## COMPREHENSIVE ZINC STUDY FOR HART-MILLER ISLAND CONTAINED DISPOSAL FACILITY, MARYLAND

## SUBMITTED TO HART-MILLER ISLAND EXTERIOR MONITORING PROGRAM DREDGING COORDINATION AND ASSESSMENT DIVISION MARYLAND DEPARTMENT OF THE ENVIRONMENT



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FREDERICK, MARYLAND



UNIVERSE TECHNOLOGIES. INC. Engineering and Scientific Solutions

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## FINAL REPORT SUBMITTED TO HART-MILLER ISLAND EXTERIOR MONITORING PROGRAM DREDGING COORDINATION AND ASSESSMENT DIVISION TECHNICAL AND REGULATORY SERVICES ADMINISTRATION MARYLAND DEPARTMENT OF THE ENVIRONMENT

**SEPTEMBER 30, 1999** 

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#### **UNIVERSE TECHNOLOGIES, INC.**

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#### **EXECUTIVE SUMMARY**

The Hart-Miller Island Contained Disposal Facility was designed to receive dredged material from navigation channel maintenance and improvement activities in Baltimore Harbor and its approaches. The facility is located in the Chesapeake Bay at the mouth of the Back River, to the northeast of Baltimore Harbor. Construction of the facility began in 1981 and was completed in 1983. Operation of the facility has continued from that time to the present.

The Hart-Miller Island Exterior Monitoring Program was designed to observe changes from baseline environmental conditions in the area surrounding the facility and to guide decisions regarding operational changes and/or corrective actions, as necessary. As part of this program, an enrichment of zinc in the sediment south and east of the facility was detected in April of 1989, the eighth monitoring year. Although the size and location of the affected area has fluctuated, as have metal concentrations within the immediate area, higher than expected zinc levels remain a concern in the vicinity of the facility.

As a result of this concern, Universe Technologies, Inc. was awarded a purchase order by the Maryland Department of the Environment to conduct a study on zinc in the sediment surrounding the Hart-Miller Contained Disposal Facility. The objectives of this study are to synthesize historical and present-day information on zinc concentrations in sediment around the facility; identify possible sources of zinc enrichments near the facility; and present the findings as a technical report (presented herein) to the Maryland Department of the Environment.

In order to accomplish these objectives, considerable data on zinc and its presence in sediments in the vicinity of the facility were reviewed. Data on zinc in other relevant areas of the Chesapeake Bay and its tributaries were also reviewed. Analysis and interpretation of these indicate that the concentration of zinc in the sediments surrounding the facility are indeed increasing, albeit at a lower rate than in previous years. Despite enrichment, these zinc concentrations are generally similar or even lower than those at other sites within the northern Chesapeake Bay including the Baltimore Harbor, Patapsco River, and Back River. Details on potential mechanisms, including sedimentation, oxidation, acidification, and precipitation, are presented to explain this apparent zinc enrichment. The sources for this zinc enrichment appear to be primarily anthropogenic.

Continued monitoring for zinc in the vicinity of the facility appears warranted but with improvements in consistency and documentation. In addition, supplemental measurements to better understand zinc speciation, bioavailability, and toxicity may be appropriate.

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#### **1.0 INTRODUCTION**

This report summarizes and interprets data collected on zinc in sediments in the vicinity of the Hart-Miller Island Contained Disposal Facility (HMI). This project was funded by the State of Maryland under the auspices of the Maryland Department of the Environment (MDE).

#### **1.1 Description of the Facility**

HMI was designed to receive dredged material from navigation channel maintenance and improvement activities in Baltimore Harbor (Patapsco River subestuary) and its approaches. The facility is located in the Chesapeake Bay at the mouth of the Back River, to the northeast of Baltimore Harbor. Construction of the facility began in 1981 and was completed in 1983. Operation of the facility, as depicted in Exhibit 1 (Maryland Department of Natural Resources, 1995), has continued from that time through the present.

Initially, a perimeter dike was constructed to an elevation of 18 feet above mean low water (mlw) using sediment dredged from what is now the dike interior. This six-mile dike connected the remnants of Hart and Miller Islands and provided a placement area of 1100 acres with a capacity of approximately 52 million cubic yards (mcy). A cross dike, constructed in 1983, separates the facility into north and south cells. The south cell, filled to capacity in 1990, is approximately 300 acres in size while the north cell consists of about 800 acres. Since its initial construction, the height of the perimeter dike has been raised increasing the total dredged material capacity to approximately 100 mcy.

As originally designed, dewatering of the dredged material was to be achieved through the semipermeable dike walls and the use of spillways scattered throughout the perimeter of the site. Spillway usage began in October of 1986 once sufficient material had been placed in the cells so that supernatant liquid could be discharged.

#### 1.2 Exterior Monitoring Program

The Hart-Miller Island Exterior Monitoring Program was developed in response to a special condition of State Wetlands License No. 72-127(R). This condition required that "water quality and biota in the facility area be frequently and comprehensively monitored". As designed, results from the monitoring would be used to observe changes from baseline environmental conditions in the area surrounding HMI and to guide decisions regarding operational changes and/or corrective actions, as necessary. Since their start in 1981, exterior monitoring activities have investigated the sedimentary environment and biota near the facility through the use of sampling cruises, typically twice a year.

As part of this program, an enrichment of zinc in the sediment south and east of Spillway #1 (northeastern shore of HMI) was detected in April of 1989, the eighth monitoring year (Hennessee and Hill, 1991). In response to this discovery, the scope of monitoring was expanded in the ninth year to include a greater number of stations distributed over a wider area around HMI. Modified versions of this enhanced sampling scheme have remained in effect since that time taking into account hydrodynamic modeling results (Wang, 1993) and HMI spillway effluent discharge activities preceding each sampling cruise. Surficial sediment sampling station



Exhibit 1, Hart-Miller Island Contained Disposal Facility

locations in the twelfth monitoring year (August 1992 – August 1993) are provided in Exhibit 2 (Hill *et al.*, 1994). Available zinc concentration data collected through the Spring of 1996 as part of the Exterior Monitoring Program is provided in Appendix A. For those stations with a significant sampling history, graphs of zinc concentration versus sampling date are also provided in Appendix A. More recent data for 1997 and beyond has not been included in this Appendix as it was not available at the time of this report.

Since the initial detection of zinc enrichment, the size and location of the affected area has fluctuated, as have metal concentrations within the immediate area. These changes appear to be related to the circulation patterns in the northern Bay as well as the rate and nature of the effluent discharges (Hill *et al.*, 1998). Despite these changes, higher than expected zinc levels remain a concern in the vicinity of HMI.

#### **1.3** Scope of Work

As a result of this concern, Universe Technologies, Inc. (UNITEC) was awarded Purchase Order # U00P8003295 by the MDE to conduct a study on zinc in the sediment surrounding HMI. The objectives of this study are to synthesize available historical and present-day information on zinc concentrations in sediment around HMI; identify possible sources of zinc enrichments near HMI; and present the findings as a technical report to the MDE.

In order to accomplish these objectives, UNITEC conducted a literature search for historical and present-day sediment zinc data in the vicinity of HMI and other relevant areas of the Chesapeake Bay and its tributaries. Once collected, this data was compiled into workable formats before being analyzed and interpreted to address various issues concerning HMI, including the following:

- Since its construction, has there been a statistical increase or enrichment in the concentrations of zinc in the sediments around HMI?
- If there have been enrichments in zinc around HMI, are these temporary/short-term changes or long-term/permanent changes?
- If there has been an enrichment in zinc around HMI, what are the likely sources?
- Has usage of various methods of chemical analysis impacted the reliability of the analytical data?

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The following sections address these issues.



Exhibit 2, Exterior Monitoring Program 12th Year Sampling Stations

#### 2.0 LITERATURE SEARCH

#### 2.1 Uses of Zinc

Zinc has been used for industrial, ornamental, or utilitarian purposes for nearly 2,000 years (National Research Council, 1979). It possesses many useful properties and has a wide range of applications. Zinc ranks fourth among metals of the world in annual consumption after iron, aluminum, and copper. Traditionally, zinc has been used for the manufacturing of alloys such as brass and bronze. One of the most extensive modern applications for zinc is galvanization on a number of other metals to prevent their oxidation. Galvanized metals have a variety of applications in the building, transportation, and appliance industries. Galvanized pipes are commonly used in domestic water delivery systems and corrosion of zinc may contribute to zinc concentrations observed in wastewater (Adriano, 1986).

Among zinc compounds, zinc oxide is the most valued. It has applications in the pharmaceutical industry for the treatment of burns, infections, skin diseases, and as an antiperspirant. Zinc oxide is used as a pigment due to its ability to completely absorb ultraviolet rays and act as a mildewcide. It is also used for photocopying applications and for the production of ceramics and glasses (National Research Council, 1979).

Many zinc compounds are ingredients of common household items such as utensils, cosmetics, powders, ointments, antiseptics and astringents, paints, varnishes, linoleum, rubber and others (Adriano, 1986). Other uses of zinc and its compounds include parchment papers, television screens, dry cell batteries, electrical apparatus, flotation reagents, fire retardants, laundry aids, concrete hardeners, wood preservatives, dental cements, lubricants, flatting agents in lacquers, waterproofing agents, and dyes. Zinc also has numerous agricultural uses such as fertilizers, insecticides and fungicides, and nutritional supplements. Annually, about 22,000 tons of zinc are used in fertilizer each year in the United States (Adriano, 1986).

#### 2.2 Characteristics of Zinc

#### 2.2.1 Zinc in Soil and Sediment

Numerous studies have been conducted on the mobility and bioavailability of zinc in soils (Adriano, 1986). Since dredged sediments serve as parent materials for the development of new soils (Fanning and Fanning, 1989), studies of zinc mobility and bioavailability in soils can be useful in predicting zinc behavior in harbor sediments under anaerobic and aerobic conditions.

Zinc is the 24th most abundant element in the earth's crust with an average concentration of 70 mg/kg (Krauskopf, 1979). Zinc is often present as a minor component of minerals, varying widely from 2 to 8900 mg/kg (Adriano, 1986). It is especially common in minerals rich in iron such as magnetite, pyroxenes, and amphiboles. When igneous and metamorphic rocks are weathered, most of the zinc is concentrated in the clay minerals of the sedimentary rocks and soils that are formed, especially in the minerals of the montmorillonite group (National Research Council, 1979).

Zinc is highly reactive and has amphoteric character, the capacity to behave as either an acid or a base. As a consequence, it forms a wide variety of compounds. Zinc is also a relatively mobile heavy metal. According to Lindsay (1979), the total zinc in soils typically ranges from 10 to 300 mg/kg. However, the widespread use of zinc-containing products in households and by industries may be increasing zinc content in the environment. For instance, total zinc in the acid sulfate soils that are formed in the Baltimore Harbor dredged materials have been found to be as high as 2000 mg/kg (Fanning *et al.*, 1988). The total zinc content in soils and sediments increases as the clay and the organic matter content increase (Udo *et al.*, 1970). The soil's organic matter and clay content, pH, and redox potential affect the distribution of zinc species in soil profiles.

Zinc is most soluble at low and high pH values due to its amphoteric character. It is the least soluble at or near neutral pH (pH of 7).

Metals in Baltimore Harbor dredged materials and in the tidal marsh sediments of the Chesapeake Bay occur mainly as sulfide-bound forms (El-Desoky *et al.*, 1988; Griffin, 1988). Sulfide ion is formed in the absence of oxygen by obligate anaerobic bacteria *Desulfovibrio desulfuricans*:

 $2CH_3$ -CHOH-COOH +  $SO_4^{2-}$  =  $2CH_3COOH + HCO_3^{-} + CO_2 + HS^{-} + H_2O$ 

These bacteria reduce sulfate to sulfide by using it as an electron sink during the oxidation of organic matter, from which they derive their energy (Ivarson *et al.*, 1982). Due to zinc sulfide's very low solubility (Ksp= $1.6 \times 10^{-23}$ ), the concentration of soluble zinc in equilibrium with zinc sulfide is extremely low. Reoxidation of the sediments on the bottom of the Bay due to resuspension has very little influence on the concentration of zinc in solution (Hirst and Aston, 1983).

Sulfides of manganese, iron, zinc, copper, and mercury are stable under flooded conditions. However, sulfides are oxidized by oxygen upon exposure to the atmosphere (Fanning and Fanning, 1989) and metals tend to be mobilized (Lindsay, 1979; Fanning *et al.*, 1988). Dredged sediments exposed to the atmosphere undergo a sulfuricization process (Fanning and Fanning, 1989). During this process, metal sulfides are oxidized and sulfuric acid is formed:

 $FeS_2 + 3.75O_2 + 3.5H_2O = 2H_2SO_4 + Fe(OH)_3$ 

The oxidation of sulfides causes a release of heavy metals into solution. Formation of sulfuric acid in the process of sulfuricization further enhances solubility and mobility of heavy metals. Under certain conditions, pH may drop below 3.5. The rate of oxygen supply is probably the main control factor on the rate of sulfuric acid production (Fanning and Fanning, 1989). Dewatering of dredged sediments increases the rate of the oxygen supply and thereby lowers pH and increases the solubility of heavy metals.

Fuller (1977) classified trace elements into three classes according to their mobility as affected by pH. In acid soils at a pH 4.2 to 6.6 (a likely pH for dredged sediments exposed to the atmosphere), cadmium, mercury, nickel, and zinc are relatively "mobile"; arsenic, beryllium, and chromium are "moderately mobile"; and copper, lead, and nickel are "slowly mobile." Thus, a decrease in pH will strongly influence zinc mobility.

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Fanning *et al.* (1988) indicated that a large part of the heavy metals in acid sulfate soils in Baltimore Harbor dredged materials were lost from the sulfuric horizon (horizon where sulfides are actively oxidizing and pH is low) to the groundwater during the sulfuricization process. Therefore, effluent discharged from a facility containing this dredged material is likely to include high concentrations of heavy metals along with a low pH. Mixing of this effluent with bay waters would increase the pH of the mixture and trigger precipitation of insoluble zinc minerals such as oxides, hydroxides, carbonates, and silicates. These precipitates would then accumulate on the bay floor where they would be transformed to zinc sulfide under anaerobic conditions. Transformation to the sulfidic form would further reduce the concentration of zinc in the solution. The pH has a great effect on the solubility of these minerals. Zinc carbonate (Ksp= $1.4x10^{-11}$ ), hydroxide (Ksp= $3.3x10^{-17}$ ), silicate, and oxide show a 100-fold decrease in their solubility per each unit increase in pH (Lindsay, 1979).

The retention of heavy metals by hydrous oxides is another mechanism that controls the concentration of zinc in solutions. Feijtel et al. (1988) found positive correlation between the concentration and the distribution of cadmium, lead, nickel, copper, and zinc and the content of iron and manganese oxides in Louisiana sediments. As much as 50% of the total content of heavy metals of these sediments were bound by iron and manganese oxides. Dutta et al. (1989) reported that the decrease in availability of zinc in acidic to near neutral soils upon flooding was due to zinc precipitation as hydroxide, carbonate, and sulfide compounds, and co-precipitation with iron. Amorphous sesquioxides, changed from crystalline oxides of iron (III) in flooded soils, bound the major portion of applied zinc (Mandal et al., 1992; Singh and Abrol, 1986). Under reducing conditions, iron and manganese oxides are unstable since iron (III) is reduced to iron (II) by anaerobic microorganisms and solubilized, thereby releasing all co-precipitated metals. Reduction of iron and manganese oxides may modify the transformation of zinc to various chemical forms due to increased solubilized iron and manganese under reduced conditions. Khalid et al. (1978) found that iron and manganese oxides govern the adsorption and co-precipitation of the available zinc in the sediment-water system of the Mississippi River. The release of the metal co-precipitated with iron oxides in these sediments is very pH and redox potential dependent. Manganese undergoes a similar process. Recent studies (Cornwell et al., 1995; Riedel et al., 1995) indicated that dissolved oxygen levels have a strong influence on the release of metals from sediments. Increasing levels of oxygen cause the release of such metals as copper and zinc whereas decreasing levels of oxygen result in binding of these metals in sediments, probably as sulfides. Therefore, the redox conditions of the sediments govern the mechanism of zinc immobilization and release.

Complexation of heavy metals with insoluble organic matter is another important mechanism that is responsible for heavy metal retention in soils. Gambrell *et al.* (1977) reported that reducing environments caused the slow degradation of organic materials and the formation of large organic complexes that are involved in metal retention. Hence, organic residues, which are undergoing anaerobic decomposition on the floor of the bay, can serve as a sink for the heavy metals. The stability of the insoluble organic complexes with copper, lead, and cadmium was reported to increase as the redox potential decreased (Gambrell *et al.*, 1977). The behavior of cadmium is very similar to that of zinc (Adriano, 1986). Thus, under anoxic conditions, zinc is expected to form insoluble organic complexes in sediments.

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Studies at the Masonville deposition site (Fanning, 1983), located 6.5 km south of Baltimore's

Inner Harbor, appear to confirm these mechanisms. The Arundel Corporation first deposited dredged materials from the Baltimore Harbor at the site in 1974. Deposition of dredged materials on the site continued until 1978. Analyses of the dredged materials in 1982 indicated zinc concentrations averaging 78 mg/kg for those materials deposited in 1974 while those materials deposited in 1978 averaged 541 mg/kg of zinc. Nitric acid-hydrochloric acid digestion and atomic absorption (Chaney *et al.*, 1977) were used in the preparation and analysis of these materials. Fanning (1983) attributed differences in the zinc concentrations for these materials primarily to the impact of four additional years (deposition in 1974 versus 1978) of sulfide oxidation and zinc leaching as per the mechanisms discussed above.

The availability of zinc to plants largely depends on the zinc speciation. Two primary variables that determine mobility and bioavailability of zinc and other metals are pH and redox potential. Therefore, measurements of these parameters are essential. Zinc that is water-soluble and adsorbed at exchange sites of colloidal materials is considered to be plant-available. The amount present in the water-soluble form is virtually nonexistent, while the amount removed by some extractants such as ammonium acetate ( $NH_4CH_3COO$ ) is very small. It is a general consensus that plant-available zinc in soil can be best predicted by the use of extractants that remove only a fraction of the total amount (Adriano, 1986). Hence, measurements of total zinc content alone are not sufficient to estimate zinc uptake by plants.

The most widely used reference levels for assessing potential sediment toxicity are guidelines called "effects range thresholds". Long *et al.* (1995) developed these guidelines from biological and chemical data collected from numerous modeling, laboratory, and field studies performed in marine and estuarine sediments. Using these data, two threshold values, ER-L and ER-M, were developed to define three concentration ranges for a particular chemical. Concentrations below the "effects range-low" (ER-L) value represent a minimal effects range in which effects would be rarely observed. Concentrations equal to and above the ER-L, but below the "effects range-median" (ER-M), represent a possible effects range within which effects would occasionally occur. Concentrations equivalent to and above the ER-M value represent probable effects range within which effects would frequently occur. For zinc, the ER-L is defined as 150 mg/kg while the ER-M value is 410 mg/kg.

#### 2.2.2 Zinc in Water

The concentration of zinc in seawater is in the range of 1 to 27  $\mu$ g/L (Goldberg, 1965; Riley and Taylor, 1972). Annually, about 700,000 metric tons of zinc are transported to sea (Bertine and Goldberg, 1971). More than 99.9% of the zinc reaching the sea in the dissolved form is eventually precipitated with oceanic sediments, chiefly with clay minerals, but partly with manganese and iron oxides and phosphorites (National Research Council, 1979). Appreciable amounts of zinc can be precipitated as sulfide in anoxic waters (Spencer *et al.*, 1972).

The zinc content in fresh waters is highly variable with an average reported value of 64  $\mu$ g/L (Kopp and Kroner, 1969). Waters in industrial and urbanized areas are significantly higher in zinc due to its widespread use in households and industrial processes. Zinc usually enters the domestic water supply from deterioration of galvanized iron and the dezincification of brass. Zinc concentrations in U.S. drinking waters range from 60 to 7000  $\mu$ g/L with a mean of 1330  $\mu$ g/L (Florida Department of Natural Resource Protection, 1998). The U.S. Environmental

Protection Agency (EPA) has established a secondary maximum contaminant level (MCL) of five parts per million (ppm) (5 ppm=5000  $\mu$ g/L) for zinc in drinking water. Secondary MCLs are based on aesthetic effects such as taste, corrosion, and staining of plumbing fixtures. Streams that drain from areas of mining activity may have zinc contents up to 21000  $\mu$ g/L (Elderfield *et al.*, 1971). Waters of such streams tend to purify themselves by precipitating zinc with clay sediments or with hydrous iron or manganese oxides (National Research Council, 1979).

#### 2.2.3 Zinc in Aquatic Plants and Animals

Zinc is an essential trace element for plant growth and human and animal nutrition, but it can be toxic (Norvell and Welch, 1993; Berry and Wallace, 1989) depending on its form and concentration in solution. The recommended daily allowance for zinc is 15 mg/day for adults. Marginal or deficient intake of zinc, rather than its toxicity, is the major health concern with zinc in the general population (Adriano, 1986).

There are two separate mechanisms of zinc uptake by aquatic plants. These are sorption processes, including adsorption and ion exchange, and metabolic assimilation. Both mechanisms may exist in the same organism, but metabolic requirements or environmental conditions often determine the pathway utilized. Some scientists have suggested that metabolic zinc uptake by algae may be a secondary process that occurs only after sorption has taken place (Gutknecht, 1961). The sorption processes are probably responsible for the large concentrations of zinc that are found in algae and other aquatic plants when compared to the zinc concentration of the ambient water (National Research Council, 1979).

The ability of aquatic plants to accumulate zinc has been reported in numerous publications, with concentrations in the range of 300 to 19,000 times that of background (National Research Council, 1979). Therefore, despite relatively low concentrations of zinc in solution, enrichment of bottom sediments with zinc might result in hyperaccumulation of zinc in aquatic plants. However, most plants are tolerant to high zinc concentrations in water. It has been reported that a critical level of 0.75 mg/L of zinc in ambient water caused lethal effects in aquatic plants (Sprague, 1968). This value applied only when zinc was in an ionic form. The presence of competing ions and chelating agents is likely to negate the toxic effects of zinc to some extent. It is also necessary to emphasize that the formation of insoluble zinc species (carbonates, hydroxides, sulfides) would preclude existence of high levels of zinc in water. Therefore, zinc toxicity in aquatic plants of a body of water such as the Baltimore Harbor may be unlikely to occur.

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Zinc is present in significant concentrations in all marine animals. The range of concentrations among species is relatively narrow, except for oysters, in which very high amounts may occur (National Research Council, 1979). Oysters may concentrate zinc to levels greater than 100,000 times the ambient concentrations in seawater (National Research Council, 1979). Other marine animals usually contain 5 to 60 mg/kg of zinc (National Research Council, 1979). Levels of zinc toxic to aquatic organisms are highly variable and depend on the environmental conditions and biology of the species.

#### 2.3 Additional Zinc Data in the Vicinity of HMI

Besides the Exterior Monitoring Program and other data sources discussed above, there have been additional sediment studies conducted in the immediate vicinity of HMI, the Baltimore Harbor, and the northern Chesapeake Bay, both before and after the construction of HMI. Those that appear relevant to this project are discussed below.

#### 2.3.1 Pre-construction Data

Prior to the construction of HMI, the Maryland Department of Natural Resources, Water Resources Administration (Allison and Butler, 1981) collected sediment samples in the immediate vicinity of HMI between 1972 and 1978. Zinc concentrations at five locations surrounding HMI were reported in the range of approximately 30 to 2500 mg/kg over this time period. Zinc concentrations in the sediments seemed to peak in 1975 at all five locations (roughly 500 to 2500 mg/kg) before leveling off to below 500 mg/kg in the late 1970s. According to a linear regression analysis presented in the first year of the Exterior Monitoring Program (Wright and Striegel, 1982), no statistically significant trend was noted in the zinc concentrations at each of these five locations from 1972 to 1982. This analysis included both the Water Resources Administration data and the first year Exterior Monitoring Program data. An illustration of this data is presented in Exhibit 3 (Wright and Striegel, 1983).

Over roughly this same time frame, Sinex and Helz (1981) reported zinc concentrations in the range of 50 to 700 mg/kg in the vicinity of the Baltimore Harbor.

#### **2.3.2 Post-Construction Data**

The MDE compiled a report (Eskin *et al.*, 1994) that summarized the results of various sediment monitoring programs within the Chesapeake Bay and some of its tributaries conducted between 1984 and 1991. Within the area of the Patapsco River and its estuary, the Baltimore Harbor, nine stations arrayed along three lines transecting the Patapsco River and parallel to the Key Bridge were monitored for metals including zinc. One station in Back River was also monitored. According to this report, zinc concentrations averaged 476 mg/kg with a range of 353 to 681 mg/kg.

Prior to dredging activities in the Baltimore Harbor and its approaches, sediments in these areas were sampled and analyzed by the U.S. Army Corps of Engineers, Baltimore District, and others. The purpose of this sampling was to determine the disposition of the material prior to placement. The Maryland Environmental Service (MES), the operator of HMI, has compiled data for the sampling years of 1985 through 1995 for materials destined for HMI (Appendix B). According to this data, the average zinc concentration is 311 mg/kg for sediment samples collected during this time frame from potential dredge sites in Baltimore's Inner Harbor (defined as the channel west of an imaginary line connecting North Point and Rock Point at the mouth of the Baltimore Harbor). For sediment samples collected from the Federal navigation channels to be potentially dredged outside of the Inner Harbor (defined as the Outer Channel), an average zinc concentration of 197 mg/kg is reported for this same time period. Overall, the materials sampled and destined for deposition at HMI from 1985 to 1995 averaged 274 mg/kg (combination of Inner Harbor and Outer Channel potential sources). Although these averages are



Exhibit 3, Sediment Zinc Concentrations From Selected Sites Around Hart and Miller Islands, 1972-1982

arithmetic means and do not take into account the volume of material deposited at HMI since volumes were not available, they still provide insight on not only the material destined for HMI but also zinc concentrations in the sediments of Baltimore Harbor and its approaches.

In early June of 1996, surficial sediment samples were collected from 80 sites scattered throughout the Baltimore Harbor, Patapsco River, Back River, and their smaller tributaries and bays. Trace metal concentrations of these samples were determined using a modified EPA method 3051 digestion (including use of a mixture of nitric and hydrochloric acids) followed by analysis using Inductively Coupled Argon Plasma. According to the results of the analyses (Baker *et al.*, 1997), total recoverable zinc concentrations varied from 40 to 2600 mg/kg with a mean value of 640 mg/kg. Zinc concentrations were found to be fairly consistent throughout the study area with two exceptions: those sediments with high sand contents indicated concentrations well below the mean and sediments in the vicinity of Sparrows Point (Bear Creek and, to a lesser extent, Old Road Bay) indicated high concentrations.

Of particular interest in the Baker study were the results of sampling conducted in Back River. Eight samples were collected in the Back River from its mouth (just west of HMI) to its upper reaches. Zinc concentrations in Back River appear to trend upwards from the mouth (sample 74 at 360.0 mg/kg) to a high (sample 80 at 899.7 mg/kg) just below the northern-most sample. Additional data from this study, including sample locations, is provided in Appendix C.

#### 2.3.3 Summary of Zinc Data in the Vicinity of HMI

Exhibit 4 summarizes the collected zinc concentration data for sediments in the immediate vicinity of HMI and the northern Chesapeake Bay and its tributaries as discussed above. Although the sampling locations varied considerably in these studies, this data nonetheless provides an indication of zinc concentrations found in the general area of HMI in the following periods of its life (Hill *et al.*, 1994):

- Pre-construction prior to Fall, 1981
- Construction Fall, 1981 to Winter, 1983
- Post-construction

Pre-discharge from Spring, 1984 to Fall, 1986 Post-discharge from Fall, 1986 to present

Study & General Location*	Sampling Dates	Total Number of Samples	Zinc Mean (mg/kg dry wgt)**	Zinc Range (mg/kg dry wgt)**
PRE-CONSTRUCTION				
Water Resources Admin. 5 locations surrounding HMI	1972 – 1978	77	***	30 - 2500
Sinex and Helz Baltimore Harbor	Pre-1981	***	***	50 - 700
<b>Ext. Monitoring Program</b> 19 locations surrounding HMI	1981	19	267	41 – 721
CONSTRUCTION				
<b>Ext. Monitoring Program</b> 28 locations surrounding HMI	1983	42	180	32 - 880
POST-CONSTRUCTION				
Eskin <i>et al.</i> 10 locations in Balto. Harbor, Patapsco and Back Rivers	1984 – 1991	80	476	353 - 681
Ext. Monitoring Program Multiple locations surrounding HMI	1984 – 1996	1,065	256	8 - 745
MES Compilation Multiple sites in Balto.Harbor and its approaches	1985 – 1995	322	274	<1-1740
Baker et al. 80 locations in Balto. Harbor, Patapsco and Back Rivers	1996	80	640	40 - 2600

\* Shaded areas of the table correspond to sampling in the immediate vicinity of HMI

\*\* All units have been converted to mg/kg

\*\*\* Not Available

Exhibit 4, Summary of Sediment Zinc Data in the Vicinity of HMI

### 3.0 CHARACTERIZATION OF EXTERIOR MONITORING PROGRAM DATA

As noted above, sampling locations varied considerably between the studies summarized in Figure 4. In addition, sampling and analytical methodologies may have also differed significantly. In some cases, such as the Water Resources Administration data, documentation on the methodologies does not appear to exist. Although all of these studies are informative, it does make direct comparisons between the studies difficult and of questionable value. Alternatively, comparisons over the years of the Exterior Monitoring Program appear to be a viable option. Unlike all of the other studies provided in Figure 4, only the Exterior Monitoring Program has been conducted in the immediate vicinity of HMI and during all phases of its life. However, even with this program, there have been differences in sample handling and analytical methods over the 15 years (1981 – 1996) examined in this report. The impact, if any, of these differences are discussed in the following.

#### 3.1 Sample Handling

Sampling under the HMI Exterior Monitoring Program began in 1981. A substantial number of samples have been collected as part of this program since that time. Due to zinc's widespread presence in the environment, procedures to avoid inadvertent sample contamination should have been closely followed (National Research Council, 1979). According to information contained in the annual reports for the Exterior Monitoring Program, sampling was conducted according to generally accepted practices. However, some sample handling deficiencies, such as insufficient cleaning of biota samples, were pointed out in the reports.

In addition, inexact replication of sampling locations may have contributed to high variations in zinc content noted in many sampling stations. Sampling sites in 1981 and 1983 were located using a Teledyne-Raydist radionavigational system. Starting in June 1984 and until at least 1994, sampling sites were located/relocated using the LORAN-C navigational system, which typically reproduced locations to within 100 meters of the original location (Hennessee and Hill, 1991). Positioning since the Fall of 1994 has apparently been accomplished using global positioning systems (GPS), capable of much better repeatability than the LORAN-C system.

Quality control documentation, such as chain-of-custody forms or laboratory director's verification, to provide assurance of the quality of the sample handling process was also not readily available. Nonetheless, the data do not contain any substantive evidence to invalidate results obtained during the years of monitoring.

#### 3.2 Analytical Methods

According to the Alliance for the Chesapeake Bay (1994), the 1988 Chesapeake Bay Basinwide Toxics Reduction Strategy identified five metals (cadmium, chromium, copper, lead, and mercury) among the 14 contaminants identified as Chesapeake Bay Toxics of Concern. Although zinc was not among these metals, it was chosen as an indicator of trace metal loading around HMI based on the consistency of its analytical data (Hennessee and Hill, 1991). The majority of the sediment trace metal analytical data were obtained from non-commercial laboratories such as the Chesapeake Biological Laboratory (University of Maryland), the EPA Central Regional Laboratory, and the Maryland Geological Survey Laboratory. HMI monitoring was performed using the standard methods of the time period with modifications as necessary to improve method efficiency. The analytical methods used for the determination of the six trace metals (iron, manganese, zinc, copper, chromium, and nickel) analyzed over the course of HMI monitoring were atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES).

AAS uses the absorption of light to measure the concentration of gas-phase atoms (Skoog, 1985). HMI sediment samples were analyzed by AAS after digestion by various methods until August of 1991 (Exhibit 5). The AAS analytical process is not convenient for the analysis of multiple elements since a specific light source is required for each element (Scimedia, 1996).

During the 9<sup>th</sup> monitoring year (August 1989 – August 1990), two changes were made to the digestion procedure to increase detection levels and reduce loss of zinc through volatilization: the ratio of sample to flux was increased and the fusion temperature was lowered from 1050 °C to 930 °C.

AES uses quantitative measurement of the optical emission from excited atoms to determine analyte concentration. Atomization sources include direct-current plasma, flame, inductivelycoupled argon plasma, laser-induced breakdown, laser-induced plasma, microwave-induced plasma, and spark (direct-current or alternating-current arc)(Scimedia, 1996). In August 1991 (11<sup>th</sup> monitoring year), the fusion-flame AAS technique was replaced by the inductively-coupled argon plasma (ICAP) analytical method. ICAP, with its multi-element capability and low detection limits, was chosen to provide better accuracy and precision, in addition to superior efficiency. Beginning with the 11<sup>th</sup> monitoring year, HMI sediment samples were also digested using a microwave/acid (hydrochloric and nitric) technique (Hennessee *et al.*, 1994). This method of digestion and analysis remained the method of choice through the spring of 1996.

The Chesapeake Biological Laboratory (University of Maryland) performed the initial trace metal sediment analyses during the first two years of the Exterior Monitoring Program. The EPA Central Regional Laboratory performed trace metal sediment analyses during the 3<sup>rd</sup> monitoring year. The available Interpretive Reports encompassing 1984 to 1994 indicate that the trace metal sediment analyses were performed by the Maryland Geological Survey (MGS). All of the analytical data indicating zinc enrichment were obtained from trace metal sediment analyses performed by MGS.

Monitoring	Analytical	Analytical Method
Year	Laboratory	
1 and 2	Chesapeake Biological Laboratory	Nitric acid digestion followed by Flame AAS
3	EPA Central Regional Laboratory	"Standard EPA procedure"
4 through 8	MGS Laboratory	Lithium metaborate fusion technique followed by Flame AAS
9 and 10	MGS Laboratory	Enhanced lithium metaborate fusion technique followed by Flame AAS
11 through 13	MGS Laboratory	Microwave digestion followed by ICAP analysis

#### Exhibit 5, Exterior Monitoring Program Analytical History

During the 12<sup>th</sup> monitoring year (Hill *et al.*, 1994), three standard reference materials (SRMs) were analyzed in an attempt to compare the fusion/flame AAS method to the microwave/ICAP method. The data for zinc indicate that the methods are comparable with the microwave/ICAP method having a precision advantage. The fusion/flame AAS method, however, produced slightly higher zinc recoveries for the SRMs than the microwave/ICAP method. Based on this data, the zinc enrichment trend (first noticed in the 8<sup>th</sup> monitoring year) would not have been enhanced by the change from the fusion/flame AAS method to the microwave/ICAP method.

Quality control measures throughout the Exterior Monitoring Program included the use of traceable reference materials, bracketing standards, blank analyses, and inter-laboratory comparisons of reference standard analyses in order to make the data comparable to other valid data. It is reasonable to assume from this that all of the referenced data can be used for interpretation and analysis.

#### 3.3 Additional Measurements

Although not required for the purpose of this study, additional measurements should be considered in future Exterior Monitoring Program efforts. These include pH and redox (Eh) measurements, both of which are inexpensive and can be performed quickly and efficiently after sampling is completed. Knowledge of pH and Eh can assist in predicting speciation of zinc in the bottom sediments. The total concentration of zinc in the sediments alone does not provide all that is necessary to determine zinc bioavailability. Sequential extraction of sediments with several extractants may be another method that allows quantitative determination of bioavailable zinc.

Besides the ongoing benthic and chemical studies, additional sediment toxicity tests were undertaken during the 11<sup>th</sup> monitoring year (Duguay, 1994) to provide direct, quantifiable information on the biological effects of sediment associated contaminants. Although these tests

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were inconclusive because the mortality of the test organisms was attributed to interactions between indigenous species in the samples rather than chemical toxicity, modified tests as recommended by Duguay (1994) should be given consideration.

# 4.0 ANALYSIS AND INTERPRETATION OF EXTERIOR MONITORING PROGRAM DATA

#### 4.1 Statistical Analysis and Interpretation

Graphical analyses of the Exterior Monitoring Program data from 1981 through 1996 are presented in Appendix A for those stations with a significant sampling history. A cursory review of this data indicates a high degree of variability in zinc concentrations over the 15 years of monitoring. This variability may be attributed to a number of factors including the hydrodynamics of the Bay in the area of HMI, the rate and nature of HMI's effluent discharges, sampling location inconsistency, and the inherent variability of the sediments.

The erratic patterns of zinc content for the majority of the sampling stations significantly restrict statistical analysis of the data. In an attempt to alleviate this problem, zinc concentrations for each monitoring year were averaged over all sampling stations (Exhibit 6). Note also that the effects range thresholds (ER-L and ER-M), discussed in section 2.2.1, are noted on this exhibit. These data were then analyzed using Statistical Analysis System (SAS) software, a combination of programs designed to perform statistical analysis on the data. Internal program checks designed to ensure data validity are presented in Appendix D.

This analysis indicates that the sampling date is statistically significant at a probability level of p=0.0001. Since its construction in 1981, HMI zinc concentration trends appear to be divided into three distinct periods. Fall 1983 – Fall 1988, Spring 1989 – Spring 1990, and Fall 1990 – Spring 1996. There are two statistical outliers that were omitted from the trend analysis: data for 1981 and Spring 1983. These outliers might be explained by non-standard analytical techniques alluded to during the early years of the Program.

Statistical trend analysis of the three periods show that zinc behavior at HMI can be described by the following equations:

1 <sup>st</sup> period (Fall 1983 – Fall 1988):	Zn (mg/kg) = 758.4 - 6.57 x Year (p=0.012)
2 <sup>nd</sup> period (Spring 1989 – Spring 1990):	Zn (mg/kg) = -3262 + 39.1 x Year (p=0.0001)
3 <sup>rd</sup> period (Fall 1990 – Spring 1996):	Zn (mg/kg) = 25.9 + 2.79 x Year (p=0.021)

All of these mathematical relationships are highly statistically significant and can be used for interpretive purposes. During the first period (Fall 1983 – Fall 1988), the concentration of zinc decreased slightly with a regression coefficient of -6.57. This time period coincides with the majority of construction activities having been completed through the initial two years of effluent discharges at HMI. During the second period (Spring 1989 – Spring 1990), sediment zinc concentrations rapidly increased with a regression coefficient of 39.1. This time period apparently corresponds to much lower volumes of effluent being released from HMI Spillway #1 (Hennessee and Hill, 1991).

With the third period (Fall 1990 – Spring 1996), sediment zinc concentrations continued to rise but at a lower rate of increase as indicated by a regression coefficient of 2.79. This drop in the rate of increase might be attributed to ameliorations to the discharge protocols implemented by MES to counteract the effects observed during the second period. In fact, Fall 1990 marked the beginning of efforts to perform crust management at HMI during periods in which inflow was suspended. The annual pattern of alternating seasons of inflow and crust management continued in subsequent years in an effort to maximize facility capacity while simultaneously maintaining the effluent discharge water quality mandated by the State effluent discharge permit.



SAS Data: Zinc Sediment Concentration Near HMI

Exhibit 6, Average Sediment Zinc Concentrations for all Exterior Monitoring Program Stations Versus Sample Date

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A limitation on the above analysis is the fact that the Exterior Monitoring Program sampling station locations and number of samples have changed over the past fifteen years. Some of these changes have been unavoidable due to the positional accuracy constraints on open water as discussed in Section 3.1. In addition, sample station locations were also revised over the years to accommodate hydrodynamic modeling results and effluent discharge activities during the months preceding each cruise.

Ideally, an analysis of only those Exterior Monitoring Program stations consistently in use since the start of the Program would alleviate this limitation. Supposedly, 22 of these stations (2, 3, 5, 6, 7, 8A, 9, 10, 11, 12, 14, 16, 19, 20, 22, 23, 24, 25, 26, 27, BC3, and BC6) have been in use since November of 1983 (Hill *et al.*, 1998). An analysis of only these 22 locations indicated zinc concentration trends remarkably similar to the previous analysis in which the entire data set was used. However, closer examination of the available data, both analytical and positional, appears to indicate that much fewer than 22 stations were consistently sampled (14 stations since November of 1983, 9 stations since 1981) making such an analysis a poor representation of the overall sediment concentrations in the vicinity of HMI. Therefore, an analysis of all stations, as per the above, appears to be the preferred method.

#### 4.2 Normalization of Data

Rather than the approach presented above, the Exterior Monitoring Program has interpreted changes in HMI zinc concentrations since the 9<sup>th</sup> monitoring year by taking into account grain size induced variability and referencing the data to a supposedly regional norm (Hennessee and Hill, 1991). This normalization of grain size induced variability of zinc concentrations was conducted to account for changes in the distribution of clay, silt, and sand since the construction of HMI. Specifically, increased clay with its high surface area would be expected to adsorb higher levels of trace metals, including zinc.

Although there does appear to be a correlation between clay content and increases in zinc, this study did not choose to normalize the data with respect to grain size, iron (as done by the Program prior to the 9<sup>th</sup> monitoring year), or any other parameter for a number of reasons (Sokal and Rohlf, 1987):

- Correlation can not be used for predictive purposes since it does not show cause and effect relationships
- By normalizing data, the normal distribution is lost making interpretations relatively inaccurate and difficult to interpret
- Normalizing data results in the loss of information about relationships between two variables

Therefore, by normalizing for grain size, the assumption is that the zinc associated with clay has not originated from HMI and there is no evidence to substantiate this. Typically, normalization of data is used when the data does not meet statistical requirements and has to be transformed in order for statistical analyses to be performed. In this case, all of the mathematical relationships shown in Section 4.1 are highly statistically significant and can be used for interpretive purposes without the need for normalization.

#### 5.0 ZINC ENRICHMENT CONCLUSIONS

The above statistical analyses supports the assertion that the concentration of zinc in the sediments surrounding HMI are increasing. The following discussion provides potential mechanisms and sources identified in the literature search for this apparent increase.

#### 5.1 Zinc Enrichment Mechanisms

Widespread use of zinc and its products in households, agriculture, and industry result in the release of zinc, carried as a fine particulate, into rivers and other bodies such as the Chesapeake Bay. The anaerobic conditions and abundance of organic substrate in the Bay provide ideal conditions for the formation of metal sulfides in sediments. Obligate anaerobic heterotrophic microorganisms such as *Desulfovibrio desulfuricans* use  $SO_4^{2-}$  as a terminal electron acceptor thereby reducing it to  $S^{2-}$ :

$$SO_4^{2-} + 8H^+ + 8e^- = S^{2-} + 4H_2O$$

Metal ions such as  $Zn^{2+}$  come in contact with  $S^{2-}$  ions and form highly insoluble precipitate zinc sulfide (ZnS):

$$S^{2-} + Zn^{2+} = ZnS$$

Formation of precipitate causes a decrease in  $Zn^{2+}$  concentration in the water layer adjacent to the sediments, which in turn causes diffusion of  $Zn^{2+}$  from the upper layers of water due to concentration gradients. This mechanism appears to be responsible for accumulation of zinc in sediments.

In addition to ZnS, other insoluble zinc compounds such as  $ZnCO_3$ ,  $Zn(OH)_2$ , and  $Zn_3(PO_4)_2$  can accumulate on the bottom via the mechanism of sedimentation. After dredging and deposition on HMI, anaerobic sediments are exposed to atmospheric oxygen, especially at low flooding conditions. Contact with atmospheric oxygen triggers oxidation of the sulfides, release of metals, and acidification of the sediments to a pH below approximately 3.5. Acidification is further enhanced by the low pH of the rainfall at HMI (average of 4.3 with a range of 3.1 to 6.6 from 1994 to 1996) (Maryland Environmental Service, 1997a). Zinc sulfides are also oxidized and  $Zn^{2+}$  is released:

$$FeS_2 + 3.75O_2 + 3.5H_2O = 2H_2SO_4 + Fe(OH)_3$$
  
ZnS + 2O<sub>2</sub> = ZnSO<sub>4</sub>

Acidification of the sediments causes dissolution of insoluble zinc compounds  $(ZnCO_3, Zn(OH)_2, and Zn_3(PO_4)_2)$  and release of  $Zn^{2+}$  into solution.

During HMI's effluent discharges, water enriched with heavy metals is released from the containment facility. The discharged effluent mixes with Bay water, with a pH typically greater than 7. In fact, Bay water in the immediate vicinity of HMI averaged 7.86 from February 1995 to November 1996 (Maryland Environmental Service, 1997b). At this pH level, several zinc minerals (ZnCO<sub>3</sub>, Zn(OH)<sub>2</sub>, and Zn  $_3(PO_4)_2$ ) become insoluble and precipitate. It is this sharp

change in pH that accounts for the apparent enrichment in zinc in the sediments surrounding HMI. Consistent with Wang's (1993) model, the hydrological regime in the vicinity of the spillways seems to largely determine the quiescent conditions where precipitates are accumulating.

The above statistical analysis shows that the concentration of zinc in the sediments surrounding HMI is increasing but at a lower rate of increase. This drop in the rate of increase might be attributed to ameliorations to the discharge protocols implemented by MES to counteract greater impacts, as discussed in Section 4.1. Once deposition onto HMI is complete and dewatering and surface disturbance ends, the concentration of the discharge should decrease as the source of the metals is depleted, consistent with the findings of Fanning (1983). As these changes continue, zinc concentrations in the vicinity of HMI should stabilize. Gradual burial of the upper layer and formation of more stable crystallized forms of zinc minerals will result in an overall decrease in zinc solubility and bioavailability. Thus, the current zinc enrichment in the vicinity of HMI can be considered temporary rather than long-term or permanent.

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#### 5.2 Potential Zinc Sources

The Chesapeake Bay watershed covers several states and includes land with significant industrial and agricultural activity as well as large, densely populated urban areas. The Chesapeake Bay airshed is even larger and extends as far as Ohio. As a result, there are many possible sources for zinc enrichment in Bay sediments including mining and concentrating; smelting and metallurgic operations; metal plating; manufacturing of various zinc products; motor vehicles; fuel oil and coal combustion; incineration; soil erosion; agriculture; sewage sludge; commercial and industrial activities.

According to the Chesapeake Bay Basinwide Toxics Reduction Reevaluation Report (Cornwell *et al.*, 1995), the majority of metal loading to the Bay basin comes from urban stormwater runoff, followed by point sources and atmospheric deposition. According to this report, metal loading is highest in the Potomac, followed by the Susquehanna, West Chesapeake, James, mainstream Bay, Patuxent, Eastern Shore, York and Rappahannock basins. The impact of the Susquehanna is especially relevant to HMI as it is the largest contributor of sediments to the upper Chesapeake Bay (U.S. Geological Survey, 1997).

Helz (1976) indicated that anthropogenic sources accounted for at least a third of the 2060 metric tons of zinc deposited annually in the northern Chesapeake Bay, including the Patapsco River and Baltimore Harbor. The Susquehanna River, by far the largest contributor of fresh water to the northern Bay, contributed almost 50% of this amount. The main sources of pollution in rivers were thought to be industries and wastewater plants.

With heavily populated areas concentrated in Baltimore and its surrounding counties, the human influence was even more strongly felt in the Baltimore Harbor, a significant source of HMI dredged materials. According to this same study (Helz, 1976), direct industrial discharge accounted for over 70% of the zinc (470 metric tons annually) in the Baltimore Harbor. The other two major sources of zinc in the Baltimore Harbor were municipal wastewater and rivers/storm drainage, contributing 80 and 70 metric tons per year, respectively. Although this data is dated by over 20 years, it still provides insight into conditions of the northern Bay and the

Baltimore Harbor. As a result of these historic inputs, heavy metals can be expected to be part of dredged materials from these locations.

Due to more strict environmental regulations such as the Clean Water Act and the Clean Air Act, industrial sources of metal contamination have been significantly reduced. Contaminants from diffuse sources such as automobile exhausts and other air deposition, storm water runoff, septic seepage, household and marine chemicals are becoming more significant than industrial sources (Maryland Geological Survey, 1997; Florida Department of Natural Resource Protection, 1998).

Another potential source of zinc/trace metals found in the sediments around HMI is Back River, which receives effluent from the Back River Wastewater Treatment Plant. Before pre-treatment programs were implemented, industrial facilities would typically discharge their wastes directly to municipal sewers. Wastewater treatment plants, therefore, have historically been major sources of heavy metal, and other contamination in receiving waters and sediments (Florida Department of Natural Resource Protection, 1998; Maryland Geological Survey, 1997; and Alliance for the Chesapeake Bay, 1994). Data from the aforementioned Baker *et al.* study (1997) indicated zinc concentrations in Back River sediments ranging from 360 to 899 mg/kg. Every two years, states are required to submit a prioritized list of water bodies that do not meet water quality standards or will not meet the standards after all technology-based pollution controls are in place (MDE, 1999a). Back River was listed on Maryland's 1996 303(d) List of Water Quality Limited Basin Segments as a low priority for nutrients, suspended sediment, and chlordane but not zinc (MDE, 1999b). However, Back River does appear on the 1998 Additions to Maryland's 303(d) List as a high priority for zinc and polychlorinated biphenyls (MDE, 1999c).

#### 5.3 Recommendations

This study has been conducted with several constraints including variations in sampling and analytical methods, inconsistent sampling station locations, multi-agency participation in the Exterior Monitoring Program, and missing or incomplete data. Nonetheless, it does appear, based on the available data, that total zinc concentrations are increasing in the sediments surrounding HMI. Despite enrichment, these zinc concentrations are generally similar to or even lower than those at other sites within the northern Chesapeake Bay including the Baltimore Harbor and the Patapsco and Back Rivers. For instance, when comparing only the post-construction data from Figure 4, the average concentration for the Exterior Monitoring Program was lower than the Eskin, Baker, and MES data. The upper range of the Exterior Monitoring Program data for this time period was also lower than all but the Eskin data.

Focusing on more recent data, the available Exterior Monitoring Program zinc data was at its highest average, 304 mg/kg, with a range of 26 to 648 mg/kg in the Spring of 1996. Even in this worse case of the Exterior Monitoring Program, this average is lower than all but the MES data average (274 mg/kg) with an upper range lower than all other non-Exterior Monitoring Program data in Figure 4. This 1996 Exterior Monitoring Program data is also lower in zinc than the Back River data collected as part of the Baker study (average of 654 mg/kg with a range of 360 to 900 mg/kg).

Although sediment zinc concentrations in the vicinity of HMI appear to be increasing, they have yet to fully reflect their northern Bay dredge sources and neighboring Back River. As such, continued monitoring appears warranted with an emphasis, when appropriate, on improved consistency and documentation.

As mentioned in Section 3.3, measurements beyond total zinc concentrations, to better understand zinc speciation, bioavailability, and toxicity, may be useful. Although defining the protocols for these tests is beyond the scope of the study, they are still worth mentioning in case they have yet to be considered.

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31

# Appendix A

Exterior Monitoring Program Zinc Data, 1981-1996


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A-1
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STA	(YEAR)	ZN (mg/kg)	Filename: trzincall_feb.xls
65.0	90.083	315.4	Maximum: 456.5 Mean: 341.7 Standard deviation: 57.67755619
65.0	90.333	456.5	Minimum: 300.3 Median: 319.5 Variance: 3326.700489
65.0	90.917	314.9	
65.0	91.333	300.3	
65.0	91.917	339.7	
65.0	92.333	323.6	
66.0	90.083	237.8	
67.0	90.083	379.3	Maximum: 390.5 Mean: 364.1 Standard deviation: 20.40403449
67.0	90.333	375.5	Minimum: 339.3 Median: 363.8 Variance: 416.3246235
67.0	90.917	347.8	
67.0	91 333	339.3	
67.0	Q1 Q17	390.5	·
67.0	92 333	352.1	
68.0	90.083	265.7	
69.0	90.083	302.5	Maximum: 395.3 Mean: 329.1 Standard deviation: 36.11401442
69.0	90.000	322.0	Minimum: 294.2 Median: 321.8 Variance: 1304.222038
69.0	90.000	339.3	
60.0 60 N	91 222	204.2	
60.0	01 017	204.2	
60.0	91.91/ 00.000	390.3	
70.0	92.333	321.3	Maximum: 556.3 Mean: 427.2 Standard deviation: 60.52303007
70.0	90.083	301.8	Minimum: 261.9 Modian: 412.0 Statuatu ueviation: 03.03.03909/
70.0	90.333	436.0	
70.0	90.917	422.2	
70.0	91.333	3/3.0	
70.0	91.917	556.3	
70.0	92.333	413.8	
71.0	90.083	266.2	Maximum: 439.6 Mean: 381.9 Standard deviation: 41.99294579
71.0	90.333	410.5	Minimum: 266.2 Median: 390.2 Vanance: 1763.407496
71.0	90.917	349.4	
71.0	91.333	350.9	Zn sediment concentrations at Station 71
71.0	91.917	388.4	
71.0	92.333	398.5	
71.0	92.917	412.4	
71.0	93.37	392.0	<b>a</b> 400.0
71.0	93.917	412.1	
71.0	94.333	374.7	<b>5</b> 300 0
71.0	94.917	368.7	ō 500.0
71.0	95.333	372.7	
71.0	95.917	410.3	
71.0	96.333	439.6	
			ğ 100.0 <u>+ </u>
			<b>O</b> 0.0 +
			80 00 01 02 02 04 05 06 07
			03 30 31 32 33 34 35 30 97
			Samula Nata (vaar)
			Sample Date (year)
72.0	90.083	237.8	
73.0	90.083	265.2	
74.0	90.083	269.2	
75.0	90.083	347.3	
76.0	90.083	305.7	
77.0	90.083	258.2	
78.0	90.083	240.9	
80.0	90.083	490.3	Maximum: 490.3 Mean: 398.0 Standard deviation: 48.30225688
80.0	90.333	392.8	Minimum: 355.3 Median: 392.4 Variance: 2333.108019
80.0 80 0	90.000	362.0	
80.0 80 0	Q1 222	355 3	
00.0 00.0	01.000	305.3 305 A	
00.0	91.91/ 00.000	393.0	
80.0	<b>∀∠.</b> 333	592.1	

1

SIA	(YEAR)	ZN (mg/kg)					File	name: trzino	all_feb.xls				
81.0	90.083	303.3	Max	imum: 339.4	4	Mean:	314.9	Standard	deviation:	21.215357	31		****
81.0	90.333	339.4	Min	imum: 302.0	)	Median:	303.3		Variance:	450.09138	57		
81.0	90.917	302.0											
82.0	90.083	268.9	**************************************		*****			******					*******
83.0	90.083	104.1	****************								*****		
84.0	90.083	73.0	~~~~~~										
85.0	90.083	65.2	Max	imum: 74.0		Mean:	64.5	Standard	deviation:	8.1142229	5		
85.0	90.333	59.3	Min	imum: 53.0		Median:	63.7		Variance:	65.8406142	25		
85.0	90.917	53.0											
85.0	91.333	62.2											
85.0	91.917	74.0											
85.0	92.333	73.1											
86.0	90.083	250.4											
87.0	90.083	304.1	Max	imum: 744.6	5	Mean:	531.9	Standard	deviation:	102.668476	56		
87.0	90.333	481.4	Mini	imum: 304.1		Median:	538.2		Variance:	10540.8160	08		
87.0	90.917	537.7											
87.0	91.333	538.7			7n c	odimo	nt or	noont	nation	a at 64	, ation (	07	
87.0	91.917	573.1		. 4	211 3	beuime		ncem	ration	s at St	ation	0/	
87.0	92.333	744.6	~	800.0 -	<u> </u>								
87.0	92.917	475.5	- D D	700.0				*					
87.0	93.37	581.2	- 16	100.0 -				/	1				
87.0	93.917	548.9	Ĕ	600.0 -			· · · · · · · · · · · · · · · · · · ·					/	
87.0	94.333	592.2	ž	500.0 -					$\Delta \mathcal{L}$				
87.0	94.917	435.3	5	400.0		Ţ			¥				
87.0	95.333	483.8	ati	400.0 -									
87.0	95.917	501.6	ţ	300.0 -	····-								
87.0	96.333	647.9	C O	200.0 -									
			õ	400.0									
				111111									
			2	100.0 -									
			Cor	- 0.0			·····	· · · · ·					
			Cor	- 0.0 - 0.0 8	  9	90	91	92	93	94	95	96	97
	·		Cor	- 0.0 8	9	90	91	92 Samp	93 le Date	94 • (year)	95	96	97
88.0	90.083	214.9	Cor	0.0 - 8	9	90	91	92 Samp	93 le Date	94 (year)	95	96	97
<u> </u>	<u>90.083</u> 90.083	<u>214.9</u> 116.8	Cor	0.0 -	89	90	91	92 Samp	93 le Date	94 (year)	95	96	97

90.083	116.8					
90.083	276.4	Maximum: 276.4	Mean: 264.0	Standard deviation:	11.91041417	
91.333	248.0	Minimum: 248.0	Median: 265.8	Variance:	141.8579656	
91.917	268.0					
92.333	263.5					
90.083	263.8		*****			
90.083	281.1	Maximum: 309.9	Mean: 281.0	Standard deviation:	18.53514625	
90.333	309.9	Minimum: 251.8	Median: 280.9	Variance:	343.5516464	
90.917	280.7					
91.333	251.8					
91.917	277.5					
92.333	285.2					
90.083	269.8					
90.083	267.9				······	
90.083	253.0		***************************************	·····		
90.083	233.2	******		****		
90.083	223.1				······	·····
90.083	229.2	·				*****
90.083	227.1					
	90.083 90.083 91.333 91.917 92.333 90.083 90.083 90.083 90.917 91.333 91.917 92.333 90.083 90.083 90.083 90.083 90.083 90.083	90.063   110.6     90.083   276.4     91.333   248.0     91.917   268.0     92.333   263.5     90.083   263.8     90.083   281.1     90.333   309.9     90.917   280.7     91.333   251.8     91.917   277.5     92.333   269.8     90.083   269.8     90.083   267.9     90.083   233.2     90.083   233.2     90.083   223.1     90.083   229.2     90.083   227.1	90.063   116.8     90.083   276.4   Maximum: 276.4     91.333   248.0   Minimum: 248.0     91.917   268.0   92.333     90.083   263.5   90.083     90.083   263.8   90.083     90.083   281.1   Maximum: 309.9     90.333   309.9   Minimum: 251.8     90.917   280.7   91.333     91.333   251.8   91.917     91.333   269.8   90.083     90.083   267.9   90.083     90.083   253.0   90.083     90.083   223.1   90.083     90.083   229.2   90.083     90.083   229.2   90.083	90.083   116.8     90.083   276.4   Maximum: 276.4   Mean: 264.0     91.333   248.0   Minimum: 248.0   Median: 265.8     91.917   268.0   92.333   263.5     90.083   263.8   90.083   263.8     90.083   281.1   Maximum: 309.9   Mean: 281.0     90.333   309.9   Minimum: 251.8   Median: 280.9     90.917   280.7   91.333   251.8     91.917   277.5   92.333   285.2     90.083   269.8   90.083   267.9     90.083   253.0   90.083   223.1     90.083   223.1   90.083   223.1     90.083   229.2   90.083   227.1	90.083 276.4 Maximum: 276.4 Mean: 264.0 Standard deviation:   91.333 248.0 Minimum: 248.0 Median: 265.8 Variance:   91.917 268.0 92.333 263.5 Variance:   90.083 263.8 Variance: 90.083 263.8   90.083 263.8 Variance: 90.083 263.8   90.083 263.8 Variance: 90.033 309.9 Minimum: 309.9 Mean: 281.0 Standard deviation:   90.333 309.9 Minimum: 251.8 Median: 280.9 Variance:   90.917 280.7 91.333 251.8 91.917 277.5   92.333 285.2 90.083 269.8 90.083 269.8   90.083 2669.8 90.083 253.0 90.083 223.1   90.083 223.1 90.083 223.1 90.083 223.1   90.083 229.2 90.083 227.1 90.083 227.1	90.083 276.4 Maximum: 276.4 Mean: 264.0 Standard deviation: 11.91041417   91.333 248.0 Minimum: 248.0 Median: 265.8 Variance: 141.8579656   91.917 268.0 92.333 263.5 Variance: 141.8579656   90.083 263.8 90.083 263.8 Variance: 141.8579656   90.083 263.8 90.083 281.1 Maximum: 309.9 Mean: 281.0 Standard deviation: 18.53514625   90.333 309.9 Minimum: 251.8 Median: 280.9 Variance: 343.5516464   90.917 280.7 91.333 251.8 91.917 277.5   91.333 251.8 91.917 277.5 92.333 285.2   90.083 269.8 90.083 267.9 90.083 253.0   90.083 253.0 90.083 253.0 90.083 223.1   90.083 223.1 90.083 223.1 90.083 223.1   90.083 229.2 90.083 227.1 90.083 227.1







## Appendix B

## MES Data Compilation, 1985-1995

PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZINC MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997) INNER HARBOR MINIMUM (1985-1997)	1740 0.04
CHANNEL ABOVE NORTH PT/ROCK PT	211
LINE INVERIOL (1905-1995)	511
CHANNEL ABOVE NORTH PT/ROCK PT	202
LINE AVERAGE (1965-1994)	202
OUTER CHANNEL AVERAGE (1985-1995)	197.18
OUTER CHANNEL MAXIMUM (1985-1995)	580
	370
	310
	640
	320
	350
	280
	410
	58
	160
Dundalk/Seagirt Marine Terminal	
	104
	12
	47

PROJECT NAME, SAMPLING DATE	ZINC
AND SAMPLE LOCATIONS	MG/K
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	31
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197.1
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
	42
	L.
Pier 4, October 1986	4.04
	100 93
American Graner 1007	
Amstar Sugar, 1987	66
MD Ship & Drydool: March 1097	
The sup of Digutes, March 1987	10
	20
	1
Sparrows Point Shipyard, April 1987	·
50' Utility Relocation. May 1987	2.
	-

PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZINC
	MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197 18
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
CSX Import Ore Pier	0.04
Canton Waterfront Park, Feb. 1988	210 430
Eastalco Aluminum Co., July 1988	588 616
Baltimore Gas & Electric, Sept. 1988	170 200
Locust Point Marine Terminal	

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0

ND SAMPLE LOCATIONS	ZINC MG/KG
IMI AVERAGE	274
NNER HARBOR AVERAGE (1985-1997)	304
NNER HARBOR MAXIMUM (1985-1997)	1740
NNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197.18
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
FOTAL VOLUME	
MPA, June 1988	481
MPA Small Boat Facility	
Oct. 1986	320
Jones Falls Waterway	
Fleet St./Falls Ave., Nov. 1988	
Stiles & Pratt Sts. Nov 1988	
Stiles & Pratt Sts., Nov. 1988	
Stiles & Pratt Sts., Nov. 1988 IIA, S. of Pratt St., Dec. 1988	
Stiles & Pratt Sts., Nov. 1988 IIA, S. of Pratt St., Dec. 1988 IIB, S. of Fleet St., Dec. 1988	1/10
Stiles & Pratt Sts., Nov. 1988 IIA, S. of Pratt St., Dec. 1988 IIB, S. of Fleet St., Dec. 1988 1A - Jones Falls Streambed	140
Stiles & Pratt Sts., Nov. 1988 IIA, S. of Pratt St., Dec. 1988 IIB, S. of Fleet St., Dec. 1988 1A - Jones Falls Streambed 1B - Jones Falls Streambed	140 150
Stiles & Pratt Sts., Nov. 1988 IIA, S. of Pratt St., Dec. 1988 IIB, S. of Fleet St., Dec. 1988 1A - Jones Falls Streambed 1B - Jones Falls Streambed 2A - Jones Falls Streambed	140 150 29
Stiles & Pratt Sts., Nov. 1988 IIA, S. of Pratt St., Dec. 1988 IIB, S. of Fleet St., Dec. 1988 1A - Jones Falls Streambed 1B - Jones Falls Streambed 2A - Jones Falls Streambed 2B - Jones Falls Streambed	140 150 29 160

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PROJECT NAME, SAMPLING DATE	ZINC
AND SAMPLE LOCATIONS	MC/KC
	WIG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197.18
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
Eastalco - MES Sample, Jan. 1989	391
CSX - Stonehouse Cove, September 1988	468
CCSC Baltimore Terminal, March 1988	
1A, 1B, 1C Composite	130
2A, 2B, 2C Composite	52
Brewerton Channel, July 1989	
B-8, B-12 Composite	231
Curtis Bay CoBayside Terminal	
November 1987	
B1-B1A	37
B2-B2A	210
(B2-B2A CONTINUED)	
B3	190

PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZIN MG/I
HMI AVERAGE	27
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	174
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	31
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	28
OUTER CHANNEL AVERAGE (1985-1995)	197.
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.6
TOTAL VOLUME	
Inner Harbor Fast Marina July 1000	4
miler marbor East Marma July, 1990	
Lady Maryland Ship Station	
Lady Maryland Ship Station September 1990	~
Lady Maryland Ship Station September 1990 1A	3
Lady Maryland Ship Station September 1990 1A 1B	3 5
Lady Maryland Ship Station September 1990 1A 1B Sparrows Point Turning Basin	3 5
Lady Maryland Ship Station September 1990 1A 1B Sparrows Point Turning Basin June 1987	3 5 2
Lady Maryland Ship Station September 1990 1A 1B Sparrows Point Turning Basin June 1987 Dundalk Marine Terminal	3 5 2
Lady Maryland Ship Station September 1990 1A 1B Sparrows Point Turning Basin June 1987 Dundalk Marine Terminal March 1991	3 5 2
Lady Maryland Ship Station September 1990 1A 1B Sparrows Point Turning Basin June 1987 Dundalk Marine Terminal March 1991 A	3 5 2 5
Lady Maryland Ship Station September 1990 1A 1B Sparrows Point Turning Basin June 1987 Dundalk Marine Terminal March 1991 A B	3 5 2 5 3
Lady Maryland Ship Station September 1990 1A 1B Sparrows Point Turning Basin June 1987 Dundalk Marine Terminal March 1991 A B C	3 5 2 5 3 2

PROJECT NAME, SAMPLING DATE	ZINC
AND SAMPLE LOCATIONS	MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NODTH DT/DOCK DT	
LINE AVERAGE (1985-1994)	282
	202
OUTER CHANNEL AVERAGE (1985-1995)	197.18
OUTER CHANNEL MAXIMUM (1985-1995)	580
FOTAL VOLUME	
August 27, 1984	
NORTH	
CENTER	
SOUTH	

PROJECT NAME, SAMPLING DATE	ZINC
AND SAMPLE LOCATIONS	MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
	107 40
OUTER CHANNEL MANDAUM (1985-1995)	197.10
OUTER CHANNEL MAXIMUM (1985-1995) OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
Amerada Hess Curtis Creek Terminal	
February 9. 1993	170
Dry weight	
SUE CREEK AREA	
SC-1A	237
SC-2A	77
SC-3A	133
SC-3A	86
SC-6A	178
SC-2B	145
SC-3B	52
SC-6C	231
	B-8

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PROJECT NAME, SAMPLING DATE	ZINC
AND SAMPLE LOCATIONS	MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997) INNER HARBOR MINIMUM (1985-1997)	1740 0.04
CHANNEL ABOVE NORTH PT/ROCK PT LINE AVERAGE (1985-1995)	311
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995) OUTER CHANNEL MAXIMUM (1985-1995) OUTER CHANNEL MINIMUM (1985-1995)	197.18 580 7.63
TOTAL VOLUME	
IPPER REAR CREEK AREA	
SC-1	560
SC-2	357
GREENHILL COVE AREA	
GH-1	239
GH-2	252
SPARROWS POINT SHIPYARD DECEMBER 14, 1993	
SP-1 ACCESS CHANNEL	296
SP-2 PIER 1/PIER 3	1230

AND SAMPLE LOCATIONS	ZIN MG/
HMI AVERAGE	2
INNER HARBOR AVERAGE (1985-1997)	30
INNER HARBOR MAXIMUM (1985-1997)	174
INNER HARBOR MINIMUM (1985-1997)	0.0
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	3
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	2
OUTER CHANNEL AVERAGE (1985-1995)	197.
OUTER CHANNEL MAXIMUM (1985-1995)	58
OUTER CHANNEL MINIMUM (1985-1995)	7.6
TOTAL VOLUME	
SP-3	17
GRAVING DOCK	
GRAVING DOCK	
SEAGIRT MARINE TERMINAL, 3/23/93	
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' +	
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16'	
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13'	
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13' AT&T COMPOSITE A,B,C 1993	
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13' AT&T COMPOSITE A,B,C 1993 U.S. Coast Guard, Curtis Bay 1995	
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13' AT&T COMPOSITE A,B,C 1993 U.S. Coast Guard, Curtis Bay 1995 BH-01	2 1 1
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13' AT&T COMPOSITE A,B,C 1993 U.S. Coast Guard, Curtis Bay 1995 BH-01 BH-02	2
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13' AT&T COMPOSITE A,B,C 1993 U.S. Coast Guard, Curtis Bay 1995 BH-01 BH-02 BH-03	2 1 1 1 1 7
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13' AT&T COMPOSITE A,B,C 1993 U.S. Coast Guard, Curtis Bay 1995 BH-01 BH-02 BH-03 BH-04	1
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13' AT&T COMPOSITE A,B,C 1993 U.S. Coast Guard, Curtis Bay 1995 BH-01 BH-02 BH-03 BH-04 BH-05	1 7 1 1
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13' AT&T COMPOSITE A,B,C 1993 U.S. Coast Guard, Curtis Bay 1995 BH-01 BH-02 BH-03 BH-04 BH-05 BH-06	2 1 1 1 7 1 1 2
SEAGIRT MARINE TERMINAL, 3/23/93 SP-1 upper elevation 16' + SP-2 middle elevation 13-16' SP-3 lower elevation 10-13' AT&T COMPOSITE A,B,C 1993 U.S. Coast Guard, Curtis Bay 1995 BH-01 BH-02 BH-03 BH-04 BH-05 BH-06 BH-07	2 1 1 1 7 1 1 2 6

PROJECT NAME, SAMPLING DATE	ZINC
AND SAMPLE LOCATIONS	MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197,18
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
BG&E Brandon Shores Facility	
August, 1995 B-1, B-2, B-3 Composite	88
FY 1995 COE Data Report (1996)	
Brewerton Reach	
BR1	375
BR2	375
BR3	366
BR4	399
Brewerton Angle Reach	
BKAI	337
BRA2	369
Ft. McHenry Reach	
	377
	350
	285
FMH4 Curtis Boy Beech	346
CD1	AFF
	455

9
AND SAMPLE LOCATIONS	ZINC MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197 18
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
CB2	45.
	154
CB3	393
CB3 CB4	393 390
CB2 CB3 CB4 Ferry Bar Reach	39: 39:
CB3 CB4 Ferry Bar Reach FB1	39: 39: 388
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3	39: 39: 38: 38: 38:
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwost Branch East Beach	39: 39: 38: 38: 38:
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach	39: 39: 38: 38: 38: 38:
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach NBE1	39( 39( 38( 38( 38( 38) 51(
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach NBE1 NBE2 Northwest Branch West Beach	39: 39: 38: 38: 38: 38: 51: 45:
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach NBE1 NBE2 Northwest Branch West Reach	39: 39: 38: 38: 38: 51: 45:
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach NBE1 NBE2 Northwest Branch West Reach NBW1 NBW2	39( 39( 38( 38( 38) 384 51( 45( 98.( 14)
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach NBE1 NBE2 Northwest Branch West Reach NBW1 NBW2 NBW3	154 39( 39( 384 384 384 51( 456 98.( 140 872
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach NBE1 NBE2 Northwest Branch West Reach NBW1 NBW2 NBW3 Clinton Street (11/22/96) composite of 3 same	154 39( 39( 38( 38) 384 51( 45( 98.( 14( 874)
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach NBE1 NBE2 Northwest Branch West Reach NBW1 NBW2 NBW3 Clinton Street (11/22/96) composite of 3 samp Clinton Street (11/28/96) (cont.)	154 393 396 388 384 384 513 456 98.6 146 874 98.6 146 874
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach NBE1 NBE2 Northwest Branch West Reach NBW1 NBW2 NBW3 Clinton Street (11/22/96) composite of 3 samp Clinton Street (11/28/96) (cont.) Pier 6. Port Covington (4/28/97)	154 39( 39( 38( 384 384 51( 456 98.6 14( 874 98.6 14( 874 98.6 98.6 14( 874) 98.6 98.6 14( 874) 98.6
CB3 CB4 Ferry Bar Reach FB1 FB2 FB3 Northwest Branch East Reach NBE1 NBE2 Northwest Branch West Reach NBW1 NBW2 NBW3 Clinton Street (11/22/96) composite of 3 samp Clinton Street (11/28/96) (cont.) Pier 6, Port Covington (4/28/97) Site 1	154 393 394 384 384 384 513 456 98.6 144 874 98.6 144 874 98.6 144 874 98.6 144 874 98.6 144 874 98.6 144 874 98.6 144 874 98.6 144 874 98.6 144 144 144 144 144 144 144 144 144 14

PROJECT NAME, SAMPLING DATE	ZINC
	MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197.18
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
Site 3	440
Site 4	410
Site 5	480
Site 6	450
Blue Circle Cement Co. 5/22/97	
Composite I	270
Composite II	200
North Locust Point Berths 4/5	110
Dundalk Marine Terminal Berth 1	40
Dundalk Marine Terminal Berths 2-6	94
Hart-Miller Island D.M.C.F.	
Dike Raising Material, May 1988	
	32
How Miller John J. D. M. C. D.	17
Diko Doioing Material Oct. 1000	
Dike Kaising Material, Oct. 1988	54
Baltimore County Projects, March 1989	

	MG/KO
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197.18
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
North Point Cove, Lynch Point Creek,	
Muddy Gut & Tabasco Cove	22
NP-2	61
NP-3	58
NP-4	101
NP-5	31
TC-1	55
TC-2	71
TC-3	63
MG-1	5
MG-2	8
	8
MG-3	4
MG-3 LP-1	
MG-3 LP-1 LP-2	50
MG-3 LP-1 LP-2 Allied Signal, January 1990	50

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PROJECT NAME, SAMPLING DATE	ZINC
AND SAMILLE LOCATIONS	MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197.18
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
•	
MR-202AX(Lower)	620
MR-204X(Upper)	830
MR-204X(Lower)	1200
MR-209X(Upper)	1200
MR-209X(Lower)	1300
MR-214X(Upper)	1700
MR-214X(Lower)	270
MR-218X(Upper)	1500
MR-218X(Lower)	900
Back River Bridge	
· · · ·	
50' Project, September 1986	
	83
1	81

PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZINC MG/K
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/POCK PT	
LINE AVERAGE (1985-1994)	282
OUTED OUANNEL AVEDAOD (1005 1005)	107 4
OUTER CHANNEL AVERAGE (1985-1995)	197.10
OUTER CHANNEL MAXIMUM (1985-1995)	762
	1
	1
	1
	1 22 26
	1 22 26 24
	1 22 26 24 20
	1 22 26 24 20 8
	1 22 26 24 20 8 6
	1 22 26 24 20 8 6 14
	1 22 26 24 20 8 6 14
	1 22 26 24 20 8 6 14 15 12
	1 22 26 24 20 8 6 14 15 12 21
	1 22 26 24 20 8 6 14 15 12 21 18
	1 22 26 24 20 8 6 14 15 12 21 18 21
	1 22 26 24 20 8 6 14 15 12 21 18 21 18 21 22
	1 22 26 24 20 8 6 14 15 12 21 18 21 22 23

PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZINC MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997) INNER HARBOR MAXIMUM (1985-1997) INNER HARBOR MINIMUM (1985-1997)	304 1740 0.04
CHANNEL ABOVE NORTH PT/ROCK PT LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995) OUTER CHANNEL MAXIMUM (1985-1995) OUTER CHANNEL MINIMUM (1985-1995)	197.18 580 7.63
TOTAL VOLUME	
	190 13 40 180 140 200 160 180 340 250
	30 210 330 320 350 250 33 310

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PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZIN
······································	MG/F
HMI AVERAGE	27
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	174
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	31
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	28
OUTER CHANNEL AVERAGE (1985-1995)	197.
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.6
TOTAL VOLUME	
TOTAL VOLUME	2
TOTAL VOLUME	2
TOTAL VOLUME	2 3 4
TOTAL VOLUME	2 3 4 4
TOTAL VOLUME Brewerton/Tolchester, March 1989	2 3 4 4
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11	2 3 4 4
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12	2 3 4 4 1 2
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13	2 3 4 4 1 2 4
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13 Core # 14	2 3 4 4 1 2 4 4
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13 Core # 14 Core # 15	2 3 4 4 1 2 4 4 4
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13 Core # 14 Core # 15 Core # 16	2 3 4 4 1 2 4 4 4 3
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13 Core # 14 Core # 15 Core # 16 Core # 17	2 3 4 4 1 2 4 4 3 3 3
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13 Core # 13 Core # 14 Core # 15 Core # 16 Core # 17 Core # 18 Core # 10	2 3 4 4 1 2 4 4 3 3 3 3 3
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13 Core # 14 Core # 15 Core # 16 Core # 17 Core # 18 Core # 19	2 3 4 4 1 2 4 4 3 3 3 3 3 3
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13 Core # 14 Core # 15 Core # 15 Core # 16 Core # 17 Core # 18 Core # 19 Core # 21 Core # 22	2 3 4 4 1 2 4 4 3 3 3 3 3 3 3
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13 Core # 14 Core # 15 Core # 16 Core # 16 Core # 17 Core # 18 Core # 19 Core # 21 Core # 21	2 3 4 4 1 2 4 4 3 3 3 3 3 3 3 3 2
TOTAL VOLUME Brewerton/Tolchester, March 1989 Core # 11 Core # 12 Core # 13 Core # 14 Core # 15 Core # 16 Core # 17 Core # 18 Core # 19 Core # 21 Core # 22 Core # 24	2 3 4 4 1 2 4 4 3 3 3 3 3 3 3 2 2 2

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PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZINC MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997) INNER HARBOR MINIMUM (1985-1997)	1740 0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197.18
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
Grab # 1	271
Grab # 2	288
Grab # 3	398
Grab # 4	290
Grab # 5	319
Grab # 6	303
Grab # 7	309
Grab # 8	275
Grab # 9	276
Grab # 10	272
Grab # 20	228
Grab # 23	304
Grab # 25	233
Craighill Channel, July 1989	
VC-1-TOP	337
VC-1-MIDDLE	
VC-1-BOTTOM	
VC-2-TOP	322

PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZIN MG/I
HMI AVERAGE	27
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	174
INNER HARBOR MINIMUM (1985-1997)	0.0
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	31
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	28
OUTER CHANNEL AVERAGE (1985-1995)	197.
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	
TOTAL VOLUME	7.63
VC-2-MIDDLE VC-2-BOTTOM	7.6
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP	7.6
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE	7.6
TOTAL VOLUME VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM	7.6
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-BOTTOM VC-3-BOTTOM VC-4-TOP	7.6
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM	7.6
TOTAL VOLUME VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM VC-5-TOP	7.6
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM VC-5-TOP VC-5-MIDDLE	7.6
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM VC-5-TOP VC-5-MIDDLE VC-5-BOTTOM	7.6
TOTAL VOLUME VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM VC-5-TOP VC-5-MIDDLE VC-5-BOTTOM VC-6-TOP	7.6
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-MIDDLE VC-4-BOTTOM VC-5-TOP VC-5-MIDDLE VC-5-BOTTOM VC-6-TOP VC-6-MIDDLE	7.6
TOTAL VOLUME VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM VC-5-TOP VC-5-MIDDLE VC-5-BOTTOM VC-6-TOP VC-6-MIDDLE VC-6-BOTTOM	7.6
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM VC-5-TOP VC-5-MIDDLE VC-5-BOTTOM VC-6-TOP VC-6-MIDDLE VC-6-BOTTOM C-10	7.6 7.6 15 17 30 17
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM VC-4-BOTTOM VC-5-TOP VC-5-MIDDLE VC-5-BOTTOM VC-6-TOP VC-6-MIDDLE VC-6-BOTTOM C-10 C-11	7.6 7.6 15 17 30 17 14
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM VC-5-TOP VC-5-MIDDLE VC-5-BOTTOM VC-6-TOP VC-6-MIDDLE VC-6-BOTTOM C-10 C-11 C-13	7.6 7.6 19 17 30 17 14 31
VC-2-MIDDLE VC-2-BOTTOM VC-3-TOP VC-3-MIDDLE VC-3-BOTTOM VC-4-TOP VC-4-MIDDLE VC-4-BOTTOM VC-5-TOP VC-5-MIDDLE VC-5-BOTTOM VC-6-TOP VC-6-MIDDLE VC-6-BOTTOM C-10 C-11 C-13 C-14	7.6 7.6 15 17 30 17 14

PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZINC
·	MG/KG
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	311
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
· · · · ·	
OUTER CHANNEL AVERAGE (1985-1995)	197.18
OUTER CHANNEL MAXIMUM (1985-1995)	- 580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
C-16	47
C-17	58
C-18	24
C-19	16
C-20	90
C-23	64
C-26	19
C-27	46
C-28	280
C-29	145
C-31	132
	234 212
	213
DT-2 DT-3	286
DT-3 DT-4	286 173
DT-2 DT-3 DT-4 DT-5	286 173 221
DT-2 DT-3 DT-4 DT-5 DT-6	286 173 221 53
DT-2 DT-3 DT-4 DT-5 DT-6 DT-7	286 173 221 53 220

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PROJECT NAME, SAMPLING DATE AND SAMPLE LOCATIONS	ZINC MG/K
HMI AVERAGE	274
INNER HARBOR AVERAGE (1985-1997)	304
INNER HARBOR MAXIMUM (1985-1997)	1740
INNER HARBOR MINIMUM (1985-1997)	0.04
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1995)	31
CHANNEL ABOVE NORTH PT/ROCK PT	
LINE AVERAGE (1985-1994)	282
OUTER CHANNEL AVERAGE (1985-1995)	197.1
OUTER CHANNEL MAXIMUM (1985-1995)	580
OUTER CHANNEL MINIMUM (1985-1995)	7.63
TOTAL VOLUME	
DT-9	223
DT-10	219
Brewerton Eastern Extension	
March 1991	
GRAB SAMPLE 1	8
GRAB SAMPLE 2	7
GRAB SAMPLE 3	8
GRAB SAMPLE 4	6
GRAB SAMPLE 5	6
GRAB SAMPLE 6	5
CORE SAMPLE 1	13
CORE SAMPLE 2	· 12
CORE SAMPLE 3	3
CORE SAMPLE 4	6

## Appendix C

Selected Data From Baker et al., 1997



Locations of surficial sediments collected during the week of June 3 to 5, 1996 in the Baltimore Harbor/Patapsco River/Back River System. Site 66 was too shallow for sampling.

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Zinc concentrations (µg/g dry wgt) in BSM sediments.

Analysis	1	2	3	4	• 5	6	7	8	9	10	11	12
<u>Grain Size (% dry weight)</u>												
Gravel	0	0	0	0.68	0	0.19	0	0	0	8.18	0	0
Sand	99.23	5.75	98.29	44.50	97.39	6.75	16.75	14.18	7.06	32.50	4.59	7.64
SIIt	0.20	33.12	0.75	25.66	1.01	35.94	46.47	55.70	61.33	22.24	38.83	36.63
Clay	0.57	61.13	0.96	29.16	1.60	57.12	36.78	30.12	31.61	37.07	56.58	55.73
water content, % (MGS)	27.18	66.72	22.71	49.22	22.39	67.84	60.33	63.47	70.28	67.23	69.41	67.75
water content, % (Baker)	27.5	74.9	28.9	53.9	32	69.5	62.5	59.8	66.5	66	70.4	69.2
Total Nitrogen	0.0113	0.2946	0.0189	0.1674	0.0243	0.2974	0.2426	0.2320	0.2916	0.2316	0.3094	0.2948
Total Carbon	0.1003	3.4370	0.3269	2.9661	0.3267	4.5077	5.3756	6.0585	5.4191	3.7652	3.7309	3.6551
Total Sulfur	BDL	0.2235	BDL	0.3036	BDL	0.2093	0.2623	0.3196	0.3817	0.3503	0.2672	0.2759
AVS												
<u>Metals (ug/g)</u>												
Cd	BDL	0.01	BDL	0.42	0.23	0.37	0.44	0.60	1.08	0.01	0.60	0.29
Cr	5.8	191.1	10.4	106.2	12.2	230.4	270.4	285.2	293.8	189.2	242.2	285.2
Cu	5.3	64.0	8.4	37.5	9.5	79.7	85.7	94.2	148.2	83.8	85.3	84.2
Fe	0.17	5.86	0.35	3.07	0.44	7.74	10.98	12.47	9.47	4.76	5.84	6.76
Mn	1054	3167	972	1586	1844	2831	2166	1331	1147	2260	3414	3072
Ni	7.6	72.6	11. <del>9</del>	38.3	16.8	71.5	61.0	49.6	48.0	56.2	81.3	74.5
Pb	5.5	77.8	10.1	36.3	5.1	125.1	260.4	265.9	244.2	66.6	95.6	93.8
Zn	48.2	440.5	69.4	225.5	78.9	652.3	1016.7	1204.1	1414.5	319.1	491.9	528.3
Hg (ng/g)	3.92	243.81	46.83	123.19	9.47	414.27	562.23	324.42	703.56	186.88	470.41	151.03
Methyl-Hg (ng/g)	0	5.53	0	0.78	0		1.31			1.15		
% Methyl		2.27		0.63			0.23			0.62		

Anaiysis	13	14	15J	15	16	17	18	19	20	21	22	23
Grain Size (% dry weight)												
Grain Gize (70 er) morging												
Gravei	0	0	0	0	0	2.84	0	0	0	0	0	0
Sand	1.15	5.41	4.71	10.06	3.73	69.17	3.07	1.19	3.14	1.57728707	48.4099748	3.27163151
Siit	35.72	41.60	28.40	28.66	21.22	12.90	41.92	26.70	33.29	28.6014721	24.1821094	38.699957
Ciay	63.13	53.00	66.89	61.28	75.05	15.10	55.02	72.11	63.57	69.8212408	27.4079158	58.0284115
water content, % (MGS)	70.51	66.50	75.52	70.34	81.23	48.81	69.86	79.97	79.57	80.01	62.40	66.59
water content, % (Baker)	71.5	68.7	0	73.1	82.2	47.8	70.8	79.8	80.5	80.4	57.4	68.1
Totai Nitrogen	0.3254	0.2849	0.4019	0.3731	0.5268	0.1284	0.3402	0.4607	0.4848	0.4736	0.1864	0.3326
Total Carbon	4.0113	3.5630	4.3338	4.1308	5.3231	2.4837	4.2545	4.6039	4.8249	4.4204	2.5554	4.5725
Totai Suifur	0.2330	0.1850	0.3723	0.2934	1.3985	0.3201	0.2141	0.5604	1.6410	1.4729	0.2666	0.2589
AVS												
<u>Metais (ug/g)</u>												
Cd	0.40	BDL	BDL	0.08	0.34	BDL	BDL	0.07	0.95	0.56	BDL	BDL
Cr	344.2	343.0	322.4	303.8	281.1	123.0	355.3	344.0	197.1	252.4	197.8	524.2
Сц	108.8	117.3	174.9	171.1	299.1	54.4	133.4	172.5	161.0	200.0	63.4	152.6
Fe	7.00	6.50	6.49	6.15	5.53	2.93	6.41	6.53	4.66	5.71	4.11	9.16
Mn	2610	2192	1276	1299	608	1053	2028	1154	405	466	1893	3381
Ni	80.7	68.6	75.6	74.3	84.3	32.0	68.8	85.0	67.3	73.9	57.7	69.7
Pb	91.6	121.4	128.8	129.0	147.2	20.2	110.0	154.4	111.7	113.9	52.0	157.0
Zn	570.7	525.0	574.0	559.7	630.4	170.8	476.9	554.3	458.2	499.4	280.1	715.0
Hg (ng/g)	284.4	183.96	135.7	325.7	143.46	77.49	114.34	25.18	303.05	85.35	143.26	518.56
Methyl-Hg (ng/g)	1.87	1.19			2.75		1.27		1.76	1.65		1.39
% Methyi	0.66	0.65			1.92		1.11		0.58	1.93		0.27

Analysis	24	25	26	27	28	29	30	31	32	33	34	35
<u>Grain Size (% dry weight)</u>												
Gravel	0	0	1.10	0	0	0	0	0	0	0	0	0
Sand	3.14861461	8.60318995	90.1292121	95.5563716	2.69277846	3.63288719	2.69121813	3.93811533	2.31303007	10.106383	7.13962946	3.46570397
Silt	33.6901763	41.7109715	3.7496833	3.0481087	37.3317013	42.4474187	37.9603399	42.7566807	44.2559753	40.2260638	55.8065974	44.2599278
Clay	63.1612091	49.6858386	5.0164682	1.39551965	59.9755202	53.9196941	59.3484419	53.3052039	53.4309946	49.6675532	37.0537732	52.2743682
water content, % (MGS)	70.93	70.71	24.21	32.08	79.82	85.75	82.27	86.56	83.59	81.69	76.64	83.65
water content, % (Baker)	73.8	68.1	65.6	28	82.3	86.7	83.6	87.4	85.2	83.7	78.2	83.4
Total Nitrogen	0.3525	0.3335	0.0728	0.0439	0.5176	0.5813	0.6103	0.7210	0.6200	0.6021	0.5476	0.6591
Total Carbon	4.6804	5.3398	2.2792	0.6385	11.3045	7.8309	7.5440	7.8635	6.8373	6.3146	5.7236	6.6376
Total Sulfur	0.4284	0.3156	0.0987	0.0000	1.6274	4.4510	1.6560	4.2948	2.8388	2.9180	2.1349	2.8886
AVS							·					
<u>Metals (ug/g)</u>												
Cd	0.08	BDL	0.01	BDL	5.34	9.28	6.54	7.65	6.63	5.31	5.95	8.35
Cr	320.7	572.3	67.9	51.9	1831.1	1536.4	1046.7	1141.7	1027.5	719.4	678.5	841.3
Cu	115.5	129.2	25.4	12.7	228.3	242.6	207.6	233.2	204.0	190.5	153.3	221.3
Fe	6.79	8.19	0.01	0.86	14.74	9.55	10.25	7.51	7.88	6.77	5.78	7.18
Mn	2009	3965	452	426	1210	630	721	555	537	364	365	460
NI	66.9	68.0	11.1	4.6	85.9	71.6	58.7	67.6	59.6	55.4	50.6	64.6
Pb	125.2	128.1	38.8	11.2	170.9	292.3	204.9	298.0	212.9	186.2	171.0	266.4
Zn	560.6	582.3	108.3	69.8	2105.4	2574.7	1762.6	2057.9	1720.2	1507.0	1786.0	2175.6
Hg (ng/g)	53.75	531.37	54.47	19.08	35.34	779.99	258.51	1219.39	62.58	166.9	602.75	1576.51
Methyl-Hg (ng/g)		1.85		0.07		1.39		1.02		2.29		1.52
% Methyl		0.35		0.37		0.18		0.08		1.37		0.1

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Analysis	36	37	38	39	40	41	42	43	44	45	46	47
<u>Grain Size (% dry weight)</u>												
Gravei	0	0	0.23016063	0	0	0	0	0	0	0	0	0
Sand	96.802589	2.91085506	63.1119636	1.87734668	1.79533214	1.00334448	3.71402043	2.11586902	2.59019426	7.12510356	7.11805556	19.0915076
Siit	1.41100324	26.1976956	17.2380724	31.9148936	33.1238779	30.5462653	31.0584958	34.2065491	23.7742831	29.0803645	29.5138889	27.8472679
Ciay	1.78640777	70.8914494	19.4198034	66.2077597	65.0807899	68.4503902	65.2274838	63.6775819	73.6355227	63.7945319	63.3680556	53.0612245
water content, % (MGS)	21.33	75.07	54.91	77.49	77.47	78.40	79.17	76.15	82.02	79.59	79.81	75.38
water content, % (Baker)	31.1	74.3	57	77.7	77.1	79.1	78.1	78.8	81.6	80	80	79.7
Total Nitrogen	0.0261	0.3198	0.1741	0.3726	0.3504	0.3226	0.3592	0.3942	0.4143	0.4125	0.4146	0.4425
Totai Carbon	0.3070	3.4713	3.0118	4.2459	4.3503	3.8608	4.5622	4.9336	4.8234	5.5735	4.9494	5.2018
Totai Suifur	0.0413	1.0840	0.8463	0.8143	0.4677	0.6894	0.7484	0.4120	0.9996	1.0470	0.9701	0.6964
AVS												
<u>Metais (ug/g)</u>												
Cd	BDL	0.93	17.60	1.68	0.74	0.65	1.35	1.33	0.48	1.73	1.56	1.49
Cr	34.3	283.6	235.9	271.1	276.1	277.0	377.7	458.2	414.0	324.8	281.2	264.4
Cu	8.6	138.5	331.3	155.1	123.7	120.8	192.1	158.4	275.9	311.2	270.8	353.7
· Fe	0.43	6.00	2.55	5.70	5.88	6.03	6.36	7.43	7.88	7.99	7.41	7.41
Mn	449	1363	310	1015	2800	2551	1934	3518	861	912	886	910
Ni	3.2	58.0	42.5	80.2	78.5	75.1	80.1	67.3	75.6	77.3	67.6	62.5
Pb	1.0	116.0	179.2	96.6	97.7	102.1	127.2	136.2	163.2	258.0	228.0	245.2
Zn	40.0	459.5	565.9	449.6	432.6	414.1	505.7	509.6	678.8	623.0	586.0	606.0
Hg (ng/g)	32.04	210.48	640.22	163.72	329.5	141.98	759.64	387.69	199.22	2340.32	· 526.67	968.88
Methyl-Hg (ng/g)			2.45	5.88		1.51		2.66	4.17		2.11	3.555
% Methyi			0.38	3.59		1.06		0.69	2.09		0.4	0.37

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Analysis	48	49	50	51	52	53	54	55	56	57	58	59
<u>Grain Size (% dry weight)</u>												
Gravel	0	0	0	0	0	0	5.71034483	0	0	0.40603248	0	0
Sand	18.1454303	4.52261307	4.3135192	4.90654206	5.28571429	27.9259492	81.462069	4.20630946	2.17391304	26.7401392	12.6822802	0.4498425
Silt	23.7491661	30.5695142	33.350868	30.0233645	31.7857143	27.8318168	5.29655172	39.4591888	47.8713768	40.4582367	51.9222271	51.506972
Clay	58.1054036	64.9078727	62.3356128	65.0700935	62.9285714	44.2422341	7.53103448	56.3345018	49.9547101	32.3955916	35.3954927	48.043184
water content, % (MGS)	82.05	82.47	81.51	81.44	80.69	72.72	26.84	77.20	72.31	63.68	71.58	73.90
water content, % (Baker)	83.2	82	82.7	82.4	81.7	72.4	40	78.3	74	64.7	66	70.2
Total Nitrogen	0.3955	0.4897	0.5151	0.5223	0.5392	0.2488	0.0728	0.4318	0.2816	0.1935	0.2139	0.2645
Total Carbon	4.3056	4.8899	5.1234	5.0827	5.2225	3.0380	1.3904	4.3777	3.6846	2.8855	3.3733	3.5385
Total Sulfur	2.6500	1.2460	1.5728	1.2939	1.3808	0.5558	0.2875	0.4605	0.3664	0.3841	0.3657	0.2801
AVS												
<u>Metals (ug/g)</u>												
Cd	2.06	0.66	1.79	1.95	1.84	0.44	0.93	2.08	0.48	0.96	1.31	1.01
Cr	288.7	226.5	138.6	160.4	132.2	270.7	129.0	216.1	193.8	179.5	185.5	187.2
Cu	438.2	294.7	184.4	215.3	175.9	138.3	77.8	113.9	131.4	127.4	129.4	148.5
Fe	8.28	6.37	4.10	4.50	3.82	4.90	2.56	4.64	5.12	4.17	4.72	5.05
Mn	928	488	357	392	313	1155	412	1333	1216	905	805	765
NI	67.2	59.1	50.0	54.4	48.0	58.6	15.2	83.5	61.2	52.4	55.2	65.8
Pb	236.6	184.3	142.6	136.1	122.1	98.5	42.5	117.1	92.1	88.1	85.9	113.9
Zn	785.5	590.8	479.9	506.6	455.9	310.0	254.4	478.0	329.8	296.4	319.0	355.3
Hg (ng/g)	867.1	842.89	119.98	185.86	200.7	370.54	20.15	450.96	557.1	413.41	436.23	398.78
Methyl-Hg (ng/g)	3.45	2.81	1.41	1.46	1.45	1.04	0.42	2.345				1.33
% Methyl	0.4	0.33	1.18	0.79	0.72	0.28	0.21	0.52				0.33

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Anaiysis	60	61	62	63	64	65	66	67	68	69	70	71
Grain Size (% dry weight)												
Gravel	0	0	0	0	0	0		2.02242251	0	Ó	3.3492823	0
Sand	3.48330914	3.08395203	1.61362618	1.13154173	2.14573089	4.21407501		57.6830073	17.1504838	18.7218722	57.7207482	11.0682111
SIIt	57.7285922	40.8909195	52.5324966	48.6916549	47.7425123	53.3080489		17.5642998	36.70337	25.1125113	17.3336233	43.6722437
Ciay	38.7880987	56.0251285	45.8538772	50.1768034	50.1117568	42.4778761		22.7302704	46.1461461	56.1656166	21.5963462	45.2595453
water content, % (MGS)	68.53	74.08	69.19	71.63	76.01	73.38		56.53	74.30	82.30	62.68	74.76
water content, % (Baker)	67.2	75.9	72.1	74.7	80.5	76.4	0	66.8	76.9	85.5	67.3	76.6
Total Nitrogen	0.2299	0.3015	0.2684	0.2958	0.3375	0.3450		0.2077	0.3706	0.4128	0.2304	0.2993
Total Carbon	3.2813	3.8228	3.5733	3.8136	4.5085	5.6975		3.4936	5.2817	6.1117	5.1820	5.5214
Totai Sulfur	0.2065	0.5192	0.2425	0.2986	0.4350	0.5802		0.6571	1.8281	2.7210	0.9544	2.1654
AVS												
<u>Metais (ug/g)</u>												
Cd	0.82	1.42	0.02	0.89	0.03	2.40		1.11	3.18	3.60	1.75	3.97
Cr	171.8	228.1	171.5	162.2	188.5	205.9		283.9	385.6	672.5	408.3	1119.3
Cu	102.1	157.7	106.9	125.4	117.1	176.3		291.0	293.1	532.1	201.3	399.7
Fe	4.90	5.19	4.94	4.73	5.04	4.08		3.56	4.45	5.69	2.98	5.12
Mn	1035	1495	1335	1195	1253	1096		1681	737	638	815	650
NI	61.1	62.5	63.3	58.0	69.7	85.9		36.3	59.6	68.5	37.7	83.2
Pb	79.1	100.9	70.9	79.0	77.8	167.4		154.7	227.9	1014.0	169.7	353.1
Zn	273.7	360.9	291.3	313.4	321.3	531.6		330.2	492.6	994.2	327.7	748.4
Hg (ng/g)	339.15	386.64	245.37	414.36	368.2	333.76		761.74	595.76	766.34	49.66\2201.8	7
Methyi-Hg (ng/g)	1.1		1.42			2.68			4.68		4.91	
% Methyi	0.32		0.58			0.8					0.22	

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Analysis	72	73	74	74J	75	76	77	78	79	80	81
<u>Grain Size (% dry weight)</u>											
Gravel	0	0	0		0	0	0	0	0	0	0
Sand	10.9665428	2.09339775	8.03757829		1.09170306	1.14285714	1.28205128	1.75746924	1.16539668	1.33667502	16.00259 <sup>•</sup>
Silt	53.7174721	37.3590982	42.5365344		50.8733624	41.9591837	42.3076923	46.8658465	43.6127297	39.0977444	49.98380
Clay	35.3159851	60.547504	49.4258873		48.0349345	56.8979592	56.4102564	51.3766842	55.2218736	59.5655806	34.01360
water content, % (MGS)	76.44	81.30	73.61		75.91	81.92	81.23	79.53	79.96	81.54	70.27
water content, % (Baker)	80	84.3	74.7	76.6	79.1	83.4	82.5	83.4	82.3	84.5	72
Total Nitrogen	0.4635	0.3675	0.3554		0.3609	0.5897	0.5979	0.5521	0.5591	0.5784	0.3282
Total Carbon	8.7522	5.8618	3.9551		3.7997	5.4694	5.5953	5.3856	5.4857	5.87 <b>1</b> 1	4.8709
Total Sulfur	1.8518	2.4951	0.3275		0.5051	0.7394	0.8116	0.7838	0.8247	0.8150	0.2680
AVS											
<u>Metals (ug/g)</u>											
Cd	2.56	3.49	0.85		0.28	3.12	4.27	4.20	3.92	5.30	2.73
Cr	247.2	891.7	155.0		238.1	321.2	345.4	329.2	343.7	405.0	325.9
Cu	225.4	396.0	69.1		151.4	179.6	187.1	174.2	209.0	229.5	140.0
Fe	4.38	4.99	4.48		4.93	4.95	4.94	4.80	4.81	5.20	3.92
Mn	<b>747</b>	745	3205		2131	1124	989	1178	1081	1011	654
NI	69.9	78.6	76.7		63.1	111.2	111.0	110.0	119.7	134.9	157.7
Pb	291.9	348.6	75.7		98.0	179.9	183.0	168.7	198.5	231.0	236.7
Zn	656.2	722.7	360.0		393.2	680.9	746.7	695.4	756.7	899.7	700.5
Hg (ng/g)	716.42	1286.49	177.53	246.02	315.25	439.54	944.68	651.89	965.6	263.49	650.44
Methyl-Hg (ng/g)		8.168	6.067	3.11	5.796	8.009	9.91	3.78	9.909	5.825	1.931
% Methyl		0.63	3.42	1.26	1.84	1.82	1.05	0.58	1.03	2.21	0.3

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# Appendix D

### SAS Results

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#### The MIXED Procedure

Class Level Information

Class Le	evels	Values
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YEAR	29	84.5 93.37 81.667 83.417
		83.917 84.917 85.333 85.917
		86.333 86.917 87.333 87.917
		88.333 88.917 89.333 89.917
		90.083 90.333 90.917 91.333
		91,917,92,333,92,917,93,917
		94 333 94 917 95 333 95 917
		96 333
CUDUTON	104	
STATION	104	1 2 3 4 5 6 7 8 9 10 11 12 13
		14 15 16 17 18 19 20 21 22 23
		24 25 26 27 28 29 30 31 32 33
		34 35 36 40 41 42 43 44 45 51
		52 53 54 55 56 58 59 60 61 63
		64 65 66 67 68 69 70 71 72 73
		74 75 76 77 78 80 81 82 83 84
		85 86 87 88 89 95 97 98 100
		102 107 109 111 114 116 231
		232 233 234 235 236 237 8.1
		21.2 24.1 25.1 28.1 233.1
		233.2 233.3 236.1

#### REML Estimation Iteration History

Iteration	Evaluations	Objective	Criterion
0	1	12011.444899	
1	3	10641.706035	0.00080370
2	4	10638.923255	0.00000947
3	1	10638.875174	0.0000004
4	1	10638.874958	0.0000000

Convergence criteria met.

Covariance Parameter Estimates (REML) Cov Parm Estimate STATION 10669.853934 Residual 4210.6290905

#### Model Fitting Information for ZN

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#### Tests of Fixed Effects

Source	NDF	DDF	Туре	III F	Pr > F
YEAR	28	1015		5.98	0.0001

#### Least Squares Means

Effect	YEAR	LSMEAN	Std Error	DF	t	Pr >  t
YEAR	84.5	234.86120136	17 19621378	537	13 66	0 0001
YEAR	93.37	293 98955364	1/ 53899258	303	20.22	0.0001
YEAR	81.667	312 32594486	19.90606090	525	20.22	0.0001
YEAR	83 417	220 50213821	18 21206009	614	10.01	0.0001
YEAR	83 917	220,00210021	10.21200009	614	12.11	0.0001
YEAR	84 917	226 38120136	17 10601000	014 537	12.74	0.0001
YEAR	85 333	220,50120130	17 19621370	537	13.16	0.0001
YEAR	85 917	232 80920136	17 19621370	531	13.82	0.0001
YEAR	86 333	221 05700331	17.19021370	537	13.54	0.0001
YEAR	86 917	221.03790331	17.160/3583	536	12.87	0.0001
YEAR	87 333	210.08431734	16 62575525	535	12.59	0.0001
YFAR	97 017	224.03244039	16.635/5535	490	13.52	0.0001
VEND	07.917	223.00916750	16.44334303	4/5~	13.56	0.0001
VEND	00.333	201.93044683	16.46862232	477	12.26	0.0001
ILAR	88.917	227.69117901	15.64098145	408	14.56	0.0001
ILAR	89.333	254.6206/6/1	16.32052583	464	15.60	0.0001
YEAR	89.917	270.17009176	16.33163960	464	16.54	0.0001
YEAR	90.083	252.09233016	13.15173806	237	19.17	0.0001
YEAR	90.333	293.22942906	13.96262125	284	21.00	0.0001
YEAR	90.917	258.22356642	13.81660679	273	18.69	0.0001
YEAR	91.333	257.63654486	13.53271336	254	19.04	0.0001
YEAR	91.917	280.59271403	13.54732706	254	20.71	0.0001
YEAR	92.333	257.13457299	13.82255555	273	18.60	0.0001
YEAR	92.917	.271.64061747	14.53899258	323	18.68	0.0001
YEAR	93.917	271.93506290	14.61151999	329	18.61	0.0001
YEAR	94.333	268.23506290	14.61151999	329	18.36	0.0001
YEAR	94.917	291.61188156	14,60742989	327	19 96	0 0001

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#### Least Squares Means

Effect	YEAR	LSMEAN	Std Error	DF	t	Pr >  t
YEAR	95.333	268.49835734	14.68320987	334	18.29	0.0001
YEAR YEAR	95.917 96.333	284.08723682 303.07089778	14.61151999	329 328	19.44 20.75	0.0001

Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	84.5	93.37	-59.12835228	16.29153429	1007	-3.63	0.0003
YEAR	84.5	81.667	-77.46474350	20.01189306	1010	-3.87	0.0001
YEAR	84.5	83.417	14.35906316	19.39671199	1010	0.74	0.4593
YEAR	84.5	83.917	3.71893458	19.23858330	1005	0.19	0.8468
YEAR	84.5	84.917	8.48000000	18.35348270	1005	0.46	0.6442
YEAR	84.5	85.333	-2.8000000	18.35348270	1005	-0.15	0.8788
YEAR	84.5	85.917	2.05200000	18.35348270	1005	0.11	0.9110
YEAR	84.5	86.333	13.80329806	18.38221439	1006	0.75	0.4529
YEAR	84.5	86.917	18.77668402	18.41164061	1006	1.02	0.3081
YEAR	84.5	87.333	10.02876098	17.87954965	1005	0.56	0.5750
YEAR	84.5	87.917	11.85203386	17.79788310	1006	0.67	0.5056
YEAR	84.5	88.333	32.93075453	17.74214515	1006	1.86	0.0637
YEAR	84.5	88.917	7.17002235	17.18239047	1008	0.42	0.6766
YEAR	84.5	89.333	-19.75947535	17.67288827	1007	-1.12	0.2638
YEAR	84.5	89.917	-35.30889040	17.64570483	1007	-2.00	0.0457
YEAR	84.5	90.083	-17.23112879	16.54414292	1069	-1.04	0.2979
YEAR	84.5	90.333	-58.36822770	16.00252675	1010	-3.65	0.0003
YEAR	84.5	90.917	-23.36236506	15.87406362	1010	-1.47	0.1414
YEAR	84.5	91.333	-22.77534349	15.88676322	1019	-1.43	0.1520
YEAR	84.5	91.917	-45.73151266	15.67544358	1010	-2.92	0.0036
YEAR	84.5	92.333	-22.27337162	15.87983229	1010	-1.40	0.1610
YEAR	84.5	92.917	-36.77941611	16.29153429	1007	-2.26	0.0242
YEAR ·	84.5	93.917	-37.07386154	16.34370785	1007	-2.27	0.0235
YEAR	84.5	94.333	-33.37386154	16.34370785	1007	-2.04	0.0414
YEAR	84.5	94.917	-56.75068020	16.47932121	1015	-3.44	0.0006
YEAR	84.5	95.333	-33.63715597	16.41810727	1007	-2.05	0.0407
YEAR	84.5	95.917	-49.22603545	16.34370785	1007	-3.01	0.0027
YEAR	84.5	96.333	-68.20969641	16.38150446	1008	-4.16	0.0001
YEAR	93.37	81.667	-18.33639122	18.03866810	1013	-1.02	0.3096
YEAR	93.37	83.417	73.48741543	17.42206150	1013	4.22	0.0001
YEAR	93.37	83.917	62.84728686	17.29769899	1007	3.63	0.0003
YEAR	93.37	84.917	67.60835228	16.29153429	1007	4.15	0.0001
YEAR	93.37	85.333	56.32835228	16.29153429	1007	3.46	0.0006
YEAR	93.37	85.917	61.18035228	16.29153429	1007	3.76	0.0002
YEAR	93.37	86.333	72.93165034	16.25976901	1007	4.49	0.0001

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Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	93.37	86.917	77.90503630	16.23050796	1007	4.80	0.0001
YEAR	93.37	87.333	69.15711326	15.69083100	1007	4.41	0.0001
YEAR	93.37	87.917	70.98038614	15.46188452	1007	4.59	0.0001
YEAR	93.37	88.333	92.05910681	15.51267723	1007	5.93	0.0001
YEAR	93.37	88.917	66.29837463	14.65901519	1009	4.52	0.0001
YEAR	93.37	89.333	39.36887693	15.37300583	1008	2.56	0.0106
YEAR	93.37	89.917	23.81946188	15.39839150	1009	1.55	0.1222
YEAR	93.37	90.083	41.89722349	13.78092698	1086	3.04	0.0024
YEAR	93.37	90.333	0.76012458	13.11868599	1011	0.06	0.9538
YEAR	93.37	90.917	35.76598722	12.92972855	1010	2.77	0.0058
YEAR	93.37	91.333	36.35300878	12.89566240	1022	2.82	0.0049
YEAR	93.37	91.917	13.39683962	12.64239119	1010	1.06	0.2895
YEAR	93.37	92.333	36.85498066	12.93109541	1010	2.85	0.0045
YEAR	93.37	92.917	22.34893617	13.38565299	1005	1.67	0.0953
YEAR	93.37	93.917	22.05449074	13.46799411	1006	1.64	0.1018
YEAR	93.37	94.333	25.75449074	13.46799411	1006	1.91	0.0561
YEAR	93.37	94.917	2.37767208	13.62461179	1016	0.17	0.8615
YEAR	93.37	95.333	25.49119631	13.54671237	1006	1.88	0.0602
YEAR	93.37	95.917	9.90231682	13.46799411	1006	0.74	0.4624
YEAR	93.37	96.333	-9.08134414	13.50254019	1007	-0.67	0.5014
YEAR	81.667	83.417	91.82380665	20.61915273	1006	4.45	0.0001
YEAR	81.667	83.917	81.18367807	20.86176924	1010	3.89	0.0001
YEAR	81.667	84.917	85.94474350	20.01189306	1010	4.29	0.0001
YEAR	81.667	85.333	74.66474350	20.01189306	1010	3.73	0.0002
YEAR	81.667	85.917	79.51674350	20.01189306	1010	3.97	0.0001
YEAR	81.667	86.333	91.26804155	20.04936928	1011	4.55	0.0001
YEAR	81.667	86.917	96.24142752	20.04547693	1011	4.80	0.0001
YEAR	81.667	87.333	87.49350447	19.50728856	1010	4.49	0.0001
YEAR	81.667	87.917	89.31677736	19.41412296	1011	4.60	0.0001
YEAR	81.667	88.333	110.39549803	19.38068052	1011	5.70	0.0001
YEAR	81.667	88.917	84.63476585	18.85023521	1013	4.49	0.0001
YEAR	81.667	89.333	57.70526815	19.32653099	1012	2.99	0.0029
YEAR	81.667	89.917	42.15585310	19.29204925	1012	2.19	0.0291
YEAR	81.667	90.083	60.23361470	18.26917845	1065	3.30	0.0010
YEAR	81.667	90.333	19.09651580	17.77622862	1016	1.07	0.2830
YEAR	81.66/	90.917	54.1023/844	17.66064340	1016	3.06	0.0022
YEAR	81.667	91.333	54.68940000	17.64128068	1023	3.10	0.0020
YEAR	81.667	91.917	31./3323083	17.48129210	1016	1.82	0.0098
YEAR	81.667	92.333	55.1913/18/	17.66523132	1010	3.12	0.0018
IEAR	81.66/	92.917	40.68532/39	10 00500010	1013	2.20	0.0243
YEAR	81.667	93.91/	40.39088195	10 00500617	1013	2.23	0.023./
ILAK	01.00/	94.333	44.09000193	10.000001146	1010	2.44 1 1/	0.0149
ILAK	01.00/	94.91/ 05 222	20./1400329	10.10001140	1013	1.14 2.10	0.2330
ILAK	01.00/	30.333	43.02/30/32	TO'T#JCJCJJ	TOTO	2.42	0.0109

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Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	81.667	95.917	28.23870804	18,08598617	1013	1 56	0 1188
YEAR	81.667	96.333	9.25504708	18.10975222	1014	0.51	0.1100
YEAR	83.417	83.917	-10.64012858	20.25684059	1009	-0.53	0.0094
YEAR	83.417	84.917	-5.87906316	19.39671199	1010	-0.30	0.3993
YEAR	83.417	85.333	-17.15906316	19.39671199	1010	-0.88	0.7019
YEAR	83.417	85.917	-12.30706316	19.39671199	1010	-0.63	0.5700
YEAR	83.417	86.333	-0.55576510	19.43238055	1010	-0.03	0.3233
YEAR	83.417	86.917	4.41762087	19.46650862	1010	0.03	0.9772
YEAR	83.417	87.333	-4.33030218	18.90635207	1010	-0.23	0.0203
YEAR	83.417	87.917	-2.50702930	18.84245378	1010	-0.13	0.0109
YEAR	83.417	88.333	18.57169137	18.77663486	1010	0 99	0.3229
YEAR	83.417	88.917	-7.18904080	18.26036137	1013	-0.39	0.5225
YEAR	83.417	89.333	-34.11853850	18.71854030	1011	-1.82	0.0686
YEAR	83.417	89.917	-49.66795355	18.68553150	1011	-2.66	0 0080
YEAR	83.417	90.083	-31.59019195	17.66297324	1068	-1.79	0.0740
YEAR	83.417	90.333	-72.72729085	17.15026988	1016	-4.24	0.0001
YEAR	83.417	90.917	-37.72142821	17.03041421	1016	-2.21	0.0270
YEAR	83.417	91.333	-37.13440665	17.01205732	1023	-2.18	0.0293
YEAR	83.417	91.917	-60.09057582	16.84436840	1016	-3.57	0.0004
YEAR	83.417	92.333	-36.63243478	17.03518785	1016	-2.15	0.0318
YEAR	83.417	92.917	-51.13847926	17.42206150	1013	-2.94	0.0034
YEAR	83.417	93.917	-51.43292470	17.47104895	1013	-2.94	0.0033
YEAR	83.417	94.333	-47.73292470	17.47104895	1013	-2.73	0.0064
YEAR	83.417	94.917	-71.10974336	17.57774349	1019	-4.05	0.0001
YEAR	83.417	95.333	-47.99621913	17.53089614	1013	-2.74	0.0063
YEAR	83.417	95.917	-63.58509861	17.47104895	1013	-3.64	0.0003
YEAR	83.417	96.333	-82.56875957	17.49623631	1014	-4.72	0.0001
YEAR	83.917	84.917	4.76106542	19.23858330	1005	0.25	0.8046
YEAR	83.917	85.333	-6.51893458	19.23858330	1005	-0.34	0.7348
YEAR	83.917	85.917	-1.66693458	19.23858330	1005	-0.09	0.9310
YEAR	83.917	86.333	10.08436348	19.27291107	1006	0.52	0.6009
YEAR	83.917	86.917	15.05774944	19.30741795	1006	0.78	0.4356
YEAR	83.917	87.333	6.30982640	18.78846899	1006	0.34	0.7371
YEAR	83.917	87.917	8.13309928	18.72300166	1006	0.43	0.6641
YEAR	83.917	88.333	29.21181995	18.65812948	1006	1.57	0.1177
YEAR	83.917	88.917	3.45108777	18.13878247	1008	0.19	0.8491
YEAR	83.917	89.333	-23.47840993	18.59846417	1007	-1.26	0.2071
YEAR	83.917	89.917	-39.02782497	18.56665495	1007	-2.10	0.0358
YEAR	83.917	90.083	-20.95006337	17.52821316	1064	-1.20	0.2323
YEAR	83.917	90.333	-62.08716228	17.02546917	1010	-3.65	0.0003
YEAR	83.917	90.917	-27.08129963	16.90480874	1010	-1.60	0.1095
YEAR	83.917	91.333	-26.49427807	16.92245628	1018	-1.57	0.1177
YEAR	83.917	91.917	-49.45044724	16.71858830	1010	-2.96	0.0032
YEAR	83.917	92.333	-25.99230620	16.91037507	1010	-1.54	0.1246

Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	83.917	92.917	-40.49835069	17.29769899	1007	-2.34	0.0194
YEAR	83.917	93.917	-40.79279612	17.34683959	1007	-2.35	0.0189
YEAR	83.917	94.333	-37.09279612	17.34683959	1007	-2.14	0.0327
YEAR	83.917	94.917	-60.46961478	17.47857589	1014	-3.46	0.0006
YEAR	83.917	95.333	-37.35609055	17.41898103	1007	-2.14	0.0322
YEAR	83.917	95.917	-52.94497003	17.34683959	1007	-3.05	0.0023
YEAR	83.917	96.333	-71.92863099	17.38448937	1008	-4.14	0.0001
YEAR	84.917	85.333	-11.28000000	18.35348270	1005	-0.61	0.5390
YEAR	84.917	85.917	-6.42800000	18.35348270	1005	-0.35	0.7262
YEAR	84.917	86.333	5.32329806	18.38221439	1006	0.29	0.7722
YEAR	84.917	86.917	10.29668402	18.41164061	1006	0.56	0.5761
YEAR	84.917	87.333	1.54876098	17.87954965	1005	0.09	0.9310
YEAR	84.917	87.917	3.37203386	17.79788310	1006	0.19	0.8498
YEAR	84.917	88.333	24.45075453	17.74214515	1006	1.38	0.1685
YEAR	84.917	88.917	-1.30997765	17.18239047	1008	-0.08	0.9392
YEAR	84.917	89.333	-28.23947535	17.67288827	1007	-1.60	0.1104
YEAR	84.917	89.917	-43.78889040	17.64570483	1007	-2.48	0.0132
YEAR	84.917	<u>9</u> 0.083	-25.71112879	16.54414292	1069	-1.55	0.1205
YEAR	84.917	90.333	-66.84822770	16.00252675	1010	-4.18	0.0001
YEAR	84.917	90.917.	-31.84236506	15.87406362	1010	-2.01	0.0451
YEAR	84.917	91.333	-31.25534349	15.88676322	1019	-1.97	0.0494
YEAR	84.917	91.917	-54.21151266	15.67544358	1010	-3.46	0.0006
YEAR	84.917	92.333	-30.75337162	15.87983229	1010	-1.94	0.0531
YEAR	84.917	92.917	-45.25941611	16.29153429	1007	-2.78	0.0056
YEAR	84.917	93.917	-45.55386154	16.34370785	1007	-2.79	0.0054
YEAR	84.917	94.333	-41.85386154	16.34370785	1007	-2.56	0.0106
YEAR	84.917	94.917	-65.23068020	16.47932121	1015	-3.96	0.0001
YEAR	84.917	95.333	-42.11715597	16.41810727	1007	-2.57	0.0105
YEAR	84.917	95.917	-57.70603545	16.34370785	1007	-3.53	0.0004
YEAR	84.917	96.333	-76.68969641	16.38150446	1008	-4.68	0.0001
YEAR	85.333	85.917	4.85200000	18.35348270	1005	0.26	0.7916
YEAR	85.333	86.333	16.60329806	18.38221439	1006	0.90	0.3666
YEAR	85.333	86.917	21.57668402	18.41164061	1006	1.17	0.2415
YEAR	85.333	87.333	12.82876098	17.87954965	1005	0.72	0.4732
YEAR	85.333	87.917	14.65203386	17.79788310	1006	0.82	0.4106
YEAR	85.333	88.333	35.73075453	17.74214515	1006	2.01	0.0443
YEAR	85.333	88.917	9.97002235	17.18239047	1008	0.58	0.5619
YEAR	85.333	89.333	-16.95947535	17.67288827	1007	-0.96	0.3375
YEAR	85.333	89.917	-32.50889040	1/.645/0483	100/	-1.84	0.0657
YEAR	85.333	90.083	-14.43112879	16.54414292	1069	-0.87	0.3833
YEAR	85.333	90.333	-55.56822770	16.00252675	1010	-3.47	0.0005
YEAR	85.333	90.91/	-20.56236506	15.8/406362	1010	-1.30	0.1955
YEAR	85.333	91.333	-19.9/534349	15.886/6322	1010	-1.26	0.2089
YEAR	85.333	91.917	-42.93151266	15.6/544358	TOTO	-2.14	0.0063

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Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	85.333	92.333	-19.47337162	15.87983229	1010	-1.23	0.2204
YEAR	85.333	92.917	-33.97941611	16.29153429	1007	-2.09	0.0373
YEAR	85.333	93.917	-34.27386154	16.34370785	1007	-2.10	0.0362
YEAR	85.333	94.333	-30.57386154	16.34370785	1007	-1.87	0.0617
YEAR	85.333	94.917	-53.95068020	16.47932121	1015	-3.27	0.0011
YEAR	85.333	95.333	-30.83715597	16.41810727	1007	-1.88	0.0606
YEAR	85.333	95.917	-46.42603545	16.34370785	1007	-2.84	0.0046
YEAR	85.333	96.333	-65.40969641	16.38150446	1008	-3.99	0.0001
YEAR	85.917	86.333	11.75129806	18.38221439	1006	0.64	0.5228
YEAR	85.917	86.917	16.72468402	18.41164061	1006	0.91	0.3639
YEAR	85.917	87.333	7.97676098	17.87954965	1005	0.45	0.6556
YEAR	85.917	87.917	9.80003386	17.79788310	1006	0.55	0.5820
YEAR	85.917	88.333	30.87875453	17.74214515	1006	1.74	0.0821
YEAR	85.917	88.917	5.11802235	17.18239047	1008	0.30	0.7659
YEAR	85.917	89.333	-21.81147535	17.67288827	1007	-1.23	0.2174
YEAR	85.917	89.917	-37.36089040	17.64570483	1007	-2.12	0.0345
YEAR	85.917	90.083	-19.28312879	16.54414292	1069	-1.17	0.2441
YEAR	85.917	90.333	-60.42022770	16.00252675	1010	-3.78	0.0002
YEAR	85.917	90.917	-25.41436506	15.87406362	1010	-1.60	0.1097
YEAR	85.917	91.333	-24.82734349	15.88676322	1019	-1.56	0.1184
YEAR	85.917	91.917	-47.78351266	15.67544358	1010	-3.05	0.0024
YEAR	85.917	92.333	-24.32537162	15.87983229	1010	-1.53	0.1259
YEAR	85.917	92.917	-38.83141611	16.29153429	1007	-2.38	0.0173
YEAR	85.917	93.917	-39.12586154	16.34370785	1007	-2.39	0.0169
YEAR	85.917	94.333	-35.42586154	16.34370785	1007	-2.17	0.0304
YEAR	85.917	94.917	-58.80268020	16.47932121	1015	-3.57	0.0004
YEAR	85.917	95.333	-35.68915597	16.41810727	1007	-2.17	0.0300
YEAR	85.917	95.917	-51.27803545	16.34370785	1007	-3.14	0.0018
YEAR	85.917	96.333	-70.26169641	16.38150446	1008	-4.29	0.0001
YEAR	86.333	86.917	4.97338596	18.38117507	1006	0.27	0.7868
YEAR	86.333	87.333	-3.77453708	17.90421016	1006	-0.21	0.8331
YEAR	86.333	87.917	-1.95126420	17.76831155	1006	-0.11	0.9126
YEAR	86.333	88.333	19.12745647	17.76536424	1006	1.08	0.2819
YEAR	86.333	88.917	-6.63327571	17.15254093	1008	-0.39	0.6990
YEAR	86.333	89.333	-33.56277340	17.64524854	1007	-1.90	0.0574
YEAR	86.333	89.917	-49.11218845	1/.66/8/611	1007	-2.78	0.0055
YEAR	86.333	. 90.083	-31.03442685	16.5236/61/	1069	-1.88	0.0606
IEAR	86.333	90.333	-/2.1/1525/5	15.9/098663	1010	-4.52	0.0001
ILAK	86.333	90.917	-3/.10566311	15.84223339	1010	-2.35	0.0192
ILAK	86.333	91.333	-36.5/864155	15.85391394	1010	-2.31	0.0212
ILAK	86.333	91.91/	-59.534810/2	15.04321439	1010	-3.81	0.0001
ILAR	86.333	92.333	-30.0/000968	10.04/92851	1002	-2.28	0.0230
ILAK	86.333	92.917	-50.582/1417	16.259/6901	1007	-3.11	0.0019
ILAK	00.333	93.91/	-20.0//12900	10.31201842	TUU/	-3.12	0.0019

Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	86.333	94.333	-47.17715960	16.31201842	1007	-2.89	0.0039
YEAR	86.333	94.917	-70.55397826	16.44715296	1014	-4.29	0.0001
YEAR	86.333	95.333	-47.44045403	16.38606039	1007	-2.90	0.0039
YEAR	86.333	95.917	-63.02933351	16.31201842	1007	-3.86	0.0001
YEAR	86.333	96.333	-82.01299447	16.34944565	1008	-5.02	0.0001
YEAR	86.917	87.333	-8.74792305	17.92969949	1006	-0.49	0.6257
YEAR	86.917	87.917	-6.92465016	17.74152439	1006	-0.39	0.6964
YEAR	86.917	88.333	14.15407051	17.78952730	1006	0.80	0.4264
YEAR	86.917	88.917	-11.60666167	17.12575144	1007	-0.68	0.4981
YEAR	86.917	89.333	-38.53615937	17.66735109	1007	-2.18	0.0294
YEAR	86.917	89.917	-54.08557442	17.69149156	1007	-3.06	0.0023
YEAR	86.917	90.083	-36.00781282	16.49205733	1069	-2.18	0.0292
YEAR	86.917	90.333	-77.14491172	15.94121841	1009	-4.84	0.0001
YEAR	86.917	90.917	-42.13904908	15.81225652	1009	-2.66	0.0078
YEAR	86.917	91.333	-41.55202752	15.82234023	1018	-2.63	0.0088
YEAR	86.917	91.917	-64.50819669	15.61287513	1009	-4.13	0.0001
YEAR	86.917	92.333	-41.05005564	15.81795356	1009	-2.60	0.0096
YEAR	86.917	92.917	-55.55610013	16.23050796	1007	-3.42	0.0006
YEAR	86.917	93.917	-55.85054556	16.28284239	1006	-3.43	0.0006
YEAR	86.917	94.333	-52.15054556	16.28284239	1006	-3.20	0.0014
YEAR	86.917	94.917	-75.52736422	16.41721171	1014	-4.60	0.0001
YEAR	86.917	95.333	-52.41384000	16.35641908	1007	-3.20	0.0014
YEAR	86.917	95.917	-68.00271948	16.28284239	1006	-4.18	0.0001
YEAR	86.917	96.333	-86.98638044	16.31977137	1008	-5.33	0.0001
YEAR	87.333	87.917	1.82327288	17.24943369	1006	0.11	0.9158
YEAR	87.333	88.333	22.90199355	17.20049906	1005	1.33	0.1833
YEAR	87.333	88.917	-2.85873862	16.61397519	1008	-0.17	0.8634
YEAR	87.333	89.333	-29.78823632	17.12471355	1007	-1.74	0.0823
YEAR	87.333	89.917	-45.33765137	17.10087505	1007	-2.65	0.0081
YEAR	87.333	90.083	-27.25988977	15.97458698	1073	-1.71	0.0882
YEAR	87.333	90.333	-68.39698867	15.39164789	1010	-4.44	0.0001
YEAR	87.333	90.917	-33.39112603	15.25794673	1010	-2.19	0.0289
YEAR	87.333	91.333	-32.80410447	15.26684865	1019	-2.15	0.0319
YEAR	87.333	91.917	-55.76027364	15.05104632	1011	-3.70	0.0002
YEAR	87.333	92.333	-32.30213260	15.26372898	1010	-2.12	0.0346
YEAR	87.333	92.917	-46.80817708	15.69083100	1007	-2.98	0.0029
YEAR	87.333	93.917	-47.10262252	15.74498460	1007	-2.99	0.0028
YEAR	87.333	94.333	-43.40262252	15.74498460	1007	-2.76	0.0059
YEAR	87.333	94.917	-66.77944118	15.88268809	1015	-4.20	0.0001
YEAR	87.333	95.333	-43.66591695	15.82059654	1007	-2.76	0.0059
YEAR	87.333	95.917	-59.25479643	15./4498460	1007	-3./6	0.0002
YEAR	87.333	96.333	-/8.23845/39	15./8262820	1008	-4.96	0.0001
YEAR	87.917	88.333	21.07872067	1/.08/34125	1005	1.23	0.21/6
YEAR	87.917	88.91/	-4,68ZU1151	10.398880032	TUU/	-0.29	0.//33

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Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	87.917	89.333	-31.61150921	16.96189322	1007	-1.86	0.0627
YEAR	87.917	89.917	-47.16092426	16.98533965	1007	-2.78	0.0056
YEAR	87.917	90.083	-29.08316265	15.75313941	1073	-1.85	0.0651
YEAR	87.917	90.333	-70.22026156	15.15911365	1010	-4.63	0.0001
YEAR	87.917	90.917	-35.21439892	15.02330942	1009	-2.34	0.0193
YEAR	87.917	91.333	-34.62737735	15.03748882	1019	-2.30	0.0215
YEAR	87.917	91.917	-57.58354652	14.81328985	1010	-3.89	0.0001
YEAR	87.917	92.333	-34.12540548	15.02923727	1010	-2.27	0.0234
YEAR	87.917	92.917	-48.63144997	15.46188452	1007	-3.15	0.0017
YEAR	87.917	93.917	-48.92589540	15.51678026	1006	-3.15	0.0017
YEAR	87.917	94.333	-45.22589540	15.51678026	1006	-2.91	0.0036
YEAR	87.917	94.917	-68.60271406	15.65401965	1015	-4.38	0.0001
YEAR	87.917	95.333	-45.48918983	15.59200221	1006	-2.92	0.0036
YEAR	87.917	95.917	-61.07806931	15.51678026	1006	-3.94	0.0001
YEAR	87.917	96.333	-80.06173028	15.55363845	1008	-5.15	0.0001
YEAR	88.333	88.917	-25.76073218	16.44569135	1008	-1.57	0.1176
YEAR	88.333	89.333	-52.69022988	16.96280781	1007	-3.11	0.0019
YEAR	88.333	89.917	-68.23964493	16.94016795	1007	-4.03	0.0001
YEAR	88.333	90.083	-50.16188332	15.79579390	1074	-3.18	0.0015
YEAR	88.333	90.333	-91.29898223	15.21017260	1010	-6.00	0.0001
YEAR	88.333	90.917	-56.29311959	15.07482898	1010	-3.73	0.0002
YEAR	88.333	91.333	-55.70609802	15.09136949	1020	-3.69	0.0002
YEAR	88.333	91.917	-78.66226719	14.86551474	1011	-5.29	0.0001
YEAR	88.333	92.333	-55.20412615	15.08082173	1010	-3.66	0.0003
YEAR	88.333	92.917	-69.71017064	15.51267723	1007	-4.49	0.0001
YEAR	88.333	93.917	-70.00461607	15.56742512	1007	-4.50	0.0001
YEAR	88.333	94.333	-66.30461607	15.56742512	1007	-4.26	0.0001
YEAR	88.333	94.917	-89.68143473	15.70579614	1015	-5.71	0.0001
YEAR	88.333	95.333	-66.56791050	15.64339471	1007	-4.26	0.0001
YEAR	88.333	95.917	-82.15678998	15.56742512	1007	-5.28	0.0001
YEAR	88.333	96.333	-101.1404509	15.60507303	1008	-6.48	0.0001
YEAR	88.917	89.333	-26.92949770	16.23937186	1007	-1.66	0.0976
YEAR	88.917	89.917	-42.47891275	16.26317164	1007	-2.61	0.0091
YEAR	88.917	90.083	-24.40115115	14.95143783	1080	-1.63	0.1030
YEAR	88.917	90.333	-65.53825005	14.37732174	1013	-4.56	0.0001
YEAR	88.917	90.917	-30.53238741	14.14976543	1011	-2.16	0.0312
YEAR	88.917	91.333	-29.94536585	14.22546846	1023	-2.11	0.0355
YEAR	88.917	91.917	-52.90153501	13.93093897	1012	-3.80	0.0002
YEAR	88.917	92.333	-29.44339397	14.23852399	1013	-2.07	0.0389
YEAR	88.917	92.917	-43.94943846	14.65901519	1009	-3.00	0.0028
YEAR	88.917	93.917	-44.24388389	14.71696019	1009	-3.01	0.0027
YEAR	88.917	94.333	-40.54388389	14.71696019	1009	-2.75	0.0060
YEAR	88.917	94.917	-63.92070255	14.87434979	1018	-4.30	0.0001
YEAR	88.917	95.333	-40.80717833	14.79384366	1009	-2.76	0.0059

Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	88.917	95.917	-56.39605781	14.71696019	1009	-3.83	0.0001
YEAR	88.917	96.333	-75.37971877	14.75337427	1010	-5.11	0.0001
YEAR	89.333	89.917	-15.54941505	16.77622059	1006	-0.93	0.3542
YEAR	89.333	90.083	2.52834655	15.66221524	1076	0.16	0.8718
YEAR	89.333	90.333	-38.60875235	15.06784579	1012	-2.56	0.0105
YEAR	89.333	90.917	-3.60288971	14.93038453	1012	-0.24	0.8094
YEAR	89.333	91.333	-3.01586815	14.94561225	1022	-0.20	0.8401
YEAR	89.333	91.917	-25.97203732	14.71891462	1012	-1.76	0.0779
YEAR	89.333	92.333	-2.51389628	14.93714129	1012	-0.17	0.8664
YEAR	89.333	92.917	-17.01994076	15.37300583	1008	-1.11	0.2685
YEAR	89.333	93.917	-17.31438619	15.42827950	1008	-1.12	0.2620
YEAR	89.333	94.333	-13.61438619	15.42827950	1008	-0.88	0.3778
YEAR	89.333	94.917	-36.99120485	15.56677082	1017	-2.38	0.0177
YEAR	89.333	95.333	-13.87768063	15.50441738	1008	-0.90	0.3710
YEAR	89.333	95.917	-29.46656011	15.42827950	1008	-1.91	0.0564
YEAR	89.333	96.333	-48.45022107	15.46567514	1010	-3.13	0.0018
YEAR	89.917	90.083	18.07776160	15.67764215	1076	1.15	0.2491
YEAR	89.917	90.333	-23.05933730	15.09303930	1012	-1.53	0.1269
YEAR	89.917	90.917	11.94652534	14.95583994	1012	0.80	0.4246
YEAR	89.917	91.333	12.53354690	14.97196354	1022	0.84	0.4027
YEAR	89.917	91.917	-10.42262227	14.74473053	1013	-0.71	0.4798
YEAR	89.917	92.333	13.03551877	14.96266033	1012	0.87	0.3838
YEAR	89.917	92.917	-1.47052571	15.39839150	1009	-0.10	0.9239
YEAR	89.917	93.917	-1.76497115	15.45359703	1009	-0.11	0.9091
YEAR	89.917	94.333	1.93502885	15.45359703	1009	0.13	0.9004
YEAR	89.917	94.917	-21.44178981	15.59251405	1017	-1.38	0.1694
YEAR	89.917	95.333	1.67173442	15.53005160	1009	0.11	0.9143
YEAR	89.917	95.917	-13.91714506	15.45359703	1009	-0.90	0.3680
YEAR	89.917	96.333	-32.90080602	15.49132085	1010	-2.12	0.0339
YEAR	90.083	90.333	-41.13709890	13.04280979	1086	-3.15	0.0017
YEAR	90.083	90.917	-6.13123626	12.91960623	1088	-0.47	0.6352
YEAR	90.083	91.333	-5.54421470	12.77562085	1093	-0.43	0.6644
YEAR	90.083	91.917	-28.50038387	12.68913241	1091	-2.25	0.0249
YEAR	90.083	92.333	-5.04224283	12.97298348	1089	-0.39	0.6976
YEAR	90.083	92.917	-19.54828731	13.78092698	1086	-1.42	0.1563
YEAR	90.083	93.917 <sup>-</sup>	-19.84273275	13.84998988	1085	-1.43	0.1522
YEAR	90.083	94.333	-16.14273275	13.84998988	1085	-1.17	0.2441
YEAR	90.083	94.917	-39.51955141	13.95149490	1090	-2.83	0.0047
YEAR	90.083	95.333	-16.40602718	13.92317151	1085	-1.18	0.2389
YEAR	90.083	95.917	-31.99490666	13.84998988	1085	-2.31	0.0211
YEAR	90.083	96.333	-50.97856762	13.86941376	1086	-3.68	0.0002
YEAR	90.333	90.917	35.00586264	12.25968763	1007	2.86	0.0044
YEAR	90.333	91.333	35.59288420	12.23295204	1020	2.91	0.0037
YEAR	90.333	91.917	12.63671503	12.04814205	1009	1.05	0.2945

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Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	90.333	92.333	36.09485607	12.32567580	1009	2.93	0.0035
YEAR	90.333	92.917	21.58881159	13.11868599	1011	1.65	0.1001
YEAR	90.333	93.917	21.29436616	13.20544524	1011	1.61	0.1072
YEAR	90.333	94.333	24.99436616	13.20544524	1011	1.89	0.0587
YEAR	90.333	94.917	1.61754750	13.34634522	1022	0.12	0.9036
YEAR	90.333	95.333	24.73107172	13.28738140	1011	1.86	0.0630
YEAR	90.333	95.917	9.14219224	13.20544524	1011	0.69	0.4889
YEAR	90.333	96.333	-9.84146872	13.23769752	1012	-0.74	0.4574
YEAR	90.917	91.333	0.58702156	12.10216958	1022	0.05	0.9613
YEAR	90.917	91.917	-22.36914761	11.83539867	1008	-1.89	0.0590
YEAR	90.917	92.333	1.08899343	12.17129597	1009	0.09	0.9287
YEAR	90.917	92.917	-13.41705105	12.92972855	1010	-1.04	0.2997
YEAR	90.917	93.917	-13.71149648	13.01628977	1010	-1.05	0.2924
YEAR	90.917	94.333	-10.01149648	13.01628977	1010	-0.77	0.4420
YEAR	90.917	94.917	-33.38831515	13.17106601	1022	-2.53	0.0114
YEAR	90.917	95.333	-10.27479092	13.09864437	1010	-0.78	0.4330
YEAR	90.917	95.917	-25.86367040	13.01628977	1010	-1.99	0.0472
YEAR	90.917	96.333	-44.84733136	13.04900082	1012	-3.44	0.0006
YEAR	91.333	91.917	-22.95616917	11.73347424	1020	-1.96	0.0507
YEAR	91.333	92.333	0.50197187	12.01818346	1019	0.04	0.9667
YEAR	91.333	92.917	-14.00407261	12.89566240	1022	-1.09	0.2778
YEAR	91.333	93.917	-14.29851805	12.98302579	1022	-1.10	0.2710
YEAR	91.333	94.333	-10.59851805	12.98302579	1022	-0.82	0.4145
YEAR	91.333	94.917	-33.97533671	13.05754698	1031	-2.60	0.0094
YEAR	91.333	95.333	-10.86181248	13.05955714	1022	-0.83	0.4058
YEAR	91.333	95.917	-26.45069196	12.98302579	1022	-2.04	0.0419
YEAR	91.333	96.333	-45.43435292	12.95751340	1021	-3.51	0.0005
YEAR	91.917	92.333	23.45814104	11.80264245	1006	1.99	0.0471
YEAR	91.917	92.917	8.95209655	12.64239119	1010	0.71	0.4790
YEAR	91.917	93.917	8.65765112	12.72929402	1010	0.68	0.4966
YEAR	91.917	94.333	12.35765112	12.72929402	1010	0.97	0.3319
YEAR	91.917	94.917	-11.01916754	12.88337694	1023	-0.86	0.3926
YEAR	91.917	95.333	12.09435669	12.81231719	1010	0.94	0.3454
YEAR	91.917	95.917	-3.49452279	12.72929402	1010	-0.27	0.7837
YEAR	91.917	96.333	-22.47818375	12.76107557	1012	-1.76	0.0785
YEAR	92.333	92.917	-14.50604449	12.93109541	1010	-1.12	0.2622
YEAR	92.333	93.917	-14.80048992	13.01779473	1010	-1.14	0.2558
YEAR	92.333	94.333	-11.10048992	13.01779473	1010	-0.85	0.3940
YEAR	92.333	94.917	-34.47730858	13.15913003	1022	-2.62	0.0089
YEAR	92.333	95.333	-11.36378435	13.09995177	1010	-0.87	0.3859
YEAR	92.333	95.917	-26.95266383	13.01779473	1010	-2.07	0.0387
YEAR	92.333	96.333	-45.93632479	13.04960813	1012	-3.52	0.0005
YEAR	92.917	93.917	-0.29444543	13.46799411	1006	-0.02	0.9826
YEAR	92.917	94.333	3.40555457	13.46799411	1006	0.25	0.8004

Effect	YEAR	_YEAR	Difference	Std Error	DF	t	Pr >  t
YEAR	92.917	94.917	-19.97126409	13.62461179	1016	-1.47	0.1430
YEAR	92.917	95.333	3.14226013	13.54671237	1006	0.23	0.8166
YEAR	92.917	95.917	-12.44661935	13.46799411	1006	-0.92	0.3556
YEAR	92.917	96.333	-31.43028031	13.50254019	1007	-2.33	0.0201
YEAR	93.917	94.333	3.70000000	13.53036696	1005	0.27	0.7846
YEAR	93.917	94.917	-19.67681866	13.68686765	1016	-1.44	0.1508
YEAR	93.917	95.333	3.43670557	13.60873117	1005	0.25	0.8007
YEAR	93.917	95.917	-12.15217391	13.53036696	1005	-0.90	0.3693
YEAR	93.917	96.333	-31.13583487	13.56501301	1007	-2.30	0.0219
YEAR	94.333	94.917	<del>-</del> 23.37681866	13.68686765	1016	-1.71	0.0879
YEAR	94.333	95.333	-0.26329443	13.60873117	1005	-0.02	0.9846
YEAR	94.333	95.917	-15.85217391	13.53036696	1005	<del>-</del> 1.17	0.2416
YEAR	94.333	96.333	-34.83583487	13.56501301	1007	-2.57	0.0104
YEAR	94.917	95.333	23.11352423	13.75778703	1016	1.68	0.0933
YEAR	94.917	95.917	7.52464475	13.68686765	1016	0.55	0.5826
YEAR	94.917	96.333	-11.45901621	13.71327626	1018	-0.84	0.4036
YEAR	95.333	95.917	-15.58887948	13.60873117	1005	-1.15	0.2523
YEAR	95.333	96.333	-34.57254044	13.63642660	1007	-2.54	0.0114
YEAR	95.917	96.333	-18.98366096	13.56501301	1007	-1.40	0.1620

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#### Differences of Least Squares Means

D-12

The SAS System



D-13

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#### The SAS System

OBS	YEAR	_TYPE_	_FREQ_	ZN
1	81.667	0	19	266.632
2	83.417	0	21	167.743
3	83.917	0	21	193.095
4	84.500	0	25	206.000
5	84.917	0	25	197.520
6	85.333	0	25	208.800
7	85.917	0	25	203.948
8	86.333	0	25	188.676
9	86.917	0	25	180.928
10	87.333	0	28	200.636
11	87.917	0	29	192.741
12	88.333	0	29	177.090
13	88.917	0	35	205.271
14	89.333	0	30	221.683
15	89.917	0	30	240.167
16	90.083	0	67	258.669
17	90.333	0	55	302.440
18	90.917	0	58	269.819
19	91.333	0	63	266.570
20	91.917	0	64	292.506
21	92.333	0	58	268.191
22	92.917	0	47	273.204
23	93.370	0	47	295.553
24	93.917	0	46	274.198
25	94.333	0	46	270.498
26	94.917	0	46	295.467
27	95.333	0	45	268.351
28	95.917	0	46	286.350
29	96.333	0	46	304.396
### The MIXED Procedure

Class Level Information

Class	Levels	Values

 STATION
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### REML Estimation Iteration History

Iteration	Evaluations	Objective	Criterion
0 1	1 5	2719.5724799 2423.5172316	0.00000498
2	1	2423.5113657	0.0000001

Convergence criteria met.

Covariance Parameter Estimates (REML)

Cov Parm	Estimate	
STATION	11225.063807	
Residual	3193.3029431	

Model Fitting Information for ZN

Value

Description

Observations	257.0000
Res Log Likelihood	-1446.09
Akaike's Information Criterion	-1448.09
Schwarz's Bayesian Criterion	-1451.63
-2 Res Log Likelihood	2892.170

### Solution for Fixed Effects

Effect	Estimate	Std Error	DF	t	Pr >  t
INTERCEPT	758.38413249	225.71537159	232	3.36	0.0009
YEAR	-6.56609776	2.60171234	228	-2.52	0.0123

## Tests of Fixed Effects

Source	NDF	DDF	Type III F	Pr > F
YEAR	1	228	6.37	0.0123

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#### The MIXED Procedure

Class Level Information

Class	Levels	Values
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 21.2

#### REML Estimation Iteration History

Iteration	Evaluations	Objective	Criterion
	_		
0	1	2651.5763230	
1	3	2464.7891281	0.00388571
2	2	2430.4574413	1.31005585
3	2	2414.3729490	0.00057125
4	-2	2413.8544887	0.00004734
5	1	2413.7947792	0.0000024
6	1	2413.7944868	0.00000000

Convergence criteria met.

### Covariance Parameter Estimates (REML)

Cov F	Parm	Estimate
STATI	ON	12532.425315
Resid	lual	3031.5572857

### Model Fitting Information for ZN

Description	Value
<b>L</b>	

Observations	246.0000
Res Log Likelihood	-1431.12
Akaike's Information Criterion	-1433.12

# Model Fitting Information for ZN

Description	Value

Schwarz's	Bayesian Criterion	-1436.62
-2 Res Log	J Likelihood	2862.236

## Solution for Fixed Effects

Effect	Estimate	Std Error	DF	t	Pr >  t
INTERCEPT	-3261.722942	533.05003379	172	-6.12	0.0001
YEAR	39.14453138	5.93190744	171	6.60	0.0001

## Tests of Fixed Effects

Source	NDF	DDF	Туре	III F	Pr > F
YEAR	1	171		43.55	0.0001

### The MIXED Procedure

Class Level Information

Class Levels Values

STATION

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 233.2
 233.3
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#### `REML Estimation Iteration History

Iteration	Evaluations	Objective	Criterion
0	1	7279,6165246	
· 1	3	6255.3364390	0.00282635
2	2	6253.9847123	0.00070433
3	1	6251.3583609	0.00010039
4	1	6251.0135076	0.00000287
5	1	6251.0043631	0.0000000

Convergence criteria met.

Covariance Parameter Estimates (REML)

Cov Pa	arm	E	Estimate
STATIC	N	14823	3.592452
Residu	ual	2925.	.8658147

Model Fitting Information for ZN

#### Description

Value

Observations	667.0000
Res Log Likelihood	-3736.60
Akaike's Information Criterion	-3738.60
Schwarz's Bayesian Criterion	-3743.10
-2 Res Log Likelihood	7473.193

# Solution for Fixed Effects

Effect	Estimate	Std Error	DF	t	Pr >  t
INTERCEPT	25.92052962	113.07327411	619	0.23	0.8188
YEAR	2.79265028	1.20798615	602	2.31	0.0211

## Tests of Fixed Effects

Source	NDF	DDF	Type III F	Pr > F
YEAR	1	602	5.34	0.0211