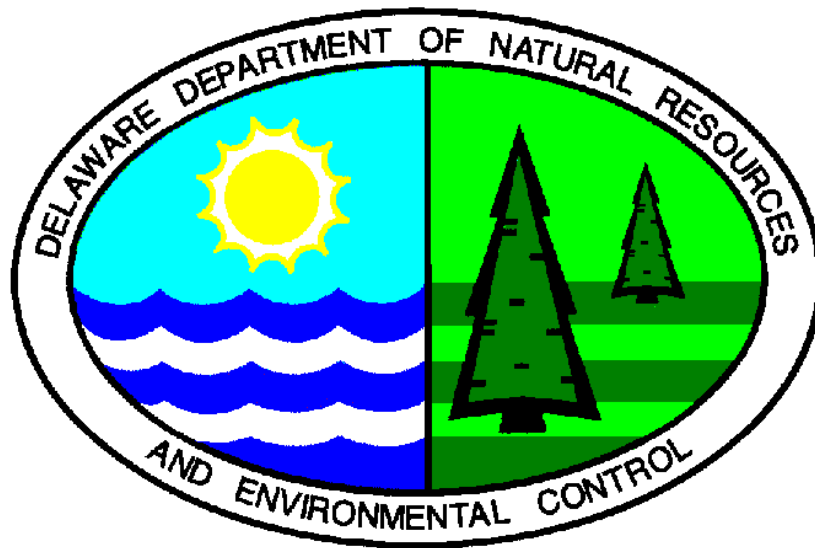


**AMENDED
TOTAL MAXIMUM DAILY LOAD (TMDL)
FOR ZINC IN THE RED CLAY CREEK**

Technical Background and Basis Document

September 15, 2008



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CONTENTS

List of Figures	ii
List of Tables	iii
Executive Summary	iv
1. Introduction	1
1.1 Purpose.....	1
1.2 Background.....	1
1.3 Report Organization.....	4
2. Environmental Setting	5
3. Applicable Water Quality Standards	8
4. Zinc Concentrations and Mass Loading in the Red Clay Creek	11
4.1 Readily Available and Existing Data.....	11
4.2 Current Zinc Concentrations.....	11
4.3 Zinc Toxicity Units.....	16
4.4 Relationship between Zinc Concentration and Stream Flow.....	20
4.5 Zinc Mass Loading	21
5. Total Maximum Daily Load	23
5.1 General Principles.....	23
5.2 Methods: Lognormal Probability Approach	24
5.3 Results: Lognormal Probability Approach	26
5.4 Margin of Safety (MOS).....	28
5.5 Seasonal Variability	28
5.6 Reasonable Assurance	28
6. Next Steps	29
7. References	30
APPENDIX 1: Zinc, Hardness, TSS, and Flow Data for the Red Clay Creek, January 2003 through April 2008	
APPENDIX 2: STATGRAPHICS Output	

List of Figures

Figure 1. Red Clay Creek Watershed, New Castle County, Delaware.....	7
Figure 2. Zinc Concentration Red Clay Creek Stateline.....	12
Figure 3. Zinc Concentration Red Clay Creek Yorklyn	12
Figure 4. Zinc Concentration Red Clay Creek Ashland	13
Figure 5. Zinc Concentration Red Clay Creek Wooddale	13
Figure 6. Zinc Concentration Red Clay Creek Stanton	14
Figure 7. Median Fraction Dissolved Zinc Below Yorklyn	16
Figure 8. Toxic Units Red Clay Creek Stateline.....	17
Figure 9. Toxic Units Red Clay Creek Yorklyn	17
Figure 10. Toxic Units Red Clay Creek Ashland	18
Figure 11. Toxic Units Red Clay Creek Wooddale	18
Figure 12. Toxic Units Red Clay Creek Stanton	19
Figure 13. Total Zinc vs Flow at Red Clay Creek Yorklyn.....	20
Figure 14. Total Zinc Load Red Clay Creek Yorklyn	21
Figure 15. Total Zinc Load vs Flow at Red Clay Creek Yorklyn.....	22

List of Tables

Table 1. Routine Water Quality Monitoring Stations in the Red Clay Creek Yorklyn.....	11
Table 2. Amended Zinc TMDL for the Red Clay Creek	27

Executive Summary

A TMDL specifies the maximum allowable mass loading of a pollutant (e.g., 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.

In December of 1999, the Department of Natural Resources and Environmental Control (DNREC) established a Total Maximum Daily Load (TMDL) regulation for zinc discharged to the Red Clay Creek (DNREC, 1999a). A TMDL was needed because ongoing release of zinc from the National Vulcanized Fiber (NVF) Company in Yorklyn, Delaware was causing frequent violations of water quality criteria designed to protect aquatic life. A TMDL of 1.81 pounds of zinc per day (1.81 #/d) was determined to be the maximum mass loading that could be present in the Red Clay Creek during critical low flow periods while still assuring that the water quality criteria for zinc are met at Yorklyn and points downstream.

The NVF Company appealed the December 1999 TMDL regulation to the State Environmental Appeals Board and the State Superior Court. Among the key technical objections raised by NVF in their appeal was that the Department improperly rejected the dynamic modeling approach that NVF had proposed during the public comment period. NVF argued that the steady-state approach used by the Department was unnecessarily stringent. In an effort to resolve the appeal, the Department entered into settlement negotiations with NVF. Those negotiations were protracted due to the complexity of the issues involved as well as the occurrence of major flooding in the Red Clay valley that forced a shut down of the NVF facility. That shut down, in turn, contributed to a bankruptcy filing by NVF.

Despite the problems, the Department and NVF remained committed to resolving the dispute and more importantly, to reducing the loading of zinc from the NVF Yorklyn facility to the Red Clay Creek. Significant progress has been made in that regard as will be fully described in this document. As a result of the pollution control actions taken at the NVF facility, the timing and magnitude of zinc loading to the Red Clay Creek has changed. Importantly, peak zinc concentrations no longer occur in the Red Clay Creek during lowest stream flows. This suggested to the Department that an alternative approach to developing a TMDL such as dynamic modeling might be acceptable provided it is fully protective of water quality.

The Department has used a particular type of dynamic modeling known as a lognormal probability analysis to develop an amended zinc TMDL for the Red Clay Creek. The method considers the simultaneous variation of upstream zinc loading, stream flow,

loading from NVF, and other variables that effect the concentration of zinc in the Red Clay Creek. This more sophisticated methodology, coupled with changed environmental conditions, indicates that the Red Clay Creek can safely receive up to 55.93 pounds of zinc per day and still meet applicable water quality criteria 99.908% of the time. This level of protection allows no more than 1 exceedance in any 3 year period, consistent with the Delaware Surface Water Quality Standards and with Federal Environmental Protection Agency (EPA) guidance.

The Department proposes to allocate the amended TMDL of 55.93 pounds of zinc per day as shown in the table below.

Amended Zinc TMDL for the Red Clay Creek

TMDL (pounds/day)	WLA ₀₀₂ + LA _{g.w.} (pounds/day)	LA _{up} (pounds/day)	MOS (pounds/day)
55.93	25.17	25.17	5.59

In this table, WLA₀₀₂ 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, WLA₀₀₂ 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 (MOS). An equal allocation was given to the NVF Yorklyn facility and all loading originating from upstream of Yorklyn. The margin of safety represents 10 % of the TMDL, which accounts for various uncertainties. 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 amended zinc TMDL for the Red Clay Creek as a State regulation. This notice will appear within the October 1, 2008 Delaware Register of Regulations. The Register will also announce a public hearing to gather comments on the proposed TMDL regulation amendment. That hearing will be held on Tuesday October 28, 2008, beginning at 6:00 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 amended TMDL regulation at the time of the public hearing, or otherwise can be submitted in writing by 4:30 p.m., November 5, 2008. All comments should be directed to the attention of Maryann Pielmeier, DNREC, Watershed Assessment Section, 820 Silver Lake Blvd., Suite 220, Dover, DE, 19904-2464, (maryann.pielmeier@state.de.us), fax: (302) 739-6140.

The DNREC expects to adopt the amended TMDL regulation following the hearing and consideration of the comments received. The DNREC will then submit the amended TMDL regulation to the U.S. EPA for their review and approval.

1. Introduction

1.1 Purpose

The purpose of this document is to provide the technical basis for the amended 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.

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.

In December of 1999, the Department of Natural Resources and Environmental Control (DNREC) established a Total Maximum Daily Load (TMDL) for zinc discharged to the Red Clay Creek (DNREC, 1999a). A TMDL was needed because ongoing release of zinc from the National Vulcanized Fiber (NVF) Company in Yorklyn, Delaware was causing frequent violations of water quality criteria designed to protect aquatic life. A TMDL of 1.81 pounds of zinc per day (1.81 #/d) was determined to be the maximum mass loading that could be present in the Red Clay Creek during critical low flow conditions while still assuring that the water quality criteria for zinc are met at Yorklyn and points downstream. The TMDL included an allocation of 1.2 #/d for all releases from the NVF property, a load allocation of 0.6 #/d for all loading from sources upstream of Yorklyn, and a margin of safety of 0.01 #/d to account for uncertainties in the relationship between mass loading and in-stream response.

The TMDL established by the Department was calculated by multiplying the acute aquatic life criterion for zinc by the 1Q10 critical low flow for the stream (DNREC, 1999b). This technique is consistent with the default approach set forth in Delaware's

Surface Water Quality Standards for Streams (DNREC, 2004), and is among the approaches recommended by the U.S. Environmental Protection Agency (EPA, 1991). Fundamentally, the approach taken by the Department presumed that: (i) the concentration of zinc immediately downstream from the NVF Yorklyn facility increases as stream flow decreases, with the peak concentration occurring at minimum flow; (ii) all conditions affecting in-stream concentration of zinc downstream of the NVF Yorklyn facility, including loading from upstream as well as loading from the NVF facility, are steady during low flow periods; and (iii) the discharge from the NVF facility mixes completely and instantaneously with the available stream flow at the point of release. These assumptions collectively produced a TMDL referred to as a steady-state, low flow, complete mix TMDL.

The U.S. Environmental Protection Agency (EPA) approved the Department's TMDL in December of 1999 (EPA, 1999). During that same month, the NVF Company filed an administrative appeal of the Department's TMDL (NVF, 1999). Among the key technical objections raised by NVF in their appeal was that the Department improperly rejected the dynamic modeling approach that NVF had proposed during the public comment period. NVF argued that the steady-state approach used by the Department was unnecessarily stringent because they claimed that peak zinc toxicity does not occur in the Red Clay Creek at lowest stream flow (counter to assumption (i) above) and that mass loading of zinc increases as stream flow increases (counter to assumption (ii) above). NVF further noted that dynamic modeling is allowable under DNREC's Surface Water Quality Standards and is actually encouraged by EPA when and where appropriate. The DNREC did not necessarily agree with NVF's arguments and position. Although arguably reviewable under DNREC's Standards, DNREC had concerns over the technical details of the dynamic modeling approach proposed by NVF (DNREC, 1999c).

Despite the Department's concerns, the prospects of revising the TMDL based on a dynamic modeling approach remained in consideration, especially if doing so could lead to a binding commitment on NVF's part to once and for all develop and implement a meaningful and aggressive pollution control strategy (PCS) to address zinc released from the facility. It was ultimately NVF's commitment to develop a PCS that convinced the Department to continue settlement negotiations with NVF. Those negotiations focused on the details of the PSC and the dynamic modeling approach. For the Department to agree to replace its steady-state, low-flow TMDL with a 'dynamic TMDL', the Department needed to see real progress on NVF's part in reducing the amount of zinc released to the Red Clay. The Department also needed to be satisfied that a 'dynamic TMDL' could be developed that would be fully protective of water quality.

Negotiations on the PCS and dynamic TMDL occurred over several years until a major flood in the Red Clay valley forced a temporary shutdown of the NVF Yorklyn facility. Not long after that flood, NVF filed for bankruptcy protection under Chapter 11 and manufacturing activity at the Yorklyn facility all but ceased.

Despite the uncertain future of the company, NVF has made significant progress on several fronts in addressing the zinc contamination problem at the Yorklyn facility. Highlights of the progress include:

- All ‘wet’ operations at the No. 1 mill were curtailed. It was discovered that subsurface piping intended to carry zinc from the No. 1 mill to a precipitator for recycling had failed, thereby allowing highly soluble zinc to directly enter the groundwater between the No. 1 mill and the Red Clay Creek. NVF stopped sending ‘new’ zinc chloride solution to the No. 1 mill, which stopped this ongoing cycle of zinc loading to the groundwater. NVF also decommissioned the failed piping.
- Recovery of soluble zinc already in the groundwater near the No. 1 mill was initiated in June of 2007 through installation/operation of a new recovery well (RW-1) located between the No. 1 mill and the Red Clay Creek. Over the 1 year period from June 2007 to June 2008, the recovery well has removed an estimated average of 1.3 pounds of zinc per day from the groundwater. This equates to 475 pounds of zinc being removed in 1 year.
- Portions of the No. 1 mill were recently demolished as part of a Removal Consent Order between NVF and the U.S. EPA. Demolition was necessary in order to allow for the safe removal of remaining liquids from process vats and to allow for the removal of contaminated soils beneath the building. These actions will further reduce the loading of zinc to the groundwater and the Red Clay near the No. 1 mill.
- NVF completed a detailed hydrogeologic investigation of the Yorklyn facility (Environmental Alliance, 2007). That investigation resulted in the discovery of another major area of zinc contamination on the property. The new area is located between the Main Paper Mill and the Red Clay Creek, just northwest of the ‘cross stream’. In response to this finding, NVF has proposed to install a groundwater recovery trench parallel to the Red Clay to intercept the contaminated groundwater plume before the plume discharges to the creek (Environmental Alliance, 2008). Preliminary calculations suggest that between 30 to 40 pounds of zinc per day may be recovered from the trench. As was the case for the No. 1 mill, a major source of the groundwater contamination in the newly discovered area is believed to have been leaks in the subsurface zinc recycle pipeline. The old piping has been replaced to prevent additional loading to the groundwater. At the time of this writing, DNREC is still reviewing the details of the groundwater recovery trench design.

As will be shown in a later chapter, the sum total of actions taken at the NVF Yorklyn facility since the original TMDL was adopted in 1999 has been lower concentrations of zinc in the Red Clay Creek. The implementation of additional actions such as installation and operation of the recovery trench and further cleanup in the vicinity of the old No. 1 mill is expected to result in further reductions in zinc concentrations and loadings. In short, development and implementation of a meaningful and aggressive Pollution Control Strategy, leveraged through settlement negotiations, is paying off and is expected to continue to pay off.

The Department is moving forward with this amended TMDL based upon the progress described above, coupled with our belief that the ‘dynamic TMDL’ is sufficiently protective. As for all TMDLs, the EPA has the ultimate authority to approve or disapprove this particular TMDL. The next section describes how the remainder of this document is organized.

1.3 Report Organization

Following the background information provided in this chapter, Chapter 2 discusses the environmental setting of the Red Clay Creek and its surrounding watershed for those who are unfamiliar with the area. Chapter 3 then identifies and discusses the applicable water quality standards that are applied to the amended TMDL. Chapter 4 follows with an update on the concentrations and mass loadings of zinc currently in the Red Clay Creek. Chapter 5 then derives the amended zinc TMDL for the Red Clay Creek based upon the lognormal probability approach. Chapter 6 identifies the next steps in the TMDL process and Chapter 7 provides a listing of references used to support the TMDL. Appendices present raw and processed data tables and selected calculations.

2. 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 (see Figure 1). 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 16,300 cubic feet per second (cfs) in 2003 to an instantaneous minimum of 2.9 cfs in 1966, with a long term (1943 to 2007) median of 44 cfs, (USGS, 2008).

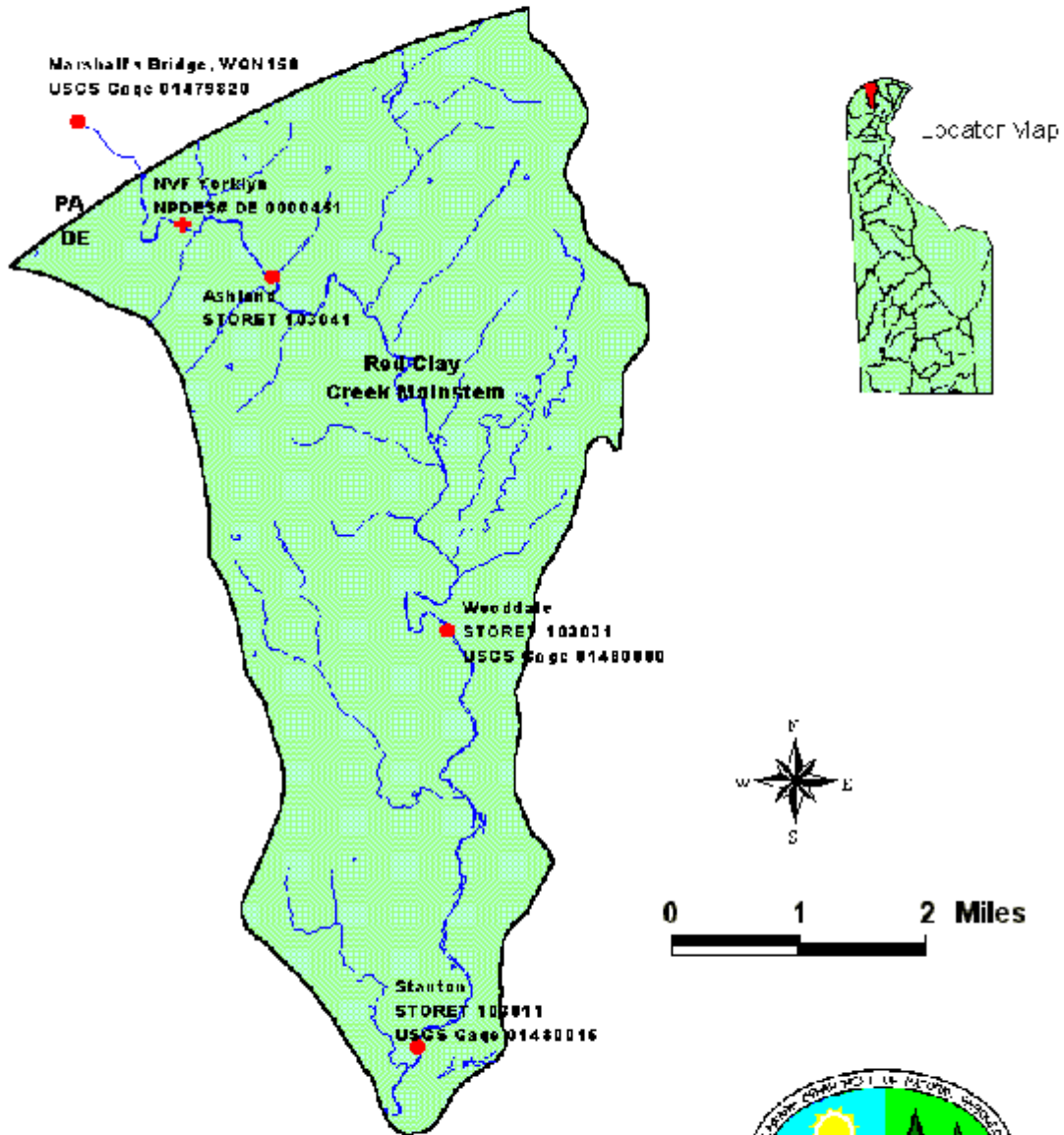
Land use/land cover in the Delaware portion of the Red Clay watershed is a mix of forest, large residential estates, agriculture, and scattered subdivisions north of the fall line. Much of this area is considered to be highly scenic and relatively undisturbed. Below the fall line, land use is primarily 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 (or attempting to remain in operation) is the National Vulcanized Fiber (NVF) facility in Yorklyn, Delaware. The facility, located along the banks of the Red Clay Creek, began operating in the early 1900s. The facility 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. No other NPDES discharges in Delaware are believed to contribute significant quantities of zinc to the Red Clay Creek.

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



The information in this map is subject to change or modification at any time. Use of the information by others is at their own risk and DNR/DEO is not responsible for any errors or omissions or for any consequences arising from the use of the information. The information is provided for general information only and does not constitute a professional representation.



3. Applicable Water Quality Standards

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. Water quality standards also contain policies and procedures that specify how the criteria are to be applied and under what conditions. An example of this is the specification of critical low flows, which are used in conjunction with other factors to develop water quality-based discharge limits for permitted discharges.

The State of Delaware Surface Water Quality Standards (As Amended, July 11, 2004) list 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; cold water fish (put-and-take), ERES for Burrough's Run (DNREC, 2004). The water quality criteria intended to protect aquatic life from adverse effects of zinc exposure are as follows:

$$\text{Freshwater Acute Criterion (ug/L)} = 0.978 * \text{EXP}^{(0.8473[\ln(\text{hardness})] + 0.884)}$$

$$\text{Freshwater Chronic Criterion (ug/L)} = 0.986 * \text{EXP}^{(0.8473[\ln(\text{hardness})] + 0.884)}$$

In both equations, EXP stands for 'e', which equals 2.71828, the base of the natural logarithm. Hardness is expressed in units of milligrams per liter (mg/L) as calcium carbonate, and the concentration of zinc calculated from the equations is expressed in units of micrograms per liter (ug/L) of dissolved zinc. The above criteria differ from those used as the basis of the 1999 Red Clay Creek zinc TMDL in that the 1999 TMDL was based on criteria expressed on a total zinc basis. The Department revised its criteria to be based on the dissolved form of the metal to better reflect the relationship between chemical bioavailability and toxicity and to be consistent with national guidance (EPA, 1993). The fact that the criteria has changed provides further justification to revise the existing TMDL.

The above criteria are based on "national" criteria developed by the EPA, (EPA, 1996). A somewhat unusual feature of the zinc criteria is that the acute criterion is more stringent than the chronic criteria for any particular hardness. Zinc is the only metal for which this is the case. This anomaly aside, the 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 decrease functional surface area for oxygen transfer and oxygen diffusion capacity.

The acute criterion listed above 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 not to be exceeded more than once in any three year period (DNREC, 2004). The averaging period defines the allowable duration of exposure and the 3 year return period defines the allowable frequency of exceedance. The concentration calculated using the criteria equation defines the allowable magnitude. Therefore, the zinc criteria being used for this amended TMDL have 3 'dimensions': a magnitude; duration; and frequency. This comports with modern water quality criteria.

As noted above, the criteria equations are a function of hardness. Substituting a range of hardness values into the equations, it is easy to verify that both the acute and chronic criteria increase as a function of water hardness. For example, at a hardness of 100 mg/L, the acute and chronic criteria are both approximately 100 ug/L of dissolved zinc. At a hardness of 200 mg/L, both criteria increase to roughly 200 ug/L. So, waters with greater hardness can have higher concentrations of zinc without adverse effects. 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."

Because the above criteria are expressed as a function of hardness, and because hardness varies over space and time for any particular waterbody, the question naturally arises as to what hardness value should be used to calculate the applicable zinc criteria. There are different approaches and thoughts on how best to handle this. Delaware's standards are sufficiently flexible to accommodate the different possibilities. Section 4.6.3.3.1.1 of Delaware's standards state that, "appropriate...hardness values...shall be determined on a case-by-case basis by the Department." (DNREC, 2004). The approach used in this TMDL is to use the measured hardness observed on the same day that zinc data were collected from the Red Clay. Therefore, if 50 separate zinc measurements are available for a particular location from the stream, and each of those measurements corresponds to a different day, then there will be 50 separate hardness values, each corresponding to the day that a paired zinc measurement was taken. This allows for a sample-by-sample assessment of the effect of hardness on the computed criteria and the associated criteria exceedance. This approach is consistent with the principles of dynamic modeling used in the amended TMDL and avoids over- or underestimation of criteria that can occur when a single value such as an average, median, or minimum is applied across all samples.

As noted earlier, water quality standards also specify critical low flows to use in conjunction with water quality criteria. Section 7 of Delaware's Surface Water Quality Standards addresses critical flows. Section 7.2 specifies that chronic aquatic life criteria only apply at flows greater than the 7Q10 low flow and that acute aquatic life criteria only apply at flows greater than the 1Q10 low flow. Section 7.3 goes on to state that:

- 7.3 These critical flows shall also be used as design flows for developing water quality-based discharge limitations for the referenced group of parameters. The Department shall consider scientifically reasonable requests for seasonally adjusted flows or the use of dynamic modeling techniques for this purpose on a case-by-case basis.

The above provision specifies that the 7Q10 and 1Q10 flows are the default flows for applying the chronic and acute aquatic life criteria, respectively, but that the Department will consider scientifically reasonable requests to use other flows or dynamic modeling on a case-by-case basis for developing water quality-based effluent limitations, and by extension, TMDLs. The Department has concluded that NVF has made a scientifically reasonable request to use dynamic modeling to revise the zinc TMDL for the Red Clay Creek. The details of the dynamic modeling approach will be addressed in chapter 5 of this document. For now, however, it is stated simply that the dynamic modeling approach considers the flows that co-occur with the concentration data. As such, dynamic modeling does not rely on a single design flow such as a 7Q10 or 1Q10. Rather, the approach considers numerous flows, thereby reflecting the ‘dynamic’ range of this variable in the waterbody. This should become more clear in chapter 5.

Another point to be made in this section is that the water quality criteria necessary to protect aquatic life from the toxic effects 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.

In summary, the controlling water quality criterion for this TMDL is the acute aquatic life criterion.

4. Zinc Concentrations and Mass Loadings

4.1 Readily Available and Existing Data

Table 1 lists the stations for which zinc data are routinely collected along the mainstem of the Red Clay. These stations are also shown on Figure 1. The NVF Company collects samples at 2 stations on a weekly frequency, while DNREC collects data from 3 stations on a monthly to bimonthly frequency. PADEP collects data from the Marshall's Bridge station on a bimonthly frequency.

Table 1. Routine Water Quality Monitoring Stations in the Red Clay Creek

Sampling Location	Station ID	River Miles Above (-) or Below (+) NVF Yorklyn	Data Collected By:
Marshalls Bridge, PA	WQN 150	-2.3	PADEP
Stateline	NA	-1.5	NVF
Ashland, DE	103041	+1.7	DNREC
Wooddale, DE	103031	+9.0	DNREC, NVF
Stanton, DE	103011	+13.1	DNREC

In addition to water quality monitoring, USGS flow gages are located at Marshalls Bridge (01479820), Wooddale (01480000), and Stanton (01480015), thereby allowing mass loading calculations to be performed.

Although there are over 3 decades of zinc data available for the Red Clay, this chapter focuses on the more recent data collected over the approximate 5 year period beginning January 2003 and ending April 2008. These data, which appear in Appendix 1 of this document, are most relevant to the amended zinc TMDL. When appropriate, the more recent data are contrasted against the older data to provide longer term perspective and to make other important points regarding the data. In addition to the measured data, this chapter also presents predicted zinc concentrations and mass loads directly downstream of the NVF Yorklyn plant. Predicted (modeled) values are presented for this location rather than measured values since poor access limits direct measurements below the plant. Further, since the NVF plant remains the single most important source of zinc to the Red Clay Creek, it is important to characterize zinc concentrations directly below this source.

4.2 Current Zinc Concentrations in Red Clay Creek

The figures shown below reflect the merged data from PADEP, DNREC, and NVF, thereby providing the most complete characterization available. Due to their close proximity, results for the Marshall's Bridge station and the Stateline station were combined and identified simply as the 'Stateline'. The figures below show the concentrations of total and dissolved zinc measured or otherwise predicted at the Stateline, Yorklyn (directly below NVF), Ashland, Wooddale, and Stanton. The ordering of the figures progresses from upstream to downstream.

Fig 2. Zinc Concentration Red Clay Creek Stateline

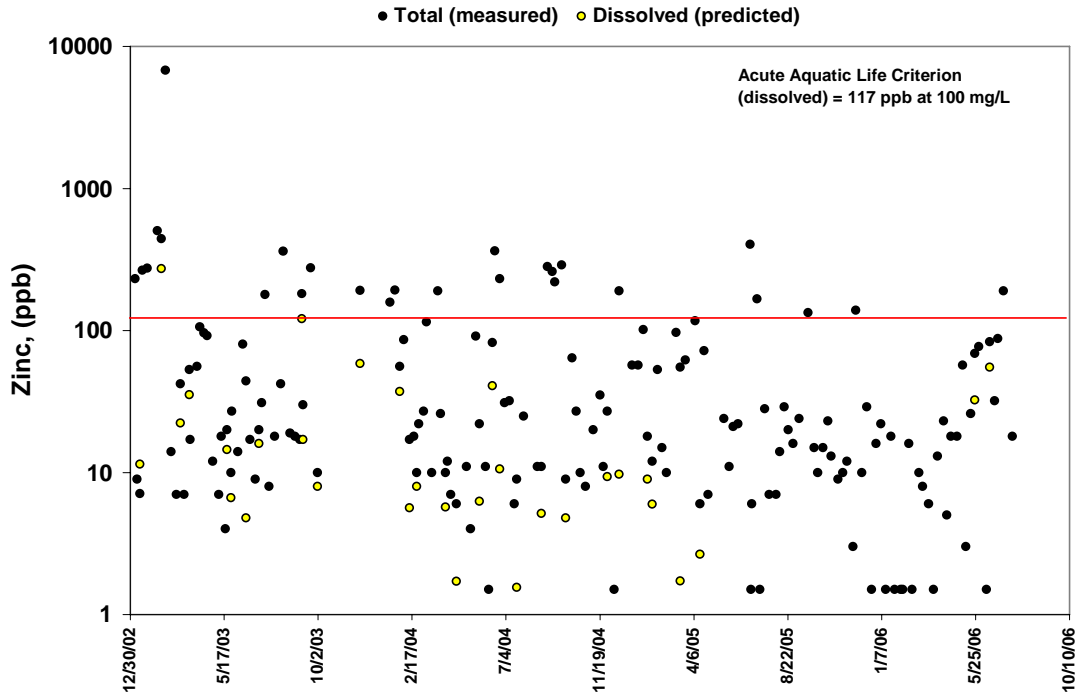


Fig 3. Zinc Concentration Red Clay Creek Yorklyn

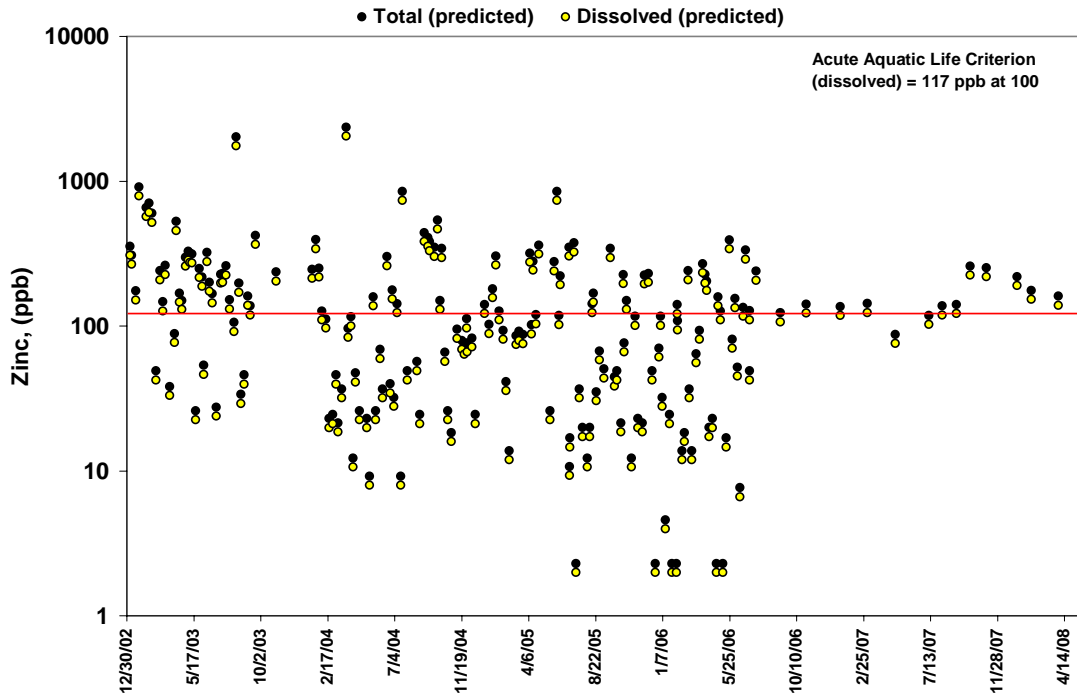


Fig. 4. Zinc Concentration Red Clay Creek Ashland

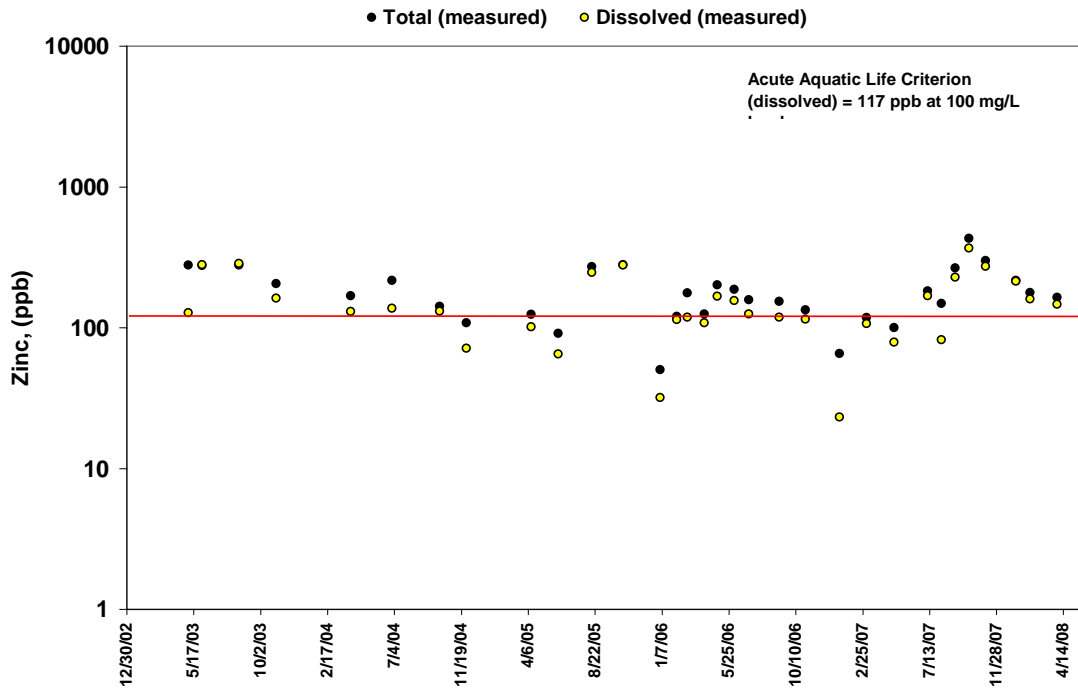


Fig. 5. Zinc Concentration Red Clay Creek Wooddale

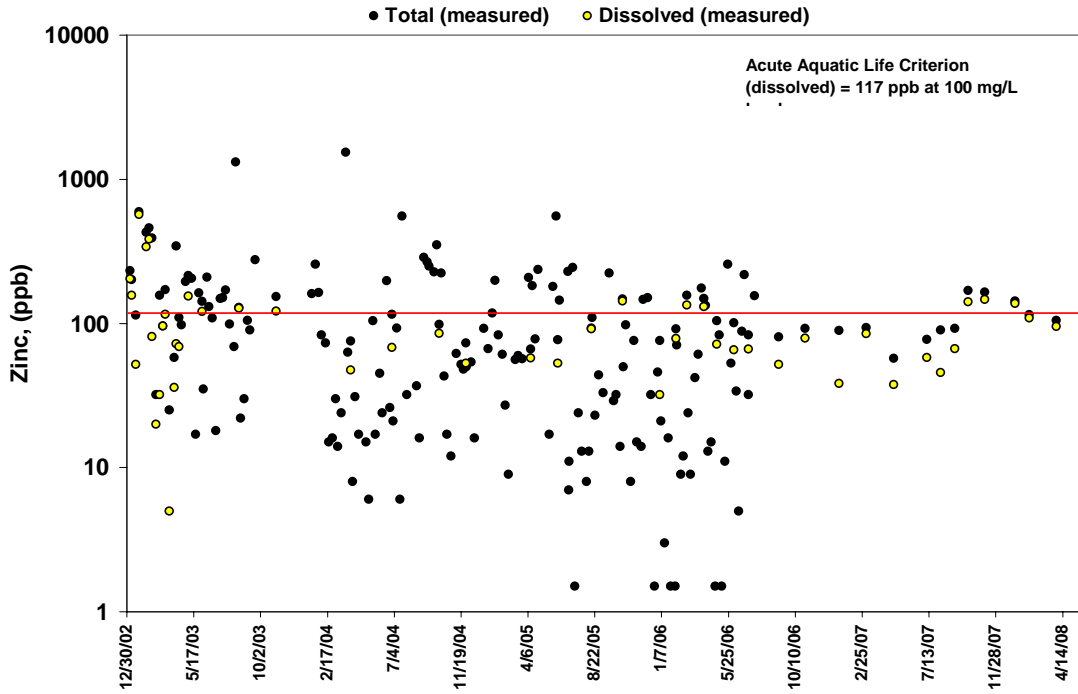
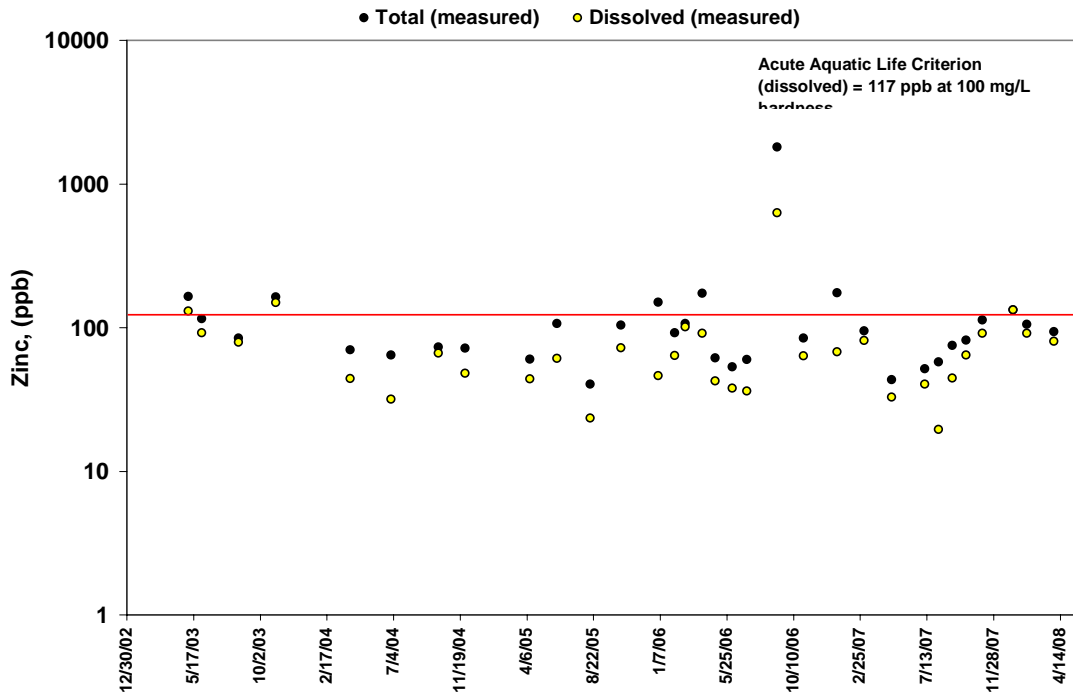


Fig. 6. Zinc Concentration Red Clay Creek Stanton



Note that the above figures all display the acute aquatic life criterion for zinc expressed on a dissolved basis and calculated at a hardness of 100 mg/L. The resulting criterion value, 117 parts per billion (ppb) or ug/L, is shown for illustrative purposes only. Results above the criterion line are not necessarily exceedances and results below the criterion line are not necessarily in compliance since the actual hardness on the day of a particular sample can be higher than or lower than 100 mg/L, which in turn alters the calculated value of the criterion. This issue will be resolved in section 4.3 when we introduce the concept of a ‘Toxicity Unit’. First, however, a brief description is offered on how zinc concentrations were predicted at Yorklyn and how dissolved concentrations were estimated in cases where only total zinc data were available.

As noted previously, zinc concentrations at Yorklyn (as shown in Fig. 3) were not measured but rather were predicted. The concentration of total zinc was predicted at Yorklyn by assuming that the mass load of zinc at Yorklyn equals the mass load of zinc at Wooddale. Since mass load is the product of concentration and flow, we start with the following relationship:

$$C_{\text{Yorklyn}} \times Q_{\text{Yorklyn}} = C_{\text{Wooddale}} \times Q_{\text{Wooddale}}, \text{ where:}$$

- C_{Yorklyn} = Concentration of total zinc at Yorklyn, (ppb or ug/L)
- Q_{Yorklyn} = Flow at Yorklyn, (cfs)
- C_{Wooddale} = Concentration of total zinc at Wooddale, (ppb or ug/L)
- Q_{Wooddale} = Flow at Wooddale, (cfs)

The above equation can be solved for C_{Yorklyn} to yield:

$$C_{\text{Yorklyn}} = C_{\text{Wooddale}} \times Q_{\text{Wooddale}}/Q_{\text{Yorklyn}}$$

C_{Wooddale} and Q_{Wooddale} are both measured values and so can be substituted directly into the above equation. Q_{Yorklyn} , on the other hand is not measured but can be estimated by assuming that the flow at Wooddale, normalized to the drainage area upstream of Wooddale (47 mi²) is equal to the flow at Yorklyn, normalized to the drainage area upstream of Yorklyn (30.7 mi²). Therefore:

$$Q_{\text{Wooddale}}/47 = Q_{\text{Yorklyn}}/30.7$$

Solving this equation for Q_{Yorklyn} , we obtain:

$$Q_{\text{Yorklyn}} = Q_{\text{Wooddale}} \times (30.7/47)$$

Substituting this equation into the equation for C_{Yorklyn} , the following simple equation results that allows us to predict C_{Yorklyn} from the measured concentration of total zinc at Wooddale and the ratio of drainage areas for the 2 locations:

$$C_{\text{Yorklyn}} = C_{\text{Wooddale}} \times (47/30.7)$$

The above equation basically says that the concentration of zinc at Yorklyn is 1.5 times greater than the concentration at Wooddale (i.e., $47/30.7 = 1.53$). The approach described above assumes that total zinc is ‘conserved’ between the Yorklyn and Wooddale stations. This is a reasonable assumption considering that: 1) Zinc does not decay; 2) Most of the zinc at these 2 stations is in the dissolved form, (as will be shown momentarily). As such, the majority of the zinc is transported along with the water, with little opportunity for particulate zinc to settle out; 3) Regression between total zinc load at Ashland and total zinc load at Wooddale reveals a slope which is not statistically different than 1. This strongly suggests that zinc is conserved between Ashland and Wooddale and by extension, between Yorklyn and Wooddale; and 4) No other major source(s) of zinc exist between Yorklyn and Wooddale that would significantly alter the amount of zinc transported between these 2 stations.

When dissolved and total zinc measurements were both available for a particular station and day, then the fraction of zinc in the dissolved form was calculated as the dissolved concentration divided by the total concentration. In situations where only total zinc measurements were available, an estimate of the associated dissolved zinc concentration was calculated using an equilibrium partition coefficient and the suspended solids concentration. The equation which describes the relationship between total and dissolved metal concentrations, the partition coefficient, and suspended solids is (Chapra, 1997):

$$C_d = C_t/(1 + K_d\text{TSS}), \text{ where:}$$

C_d = dissolved zinc concentration, (mg/L)

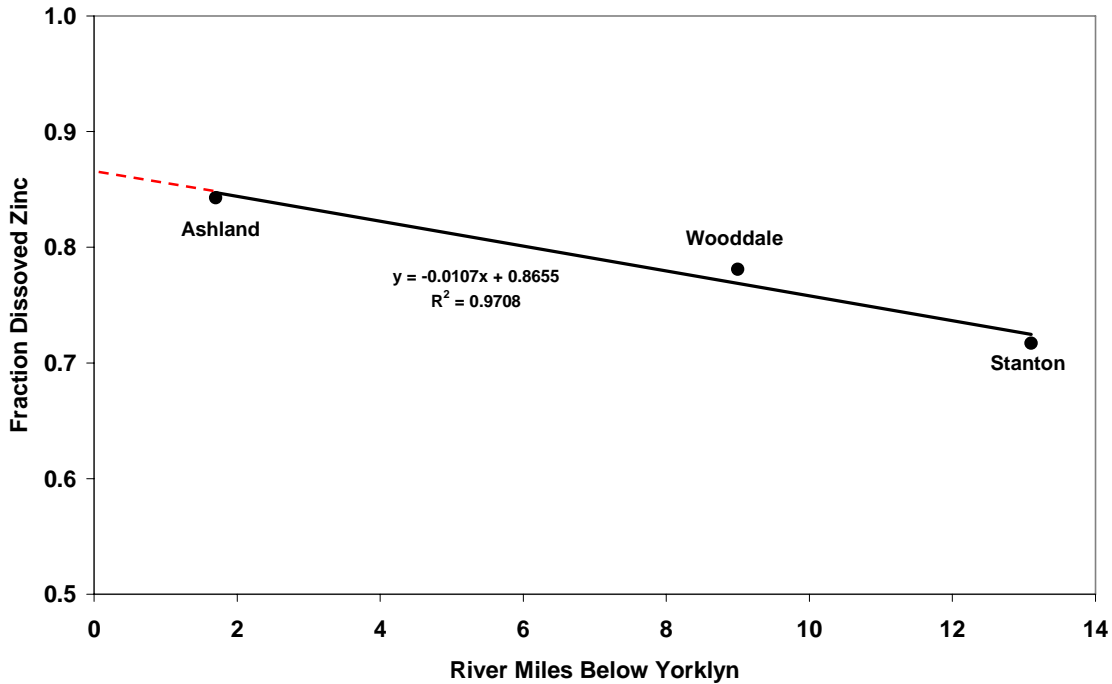
C_t = total zinc concentration, (mg/L)

K_d = partition coefficient for zinc, (L/kg)

TSS = suspended solids concentration, (mg/L)

For purposes of the present analysis, a median log K_d of 5.1 was used (EPA, 2005). A log K_d of 5.1 equates to a K_d of $10^{5.1}$ or 125,893 L/kg. For the Stateline samples, the fraction of zinc predicted to be in the dissolved form ranged from a minimum of 3.1% to a maximum of 100% with an average of 47.2% and a median of 49.8%. For the Ashland, Wooddale, and Stanton stations where paired measurements of total and dissolved zinc are available, median dissolved fractions were calculated as 84.3%, 78.1%, and 71.7%, respectively. These percentages are much higher than the Stateline estimates, presumably due to the high proportion of dissolved zinc which enters the Red Clay Creek via groundwater discharge at the NVF Yorklyn plant. Regressing the median dissolved fractions at Ashland, Wooddale, and Stanton against river miles below Yorklyn, and then extrapolating the resulting relationship upstream to Yorklyn, the median percentage of zinc in the dissolved form at Yorklyn is estimated to be 86.6% (see Fig. 7 below). Note that this is an estimated median and so some values will be higher, even approaching 100%.

Fig. 7. Median Fraction Dissolved Zinc Below Yorklyn



4.3 Zinc Toxicity Units

A toxicity unit (T.U.) is the ratio of the measured (or predicted) zinc concentration on a particular day to the criterion calculated using the hardness concentration measured on that same day. A toxicity unit greater than 1 indicates that the measured (or predicted) concentration exceeds the criterion for the particular sample, while a toxicity unit less than 1 means the measured (or predicted) concentration is less than the criterion for the sample. Expressing results in terms of toxicity units is not only preferable from a toxicological standpoint; it's actually integral to the lognormal probability approach, as will become clear in Chapter 5.

Figures 8 through 12 below show the acute toxicity units for total and dissolved zinc at the Stateline, Yorklyn, Ashland, Wooddale, and Stanton stations.

Fig. 8. Toxic Units Red Clay Creek Stateline

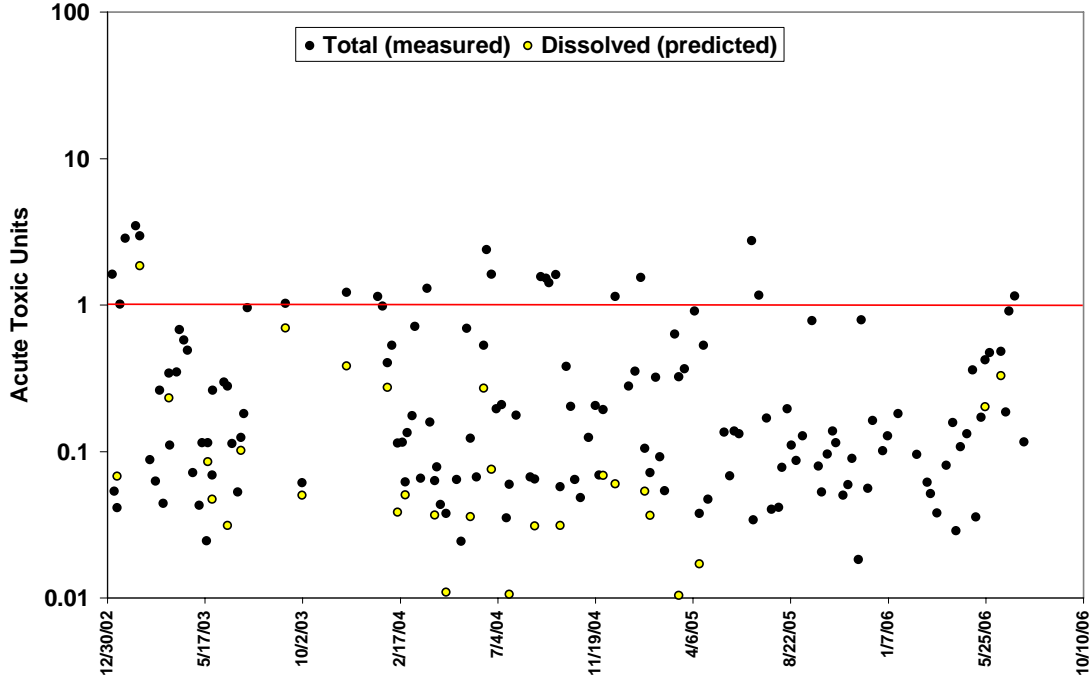


Fig. 9. Predicted Toxic Units Red Clay Creek Yorklyn

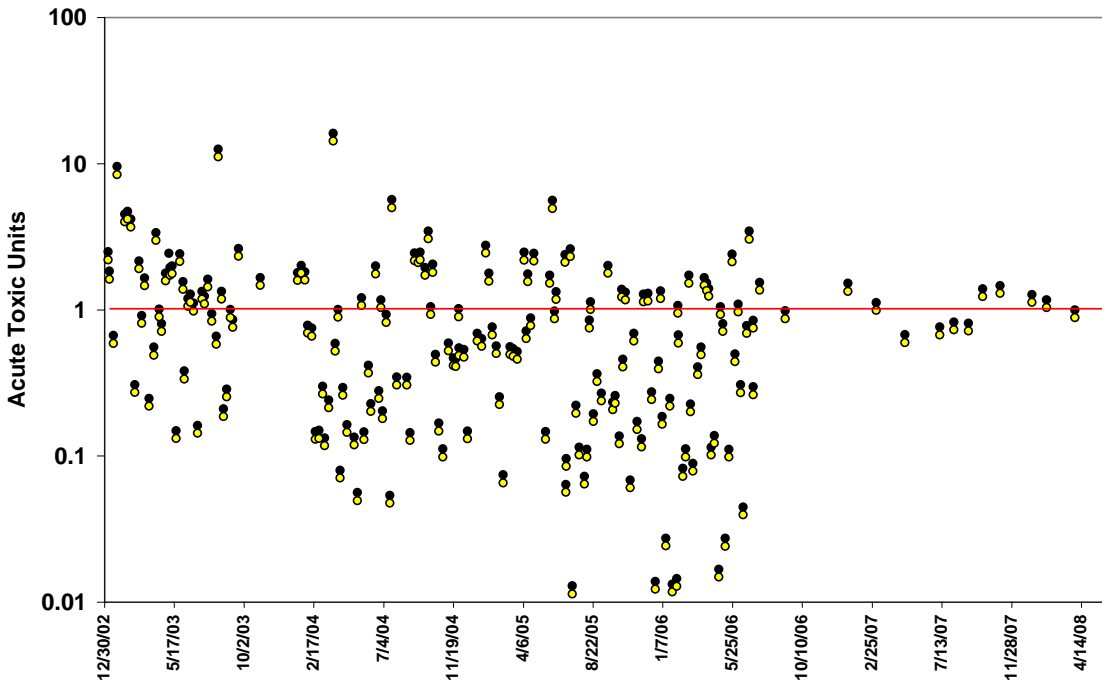


Fig. 10. Measured Toxic Units Red Clay Creek Ashland

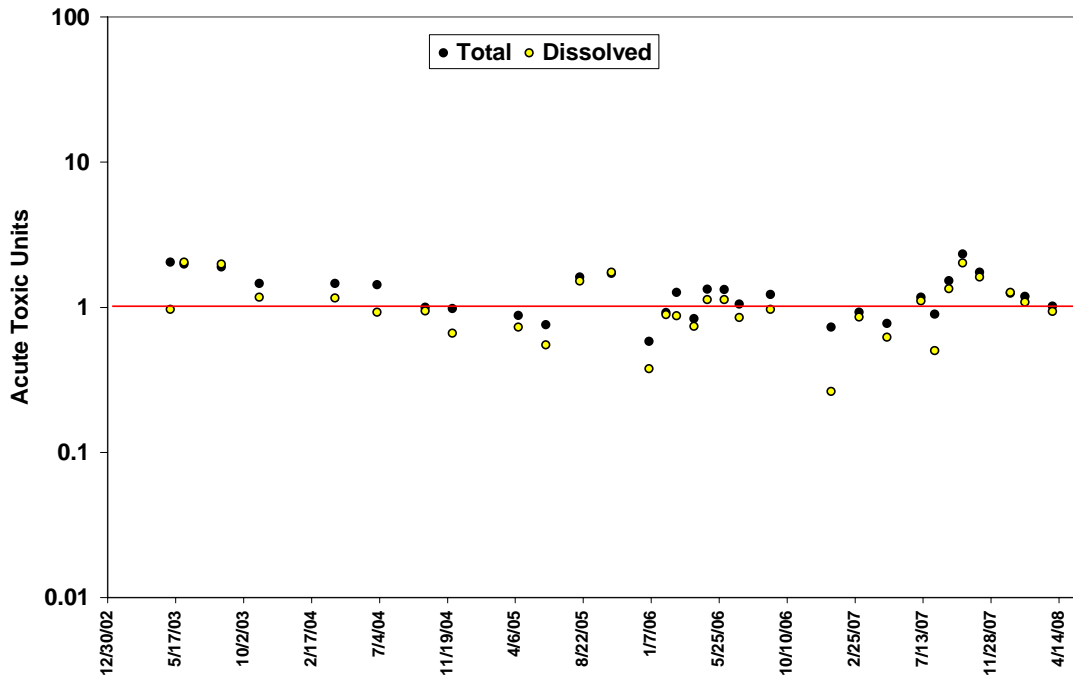


Fig. 11. Measured Toxic Units Red Clay Wooddale

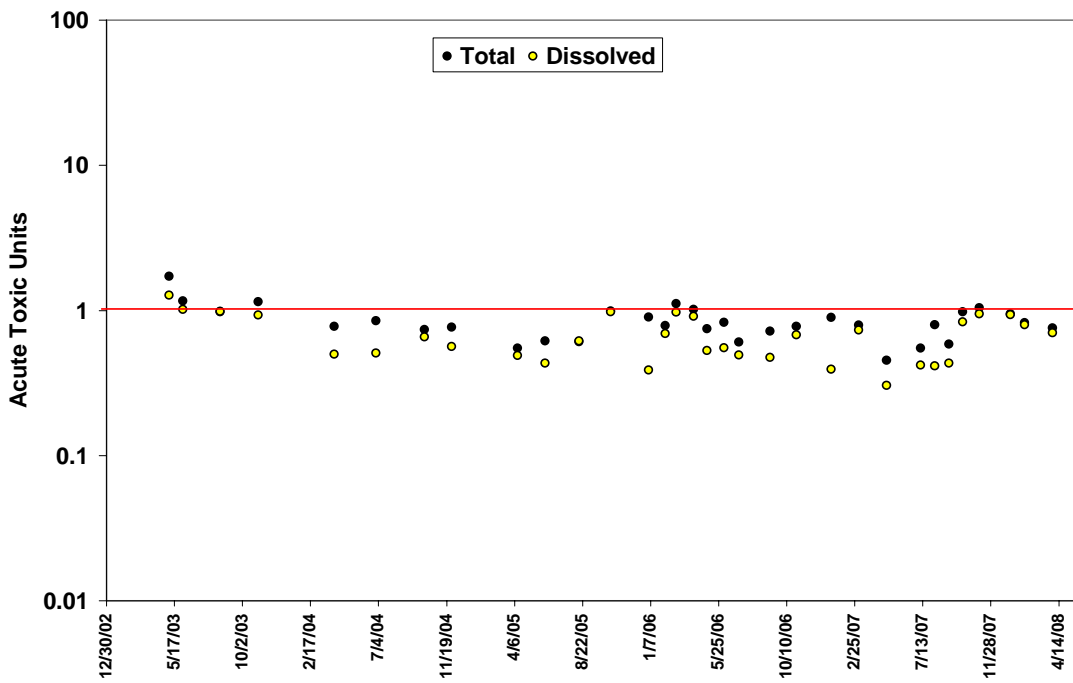
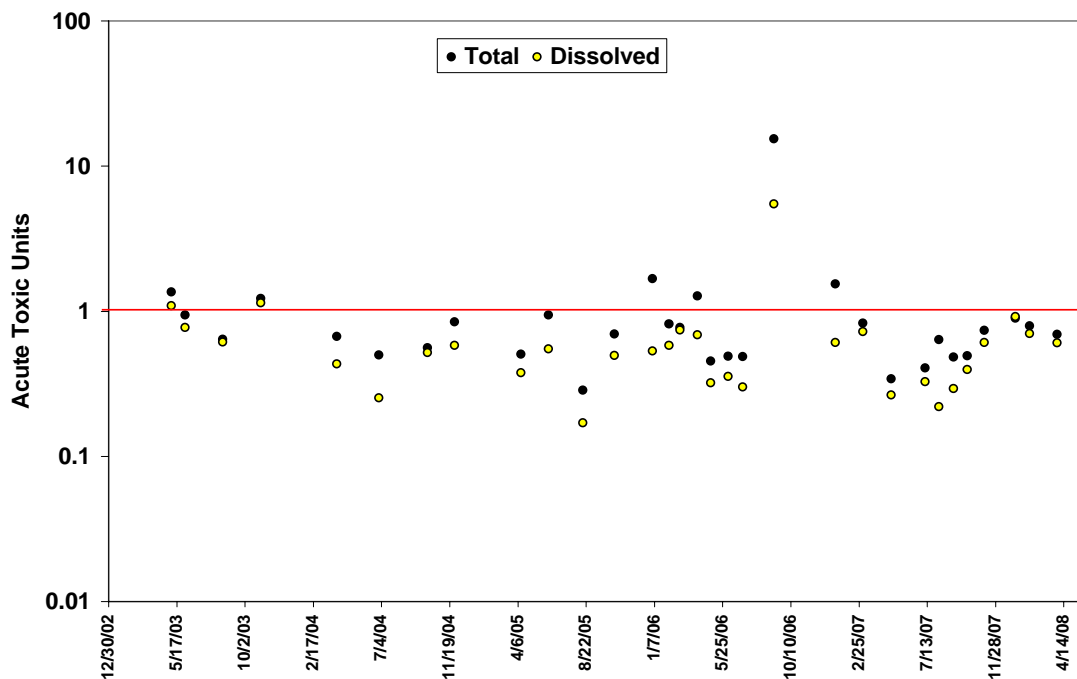


Fig. 12. Measured Toxic Units Red Clay Creek Stanton



In Fig. 9 above, note that the hardness at Yorklyn was assumed to be equal to the hardness measured at the PA/DE stateline by NVF and at Marshalls Bridge by PADEP. The assumption inherent in this extrapolation is that hardness behaves conservatively between Marshalls Bridge, the stateline, and Yorklyn. The distance between these 3 locations is quite short (~2 mi.) and there is little to no change in land use until one actually reaches Yorklyn. There were several days were NVF reported the concentration of total zinc at the stateline but did not report a corresponding hardness value. Hardness on those days was estimated as the average of the otherwise measured values at the stateline and Marshalls Bridge. An alternative approach of estimating hardness at the stateline based upon flow at Marshalls Bridge was not used due to low correlation between flow and hardness at the station.

From the above figures, we see that there was only a single exceedance of the dissolved acute criterion at the Stateline station. That exceedance occurred in early 2003. In contrast, there were numerous exceedances of the dissolved acute criterion at Yorklyn and Ashland over the period considered. Exceedance frequencies at those 2 stations were on the order of 40%. At Wooddale and Stanton, the 2 stations further down in the watershed, there were only 2 and 3 exceedances, respectively.

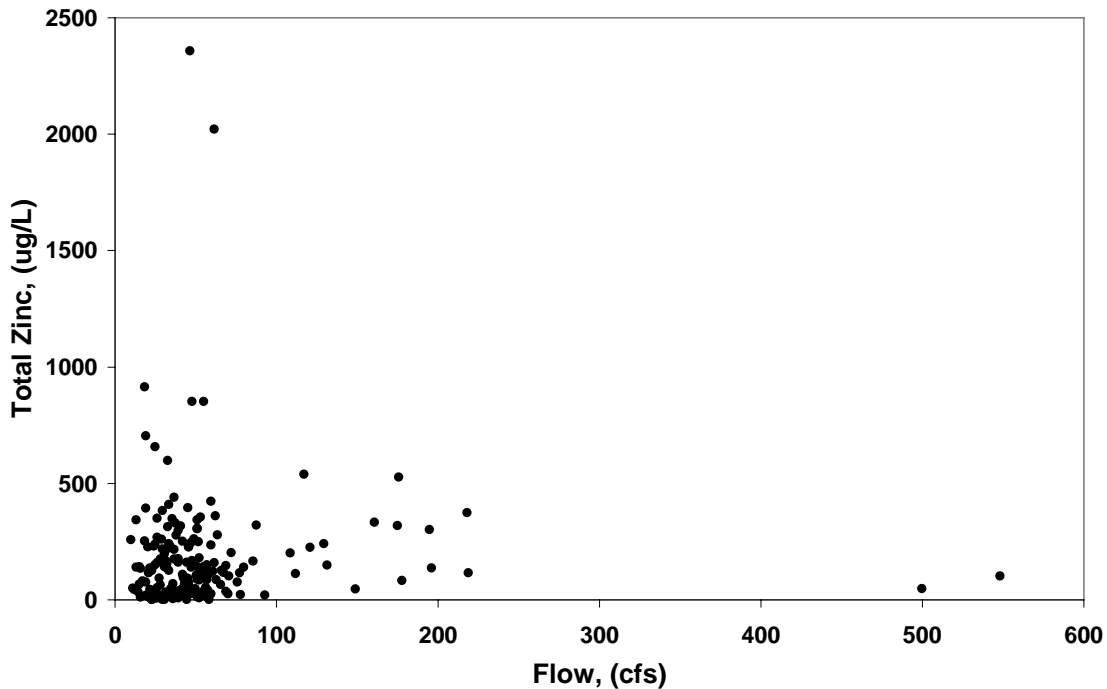
Although the zinc criterion is still being regularly exceeded at the Yorklyn and Ashland stations, the frequency and magnitude of exceedances have dropped significantly in comparison to data collected in the 1990s and earlier. For instance, the dissolved acute criterion was exceeded nearly 96% of the time at the Ashland station during the 1990s (DNREC, 1999b). At the Wooddale station during this same time period, the dissolved acute criterion was exceeded 89% of the time (DNREC, 1999b). The current exceedance

frequency at Wooddale is less than half that in comparison to the previous decade. The overall picture that emerges is that the magnitude, frequency, and spatial extent of exceedance of the zinc criterion have dropped in the current decade in comparison to earlier periods. This is a move in the right direction but there is still more improvement needed based upon on the ongoing exceedances at Yorklyn and Ashland.

4.4 Relationship Between Zinc Concentration and Stream Flow

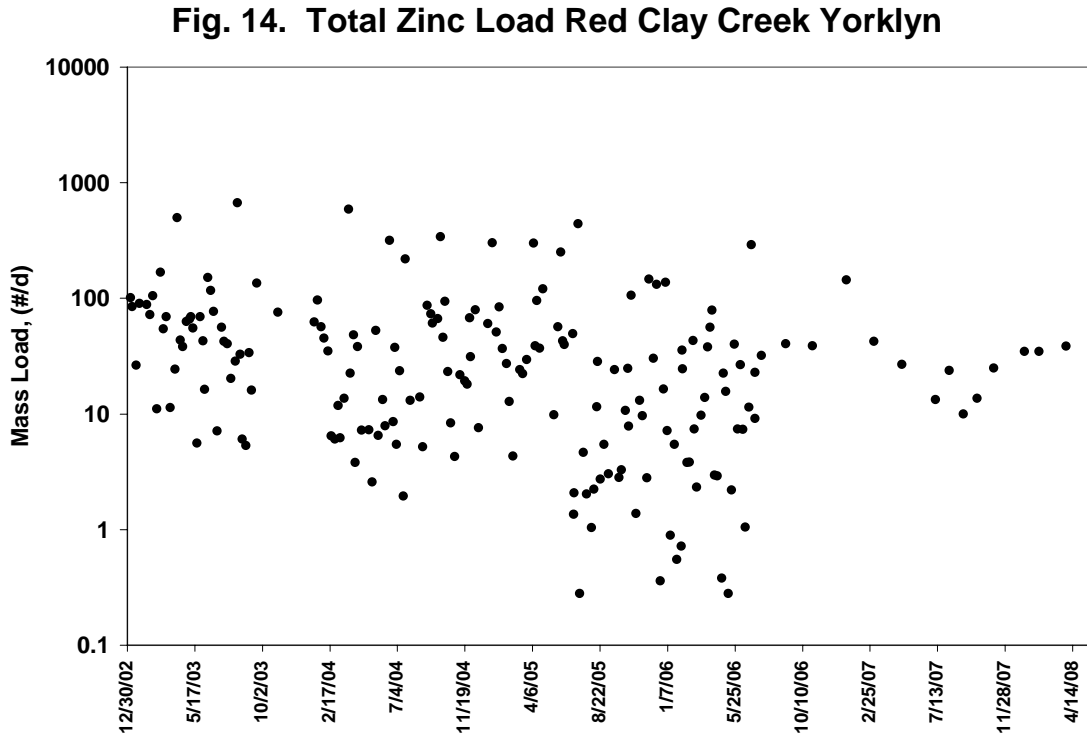
It is important in any water quality assessment, and in particular to TMDLs, to evaluate the relationship, if any, between pollutant concentrations and stream flows. Figure 13 below shows a cross plot of flow versus total zinc at Yorklyn for the period January 2003 through April 2008. The figure reveals no clear relationship between flow and concentration. Notably, the highest concentrations did not occur during the lowest flows. Further, the lowest concentrations did not occur during the highest flows. In fact, some of the lowest concentrations occurred during the lowest flows. This is in sharp contrast to the situation in the 1990s when there was a statistically significant inverse relationship between flow and zinc concentration below Yorklyn (DNREC, 1999b). Such a relationship apparently no longer exists, presumably because pollution controls put into place at the NVF Yorklyn facility in response to the original TMDL as well as in response to the EPA Consent Decree have fundamentally changed the magnitude and timing of zinc loading to the Red Clay from the NVF plant.

Fig. 13. Total Zinc vs Flow at Red Clay Creek Yorklyn



4.5 Zinc Mass Loading

Because TMDLs are typically expressed in terms of mass loading, it is important to characterize existing mass loading in order to be able to determine how far the load must be reduced in order to meet applicable water quality criteria. Figure 14 shows the mass loading of total zinc at Yorklyn for the period January 2003 to April 2008. Figure 15 shows these same loads plotted against flow.



The above plot shows that total zinc mass loads have varied widely from approximately 1 pound per day up to nearly 1000 pounds per day. The figure also reveals a slow but discernable drop in mass loads over time.

Fig. 15. Total Zinc Load vs Flow at Red Clay Yorklyn

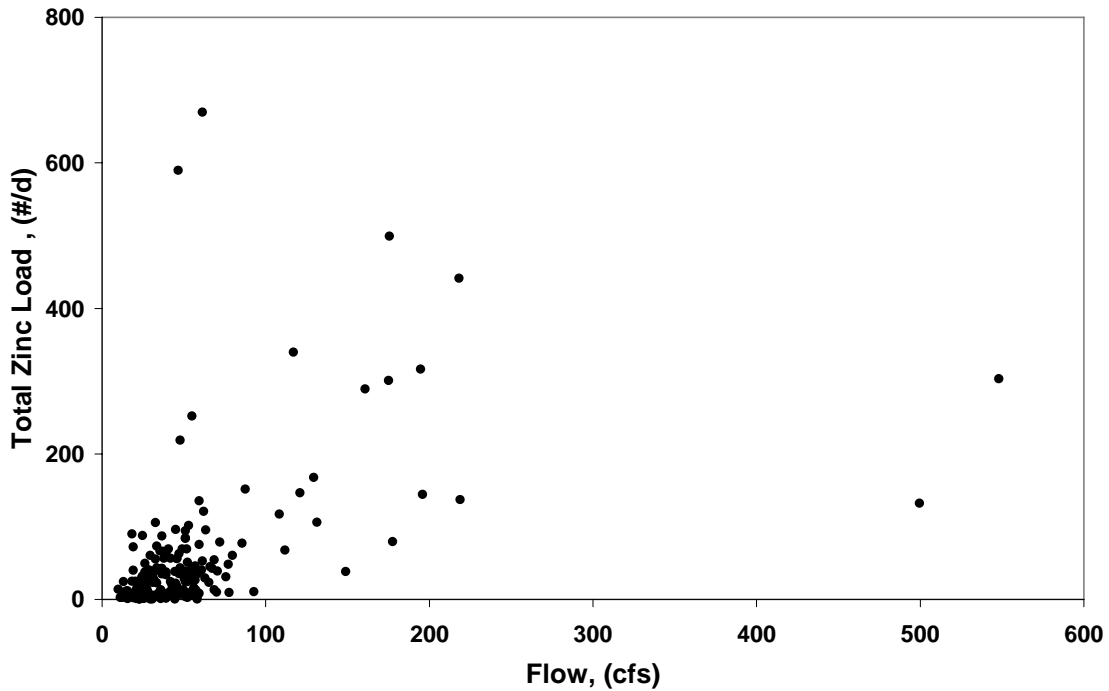


Figure 15 shows that the lowest mass loads appear to occur during the lowest flows and higher loads tend to occur during higher flows. The relationship between load and flow, however, is less than clear. One thing is clear: If the load from the NVF facility was constant or nearly so as presumed in a steady-state low flow TMDL, then the in stream mass load at Yorklyn would show far less variability with flow than is indicated in Figure 15, assuming of course that the load upstream of Yorklyn is less important than the load from NVF. As it turns out, the lognormal probability approach described in the next chapter accounts explicitly and simultaneously for the role of flow, hardness, and zinc concentrations in establishing a TMDL.

5. Total Maximum Daily Load Methods and Results

5.1 General Principles

A TMDL specifies the maximum allowable mass loading of a pollutant (e.g., pounds per day) that can be delivered to a waterbody while still assuring that applicable water quality criteria are met and associated water uses are protected. A TMDL is composed of three parts: 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. Therefore, a TMDL can be expressed mathematically as:

$$\text{TMDL} = \text{WLA} + \text{LA} + \text{MOS}$$

This chapter describes how the amended zinc TMDL for the Red Clay Creek was determined and how the individual parts (WLA, LA, and MOS) were allocated. As noted earlier, this amended TMDL is based on a lognormal probability analysis, which is a type of dynamic modeling technique that can be used, provided certain conditions are met (DiToro, 1984; EPA, 1991; EPA, 1993; EPA, 1996). Before describing the lognormal probability approach and underlying assumptions, it is first useful to briefly review steady-state, low flow TMDL modeling since it provides a point of departure for the more complex lognormal probability approach.

Steady-state, low flow TMDLs assume that the highest concentrations in a stream occur during low flow conditions and that all factors affecting the concentration in the water (e.g., upstream loading, point source loading, and stream flow) are constant or relatively constant for periods relevant to the applicable criteria. Since low flows are statistically defined, relatively uncommon events, the presumption is that TMDLs based on low flows will ensure that water quality criteria will be met (and uses protected) at all flows greater than the low flow. For example, if a TMDL is based on a 7Q10 design flow, which only occurs about 1% of the time, then water quality criteria should be met approximately 99% of the time. If, however, the assumptions inherent in a steady-state, low flow TMDL don't actually hold, then the resulting TMDL may be far more, or far less, stringent than necessary to ensure protection of water quality. Neither case is desirable from an overall societal perspective.

Although the assumptions inherent in a steady-state, low flow TMDL were valid at the time the original zinc TMDL was developed, it is clear that conditions have since changed. It was shown in the previous chapter that peak zinc concentrations at Yorklyn no longer occur during lowest stream flows. Since peak concentrations no longer occur at lowest stream flows, there is less justification for and need to retain a steady-state, low flow TMDL. Further, as discussed in Chapter 3 of this document, Delaware Surface Water Quality Standards require DNREC to consider scientifically reasonable requests for alternative flows and dynamic modeling when establishing water quality based

control. DNREC has concluded that NVF's request to use dynamic modeling as the basis of an amended TMDL is scientifically reasonable.

5.2 Methods: Lognormal Probability Approach

The basic idea of the lognormal probability approach is to first describe the distribution of toxicity units as a lognormal distribution. Since some or all of the data points in the distribution exceed the applicable water quality criterion, this distribution is referred to as the noncompliant distribution. The noncompliant distribution is then shifted downward until the uppermost quantile of the distribution intersects the allowable criterion exceedance frequency (e.g., 1 day in 3 yrs). The resulting distribution of T.U. values becomes the desired compliant distribution. The individual T.U.s in the compliant distribution are then multiplied by the corresponding hardness dependent criterion and flow for the associated days to produce a series of compliant mass loads. Those loads are fit to a lognormal distribution and the upper quantile is calculated, which equates to the TMDL. The specific steps in the approach are detailed below.

Step 1. Merge the NVF, PADEP, DNREC, and USGS data into a single table sorted by sample date and partitioned based upon sampling station. That table appears in Appendix 1 of this document.

Step 2. Calculate the zinc water quality criteria as a function of hardness. This was done for each sample date and for each sampling station.

Step 3. Calculate the concentration of zinc at Yorklyn by multiplying the concentration of zinc at Wooddale by the ratio of the drainage area at Wooddale (47 mi²) to that at Yorklyn (30.7 mi²). Similarly, use the DNREC data collected at Ashland to estimate additional zinc values at Yorklyn by multiplying the concentration at Ashland by the ratio of the drainage area at Ashland (33.1 mi²) to that at Yorklyn.

Step 4. Calculate the acute and chronic toxicity units at Yorklyn by dividing the concentration of zinc at Yorklyn (from step 3) by the water quality criteria (from step 2).

Step 5. Estimate the fraction of zinc at each station that is in the dissolved vs. sorbed form. For stations with both total and dissolved zinc measurements from the same sample, calculate the fraction dissolved as the ratio of the dissolved result to the total result. For samples without dissolved and total zinc measurements but otherwise having total zinc and TSS results for the same sample, estimate the fraction dissolved using equilibrium partitioning theory.

Step 6. For the Yorklyn station, calculate the base 10 logarithm of the toxic unit values from step 4. Test whether the logarithm of the toxic unit values follows a normal distribution. Calculate the average and standard deviation of the log transformed toxic unit values. The average and standard deviation of the individual values describe the noncompliant toxic unit distribution at Yorklyn. It is this distribution that we ultimately seek to drive down.

Step 7. Calculate the required water quality criteria compliance frequency associated with 1 allowable exceedance in any 3 year period. Three (3) years is the same as 3×365.25 days/yr = 1095.75 days. The required compliance frequency is therefore calculated as $100*[1 - (1/1095.75)] = 99.9087 \%$.

8. Calculate the 99.908 percentile value of the noncompliant log transformed toxic unit values using the following equation (Berthouex and Brown, 1994):

$$X_{99.908} = \text{antilog}[y_1 + Z_{99.908} * S_1], \text{ where:}$$

y_1 and S_1 are the mean and standard deviation of the noncompliant toxic unit distribution (from step 6).

Z_p = standard normal deviate for the required compliance frequency = 3.108 (from standard statistics text).

Step 9. Determine the magnitude of the shift needed to drive the noncompliant toxic unit distribution into compliance where 1 toxic unit is considered compliant. The required shift is therefore calculated as $X_{99.908}$ (from step 8) minus 1 (which is compliant). Calculate the base 10 logarithm of the shift for the next step.

Step 10. Shift the individual noncompliant toxic unit values downward to produce a distribution of compliant toxic unit values at Yorklyn. This is done using the following equation:

$$\text{Compliant log T.U.} = \text{antilog}[\log \text{ noncompliant T.U.} - \log \text{ of required shift}]$$

Step 11. With the compliant T.U.s at Yorklyn in hand, next calculate the associated compliant zinc loads at Yorklyn by multiplying the compliant T.U.s by the hardness dependent criteria and daily stream flow at Yorklyn. Daily stream flow at Yorklyn was estimated by multiplying the daily flow at Wooddale by the ratio of the drainage at Yorklyn by that at Wooddale.

Step 12. Calculate the base 10 logarithm of the compliant zinc loads at Yorklyn and then calculate the mean and standard deviation of the individual values. Test whether the log transformed compliant zinc loads at Yorklyn are reasonably described as a normal distribution. This is equivalent to testing whether the nontransformed compliant zinc loads are lognormally distributed. All statistical tests were performed with the aid of the commercial software package Statgraphics Plus. Results of those tests are summarized in the Results section below and full output appears in Appendix 2.

Step 13. Specify the required compliance frequency for the TMDL. This is the same as the required compliance frequency for the water quality criteria, which from step 7 is 99.908%.

Step 14. Calculate the TMDL, which is the 99.908 percentile value of the compliant log transformed zinc loads at Yorklyn, using the following equation (Berthouex and Brown, 1994):

$X_{99.908} = \text{antilog}[y_2 + Z_{99.908} * S_{y2}]$, where:

y_2 and S_2 are the mean and standard deviation of the compliant zinc load distribution (from step 12).

Z_p = standard normal deviate for the required compliance frequency = 3.108 (as before).

Step 15. Allocate the TMDL among wasteload allocation (WLA), load allocation (LA), and a margin of safety (MOS) to account for uncertainties between loading to the stream and resulting in-stream concentrations. In this case, the WLA is defined as the mass loading of zinc associated with the NVF Yorklyn facility, which includes the combined loading from contaminated groundwater and NPDES discharge 002. LA, in this case, is all mass loading of zinc entering the Red Clay Creek from points upstream of the NVF Yorklyn facility. That loading is, in essence, all loading entering Delaware from the Pennsylvania portion of the Red Clay Creek watershed.

A spreadsheet is available which documents all of the steps listed above (DNREC, 2008).

5.3 Results: Lognormal Probability Approach

- When considered over the period 1/6/03 through 4/1/08, the log transformed acute toxic unit values at Yorklyn met some but not all of the diagnostic tests for normality. This means that we cannot reasonably describe the untransformed acute toxic unit values as a lognormal distribution. However, it is clear that zinc concentrations below Yorklyn during 2003 and 2004 were dropping rapidly and as such represent a non-representative transition period, presumably in response to NVF's action to curtail wet operations in the No. 1 mill. For this reason, the early part of the record was not used to develop the amended TMDL. Inspection of Figure 3 reveals the period between 9/8/05 through 9/6/06 to be without significant temporal trend, relatively data rich (n = 53 with basically 1 result per week), and having robust variation. All three of these attributes are desirable for a distributional approach like a lognormal probability analysis. Note that the period after September 2006 was also not used for the TMDL calculations because data were comparatively sparse.
- For the reasons noted in the previous bullet, acute toxic unit values for Yorklyn for the period 9/8/05 through 9/6/06 were used to develop the amended TMDL.
- As shown in Appendix 2, the logs of the acute toxic unit values at Yorklyn for the period 9/8/05 through 9/6/06 are normally distributed. Stated in another way, the untransformed acute toxic unit values at Yorklyn follow a lognormal distribution. The mean and standard deviation of the noncompliant acute toxic unit distribution are -0.4926 and 0.6393, respectively.
- The log transformed compliant zinc loads for the period 9/8/05 through 9/6/06 (again, n = 53 samples) also follow a normal distribution (see Appendix 2). This is equivalent to saying that the untransformed compliant zinc loads at Yorklyn are

lognormally distributed. The mean and standard deviation of the lognormal compliant zinc load distribution are -0.5100 and 0.7264, respectively.

- Following the procedure listed in Step 14 of Section 5.2, a TMDL of 55.93 pounds per day was calculated. This TMDL makes the conservative assumption that all of the zinc in the Red Clay Creek at Yorklyn is in the dissolved form. Although this is a conservative assumption, it is nevertheless reasonable given that 84.3% of the zinc at Ashland, nearly 2 miles downstream from Yorklyn, is in the dissolved form. Further, the mass loading from the NVF Yorklyn facility is thought to enter the Red Clay primarily as dissolved zinc from contaminated groundwater discharge.
- The final step is to allocate the TMDL among a MOS, the WLA, and a LA. This was done by first setting the MOS equal to 10% of the TMDL (i.e., 5.59 pounds/day). After subtracting out this explicit MOS from the TMDL, the remainder was allocated equally between the NVF facility and a LA for upstream. In this case, the NVF allocation includes 2 components: a WLA for NPDES outfall 002 and a LA for contaminated groundwater discharge ($LA_{g.w.}$) from the facility. The upstream LA (LA_{up}) is allocated to the entire Red Clay watershed upstream of the NVF Yorklyn facility. With an equal split between upstream and the NVF facility, each was allocated 25.17 pounds/day. The resulting TMDL is summarized as follows:

Table 2. Amended Zinc TMDL for the Red Clay Creek

TMDL (pounds/day)	$WLA_{002} + LA_{g.w.}$ (pounds/day)	LA_{up} (pounds/day)	MOS (pounds/day)
55.93	25.17	25.17	5.59

The above TMDL is designed to ensure that the applicable water quality criterion is met 99.908% of the time. This compliance frequency allows only a single exceedance of the acute criterion in any three year period.

The Department recognizes that the amended TMDL (55.93 pounds per day) is considerably greater than the existing zinc TMDL for the Red Clay Creek (1.8 pounds per day). The primary reason the amended TMDL is so much greater has to do with, ironically, pollution controls implemented at the NVF Yorklyn facility. As explained in Chapter 1, pollution controls there have focused primarily on: 1) stopping additional zinc from entering the groundwater; and 2) recovering the zinc already in the groundwater. These actions have fundamentally changed the relationship between zinc loading from the NVF facility and the resulting concentrations of zinc in the Red Clay Creek. As before, zinc loading from the facility still enters the Red Clay primarily through the discharge of contaminated groundwater. Now, however, the zinc available to be discharged is limited to the inventory previously accumulated in the groundwater due to the failed subsurface piping. Since the subsurface piping has been decommissioned or otherwise repaired, new zinc is no longer being loaded to the groundwater. In essence, the ongoing release of additional zinc associated with manufacturing has been eliminated

or at least drastically reduced. Less zinc reaching the groundwater ultimately means less zinc reaching the Red Clay. Further, the more zinc that is recovered from the groundwater, the less there is available to discharge to the Creek.

The point of the above discussion is that the rate/timing of zinc discharged from the NVF facility has changed. As a result, the peak concentration of zinc in the Red Clay Creek no longer occurs at the lowest stream flows and there is no longer a need for a traditional low flow TMDL. This new TMDL addresses the new conditions by accounting for the simultaneous, covarying effects of upstream load, groundwater loading from NVF, stream flow, and hardness while assuring that the applicable criterion is met 99.908% of the time.

5.4 Margin of Safety (MOS)

The explicit MOS listed in Table 2 above reflects uncertainty in future loading when, as, and if the NVF facility ramps production back up. It also reflects uncertainty in upstream loading which appears to have increased over time. Finally, the MOS also accounts for possible flux of dissolved zinc out of contaminated bottom sediments and into the water column of the Red Clay below Yorklyn. This issue was addressed in some detail in the original TMDL Background and Basis Document (DNREC, 1999b) and remains relevant now. Another consideration in setting the MOS at 10% is the general lack of experience, regionally and nationally, in developing TMDLs based on the lognormal probability approach, let alone one involving substantial groundwater contamination.

5.5 Seasonal Variability

Federal regulations (40 CFR, Part 130.7) require that TMDLs consider seasonal variations and critical conditions for stream flow, loading, and water quality. As noted above, variation, (more formally, the covariation) in stream flow, loading, hardness, and zinc were explicitly considered in the development of this TMDL. As such, seasonal variation is fully considered in this TMDL.

5.6 Reasonable Assurance:

Based on the reduced magnitude, frequency and spatial extent of zinc criteria exceedances below Yorklyn following adoption of the original TMDL, coupled with the pollution control commitments secured from NVF during the settlement negotiations, the Department fully expects this TMDL to be met in a matter of a few years (e.g., less than 5 years). The Department will continue to monitor zinc concentrations and loads in the Red Clay Creek to track the expected improvements over time.

6. Next Steps

This chapter identifies the next steps in the amended Red Clay Creek zinc TMDL process. First, the amended TMDL and its component parts will be published as a proposed regulation in the October 1, 2008 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 hearing will be held to take comments on the regulatory articles. The hearing will also be announced in the News Journal and Delaware State News.

The hearing is scheduled as follows:

Public Hearing

The hearing will be held on Tuesday, October 28, 2008, beginning at 6:00 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. People should enter from the rear of the building and proceed to Conference Room A.

Oral and/or written comments can be provided concerning the amended TMDL regulation at the time of the public hearing, or otherwise can be submitted in writing by 4:30 p.m., November 5, 2008. All comments should be directed to the attention of Maryann Pielmeier, DNREC, Watershed Assessment Section, 820 Silver Lake Blvd., Suite 220, Dover, DE, 19904-2464, (maryann.pielmeier@state.de.us), fax: (302) 739-6140.

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 may be published in the Delaware Register of Regulations as early as December 1, 2008, (tentatively). The final articles and supporting documentation will then be submitted to the U.S. EPA for their review and approval.

7. References

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APPENDICES

1. Zinc, Hardness, TSS, and Flow Data for the Red Clay Creek, January 2003 through April 2008
2. STATGRAPHICS Output

APPENDIX 1

Data Source	Date	Predicted				
		Zn_t (ug/L) Stateline	Zn_d (ug/L) Stateline	Hardness Stateline	TSS (mg/L) Stateline	Flow (cfs) Marshalls Br
NVF	1/6/03	231		123		42
NVF	1/9/03	9		149		39
PADEP	1/13/03	7.1	11.4	153	6	28
NVF	1/17/03	266		252		26
NVF	1/24/03	274		77		21
NVF	2/8/03	505		126		24
NVF	2/14/03	443	271.9	130	5	21
NVF	2/20/03	6810		124		28
NVF	2/28/03	14		140		40
NVF	3/8/03	7		92		129
NVF	3/14/03	42	22.3	141.4	7	53
NVF	3/19/03	7		139		39
PADEP	3/27/03	53	35.2	136	4	51
NVF	3/28/03	17		135		43
NVF	4/7/03	56		141		35
NVF	4/11/03	106		137		166
NVF	4/17/03	96		148		34
NVF	4/22/03	92		169		35
NVF	4/30/03	12		149	ND(<4)	30
DNREC	5/6/03					
NVF	5/9/03	7		144		33
NVF	5/13/03	18		138		28
NVF	5/19/03	4		144		28
NVF	5/21/03	20	14.5	156	3	37
PADEP	5/27/03	10	6.7	125	4	55
NVF	5/28/03	27		84		46
DNREC	6/3/03					
NVF	6/6/03	14		121		54
NVF	6/13/03	80		260		69
NVF	6/18/03	44	4.8	138	65	107
NVF	6/24/03	17		131		63
NVF	7/2/03	9		152		38
PADEP	7/7/03	20	16.0	141	2	40
NVF	7/11/03	31		152		38
NVF	7/16/03	179		169		28
NVF	7/22/03	8		141.4		22
NVF	7/30/03	18		141.4	ND(<4)	20
NVF	8/8/03	42		141.4		31
NVF	8/12/03	362		141.4		33
DNREC	8/18/03					
NVF	8/22/03	19		141.4		26
NVF	8/29/03	18		141.4	ND(<4)	19
NVF	9/5/03	17		141.4		29
PADEP	9/8/03	182	121.0	159	4	17
NVF	9/10/03	30	17.1	141.4	6	16
NVF	9/21/03	276		141.4		19
PADEP	10/1/03	10	8.0	144	2	43

DNREC	11/3/03					
PADEP	12/3/03	191	58.5	137	18	51
NVF	1/16/04	158		118		45
NVF	1/23/04	193		179		42
NVF	1/30/04	56	37.2	119	4	43
NVF	2/5/04	86		143		66
NVF	2/13/04	17	5.6	130	16	52
NVF	2/20/04	18		137		46
PADEP	2/24/04	10	8.0	142	2	45
NVF	2/27/04	22		145		41
NVF	3/5/04	27		134	ND(<4)	46
NVF	3/9/04	115		142		48
NVF	3/17/04	10		133		63
NVF	3/26/04	190		127		44
NVF	3/30/04	26		145		41
DNREC	4/5/04					
PADEP	4/6/04	10	5.7	139	6	52
NVF	4/9/04	12		134		51
NVF	4/14/04	7		142		124
NVF	4/22/04	6	1.7	140	20	43
NVF	5/7/04	11		152		52
NVF	5/13/04	4		145		42
NVF	5/21/04	91		112		60
NVF	5/26/04	22	6.3	160	20	41
NVF	6/4/04	11		146		32
NVF	6/9/04	1.5	0.6	142	12	35
PADEP	6/14/04	82	40.9	135	8	36
NVF	6/18/04	363		132		147
NVF	6/25/04	231	10.5	123	166	41
DNREC	6/29/04					
NVF	7/2/04	31		139		25
NVF	7/9/04	32		134		28
NVF	7/16/04	6		152		35
NVF	7/20/04	9	1.6	131	38	39
NVF	7/30/04	25		122		43
NVF	8/19/04	11		145		42
NVF	8/25/04	11	5.2	151	9	40
NVF	9/3/04	281		162		38
NVF	9/10/04	261		153		36
NVF	9/14/04	219		135		34
NVF	9/24/04	289		161		36
NVF	9/30/04	9	4.8	137	7	90
DNREC	10/5/04					
NVF	10/9/04	64		149		51
NVF	10/15/04	27		113		79
NVF	10/21/04	10		136		61
NVF	10/29/04	8		146	ND(<4)	49
NVF	11/9/04	20		141		50
NVF	11/19/04	35		151		51
NVF	11/24/04	11		140		55
DNREC	11/29/04					
NVF	11/30/04	27	9.3	120	15	72

NVF	12/10/04	1.5		135		172
NVF	12/17/04	190	9.7	147	147	56
NVF	1/5/05	57		188		82
NVF	1/14/05	57		142		558
NVF	1/22/05	101		49		51
NVF	1/28/05	18	9.0	153	8	52
NVF	2/4/05	12	6.0	148	8	53
NVF	2/12/05	53		146		55
NVF	2/18/05	15		144		55
NVF	2/25/05	10		168		57
NVF	3/11/05	97		134		53
NVF	3/17/05	55	1.7	151	245	48
NVF	3/25/05	62		150		61
NVF	4/8/05	117		109		150
DNREC	4/12/05					
NVF	4/15/05	6	2.7	140	10	63
NVF	4/21/05	72		116		58
NVF	4/27/05	7		129		62
NVF	5/20/05	24		159		72
NVF	5/28/05	11		142		41
NVF	6/3/05	21		133		57
DNREC	6/7/05					
NVF	6/10/05	22		148		36
NVF	6/28/05	404		127		30
NVF	6/29/05	1.5		149	ND(<4)	28
NVF	6/30/05	6		157		27
NVF	7/8/05	167		124		234
NVF	7/12/05	1.5	0.8	160	7	22
NVF	7/19/05	28		147		22
NVF	7/26/05	7		155		19
NVF	8/5/05	7		150		15
NVF	8/10/05	14		161	ND(<4)	20
DNREC	8/15/05					
NVF	8/17/05	29		129		29
NVF	8/23/05	20		163		14
NVF	8/30/05	16		167		20
NVF	9/8/05	24		170		17
NVF	9/21/05	133		152		19
NVF	9/30/05	15		172		19
NVF	10/5/05	10		172		19
NVF	10/13/05	15		137		88
DNREC	10/18/05					
NVF	10/20/05	23	0.7	148	246	26
NVF	10/25/05	13		94		151
NVF	11/4/05	9		161		29
NVF	11/11/05	10		150	ND(<4)	34
NVF	11/17/05	12		114		84
NVF	11/26/05	3		145		33
NVF	11/30/05	139		157		132
NVF	12/9/05	10		160	ND(<4)	34
NVF	12/16/05	29		160		497
NVF	12/23/05	1.5		147		28

NVF	12/30/05	16		139		31
DNREC	1/3/06					
NVF	1/6/06	22		154		31
NVF	1/13/06	1.5		149	ND(<4)	31
NVF	1/21/06	18		80		37
NVF	1/26/06	1.5		155		39
NVF	2/4/06	1.5		139		53
DNREC	2/6/06					
NVF	2/7/06	1.5		143	ND(<4)	29
NVF	2/16/06	16		149		39
NVF	2/21/06	1.5		146		27
DNREC	2/28/06					
NVF	3/3/06	10		143		27
NVF	3/8/06	8		136		26
NVF	3/17/06	6		139		27
NVF	3/24/06	1.5		149	ND(<4)	26
NVF	3/30/06	13		143		26
DNREC	4/4/06					
NVF	4/8/06	23		126		63
NVF	4/13/06	5		155	ND(<4)	25
NVF	4/19/06	18		148		23
NVF	4/28/06	18		117		26
DNREC	5/1/06					
NVF	5/6/06	57		139		21
NVF	5/11/06	3		66	ND(<4)	21
NVF	5/18/06	26		132		20
NVF	5/24/06	69	32.3	145	9	17
NVF	5/30/06	77		144		16
DNREC	6/5/06					
NVF	6/10/06	1.5		151		19
NVF	6/15/06	83	55.2	153	4	19
NVF	6/22/06	32		154		11
NVF	6/27/06	88		78		141
DNREC	7/5/06					
NVF	7/5/06	190		146		30
NVF	7/18/06	18		136		21
DNREC	8/1/06					
DNREC	9/6/06					
DNREC	10/30/06					37
DNREC	1/8/07					185
DNREC	3/5/07					50
DNREC	5/1/07					53
DNREC	7/9/07					21
DNREC	8/6/07					31
DNREC	9/4/07					13
DNREC	10/2/07					13
DNREC	11/5/07					20
DNREC	1/7/08					30
DNREC	2/5/08					41
DNREC	4/1/08					46

Notes:

1. Zinc concentrations in BOLD were reported as Nondetected (ND).
Value shown is one-half the detection limit of 3 ug/L.
2. Hardness values highlighted in green equal the average of the otherwise measured values.

Data Source	Date	Predicted Zn_t (ug/L) Yorklyn	Predicted Zn_d (ug/L) Yorklyn	Predicted Flow (cfs) Yorklyn
NVF	1/6/03	355.2	307	52.91
NVF	1/9/03	307.7	266	50.95
PADEP	1/13/03			
NVF	1/17/03	174.5	151	28.09
NVF	1/24/03	914.0	791	18.29
NVF	2/8/03	656.8	568	24.82
NVF	2/14/03	704.2	610	18.94
NVF	2/20/03	598.6	518	32.66
NVF	2/28/03	49.0	42	41.80
NVF	3/8/03	240.4	208	129.33
NVF	3/14/03	147.0	127	68.59
NVF	3/19/03	261.8	227	48.99
PADEP	3/27/03			
NVF	3/28/03	38.3	33	54.87
NVF	4/7/03	88.8	77	50.95
NVF	4/11/03	526.6	456	175.71
NVF	4/17/03	168.4	146	47.68
NVF	4/22/03	150.0	130	47.03
NVF	4/30/03	298.5	258	39.19
DNREC	5/6/03	329.2	285	37.23
NVF	5/9/03	316.9	274	40.50
NVF	5/13/03	313.8	272	32.66
NVF	5/19/03			31.35
NVF	5/21/03	26.0	23	39.84
PADEP	5/27/03			
NVF	5/28/03	249.5	216	51.60
DNREC	6/3/03	217.4	188	36.58
NVF	6/6/03	53.6	46	56.17
NVF	6/13/03	321.5	278	87.53
NVF	6/18/03	200.6	174	108.43
NVF	6/24/03	166.9	144	85.57
NVF	7/2/03	27.6	24	47.68
PADEP	7/7/03			
NVF	7/11/03	228.1	197	45.72
NVF	7/16/03	231.2	200	33.97
NVF	7/22/03	260.3	225	28.74
NVF	7/30/03	151.6	131	24.82
NVF	8/8/03	105.6	91	50.30
NVF	8/12/03	2020.8	1749	61.40
DNREC	8/18/03	197.5	171	30.70
NVF	8/22/03	33.7	29	33.31
NVF	8/29/03	45.9	40	21.56
NVF	9/5/03	160.7	139	39.19
PADEP	9/8/03			
NVF	9/10/03	137.8	119	21.56
NVF	9/21/03	422.5	366	59.44
PADEP	10/1/03			

DNREC	11/3/03	235.8	204	59.44
PADEP	12/3/03			
NVF	1/16/04	246.5	213	47.03
NVF	1/23/04	395.0	342	45.07
NVF	1/30/04	251.1	217	41.80
NVF	2/5/04	127.1	110	65.97
NVF	2/13/04	111.8	97	58.13
NVF	2/20/04	23.0	20	52.26
PADEP	2/24/04			
NVF	2/27/04	24.5	21	45.72
NVF	3/5/04	45.9	40	47.68
NVF	3/9/04	21.4	19	53.56
NVF	3/17/04	36.7	32	68.59
NVF	3/26/04	2357.7	2041	46.38
NVF	3/30/04	96.4	83	43.11
DNREC	4/5/04	115.7	100	77.08
PADEP	4/6/04			
NVF	4/9/04	12.2	11	57.48
NVF	4/14/04	47.5	41	148.93
NVF	4/22/04	26.0	23	51.60
NVF	5/7/04	23.0	20	58.79
NVF	5/13/04	9.2	8	52.26
NVF	5/21/04	159.2	138	61.40
NVF	5/26/04	26.0	23	46.38
NVF	6/4/04	68.9	60	35.93
NVF	6/9/04	36.7	32	39.84
PADEP	6/14/04			
NVF	6/18/04	301.6	261	194.65
NVF	6/25/04	39.8	34	39.84
DNREC	6/29/04	177.6	154	39.19
NVF	7/2/04	32.1	28	31.35
NVF	7/9/04	142.4	123	30.70
NVF	7/16/04	9.2	8	39.19
NVF	7/20/04	851.2	737	47.68
NVF	7/30/04	49.0	42	49.64
NVF	8/19/04	56.6	49	45.72
NVF	8/25/04	24.5	21	39.19
NVF	9/3/04	440.9	382	36.58
NVF	9/10/04	408.8	354	33.31
NVF	9/14/04	382.7	331	29.39
NVF	9/24/04	349.1	302	35.27
NVF	9/30/04	538.9	466	116.92
DNREC	10/5/04	150.2	130	56.83
NVF	10/9/04	342.9	297	50.95
NVF	10/15/04	65.8	57	65.32
NVF	10/21/04	26.0	23	59.44
NVF	10/29/04	18.4	16	43.11
NVF	11/9/04	94.9	82	42.46
NVF	11/19/04	79.6	69	45.07
NVF	11/24/04	73.5	64	45.72
DNREC	11/29/04	112.1	97	111.70
NVF	11/30/04	76.5	66	75.77

NVF	12/10/04	82.7	72	177.67
NVF	12/17/04	24.5	21	57.48
NVF	1/5/05	140.8	122	79.69
NVF	1/14/05	102.6	89	548.03
NVF	1/22/05	180.7	156	52.26
NVF	1/28/05	304.7	264	50.95
NVF	2/4/05	127.1	110	53.56
NVF	2/12/05	93.4	81	54.21
NVF	2/18/05	41.3	36	57.48
NVF	2/25/05	13.8	12	58.13
NVF	3/11/05	85.7	74	52.26
NVF	3/17/05	91.9	80	45.07
NVF	3/25/05	87.3	76	62.71
NVF	4/8/05	318.4	276	175.06
DNREC	4/12/05	101.7	88	70.54
NVF	4/15/05	280.2	242	63.36
NVF	4/21/05	119.4	103	57.48
NVF	4/27/05	361.3	313	62.05
NVF	5/20/05	26.0	23	69.89
NVF	5/28/05	277.1	240	37.89
NVF	6/3/05	851.2	737	54.87
DNREC	6/7/05	118.0	102	67.28
NVF	6/10/05	222.0	192	33.31
NVF	6/28/05	350.6	303	26.13
NVF	6/29/05	10.7	9	23.51
NVF	6/30/05	16.8	15	22.86
NVF	7/8/05	375.1	325	218.17
NVF	7/12/05	2.3	2	22.86
NVF	7/19/05	36.7	32	23.51
NVF	7/26/05	19.9	17	18.94
NVF	8/5/05	12.2	11	15.68
NVF	8/10/05	19.9	17	20.90
DNREC	8/15/05	142.5	123	15.02
NVF	8/17/05	168.4	146	31.35
NVF	8/23/05	35.2	30	14.37
NVF	8/30/05	67.4	58	15.02
NVF	9/8/05	50.5	44	11.10
NVF	9/21/05	342.9	297	13.06
NVF	9/30/05	44.4	38	11.76
NVF	10/5/05	49.0	42	12.41
NVF	10/13/05	21.4	19	92.75
DNREC	10/18/05	226.6	196	20.25
NVF	10/20/05	76.5	66	18.94
NVF	10/25/05	150.0	130	131.29
NVF	11/4/05	12.2	11	20.90
NVF	11/11/05	116.4	101	20.90
NVF	11/17/05	23.0	20	77.73
NVF	11/26/05	21.4	19	24.17
NVF	11/30/05	225.0	195	120.84
NVF	12/9/05	231.2	200	24.17
NVF	12/16/05	49.0	42	499.69
NVF	12/23/05	2.3	2	29.39

NVF	12/30/05	70.4	61	43.11
DNREC	1/3/06	116.4	101	218.82
NVF	1/6/06	32.1	28	41.15
NVF	1/13/06	4.6	4	35.93
NVF	1/21/06	24.5	21	41.15
NVF	1/26/06	2.3	2	44.42
NVF	2/4/06	2.3	2	58.13
DNREC	2/6/06	140.2	121	47.03
NVF	2/7/06	108.7	94	41.80
NVF	2/16/06	13.8	12	50.95
NVF	2/21/06	18.4	16	38.54
DNREC	2/28/06	240.4	208	33.31
NVF	3/3/06	36.7	32	37.23
NVF	3/8/06	13.8	12	31.35
NVF	3/17/06	64.3	56	28.09
NVF	3/24/06	93.4	81	27.43
NVF	3/30/06	269.4	233	26.13
DNREC	4/4/06	228.1	197	45.72
NVF	4/8/06	203.6	176	71.85
NVF	4/13/06	19.9	17	27.43
NVF	4/19/06	23.0	20	23.51
NVF	4/28/06	2.3	2	30.70
DNREC	5/1/06	159.2	138	26.13
NVF	5/6/06	127.1	110	22.86
NVF	5/11/06	2.3	2	22.86
NVF	5/18/06	16.8	15	24.17
NVF	5/24/06	393.5	341	18.94
NVF	5/30/06	81.1	70	16.98
DNREC	6/5/06	154.6	134	32.01
NVF	6/10/06	52.1	45	26.13
NVF	6/15/06	7.7	7	25.47
NVF	6/22/06	134.7	117	15.68
NVF	6/27/06	333.7	289	160.69
DNREC	7/5/06	127.4	110	33.31
NVF	7/5/06	49.0	42	34.62
NVF	7/18/06	238.8	207	24.82
DNREC	8/1/06			18.94
DNREC	9/6/06	123.5	107	60.75
DNREC	10/30/06	141.5	122	50.95
DNREC	1/8/07	136.4	118	195.96
DNREC	3/5/07	143.0	124	54.87
DNREC	5/1/07	87.6	76	56.83
DNREC	7/9/07	118.3	102	20.90
DNREC	8/6/07	137.6	119	32.01
DNREC	9/4/07	141.0	122	13.06
DNREC	10/2/07	258.7	224	9.80
DNREC	11/5/07	252.6	219	18.29
DNREC	1/7/08	218.9	189	29.39
DNREC	2/5/08	176.1	152	36.58
DNREC	4/1/08	160.7	139	44.42

Data Source	Date	Zn_t (ug/L) Ashland	Zn_d (ug/L) Ashland	Hardness Ashland	Predicted Flow (cfs) Ashland
NVF	1/6/03				57.04
NVF	1/9/03				54.93
PADEP	1/13/03				0.00
NVF	1/17/03				30.28
NVF	1/24/03				19.72
NVF	2/8/03				26.76
NVF	2/14/03				20.42
NVF	2/20/03				35.21
NVF	2/28/03				45.07
NVF	3/8/03				139.44
NVF	3/14/03				73.95
NVF	3/19/03				52.82
PADEP	3/27/03				0.00
NVF	3/28/03				59.16
NVF	4/7/03				54.93
NVF	4/11/03				189.44
NVF	4/17/03				51.41
NVF	4/22/03				50.71
NVF	4/30/03				42.26
DNREC	5/6/03	278	128	116	40.14
NVF	5/9/03				43.66
NVF	5/13/03				35.21
NVF	5/19/03				33.80
NVF	5/21/03				42.96
PADEP	5/27/03				0.00
NVF	5/28/03				55.64
DNREC	6/3/03	276	280	120	39.44
NVF	6/6/03				60.57
NVF	6/13/03				94.37
NVF	6/18/03				116.91
NVF	6/24/03				92.26
NVF	7/2/03				51.41
PADEP	7/7/03				0.00
NVF	7/11/03				49.30
NVF	7/16/03				36.62
NVF	7/22/03				30.99
NVF	7/30/03				26.76
NVF	8/8/03				54.23
NVF	8/12/03				66.20
DNREC	8/18/03	279	286	128	33.10
NVF	8/22/03				35.92
NVF	8/29/03				23.24
NVF	9/5/03				42.26
PADEP	9/8/03				0.00
NVF	9/10/03				23.24
NVF	9/21/03				64.09
PADEP	10/1/03				0.00

DNREC	11/3/03	206	162	122	64.09
PADEP	12/3/03				0.00
NVF	1/16/04				50.71
NVF	1/23/04				48.59
NVF	1/30/04				45.07
NVF	2/5/04				71.13
NVF	2/13/04				62.68
NVF	2/20/04				56.34
PADEP	2/24/04				0.00
NVF	2/27/04				49.30
NVF	3/5/04				51.41
NVF	3/9/04				57.75
NVF	3/17/04				73.95
NVF	3/26/04				50.00
NVF	3/30/04				46.48
DNREC	4/5/04	168	130	95.4	83.10
PADEP	4/6/04				0.00
NVF	4/9/04				61.97
NVF	4/14/04				160.57
NVF	4/22/04				55.64
NVF	5/7/04				63.38
NVF	5/13/04				56.34
NVF	5/21/04				66.20
NVF	5/26/04				50.00
NVF	6/4/04				38.73
NVF	6/9/04				42.96
PADEP	6/14/04				0.00
NVF	6/18/04				209.87
NVF	6/25/04				42.96
DNREC	6/29/04	217	137	132	42.26
NVF	7/2/04				33.80
NVF	7/9/04				33.10
NVF	7/16/04				42.26
NVF	7/20/04				51.41
NVF	7/30/04				53.52
NVF	8/19/04				49.30
NVF	8/25/04				42.26
NVF	9/3/04				39.44
NVF	9/10/04				35.92
NVF	9/14/04				31.69
NVF	9/24/04				38.03
NVF	9/30/04				126.06
DNREC	10/5/04	142	131	123	61.27
NVF	10/9/04				54.93
NVF	10/15/04				70.43
NVF	10/21/04				64.09
NVF	10/29/04				46.48
NVF	11/9/04				45.78
NVF	11/19/04				48.59
NVF	11/24/04				49.30
DNREC	11/29/04	108	71.5	90.9	120.43
NVF	11/30/04				81.69

NVF	12/10/04				191.56
NVF	12/17/04				61.97
NVF	1/5/05				85.92
NVF	1/14/05				590.87
NVF	1/22/05				56.34
NVF	1/28/05				54.93
NVF	2/4/05				57.75
NVF	2/12/05				58.45
NVF	2/18/05				61.97
NVF	2/25/05				62.68
NVF	3/11/05				56.34
NVF	3/17/05				48.59
NVF	3/25/05				67.61
NVF	4/8/05				188.74
DNREC	4/12/05	124	101	122	76.06
NVF	4/15/05				68.31
NVF	4/21/05				61.97
NVF	4/27/05				66.90
NVF	5/20/05				75.36
NVF	5/28/05				40.85
NVF	6/3/05				59.16
DNREC	6/7/05	91.3	65	101	72.54
NVF	6/10/05				35.92
NVF	6/28/05				28.17
NVF	6/29/05				25.35
NVF	6/30/05				24.65
NVF	7/8/05				235.22
NVF	7/12/05				24.65
NVF	7/19/05				25.35
NVF	7/26/05				20.42
NVF	8/5/05				16.90
NVF	8/10/05				22.54
DNREC	8/15/05	271	248	149	16.20
NVF	8/17/05				33.80
NVF	8/23/05				15.49
NVF	8/30/05				16.20
NVF	9/8/05				11.97
NVF	9/21/05				14.09
NVF	9/30/05				12.68
NVF	10/5/05				13.38
NVF	10/13/05				100.00
DNREC	10/18/05	280	279	145	21.83
NVF	10/20/05				20.42
NVF	10/25/05				141.56
NVF	11/4/05				22.54
NVF	11/11/05				22.54
NVF	11/17/05				83.81
NVF	11/26/05				26.06
NVF	11/30/05				130.29
NVF	12/9/05				26.06
NVF	12/16/05				538.76
NVF	12/23/05				31.69

NVF	12/30/05				46.48
DNREC	1/3/06	50.2	31.8	68	235.93
NVF	1/6/06				44.37
NVF	1/13/06				38.73
NVF	1/21/06				44.37
NVF	1/26/06				47.89
NVF	2/4/06				62.68
DNREC	2/6/06	120	114	111	50.71
NVF	2/7/06				45.07
NVF	2/16/06				54.93
NVF	2/21/06				41.55
DNREC	2/28/06	177	119	120	35.92
NVF	3/3/06				40.14
NVF	3/8/06				33.80
NVF	3/17/06				30.28
NVF	3/24/06				29.58
NVF	3/30/06				28.17
DNREC	4/4/06	125	108	130	49.30
NVF	4/8/06				77.47
NVF	4/13/06				29.58
NVF	4/19/06				25.35
NVF	4/28/06				33.10
DNREC	5/1/06	202	167	132	28.17
NVF	5/6/06				24.65
NVF	5/11/06				24.65
NVF	5/18/06				26.06
NVF	5/24/06				20.42
NVF	5/30/06				18.31
DNREC	6/5/06	187	156	122	34.51
NVF	6/10/06				28.17
NVF	6/15/06				27.47
NVF	6/22/06				16.90
NVF	6/27/06				173.25
DNREC	7/5/06	158	125	131	35.92
NVF	7/5/06				37.33
NVF	7/18/06				26.76
DNREC	8/1/06			137	20.42
DNREC	9/6/06	154	119	106	65.50
DNREC	10/30/06	134	115		54.93
DNREC	1/8/07	65.5	23.2	71.5	211.28
DNREC	3/5/07	118	107	108	59.16
DNREC	5/1/07	100	78.8	110	61.27
DNREC	7/9/07	182	168	136	22.54
DNREC	8/6/07	149	81.8	148	34.51
DNREC	9/4/07	265	229	156	14.09
DNREC	10/2/07	431	367	168	10.56
DNREC	11/5/07	300	273	154	19.72
DNREC	1/7/08	216	214	154	31.69
DNREC	2/5/08	178	160	131	39.44
DNREC	4/1/08	164	147	142	47.89

Data Source	Date	Zn_t (ug/L) Wooddale	Zn_d (ug/L) Wooddale	Hardness Wooddale	Measured Flow (cfs) Wooddale
NVF	1/6/03	232	204		81
NVF	1/9/03	201	157		78
PADEP	1/13/03				
NVF	1/17/03	114	52		43
NVF	1/24/03	597	570		28
NVF	2/8/03	429	340		38
NVF	2/14/03	460	384		29
NVF	2/20/03	391	81		50
NVF	2/28/03	32	20		64
NVF	3/8/03	157	32		198
NVF	3/14/03	96	96		105
NVF	3/19/03	171	116		75
PADEP	3/27/03				
NVF	3/28/03	25	5		84
NVF	4/7/03	58	36		78
NVF	4/11/03	344	72		269
NVF	4/17/03	110	69		73
NVF	4/22/03	98			72
NVF	4/30/03	195			60
DNREC	5/6/03	215	155	105	57
NVF	5/9/03	207			62
NVF	5/13/03	205			50
NVF	5/19/03				48
NVF	5/21/03	17			61
PADEP	5/27/03				
NVF	5/28/03	163			79
DNREC	6/3/03	142	121	102	56
NVF	6/6/03	35			86
NVF	6/13/03	210			134
NVF	6/18/03	131			166
NVF	6/24/03	109			131
NVF	7/2/03	18			73
PADEP	7/7/03				
NVF	7/11/03	149			70
NVF	7/16/03	151			52
NVF	7/22/03	170			44
NVF	7/30/03	99			38
NVF	8/8/03	69			77
NVF	8/12/03	1320			94
DNREC	8/18/03	129	127	112	47
NVF	8/22/03	22			51
NVF	8/29/03	30			33
NVF	9/5/03	105			60
PADEP	9/8/03				
NVF	9/10/03	90			33
NVF	9/21/03	276			91
PADEP	10/1/03				

DNREC	11/3/03	154	122	114	91
PADEP	12/3/03				
NVF	1/16/04	161			72
NVF	1/23/04	258			69
NVF	1/30/04	164			64
NVF	2/5/04	83			101
NVF	2/13/04	73			89
NVF	2/20/04	15			80
PADEP	2/24/04				
NVF	2/27/04	16			70
NVF	3/5/04	30			73
NVF	3/9/04	14			82
NVF	3/17/04	24			105
NVF	3/26/04	1540			71
NVF	3/30/04	63			66
DNREC	4/5/04	75.6	47.5	78.3	118
PADEP	4/6/04				
NVF	4/9/04	8			88
NVF	4/14/04	31			228
NVF	4/22/04	17			79
NVF	5/7/04	15			90
NVF	5/13/04	6			80
NVF	5/21/04	104			94
NVF	5/26/04	17			71
NVF	6/4/04	45			55
NVF	6/9/04	24			61
PADEP	6/14/04				
NVF	6/18/04	197			298
NVF	6/25/04	26			61
DNREC	6/29/04	116	68	117	60
NVF	7/2/04	21			48
NVF	7/9/04	93			47
NVF	7/16/04	6			60
NVF	7/20/04	556			73
NVF	7/30/04	32			76
NVF	8/19/04	37			70
NVF	8/25/04	16			60
NVF	9/3/04	288			56
NVF	9/10/04	267			51
NVF	9/14/04	250			45
NVF	9/24/04	228			54
NVF	9/30/04	352			179
DNREC	10/5/04	98.1	85.5	113	87
NVF	10/9/04	224			78
NVF	10/15/04	43			100
NVF	10/21/04	17			91
NVF	10/29/04	12			66
NVF	11/9/04	62			65
NVF	11/19/04	52			69
NVF	11/24/04	48			70
DNREC	11/29/04	73.2	52.9	76.7	171
NVF	11/30/04	50			116

NVF	12/10/04	54			272
NVF	12/17/04	16			88
NVF	1/5/05	92			122
NVF	1/14/05	67			839
NVF	1/22/05	118			80
NVF	1/28/05	199			78
NVF	2/4/05	83			82
NVF	2/12/05	61			83
NVF	2/18/05	27			88
NVF	2/25/05	9			89
NVF	3/11/05	56			80
NVF	3/17/05	60			69
NVF	3/25/05	57			96
NVF	4/8/05	208			268
DNREC	4/12/05	66.4	57.7	101	108
NVF	4/15/05	183			97
NVF	4/21/05	78			88
NVF	4/27/05	236			95
NVF	5/20/05	17			107
NVF	5/28/05	181			58
NVF	6/3/05	556			84
DNREC	6/7/05	77.1	52.8	105	103
NVF	6/10/05	145			51
NVF	6/28/05	229			40
NVF	6/29/05	7			36
NVF	6/30/05	11			35
NVF	7/8/05	245			334
NVF	7/12/05	1.5			35
NVF	7/19/05	24			36
NVF	7/26/05	13			29
NVF	8/5/05	8			24
NVF	8/10/05	13			32
DNREC	8/15/05	93.1	91.9	133	23
NVF	8/17/05	110			48
NVF	8/23/05	23			22
NVF	8/30/05	44			23
NVF	9/8/05	33			17
NVF	9/21/05	224			20
NVF	9/30/05	29			18
NVF	10/5/05	32			19
NVF	10/13/05	14			142
DNREC	10/18/05	148	143	130	31
NVF	10/20/05	50			29
NVF	10/25/05	98			201
NVF	11/4/05	8			32
NVF	11/11/05	76			32
NVF	11/17/05	15			119
NVF	11/26/05	14			37
NVF	11/30/05	147			185
NVF	12/9/05	151			37
NVF	12/16/05	32			765
NVF	12/23/05	1.5			45

NVF	12/30/05	46			66
DNREC	1/3/06	76	32.1	66.3	335
NVF	1/6/06	21			63
NVF	1/13/06	3			55
NVF	1/21/06	16			63
NVF	1/26/06	1.5			68
NVF	2/4/06	1.5			89
DNREC	2/6/06	91.6	78.4	96.4	72
NVF	2/7/06	71			64
NVF	2/16/06	9			78
NVF	2/21/06	12			59
DNREC	2/28/06	157	134	121	51
NVF	3/3/06	24			57
NVF	3/8/06	9			48
NVF	3/17/06	42			43
NVF	3/24/06	61			42
NVF	3/30/06	176			40
DNREC	4/4/06	149	131	127	70
NVF	4/8/06	133			110
NVF	4/13/06	13			42
NVF	4/19/06	15			36
NVF	4/28/06	1.5			47
DNREC	5/1/06	104	71.8	119	40
NVF	5/6/06	83			35
NVF	5/11/06	1.5			35
NVF	5/18/06	11			37
NVF	5/24/06	257			29
NVF	5/30/06	53			26
DNREC	6/5/06	101	65.7	102	49
NVF	6/10/06	34			40
NVF	6/15/06	5			39
NVF	6/22/06	88			24
NVF	6/27/06	218			246
DNREC	7/5/06	83.2	66.2	118	51
NVF	7/5/06	32			53
NVF	7/18/06	156			38
DNREC	8/1/06			121	29
DNREC	9/6/06	80.7	52	92.7	93
DNREC	10/30/06	92.4	78.9	98.9	78
DNREC	1/8/07	89.1	38.4	80.7	300
DNREC	3/5/07	93.4	85	98.6	84
DNREC	5/1/07	57.2	37.6	106	87
DNREC	7/9/07	77.3	57.8	121	32
DNREC	8/6/07	89.9	45.7	92.9	49
DNREC	9/4/07	92.1	66.8	138	20
DNREC	10/2/07	169	141	154	15
DNREC	11/5/07	165	147	139	28
DNREC	1/7/08	143	138	131	45
DNREC	2/5/08	115	109	120	56
DNREC	4/1/08	105	95.2	119	68

Data Source	Date	Zn_t (ug/L) Stanton	Zn_d (ug/L) Stanton	Hardness Stanton
NVF	1/6/03			
NVF	1/9/03			
PADEP	1/13/03			
NVF	1/17/03			
NVF	1/24/03			
NVF	2/8/03			
NVF	2/14/03			
NVF	2/20/03			
NVF	2/28/03			
NVF	3/8/03			
NVF	3/14/03			
NVF	3/19/03			
PADEP	3/27/03			
NVF	3/28/03			
NVF	4/7/03			
NVF	4/11/03			
NVF	4/17/03			
NVF	4/22/03			
NVF	4/30/03			
DNREC	5/6/03	165	130	102
NVF	5/9/03			
NVF	5/13/03			
NVF	5/19/03			
NVF	5/21/03			
PADEP	5/27/03			
NVF	5/28/03			
DNREC	6/3/03	115	92.2	102
NVF	6/6/03			
NVF	6/13/03			
NVF	6/18/03			
NVF	6/24/03			
NVF	7/2/03			
PADEP	7/7/03			
NVF	7/11/03			
NVF	7/16/03			
NVF	7/22/03			
NVF	7/30/03			
NVF	8/8/03			
NVF	8/12/03			
DNREC	8/18/03	84.5	79	112
NVF	8/22/03			
NVF	8/29/03			
NVF	9/5/03			
PADEP	9/8/03			
NVF	9/10/03			
NVF	9/21/03			
PADEP	10/1/03			

DNREC	11/3/03	164	149	114
PADEP	12/3/03			
NVF	1/16/04			
NVF	1/23/04			
NVF	1/30/04			
NVF	2/5/04			
NVF	2/13/04			
NVF	2/20/04			
PADEP	2/24/04			
NVF	2/27/04			
NVF	3/5/04			
NVF	3/9/04			
NVF	3/17/04			
NVF	3/26/04			
NVF	3/30/04			
DNREC	4/5/04	70	44.1	84.8
PADEP	4/6/04			
NVF	4/9/04			
NVF	4/14/04			
NVF	4/22/04			
NVF	5/7/04			
NVF	5/13/04			
NVF	5/21/04			
NVF	5/26/04			
NVF	6/4/04			
NVF	6/9/04			
PADEP	6/14/04			
NVF	6/18/04			
NVF	6/25/04			
DNREC	6/29/04	64.3	31.8	109
NVF	7/2/04			
NVF	7/9/04			
NVF	7/16/04			
NVF	7/20/04			
NVF	7/30/04			
NVF	8/19/04			
NVF	8/25/04			
NVF	9/3/04			
NVF	9/10/04			
NVF	9/14/04			
NVF	9/24/04			
NVF	9/30/04			
DNREC	10/5/04	73.4	66.4	111
NVF	10/9/04			
NVF	10/15/04			
NVF	10/21/04			
NVF	10/29/04			
NVF	11/9/04			
NVF	11/19/04			
NVF	11/24/04			
DNREC	11/29/04	71.7	48.1	66.5
NVF	11/30/04			

NVF	12/10/04			
NVF	12/17/04			
NVF	1/5/05			
NVF	1/14/05			
NVF	1/22/05			
NVF	1/28/05			
NVF	2/4/05			
NVF	2/12/05			
NVF	2/18/05			
NVF	2/25/05			
NVF	3/11/05			
NVF	3/17/05			
NVF	3/25/05			
NVF	4/8/05			
DNREC	4/12/05	60.5	44	99.8
NVF	4/15/05			
NVF	4/21/05			
NVF	4/27/05			
NVF	5/20/05			
NVF	5/28/05			
NVF	6/3/05			
DNREC	6/7/05	107	61.1	94.3
NVF	6/10/05			
NVF	6/28/05			
NVF	6/29/05			
NVF	6/30/05			
NVF	7/8/05			
NVF	7/12/05			
NVF	7/19/05			
NVF	7/26/05			
NVF	8/5/05			
NVF	8/10/05			
DNREC	8/15/05	40.3	23.4	121
NVF	8/17/05			
NVF	8/23/05			
NVF	8/30/05			
NVF	9/8/05			
NVF	9/21/05			
NVF	9/30/05			
NVF	10/5/05			
NVF	10/13/05			
DNREC	10/18/05	104	72.5	130
NVF	10/20/05			
NVF	10/25/05			
NVF	11/4/05			
NVF	11/11/05			
NVF	11/17/05			
NVF	11/26/05			
NVF	11/30/05			
NVF	12/9/05			
NVF	12/16/05			
NVF	12/23/05			

NVF	12/30/05			
DNREC	1/3/06	150	46.4	70.8
NVF	1/6/06			
NVF	1/13/06			
NVF	1/21/06			
NVF	1/26/06			
NVF	2/4/06			
DNREC	2/6/06	91.9	64	92.8
NVF	2/7/06			
NVF	2/16/06			
NVF	2/21/06			
DNREC	2/28/06	107	101	119
NVF	3/3/06			
NVF	3/8/06			
NVF	3/17/06			
NVF	3/24/06			
NVF	3/30/06			
DNREC	4/4/06	173	91.6	116
NVF	4/8/06			
NVF	4/13/06			
NVF	4/19/06			
NVF	4/28/06			
DNREC	5/1/06	61.7	42.5	116
NVF	5/6/06			
NVF	5/11/06			
NVF	5/18/06			
NVF	5/24/06			
NVF	5/30/06			
DNREC	6/5/06	53.5	37.8	89.5
NVF	6/10/06			
NVF	6/15/06			
NVF	6/22/06			
NVF	6/27/06			
DNREC	7/5/06	59.9	36.1	103
NVF	7/5/06			
NVF	7/18/06			
DNREC	8/1/06			117
DNREC	9/6/06	1810	629	97.8
DNREC	10/30/06	84.5	63.7	
DNREC	1/8/07	175	67.6	94
DNREC	3/5/07	95	81.5	95.2
DNREC	5/1/07	43.3	32.9	107
DNREC	7/9/07	51.7	40.5	107
DNREC	8/6/07	57.8	19.6	72.3
DNREC	9/4/07	75.3	44.6	136
DNREC	10/2/07	82	64.5	148
DNREC	11/5/07	113	91.2	134
DNREC	1/7/08	133	133	129
DNREC	2/5/08	105	91.1	113
DNREC	4/1/08	93.7	80.1	116

APPENDIX 2

Analysis Summary

This analysis shows the results of fitting a normal distribution to the data for LogTUa_Tot. The estimated parameters of the fitted distribution are shown below.

53 values ranging from -1.8787 to 0.5363

Fitted normal distribution:

mean = -0.492575

standard deviation = 0.639313

Tests for Normality for LogTUa_Tot

This shows the results of several tests run to determine whether LogTUa_Tot can be adequately modeled by a normal distribution. The chi-square test divides the range of LogTUa_Tot into 19 equally probable classes and compares the number of observations in each class to the number expected. The standardized skewness test looks for lack of symmetry in the data. The standardized kurtosis test looks for distributional shape which is either flatter or more peaked than the normal distribution.

Computed Chi-Square goodness-of-fit statistic = 24.7925

P-Value = 0.0735688

Z score for skewness = 1.3374

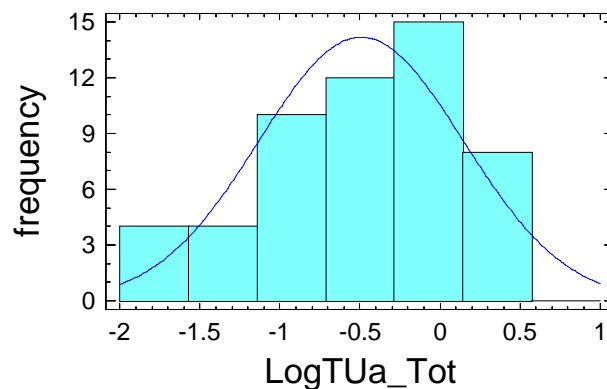
P-Value = 0.181091

Z score for kurtosis = -0.630184

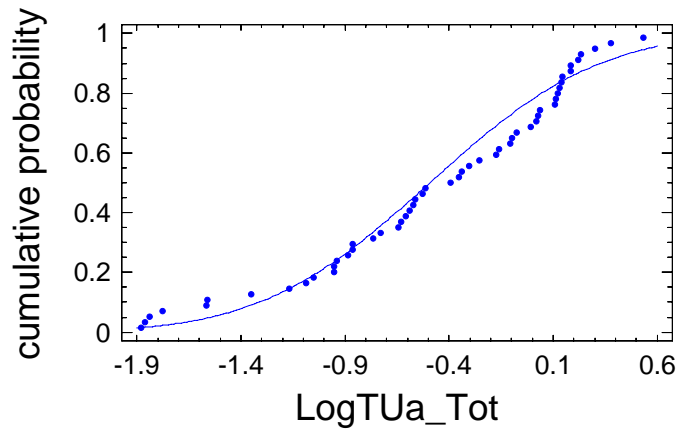
P-Value = 0.528571

The lowest P-value amongst the tests performed equals 0.0735688. Because the P-value for this test is greater than or equal to 0.05, we can not reject the idea that LogTUa_Tot comes from a normal distribution with 95% or higher confidence.

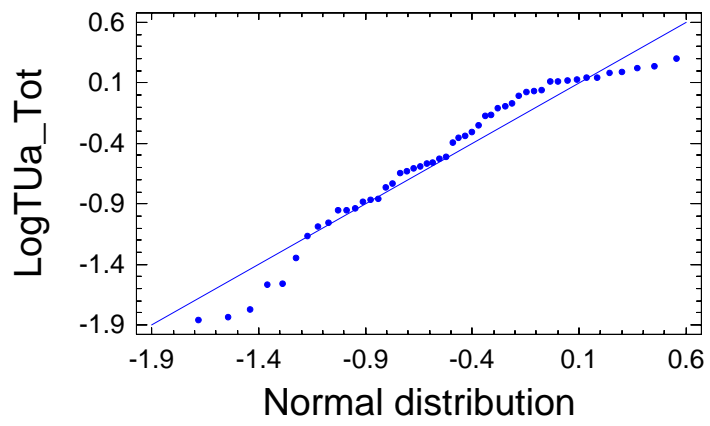
Histogram for LogTUa_Tot



Normal Distribution



Quantile-Quantile Plot



Analysis Summary

This analysis shows the results of fitting a normal distribution to the data on Log Load_Compl. The estimated parameters of the fitted distribution are shown above.

53 values ranging from -2.0 to 0.9809

Fitted normal distribution:

mean = -0.51007

standard deviation = 0.72641

Tests for Normality for Log Load Compl

This shows the results of several tests run to determine whether Log Load_Compl can be adequately modeled by a normal distribution. The chi-square test divides the range of Log Load_Compl into 19 equally probable classes and compares the number of observations in each class to the number expected. The standardized skewness test looks for lack of symmetry in the data. The standardized kurtosis test looks for distributional shape which is either flatter or more peaked than the normal distribution.

Computed Chi-Square goodness-of-fit statistic = 19.7736

P-Value = 0.230592

Z score for skewness = 0.542297

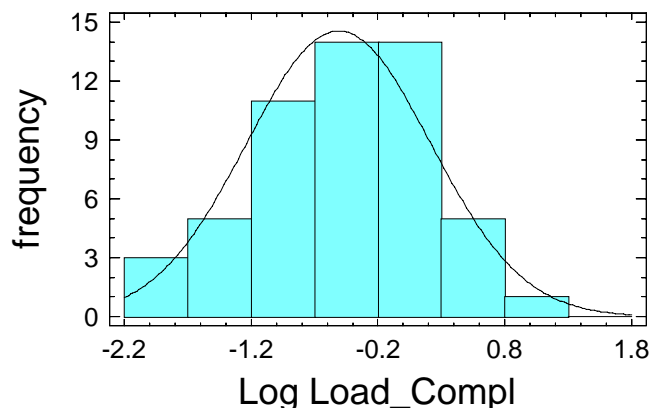
P-Value = 0.587611

Z score for kurtosis = -0.533731

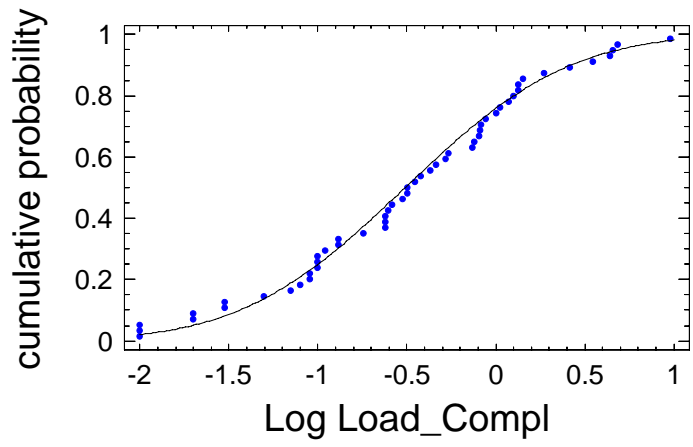
P-Value = 0.593525

The lowest P-value amongst the tests performed equals 0.230592. Because the P-value for this test is greater than or equal to 0.10, we can not reject the idea that Log Load_Compl comes from a normal distribution with 90% or higher confidence.

Histogram for Log Load_Compl



Normal Distribution



Quantile-Quantile Plot

