such dam below the NVF facility, is located approximately 0.5 miles downstream of the NVF site. Several of the key findings of that work are summarized below.

- ▶ Zinc concentrations in the Red Clay Creek above the NVF Yorklyn facility are low, while concentrations below the NVF facility are high. For example, total zinc measured upstream at Marshall's Bridge Road on October 21, 1988 was 80 ug/L, compared to a downstream concentration of 1050 ug/L for the water flowing over the dam on this same day.
- ▶ Most of the zinc in the Red Clay Creek below NVF Yorklyn is in a dissolved form and it originates from an [active] source. Once this source delivers zinc to the Creek, the zinc is transported with only a modest amount of deposition and without substantial contributions from the zinc stored in the sediments.
- ▶ Zinc concentrations decrease in the downstream direction below Yorklyn primarily because tributaries and [non-contaminated] groundwater progressively dilute the Creek with water containing very low concentrations of zinc. The researchers note, however, that some zinc is removed from the water column [due to deposition of particulate zinc].
- ▶ Red Clay Creek sediments consist primarily of course to very course grained sand, with some muddy deposits on the insides of bends and behind obstructions. The concentration of zinc in the sediments (dry weight basis) ranged from 8 ug/g up to 936 ug/g, with an average of about 200 ug/g. Zinc was generally found to decrease with depth and not to vary with grain size, organic content, or depositional environment. Zinc concentrations were also found to be elevated in adjacent flood plain soils.

The results of Pizzuto and Church are consistent with, and add further support to, the findings presented in Sections 2.3.1 and 2.3.2 of this report.

2.3.4 U.S. Fish & Wildlife Service Study of Red Clay Creek Sediments

In 1989, the USFWS conducted a watershed-scale study of organic and trace metal contaminants in the sediments and floodplain soils of the Red Clay Creek in Pennsylvania and Delaware, (Rice, 1993). Sediments in the watershed were found to be predominantly sand, consistent with the observations of Pizzuto and Church (1990). The table below presents the concentrations of zinc detected in the surficial sediments of the Red Clay Creek between Marshall's Bridge, PA and the

Creek mouth near Stanton, DE. For brevity, only main stem results and results for the NVF “cross stream” are shown.

Table 6. Selected Zinc Results Reported by the USFWS, Red Clay Creek Sediments

Sample ID	Location	Zn, (ug/g dry)
PA 27	Red Clay Creek near Marshall’s Bridge	57
DE/PA 18	Red Clay Creek at PA/DE Line, below dam	79.5
DE 13	Red Clay Creek just above dam at Sharpless Rd. (near Ashland)	512
DE 6	Red Clay Creek approx. 0.4 mi. upstream of Hoopes outlet (near Wooddale)	550
DE 2	Red Clay Creek just upstream from mouth	656
DE 17	Cross stream approx. 0.4 mi. upstream of NVF facility	87.2
DE 16	Cross stream mouth just before discharge to Red Clay Creek (NVF outfall 002)	1,110

The first 5 results shown in the table are presented in an upstream to downstream sequence. Of those results, the first two (PA 27 and DE/PA 18) are from stations upstream of NVF Yorklyn, while the next three (DE 13, DE 6, and DE 2) are from stations downstream of NVF Yorklyn. The two upstream stations had zinc sediment concentrations of 57 and 79.5 ug/g, and the three downstream stations had zinc concentrations substantially higher at 512, 550, and 656 ug/g. Finally, the upstream location for the cross stream had a zinc sediment concentration of 87.2 ug/g, while the downstream location for the cross stream, (i.e., NVF outfall 002), had a zinc sediment concentration of 1,110 ug/g. The USFWS noted that the zinc results from stations DE 13, DE 6, DE 2, and DE 16 are “enriched” based on aluminum normalization calculations.

2.3.5 DNREC Surveys of Zinc in Red Clay Creek Sediments

2.3.5.1 March 1987 Synoptic Survey

DNREC conducted a limited survey of sediment contamination in the Red Clay Creek in March of 1987. That survey involved the collection of surficial sediment samples from 5 depositional areas between the PA/DE border down to Mount Cuba, which is a short distance upstream from Hoopes Reservoir and Wooddale. The zinc results from that survey were previously presented by Dobroski and Salamon (1988) on behalf of the DNREC. The results are repeated below for completeness.

Table 7. Zinc Results of March, 1987 DNREC Survey, Red Clay Creek Sediments

Sample ID	Location	Zn, (ug/g dry)
#1	Red Clay Creek at PA/DE Line, behind dam	107
#3	Red Clay Creek at Rd 253, between PA/DE Line and NVF Yorklyn	83
#4	Red Clay Creek behind first dam below NVF Yorklyn (same as Pizzuto study area)	1064
#5	Red Clay Creek at Sharpless Rd, just upstream from Ashland	404
#6	Red Clay Creek behind dam near Mount Cuba, upstream from Wooddale	842

Once again, the results are presented in an upstream to downstream sequence. Samples 1 and 3 are located upstream of NVF Yorklyn and samples 4, 5, and 6 are located downstream of NVF Yorklyn. The downstream results are considerably higher than the upstream results, with a maximum value of 1064 ug/g detected at the first station below NVF Yorklyn.

2.3.5.2 Sediment Contamination Study of the Red Clay Creek Near Glenville, DE

The DNREC participated in a small study that was performed in May of 1997 to determine the nature and extent of chemical contamination in channel and overbank sediment samples from the Red Clay Creek in the vicinity of Glenville, Delaware. Glenville lies along the east bank of the Red Clay Creek near the confluence of the Creek. That study included the collection of 5 core samples from the Red Clay Creek and 2 overbank sediment samples from the adjacent floodplain. The Creek samples were composited over an approximate 2 foot depth. The full results of the survey are documented elsewhere, (Greene, 1998). The zinc results for the 5 Creek samples were (dry weight basis): 1,068 ug/g, 941 ug/g, 234 ug/g, 866 ug/g, and 1008 ug/g, with an average of 823 ug/g and a median of 941 ug/g. The concentrations of zinc in the overbank sediments were 883 ug/g and 210 ug/g.

Among the conclusions in the report, it was noted that zinc is particularly elevated and poses an ecological risk to benthic organisms. The Glenville zinc concentrations were placed into broader geographic context by comparing those results to results from a large, regional study. It was noted that the median zinc concentration for the Glenville sediments (941 ug/g) is greater than the maximum concentration for 425 sediment samples taken from the entire Virginian Province, which spans a coastal area from Cape Cod, Massachusetts to Cape Henry, Virginia. Furthermore,

the minimum from Glenville is more than twice the Virginian Province median.

A final point to be made in this section is that the lower reach of the Red Clay Creek (where the Glenville samples were taken) is a sediment deposition zone. This reach is literally “at the bottom of the hill” where the Piedmont portion of the Red Clay watershed drops its suspended sediment load onto the Coastal Plain. This process, referred to as fluvial transport, is a natural phenomenon that has worked over decades to determine the ultimate fate and accumulation of zinc in the sediments of the lower Red Clay Creek.

2.3.6 DNREC Surveys of Zinc in Red Clay Creek Fish Tissue

Zinc is known to accumulate in fish tissue, and therefore elevated concentrations in tissue are a good indicator of contamination, (Sorensen, 1991). The DNREC maintains a statewide fish tissue monitoring program that tests for zinc, among several other parameters. Since 1994, a total of 135 fish samples from various locations throughout the State of Delaware have been analyzed for zinc content. All of these samples have been analyzed by the DNREC laboratory. Further, all of these samples have been analyzed as fillets, or otherwise as edible portions. Among the samples analyzed were 4 composite samples collected from the Red Clay Creek during September of 1995. Two of the samples were from Ashland and two were from Stanton. The first Ashland sample was composed of 5 adult white suckers and the other Ashland sample was made up of 4 medium-sized American eels. At Stanton, one sample was composed of 5 adult white suckers and the other was composed of 5 adult redbreast sunfish.

For the Ashland samples, the zinc concentrations (wet weight basis) were 37.4 ug/g and 29.6, respectively, for the sucker and eel. At Stanton, the zinc concentrations were 20 ug/g and 15.2 ug/g for the sucker and sunfish, respectively. In comparison, the median (50th percentile) zinc concentration among the 135 fish samples taken Statewide is 7.3 ug/g. Further, the 95th percentile concentration for the overall dataset is 18.5 ug/g and the 99th percentile value is 29.6 ug/g. Therefore, 99% of the values Statewide are at or below the values observed in the Ashland samples. Furthermore, although the fish tissue zinc concentrations are quite a bit lower at the Stanton station than at the Ashland station, the Stanton values are still well above the Statewide median and easily within the upper 10% of the data distribution.

It is not known at present whether the elevated levels of zinc detected in the fish are causing any adverse physiological effects to the fish. However, because the concentrations of zinc in the water that surrounds the fish far exceed applicable water quality criteria, it is presumed that adverse effects are at least possible if not likely.

2.4 Mass Loading of Zinc From NVF, Yorklyn

This section summarizes data on the amount of zinc released from the NVF Yorklyn facility. Two categories of data are presented. First, monthly monitoring data are presented for NVF's NPDES discharge to the Red Clay Creek. Second, data are presented on the total amount of zinc released from the facility based on information contained in the Toxics Release Inventory, (TRI). Both categories of data are "self-reporting," meaning that NVF collects and submits the data in order to satisfy regulatory requirements.

2.4.1 NPDES Outfall 002

The NVF Yorklyn facility holds a National Pollutant Discharge Elimination System (NPDES) permit (DE0000451) that allows them to discharge zinc to the Red Clay Creek through outfall 002. NVF's effluent limitations for total zinc are presented in the table below.

Table 8. Effluent Limitations for Total Zinc Discharged from NVF Yorklyn Outfall 002

	Concentration (ug/L)	Mass Loading (pounds/day)
Daily Average	70	1.3
Daily Maximum	110	1.98
Instantaneous Maximum	140	-

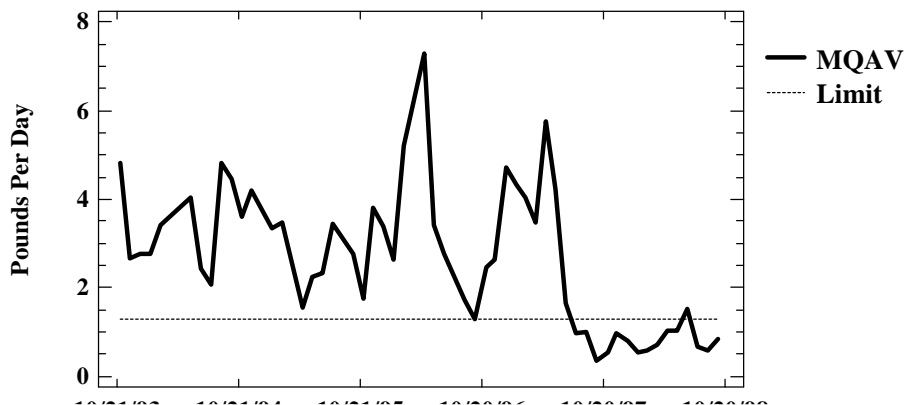
As noted previously, discharge 002 is composed primarily of cooling water withdrawn from the Red Clay Creek plus flow added from the "cross stream." Miscellaneous waste flows such as steam condensate, boiler blowdown, and zeolite regeneration are also allowed to be added to discharge 002. Interestingly, process wastes containing zinc are not allowed to be added to discharge 002. However, because the channel through which discharge 002 is conveyed is an unlined, earthened ditch, zinc is able to enter 002 through shallow groundwater flow and "leaky" processes at the plant. In addition, zinc is also present in discharge 002 as a result of low levels present in the cooling water and cross stream prior to flowing onto the NVF property.

Monitoring to determine compliance with the limits presented above involves the collection of 24-hour composite water samples from discharge 002 once per week, plus continuous flowrate monitoring. The total zinc concentrations observed in each of the weekly samples is averaged over the calendar month and the resulting average is compared to the daily average concentration limit, referred to as the MCAV. The maximum of the four concentrations observed during the month is compared to the daily maximum concentration limit, which is abbreviated as MCMX. By extension, compliance with the daily average mass loading limitation, abbreviated MQAV, is determined by multiplying the measured concentrations by the associated flows, averaging the

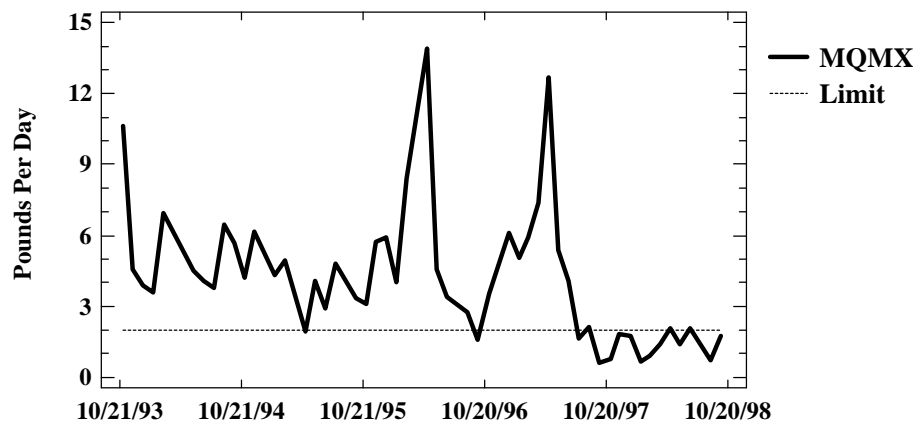
four values, and comparing the result to 1.3 pounds per day. The maximum daily mass loading limitation, MQMX, is the largest of the four daily mass loading values. Finally, the instantaneous maximum concentration limit of 140 ug/L is only used to compare total zinc concentrations in grab samples.

Appendix B of this report presents the monitoring data reported by NVF for discharge 002 over the period spanning from October 1993 through September of 1998. This period was chosen to coincide with the ambient water quality data presented in Appendix A and discussed in Section 2.3.1 of this report. Appendix B also compares the effluent monitoring data to the appropriate effluent limitations. The comparison is shown as the ratio of the reported value to the effluent limit, with ratios greater than 1 indicating a permit violation. Figure 10 below plots the reported average monthly mass loading of zinc for discharge 002 against the MQAV and Figure 11 plots the reported maximum monthly mass loading against the MQMX.

**Figure 10. Daily Average Zinc Mass Loading Versus Effluent Limit
NVF Yorklyn Outfall 002**



**Figure 11. Daily Max Zinc Mass Loading Versus Effluent Limit
NVF Yorklyn Outfall 002**



From the above figures, we see that there is a high frequency of violation of both the MQAV and MQMX limits when the full record is considered. However, note that compliance greatly improved beginning in July of 1997, with only 1 violation of the MQAV and 3 violations of the MQMX. In terms of actual mass loading since that time, daily average loading has dropped to less than 1 pound per day, (with 1 exception), and daily maximums have dropped to an average of 1.4 pounds per day.

Despite these improvements, data presented in Section 2.3.5 of this report indicates that total zinc mass loading in the Red Clay Creek below the NVF Yorklyn facility remains high. Further, and more importantly, simple mass balance calculations show that the mass loadings of zinc below the NVF Yorklyn facility (i.e., ~ 87 pounds per day at Ashland during water year 1998) cannot be accounted for based upon the mass loading of zinc coming from upstream (~ 0.6 pounds per day at Marshall's Bridge), plus the mass loading from the NVF discharge 002 (~0.5 to 2 pounds per day). In fact, the mass loading from discharge 002 is a very small fraction of the total mass loading of zinc observed in the Creek below the NVF facility. The source of the remaining zinc that serves to close this mass balance will be discussed next.

2.4.2 Toxics Release Inventory Data

The NVF Yorklyn facility reports annually on the amount of zinc released to the surrounding air, water, and land. This reporting is required under Title III, Section 313, of the federal Superfund Amendments and Reauthorization Act. The database produced from this reporting is known as the Toxics Release Inventory, or TRI for short. TRI data for zinc released from the NVF Yorklyn facility is available for reporting years 1987 through 1997 (DNREC, 1999) and is shown in Table 9. The data presented in the second and third columns of the table were self-reported by the NVF Company. Figures in the fourth column were computed by the author by dividing the annualized numbers appearing in the second column by 365.

Table 9. Toxics Release Inventory (TRI) Data for Zinc Released from NVF Yorklyn

Year	Zinc Released to the Red Clay Creek (pounds per year)	Zinc Released to the NCC Sewer (pounds per year)	Ave. Daily Zinc Release to the Red Clay Creek (pounds per day)
1987	28,580	115,662	78.3
1988	61,138	12,803	167.5
1989	61,138	13,217	167.5
1990	61,138	8,520	167.5
1991	53,034	10,816	145.3
1992	35,476	10,272	97.2
1993	21,389	16,377	58.6
1994	31,901	11,157	87.4
1995	30,295	7,051	83.0
1996	28,313	6,851	77.6
1997	22,703	5,568	62.2

Note first from the table that the computed release figures in the last column are much greater than the amount of zinc that is discharged through outfall 002 alone. Second, note that the figures in the fourth column are very similar to the mass loading statistics provided for the ambient monitoring data at Ashland, which is located downstream from the NVF facility. Although the numbers are not directly comparable because of slightly different averaging periods, note in particular that the release figures for calendar years '94 through '97 are in general agreement with the Ashland loads for water years '94 through '97. Therefore, the TRI release data serves to explain, and actually close, the mass balance on zinc in the Red Clay Creek. In other words, the zinc mass loading from upstream, plus the mass loading listed in the table above, (which includes the load from 002), equals the mass load of zinc in the Red Clay Creek below the NVF Yorklyn facility. As a simple example, consider July of 1997. The mass loading of total zinc from upstream (Marshall's Bridge Road) was 0.57 pounds per day, and the mass loading downstream at Ashland was 67.42 pounds per day. Further, the 1997 annual average release from NVF (including 002) was calculated as 62.2 pounds per day. Therefore, the upstream load (0.57 #/d), plus the release from NVF (62.2 #/d) is very nearly equal to the load observed downstream (67.42 #/d). These numbers are not expected to match exactly because of the different monitoring dates and averaging periods of the data used. The example nevertheless demonstrates the point that on-going release of zinc from NVF is responsible for the zinc loads and concentrations observed downstream.

Because the release data presented in the above table is self-reported, it is concluded that NVF has been aware of a major, on-going release of zinc to the Red Clay Creek from their Yorklyn facility for some time. The question remains as to exactly where on the NVF facility this additional mass loading is coming from and whether NVF is aware of the source. A number of factors strongly point to the discharge of contaminated groundwater under the site as the pathway through which the additional zinc is reaching the Red Clay Creek. These factors include the following:

- ▶ The extremely high concentrations of zinc in the shallow groundwater reported in Section 2.3.2, the close proximity of the monitoring wells to the Red Clay Creek, and sufficiently porous soils, all point to a groundwater source and release pathway;
- ▶ Zinc transported in groundwater is primarily dissolved, whereas zinc transported in overland flow is mainly particulate. As pointed out in Section 2.3.1, the majority of zinc in the Red Clay Creek is in the dissolved form.
- ▶ When streamflows are low, the percentage of the flow in the Creek that is derived directly from groundwater increases, thereby magnifying the influence of any contaminants present in the groundwater. Based on the relationships presented in Section 2.3.1, we know that there is a strong inverse relationship between zinc concentration in the Creek and streamflow below Yorklyn.
- ▶ The presence of zinc in discharge 002, which does not receive process waste flows containing zinc, suggests that zinc is able to reach discharge 002 via groundwater flow.
- ▶ There is no obvious, visible point source discharge that releases zinc from the site other than outfall 002. This suggests the source is located below ground.

Although it is quite clear at this point that zinc is reaching the Red Clay Creek almost exclusively through a groundwater flow pathway, how that zinc reached the groundwater in the first place and whether a source continues to release zinc to the groundwater are unknowns. It would appear, based upon the on-going, sustained loads of zinc in the Red Clay Creek, that there is still an active source within the manufacturing process that continues to loose zinc to the groundwater. It is likely, although not certain, that subsurface piping or tankage designed to carry or hold a zinc solution has failed. Whether the source is a broken pipe or not, the data collected during EPA's May, 1997 multi-media Superfund investigation suggests that the major source is located in the vicinity of NVF's # 1 Mill. That mill is located very close to the Red Clay Creek and is the furthest "downstream" building on the NVF property.

3. TOTAL MAXIMUM DAILY LOAD

This chapter derives the zinc TMDL for the Red Clay Creek and documents the assumptions used in that derivation. As noted in the introduction, a TMDL specifies the maximum allowable mass loading of a pollutant (i.e., pounds per day) that can be delivered to a waterbody while still assuring that applicable water quality standards are met. In simple terms, a TMDL attempts to match the strength, location, and timing of pollution sources within a watershed with the inherent ability of the receiving water to assimilate the pollutant without adverse impact. Also as discussed in the introduction, a TMDL is composed of three components, including a Waste Load Allocation (WLA) for point source discharges, a Load Allocation (LA) for nonpoint sources, and a Margin of Safety (MOS) to account for uncertainties regarding the relationship between mass loading and resulting water quality.

In order to derive a zinc TMDL for the Red Clay Creek, it is first necessary to identify the critical, or design, conditions upon which the TMDL is to be based. The specification of design conditions is important because these conditions determine the frequency at which water quality criteria would be expected to be met under the TMDL. As was shown in the previous chapter, the concentration of zinc in the Red Clay Creek downstream from Yorklyn increases as streamflow decreases. It is logical then to specify a critical low flow in the Creek above which we desire the water quality criteria to always be met. Consistent with this concept, the State of Delaware Surface Water Quality Standards specifies that the 1Q10 flow, which is the lowest 1 day average flow that occurs once in any 10-year period, be used with acute aquatic life criteria. Similarly, the Delaware Standards specify that the 7Q10 flow, which is the lowest 7 day average flow that occurs once in any 10-year period, be used with chronic aquatic life criteria.

Because 1Q10 and 7Q10 streamflows are not available at the point where NVF's zinc loading enters the Red Clay Creek, it was necessary to estimate the 1Q10 and 7Q10 at that point by extrapolating flows from the nearest USGS gaging station, which is located at Marshall's Bridge Road, just upstream in Pennsylvania. The USGS recently published 1Q10 and 7Q10 flows at Marshall's Bridge of 3 cubic feet per second (cfs) and 2.5 cfs, respectively, (Schreffler, 1998). Those flows were extrapolated downstream to Yorklyn based upon the following equation:

$$\text{Flow at Yorklyn} = [\text{Flow at M.B.} \times (\text{Area above Yorklyn}/\text{Area above M.B.})] - \text{NVF withdrawal},$$

where, based upon the information presented in Section 2.3.1 of this report, the area above Marshall's Bridge is 28.3 square miles and the permanent NVF withdrawal is 0.5 million gallons per day (0.7736 cfs). The additional drainage area between Marshall's Bridge and Yorklyn was determined to be 2.4 square miles through the use of a planimeter, making the total drainage area above Yorklyn 30.7 square miles. Substituting these figures into the equation above, the 1Q10 at Yorklyn is estimated to be 1.94 cfs, and the 7Q10 at Yorklyn is estimated to be 2.48 cfs.

In addition to streamflow, the other important design variable for this TMDL is the hardness of the Creek at the point of discharge. As previously discussed in Section 2.2, this variable is important because the applicable water quality criteria for zinc are expressed as a function of hardness. Hardness data were not available right at the point of NVF's discharge but were available just upstream at Marshall's Bridge Road; hence, the Marshall's Bridge data were used. As shown in Section 2.3.1, hardness is inversely related to flow at Marshall's Bridge for flows less than 12 cfs. In other words, hardness increases at this station as flow decreases and vice versa, again, during low flow conditions. However, water quality criteria increase as hardness increases. Faced with these 2 countervailing effects of hardness, two separate approaches were considered for specifying the design hardness for this TMDL, both of which are considered protective.

The first approach was to use the regression equation relating hardness and flow at Marshall's Bridge presented in Section 2.3.1 to predict the hardness at the 1Q10 and 7Q10 flows at Yorklyn. The second approach considered was to simply select the hardness value that was observed at Marshall's Bridge Road on the day when flows there were at their closest point to the 1Q10 and 7Q10. The second approach was selected, resulting in a design hardness of 159 mg/L. This approach was taken despite the fact that doing so resulted in a slightly higher design hardness (and slightly higher computed zinc criteria) than if the first approach had been taken. In this case, it was felt that it would be better to rely upon an actual observation that was close to the critical flows than to resort to forecasting a value from a regression equation which only introduces additional uncertainty. This uncertainty arises because the dataset upon which the regression is based only had a single flow value at or below the 1Q10 and 7Q10, (i.e., 0.94 cfs on 9/11/95). The next smallest flow jumped to 10 cfs. Therefore, the equation is rather "thin" at the particular flow rates for which it would be used to predict hardness, (i.e., 1.94 cfs and 2.48 cfs). From a larger perspective, and within the context of the TMDL, it is stated without exhaustive proof that the ultimate consequence of this decision amounts to less than 0.01 pounds of zinc per day to the TMDL, which is minor and easily accommodated in the Margin of Safety.

At the design hardness of 159 mg/L, the applicable freshwater acute criterion for this TMDL is computed as 173.3 ug/L. The applicable freshwater chronic criterion at the design hardness is 157.0 ug/L. Both of these criteria are expressed on a total zinc basis.

With the above critical flows and applicable criteria in hand, the zinc TMDL for the Red Clay Creek can now be determined. The total amount of zinc that the Red Clay Creek can accommodate at Yorklyn and points downstream and still meet the acute criterion under design conditions is computed as the product of the 1Q10 design flow and the acute criterion. This product is the TMDL for acute impacts, which shall be abbreviated in this report as TMDL_a. In a similar manner, in order to ensure that the chronic criterion is met under the design conditions, the total amount of zinc that the Red Clay Creek can accommodate at Yorklyn and points downstream is computed as the product of the 7Q10 design flow and the chronic criterion. This product is the TMDL for chronic impacts, which is abbreviated as TMDL_c in this report. These two calculations appear below.

$$TMDL_a = (173.3 \text{ ug/L})(1.94 \text{ cfs})(0.005394) = 1.81 \text{ pounds per day}$$

$$TMDL_c = (157.0 \text{ ug/L})(2.48 \text{ cfs})(0.005394) = 2.10 \text{ pounds per day}$$

To ensure that both the acute and chronic criteria are met under the design conditions, the more stringent of the two TMDLs listed above must be met. Therefore, the zinc TMDL for the Red Clay Creek is 1.81 pounds per day. The basic assumption of this formulation is that zinc acts as a conservative substance which exhibits its maximum in-stream concentration at Yorklyn, Delaware, immediately downstream from the NVF facility. The other fundamental assumption is that zinc released from the NVF facility to the Red Clay Creek mixes rapidly and completely with the background, or upstream, loading of zinc. Although detailed mixing studies have not been performed to verify this assumption, the narrow width, shallow depth, moderate slope, and sinuous course of the Creek channel all promote rapid mixing and justify the “complete mix” assumption. Finally, this TMDL assumes that zinc in the Creek sediments below Yorklyn do not significantly contribute zinc to the overlying water column during design conditions.

This final assumption is supported by the findings of Pizzuto and Church (1990) as well as theoretical calculations appearing in Appendix C of this report that estimate the diffusive flux of dissolved zinc from the sediment pore water to the overlying water column. Those calculations indicate that less than 0.01 pounds of zinc per day are expected to diffusive from the sediments to the water column in the reach from the NVF facility, downstream 0.5 miles to the first low head dam. The calculations upon which this flux estimate is based make the conservative assumption that the average concentration of zinc in the bulk sediments in this reach is 500 ug/g, as opposed to the average of 200 ug/g reported by Pizzuto and Church. Further, the calculations were performed under the future, hypothetical scenario that the water column concentration of zinc has dropped to a controlling criterion concentration of 173.3 ug/L. This too is a conservative assumption insofar as diffusive flux increases as the difference between the pore water concentration and concentration in the water column becomes greater. Because of these conservative assumptions, it is unlikely that the true flux is, or will be, greater than 0.01 pound of zinc per day in the area of greatest impact. Further, it is stated without formal proof that the rate at which clean baseflow and tributary inflow tend to dilute water column zinc concentrations in the downstream direction outpaces the rate at which diffusive flux adds zinc to the water column. This supposition is consistent with the basic assumption made above that zinc in the Red Clay Creek exhibits its maximum in-stream concentration immediately downstream from the NVF facility.

Although diffusive flux is not expected to significantly contribute to the mass loading of zinc in the Red Clay Creek, the possibility exists that the concentration of zinc in the sediment pore water is toxic to benthic organisms. This TMDL does not address that possibility because no relevant and applicable data are available to make such a determination. As a separate, but certainly related effort, a detailed assessment of sediment toxicity below NVF could be performed in the

future. To provide the greatest level of confidence, any such assessment should take the so-called “triad” approach, where solid phase toxicity testing, macroinvertebrate assessment, and chemical testing are all performed on the samples.

The final technical requirement to complete the zinc TMDL for the Red Clay Creek is to specify the individual components of the TMDL. In this case, the major components of the TMDL include a wasteload allocation for NVF discharge 002 (WLA_{002}), a load allocation for contaminated groundwater released from the NVF site ($LA_{g.w.}$), a load allocation to account for zinc loading in the Creek immediately upstream and just prior to mixing with NVF’s load (LA_{up}), and a Margin of Safety (MOS) for uncertainties. This is expressed mathematically in the equation below.

$$TMDL = WLA_{002} + LA_{g.w.} + LA_{up} + MOS$$

We start with the background loading from upstream, LA_{up} . As was shown in Section 2.3.1, total zinc and streamflow are not related at the upstream Marshall’s Bridge station. In other words, total zinc concentration is as likely to increase during low flows as during high flows.

Furthermore, an examination of the mass loadings at that site revealed that the data are not normally distributed. For these reasons, the median mass loading over the record considered was specified for LA_{up} . From Appendix A, this value is 0.6 pounds of zinc per day. It is assumed that the concentration and mass loading of zinc in the Red Clay Creek do not change appreciable between Marshall’s Bridge and Yorklyn, and that therefore, the Marshall’s Bridge data is reflective of conditions immediately above NVF Yorklyn. This assumption is supported by the limited test results available for samples taken immediately upstream of the NVF Yorklyn facility.

The Margin of Safety (MOS) for this TMDL has been set at 0.01 pounds of zinc per day. This small margin of safety, which is less than 1% of the TMDL, reflects the robust data set and the conservative approach used to establish the TMDL, while at the same time accounting for the uncertainty associated with specifying the design hardness and the possibility that dissolved zinc may diffuse to the water column.

The final 2 components of the TMDL that need to be specified are the wasteload allocation for NVF discharge 002 and the load allocation for the NVF groundwater. The maximum combined loading from these two sources can be determined by rearranging the equation above and substituting in the numeric values previously determined for TMDL, LA_{up} , and MOS. Doing so yields the following allowable site loading:

$$\begin{aligned} (WLA_{002} + LA_{g.w.}) &= TMDL - LA_{up} - MOS \\ &= 1.81 - 0.6 - 0.01 \\ &= 1.2 \text{ pounds of zinc per day} \end{aligned}$$

There is merit to combining these two sources within this TMDL for a variety of reasons. First and foremost, the Red Clay Creek does not distinguish between zinc discharged from outfall 002 and zinc coming from the contaminated groundwater. In fact, the zinc from the groundwater and the zinc discharged from outfall 002 are one-and-the-same since the zinc in outfall 002 is derived from the contaminated site groundwater. Second, controlling the major groundwater contamination problem will solve the less serious loading problem associated with discharge 002. Third, because the NVF Company is ultimately responsible for both of these sources, combining them provides added flexibility in arriving at an overall engineering solution. For these reasons, this TMDL advocates combining the allowable wasteloading from discharge 002 and the contaminated groundwater into a single site allocation. However, because this combined site allocation is more stringent than the currently permitted mass loading limits for discharge 002 alone, an administrative mechanism/compliance schedule will be needed to accomplish load reductions at the site, while still allowing plant operations to continue. This issue, and others, will be the subject of a Pollution Control Strategy (PCS) that will be developed to guide implementation of this TMDL.

The table below provides a final summary of the zinc TMDL for the Red Clay Creek. This TMDL covers the entire main stem of the Red Clay Creek from the PA/DE border to its confluence with the White Clay Creek in Stanton, Delaware. Based upon the analyses contained herein, the DNREC concludes with a reasonable degree of scientific certainty that water quality standards for zinc will be met in the Red Clay Creek once the mass loading requirements listed in the table are reached.

Table 10. Zinc TMDL for the Red Clay Creek, New Castle County, Delaware

TMDL (#/d)	$WLA_{002} + LA_{g.w.}$ (#/d)	LA_{up} (#/d)	MOS (#/d)
1.81	1.20	0.60	0.01

4. NEXT STEPS

This chapter concludes by identifying the next steps in the Red Clay Creek zinc TMDL process. First, the TMDL and its component parts will be published as proposed regulations in the August 1, 1999 State of Delaware Register of Regulations. The TMDL and its component parts will be identified as individual regulatory articles. On this same date in the Delaware Register, an announcement will be made that a public workshop and public hearing will be held to answer questions concerning the proposed TMDL and to take formal comments on the regulatory articles, respectively. The workshop and hearing will also be announced on August 1st and 4th, 1999, in the News Journal and Delaware State News.

The workshop and hearing are scheduled as follows:

Public Workshop

The workshop will be held on Tuesday, September 7, 1999, between 3:00 and 4:00 p.m., at the New Castle office of the Division of Air and Waste Management, Delaware Department of Natural Resources and Environmental Control, 391 Lukens Drive, New Castle, Delaware.

Public Hearing

The hearing will be held on Tuesday, September 7, 1999, between 7:00 and 8:00 p.m., at the New Castle office of the Division of Air and Waste Management, Delaware Department of Natural Resources and Environmental Control, 391 Lukens Drive, New Castle, Delaware.

Oral and/or written comments can be provided on the proposed regulatory articles at the time of the public hearing, or otherwise can be submitted in writing by 4:30 p.m., September 15, 1999. All comments should be directed to the attention of Mr. Rod Thompson, Hearing Officer, DNREC, 89 Kings Highway, Dover, DE, 19901; facsimile: (302) 739-6242.

Following the close of the hearing record, the Hearing Officer will evaluate the comments received and will make a recommendation to the Secretary of the Department of Natural Resources and Environmental Control to adopt one or more of the articles as proposed, withdrawal one or more of the articles, or to modify one or more of the articles based upon the record. The Secretary will accept or reject the recommendations and will promptly publish a Secretary's Order and final regulation. The Order and final regulatory articles will be published in the Delaware Register of Regulations on November 1, 1999, (tentatively). The final articles and supporting documentation will then be submitted to the U.S. EPA for their review and approval. As noted in the introductory chapter, if the State fails to establish this TMDL by December 31, 1999, the EPA will have one additional year to do so.

Under the assumption that this TMDL will be established by December 31, 1999, the State will then proceed to develop a Pollution Control Strategy (PCS) to guide implementation of the TMDL. The PCS will be developed by the DNREC in concert with affected parties, the interested public, and the DNREC's ongoing Whole basin Management Program. As a goal, the PCS will be completed within 1 year of the TMDL adoption date.

5. REFERENCES

- American Littoral Society and Sierra Club. 1996. Citizen law suit concerning the administration of the TMDL program in the State of Delaware. Case filed in June, 1996 and identified by the Court as: American Littoral Society, et. al. v. U.S. Environmental Protection Agency, et. al., C.A. No. 96-591 (SLR).
- DiToro, D.M., D.J. O'Connor, R.V. Thomann, and J.P. St. John. 1981. Analysis of Fate of Chemicals in Receiving Waters, Phase 1. Chemical Manufacturers Association, Washington, D.C., Prepared by HydroQual, Inc., Mahwah, N.J.
- DNREC. 1993. State of Delaware Surface Water Quality Standards (As Amended, February 26, 1993). Delaware Department of Natural Resources and Environmental Control, Division of Water Resources, Dover, DE.
- DNREC. 1996. Final Determination State of Delaware 1996 Clean Water Act Section 303(d) List of Waters Needing TMDLs and Supporting Rationale. Delaware Department of Natural Resources and Environmental Control, Division of Water Resources, Dover, DE.
- DNREC. 1998a. Final Determination State of Delaware 1998 Clean Water Act Section 303(d) List of Waters Needing TMDLs and Supporting Rationale. Delaware Department of Natural Resources and Environmental Control, Division of Water Resources, Dover, DE.
- DNREC. 1998b. Piedmont Basin Preliminary Assessment Report. Delaware Department of Natural Resources and Environmental Control, Whole Basin Management Program, Dover, DE.
- DNREC/EPA. 1997. Memorandum of Understanding between Delaware Department of Natural Resources and Environmental Control and United States Environmental Protection Agency Region III regarding Sections 303(d) and 303(e) of the Clean Water Act. Delaware Department of Natural Resources and Environmental Control, Division of Water Resources, Dover, DE.
- DNREC. 1999. Toxics Release Inventory (TRI) Data for Calendar Years 1987 Through 1997 for the National Vulcanized Fiber, Yorklyn Facility. Delaware Department of Natural Resources and Environmental Control, Division of Air and Waste Management, Dover, DE.
- Dobroski, C.J. and K.J. Salamon. 1988. Synoptic Report on Toxic Substances Contamination of Red Clay Creek. Report prepared by Roy F. Weston, Inc. on behalf of the State of Delaware, Department of Natural Resources and Environmental Control, Division of Water Resources, Dover, DE.
- EPA. 1987. Ambient Water Quality Criteria for Zinc - 1987 (EPA-440/5-87-003). U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Criteria and Standards Division, Washington, DC.

EPA. 1999. AQUIRE (Aquatic Toxicity Information Retrieval) Online Database System. U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Duluth, MN.

EPA. 1997. Trip Report prepared by Roy F. Weston Site Assessment Technical Assistance Team regarding the NVF - Yorklyn Site, TDD No. 9701-53, Contract No. 68-S5-3002.

EPA. 1998. Administrative Order by Consent for Removal Response Action (Concerning the NVF Yorklyn Site), EPA Docket No. III-98-007-DC. U.S. Environmental Protection Agency, Region III, Removal Enforcement and Oil Section, Philadelphia, PA.

Greene, R.W. 1995. Potential Human Health Effects Associated With Ingesting Zinc in Red Clay Creek and White Clay Creek Drinking Water. Delaware Department of Natural Resources and Environmental Control, Division of Water Resources, Dover, DE.

Greene, R.W. 1998. Chemical Contaminants in Sediments of the Red Clay Creek in the Vicinity of Glenville, Delaware. Delaware Department of Natural Resources and Environmental Control, Division of Water Resources, Dover, DE.

James, R.W., R.W. Saffer, and A.J. Tallman. 1999. Water Resources Data - Maryland and Delaware, Water Year 1998, Volume 1. Surface-Water Data. United States Geological Survey, Water Resources Division, Baltimore, MD.

Marler, E.H. 1987. Natural History and Heritage of the Red Clay Creek. Report prepared by the Delaware Nature Education Society under contract to the Delaware Department of Natural Resources and Environmental Control, Division of Water Resources, Dover, DE.

NVF. 1999. (EPA Approved) Response Action Plan NVF Company Yorklyn, Delaware. April 1, 1999 Work Plan prepared by URS Greiner Woodward Clyde for NVF Company. National Vulcanized Fiber Company, Yorklyn, DE.

Pizzuto, J.E. and T.M. Church. 1990. Zinc Contamination in the waters and Sediments of the Red Clay Creek, New Castle County, Delaware. University of Delaware, College of Geology and College of Marine Studies, Newark, DE.

Rice, C.L. 1993. Environmental Contaminants in Soils and Sediments from the Red Clay Creek Watershed, Pennsylvania and Delaware (Special Project report 93-7). U.S. Fish & Wildlife Service, State College, PA.

Schreffler, C.L. 1998. Low-Flow Statistics of Selected Streams in Chester County, Pennsylvania (Water-Resources Investigations Report 98-4117). United States Geological Survey, Lemoyne, PA.

Sorensen, E.M.B. 1991. Metal Poisoning in Fish. CRC Press, Inc., Boca Raton, FLA.

Stephan, C.E. 1995. Derivation of Conversion Factors for the Calculation of Dissolved Freshwater Aquatic Life Criteria for Metals. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Duluth, MN.

Thomann, R.V and J.A. Mueller. 1987. Principles of Surface Water Quality Modeling and Control. Harper & Row, Publishers, Inc., New York, NY.

USGS. 1999. United States NWIS-W Data Retrieval (Current and Historical Daily Streamflow Data Online). United States Geological Survey, Water Resources Division, Reston, VA.

APPENDIX A

**Summary of Routine Ambient Monitoring Data for the Red Clay Creek
(Period Generally Covering Fall, 1993 Through Fall, 1998)**

Red Clay PA WQN 150 (Marshalls Bridge)										
Streamflow, Concentration, and Mass Loading										
	Flow at					TZinc with	DZinc with	Percent	Mass Load	Mass Load
	Marshalls Br	TZinc	TZinc	DZinc	DZinc	NDs=1/2DL	NDs=1/2DL	Dissolved	Total Zn	Dissolved Zn
Date	(cfs)	(ug/L)	DQC	(ug/L)	DQC	(ug/L)	(ug/L)	Zinc	(lb/day)	(lb/day)
01/25/94	25	17.9		5.83		17.9	5.83	32.6	2.41	0.79
02/15/94	27	6.53		6.17		6.53	6.17	94.5	0.95	0.90
03/15/94	99			5.84		NA	5.84	NA		3.12
04/18/94	50	5	<	18.9		2.5	18.9	100.0	0.67	5.10
06/20/94	21	6.1		5.63		6.1	5.63	92.3	0.69	0.64
07/19/94	19	5	<	5	<	2.5	2.5	100.0	0.26	0.26
08/15/94	20	5.58		5	<	5.58	2.5	44.8	0.60	0.27
09/12/94	11	5	<	5	<	2.5	2.5	100.0	0.15	0.15
10/17/94	9.5	8.37		5.88		8.37	5.88	70.3	0.43	0.30
11/15/94	12	9.99		29.8		9.99	29.8	100.0	0.65	1.93
12/12/94	25	5	<	5	<	2.5	2.5	100.0	0.34	0.34
01/17/95	25	5.29		5.29		5.29	5.29	100.0	0.71	0.71
02/13/95	15	7.87		6.92		7.87	6.92	87.9	0.64	0.56
03/13/95	38	5	<	5	<	2.5	2.5	100.0	0.51	0.51
04/18/95	26	5.62		5.62		5.62	5.62	100.0	0.79	0.79
05/15/95	25	5	<	5	<	2.5	2.5	100.0	0.34	0.34
06/19/95	11	5	<	5	<	2.5	2.5	100.0	0.15	0.15
07/17/95	20	5.7		5.5		5.7	5.5	96.5	0.61	0.59
08/14/95	12	5.1		5	<	5.1	2.5	49.0	0.33	0.16
09/11/95	0.94	5	<	5	<	2.5	2.5	100.0	0.01	0.01
10/16/95	25	5	<	5	<	2.5	2.5	100.0	0.34	0.34
11/13/95	50	5.1		5	<	5.1	2.5	49.0	1.38	0.67
12/11/95	17	5.95		5	<	5.95	2.5	42.0	0.55	0.23
01/29/96	55	6.2		5	<	6.2	2.5	40.3	1.84	0.74
02/12/96	42	7.7		7.7		7.7	7.7	100.0	1.74	1.74
03/11/96	41	5	<	5	<	2.5	2.5	100.0	0.55	0.55
04/15/96	43	11.8		5	<	11.8	2.5	21.2	2.74	0.58
05/13/96	49	6.4		6.1		6.4	6.1	95.3	1.69	1.61
06/10/96	41	8.7		5	<	8.7	2.5	28.7	1.92	0.55
07/15/96	39	5.1		5	<	5.1	2.5	49.0	1.07	0.53
08/12/96	34	5	<	5	<	2.5	2.5	100.0	0.46	0.46
09/17/96	154	5	<	5	<	2.5	2.5	100.0	2.08	2.08
10/17/96	31	5	<	5	<	2.5	2.5	100.0	0.42	0.42
11/18/96	39	5	<	5	<	2.5	2.5	100.0	0.53	0.53
12/17/96	83	23.4		5	<	23.4	2.5	10.7	10.48	1.12
01/13/97	43	5	<	8.9		2.5	8.9	100.0	0.58	2.06
02/19/97	50	5	<	5	<	2.5	2.5	100.0	0.67	0.67
03/17/97	57	5	<	5	<	2.5	2.5	100.0	0.77	0.77
04/21/97	42	5	<	5	<	2.5	2.5	100.0	0.57	0.57
05/27/97	34	5	<	5	<	2.5	2.5	100.0	0.46	0.46
06/16/97	24	6		5	<	6	2.5	41.7	0.78	0.32
07/21/97	15	7		5	<	7	2.5	35.7	0.57	0.20
08/18/97	12	5	<	5	<	2.5	2.5	100.0	0.16	0.16
09/15/97	15	17.8		8.3		17.8	8.3	46.6	1.44	0.67
10/16/97	16	8.3		6.7		8.3	6.7	80.7	0.72	0.58
11/17/97	22	5	<	5	<	2.5	2.5	100.0	0.30	0.30
12/17/97	18	6.7		7.6		6.7	7.6	100.0	0.65	0.74
01/12/98	21	5.2		5	<	5.2	2.5	48.1	0.59	0.28
02/17/98	44	5		5.2		5	5.2	100.0	1.19	1.23
03/16/98	43	5		5	<	5	2.5	50.0	1.16	0.58
04/20/98	52	5	<	5	<	2.5	2.5	100.0	0.70	0.70
05/18/98	37	5	<	5	<	2.5	2.5	100.0	0.50	0.50
06/17/98	29	5	<	5	<	2.5	2.5	100.0	0.39	0.39
07/13/98	19	5	<	5	<	2.5	2.5	100.0	0.26	0.26
08/24/98	14	5.6		5	<	5.6	2.5	44.6	0.42	0.19

Red Clay PA WQN 150 (Marshalls Bridge)
Summary Statistics for Zinc Concentration and Mass Loading

CONC. STATS FOR 1/25/94 - 8/24/98			MASS LOADING STATS FOR 1/25/94 - 8/24/98		
	TZinc (ug/L)	DZinc (ug/L)		TZinc (#/day)	DZinc (#/day)
avg	5.44	4.44	avg	0.96	0.75
median (50%tile)	5.05	2.50	median (50%tile)	0.60	0.55
minimum	2.50	2.50	minimum	0.01	0.01
maximum	23.40	29.80	maximum	10.48	5.10
CONC. STATS FOR 1/25/94 - 9/12/94 (WY '94, partial)			MASS LOAD STATS FOR 1/25/94-9/12/94 (WY '94, partial)		
avg	6.23	6.23	avg	0.82	1.40
median (50%tile)	5.58	5.73	median (50%tile)	0.67	0.71
minimum	2.50	2.50	minimum	0.15	0.15
maximum	17.90	18.90	maximum	2.41	5.10
CONC. STATS FOR 10/17/94 - 9/11/95 (WY '95)			MASS LOADING STATS FOR 10/17/94 - 9/11/95 (WY '95)		
avg	5.04	6.17	avg	0.46	0.53
median (50%tile)	5.20	3.90	median (50%tile)	0.47	0.42
minimum	2.50	2.50	minimum	0.01	0.01
maximum	9.99	29.80	maximum	0.79	1.93
CONC. STATS FOR 10/16/95 - 9/17/96 (WY '96)			MASS LOADING STATS FOR 10/16/95 - 9/17/96 (WY '96)		
avg	5.58	3.23	avg	1.36	0.84
median (50%tile)	5.53	2.50	median (50%tile)	1.53	0.57
minimum	2.50	2.50	minimum	0.34	0.23
maximum	11.80	7.70	maximum	2.74	2.08
CONC. STATS FOR 11/17/96 - 9/15/97 (WY '97)			MASS LOADING STATS FOR 11/17/96 - 9/15/97 (WY '97)		
avg	6.18	3.52	avg	1.45	0.66
median (50%tile)	2.50	2.50	median (50%tile)	0.57	0.55
minimum	2.50	2.50	minimum	0.16	0.16
maximum	23.40	8.90	maximum	10.48	2.06
CONC. STATS FOR 10/16/97 - 8/24/98 (WY '98)			MASS LOADING STATS FOR 10/16/97 - 8/24/98 (WY '98)		
avg	4.39	3.59	avg	0.62	0.52
median (50%tile)	5.00	2.50	median (50%tile)	0.59	0.50
minimum	2.50	2.50	minimum	0.26	0.19
maximum	8.30	7.60	maximum	1.19	1.23

MARSHALL'S BRIDGE					
Freshwater Aquatic Life Criteria for Zinc					
(note: DE criteria applied to PA waters)					
Date	THard (mg/L)	CMC_t (ug/L)	CCC_t (ug/L)	CMC_d (ug/L)	CCC_d (ug/L)
01/25/94	124	140.4	127.2	137.3	125.4
02/15/94	117	133.7	121.1	130.7	119.4
03/15/94	87	104.0	94.2	101.7	92.9
04/18/94	118	134.6	121.9	131.7	120.2
06/20/94	121	137.5	124.6	134.5	122.8
07/19/94	126	142.3	128.9	139.2	127.1
08/15/94	120	136.6	123.7	133.6	122.0
09/12/94	141	156.6	141.8	153.1	139.8
10/17/94	138	153.7	139.2	150.4	137.3
11/15/94	125	141.4	128.1	138.3	126.3
12/12/94	122	138.5	125.4	135.4	123.7
01/17/95	95	112.0	101.5	109.6	100.1
02/13/95	134	150.0	135.8	146.7	133.9
03/13/95	121	137.5	124.6	134.5	122.8
04/18/95	138	153.7	139.2	150.4	137.3
05/15/95	127	143.3	129.8	140.1	128.0
06/19/95	132	148.1	134.1	144.8	132.2
07/17/95	129	145.2	131.5	142.0	129.7
08/14/95	144	159.4	144.4	155.9	142.3
09/11/95	159	173.3	157.0	169.5	154.8
10/16/95	125	141.4	128.1	138.3	126.3
11/13/95	130	146.2	132.4	142.9	130.5
12/11/95	142	157.5	142.7	154.0	140.7
01/29/96	123	139.5	126.3	136.4	124.5
02/12/96	120	136.6	123.7	133.6	122.0
03/11/96	122	138.5	125.4	135.4	123.7
04/15/96	124.6	141.0	127.7	137.9	125.9
05/13/96	118.9	135.5	122.7	132.5	121.0
06/10/96	112.2	129.0	116.9	126.2	115.2
07/15/96	116.3	133.0	120.5	130.1	118.8
08/12/96	120	136.6	123.7	133.6	122.0
09/17/96	143	158.4	143.5	155.0	141.5
10/17/96	79	95.8	86.8	93.7	85.6
11/18/96	136	151.8	137.5	148.5	135.6
12/17/96	45	59.5	53.9	58.2	53.1
01/13/97	122	138.5	125.4	135.4	123.7
02/19/97	122	138.5	125.4	135.4	123.7
03/17/97	111	127.8	115.8	125.0	114.2
04/21/97	55	70.5	63.9	69.0	63.0
05/27/97	116	132.7	120.2	129.8	118.5
06/16/97	113	129.8	117.6	126.9	115.9
07/21/97	136	151.8	137.5	148.5	135.6
08/18/97	138	153.7	139.2	150.4	137.3
09/15/97	136	151.8	137.5	148.5	135.6
10/16/97	131	147.1	133.2	143.9	131.4
11/17/97	121	137.5	124.6	134.5	122.8
12/17/97	132	148.1	134.1	144.8	132.2
01/12/98	116	132.7	120.2	129.8	118.5
02/17/98	121	137.5	124.6	134.5	122.8
03/16/98	115	131.7	119.3	128.8	117.6
04/20/98	107	123.9	112.2	121.2	110.7
05/18/98	132	148.1	134.1	144.8	132.2
06/17/98	128	144.2	130.7	141.1	128.8
07/13/98	161	175.2	158.7	171.3	156.5
08/24/98	145	160.3	145.2	156.8	143.2

MARSHALL'S BRIDGE				
Zinc Criteria Exceedance				
	CMC_t	CCC_t	CMC_d	CCC_d
	Ecorisk	Ecorisk	Ecorisk	Ecorisk
Date	Index	Index	Index	Index
01/25/94	0.127	0.141	0.042	0.046
02/15/94	0.049	0.054	0.047	0.052
03/15/94	NA	NA	0.057	0.063
04/18/94	0.019	0.021	0.144	0.157
06/20/94	0.044	0.049	0.042	0.046
07/19/94	0.018	0.019	0.018	0.020
08/15/94	0.041	0.045	0.019	0.020
09/12/94	0.016	0.018	0.016	0.018
10/17/94	0.054	0.060	0.039	0.043
11/15/94	0.071	0.078	0.216	0.236
12/12/94	0.018	0.020	0.018	0.020
01/17/95	0.047	0.052	0.048	0.053
02/13/95	0.052	0.058	0.047	0.052
03/13/95	0.018	0.020	0.019	0.020
04/18/95	0.037	0.040	0.037	0.041
05/15/95	0.017	0.019	0.018	0.020
06/19/95	0.017	0.019	0.017	0.019
07/17/95	0.039	0.043	0.039	0.042
08/14/95	0.032	0.035	0.016	0.018
09/11/95	0.014	0.016	0.015	0.016
10/16/95	0.018	0.020	0.018	0.020
11/13/95	0.035	0.039	0.017	0.019
12/11/95	0.038	0.042	0.016	0.018
01/29/96	0.044	0.049	0.018	0.020
02/12/96	0.056	0.062	0.058	0.063
03/11/96	0.018	0.020	0.018	0.020
04/15/96	0.084	0.092	0.018	0.020
05/13/96	0.047	0.052	0.046	0.050
06/10/96	0.067	0.074	0.020	0.022
07/15/96	0.038	0.042	0.019	0.021
08/12/96	0.018	0.020	0.019	0.020
09/17/96	0.016	0.017	0.016	0.018
10/17/96	0.026	0.029	0.027	0.029
11/18/96	0.016	0.018	0.017	0.018
12/17/96	0.393	0.434	0.043	0.047
01/13/97	0.018	0.020	0.066	0.072
02/19/97	0.018	0.020	0.018	0.020
03/17/97	0.020	0.022	0.020	0.022
04/21/97	0.035	0.039	0.036	0.040
05/27/97	0.019	0.021	0.019	0.021
06/16/97	0.046	0.051	0.020	0.022
07/21/97	0.046	0.051	0.017	0.018
08/18/97	0.016	0.018	0.017	0.018
09/15/97	0.117	0.129	0.056	0.061
10/16/97	0.056	0.062	0.047	0.051
11/17/97	0.018	0.020	0.019	0.020
12/17/97	0.045	0.050	0.052	0.057
01/12/98	0.039	0.043	0.019	0.021
02/17/98	0.036	0.040	0.039	0.042
03/16/98	0.038	0.042	0.019	0.021
04/20/98	0.020	0.022	0.021	0.023
05/18/98	0.017	0.019	0.017	0.019
06/17/98	0.017	0.019	0.018	0.019
07/13/98	0.014	0.016	0.015	0.016
08/24/98	0.035	0.039	0.016	0.017

**Red Clay STORET No. 103041 (Ashland)
Streamflow, Concentration, and Mass Loading**

	Flow at	Flow at					TZinc with	DZinc with	Percent	Mass Load	Mass Load
	M. B.	Ashland	TZinc	TZinc	DZinc	DZinc	NDs=1/2DL	NDs=1/2DL	Dissolved	Total Zn	Dissolved Zn
Date	(cfs)	(cfs)	(ug/L)	DQC	(ug/L)	DQC	(ug/L)	(ug/L)	Zinc	(lb/day)	(lb/day)
93/07/21	15	16.77	472.8		412.1		472.8	412.1	87.2	42.78	37.28
93/08/18	15	16.77	629.4		316.1		629.4	316.1	50.2	56.94	28.60
93/09/23	32	36.65	1306		1212		1306	1212	92.8	258.24	239.66
93/10/19	15	16.77	562		576.4		562	576.4	100.0	50.85	52.15
93/11/15	22	24.96	470		468.1		470	468.1	99.6	63.28	63.02
93/12/14	48	55.37	313.8		319.4		313.8	319.4	100.0	93.73	95.40
94/01/24	23	26.13	281.3		281.9		281.3	281.9	100.0	39.65	39.73
94/03/14	122	141.92	241.9		censored		241.9			185.20	
94/04/18	50	57.71	274.8		282		274.8	282	100.0	85.55	87.79
94/05/16	69	79.93	143.2		73.6		143.2	73.6	51.4	61.75	31.74
94/06/14	26	29.64	431.7		331.1		431.7	331.1	76.7	69.02	52.94
94/07/18	23	26.13	538		470.2		538	470.2	87.4	75.83	66.27
94/08/15	20	22.62	414.1		365.4		414.1	365.4	88.2	50.53	44.59
94/09/12	11	12.09	1137.8		1011.4		1137.8	1011.4	88.9	74.22	65.98
94/10/17	9.5	10.34	1212.2		1200.8		1212.2	1200.8	99.1	67.60	66.97
94/12/12	25	28.47	493.2		468.9		493.2	468.9	95.1	75.74	72.01
95/01/17	25	28.47	587.6		581.2		587.6	581.2	98.9	90.24	89.25
95/02/13	15	16.77	728.7		757.5		728.7	757.5	100.0	65.93	68.53
95/03/13	38	43.67	396.5		397.2		396.5	397.2	100.0	93.41	93.58
95/04/17	26	29.64	739.5		688.5		739.5	688.5	93.1	118.23	110.08
95/05/15	25	28.47	567.9		544.3		567.9	544.3	95.8	87.21	83.59
95/06/19	11	12.09	1241		1002.6		1241	1002.6	80.8	80.95	65.40
95/07/17	20	22.62	611.2		465.3		611.2	465.3	76.1	74.58	56.78
95/08/14	12	13.26	1296.4		1104.7		1296.4	1104.7	85.2	92.75	79.03
95/09/11	0.94	0.33	2010.3		1509		2010.3	1509	75.1	3.53	2.65
95/10/16	25	28.47	740.9		642.7		740.9	642.7	86.7	113.78	98.70
95/11/13	50	57.71	440.1		422		440.1	422	95.9	137.01	131.37
96/01/29	55	63.56	349		280.7		349	280.7	80.4	119.66	96.24
96/02/12	42	48.35	261.6		244.1		261.6	244.1	93.3	68.23	63.67
96/03/11	41	47.18	538.3		564.4		538.3	564.4	100.0	137.01	143.65
96/04/15	43	49.52	326.9		353.3		326.9	353.3	100.0	87.33	94.38
96/05/13	49	56.54	278.6		292.1		278.6	292.1	100.0	84.97	89.09
96/06/10	41	47.18	353.4		336.9		353.4	336.9	95.3	89.95	85.75
96/07/15	39	44.84	418.7		405.4		418.7	405.4	96.8	101.29	98.07
96/09/17	154	179.35	81.8		30.4		81.8	30.4	37.2	79.14	29.41
96/11/18	46	53.03	400		425		400	425	100.0	114.43	121.58
97/01/13	49	56.54	326		193		326	193	59.2	99.43	58.87
97/03/17	57	65.89	249.5		240.7		249.5	240.7	96.5	88.69	85.56
97/05/27	34	38.99	363		280		363	280	77.1	76.36	58.90
97/07/14	17	19.11	654		533		654	533	81.5	67.42	54.95
97/09/15	15	16.77	828.5		767.2		828.5	767.2	92.6	74.96	69.41
97/11/17	22	24.96	647.3		630.2		647.3	630.2	97.4	87.15	84.85
98/01/12	21	23.79	729.8		542.9		729.8	542.9	74.4	93.66	69.67
98/03/18	50	57.71	366.6		311		366.6	311	84.8	114.13	96.82
98/05/19	36	41.33	380		314		380	314	82.6	84.73	70.01
98/09/15	11	12.09	1118		920		1118	920	82.3	72.93	60.01

Red Clay STORET No. 103041 (Ashland)					
Summary Statistics for Zinc Concentration and Mass Loading					
CONC. STATS FOR 7/21/93 - 9/15/98			MASS LOADING STATS FOR 7/21/93 - 9/15/98		
	TZinc (ug/L)	DZinc (ug/L)		TZinc (#/day)	DZinc (#/day)
avg	585.94	523.75	avg	88.04	76.76
median (50%tile)	471.40	425.00	median (50%tile)	84.85	69.67
minimum	81.80	30.40	minimum	3.53	2.65
maximum	2010.30	1509.00	maximum	258.24	239.66
CONC. STATS FOR 10/19/93 - 9/12/94 (WY '94)			MASS LOADING STATS FOR 10/19/93 - 9/12/94 (WY '94)		
avg	437.15	417.95	avg	77.24	59.96
median (50%tile)	414.10	348.25	median (50%tile)	69.02	57.98
minimum	143.20	73.60	minimum	39.65	31.74
maximum	1137.80	1011.40	maximum	185.20	95.40
CONC. STATS FOR 10/17/94 - 9/11/95 (WY '95)			MASS LOADING STATS FOR 10/17/94 - 9/11/95 (WY '95)		
avg	898.59	792.73	avg	77.29	71.62
median (50%tile)	728.70	688.50	median (50%tile)	80.95	72.01
minimum	396.50	397.20	minimum	3.53	2.65
maximum	2010.30	1509.00	maximum	118.23	110.08
CONC. STATS FOR 10/16/95 - 9/17/96 (WY '96)			MASS LOADING STATS FOR 10/16/95 - 9/17/96 (WY '96)		
avg	378.93	357.20	avg	101.84	93.03
median (50%tile)	351.20	345.10	median (50%tile)	95.62	95.31
minimum	81.80	30.40	minimum	68.23	29.41
maximum	740.90	642.70	maximum	137.01	143.65
CONC. STATS FOR 11/18/96 - 9/15/97 (WY '97)			MASS LOADING STATS FOR 11/18/96 - 9/15/97 (WY '97)		
avg	470.17	406.48	avg	86.88	74.88
median (50%tile)	381.50	352.50	median (50%tile)	82.53	64.15
minimum	249.50	193.00	minimum	67.42	54.95
maximum	828.50	767.20	maximum	114.43	121.58
CONC. STATS FOR 11/17/97 - 9/15/98 (WY '98)			MASS LOADING STATS FOR 11/17/97 - 9/15/98 (WY '98)		
avg	648.34	543.62	avg	90.52	76.27
median (50%tile)	647.30	542.90	median (50%tile)	87.15	70.01
minimum	366.60	311.00	minimum	72.93	60.01
maximum	1118.00	920.00	maximum	114.13	96.82

ASHLAND					
Freshwater Aquatic Life Criteria for Zinc					
Date	THard (mg/L)	CMC_t (ug/L)	CCC_t (ug/L)	CMC_d (ug/L)	CCC_d (ug/L)
93/07/21	110	126.9	114.9	124.1	113.3
93/08/18	140	155.6	141.0	152.2	139.0
93/09/23	98	115.0	104.2	112.5	102.7
93/10/19	104	121.0	109.6	118.3	108.0
93/11/15	100	117.0	106.0	114.4	104.5
93/12/14	84	101.0	91.4	98.7	90.2
94/01/24	66	82.3	74.5	80.5	73.5
94/03/14	88	105.0	95.1	102.7	93.8
94/04/18	110	126.9	114.9	124.1	113.3
94/05/16	108	124.9	113.1	122.2	111.5
94/06/14	140	155.6	141.0	152.2	139.0
94/07/18	128	144.2	130.7	141.1	128.8
94/08/15	140	155.6	141.0	152.2	139.0
94/09/12	160	174.3	157.8	170.4	155.6
94/10/17	160	174.3	157.8	170.4	155.6
94/12/12	112	128.8	116.7	126.0	115.0
95/01/17	124	140.4	127.2	137.3	125.4
95/02/13	130	146.2	132.4	142.9	130.5
95/03/13	118	134.6	121.9	131.7	120.2
95/04/17	132	148.1	134.1	144.8	132.2
95/05/15	124	140.4	127.2	137.3	125.4
96/06/19	154	168.7	152.8	165.0	150.7
95/07/17	110	126.9	114.9	124.1	113.3
95/08/14	168	181.6	164.5	177.6	162.2
95/09/11	176	188.9	171.1	184.8	168.7
95/10/16	122	138.5	125.4	135.4	123.7
95/11/13	104	121.0	109.6	118.3	108.0
96/01/29	100	117.0	106.0	114.4	104.5
96/02/12	100	117.0	106.0	114.4	104.5
96/03/11	140	155.6	141.0	152.2	139.0
96/04/15	102	119.0	107.8	116.4	106.3
96/05/13	108	124.9	113.1	122.2	111.5
96/06/10	114	130.8	118.4	127.9	116.8
96/07/15	116	132.7	120.2	129.8	118.5
96/09/17	124	140.4	127.2	137.3	125.4
96/11/18	128	144.2	130.7	141.1	128.8
97/01/13	102	119.0	107.8	116.4	106.3
97/03/17	110	126.9	114.9	124.1	113.3
97/05/27	108	124.9	113.1	122.2	111.5
97/07/14	150	165.0	149.4	161.4	147.4
97/09/15	142	157.5	142.7	154.0	140.7
97/11/17	130	146.2	132.4	142.9	130.5
98/01/12	144	159.4	144.4	155.9	142.3
98/03/18	120	136.6	123.7	133.6	122.0
98/05/19	133	149.0	135.0	145.7	133.1
98/09/15	148	163.1	147.8	159.5	145.7

ASHLAND				
Zinc Criteria Exceedance				
	CMC_t	CCC_t	CMC_d	CCC_d
	Ecorisk	Ecorisk	Ecorisk	Ecorisk
Date	Index	Index	Index	Index
93/07/21	3.727	4.115	3.321	3.637
93/08/18	4.044	4.465	2.077	2.274
93/09/23	11.353	12.534	10.773	11.797
93/10/19	4.646	5.129	4.872	5.335
93/11/15	4.016	4.434	4.090	4.479
93/12/14	3.108	3.432	3.235	3.543
94/01/24	3.418	3.774	3.503	3.836
94/03/14	2.304	2.543	NA	NA
94/04/18	2.166	2.392	2.273	2.489
94/05/16	1.146	1.266	0.602	0.660
94/06/14	2.774	3.063	2.175	2.382
94/07/18	3.730	4.118	3.333	3.650
94/08/15	2.661	2.938	2.401	2.629
94/09/12	6.529	7.208	5.934	6.499
94/10/17	6.956	7.680	7.046	7.716
94/12/12	3.829	4.227	3.722	4.076
95/01/17	4.185	4.620	4.232	4.635
95/02/13	4.986	5.505	5.299	5.803
95/03/13	2.945	3.251	3.016	3.303
95/04/17	4.995	5.514	4.755	5.207
95/05/15	4.044	4.465	3.963	4.340
96/06/19	7.356	8.121	6.076	6.654
95/07/17	4.818	5.319	3.750	4.107
95/08/14	7.138	7.881	6.219	6.811
95/09/11	10.641	11.748	8.167	8.944
95/10/16	5.350	5.906	4.745	5.196
95/11/13	3.638	4.016	3.567	3.906
96/01/29	2.982	3.293	2.453	2.686
96/02/12	2.235	2.468	2.133	2.336
96/03/11	3.459	3.819	3.708	4.061
96/04/15	2.747	3.033	3.036	3.324
96/05/13	2.230	2.463	2.391	2.619
96/06/10	2.703	2.984	2.634	2.885
96/07/15	3.155	3.484	3.124	3.421
96/09/17	0.583	0.643	0.221	0.242
96/11/18	2.773	3.062	3.013	3.299
97/01/13	2.739	3.025	1.658	1.816
97/03/17	1.967	2.171	1.940	2.124
97/05/27	2.906	3.209	2.292	2.510
97/07/14	3.964	4.376	3.303	3.617
97/09/15	5.260	5.807	4.980	5.454
97/11/17	4.429	4.890	4.409	4.828
98/01/12	4.579	5.055	3.483	3.814
98/03/18	2.684	2.964	2.328	2.550
98/05/19	2.550	2.816	2.155	2.360
98/09/15	6.853	7.567	5.767	6.315

Red Clay STORET No. 103031 (Wooddale)										
Streamflow, Concentration, and Mass Loading										
	Flow at					TZinc with	DZinc with	Percent	Mass Load	Mass Load
	Wooddale	TZinc	TZinc	DZinc	DZinc	NDs=1/2DL	NDs=1/2DL	Dissolved	Total Zn	Dissolved Zn
Date	(cfs)	(ug/L)	DQC	(ug/L)	DQC	(ug/L)	(ug/L)	Zinc	(lb/day)	(lb/day)
07/21/93	27	192.8		177		192.8	177	91.8	28.08	25.78
08/18/93	23	291.5		147.9		291.5	147.9	50.7	36.17	18.35
09/23/93	26	273.3		247.3		273.3	247.3	90.5	38.33	34.69
10/19/93	25	353.4		363.3		353.4	363.3	100.0	47.66	49.00
11/15/93	33	278.3		265.7		278.3	265.7	95.5	49.54	47.30
12/14/93	52	273.4		279.2		273.4	279.2	100.0	76.70	78.32
01/24/94	63	245.2		267.3		245.2	267.3	100.0	83.33	90.85
03/14/94	249	226		125.3		226	125.3	55.4	303.58	168.31
04/18/94	82	166.3		144.7		166.3	144.7	87.0	73.57	64.01
05/16/94	143	122.5		79.3		122.5	79.3	64.7	94.50	61.18
06/14/94	38	185.4		132.5		185.4	132.5	71.5	38.01	27.16
07/18/94	35	188.4		110.4		188.4	110.4	58.6	35.57	20.85
08/15/94	29	393.9		358.4		393.9	358.4	91.0	61.62	56.07
09/12/94	20	328.1		301.6		328.1	301.6	91.9	35.40	32.54
10/17/94	15	754.5		740.2		754.5	740.2	98.1	61.05	59.90
12/12/94	42	323.2		305.5		323.2	305.5	94.5	73.23	69.22
01/17/95	36	388.3		381		388.3	381	98.1	75.41	73.99
02/13/95	26	463.8		477.9		463.8	477.9	100.0	65.05	67.03
03/13/95	48	319.3		323.5		319.3	323.5	100.0	82.68	83.77
04/17/95	31	456.4		436.9		456.4	436.9	95.7	76.33	73.07
05/15/95	33	487.6		455.6		487.6	455.6	93.4	86.80	81.11
06/19/95	23	276.6		214.2		276.6	214.2	77.4	34.32	26.58
07/17/95	23	285.9		165.3		285.9	165.3	57.8	35.47	20.51
08/14/95	20	328.5		305.5		328.5	305.5	93.0	35.44	32.96
09/11/95	6	720.2		603.6		720.2	603.6	83.8	23.31	19.54
10/16/95	32	417.2		337.7		417.2	337.7	80.9	72.02	58.30
11/13/95	56	280.6		236		280.6	236	84.1	84.77	71.30
12/11/95	28	586.8		538.6		586.8	538.6	91.8	88.64	81.36
01/29/96	91	245.5		191.6		245.5	191.6	78.0	120.52	94.06
02/12/96	68	281.1		280		281.1	280	99.6	103.12	102.71
03/11/96	64	298.4		327.4		298.4	327.4	100.0	103.03	113.04
04/15/96	76	224.9		182.6		224.9	182.6	81.2	92.21	74.87
05/13/96	94	176.2		143.5		176.2	143.5	81.4	89.35	72.77
06/10/96	85	164.9		128.2		164.9	128.2	77.7	75.61	58.79
07/15/96	71	156.9		144.3		156.9	144.3	92.0	60.10	55.27
09/17/96	274	129		24		129	24	18.6	190.68	35.48
11/18/96	60	332		346		332	346	100.0	107.46	111.99
01/13/97	82	231		224		231	224	97.0	102.19	99.09
03/17/97	96	190.2		197.4		190.2	197.4	100.0	98.50	102.23
05/27/97	58	169		140		169	140	82.8	52.88	43.80
07/14/97	22	237		199		237	199	84.0	28.13	23.62
09/15/97	17	334.5		302.5		334.5	302.5	90.4	30.68	27.74
11/17/97	25	434.5		417.9		434.5	417.9	96.2	58.60	56.36
98/01/12	26	447.3		377.7		447.3	377.7	84.4	62.74	52.98
98/03/18	60	264.7		223.5		264.7	223.5	84.4	85.68	72.34
98/05/19	45	207		169		207	169	81.6	50.25	41.03
98/09/15	13	445		385		445	385	86.5	31.21	27.00

Red Clay STORET No. 103031 (Wooddale)					
Summary Statistics for Zinc Concentration and Mass Loading					
CONC. STATS FOR 7/21/93 - 9/15/98			MASS LOADING STATS FOR 7/21/93 - 9/15/98		
	TZinc (ug/L)	DZinc (ug/L)		TZinc (#/day)	DZinc (#/day)
avg	310.14	275.00	avg	73.18	60.81
median (50%tile)	280.60	265.70	median (50%tile)	72.02	58.79
minimum	122.50	24.00	minimum	23.31	18.35
maximum	754.50	740.20	maximum	303.58	168.31
CONC. STATS FOR 10/19/93 - 9/12/94 (WY '94)			MASS LOADING STATS FOR 10/19/93 - 9/12/94 (WY '94)		
avg	250.99	220.70	avg	81.77	63.23
median (50%tile)	245.20	265.70	median (50%tile)	61.62	56.07
minimum	122.50	79.30	minimum	35.40	20.85
maximum	393.90	363.30	maximum	303.58	168.31
CONC. STATS FOR 10/17/94 - 9/11/95 (WY '95)			MASS LOADING STATS FOR 10/17/94 - 9/11/95 (WY '95)		
avg	436.75	400.84	avg	59.01	55.24
median (50%tile)	388.30	381.00	median (50%tile)	65.05	67.03
minimum	276.60	165.30	minimum	23.31	19.54
maximum	754.50	740.20	maximum	86.80	83.77
CONC. STATS FOR 10/16/95 - 9/17/96 (WY '96)			MASS LOADING STATS FOR 10/16/95 - 9/17/96 (WY '96)		
avg	269.23	230.35	avg	98.19	74.36
median (50%tile)	245.50	191.60	median (50%tile)	89.35	72.77
minimum	129.00	24.00	minimum	60.10	35.48
maximum	586.80	538.60	maximum	190.68	113.04
CONC. STATS FOR 11/18/96 - 9/15/97 (WY '97)			MASS LOADING STATS FOR 11/18/96 - 9/15/97 (WY '97)		
avg	248.95	234.82	avg	69.97	68.08
median (50%tile)	234.00	211.50	median (50%tile)	75.69	71.45
minimum	169.00	140.00	minimum	28.13	23.62
maximum	334.50	346.00	maximum	107.46	111.99
CONC. STATS FOR 11/17/97 - 9/15/98 (WY '98)			MASS LOADING STATS FOR 11/17/97 - 9/15/98 (WY '98)		
avg	359.70	314.62	avg	57.70	49.94
median (50%tile)	434.50	377.70	median (50%tile)	58.60	52.98
minimum	207.00	169.00	minimum	31.21	27.00
maximum	447.30	417.90	maximum	85.68	72.34

WOODDALE					
Freshwater Aquatic Life Criteria for Zinc					
Date	THard (mg/L)	CMC_t (ug/L)	CCC_t (ug/L)	CMC_d (ug/L)	CCC_d (ug/L)
93/07/21	108	124.9	113.1	122.2	111.5
93/08/18	112	128.8	116.7	126.0	115.0
93/09/23	82	98.9	89.6	96.7	88.3
93/10/19	86	103.0	93.3	100.7	92.0
93/11/15	92	109.0	98.8	106.6	97.4
93/12/14	86	103.0	93.3	100.7	92.0
94/01/24	64	80.2	72.6	78.4	71.6
94/03/14	90	107.0	96.9	104.7	95.6
94/04/18	140	155.6	141.0	152.2	139.0
94/05/16	92	109.0	98.8	106.6	97.4
94/06/14	120	136.6	123.7	133.6	122.0
94/07/18	108	124.9	113.1	122.2	111.5
94/08/15	132	148.1	134.1	144.8	132.2
94/09/12	108	124.9	113.1	122.2	111.5
94/10/17	140	155.6	141.0	152.2	139.0
94/12/12	100	117.0	106.0	114.4	104.5
95/01/17	112	128.8	116.7	126.0	115.0
95/02/13	120	136.6	123.7	133.6	122.0
95/03/13	118	134.6	121.9	131.7	120.2
95/04/17	118	134.6	121.9	131.7	120.2
95/05/15	120	136.6	123.7	133.6	122.0
95/06/19	126	142.3	128.9	139.2	127.1
95/07/17	82	98.9	89.6	96.7	88.3
95/08/14	136	151.8	137.5	148.5	135.6
95/09/11	150	165.0	149.4	161.4	147.4
95/10/16	114	130.8	118.4	127.9	116.8
95/11/13	90	107.0	96.9	104.7	95.6
95/12/11	126	142.3	128.9	139.2	127.1
96/01/29	92	109.0	98.8	106.6	97.4
96/02/12	106	122.9	111.4	120.2	109.8
96/03/11	108	124.9	113.1	122.2	111.5
96/04/15	102	119.0	107.8	116.4	106.3
96/05/13	92	109.0	98.8	106.6	97.4
96/06/10	92	109.0	98.8	106.6	97.4
96/07/15	98	115.0	104.2	112.5	102.7
96/09/17	104	121.0	109.6	118.3	108.0
96/11/18	114	130.8	118.4	127.9	116.8
97/01/13	102	119.0	107.8	116.4	106.3
97/03/17	108	124.9	113.1	122.2	111.5
97/05/27	88	105.0	95.1	102.7	93.8
97/07/14	124	140.4	127.2	137.3	125.4
97/09/15	122	138.5	125.4	135.4	123.7
97/11/17	122	138.5	125.4	135.4	123.7
98/01/12	132	148.1	134.1	144.8	132.2
98/03/18	114	130.8	118.4	127.9	116.8
98/05/19	117	133.7	121.1	130.7	119.4
98/09/15	142	157.5	142.7	154.0	140.7

WOODDALE				
Zinc Criteria Exceedance				
	CMC_t	CCC_t	CMC_d	CCC_d
	Ecorisk Index	Ecorisk Index	Ecorisk Index	Ecorisk Index
Date				
93/07/21	1.544	1.704	1.449	1.587
93/08/18	2.263	2.498	1.174	1.286
93/09/23	2.763	3.051	2.556	2.800
93/10/19	3.432	3.789	3.607	3.950
93/11/15	2.552	2.818	2.492	2.729
93/12/14	2.655	2.931	2.772	3.036
94/01/24	3.058	3.377	3.409	3.733
94/03/14	2.112	2.331	1.197	1.311
94/04/18	1.069	1.180	0.951	1.041
94/05/16	1.123	1.240	0.744	0.814
94/06/14	1.358	1.499	0.992	1.086
94/07/18	1.508	1.665	0.904	0.990
94/08/15	2.660	2.937	2.475	2.711
94/09/12	2.627	2.900	2.469	2.704
94/10/17	4.848	5.353	4.863	5.326
94/12/12	2.762	3.049	2.669	2.923
95/01/17	3.014	3.328	3.024	3.312
95/02/13	3.396	3.749	3.578	3.918
95/03/13	2.372	2.618	2.457	2.690
95/04/17	3.390	3.743	3.318	3.634
95/05/15	3.570	3.942	3.411	3.735
95/06/19	1.943	2.146	1.539	1.685
95/07/17	2.890	3.191	1.709	1.871
95/08/14	2.163	2.388	2.057	2.253
95/09/11	4.365	4.819	3.741	4.096
95/10/16	3.191	3.523	2.641	2.892
95/11/13	2.622	2.895	2.255	2.469
95/12/11	4.123	4.552	3.869	4.237
96/01/29	2.251	2.486	1.797	1.968
96/02/12	2.286	2.524	2.329	2.550
96/03/11	2.389	2.638	2.680	2.935
96/04/15	1.890	2.087	1.569	1.718
96/05/13	1.616	1.784	1.346	1.474
96/06/10	1.512	1.670	1.202	1.317
96/07/15	1.364	1.506	1.283	1.405
96/09/17	1.066	1.177	0.203	0.222
96/11/18	2.539	2.803	2.706	2.963
97/01/13	1.941	2.143	1.925	2.108
97/03/17	1.523	1.681	1.616	1.770
97/05/27	1.609	1.777	1.363	1.493
97/07/14	1.688	1.863	1.449	1.587
97/09/15	2.415	2.667	2.233	2.446
97/11/17	3.137	3.464	3.085	3.379
98/01/12	3.021	3.336	2.608	2.857
98/03/18	2.024	2.235	1.748	1.914
98/05/19	1.549	1.710	1.293	1.416
98/09/15	2.825	3.119	2.499	2.737

Red Clay STORET No. 103011 (Stanton)										
Streamflow, Concentration, and Mass Loading										
	Flow at					TZinc with	DZinc with	Percent	Mass Load	Mass Load
	Stanton	TZinc	TZinc	DZinc	DZinc	NDs=1/2DL	NDs=1/2DL	Dissolved	Total Zn	Dissolved Zn
Date	(cfs)	(ug/L)	DQC	(ug/L)	DQC	(ug/L)	(ug/L)	Zinc	(lb/day)	(lb/day)
03/14/94	225	127.2		89.1		127.2	89.1	70.0	154.40	108.15
04/18/94	88	128.2		115.7		128.2	115.7	90.2	60.86	54.93
05/16/94	151	174.9		62.9		174.9	62.9	36.0	142.47	51.24
06/14/94	40	364.9		77.2		364.9	77.2	21.2	78.74	16.66
07/18/94	42	105.5		57.4		105.5	57.4	54.4	23.90	13.01
08/15/94	31	128.4		72.4		128.4	72.4	56.4	21.47	12.11
09/12/94	20	185.8		144.9		185.8	144.9	78.0	20.05	15.63
10/17/94	19	460		407.7		460	407.7	88.6	47.15	41.79
12/12/94	46	246.6		214.8		246.6	214.8	87.1	61.20	53.30
01/17/95	36	289.8		265.6		289.8	265.6	91.6	56.28	51.58
02/13/95	37	477.5		473.9		477.5	473.9	99.2	95.31	94.59
03/13/95	53	242.5		232.6		242.5	232.6	95.9	69.34	66.50
04/17/95	37	277.4		235.1		277.4	235.1	84.8	55.37	46.93
05/15/95	37	301.5		232.9		301.5	232.9	77.2	60.18	46.49
06/19/95	25	144.8		100.8		144.8	100.8	69.6	19.53	13.59
07/17/95	31	207.7		83.7		207.7	83.7	40.3	34.73	14.00
08/14/95	23	116.7		87.6		116.7	87.6	75.1	14.48	10.87
09/11/95	9	98.4		79		98.4	79	80.3	4.78	3.84
10/16/95	40	247.3		176.8		247.3	176.8	71.5	53.36	38.15
11/13/95	62	197.7		143.9		197.7	143.9	72.8	66.12	48.13
12/11/95	41	523		533.1		523	533.1	100.0	115.68	117.91
01/29/96	108	189.7		141.5		189.7	141.5	74.6	110.52	82.44
02/12/96	81	260.4		260.6		260.4	260.6	100.0	113.79	113.87
03/11/96	75	272.9		291.2		272.9	291.2	100.0	110.42	117.82
04/15/96	90	208.6		155.3		208.6	155.3	74.4	101.28	75.40
05/13/96	104	131.3		105		131.3	105	80.0	73.67	58.91
06/10/96	102	174.5		134.5		174.5	134.5	77.1	96.02	74.01
07/15/96	80	108.4		81.8		108.4	81.8	75.5	46.78	35.30
09/17/96	299	691		57		691	57	8.2	1114.59	91.94
11/18/96	62	293		311		293	311	100.0	98.00	104.02
01/13/97	98	241		224		241	224	92.9	127.41	118.42
03/17/97	108	168.7		160.1		168.7	160.1	94.9	98.29	93.28
05/27/97	60	124.1		79.3		124.1	79.3	63.9	40.17	25.67
07/14/97	24	114		66.7		114	66.7	58.5	14.76	8.64
09/15/97	21	185.2		140.5		185.2	140.5	75.9	20.98	15.92
11/17/97	31	337.2		318.7		337.2	318.7	94.5	56.39	53.30
01/12/98	34	379.3		311.4		379.3	311.4	82.1	69.57	57.12
03/17/98	58	209.9		184.9		209.9	184.9	88.1	65.68	57.85
05/19/98	57	150		105		150	105	70.0	46.12	32.29
09/15/98	13	183		131		183	131	71.6	12.83	9.19

Red Clay STORET No. 103011 (Stanton)						
Summary Statistics for Zinc Concentration and Mass Loading						
CONC. STATS FOR 3/14/94 - 9/15/98			MASS LOADING STATS FOR 3/14/94 - 9/15/98			
	TZinc (ug/L)	DZinc (ug/L)		TZinc (#/day)	DZinc (#/day)	
avg	236.70	178.67	avg	91.82	53.62	
median (50%tile)	202.70	142.70	median (50%tile)	61.03	51.41	
minimum	98.40	57.00	minimum	4.78	3.84	
maximum	691.00	533.10	maximum	1114.59	118.42	
CONC. STATS FOR 3/14/94 - 9/12/94 (WY '94, partial)			MASS LOAD STATS FOR 3/14/94-9/12/94(WY '94, partial)			
avg	173.56	88.51	avg	71.70	38.82	
median (50%tile)	128.40	77.20	median (50%tile)	60.86	16.66	
minimum	105.50	57.40	minimum	20.05	12.11	
maximum	364.90	144.90	maximum	154.40	108.15	
CONC. STATS FOR 10/17/94 - 9/11/95 (WY '95)			MASS LOADING STATS FOR 10/17/94 - 9/11/95 (WY '95)			
avg	260.26	219.43	avg	47.12	40.32	
median (50%tile)	246.60	232.60	median (50%tile)	55.37	46.49	
minimum	98.40	79.00	minimum	4.78	3.84	
maximum	477.50	473.90	maximum	95.31	94.59	
CONC. STATS FOR 10/17/94 - 9/11/95 (WY '95)			MASS LOADING STATS FOR 10/17/94 - 9/11/95 (WY '95)			
avg	273.16	189.15	avg	182.02	77.63	
median (50%tile)	208.60	143.90	median (50%tile)	101.28	75.40	
minimum	108.40	57.00	minimum	46.78	35.30	
maximum	691.00	533.10	maximum	1114.59	117.91	
CONC. STATS FOR 11/18/96 - 9/15/97 (WY '97)			MASS LOADING STATS FOR 11/18/96 - 9/15/97 (WY '97)			
avg	187.67	163.60	avg	66.60	60.99	
median (50%tile)	176.95	150.30	median (50%tile)	69.08	59.47	
minimum	114.00	66.70	minimum	14.76	8.64	
maximum	293.00	311.00	maximum	127.41	118.42	
CONC. STATS FOR 11/17/97 - 9/15/98 (WY '98)			MASS LOADING STATS FOR 11/17/97 - 9/15/98 (WY '98)			
avg	251.88	210.20	avg	50.12	41.95	
median (50%tile)	209.90	184.90	median (50%tile)	56.39	53.30	
minimum	150.00	105.00	minimum	12.83	9.19	
maximum	379.30	318.70	maximum	69.57	57.85	

		STANTON				
		Freshwater Aquatic Life Criteria for Zinc				
Date	THard (mg/L)	CMC_t (ug/L)	CCC_t (ug/L)	CMC_d (ug/L)	CCC_d (ug/L)	
94/03/14	80	96.9	87.7	94.7	86.5	
94/04/18	110	126.9	114.9	124.1	113.3	
94/05/16	84	101.0	91.4	98.7	90.2	
94/06/14	110	126.9	114.9	124.1	113.3	
94/07/18	106	122.9	111.4	120.2	109.8	
94/08/15	114	130.8	118.4	127.9	116.8	
94/09/12	116	132.7	120.2	129.8	118.5	
94/10/17	120	136.6	123.7	133.6	122.0	
94/12/12	102	119.0	107.8	116.4	106.3	
95/01/17	114	130.8	118.4	127.9	116.8	
95/02/13	124	140.4	127.2	137.3	125.4	
95/03/13	110	126.9	114.9	124.1	113.3	
95/04/17	124	140.4	127.2	137.3	125.4	
95/05/15	116	132.7	120.2	129.8	118.5	
95/06/19	130	146.2	132.4	142.9	130.5	
95/07/17	78	94.8	85.9	92.7	84.7	
95/08/14	118	134.6	121.9	131.7	120.2	
95/09/11	140	155.6	141.0	152.2	139.0	
95/10/16	100	117.0	106.0	114.4	104.5	
95/11/13	82	98.9	89.6	96.7	88.3	
95/12/11	118	134.6	121.9	131.7	120.2	
96/01/29	86	103.0	93.3	100.7	92.0	
96/02/12	98	115.0	104.2	112.5	102.7	
96/03/11	106	122.9	111.4	120.2	109.8	
96/04/15	100	117.0	106.0	114.4	104.5	
96/05/13	88	105.0	95.1	102.7	93.8	
96/06/10	84	101.0	91.4	98.7	90.2	
96/07/15	108	124.9	113.1	122.2	111.5	
96/09/17	122	138.5	125.4	135.4	123.7	
96/11/18	112	128.8	116.7	126.0	115.0	
97/01/13	110	126.9	114.9	124.1	113.3	
97/03/17	104	121.0	109.6	118.3	108.0	
97/05/27	84	101.0	91.4	98.7	90.2	
97/07/14	134	150.0	135.8	146.7	133.9	
97/09/15	112	128.8	116.7	126.0	115.0	
97/11/17	118	134.6	121.9	131.7	120.2	
98/01/12	128	144.2	130.7	141.1	128.8	
98/03/18	118	134.6	121.9	131.7	120.2	
98/05/19	123	139.5	126.3	136.4	124.5	
98/09/15	133	149.0	135.0	145.7	133.1	

	STANTON			
	Zinc Criteria Exceedance			
	CMC_t	CCC_t	CMC_d	CCC_d
	Ecorisk	Ecorisk	Ecorisk	Ecorisk
Date	Index	Index	Index	Index
94/03/14	1.313	1.450	0.941	1.030
94/04/18	1.011	1.116	0.933	1.021
94/05/16	1.733	1.913	0.637	0.698
94/06/14	2.876	3.176	0.622	0.681
94/07/18	0.858	0.947	0.477	0.523
94/08/15	0.982	1.084	0.566	0.620
94/09/12	1.400	1.546	1.116	1.223
94/10/17	3.368	3.719	3.052	3.343
94/12/12	2.072	2.288	1.846	2.021
95/01/17	2.216	2.447	2.077	2.274
95/02/13	3.401	3.754	3.451	3.779
95/03/13	1.911	2.110	1.875	2.053
95/04/17	1.976	2.181	1.712	1.875
95/05/15	2.272	2.508	1.795	1.965
95/06/19	0.991	1.094	0.705	0.772
95/07/17	2.191	2.419	0.903	0.989
95/08/14	0.867	0.957	0.665	0.729
95/09/11	0.632	0.698	0.519	0.568
95/10/16	2.113	2.333	1.545	1.692
95/11/13	1.999	2.207	1.488	1.629
95/12/11	3.884	4.289	4.049	4.434
96/01/29	1.842	2.034	1.405	1.539
96/02/12	2.264	2.499	2.316	2.537
96/03/11	2.220	2.451	2.422	2.652
96/04/15	1.783	1.968	1.357	1.486
96/05/13	1.250	1.380	1.022	1.120
96/06/10	1.729	1.908	1.362	1.492
96/07/15	0.868	0.958	0.670	0.733
96/09/17	4.989	5.509	0.421	0.461
96/11/18	2.275	2.511	2.469	2.703
97/01/13	1.900	2.097	1.805	1.977
97/03/17	1.394	1.540	1.353	1.482
97/05/27	1.229	1.357	0.803	0.880
97/07/14	0.760	0.839	0.455	0.498
97/09/15	1.438	1.587	1.115	1.221
97/11/17	2.504	2.765	2.420	2.650
98/01/12	2.630	2.903	2.207	2.417
98/03/18	1.559	1.721	1.404	1.538
98/05/19	1.076	1.188	0.770	0.843
98/09/15	1.228	1.356	0.899	0.984

APPENDIX B

**Summary of Effluent Monitoring Data for NVF Discharge 002
(Period Generally Covering Fall, 1993 Through Fall, 1998)**

NVF YORKLYN OUTFALL 002 SELF-REPORTING DATA FROM DISCHARGE MONITORING REPORTS						NVF YORKLYN OUTFALL 002 RATIO OF REPORTED VALUE TO EFFLUENT LIMIT			
PARAM	MVDT	MQAV	MQMX	MCAV	MCMX	MQAV	MQMX	MCAV	MCMX
(measured parameter)	(end of month reporting date)	(monitored mass loading, ave.)	(monitored mass loading, max)	(monitored conc. ,ave.)	(monitored conc. ,max.)	(monitored mass loading, ave.)	(monitored mass loading, max)	(monitored conc. ,ave.)	(monitored conc. ,max.)
		units: #/day	units: #/day	units: mg/L	units: mg/L	units: #/day	units: #/day	units: mg/L	units: mg/L
ZINC, (total)	10/31/93	4.80	10.60	0.30	0.67	3.7	5.4	4.3	6.1
ZINC, (total)	11/30/93	2.66	4.57	0.19	0.34	2.0	2.3	2.7	3.1
ZINC, (total)	12/31/93	2.76	3.89	0.20	0.36	2.1	2.0	2.9	3.3
ZINC, (total)	01/31/94	2.77	3.57	0.25	0.32	2.1	1.8	3.6	2.9
ZINC, (total)	02/28/94	3.40	6.92	0.20	0.38	2.6	3.5	2.9	3.5
ZINC, (total)	03/31/94	NA	NA	NA	NA	NA	NA	NA	NA
ZINC, (total)	05/31/94	4.02	4.53	0.22	0.24	3.1	2.3	3.1	2.2
ZINC, (total)	06/30/94	2.45	4.06	0.14	0.20	1.9	2.1	2.0	1.8
ZINC, (total)	07/31/94	2.08	3.79	0.13	0.22	1.6	1.9	1.9	2.0
ZINC, (total)	08/31/94	4.80	6.44	0.29	0.39	3.7	3.3	4.1	3.5
ZINC, (total)	09/30/94	4.46	5.68	0.29	0.39	3.4	2.9	4.1	3.5
ZINC, (total)	10/31/94	3.60	4.21	0.25	0.29	2.8	2.1	3.6	2.6
ZINC, (total)	11/30/94	4.20	6.13	0.30	0.44	3.2	3.1	4.3	4.0
ZINC, (total)	01/31/95	3.36	4.34	0.35	0.46	2.6	2.2	5.0	4.2
ZINC, (total)	02/28/95	3.48	4.96	0.37	0.61	2.7	2.5	5.3	5.5
ZINC, (total)	04/30/95	1.55	1.92	0.15	0.17	1.2	1.0	2.1	1.5
ZINC, (total)	05/31/95	2.23	4.10	0.16	0.27	1.7	2.1	2.3	2.5
ZINC, (total)	06/30/95	2.33	2.90	0.17	0.20	1.8	1.5	2.4	1.8
ZINC, (total)	07/31/95	3.46	4.79	0.24	0.35	2.7	2.4	3.4	3.2
ZINC, (total)	09/30/95	2.76	3.36	0.22	0.29	2.1	1.7	3.1	2.6
ZINC, (total)	10/31/95	1.74	3.09	0.13	0.26	1.3	1.6	1.9	2.4
ZINC, (total)	11/30/95	3.82	5.72	0.27	0.36	2.9	2.9	3.9	3.3
ZINC, (total)	12/31/95	3.38	5.89	0.41	0.63	2.6	3.0	5.9	5.7
ZINC, (total)	01/31/96	2.62	4.01	0.24	0.33	2.0	2.0	3.4	3.0
ZINC, (total)	02/29/96	5.20	8.43	0.48	0.85	4.0	4.3	6.9	7.7
ZINC, (total)	04/30/96	7.28	13.90	0.39	0.87	5.6	7.0	5.6	7.9
ZINC, (total)	05/31/96	3.41	4.54	0.22	0.29	2.6	2.3	3.1	2.6
ZINC, (total)	06/30/96	2.77	3.41	0.18	0.27	2.1	1.7	2.6	2.5
ZINC, (total)	08/31/96	1.73	2.72	0.10	0.16	1.3	1.4	1.4	1.5
ZINC, (total)	09/30/96	1.29	1.57	0.11	0.14	1.0	0.8	1.6	1.3
ZINC, (total)	10/31/96	2.46	3.52	0.20	0.25	1.9	1.8	2.9	2.3
ZINC, (total)	11/30/96	2.63	4.65	0.18	0.30	2.0	2.2	2.6	2.7

(cont.)									
NVF YORKLYN OUTFALL 002					NVF YORKLYN OUTFALL 002				
SELF-REPORTING DATA FROM DISCHARGE MONITORING REPORTS					RATIO OF REPORTED VALUE TO EFFLUENT L				
PARAM	MVDT	MQAV	MQMX	MCAV	MCMX	MQAV	MQMX	MCAV	MCM
(measured parameter)	(end of month reporting date)	(monitored mass loading, ave.)	(monitored mass loading, max)	(monitored conc. ,ave.)	(monitored conc. ,max.)	(monitored mass loading, ave.)	(monitored mass loading, max)	(monitored conc. ,ave.)	(monitored conc. ,max.)
		units: #/day	units: #/day	units: mg/L	units: mg/L	units: #/day	units: #/day	units: mg/L	units: mg/L
ZINC, (total)	01/31/97	4.31	5.08	0.29	0.35	3.3	2.6	4.1	3.2
ZINC, (total)	02/28/97	4.04	5.89	0.27	0.39	3.1	3.0	3.9	3.5
ZINC, (total)	03/31/97	3.49	7.36	0.23	0.51	2.7	3.7	3.3	4.6
ZINC, (total)	04/30/97	5.76	12.70	0.32	0.71	4.4	6.4	4.6	6.5
ZINC, (total)	05/31/97	4.22	5.34	0.26	0.34	3.2	2.7	3.7	3.1
ZINC, (total)	06/30/97	1.67	4.08	0.10	0.23	1.3	2.1	1.4	2.1
ZINC, (total)	07/31/97	0.97	1.62	0.06	0.09	0.7	0.8	0.9	0.8
ZINC, (total)	08/31/97	1.00	2.12	0.07	0.16	0.8	1.1	1.0	1.5
ZINC, (total)	09/30/97	0.34	0.57	0.02	0.03	0.3	0.3	0.3	0.3
ZINC, (total)	10/31/97	0.55	0.77	0.04	0.06	0.4	0.4	0.6	0.5
ZINC, (total)	11/30/97	0.96	1.83	0.06	0.09	0.7	0.9	0.9	0.8
ZINC, (total)	12/31/97	0.82	1.76	0.06	0.09	0.6	0.9	0.9	0.8
ZINC, (total)	01/31/98	0.55	0.66	0.04	0.05	0.4	0.3	0.6	0.5
ZINC, (total)	02/28/98	0.57	0.92	0.04	0.07	0.4	0.5	0.6	0.6
ZINC, (total)	03/31/98	0.70	1.40	0.06	0.12	0.5	0.7	0.9	1.1
ZINC, (total)	04/30/98	1.05	2.09	0.07	0.14	0.8	1.1	1.0	1.3
ZINC, (total)	05/31/98	1.05	1.38	0.07	0.11	0.8	0.7	1.0	1.0
ZINC, (total)	06/30/98	1.54	2.08	0.11	0.14	1.2	1.1	1.6	1.3
ZINC, (total)	07/31/98	0.69	1.42	0.06	0.10	0.5	0.7	0.9	0.9
ZINC, (total)	08/31/98	0.58	0.73	0.04	0.06	0.4	0.4	0.6	0.5
ZINC, (total)	09/30/98	0.84	1.75	0.06	0.14	0.6	0.9	0.9	1.3

APPENDIX C

Estimate of Diffusive Flux of Zinc from Red Clay Creek Sediments

1. Introduction

Contaminants can move between the water column and bottom sediments in a variety of ways. One way this can happen is when particles in the water column (i.e., suspended solids) settle to the creek bed, carrying any adsorbed contaminants with them. Once settled, these particles (and adsorbed contaminants) will either be resuspended to the water column, move downstream as a part of the bedload or will become buried by other sediments. The movement of the contaminant in these cases is largely dictated by the movement of the particles.

In addition to the physical processes of settling and resuspension, contaminants can also be exchanged between bed sediments and the water column when sediment-dwelling organisms shred, graze, or otherwise “work” the sediments. This process, which can act to transfer contaminants to the water column, is often referred to as “bioturbation.” Finally, contaminants can be exchanged between the water and sediment by the chemical process of diffusion. As will be further discussed below, diffusion can result in the transfer of contaminants from bottom sediments to the water column or from the water column to the sediments.

The physical, chemical, and biological processes just mentioned occur within all waterbodies at different times and to different degrees. Which process or processes predominant depends upon the particular situation under consideration. For the case of the Red Clay Creek, very little of the zinc in the water column immediately downstream of the NVF Yorklyn facility is in the particulate form. Therefore, we would not expect settling to be a significant process in this reach. The work of Pizzuto and Church (1990) support this premise. Further, during steady-state, low flow conditions, the flow in the Creek is calm and would not be expected to cause significant resuspension or bedload movement. In addition, although the degree of bioturbation directly below the NVF facility is unknown, it is assumed to be negligible due to the sparse macroinvertebrate assemblage observed there in the past. Diffusive flux, on the other hand, was worthy of closer examination for two reasons. First, the concentration of zinc in the sediments below the NVF Yorklyn facility are elevated, thereby providing a reservoir of zinc that could potentially be returned to the water column. Second, the steady-state, low flow conditions of the TMDL offer the conditions that are favorable for diffusion to occur.

There are two basic approaches that can be used to develop estimates of diffusive flux of contaminants to/from sediments. The first approach is to perform detailed laboratory and field experiments to gather empirical data on the flux. The major advantage of this approach is that it yields site-specific data. The major cons, however, are that these studies can be costly, are fraught with all the usual logistical challenges of specialized lab and field studies, and the resulting mass transfer rates are not necessarily applicable to future condition. The second approach to determine diffusive flux is through mathematical modeling. The major advantages here are low cost, short turn-around time, and the ability to consider any number of hypothetical scenarios. The major con is that the modeled fluxes are just that, modeled. Given the time constraints associated with the development of the zinc TMDL for the Red Clay Creek, and in consideration of the work of Pizzuto and Church which suggests minimal diffusive exchange, the latter approach was taken.

The discussion that follows provides a brief overview of diffusion theory and presents the governing equations used to model the process. Available information for the Red Clay Creek is applied to estimate the diffusive flux of zinc from/to the sediments in the ½ mile reach below the NVF Yorklyn facility.

2. Overview of Sediment-Water Diffusion Theory

Just as a contaminant will partition itself in the water column between dissolved and adsorbed (particulate) phases, so will a contaminant partition between these phases in sediment. In sediments, the particulate phase is primarily associated with the sediment particles themselves, although some particulate contaminant may also be adsorbed to finely divided particles suspended in the sediment pore water. The dissolved contaminant is found primarily in the sediment pore water. During steady-state, quiescent conditions, the movement of a contaminant between the sediment and overlying water column can be treated as a classical diffusion process where the magnitude of the exchange depends upon the concentration gradient, the interfacial area between the 2 zones, and a rate constant. In this case, the gradient that drives the process is the difference between the dissolved concentration of the contaminant in the sediment pore water and the dissolved concentration in the overlying water. When the dissolved concentration is greater in the sediment pore water than in the overlying water, then dissolved contaminant will diffuse from the pore water to the water column. When the dissolved concentration is greater in the water column, then the opposite will happen and the contaminant will diffuse from the water column into the sediment pore water.

3. Model Equations

Thomann and Mueller (1987) present the following equation to describe the diffusive flux of a contaminant between sediment and the water column:

$$\text{Diffusive Flux} = K_f A_s (C_{d2} - C_{d1})$$

In the above equation, K_f is the sediment-water diffusive transfer coefficient, A_s is the interfacial area between the sediment and the overlying water column, and C_{d2} and C_{d1} are the dissolved concentrations of the contaminant in the pore water of the sediment and water column, respectively. In this and other equations to be presented, the subscript “2” refers to the bed sediments, while the subscript “1” refers to the water column.

DiToro *et. al.* (1981) have shown that K_f (in units of cm/day) can be estimated through the following equation, where ϕ_2 is the sediment porosity and MW is the molecular weight of the contaminant:

$$K_f = 19 \phi_2 (MW)^{-2/3}$$

Pizzuto and Church (1990) used a porosity 0.3 in their work to estimate zinc inventories in the sediments below Yorklyn. When this porosity is substituted into the equation above along with a molecule weight of 65.38 for zinc, a value of 0.3512 cm/day is computed for K_f . This is within the expected range of 0.1-1.0 cm/day noted by Thomann and Mueller (1987).

The interfacial area, A_s , over which we wish to compute diffusive flux was computed by multiplying the length of the reach by the average width. The length was taken as the full ½ mile from the NVF facility down to the first low head dam. Based on previous stream surveys, the average width of the Creek in the area between Yorklyn and Ashland is approximately 30 feet. In SI units, the computed area therefore becomes 7,356.348 m².

For purposes of the TMDL, we ultimately want to see dissolved concentrations of zinc in the water column, C_{d1} , to be at or below the acute aquatic life criterion. In this case, we must convert the total zinc criterion to a dissolved basis. For a total zinc criterion of 173.3 ug/L under design conditions, and a total to dissolved conversion factor of 0.978, the dissolved acute criterion is 169.49 ug/L. This is the value used in the flux calculations for C_{d1} .

The last, and most difficult, parameter that needs to be determined before we can estimate flux is the concentration of zinc in the sediment pore water, C_{d2} . This value has not been directly determined through previous testing, so modeling techniques were used. The solution strategy for determining C_{d2} was as follows:

- ▶ Using the fraction of dissolved zinc in the water column, f_{d1} , and the suspended solids concentration in the water column, m_1 , first estimate the partition coefficient for dissolved and particulate zinc in the water column, Π_1 . Assume local equilibrium and that sorption kinetics are linear and reversible. Use the following equation, (Thomann and Mueller, 1987):

$$\Pi_1 = (1 - f_{d1})/m_1 f_{d1}$$

Recall from Section 2.3.1 that the geometric mean of the dissolved fraction of zinc at the Ashland station is 85.9 %. As a decimal fraction, this percentage is equivalent to 0.859. Because Ashland is a short distance downstream from the area of interest for the flux calculations, the dissolved fraction from Ashland was used in the above equation for the ½ mile reach directly below NVF Yorklyn. Furthermore, the median suspended solids concentration at Ashland over water years '93 through '98 was used as an estimate of suspended solids concentrations in the reach of interest for the flux calculations. That median is 6 mg/L. Substituting these values into the above equation and multiplying by 10⁶ for unit conversions, the partition coefficient for the water column, Π_1 , becomes 27,357.4 L/kg. Expressed in base 10 notation, Π_1 becomes 10^{4.4} L/kg. This value is nearly in the middle of the range (10⁴ - 10⁵) reported by Thomann and Mueller (1987) for the heavy metals cadmium, copper, lead, and zinc.

- ▶ Estimate the partition coefficient for dissolved and particulate zinc in the sediments, Π_2 , by assuming that Π_2 is some fraction of the partition coefficient in the water column, Π_1 . Thomann and Mueller (1987) note that partition coefficients for sediments are generally less than partition coefficients in the overlying water column. They present examples in which Π_1 ranges between 5 and 16 times greater than Π_2 . For purposes of evaluating the flux of zinc from/to the Red Clay Creek sediments, this analysis assumed that Π_1 is 5 times Π_2 . The implication of this choice will be discussed later within the context of model sensitivity. For now, assuming a 5-fold difference between Π_1 and Π_2 , the partition coefficient between dissolved and particulate zinc in the sediments, Π_2 , is computed as 5,471.5 L/kg, which, in base 10 notation is $10^{3.7}$ L/kg.
- ▶ Estimate the solids concentration in the bed sediment on a bulk volume basis, m_2 , from the density of the particles in the bed, ρ_s , and the bed porosity, ϕ_2 . Thomann and Mueller (1987) provide the following equation for m_2 in units of mg/L, where ρ_s is entered in units of g/cm³:

$$m_2 = \rho_s(1 - \phi_2)10^6$$

As noted previously, Pizzuto and Church (1990) used a porosity 0.3 in their work to estimate zinc inventories in the sediments below Yorklyn. Also as a part of those calculations, they used a particle density of 2.65 g/cm³. When these values are substituted into the equation above, m_2 is computed as 1,855,000 mg/L. This value may seem high, but this is only because we are more familiar with total suspended solids concentrations in the water column, which generally fall below 100 mg/L. Remember, however, that bed sediments are mostly particles, so the solids concentration in the bed on a bulk volume basis is going to be very high. Finally in this section, it is noted that although the density of the bed solids was assumed to be constant in these calculations, the implication of using different porosity values was evaluated and will be discussed later under model sensitivity.

- ▶ Estimate the dissolved fraction of zinc in the sediments, f_{d2} , from Π_2 and m_2 . Again, local equilibrium between dissolved and particulate zinc is assumed along with linear and reversible sorption kinetics. Thomann and Mueller (1987) provide the following equation for f_{d2} :

$$f_{d2} = 1/(1 + \Pi_2 m_2)$$

For Π_2 and m_2 equal to 5471.48 L/kg and 1,855,000 mg/L, respectively, and multiplying the above equation by 10^6 to handle unit conversions, f_{d2} is computed as 0.0000985.

- ▶ Estimate the total zinc concentration in the sediment on a bulk volume basis, C_{T2} , by a two-step calculation. First, multiply the zinc concentration in the bed sediments on a dry weight basis, r_2 , by the solids concentration in the bed, m_2 . This product represents the concentration of particulate zinc in the sediments expressed on a bulk volume basis, C_{p2} .

C_{p2} is then divided by the fraction of zinc in the particulate form in the sediments, f_{p2} , which is the same as 1 minus f_{d2} determined above.

$$C_{T2} = (r_2 m_2)/(1 - f_{d2})$$

Pizzuto and Church (1990) reported an average dry weight concentration of zinc in the sediments below NVF Yorklyn of 200 ug/g. That average value, however, included results from surficial sediments as well as deeper sediments, which, they point out, were generally less contaminated. For this reason, and because various other agencies reported somewhat higher dry weight zinc concentrations for surficial sediments below NVF, the flux calculations presented in this Appendix are based on a dry weight sediment zinc concentration of 500 ug/g. Using this value for r_2 and the values presented previously for m_2 and f_{d2} , and dividing by 10^6 to take care of units, the total zinc concentration in the sediment on a bulk volume basis, C_{T2} , is computed as 927.59 mg/L.

- ▶ The dissolved concentration of zinc in the sediment pore water, C_{d2} , can now be computed by multiplying the dissolved fraction of zinc in the sediments, f_{d2} , by the total zinc concentration in the sediment on a bulk volume basis, C_{T2} , and then dividing the resulting product by the porosity of the bed, ϕ_2 . This calculation yields a concentration of dissolved zinc in the pore water of the sediments of 0.3046 mg/L, which is equal to 304.6 ug/L. As a final note in this section, it is pointed out without proof that the above equations can be combined to yield the rather simple result for C_{d2} :

$$C_{d2} = r_2 / (\Pi_2 \phi_2)$$

At this point, estimates for all of the parameters in the original flux equation are available. The flux equation is repeated below for convenience, as are the values of the parameters.

$$\text{Diffusive Flux} = K_f A_s (C_{d2} - C_{d1}),$$

where:

$$K_f = \text{diffusive transfer coefficient} = 0.3512 \text{ cm/d}$$

$$A_s = \text{interfacial area between water and bed} = 7356.348 \text{ m}^2$$

$$C_{d2} = \text{dissolved zinc conc. in the sediment pore water} = 304.6 \text{ ug/L, and}$$

$$C_{d1} = \text{desired dissolved zinc conc. in the water column} = 169.49 \text{ ug/L}$$

Substituting these values into the flux equation and making appropriate unit conversions, we obtain the final result that we would expect no more than 0.0077 pounds of zinc per day to diffuse out of the sediments in the ½ mile reach below the NVF Yorklyn facility during low flow conditions. This is a small fraction of the TMDL (1.81 #/d) which can be easily accommodated by a MOS of 0.01 #/d.

The table on the following page demonstrates the effect of choosing different values for porosity

and different multipliers between Π_1 and Π_2 . The highlighted row represents the best estimate based upon the available information. The other rows represent alternative flux estimates for different porosity and Π_2/Π_1 ratios. Note from the table that as porosity increases, the dissolved concentration in the pore water decreases, acting to reduce the likelihood that zinc would be released from the sediments. However, as Π_1 becomes ever greater than Π_2 , the dissolved concentration in the pore water increases, making it more likely that zinc would be released from the sediments. The other observation that should be made from the table is that the magnitude of the flux is small in comparison to the TMDL, regardless of the values selected for porosity and the partition coefficients.

Spreadsheet to Estimate Diffusive Flux of Zinc to/from Red Clay Creek Sediments

BED CHARACTERISTICS											PARTITION COEFFICIENTS				
r ₂ (ug tox/g dry wt)	porosity	density (g/cm ³)	m ₂ (mg/L)	Length (m)	Width (m)	f _{d1}	m ₁ (mg/L)	Pi ₁ (L/kg)	Pi ₂ /Pi ₁	Pi ₂ (L/kg)					
500	0.3	2.65	1855000	804.5	9.144	0.859	6	27357.39	1	27357.39					
500	0.3	2.65	1855000	804.5	9.144	0.859	6	27357.39	0.5	13678.70					
500	0.3	2.65	1855000	804.5	9.144	0.859	6	27357.39	0.2	5471.48					
500	0.3	2.65	1855000	804.5	9.144	0.859	6	27357.39	0.1	2735.74					
500	0.5	2.65	1325000	804.5	9.144	0.859	6	27357.39	1	27357.39					
500	0.5	2.65	1325000	804.5	9.144	0.859	6	27357.39	0.5	13678.70					
500	0.5	2.65	1325000	804.5	9.144	0.859	6	27357.39	0.2	5471.48					
500	0.5	2.65	1325000	804.5	9.144	0.859	6	27357.39	0.1	2735.74					
500	0.7	2.65	795000	804.5	9.144	0.859	6	27357.39	1	27357.39					
500	0.7	2.65	795000	804.5	9.144	0.859	6	27357.39	0.5	13678.70					
500	0.7	2.65	795000	804.5	9.144	0.859	6	27357.39	0.2	5471.48					
500	0.7	2.65	795000	804.5	9.144	0.859	6	27357.39	0.1	2735.74					
DIFFUSIVE TRANSFER COEFFICIENT		DISSOLVED ZINC CONCENTRATIONS				FLUX ESTIMATES									
M.W. (g/mole)	K _f (cm/d)	C _{T1} (ug/L)	C.F.	C _{d1} (ug/L)	C _{d2} (ug/L)	FLUX (ug/d)	FLUX (#/d)	Direction							
65.38	0.3512	173.3	0.978	169.49	60.92	-2.80E+06	-0.0062	into sediment							
65.38	0.3512	173.3	0.978	169.49	121.84	-1.23E+06	-0.0027	into sediment							
65.38	0.3512	173.3	0.978	169.49	304.61	3.49E+06	0.0077	out of sediment							
65.38	0.3512	173.3	0.978	169.49	609.22	1.14E+07	0.0251	out of sediment							
65.38	0.5854	173.3	0.978	169.49	36.55	-5.72E+06	-0.0126	into sediment							
65.38	0.5854	173.3	0.978	169.49	73.11	-4.15E+06	-0.0092	into sediment							
65.38	0.5854	173.3	0.978	169.49	182.77	5.72E+05	0.0013	out of sediment							
65.38	0.5854	173.3	0.978	169.49	365.53	8.44E+06	0.0186	out of sediment							
65.38	0.8195	173.3	0.978	169.49	26.11	-8.64E+06	-0.0191	into sediment							
65.38	0.8195	173.3	0.978	169.49	52.22	-7.07E+06	-0.0156	into sediment							
65.38	0.8195	173.3	0.978	169.49	130.55	-2.35E+06	-0.0052	into sediment							
65.38	0.8195	173.3	0.978	169.49	261.09	5.52E+06	0.0122	out of sediment							