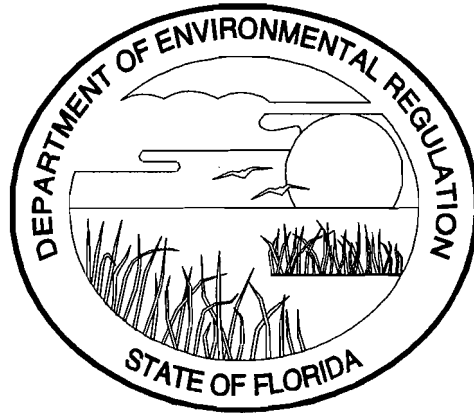


LONG-TERM PERFORMANCE EVALUATION OF THE ALUM STORMWATER TREATMENT SYSTEM AT LAKE ELLA, FLORIDA



FINAL REPORT

for

FDER Project WM339

December 1990

Submitted to:

Florida Department of Environmental Regulation

Eric H. Livingston
Project Administrator

Prepared By:

Environmental Research & Design, Inc.

3419 Trentwood Blvd., Suite 101
Orlando, FL 32812

Harvey H. Harper, Ph.D., P.E.

TABLE OF CONTENTS

| | <u>Page</u> |
|---|-------------|
| LIST OF TABLES | v |
| LIST OF FIGURES | ix |
| CHAPTER | |
| 1. INTRODUCTION | 1 |
| Scope and Objectives | 2 |
| Units of Measurement | 3 |
| 2. LITERATURE REVIEW: ENVIRONMENTAL CHEMISTRY AND TOXICITY OF ALUMINUM | 4 |
| Aluminum Cycle | 4 |
| Speciation in Natural Waters | 7 |
| Environmental Chemistry of Aluminum | 9 |
| Removal of Phosphorus and Heavy Metals by Aluminum Ions | 10 |
| Alum Treatment of Lakes | 14 |
| Biological Cycling of Aluminum | 15 |
| Potential Toxicity of Aluminum to Fish Species | 16 |
| Water Quality Criteria for Aluminum | 20 |
| Effects of Aluminum on Humans | 23 |
| Toxicity of Alum Sludge | 26 |
| 3. DESCRIPTION OF LAKE ELLA AND THE ALUM STORMWATER TREATMENT SYSTEM | 31 |
| Historical Conditions and Water Quality Problems | 31 |
| Evaluation of the Feasibility of Alum Treatment of Stormwater | 43 |
| Description of the Alum Injection System | 46 |
| Additional Improvements to Lake Ella | 50 |
| Start-up of the Alum Injection System | 53 |
| Chemical Requirements | 57 |

| | <u>Page</u> |
|--|-------------|
| 4. FIELD LABORATORY PROCEDURES | 60 |
| Water Quality Monitoring | 60 |
| Sediment Studies | 64 |
| Benthic Survey | 64 |
| Sediment Metal Accumulation and Migration | 64 |
| Chemical Speciation of Sediment Cores | 67 |
| Soluble | 68 |
| Exchangeable | 68 |
| Bound to Carbonates | 68 |
| Bound to Fe-Mn Oxides | 69 |
| Bound to Organic Matter | 69 |
| Fractionation of Sediment Phosphorus/Aluminum | 70 |
| The Influence of pH and Redox Potential on the | |
| Stability of Phosphorus and Heavy Metals | |
| in Alum Treated Sediments | 70 |
| Sediment Disposal and Toxicity Studies | 76 |
| Rate Experiments | 78 |
| Biotoxicity Testing | 79 |
| Fathead Minnow Toxicity Test | 80 |
| Long-Term Biotoxicity Tests | 82 |
| Analytical Methods | 85 |
| 5. RESULTS AND DISCUSSION | 86 |
| Water Quality Characteristics of Lake Ella Following | |
| Alum Treatment of Stormwater | 86 |
| Benthic Survey | 103 |
| Metal Accumulation and Migration | 106 |
| Speciation of Heavy Metals and Phosphorus in | |
| Lake Ella Sediments | 126 |
| Fractionation of Sediment Phosphorus | 131 |
| Influence of pH and Redox Potential on the Stability | |
| of Heavy Metals in Alum Treated Sediments | 140 |
| Estimates of Floc Accumulation | 149 |
| Sludge Production | 153 |
| Sludge Disposal | 157 |
| Rate Experiments | 161 |
| Bioassay and Toxicity Testing | 163 |
| Fathead Minnow Toxicity Tests | 165 |
| Long-Term Biotoxicity Tests | 175 |

| | <u>Page</u> |
|---|-------------|
| 6. SUMMARY AND CONCLUSIONS | 179 |
| Summary | 179 |
| Historical Characteristics of Lake Ella | 179 |
| Description of the Alum Injection System | 180 |
| Water Quality Characteristics of Lake Ella | |
| Following Alum Treatment of Stormwater | 182 |
| Effects of Alum Stormwater Treatment on | |
| Benthic Populations | 184 |
| Accumulation and Migration of Heavy Metals in | |
| Lake Ella Sediments | 185 |
| Speciation of Heavy Metals and Phosphorus in | |
| Lake Ella Sediments | 186 |
| Speciation of Sediment Phosphorus | 187 |
| Influence of pH and Redox Potential on the | |
| Stability of Heavy Metals in Alum Treated | |
| Sediments | 189 |
| Estimates of Flocculation Accumulation in Lake Ella | 190 |
| Sludge Production | 191 |
| Sludge Disposal | 191 |
| Rate Experiments | 192 |
| Bioassay and Toxicity Testing | 193 |
| Conclusions | 194 |
| REFERENCES | 199 |

LIST OF TABLES

| | <u>Page</u> |
|--|-------------|
| 2-1. Acute Toxicity of Aluminum to Aquatic Freshwater Species of Potential Significance | 21 |
| 2-2. Toxicity of Aluminum to Aquatic Freshwater Plants | 22 |
| 2-3. Chronic Toxicity of Aluminum to Selected Freshwater Aquatic Species | 24 |
| 2-4. Other Studies on the Effects of Aluminum to Freshwater Aquatic Species | 25 |
| 2-5. Estimated Aluminum Concentrations of Selected Foods | 27 |
| 2-6. Type and Source of Metal Concentrations in Alum Sludge from Durham, North Carolina | 29 |
| 3-1. Physical Characteristics of Lake Ella Before Restoration | 32 |
| 3-2. Physical Characteristics of Sub-Watershed Areas in the Lake Ella Drainage Basin | 35 |
| 3-3. Water Quality Characteristics of Lake Ella Prior to Alum Treatment of Stormwater | 41 |
| 3-4. Summary of Runoff Characteristics Entering Lake Ella During 1974 | 42 |
| 3-5. Physical and Chemical Characteristics of Alum | 44 |
| 3-6. Summary of Alum Treatment Performance Using a Dose of 20 mg/l as Al ₂ O ₃ and a Settling Time of 24 Hours | 45 |
| 3-7. Summary of Alum Injection System Costs | 52 |
| 3-8. Physical Characteristics of Lake Ella Before and After Restoration | 54 |
| 3-9. Operational Experience at Lake Ella | 56 |
| 3-10. Summary of Chemical Requirements for Alum Injection of Stormwater at Lake Ella | 59 |

| | <u>Page</u> |
|--|-------------|
| 4-1. Analytical Methods Used for the Lake Ella Study | 63 |
| 4-2. Summary of Toxicity Test Conditions for the Fathead Minnow (<i>Pimephales Promelas</i>) Seven-Day Larval Survival and Growth Test | 81 |
| 4-3. Summary of Experimental Test Conditions Used in Long-Term Bioassay Experiments | 84 |
| 5-1. Summary of Water Quality Characteristics in Lake Ella from 1/88 to 5/90 with Alum Treatment of Stormwater at a Dose of 10 mg/l | 87 |
| 5-2. Comparison of Water Quality Characteristics of Lake Ella Before and After Initiation of Alum Stormwater Treatment | 91 |
| 5-3. Concentrations of Heavy Metals in Lake Ella from 1/88 to 5/90 with Alum Treatment of Stormwater at a Dose of 10 mg/l | 97 |
| 5-4. Comparison of Pre- and Post-Modification Trophic States in Lake Ella | 102 |
| 5-5. Results of Benthic Survey Conducted in Lake Ella on May 25, 1990 | 105 |
| 5-6. Comparison of Benthic Surveys Conducted in Lake Ella from 1985-1990 | 107 |
| 5-7. General Characteristics of Sediment Core Samples Collected in Lake Ella on 2/21/87 (Before Alum Treatment of Stormwater) | 109 |
| 5-8. General Characteristics of Sediment Core Samples Collected in Lake Ella on 11/11/88 (After Alum Treatment of Stormwater) | 110 |
| 5-9. Summary of Mean Characteristics of Sediments in Lake Ella Before and After Alum Treatment of Stormwater | 111 |
| 5-10. Sediment Metal Concentrations in Core Samples Collected in Lake Ella on 2/21/87 (Before Alum Treatment of Stormwater) | 115 |
| 5-11. Sediment Metal Concentrations in Core Samples Collected in Lake Ella on 11/11/88 (After Alum Treatment of Stormwater) | 116 |

| | <u>Page</u> |
|--|-------------|
| 5-12. Comparison of Mean Heavy Metal Concentrations in Sediments from Lake Ella Before and After Treatment of Stormwater | 118 |
| 5-13. Sediment Speciation of Heavy Metals and Phosphorus in Composite Core Samples in Lake Ella on 2/21/87 (Before Alum Treatment of Stormwater) | 127 |
| 5-14. Sediment Speciation of Heavy Metals and Phosphorus in Composite Core Samples in Lake Ella on 11/11/88 (After Alum Treatment of Stormwater) | 129 |
| 5-15. Comparison of Sediment Speciation of Heavy Metals and Phosphorus in the Top 25 cm of Lake Ella Before and After Alum Treatment of Stormwater | 130 |
| 5-16. Sediment Phosphorus Associations in Sediment Core Samples Collected in Lake Ella on 2/21/87 (Before Alum Treatment of Stormwater) | 133 |
| 5-17. Sediment Phosphorus Associations in Sediment Core Samples Collected in Lake Ella on 11/11/88 (After Alum Treatment of Stormwater) | 134 |
| 5-18. Comparison of Sediment Phosphorus Associations in Lake Ella Before and After Alum Treatment of Stormwater | 135 |
| 5-19. Comparison of Total Sediment Phosphorus Release During Fractionation Procedures Before and After Alum Treatment of Stormwater | 139 |
| 5-20. Release of Heavy Metals and Phosphorus from Lake Ella Alum Sludge Under Various Redox Potentials and pH Values | 141 |
| 5-21. Measurements of Alum Flocc Accumulation in Lake Ella Based on Core Samples Collected on May 25, 1990 | 150 |
| 5-22. Maximum Anticipated Production of Alum Sludge from Alum Treatment of Stormwater at Various Doses | 154 |
| 5-23. Chemical Characteristics of Alum Sludge Leachate | 158 |
| 5-24. Characteristics of the Alum Sludge Used for Disposal Studies | 160 |
| 5-25. Routine Chemical and Physical Measurements Conducted During the Fathead Minnow Larval Survival and Growth Test | 166 |

| | <u>Page</u> |
|---|-------------|
| 5-26. Survival Data for Fathead Minnow Larval Survival and Growth Test | 170 |
| 5-27. Final Larval Weight Data for the Fathead Minnow Larval Survival and Growth Test | 173 |
| 5-28. Measured Values of pH and Dissolved Aluminum in Long-Term Bioassay Experiments | 177 |

LIST OF FIGURES

| | <u>Page</u> |
|--|-------------|
| 2-1. Representation of the Aluminum Cycle | 5 |
| 2-2. Equilibrium Diagrams of Hydroxo Aluminum Complexes for (a) Freshly Precipitated $\text{Al}(\text{OH})_3$ and (b) Aged $\text{Al}(\text{OH})_3$, Gibbsite | 8 |
| 2-3. Equilibrium Diagrams for the Simultaneous Existence of $\text{Al}(\text{OH})_3(\text{s})$ and $\text{AlPO}_4(\text{s})$ Precipitates as a Function of pH | 12 |
| 3-1. Lake Ella Stormsewer System Prior to Construction of the Alum Stormwater Treatment System | 33 |
| 3-2. Contributing Watershed Areas to Lake Ella | 34 |
| 3-3. Physical-Chemical Profiles in Lake Ella on 11/29/85 | 39 |
| 3-4. Lake Ella Stormwater System After Modification for Alum Treatment | 47 |
| 3-5. Typical Cross-Section of Alum Injection System Modifications | 49 |
| 3-6. Typical Sonic Meter Installation | 51 |
| 4-1. Sample Locations for Water Quality and Sediment Sampling in Lake Ella | 62 |
| 4-2. Schematic of the Sediment Core Collection Device | 66 |
| 4-3. Schematic of the Incubation Apparatus Used for pH and Redox Studies | 71 |
| 4-4. Apparatus for Filtering Supernatant Solutions Under a Nitrogen Atmosphere: (1) Pipette in N_2 Purge Position and (b) Pipette in Filtering Position | 75 |
| 4-5. Drying Bed Used for Evaluation of Sludge Characteristics | 77 |
| 5-1. Comparison of Pre-Treatment and Post-Treatment Physical-Chemical Profiles in Lake Ella | 94 |

| | <u>Page</u> |
|--|-------------|
| 5-2. Fluctuations in pH, Phosphorus, Dissolved Oxygen and Chlorophyll-a in Lake Ella from 6/87 to 5/90 | 95 |
| 5-3. Fluctuations in Aluminum Concentrations in Lake Ella from 6/87 to 5/90 | 98 |
| 5-4. Relationships Between pH and Dissolved Aluminum Levels in Lake Ella from 7/88 to 5/90 | 100 |
| 5-5. Comparison of Sediment Concentrations of Nitrogen and Phosphorus in Lake Ella Based on Core Samples Collected on 2/21/87 and 11/11/88 | 112 |
| 5-6. Comparison of Pre-Treatment and Post-Treatment Sediment Concentrations of Zinc, Lead and Copper in Lake Ella | 119 |
| 5-7. Comparison of Sediment Concentrations of Aluminum at the Four Sample Locations in Pre- and Post-Treatment Sediments in Lake Ella | 121 |
| 5-8. Comparison of Sediment Concentrations of Zinc at the Four Sample Locations in Pre- and Post-Treatment Sediments in Lake Ella | 122 |
| 5-9. Comparison of Sediment Concentrations of Copper at the Four Sample Locations in Pre- and Post-Treatment Sediments in Lake Ella | 123 |
| 5-10. Comparison of Sediment Concentrations of Lead at the Four Sample Locations in Pre- and Post-Treatment Sediments in Lake Ella | 125 |
| 5-11. Comparison of Pre- and Post-Treatment Phosphorus Fractions in Lake Ella | 137 |
| 5-12. Comparison of Sediment Release of Aluminum Under Various Conditions of pH and Redox Potential in Lake Ella and in a Highway Detention Pond | 144 |
| 5-13. Comparison of Sediment Release of Copper Under Various Conditions of pH and Redox Potential in Lake Ella and in a Highway Detention Pond | 145 |
| 5-14. Comparison of Sediment Release of Lead Under Various Conditions of pH and Redox Potential in Lake Ella and in a Highway Detention Pond | 147 |
| 5-15. Comparison of Sediment Release of Iron Under Various Conditions of pH and Redox Potential in Lake Ella and in a Highway Detention Pond | 148 |

| | <u>Page</u> |
|--|-------------|
| 5-16. Typical Consolidation of Alum Flocculation with Time After Stormwater Treatment | 152 |
| 5-17. Relationship Between Alum Sludge Production and Alum Treatment Dose | 156 |
| 5-18. Changes in Concentrations of Monomeric Dissolved Aluminum with Time After Addition of Alum to Stormwater Runoff Collected on 3/27/89 | 162 |
| 5-19. Changes in Concentrations of Monomeric Dissolved Aluminum with Time After Addition of Alum to Stormwater Runoff Collected on 4/4/89 | 164 |
| 5-20. Survival Results for the Fathead Minnow Larval Survival and Growth Test | 171 |
| 5-21. Relationship Between Survival of Fathead Minnows and Dissolved Aluminum Levels in Short-Term Chronic Biototoxicity Tests | 174 |
| 5-22. Results of Long-Term Bioassay Experiments Using <i>Gambusia sp.</i> | 178 |

CHAPTER 1

INTRODUCTION

For several decades, new land development projects constructed within the State of Florida have been required to utilize stormwater management practices such as retention or detention ponds, filtration systems or swales to minimize post-development discharges of pollutants to receiving water bodies. However, much of the existing land development in Florida occurred prior to implementation of the current stormwater regulations. Most of these areas contain no facilities for management of runoff, and therefore, discharge untreated stormwater runoff to lakes and other surface water bodies. Many of these areas are highly urbanized and fully developed with little available space for retrofitting activities using traditional stormwater management techniques. Therefore, interest has risen recently in developing a rapid and efficient method of reducing pollutant concentrations in nonpoint source discharges to surface waters which does not require a large commitment of often unavailable land area.

In 1986, a prototype system was introduced in a lake restoration project on Lake Ella in Tallahassee, Florida based on the flow-weighted injection of liquid aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, commonly called alum, into the runoff flow inside stormsewer lines prior to discharge into the lake. Alum is an acid salt of aluminum which has been used for many years in treatment of drinking water, for phosphorus removal in the wastewater industry, and also in lake restoration projects for water column clarification and as a method of inactivating sediment release of phosphorus into the overlying water column during anaerobic conditions. However,

prior to the Lake Ella project, alum had not been used for treatment of stormwater inputs into a receiving water body.

Alum forms harmless non-toxic precipitates of $\text{Al}(\text{PO}_4)$ and $\text{Al}(\text{OH})_3$ which combine with phosphorus, suspended solids, and heavy metals, causing them to be deposited into the sediments in a stable inactive state. The insoluble precipitates formed between alum and phosphorus in the sediments are exceptionally stable since they are immune to changes in sediment redox potential, and to a lesser degree, pH as well.

The alum stormwater treatment system resulted in immediate and substantial improvements to water quality in Lake Ella and appears promising for use in other locations. However, many questions need to be addressed concerning long-term pollutant removal efficiencies, floc accumulation and stability, ultimate floc disposal, and potential toxicity problems before these systems can be permitted for general use.

Scope and Objectives

The research efforts described in this document are intended to generate further information on the performance and long-term impacts of the alum injection system constructed at Lake Ella in Tallahassee. The specific objectives of these research efforts were to:

1. Evaluate the long-term pollutant removal efficiencies of the alum treatment process and resulting water quality characteristics of Lake Ella;
2. Examine the accumulation rate and migration of alum floc and heavy metals in the bottom sediments;
3. Determine the stability of phosphorus and heavy metal sediment associations in Lake Ella before and after initiation of the alum treatment system;
4. Examine the effects of change in pH and redox potential on stability of phosphorus and heavy metals in alum treated sediments;

5. Examine the toxicity and characteristics of floc accumulations with respect to ultimate disposal;
6. Examine the chemical speciation of the aluminum ions formed during precipitation reactions and their relationship to potential toxicity; and
7. Examine the effects of alum floc accumulations on populations of benthic organisms.

Units of Measurement

Research efforts described in this report were conducted almost exclusively with metric units of measurement. In general, all data, measurements and descriptions given in this report are presented in metric form with English equivalent units given in parentheses for measurements of length, area and volume. The only exception to this format is in the presentation of elevation data referenced to mean sea level (MSL) which is given in terms of English units (i.e., feet) only.

CHAPTER 2

LITERATURE REVIEW: ENVIRONMENTAL CHEMISTRY AND TOXICITY OF ALUMINUM

Aluminum Cycle

Aluminum is the most abundant metallic element in the lithosphere and the third most abundant element in the earth, comprising approximately 8% of the earth's crust (Hem, 1986). Although quantitatively important, the aluminum cycle is complicated and poorly understood. Aqueous, particulate (soil/sediment) and biological transformations of aluminum may be conceptualized through a schematic representation of the aluminum cycle as shown in Figure 2-1. This cycle is a series of pools of aqueous, particulate and living biomass with many fluxes that regulate pool sizes. Although some information is available on aluminum pools within the natural environment, it is largely based on operationally defined methods. Unfortunately, there is little information available on the relative importance of the pathways linking the pools or rates of these transformations.

Soil represents the largest pool of aluminum at the earth's surface. Within the lithosphere, aluminum is associated largely with aluminosilicate minerals, most commonly as feldspars in metamorphic and igneous rocks, and as clay minerals in well-weathered soils. In this form, aluminum is generally unavailable for chemical and biological reactions. Through soil development, highly crystalline aluminosilicate minerals are decomposed and a small fraction of their aluminum becomes available to participate in biogeochemical processes.

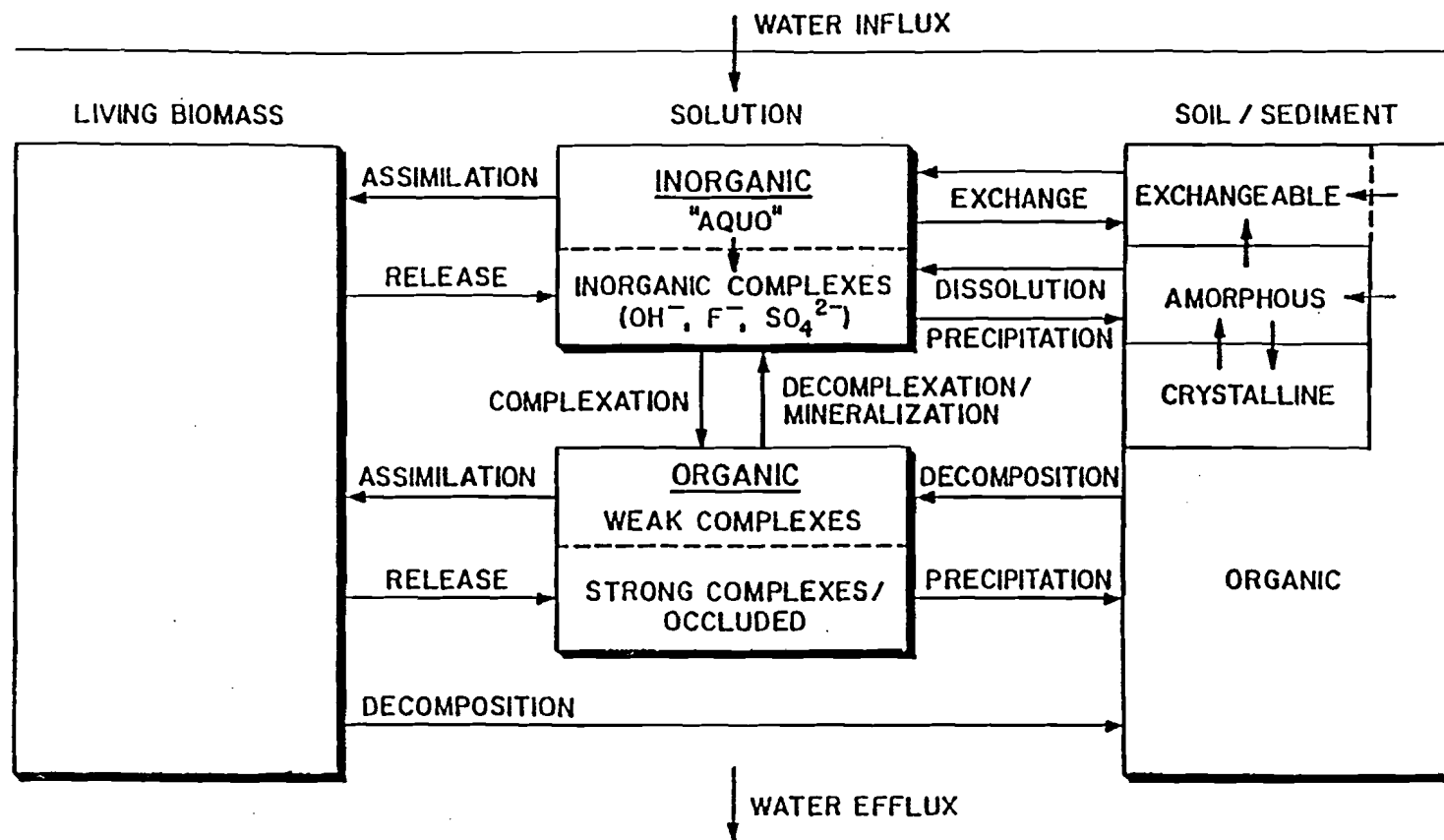


Figure 2-1. Representation of the Aluminum Cycle.

Many processes contribute to free soil and sediment aluminum pools. For example, the weathering of aluminosilicate minerals by carbonic acid dissolution, strong acid dissolution, or neutral hydrolysis (Johnson et al., 1981), followed by the secondary precipitation of aluminum, produces amorphous mineral forms. Soil aluminum is also retained on charged surfaces associated with soil organic matter and/or clay minerals (Bohn et al., 1985). Free soil or sediment aluminum may also be bound with organic matter through microbial/plant transformations (Messenger, 1975; Messenger et al., 1978) or formed by precipitation with organic solutes (Schnitzer and Skinner, 1963a; Schnitzer and Skinner, 1963b) within soil solutions.

All forms of soil/sediment aluminum potentially exert control over solution concentrations of aluminum. However, the release of aluminum from highly crystalline minerals is very slow (Bloom, 1983). Although the mechanisms regulating the concentration of aluminum in the environment are not clearly established, it is likely that aqueous aluminum is derived largely from free-soil/sediment pools, including exchange from cation-exchange sites, dissolution from amorphous mineral phases, or decomposition/mineralization of organic forms.

Solution aluminum is the most chemically and biologically available form, although this pool represents an extremely small fraction of the total aluminum in the environment. Aluminum is a strongly hydrolyzing metal and is somewhat insoluble in the neutral pH range of 6.0 to 8.0 (Stumm and Morgan, 1970). Under acidic (pH < 6.0) or alkaline (pH > 8.0) conditions, and/or in the presence of complexing ligands, the solubility of aluminum is enhanced, making it more available for biogeochemical transformations. Within the aqueous phase, aluminum may be associated with a variety of inorganic and organic complexes. The extent of complexation depends on the availability of soil aluminum, solution pH value, concentrations of complexing ligands, ionic strength, and temperature.

Speciation in Natural Waters

The chemistry of aluminum in natural waters is quite complex. Its high ionic charge and small crystalline radius combine to yield a level of reactivity unmatched by any other soluble metal. The Al-O bond is thought to be about 40 percent covalent and 60 percent ionic (Hsu, 1988). Aluminum is exceptional in this respect, since covalence plays a minor role in the overall structure of most minerals, aside from Si-O. Almost all of the metal-oxygen bonds that occur in minerals are ionic (Johnson et al., 1981).

A pC versus pH diagram for freshly precipitated $\text{Al}(\text{OH})_3$ is shown in Figure 2-2a. As the pH of a solution of pure water and aluminum ions is raised above 4.0, Al^{+3} gives way to mononuclear species such as $\text{Al}(\text{OH})^{+2}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3(\text{s})$ and $\text{Al}(\text{OH})_4^-$ (Baes and Mesmer, 1976). In addition, larger polynuclear hydroxy-Al species may form metastable intermediates in the precipitation of solid phase $\text{Al}(\text{OH})_3$ (Hsu, 1964). Inorganic ligands such as sulfate and fluoride (Roberson and Hem, 1967), as well as a host of organic compounds (Lind and Hem, 1975), may also form strong complexes with aluminum. It is well established that aluminum forms strong complexes with OH^- , F^- , and SO_4^{-2} (Roberson and Hem, 1967). Aluminum also forms strong complexes with natural organic matter such as tannins and ligands (Lind and Hem, 1975).

As freshly precipitated $\text{Al}(\text{OH})_3$ ages, it forms a continuous series of heximeric ring complexes with the basic form $[\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}]^{+6}$. These rings are believed to coalesce with aging via deprotonation of edge-group water molecules, with the subsequent formation of double hydroxide bridges between units. Thus, the polymerization process involves continued growth of the heximeric ring units, with the resulting polymers prefiguring the crystal structure of the aluminum trioxide polymorphs, gibbsite, bayerite and nordstrandite (Hsu and Bates, 1964; Stol et al., 1976; Hem and Roberson, 1967). A pC versus pH diagram for aged $\text{Al}(\text{OH})_3(\text{s})$ is shown in Figure 2-2b.

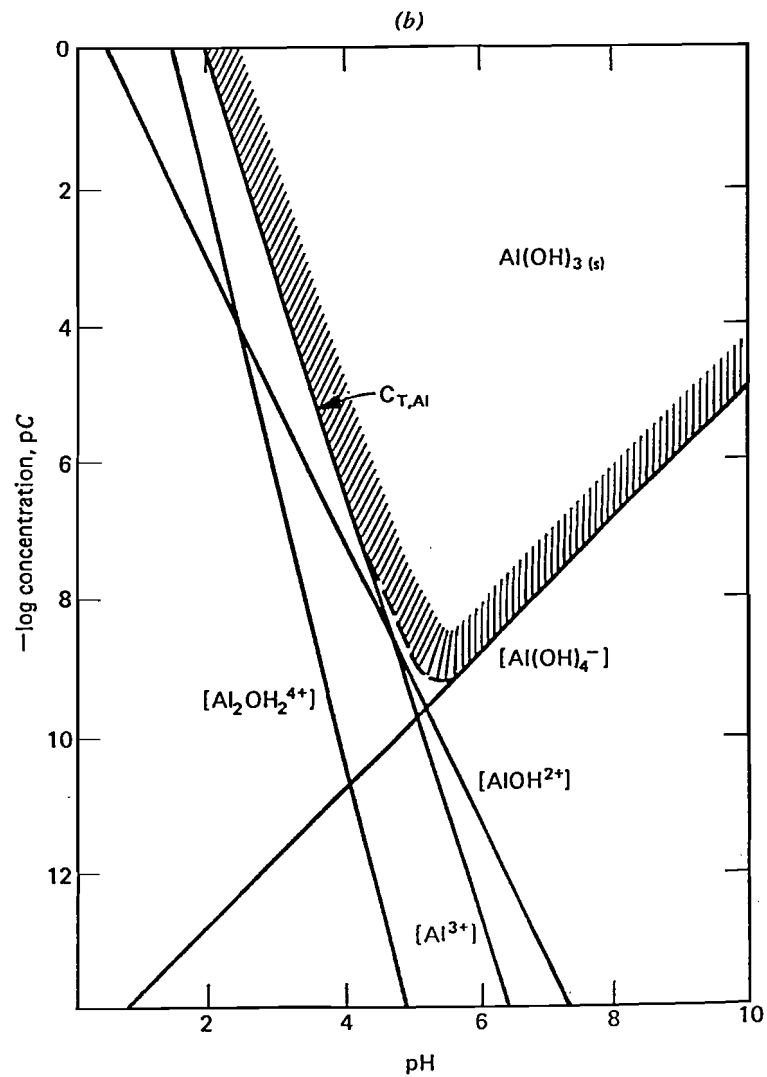
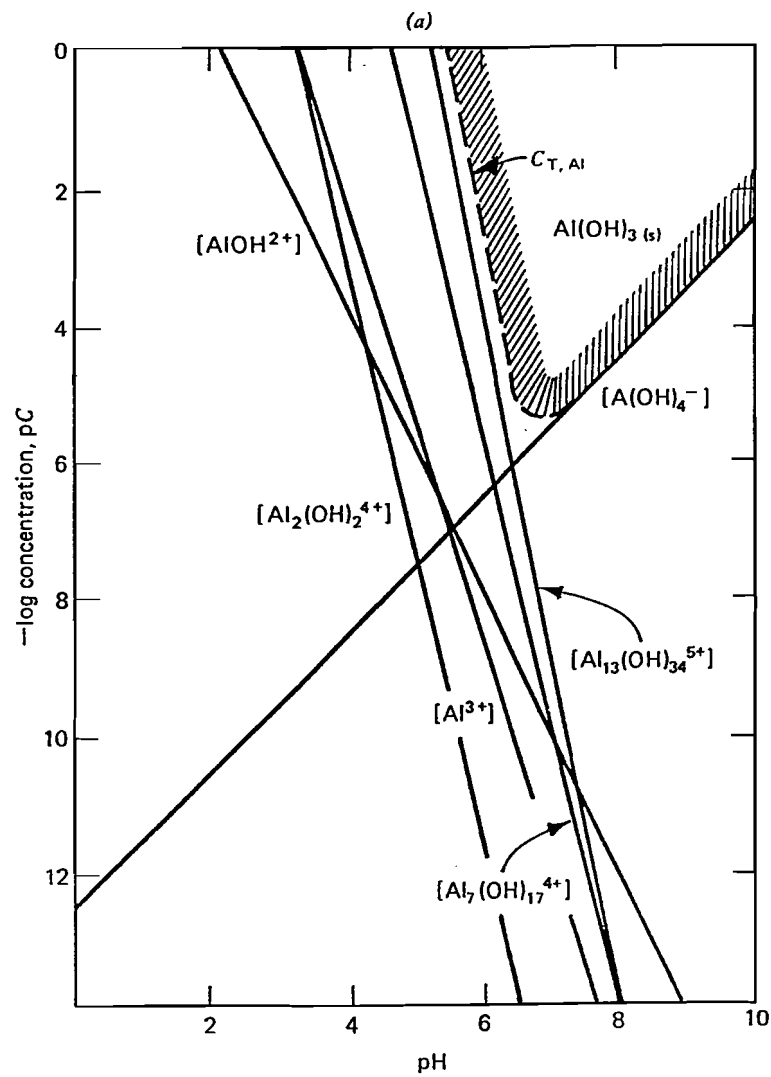
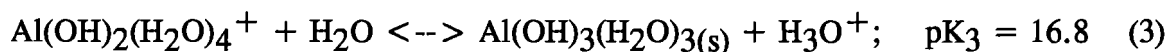
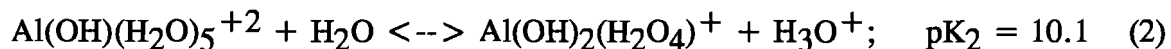
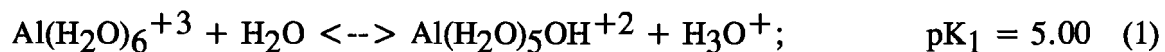


Figure 2-2. Equilibrium diagrams of hydroxo aluminum complexes for (a) freshly precipitated $\text{Al}(\text{OH})_3$ and (b) aged $\text{Al}(\text{OH})_3$, gibbsite.

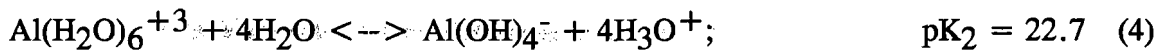
The solubility of aluminum in equilibrium with freshly precipitated sludges is higher than the solubility level expected from aged sludge, often termed gibbsite. These solubility differences occur since aluminum exists as amorphous aluminum hydroxide in freshly precipitated sludge which is more reactive and more soluble than the crystallized gibbsite. The crystallization of aluminum hydroxide to gibbsite is slow and may take a year or more. As can be seen in Figure 2-2b, gibbsite predominates over a much larger pH range than freshly precipitated $\text{Al}(\text{OH})_3$. The minimum solubility of freshly precipitated $\text{Al}(\text{OH})_3$ occurs at a pH of approximately 7. However, the minimum solubility of crystallized gibbsite occurs at a lower pH level of approximately 5.5.

Environmental Chemistry of Aluminum

When aluminum sulfate (alum), $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, or sodium aluminate, NaAlO_2 , is added to water, free Al^{+3} ions are formed. These ions are quickly coordinated by six water molecules in an octahedral configuration which can be represented by the formula $\text{Al}(\text{H}_2\text{O})_6^{+3}$. The Al^{+3} ion has a considerably smaller ionic radius (0.51 angstroms) than other commonly encountered trivalent metal ions and polarizes solvated water ions very strongly. This gives rise to several hydrolytic species that are produced by a successive loss of hydration shell protons to water molecules in the surrounding bulk solution. The hydrolysis reactions can be written:



The final product of these hydrolysis reactions, $\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3$, is alum precipitate or floc and is most commonly written as $\text{Al}(\text{OH})_3$ without the hydrated water molecules. Under alkaline conditions, the hydrolysis reactions can undergo an additional reaction according to:



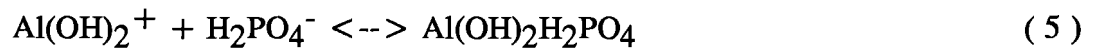
In addition to the monomeric aluminum species indicated previously, many authors have postulated the existence of polymeric aluminum species. Some of the more commonly suggested species are $\text{Al}_2(\text{OH})_2^{+4}$, $\text{Al}_8(\text{OH})_{20}(\text{H}_2\text{O})_x^{+4}$, $\text{Al}_{16}(\text{OH})_{12}(\text{H}_2\text{O})_{12}^{+6}$ through $\text{Al}_{54}(\text{OH})_{144}(\text{H}_2\text{O})_{36}^{+18}$ and the $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{+7}$ species. Of these, there is conclusive, direct evidence indicating that the $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{+7}$ species exists and is an important polymer in water treatment processes. A complete analysis of aluminum hydrolysis has been published by Bertsch (1989).

Removal of Phosphorus and Heavy Metals by Aluminum Ions

When aluminum or sodium aluminate is added to water, phosphorus is removed by three primary mechanisms: (1) forming insoluble AlPO_4 , (2) by sorption on the surface of $\text{Al}(\text{OH})_3$ polymer or floc, and (3) by entrapment of phosphorus-containing particulate matter in the $\text{Al}(\text{OH})_3$ floc (Cooke and Kennedy, 1981). Phosphorus removal or entrapment can occur by several mechanisms, depending on the solution pH. At lower pH values and higher inorganic phosphorus concentrations, the formation of AlPO_4 is favored. Theoretically, under these conditions, the removal or inactivation of one mole of phosphorus as AlPO_4 would require one mole of aluminum. Yet, due to incomplete reaction and competition by other species,

aluminum/phosphorus ratios are often greater than one in practice. Eisenreich et al. (1977) reported maximum inorganic phosphorus removal at Al:P ratios greater than 500 in Lake Mendota. Inorganic phosphorus is most effectively removed by sorption to the $\text{Al}(\text{OH})_3$ floc. Removal of particulate phosphorus is most effective in the pH range of 6 to 8 when maximum floc occurs (Cooke and Kennedy, 1981). At higher pH values, OH^- begins to compete with phosphate ions for aluminum ions and aluminum hydroxide-phosphate complexes begin to form:

Phosphorus adsorption by $\text{Al}(\text{OH})_3$ floc can occur by ion-pair formation with positively charged surface sites according to equation 5:



or by ligand exchange with surface hydroxyl ions according to equation 6 (Hingston et al., 1972; Hingston et al., 1974; Huang, 1975; Hingston et al., 1971; Kyle et al., 1975; Davis and Lecki, 1980):



Since ligand exchange reactions replace hydroxyl ions, the adsorption of anions usually increases with decreasing pH (Hingston et al., 1972; Hingston et al., 1974). Phosphate sorption and reversibility is influenced significantly by the age of the precipitate, and continued uptake of phosphorus can continue for months (Lijlema, 1980; Bolan et al., 1985). A solubility equilibrium diagram for $\text{Al}(\text{OH})_3(\text{s})$ and $\text{AlPO}_4(\text{s})$ as a function of pH is given in Figure 2-3. Because AlPO_4 is more stable than $\text{Al}(\text{OH})_3$ under neutral to slightly acidic conditions (Chen et al., 1973), then slow phosphate sorption by diffusion into the precipitate may eventually convert $\text{Al}(\text{OH})_3$ to

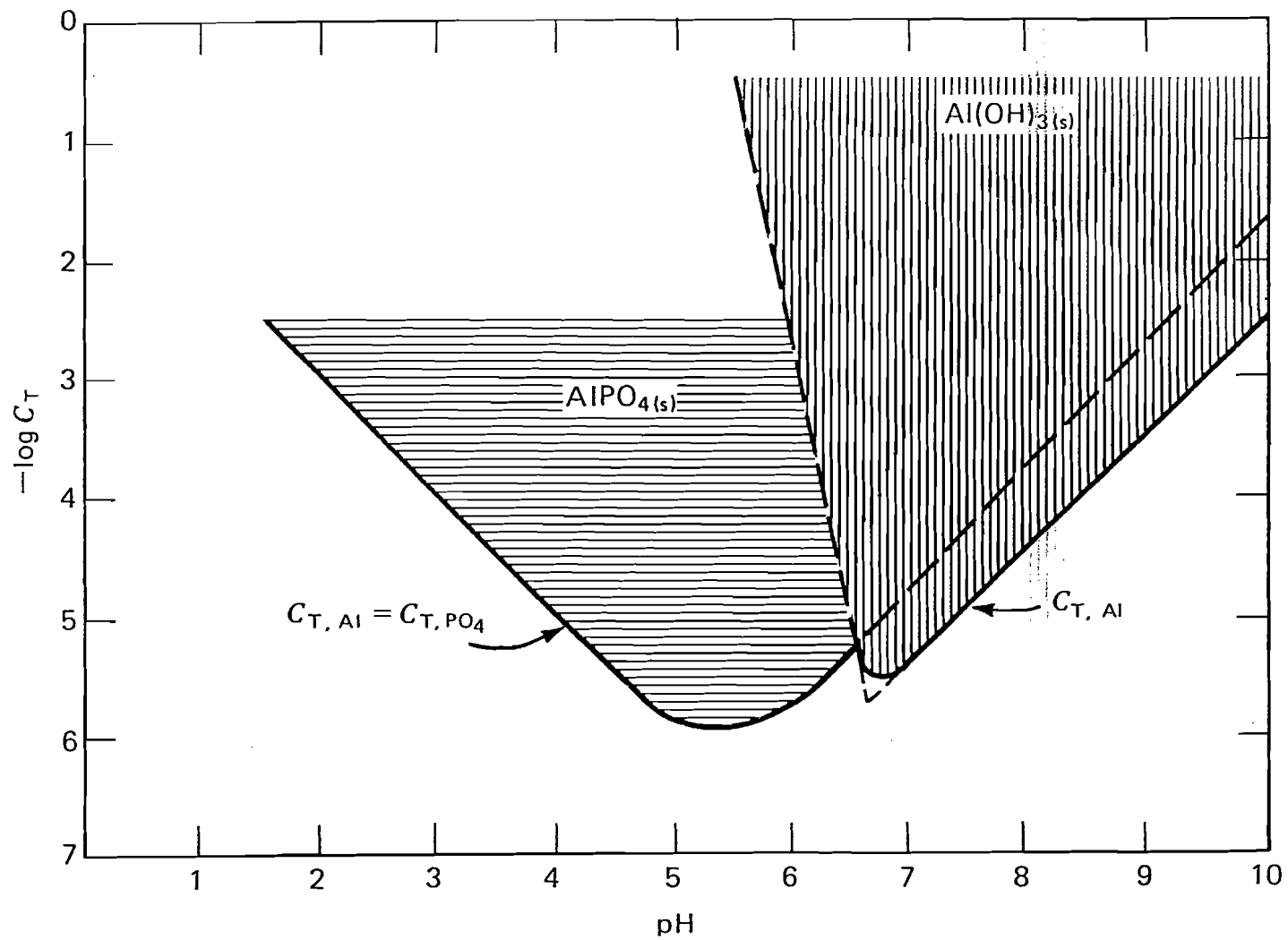


Figure 2-3. Equilibrium diagrams for the simultaneous existence of $\text{Al(OH)}_3(\text{s})$ and $\text{AlPO}_4(\text{s})$ precipitates as a function of pH.

AlPO_4 (Davis and Hem, 1989). Thus, effective phosphorus removal and inactivation from the water column and sediments is dependent on the quantity and quality of floc formed during application. If sufficient aluminum is added, the $\text{Al}(\text{OH})_3$ floc which settles on the lake bottom will continue to sorp phosphorus from interstitial water to form AlPO_4 , depending on pH, phosphorus concentration, and the amount of aluminum present (Kennedy, 1978).

In addition to the adsorption of phosphorus onto $\text{Al}(\text{OH})_3$ floc, numerous studies have been conducted on the adsorption of metal ions on aluminum oxides and hydroxides. It has often been demonstrated that the mechanisms of metal ion association with hydrous oxide surfaces involves an ion exchange process in which the adsorbed metal ions replace bound protons (Huang and Stumm, 1973; Kurbatov et al., 1951; Dugger et al., 1964; Schindler, 1981). The adsorption of metal ions from dilute solution onto alumina surfaces is highly dependent on pH. Benjamin and Leckie (1980) conducted numerous experiments to investigate the adsorption mechanisms for Pb^{+2} and Cd^{+2} on Al_2O_3 . These authors were among the first to demonstrate that the pH region in which adsorption processes increase rapidly (the "adsorption edge") depends on the metal concentration. A consequence of this phenomenon is that adsorption isotherms for metal ions usually are best described by the Freundlich equation:

$$\Gamma_M = C_M^b \quad (7)$$

where:

Γ_M = the adsorption density of the metal ion

C_M = the equilibrium concentration of the metal ion

a, b = constants (the parameter b usually has a value in the range of 0.5 to 0.7)

Alum Treatment of Lakes

Since at least Roman times, salts of aluminum have been added to drinking water to improve its appearance. Both aluminum and iron are used in the United States in water treatment plants to remove phosphorus and turbidity. Hershell (1977) reported that 20 percent of the water systems in the United States used coagulation with either aluminum or iron on all or some of their proposed water.

Jernelov apparently was the first to use aluminum sulfate to remove phosphorus from the water column of a lake as part of a restoration project on Lake Langsjon, Sweden (Jernelov, 1970). Previously, alum has been used exclusively as a flocculating agent in the treatment of water and wastewater. The Wisconsin Department of Natural Resources pioneered the use of aluminum sulfate to improve water quality of lakes in the United States (Cooke et al., 1986). The first U.S. lake to be treated with alum was Horseshoe Lake which received a 2.6 mg/l aluminum surface application in May 1970. Twelve years later, phosphorus concentrations were still below the pre-treatment levels (Garrison and Knauer, 1984). Although aluminum treatment methods and doses have varied, nearly all have brought about a reduction in phosphorus concentration and an improvement in trophic state (Cooke et al., 1986).

Aluminum is the metal most often chosen for phosphorus precipitation and inactivation applications because it forms complexes and polymers which are inert to redox changes such as occur in an anoxic hypolimnion. This unusual characteristic is due primarily to the fact that aluminum exists only in the +3 oxidation state under both oxidized and reduced conditions. Phosphorus bound to these aluminum complexes should remain so, even under strongly reduced conditions. In contrast, iron becomes reduced from the Fe^{+3} state to the Fe^{+2} state and releases phosphorus as the redox potential falls during the development of anoxia. Aluminum complexes are also more efficient than iron in entrapment and removal of particulate and inorganic phosphorus.

Virtually every reported application of aluminum to the surface of lakes has been successful in bringing about an immediate reduction in phosphorus concentration and an improvement in trophic state. Treatment areas up to 121 hectares in Annabessacook Lake, Maine (Dominie, 1980), doses up to 936 metric tons on Medical Lake, Washington (Gasperino et al., 1980), and treatment effectiveness up to 12 years (Garrison and Knauer, 1984) have been reported for alum treatments involving surface waters and sediments.

A 12.2 mg/l aluminum treatment at Medical Lake in the fall of 1977 produced a greatly improved trophic state as long as three years after treatment (Gasperino et al., 1980; Soltero et al., 1981). Mean orthophosphorus was reduced 90 percent and total phosphorus 30 percent (Soltero et al., 1981). The overall chlorophyll was reduced 87 percent. Following an alum treatment of 26 mg/l aluminum to West Twin Lake, mean total phosphorus concentration for the entire water column was reduced from 79 $\mu\text{g/l}$ in 1974 to 32 $\mu\text{g/l}$ in 1976 one year after treatment.

Biological Cycling of Aluminum

The biological cycling of aluminum is generally assumed to be unimportant quantitatively. Aluminum is not a plant or animal nutrient (Bohn et al., 1985) and, therefore, it generally does not accumulate in living tissue. However, elevated concentrations of aluminum have been shown to be toxic to a variety of organisms (Driscoll et al., 1980; Hall et al., 1985; Helliwell et al., 1983; Pavan et al., 1982). Wood (1985), among others, has hypothesized that the selection and use of elements in the biochemical evolution of organisms was dictated by their abundance in the earth's crust, and their solubility under the anaerobic conditions that occurred during that period, about 4×10^9 years ago. Although abundant, aluminum was insoluble under the conditions in which life evolved and, therefore, probably unavailable for transport into

primitive anaerobic bacteria. Because most organisms have not adapted to elevated concentrations of bioavailable aluminum, they cannot survive large intracellular accumulation. Nevertheless, organisms do assimilate limited quantities of aluminum, with some plants accumulating high concentrations (Foy, 1974). Biological uptake and release, therefore, represent a potential pathway of aluminum transfer to soil and aqueous environments.

Potential Toxicity of Aluminum to Fish Species

Early in this century, Hartwell and Pember (1918) postulated the toxicity of soluble aluminum to plants in acidic soils. The relationships between the aqueous chemistry of aluminum in soils and toxicity are still not fully understood. Recently, there has been considerable interest on the effects of increased aluminum mobilization from the edaphic to the aquatic environment and corresponding reductions in fish populations (Burrows, 1977; Schofield and Trojnar, 1980; Ulrich et al., 1980; Hutchinson and Sprague, 1986).

The toxicity of aluminum in aquatic and terrestrial systems is not well correlated with total aluminum concentrations, but is a function of the concentration of the biologically active fraction of the total. In terms of acute toxicity, the inorganic monomeric form of aluminum, Al^{+3} , is believed to be the most toxic. However, organically bound species may also be capable of crossing biological membranes and contributing to chronic bioaccumulation.

Elevated levels of aluminum may have serious effects on aquatic organisms, particularly fish under acidic stress. Dissolved aluminum, mobilized from the sediments and suspended matter at increased acidities, was implicated in fish deaths in waters of pH 4.5-5.0 (Burrows, 1977; Schofield and Trojnar, 1980; Hutchinson and Sprague, 1986). Surges of labile aluminum during snowmelt and heavy rainfall were shown to be potentially lethal to fish eggs and fry (Driscoll et al., 1980).

Woodward et al. (1989) reported that at low pH, as little as 50 $\mu\text{g/l}$ aluminum decreased growth and reduced survival of cutthroat trout (*Oncorhynchus clarki*). Similar concentrations have been reported to exhibit chronic toxicity to larval small-mouth bass (*Micropterus dolomieu*) at pH 5.1 (Kane and Rabeni, 1987) and for post-larval white suckers (*Catostomus commersoni*) at pH values less than 4.5 (Baker and Schofield, 1982). Gunn and Noakes (1987) reported no increased mortality to lake trout embryos subjected to pulse exposures of 0, 100 and 200 $\mu\text{g/l}$ aluminum at pH 5.0, but noted that alevins from the high aluminum exposure were smaller, had reduced (18-22%) whole-body concentrations of calcium and potassium, and were less effective predators on *Daphnia magna*.

The toxicity of aluminum appears to vary with the life history stage of fish. In acidic solutions (pH 4.2-4.8), the presence of aluminum improves egg survival and growth of white suckers (*Catostomus commersoni*) and brook trout sac fry (Baker and Schofield, 1982). Similarly, McCormick et al. (1989) reported that aluminum concentrations of 30 to 35 $\mu\text{g/l}$ may provide some protection against the effects of pH at 5.5, but offered no protection at pH 5.2 and was toxic at 60 $\mu\text{g/l}$ at pH 5.0 in a study of juvenile fathead minnows.

The extent of aluminum toxicity appears to be dependent on the concentration and the speciation of aqueous aluminum. Driscoll et al. (1980) demonstrated that excess fluoride, citrate and humic matter decreased the toxicity of aluminum to brook trout and white suckers (*Catostomus commersoni*) at the pH range between 4.4 and 5.2. Moreover, the survival of brook trout and white sucker fry in acidic Adirondack waters was correlated with both inorganic monomeric aluminum concentrations and pH. Aluminum toxicity appears to be acute in acidic solutions that are oversaturated with respect to $\text{Al}(\text{OH})_3$ solubility (Baker and Schofield, 1982).

Environmental calcium has been shown to reduce the impact of low pH and elevated aluminum on fish (Wright and Snekivik, 1978; Brown, 1983; McDonald,

1983; Saddler and Lynam, 1988). Aluminum exacerbated the pH-dependent net losses of sodium and chloride from adult brook trout (*Salvelinus fontinalis*) but this loss was reduced by elevated calcium concentrations (Booth et al., 1988). The protective role of calcium in acid-stressed fish may be due to an influence on membrane permeability and associated osmoregulation (Maetz, 1974).

The mechanism of aluminum toxicity to fish has been attributed to the inability of fish to maintain their osmoregulatory balance as well as respiratory problems associated with coagulation of mucus on the gills. Baker and Schofield (1982) observed that larvae and juvenile forms were the most susceptible to oversaturated solutions of aluminum. They suggested that the mechanisms of the toxicity involved precipitation and coagulation of aluminum oxide on the gills or other surfaces or the adsorption and nucleation of aluminum polymers at surface interfaces. Buerger and Soltero (1983) found differential accumulation of aluminum in tissues of rainbow trout from an alum-treated lake, an untreated lake and a hatchery. Aluminum concentrations in fish from all three sources were highest in gill tissue and lowest in muscle.

Muniz and Leivestad (1980) reported the loss of Na^+ and Cl^- from the blood of brown trout (*Salmo trutta*) in solutions containing 190 $\mu\text{g/l}$ aluminum at a pH of 5.0. Reader et al. (1988) reported aluminum impaired gross development, net uptake of calcium, potassium and sodium, calcium deposition in the skeleton, and increased the net loss of magnesium in brown trout following aluminum addition to a New Hampshire stream. The drift rate of immature aquatic insects generally increased with increasing concentrations of added inorganic aluminum, suggesting a stress avoidance response that was a function of aluminum concentration. Helliwell et al. (1983) evaluated the effects of aluminum on the algae *Chlorella pyrenoidosa* and found that maximum toxicity occurred at pH 5.8-6.2. They implicated $\text{Al}(\text{OH})_2^+$ as the toxic species of aluminum.

Research conducted by Lamb and Bailey (1981) focused on the effects of using alum to treat eutrophic lakes. They studied the effects of aluminum hydroxide to *Tanytarsus dissimilis*. *T. dissimilis* is a representative of the chironomidae, the family of organisms that occupies a significant portion of the benthic invertebrate community of lakes. The acute tests were conducted by adding concentrations of up to 960 mg/l of alum to beakers at pH 7.8. The results of the acute bioassay indicated no apparent effects. However, mortalities in the chronic assays were recorded at all alum doses. They concluded that there was some chemical toxicity but did not believe that the solid hydroxide itself was toxic, but that the aluminate ion concentration was responsible. They suggested that instantaneous deposition of a heavy floc layer on the lake bottom, such as occurred in their laboratory studies at high alum dose rates, could inhibit pupae from reaching the surface and deposited eggs from reaching the sediment.

In contrast, Narf (1978) reported there have been no indications of short- or long-term toxicity to benthic invertebrates in Horseshoe Lake from an alum surface application conducted in 1970. Malley and Donkersloot (1988) reported that floater mussels (*Anodonta grandis grandis*) suffered almost no mortality in an Ontario lake after the addition of alum. Although Moffett (1979) found a significant decrease in the species diversity of planktonic, microcrustacea in West Twin Lake, Ohio in two years of post-treatment sampling following an alum treatment, the diversity change could not be attributed to dissolved aluminum in the water column because concentrations were always below detection limits ($< 2 \mu\text{g/l}$ aluminum) at pH levels from 7-9 and alkalinity values of 100-150 mg/l as CaCO_3 . Rather, the shift in diversity was related to a change in algal food sources from blue-green to dinoflagellates and to increased predation by fish due to improvements in water column visibility.

Water Quality Criteria for Aluminum

Although many studies have illustrated the potential toxicity of aluminum at pH values less than 5.0-5.5 to a variety of aquatic species, there is virtually universal agreement that aluminum concentrations in the range of 50-100 $\mu\text{g/l}$ at pH values in the range of 6.5-8.0 pose little potential toxicity to organisms. Studies by Biesinger and Christensen (1972), Everhart and Freeman (1973), Lamb and Bailey (1981), and Peterson et al. (1974) indicate that a dissolved aluminum concentration below 50 $\mu\text{g/l}$ aluminum will have no harmful effects on *Daphnia magna*, rainbow trout (*Salmo gairdneri*), or chironomid larvae (*Tanytarsus dissimilus*).

In 1988, the U.S. Environmental Protection Agency published recommendations on ambient water quality criteria for the protection of aquatic organisms from the toxic effects of aluminum. As part of the process for establishment of ambient water quality criteria for aluminum, the U.S. Environmental Protection Agency conducted a careful analysis of the latest toxicological information available to EPA on the adverse effects of aluminum on aquatic vertebrates, invertebrates and plants. Acute toxicity data for 20 species of freshwater organisms and chronic toxicity data for five species of freshwater organisms were used to develop these criteria. A summary of information gathered by EPA on the acute toxicity of aluminum to aquatic freshwater species of potential significance is given in Table 2-1.

Evaluation of available acute toxicity data indicate that the most sensitive freshwater vertebrate is the juvenile brook trout (*Salvelinus fontinalis*) with an LC50 of 3600 $\mu\text{g/l}$ (Decker and Menendez, 1974). The most sensitive freshwater invertebrate is a cladoceran, *Ceriodaphnia dubis*, with an LC50 of 1900 $\mu\text{g/l}$ (McCauley et al., 1986).

A summary of information gathered by EPA on the toxicity of aluminum to aquatic freshwater plants is given in Table 2-2. The most sensitive freshwater alga is

TABLE 2-1

ACUTE TOXICITY OF ALUMINUM TO AQUATIC FRESHWATER SPECIES OF POTENTIAL SIGNIFICANCE

| TEST SPECIES | | TEST CONDITIONS | | LC VALUE ($\mu\text{g/l}$) | REFERENCE |
|----------------------------|--------------------------------|-------------------------------|-----------|------------------------------------|-------------------------------|
| COMMON NAME | TAXONOMIC NAME | HARDNESS (mg/l) | pH | | |
| Planarian (adult) | <i>Dugesia tigrina</i> | 47.4 | 7.48 | >23,000 | Brooke et al., 1985 |
| Snail (adult) | <i>Physa sp.</i> | 47.4 | 7.46 | 55,000 | Call, 1984 |
| Snail (adult) | <i>Physa sp.</i> | 47.4 | 6.59 | >23,000 | Call, 1984 |
| Snail (adult) | <i>Physa sp.</i> | 47.4 | 7.55 | 30,600 | Call, 1984 |
| Snail (adult) | <i>Physa sp.</i> | 47.4 | 8.17 | >24,700 | Call, 1984 |
| Cladoceran (<16 hr) | <i>Ceriodaphnia dubia</i> | 50.0 | 7.4 | 1,900 | McCauley et al., 1986 |
| Cladoceran (<24 hr) | <i>Ceriodaphnia sp.</i> | 47.4 | 7.68 | 3,690 | Call, 1984 |
| Cladoceran | <i>Daphnia magna</i> | 45.3 | 6.5-7.5 | 3,900 | Biesinger & Christensen, 1972 |
| Cladoceran | <i>Daphnia magna</i> | 45.4 | 7.61 | >25,300 | Brooke et al., 1985 |
| Amphipod (adult) | <i>Gammarus pseudolimnaeus</i> | 47.4 | 7.53 | 22,000 | Call, 1984 |
| Stonefly (numph) | <i>Acroneuria sp.</i> | 47.4 | 7.46 | >22,000 | Call, 1984 |
| Midge (larva) | <i>Tanytarsus dissimilis</i> | 17.43 | 7.71-6.85 | >79,000 | Lamb & Bailey, 1981 |
| Fathead Minnow (adult) | <i>Pimephales promelas</i> | -- | 7.6 | >18,900 | Boyd, 1979 |
| Fathead Minnow (juvenile) | <i>Pimephales promelas</i> | -- | 7.61 | >48,200 | Call, 1984 |
| Fathead Minnow (juvenile) | <i>Pimephales promelas</i> | -- | 8.05 | >49,800 | Call, 1984 |
| Channel Catfish (juvenile) | <i>Ictalurus punctatus</i> | 47.4 | 7.54 | >47,900 | Call, 1984 |
| Green Sunfish (juvenile) | <i>Lepomis cyanellus</i> | 47.4 | 7.55 | >50,000 | Call, 1984 |
| Yellow Perch (juvenile) | <i>Perca flavescens</i> | 47.4 | 7.55 | >49,800 | Call, 1984 |
| Brook Trout (juvenile) | <i>Salvelinus fontinalis</i> | -- | 6.5 | 3,600 | Decker & Menendez, 1974 |

NOTE: All tests conducted as static bioassay experiments.

SOURCE: U.S. Environmental Protection Agency, 1988.

TABLE 2-2

TOXICITY OF ALUMINUM TO AQUATIC FRESHWATER PLANTS

| TEST SPECIES | | TEST CONDITIONS | | TEST DURATION (days) | EFFECT | CONC. ($\mu\text{g/l Al}$) | REFERENCE |
|--------------------------|----------------------------------|-----------------|-----|----------------------|---------------------------------------|------------------------------|--------------------------|
| COMMON NAME | TAXONOMIC NAME | HARDNESS (mg/l) | pH | | | | |
| Diatom | <i>Cyclotella meneghiniana</i> | -- | 7.9 | 8 | Inhibited growth Algistatic | 810 3,240 | Rao & Subramanian |
| Green Alga | <i>Selenastrum capricornutum</i> | 15 | 7.0 | 14 | Reduced cell counts and dry weight | 900-1,320 | Peterson et al., 1974 |
| Green Alga | <i>Selenastrum capricornutum</i> | 14.9 | 7.6 | 4 | EC50 (biomass) | 570 | Call, 1984 |
| Green Alga | <i>Selenastrum capricornutum</i> | 14.9 | 8.2 | 4 | EC50 (biomass) | 460 | Call, 1984 |
| Eurasian Watermilfoil | <i>Myriophyllum spicatum</i> | -- | -- | 32 | EC50 (not weight) | 2,500 | Stanley, 1974 |
| Duckweed | <i>Lemna minor</i> | 14.9 | 7.6 | 4 | Reduced frond production | > 45,700 | Call, 1984 |
| Duckweed | <i>Lemna minor</i> | 14.9 | 8.2 | 4 | Reduced frond production | > 45,700 | Call, 1984 |

SOURCE: U.S. Environmental Protection Agency, 1988.

Selenastrum capricornutum with an EC50 of 460 $\mu\text{g/l}$ (Call, 1984). A review of the available data on the chronic toxicity of aluminum is given in Table 2-3. *Daphnia magna* is the most sensitive invertebrate species tested with a chronic value of 742 $\mu\text{g/l}$.

A summary of other studies on the effects of aluminum on aquatic organisms conducted by Cleveland et al. (1989) and Buckler et al. (1989) is given in Table 2-4 using brook trout larva (*Salvelinus fontinalis*) and striped bass (*Morone saxatilis*) as test species. In studies conducted by Cleveland et al. (1989) during a 60-day period at a pH of 6.5-6.6, brook trout exhibited a 48% mortality at an aluminum level of 350 $\mu\text{g/l}$, a 3% death rate and a 24% reduction in body weight at 169 $\mu\text{g/l}$, but only a 4% reduction in body weight at 88 $\mu\text{g/l}$. Similar results were reported by Buckler et al. (1989) with no mortality after 7 days at a pH level of 6.5 and a dissolved aluminum concentration of 87 $\mu\text{g/l}$. Significant mortality rates were observed at higher aluminum levels. These studies form the basis of the chronic criterion for aluminum established by the EPA.

Based on a review of the previously described studies and reports, the EPA established guidelines for aluminum concentrations based upon protection of the most sensitive important aquatic species. As a result, the criteria are generally conservative. The criteria recommend that the four-day average concentration of dissolved aluminum not exceed 87 $\mu\text{g/l}$ more than once every three years on the average when the ambient pH is between 6.5 and 9.0 to provide protection from chronic toxicity. The criteria also recommend that the one-hour average concentration of dissolved aluminum not exceed 750 $\mu\text{g/l}$ more than once every three years on the average when the ambient pH is between 6.5 and 9.0 to provide protection from acute toxicity.

Effects of Aluminum on Humans

Aluminum has generally been regarded as a benign element with respect to human toxicity for many years. However, in the last decade or two, a considerable

TABLE 2-3

CHRONIC TOXICITY OF ALUMINUM TO SELECTED FRESHWATER AQUATIC SPECIES

| TEST SPECIES | | TEST CONDITIONS | | TYPE OF TEST | RANGE RESTED ($\mu\text{g/l Al}$) | CHRONIC VALUE ($\mu\text{g/l}$) | REFERENCE |
|----------------|----------------------------|-------------------------------|-----------|------------------|--|--------------------------------------|------------------------|
| COMMON NAME | TAXONOMIC NAME | HARDNESS (mg/l) | pH | | | | |
| Cladoceran | <i>Ceriodaphnia dubia</i> | 50 | 7.15 | Life-cycle | 1,400-2,600 | 1,908 | McCauley, et al., 1986 |
| Cladocern | <i>Daphnia magna</i> | 220 | 8.30 | Life-cycle | 540-1,020 | 742 | Kimball, Manuscript |
| Fathead Minnow | <i>Pimephales promelas</i> | 220 | 7.24-8.15 | Early Life-stage | 2,300-4,700 | 3,288 | Kimball, Manuscript |

SOURCE: U.S. Environmental Protection Agency, 1988.

TABLE 2-4

OTHER STUDIES ON THE EFFECTS OF ALUMINUM
TO FRESHWATER AQUATIC SPECIES

| TEST SPECIES | | TEST CONDITIONS | | DURATION (days) | ALUMINUM CONC. ($\mu\text{g}/\text{l}^{-1}$) | EFFECT | REFERENCE |
|--------------------------------------|----------------------------------|---|--------------------------|--------------------|--|-------------------------|------------------------------------|
| COMMON NAME | TAXONOMIC NAME | HARDNESS (mg/l^{-1} as CaCO_3) | pH | | | | |
| Brook Trout (embryo, larva) | <i>Salvelinus fontinalis</i> | 12.3 | 6.5- 6.6 | 60 | 350 | 48% dead | Cleveland et al., Manuscript |
| | | | | | 169 | 3% dead | |
| | | | | | 169 | 24% reduction in weight | |
| | | | | | 88 | 4% reduction in weight | |
| Striped Bass (160 days) | <i>Morone saxatilis</i> | -- | 6.5 6.5 7.2 7.2 | 7 | 87.2 | 0% dead | Buckler et al., Manuscript |
| | | | | | 174.4 | 58% dead | |
| | | | | | 174.4 | 2% dead | |
| | | | | | 348.8 | 100% dead | |

body of evidence has been accumulated implicating aluminum in a variety of dysfunctions, both neurological (e.g., Alzheimer's Disease, dialysis encephalopathy, amyotrophic lateral sclerosis) and osteological (e.g., osteoporosis, osteomalacia). The role played by aluminum in each of these conditions is poorly understood, and there remains controversy over whether it is involved at all.

The average North American diet contains from 20-30 mg/day of aluminum, but this can be far exceeded, for example, by individuals who consume significant quantities of aluminum-based antacids (Greger, 1985). Lione (1985) estimated that 840-5000 mg aluminum and 126-728 mg aluminum were possible daily doses of aluminum in antacids and in buffered analgesics, respectively. A list of aluminum content of some common food products is given in Table 2-5.

Based upon the values presented in Table 2-4, it is obvious that the primary source of aluminum intake for humans is through the diet rather than through drinking water sources. Steeped tea contains an average of 4600 $\mu\text{g}/\text{l}$ aluminum, while milk contains 700 $\mu\text{g}/\text{l}$. Aluminum concentrations in these common foods are 1-2 orders of magnitude greater than the 50-100 $\mu\text{g}/\text{l}$ aluminum normally found in drinking water or lake water treated with alum. Although references related to aluminum content in foods were abundant, no references were found related to maximum recommended levels of aluminum through skin contact.

Toxicity of Alum Sludge

The majority of research related to the potential toxicity of alum sludge has concentrated on the constituents which become entrained in the sludge during the precipitation process. Pollutants removed from the water column become concentrated in the sludge by a factor of approximately 10,000. Toxic components enter the sludge as contaminants in commercial alum as well as from the raw water source. Analysis of

TABLE 2-5

ESTIMATED ALUMINUM CONCENTRATIONS OF SELECTED FOODS

| FOOD | ALUMINUM CONCENTRATIONS ¹ ($\mu\text{g/g}$) | FOOD | ALUMINUM CONCENTRATIONS ($\mu\text{g/g}$) |
|---------------------------|---|----------------------------------|--|
| Animal Products | | Vegetables | |
| Beef, cooked ² | 0.2 | Asparagus | 4.4 |
| Cheese, natural | 15.7 | Beans, green cooked ² | 3.4 |
| Cheese, processed | 297 | Cabbage, raw | 0.1 |
| Eggs, cooked ² | 0.1 | Cauliflower, cooked ² | 0.2 |
| Milk | 0.7 | Cucumber | 1.7 |
| Fruits | | Lettuce | 0.6 |
| Bananas | 0.4 | Peas, cooked ² | 1.9 |
| Grapes | 0.4 | Potatoes, unpeeled | 0.1 |
| Orange Juice | 0.05 | Potatoes, with skin | 2.4 |
| Grains | | Tomatoes, cooked ² | 0.1 |
| Bread, white | 3.0 | Other | |
| Bread, whole wheat | 5.4 | Baking powder | 23,000 |
| Rice, cooked ² | 1.7 | Cocoa | 45 |
| Herbs | | Coffee, brewed | 0.4 |
| Basil | 308 | Pickles, with alum | 39.2 |
| Bay | 436 | Salt with aluminum | 164 |
| Celery seed | 465 | Tea in bag, dry | 1280 |
| Oregano | 600 | Tea, steeped | 4.6 |
| Pepper, black | 143 | | |
| Sage | 404 | | |
| Thyme | 750 | | |

1. Values are arithmetic averages of sometimes widely differing individual values.
2. Food not cooked or stored in aluminum pans, trays or foils.

the sludge can be accomplished by using the extraction procedure (EP) toxicity test or through a total dissolution of the sludge. An analysis for alum sludge obtained from the city of Durham, NC is given in Table 2-6. Values are shown in terms of total metal present (mg/l) and are normalized to μg of metal/mg of aluminum. Also given are the concentrations of metals that were in the commercial alum used at this plant. The source of some metals was the alum, whereas other metals originated in the raw water source. Of course, the values are site-specific and must be evaluated for each situation.

Virtually all research conducted on the toxicity and leeching characteristics of alum sludge has indicated that most pollutants are tightly bound to the aluminum matrix with little or no affinity for release from either the dried or wet sludge forms. Leeching or contamination of surface or groundwaters with pollutants from alum sludge appears unlikely. It appears that the only feasible method by which alum sludge could pose a health risk to humans is through direct injection of the alum floc, which is unlikely to occur.

A potential health risk associated with alum sludge present is the concentration of bacteria and viruses from the water column into the sludge layer. Bulson et al. (1984) observed that during two separate alum treatments of a eutrophic lake, 90% of the fecal coliform (FC) population and 70% of the fecal streptococci population were removed from the water column within 72 hours. The number of fecal coliforms in the floc on the lake bottom exceeded 2400 FC/100 ml after 120 hours compared with pre-treatment concentrations of 30 FC/ml. Inactivation of the fecal coliforms in the floc proceeded at a rate of 200 FC/100 ml/24 hours. In a second alum application, 95% of the total culturable bacterial population was removed from the water column. In a laboratory column study of the survival and release rates, over 90% of an *Escherichia coli* suspension was concentrated in the floc formed at the bottom. *E. coli*

TABLE 2-6

TYPE AND SOURCE OF METAL CONCENTRATIONS IN ALUM SLUDGE FROM DURHAM, NORTH CAROLINA

| METAL | CONCENTRATION OF METAL IN COMMERCIAL ALUM | | CONCENTRATION IN 2.5 PERCENT SLUDGE | | PERCENT OF METALS FROM ALUM |
|-----------|---|---------------------------|-------------------------------------|---------------------------|-----------------------------|
| | mg/l | $\mu\text{g Metal/mg Al}$ | mg/l | $\mu\text{g Metal/mg Al}$ | |
| Cadmium | * | 0 | * | 0 | |
| Chromium | 9.5 | 0.2 | 0.6 | 0.3 | 66 |
| Copper | 0.1 | 0.002 | 0.6 | 0.3 | 0 |
| Iron | 1,160 | 18.4 | 292 | 146 | 12 |
| Sodium | 57 | 0.9 | 6.5 | 3.3 | 27 |
| Potassium | 5.6 | 0.1 | 6.1 | 3.0 | 3 |
| Manganese | 1.7 | 0.03 | 255 | 127 | 0 |
| Nickel | 0.1 | 0.002 | 0.06 | 0.03 | 0 |
| Lead | 1.5 | 0.02 | 0.03 | 0.02 | 100 |
| Zinc | 1.1 | 0.02 | 1.7 | 0.9 | 2 |
| Calcium | 6.3 | 0.1 | 2.8 | 1.4 | 7 |
| Magnesium | 12.5 | 0.2 | 5.5 | 2.7 | 7 |
| Aluminum | 63,000 | | 1,970 | | |
| Silicon | 14.2 | 0.2 | 8.5 | 4.2 | 5 |
| Barium | 0.5 | 0.01 | 0.3 | 0.1 | 10 |
| Silver | 0.4 | 0.01 | * | 0 | 100 |
| Arsenic | 3.0 | 0.05 | 1.1 | 0.05 | 100 |
| Selenium | * | 0 | * | 0 | |
| Mercury | 0.001 | 0 | 0.002 | 0 | |

* Below Detection Limit

was not released from the floc. The number of *E. coli* in the floc suggested the probable concentration of other enteric organisms, including pathogens. Thus, the floc poses a potential human health risk if ingested by swimmers.

Researchers have reported 80-90% virus removal at 18-50 mg/l alum dosages (Chang and Jackson, 1959; Manwaring et al., 1971; Chaudhuri and Engelbrect, 1970; York and Drewry, 1974; Pasco, 1956; Guy and McIver, 1977; Malek et al., 1981). Malek et al. (1981) suggest that virus removal was due to entrapment of the virus within the precipitating floc. Chaudhuri and Engelbrect (1970) reported that coagulants initially form a coordination complex between the virus and aluminum. They believed that aluminum coordinated with carboxyl groups in the protein coat of the virus. The complex was subsequently incorporated into the precipitating aluminum hydroxide floc. However, the viruses were not inactivated but could be partially recovered from the sludge. The presence of organic matter was shown to decrease the amount of virus removal due to competition.

CHAPTER 3
DESCRIPTION OF LAKE ELLA
AND THE ALUM STORMWATER TREATMENT SYSTEM

Historical Conditions and Water Quality Problems

Lake Ella is a small 5.38 hectare (13.29 ac) land-locked lake located in Tallahassee, Florida. The shoreline areas surrounding Lake Ella are heavily used for recreational activities such as jogging and picnics, and the lake is the site for many cultural events throughout the year. Aesthetically, this lake is of tremendous value to the residents in the surrounding neighborhoods and all of Tallahassee. Physical characteristics of Lake Ella prior to installation of the alum treatment system are given in Table 3-1.

Lake Ella receives large quantities of stormwater runoff from a highly urbanized watershed of approximately 63.7 hectare (157.2 ac). A schematic of the Lake Ella stormsewer system prior to construction of the alum injection system is given in Figure 3-1. Prior to restoration activities, 18 active storm drains discharged untreated stormwater runoff into Lake Ella.

Contributing drainage sub-basins to Lake Ella are outlined in Figure 3-2. There are 13 separate areas which drain into Lake Ella through individual stormsewer lines or by overland flow. Physical characteristics of sub-basin areas are given in Table 3-2. Geographic relief in the watershed areas surrounding Lake Ella is generally quite steep. Soil types within the Lake Ella watershed are classified in Hydrologic Soil Group C and consist of combinations of silty sand, clayey sand and lean sand. Runoff potential from pervious areas with these characteristics is considered to be moderate to high.

TABLE 3-1
 PHYSICAL CHARACTERISTICS
 OF LAKE ELLA BEFORE RESTORATION

| PARAMETER | QUANTITY |
|-----------------------------|--|
| Surface Area | 5.38 ha (13.29 acres) |
| Volume | $1.13 \times 10^5 \text{ m}^3$ (91.4 acre-feet) |
| Mean Depth | 2.10 m (6.87 feet) |
| Maximum Depth | 2.7 m (9.0 feet) |
| Length of Shoreline | 983 m (3225 feet) |
| Shoreline Development | 1.20 |
| Volume Development | 2.29 |
| Mean Height Above Sea Level | 48.0 m (157.5 feet) |

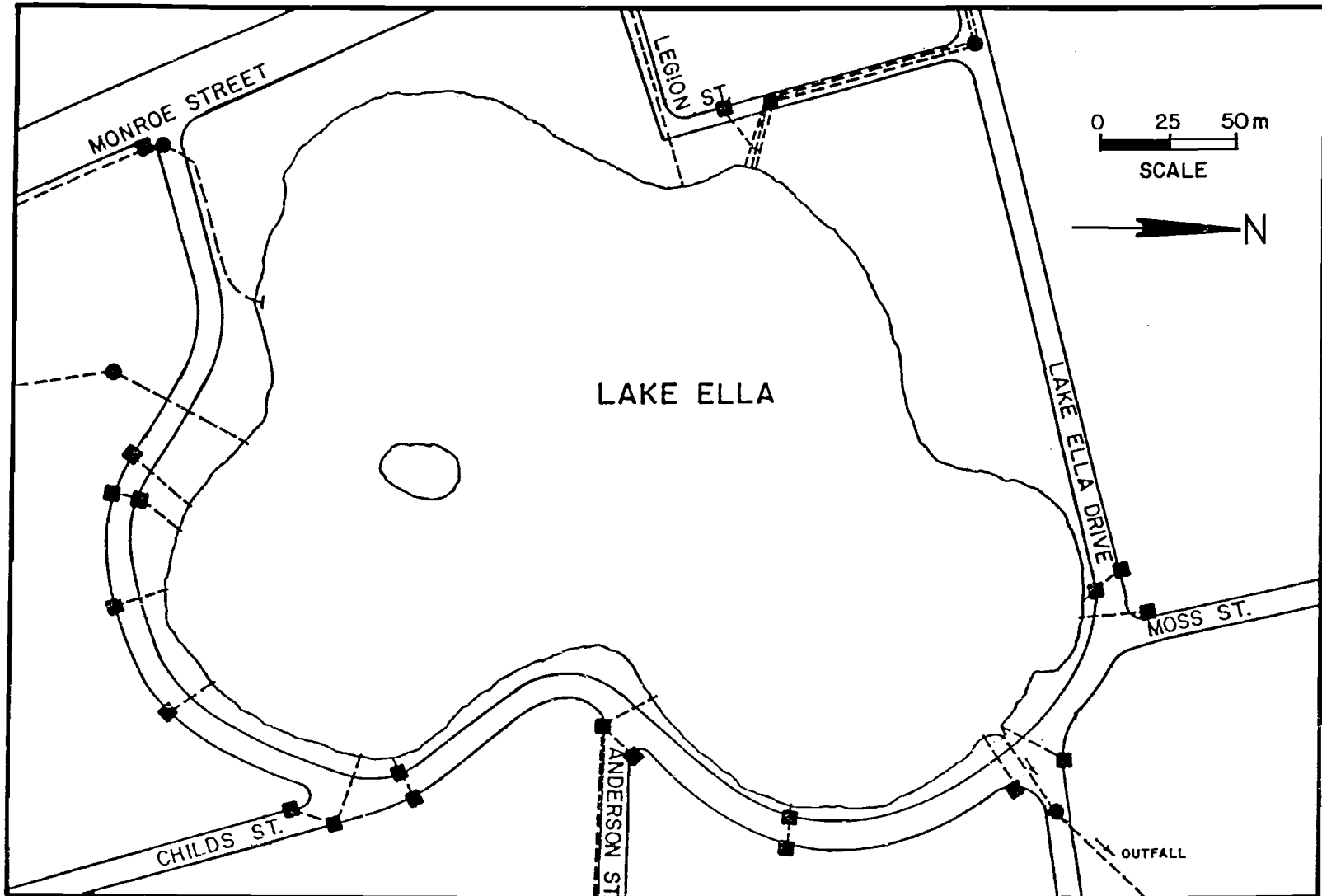


Figure 3-1. Lake Ella Stormsewer System Prior to Construction of the Alum Stormwater Treatment System.

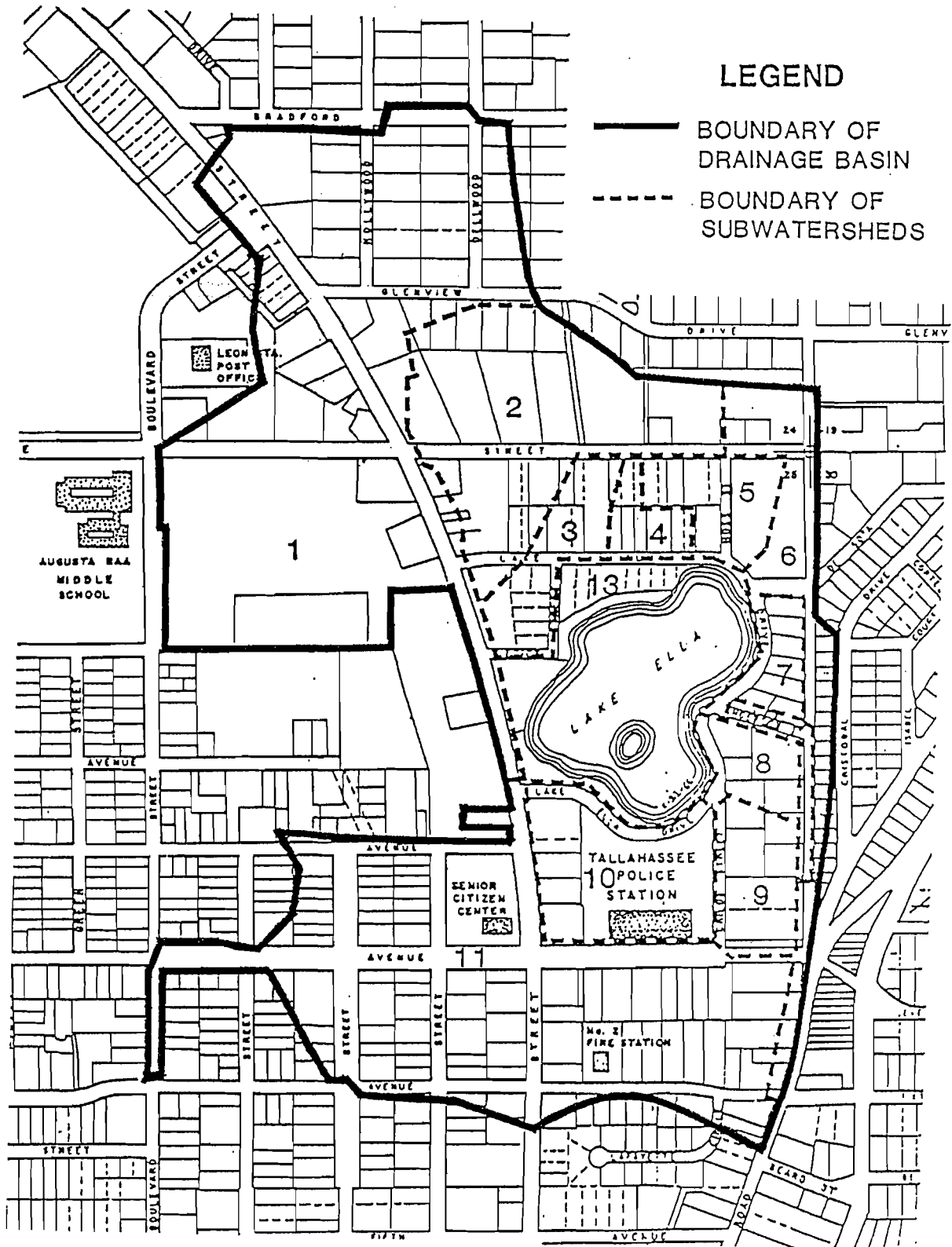


Figure 3-2. Contributing Watershed Areas to Lake Ella.

TABLE 3-2

PHYSICAL CHARACTERISTICS OF SUB-WATERSHED AREAS IN THE LAKE ELLA DRAINAGE BASIN

| BASIN | AREA | GENERAL DESCRIPTION | OBSERVED CHARACTERISTICS | |
|-------|------------------------|----------------------------|---|---|
| 1 | 21.47 ha (53.02 ac) | Commercial/ Residential | Divided into a commercial area and a dense residential area: | |
| | | | Commercial | Includes K-Mart, Albertsons and the businesses lining both sides of Monroe Street as well as the north side of Tharpe Street. Most drain directly or indirectly into stormdrains along Monroe Street. Characterized by a high degree of imperviousness with steep slopes. |
| | | | Residential | Dense area of single-family homes north of Glenview Drive. Drainage is generally through grassed swales which ultimately discharge into stormsewers along Monroe Street. Percent impervious estimated at 40%. |
| 2 | 7.40 ha (18.28 ac) | Commercial/ Residential | Divided into a commercial area and a densely wooded residential area: | |
| | | | Commercial | A small area located in the southwest corner of the sub-watershed which includes a restaurant, gas station and several small businesses. Area is predominantly impervious with relatively steep slopes. Drainage occurs by overland flow and is collected by inlets along the eastern portion of this area. |
| | | | Residential | A medium density residential area which is heavily wooded with a dense ground cover. Average slope is approximately 0.069. Runoff potential from this type of land use is generally low, but is increased in this case by the steep slope. Drainage is collected along Tharpe Street and enters stormsewer lines. |
| 3 | 2.35 ha (5.81 ac) | Commercial/ Residential | Divided into a commercial area and a wooded residential area: | |
| | | | Commercial | An area along Monroe Street of small cottage-type businesses. Area is either paved or clay with high runoff potentials. Drainage flows to an open inlet along Legion Street. |
| | | | Residential | A densely wooded residential area with both single and multi-family uses. Average land slope is 0.0705. Wooded area is covered with dense ground litter. Drainage is collected along Lake Ella Drive. Runoff potential is generally low, but is increased as a result of the steep land slope. |

TABLE 3-2 -- CONTINUED

| BASIN | AREA | GENERAL DESCRIPTION | OBSERVED CHARACTERISTICS |
|-------|-----------------------|--------------------------------|--|
| 4 | 0.81 ha (2.00 ac) | Densely Wooded/ Residential | A densely wooded, low density, single-family residential area. Drainage is overland flow which is collected along Lake Ella Drive. Percent impervious estimated at 40%. Runoff potential is generally low for this land use, but is increased by the steep average land slope of 0.0918. |
| 5 | 1.35 ha (3.33 ac) | Church with Open Spaces | Area consists of a church with associated parking lots and grassed areas. Impervious areas are generally steep with a high and a rapid runoff potential. Grassed areas are also relatively steep with a moderate runoff potential. Drainage is by sheet flow to an inlet along Lake Ella Drive. |
| 6 | 3.72 ha (9.19 ac) | Open Spaces | Consists of roadway areas along Tharpe Street and Meridian Road with a small wooded area in the northwest corner and open grassed areas in the southern portion. Runoff potential for roadways and grassed areas is high. Drainage is by overland flow to inlets along Meridian Road. Average slope of the wooded area is 0.0700. |
| 7 | 1.17 ha (2.89 ac) | Residential | Area consists of a dense residential area with an average slope of 0.0867. Pervious areas are generally grassed. Runoff potential from this area is generally low. Drainage occurs by overland flow to an inlet along Lake Ella Drive. |
| 8 | 1.31 ha (3.24 ac) | Residential | A dense area similar to sub-watershed 7. Pervious areas are generally grassed. Average slope is 0.0817, but runoff potential is low due to the low percentage of impervious areas. Drainage occurs by overland flow and is collected by inlets along Lake Ella Drive. |
| 9 | 2.32 ha (5.73 ac) | Residential | A residential area with low density single-family housing and a large apartment complex. The apartment complex is largely impervious with numerous parking lots. Average drainage slope is approximately 0.0543. Pervious areas are mainly grassed. Drainage occurs by overland flow to Childs Street where it is collected by inlets. Runoff potential is high. |
| 10 | 4.35 ha (10.74 ac) | Commercial/ Office | A large sub-watershed which includes the entire block area bounded by Monroe Street, Seventh Avenue, Childs Street and Lake Ella Drive. Southern portion is occupied by a police station with commercial use along Monroe Street. The northern area is open with a thin grass cover. Average slope is 0.0317 with a moderate runoff potential. Drainage occurs by overland flow to inlets along Lake Ella Drive. |

TABLE 3-2 -- CONTINUED

| BASIN | AREA | GENERAL DESCRIPTION | OBSERVED CHARACTERISTICS | |
|-------|------------------------|----------------------------|---|---|
| 11 | 15.17 ha (37.46 ac) | Commercial/ Residential | This area is divided into a commercial area and a dense residential area: | |
| | | | Commercial | Located mainly along and adjacent to Monroe Street. Area is largely impervious with a high runoff potential. Runoff is collected by inlets along Monroe Street. |
| | | | Residential | Located in western and eastern portions of the sub-watershed. Housing is dense with pervious areas grassed. Stormwater is collected by inlets along Seventh Avenue and discharged to stormsewers along Monroe Street. Average slope is 0.008. |
| 12 | 0.39 ha (0.96 ac) | Street | Consists of portions of Meridian Road and Anderson Street with a small amount of residential drainage. Average slope is 0.080 with a high runoff potential. | |
| 13 | 1.97 ha (4.86 ac) | Park Land | Consists of park land areas immediately surrounding Lake Ella. The low slope of 0.024 makes the runoff potential low for low intensity events. A small area of commercial use is located along Monroe Street. | |

The estimated weighted runoff coefficient for the Lake Ella watershed is 0.434. Water levels within the lake are controlled by a 38 cm (15 in) outfall line which discharges to a downstream county drainage system.

As a result of continual stormwater loadings, algal productivity in Lake Ella increased substantially during the 1970s and early 1980s. Algal blooms were a frequent and often persistent occurrence. Build-up of flocculant sediment matter increased rapidly. Large masses of algae could be seen floating along the shoreline, and fish and duck kills were reported periodically. Rapid increases in the growth of rooted aquatic weeds were also reported. Plumes of settled suspended solids accumulated around the outfall pipes, several of which were exposed much of the time. Measurements of dissolved oxygen in Lake Ella often indicated very high concentrations near the surface as a result of the high rate of algal productivity. However, dissolved oxygen levels declined rapidly with increasing depth due to the oxygen demand created by the accumulated sediment material.

A summary of physical-chemical profiles collected in Lake Ella on November 29, 1985 is given in Figure 3-3. Although significant thermal stratification was not observed in the water column, measured values of both dissolved oxygen and redox potential (ORP) decreased rapidly at water depths greater than 1 meter. At depths below 2 meters, dissolved oxygen levels were less than 1 mg/l, and the water column became reduced. Because of low dissolved oxygen conditions near the sediment-water interface, internal recycling of phosphorus from bottom sediments was thought to be a significant nutrient source to the water column.

Historical water quality data on Lake Ella is somewhat limited and does not exist prior to 1975. From 1975 to 1985, a total of 15 water quality samples were collected by City of Tallahassee personnel primarily from surface water layers near the shoreline or at the outfall. A summary of mean characteristics for available water

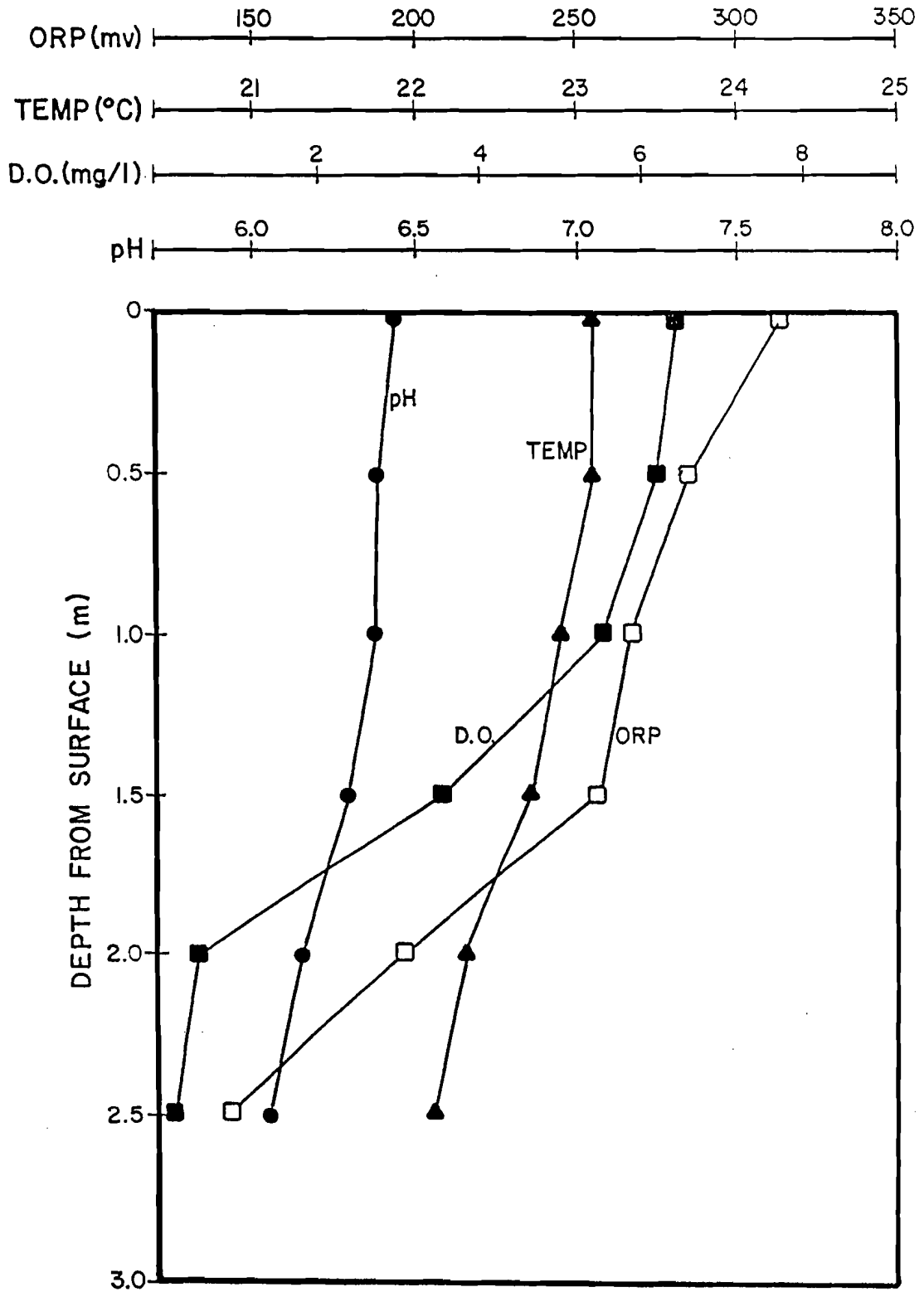


Figure 3-3. Physical-Chemical Profiles in Lake Ella on 11/29/85.

quality data is given in Table 3-3. Prior to construction of the alum injection system, Lake Ella was characterized by high levels of turbidity, total phosphorus, BOD and extremely high levels of chlorophyll a. Secchi disk transparency was generally less than 0.5 meter at all times.

Characterization of stormwater quality within the Lake Ella basin was conducted as part of the restoration feasibility study by collection of stormwater samples from seven major stormsewers during three storm events in May and June 1984. Samples were collected during storm events on 5/23/84, 5/29/84 and 6/14/84 from each of the seven major stormsewer lines. Sample locations were selected to include watersheds of varying size and land use classifications. In general, stormwater samples were collected in the man-hole immediately upstream of the points of discharge into the lake. A summary of mean weighted runoff characteristics from the three monitoring events is given in Table 3-4.

Runoff entering Lake Ella was characterized by a pH slightly less than neutral with a mean alkalinity of only 19 mg/l. Concentrations of total nitrogen were relatively high and were comprised primarily of nitrate and organic nitrogen. Total phosphorus and orthophosphorus concentrations in stormwater were found to be extremely high with a mean total phosphorus concentration of 750 $\mu\text{g/l}$ and an orthophosphorus concentration of 490 $\mu\text{g/l}$. Measured values for BOD and suspended solids were also extremely high in runoff inputs with averages of 25.5 and 111 mg/l, respectively.

In contrast, concentrations of heavy metals measured in stormwater runoff in the Lake Ella basin were generally low in comparison to heavy metal concentrations normally measured in urban runoff. Cadmium and chromium were present in concentrations below or near detection limits. Concentrations of iron, nickel, lead and copper, which are often abundant in urban runoff, were also found to be relatively low.

TABLE 3-3
 WATER QUALITY CHARACTERISTICS OF LAKE
 ELLA PRIOR TO ALUM TREATMENT OF STORMWATER

| PARAMETER | UNITS | MEAN CHEMICAL CHARACTERISTICS PRIOR TO ALUM INJECTION 1974-85 ¹ |
|--------------------------------------|-------------------------|--|
| pH | s.u. | 7.41 |
| Spec. Conductivity | $\mu\text{S}/\text{cm}$ | 91 |
| Dissolved O ₂ (1 m) | mg/l | 3.5 |
| Alkalinity | mg/l | 25.3 |
| Turbidity | NTU | 22 |
| NH ₃ -N | $\mu\text{g}/\text{l}$ | 276 |
| NO ₂ + NO ₃ -N | $\mu\text{g}/\text{l}$ | 50 |
| Diss. Organic N | $\mu\text{g}/\text{l}$ | -- |
| Part. Organic N | $\mu\text{g}/\text{l}$ | 1550 |
| Ortho-P | $\mu\text{g}/\text{l}$ | 23 |
| Total P | $\mu\text{g}/\text{l}$ | 232 |
| SO ₄ ⁻² | mg/l | -- |
| Chlorophyll-a | mg/m ³ | 180 |
| BOD | mg/l | 41 |
| Secchi Disk Depth | m | <0.5 |

1. n = 15 samples

TABLE 3-4
 SUMMARY OF RUNOFF CHARACTERISTICS
 ENTERING LAKE ELLA DURING 1974

| PARAMETER | UNITS | CONCENTRATION | MASS LOADING (kg/year) |
|--------------------|-------|---------------|---------------------------|
| pH | s.u. | 6.34 | - |
| Alkalinity | mg/l | 19.0 | 7993 |
| NH ₃ -N | μg/l | 220 | 92.6 |
| NO ₃ -N | μg/l | 1320 | 555 |
| Organic N | μg/l | 1810 | 761 |
| Total N | μg/l | 3350 | 1410 |
| Ortho-P | μg/l | 490 | 206 |
| Total P | μg/l | 750 | 316 |
| BOD | mg/l | 25.5 | 10,727 |
| TSS | mg/l | 111 | 46,697 |
| Cd - Dissolved | μg/l | 0.12 | 0.050 |
| Total | | 0.14 | 0.059 |
| Cu - Dissolved | μg/l | 6.0 | 2.52 |
| Total | | 9.2 | 3.87 |
| Fe - Dissolved | μg/l | 142 | 59.7 |
| Total | | 201 | 84.6 |
| Pb - Dissolved | μg/l | 19.8 | 8.33 |
| Total | | 29.8 | 12.5 |
| Zn - Dissolved | μg/l | 243 | 102 |
| Total | | 289 | 122 |
| Ni - Dissolved | μg/l | 7.8 | 3.28 |
| Total | | 12.1 | 5.09 |

Zinc was the only measured heavy metal which was found in significant amounts in the Lake Ella runoff.

Evaluation of the Feasibility of Alum Treatment of Stormwater

After a detailed watershed analysis and evaluation of restoration alternatives, it was decided that conventional stormwater management techniques such as retention ponds, detention ponds, filtration systems or underground exfiltration systems were not feasible within the Lake Ella watershed due to limitations of available space and soil characteristics. A pilot study was conducted to evaluate the feasibility of using alum to treat stormwater runoff within the stormsewer system prior to discharge into Lake Ella.

Physical and chemical characteristics of alum are presented in Table 3-5. Commercial liquid alum is generally sold as a yellow-green solution consisting of approximately 48.5 percent dry aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in water which contains 8.3 percent Al_2O_3 . In this form, alum is acidic, with a pH of approximately 1.5. Liquid alum is approximately 33 percent heavier and substantially more viscous than water.

The feasibility of alum treatment for stormwater inputs into Lake Ella was evaluated in a series of jar tests conducted on stormwater runoff collected within the Lake Ella drainage basin during May and June 1984 to provide estimates of expected removal rates and to define the optimum alum dose. The optimum alum dose was defined as the minimum alum dose necessary to provide reductions in total phosphorus of approximately 90% or more while maintaining a pH level within the range of 6.0 to 6.5. Based upon this criteria, the results of the laboratory tests defined the optimum alum dose as approximately 20 mg/l as Al_2O_3 .

A summary of removal efficiencies obtained by alum treatment of stormwater at a dose of 20 mg/l and a settling time of 24 hours is presented in Table 3-6. Addition

TABLE 3-5

PHYSICAL AND CHEMICAL CHARACTERISTICS OF ALUM

| PRODUCT DESCRIPTION OF ALUMINUM SULFATE, LIQUID | |
|---|---|
| Formula | Approximately 48.5% dry aluminum sulfate in water |
| Appearance | Light green to light yellow liquid |
| Specific Gravity (60° F) | 1.335 |
| pH of 1% Solution | 3.5 (approximate) |
| Baume (60° F) | 36.4 |
| lb/gal (U.S.) | 11.1 |
| lb/gal (Imperial) | 13.3 |
| lb alum/gal (U.S.) | 5.4 |
| lb alum/gal (Imperial) | 6.5 |

| TYPICAL ANALYSES OF ALUMINUM SULFATE, LIQUID | | |
|--|------------|-----------|
| GRADE | COMMERCIAL | IRON-FREE |
| Total Al ₂ O ₃ | 8.3 | 8.3 |
| Free Al ₂ O ₃ | 0.1 | 0.1 |
| Total Iron as Fe ₂ O ₃ (%) | 0.2 | 0.004 |
| Actual Fe ₂ O ₃ (%) | 0.03 | - |
| Insoluble in Water (%) | 0.01 | 0.004 |

SOURCE: General Chemical

TABLE 3-6

SUMMARY OF ALUM TREATMENT PERFORMANCE USING A DOSE OF 20 mg/l AS Al₂O₃ AND A SETTLING TIME OF 24 HOURS

| PARAMETER | UNITS | MEAN RUNOFF CONC. | MEAN CONC. AFTER ALUM TREATMENT | AVERAGE PERCENT CHANGE |
|--------------------------------------|------------|-------------------|---------------------------------|------------------------|
| Spec. Conductivity | μS/cm | 119 | 170 | +70 |
| Alkalinity | mg/l | 35.5 | 10.5 | -73 |
| NH ₃ -N | μg/l | 107 | 40 | -52 |
| NO ₂ + NO ₃ -N | μg/l | 923 | 868 | -6 |
| Diss. Organic N | μg/l | 330 | < 10 | -99 |
| Part. Organic N | μg/l | 394 | 125 | -69 |
| Total N | μg/l | 1753 | 1092 | -47 |
| Diss. Ortho-P | μg/l | 47 | 1 | -98 |
| Diss. Organic P | μg/l | 102 | 7 | -94 |
| Total P | μg/l | 417 | 40 | -91 |
| Sulfates | mg/l | 13 | 67 | +919 |
| BOD | mg/l | 20.7 | 11.8 | -42 |
| T.D.S. | mg/l | 103 | 125 | +31 |
| S.S. | mg/l | 49.3 | 7.5 | -85 |
| Turbidity | NTU | 52.9 | 7.7 | -86 |
| Total Coliform | No./100 ml | 4680 | 305 | -94 |
| Fecal Coliform | No./100 ml | 1020 | 95 | -91 |
| Diss. Al | μg/l | 287 | 39 | -86 |
| Total Al | μg/l | 947 | 156 | -84 |

n = 6 tests

of alum to stormwater runoff at a dose of 20 mg/l was found to reduce concentrations of ammonia by 52%, total nitrogen by 47%, dissolved orthophosphorus by 98%, total phosphorus by 91%, BOD by 42%, suspended solids by 85%, turbidity by 86%, total coliform by 94% and fecal coliform by 91%. Concentrations of both dissolved and total aluminum were found to be substantially less following the alum treatment than measured in the raw runoff prior to treatment as a result of pH modifications into the range of minimum aluminum solubility. The pH of the raw stormwater was reduced from an average value of 6.73 to an average value of 6.31 at an alum dose of 20 mg/l.

Complete settling of the floc particles was observed to be approximately 90% complete within 30 minutes. These particles formed a thin layer on the bottom of each test chamber. The supernatant waters were clear and free of visible particles. Based upon these impressive laboratory results, a treatment system was designed to inject liquid alum into stormwater entering Lake Ella at an initial dose of 20 mg/l as Al_2O_3 .

Description of the Alum Injection System

The alum stormwater treatment system for Lake Ella was designed using sonic flow meters and variable speed injection pumps to automatically inject liquid alum into the stormsewer line upstream of the lake at a flow proportioned rate. Mixing of the alum and stormwater occurs as a result of turbulence in the stormsewer line, and the floc produced settles on the lake bottom providing an added benefit of nutrient inactivation in the sediments.

A plan view of the stormsewer modifications required for the alum stormwater treatment system at Lake Ella is shown in Figure 3-4. Several of the smaller individual stormsewer lines were combined and connected together to consolidate points of discharge into the lake from the original 18 inlets to 10 inlets. Six of these 10 inputs,

Figure 3-4 is missing from original document.

representing 95% of the annual runoff inputs into Lake Ella, are equipped with points of alum injection as indicated in Figure 3-4. The alum is introduced into the stormwater flow approximately 30-150 meters (100-500 feet) upstream of the point of discharge into the lake to allow adequate time for mixing of the alum and stormwater flow. Bar type trash traps with fine mesh stainless steel screens were also constructed on each stormsewer to reduce the amount of debris and leaves entering the lake.

The alum injection system is designed to inject liquid alum into the six stormsewer lines at points upstream of the lake on a flow-weighted basis to achieve the desired alum dose regardless of the incoming stormwater flow. Standard triplex metering pumps, common in wastewater applications, are used as the injection pumps. Pumps and control devices for the injection system are housed in an above-ground structure constructed on the south shore of Lake Ella adjacent to the existing park area. A 22,700 liter (6000 gal) above-ground alum storage tank is located next to the pump station facility. Underground conduits for alum feed, power and flow meter transmitter signals were run from the pump station to each of the six flow monitoring and injection locations.

A typical cross-section of alum injection system modifications is given in Figure 3-5. Alum feed lines were inserted into each man-hole, and the alum is pumped as a small stream into the stormwater flow. A check valve was placed on the end of each discharge line to prevent the accidental discharge of alum except under pumped conditions. Upon entering the stormwater flow, the alum mixes with the stormwater due to the natural turbulence which exists in the stormsewer line.

The operation of each injection pump is regulated by a single sonic flow meter device attached to the specific stormwater line. A total of six sonic flow meters are used to operate the six injection pumps. Locations of the sonic meters are indicated in

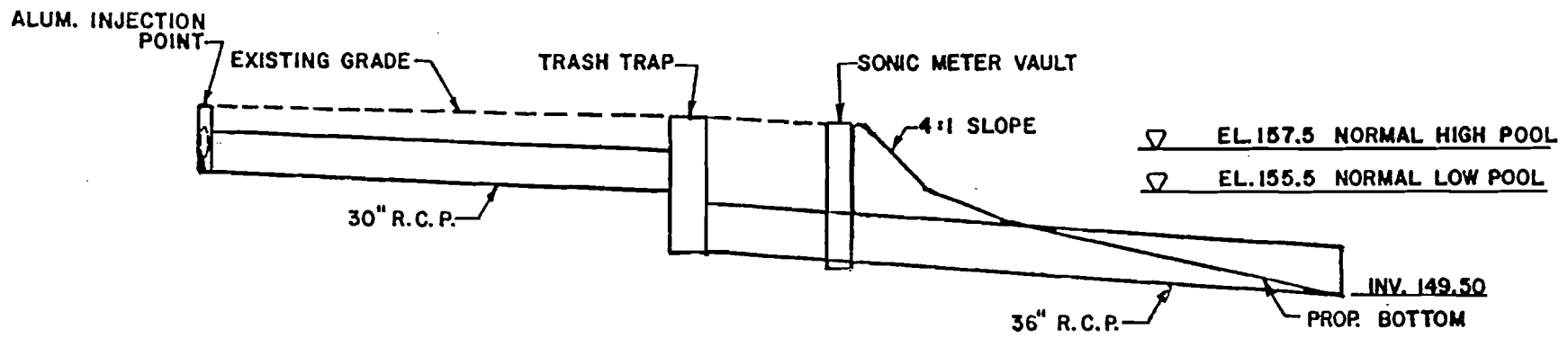
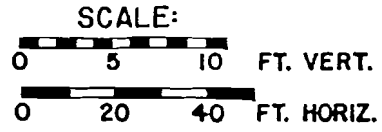


Figure 3-5. Typical Cross-Section of Alum Injection System Modifications.

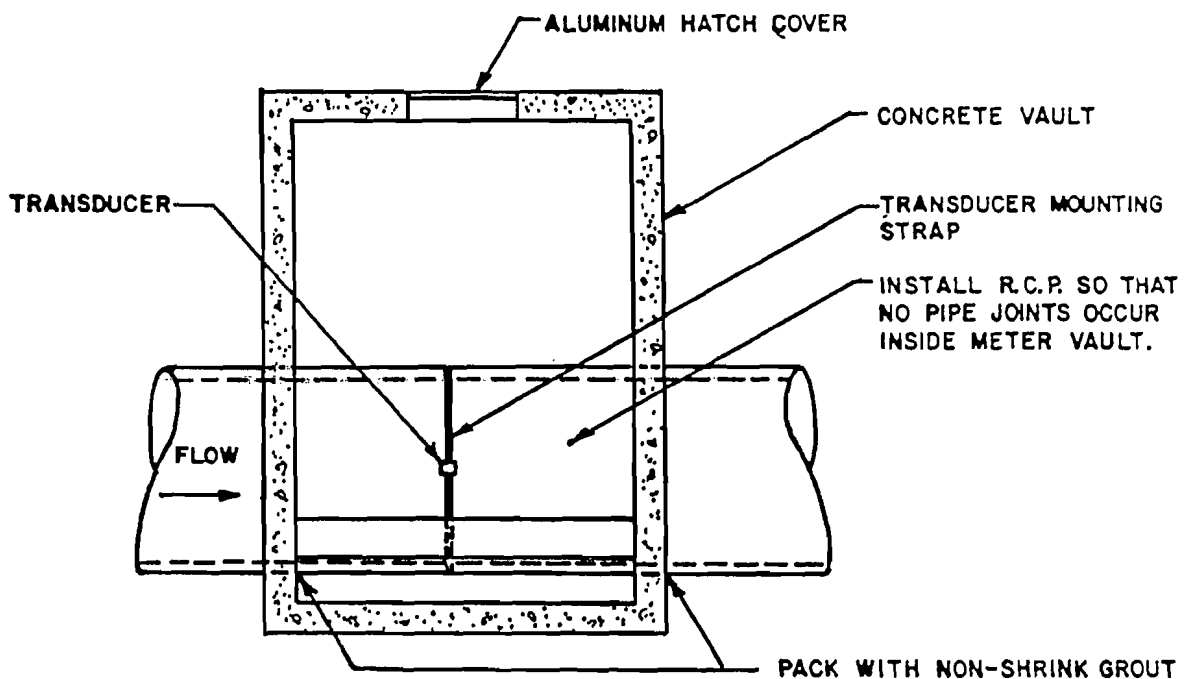
Figures 3-4 and 3-5. Operation of the sonic flow meters requires that the stormsewer pipe be totally full at all times. This requirement necessitated modification and lowering of each of the six stormsewer lines as part of the restoration process. During flow conditions, each sonic meter produces a 4-20 milliamp DC signal which is proportional to the stormsewer flow. This signal is transmitted through underground cables to the pump station where the milliamp signals are used to operate the variable speed metering pumps.

A typical sonic meter installation is shown in Figure 3-6. Each sonic meter installation consists of two transducers which both send and receive sonic signals into the stormwater flow. Changes in the sonic signals are translated into flow rates occurring within the pipes. These signals are sent by transducer cable to an above-ground sonic meter transmitter which transmits the 4-20 milliamp DC signal back to the pump station.

A summary of capital construction costs for the alum injection system is provided in Table 3-7. The total cost of the alum injection system components, excluding the extensions of stormsewer lines into the lake, was approximately \$200,400. Almost 50% of this cost was for the alum injection pumps themselves which cost approximately \$15,000 each. This capital cost is approximately \$3,141 per hectare (\$1,270 per acre) of watershed area treated. In general, the capital costs involved in constructing an alum injection system are relatively independent of watershed size and depend primarily upon the number of outfall locations treated.

Additional Improvements to Lake Ella

In addition to the alum treatment system modifications described previously, several other alterations were made to Lake Ella as part of the overall maintenance and restoration effort. A substantial dredging and recontouring process was conducted



TYPICAL SECTION THRU METER VAULT

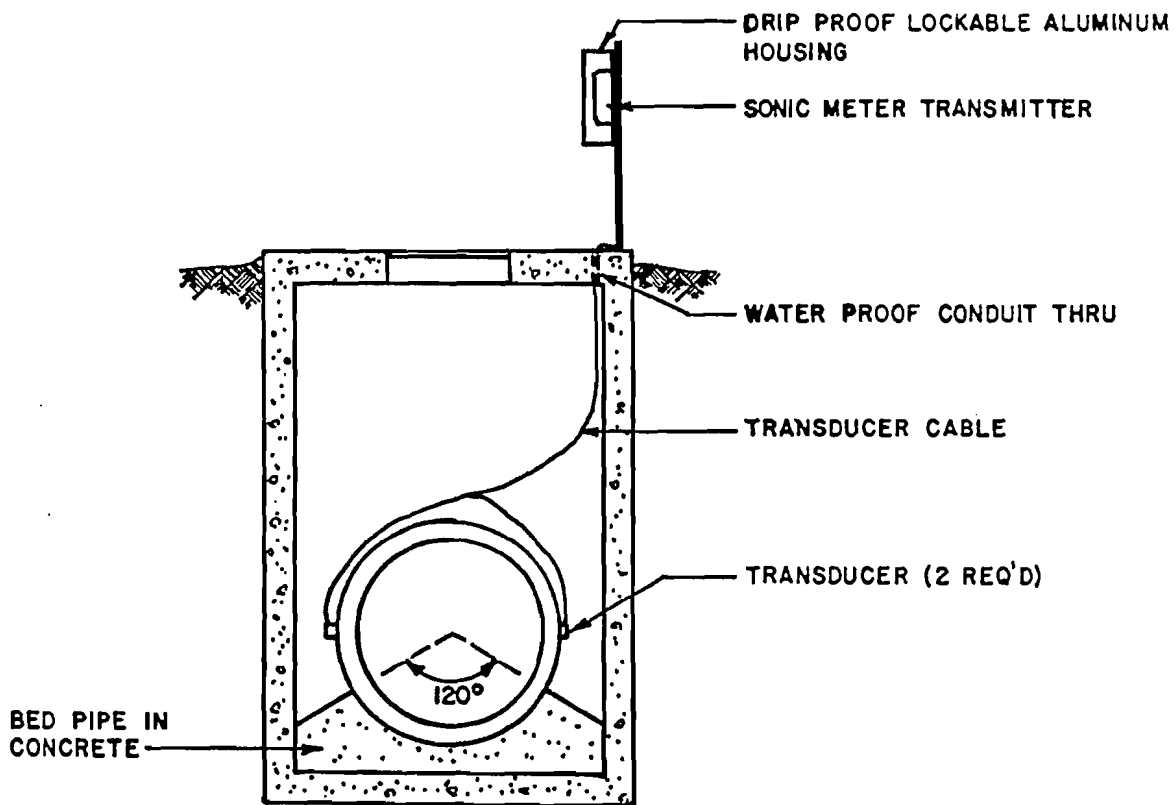


Figure 3-6. Typical Sonic Meter Installation.

TABLE 3-7

SUMMARY OF ALUM INJECTION SYSTEM COSTS

| NO. | ITEM | COST |
|-------|---|-----------|
| 1 | Pump Building (with mechanical) | \$ 35,000 |
| 2 | Alum Storage Tank - 22,710 liter (6000 gallon, fiberglass) | 13,900 |
| 3 | Alum Injection Pumps (6 at \$15,000 each) | 90,000 |
| 4 | Sonic Flow Meters (6 at \$5,650 each) | 33,900 |
| 5 | Transmitter Housing Near Sonic Meter (6 at \$850 each) | 5,100 |
| 6 | Installation of Underground Alum Lines and Transmitter Cables | 20,000 |
| 7 | System Testing | 2,500 |
| TOTAL | | \$200,400 |

which removed approximately 38,260 m³ (50,000 yd³) of accumulated sand, debris and muck from the bottom of Lake Ella. This process resulted in a lowering of the average bottom elevation in Lake Ella by approximately 0.6 m (2 ft). The majority of this excess material was transported to an off-site location as fill material. However, a portion of the excavated material was used to construct a peninsula on the south end of Lake Ella extending approximately 100 meters (330 feet) into the lake connecting an existing small island with the shore. Following removal of the dredged material, the bottom of Lake Ella was recontoured with a gradual slope toward the outfall control structure located at the northeast corner of the lake.

A comparison of physical characteristics of Lake Ella before and after the lake restoration efforts is given in Table 3-8. As a result of the addition of the peninsula, the surface area of the lake was reduced from 5.38 hectare (13.3 ac) to 4.77 hectare (11.8 ac). As indicated previously, the bottom elevation of the lake was lowered approximately 0.6 meter (2 ft) during the excavation of excess material from the lake. However, the normal water elevation within the lake was also lowered by this same amount to allow for increased storage and flood protection within the lake during extreme rain events. As a result, the mean depth of the lake was virtually unchanged following the restoration activity. However, the volume of the lake decreased approximately 27% as a result of the decrease in available surface area.

Start-up of the Alum Injection System

Construction of the alum injection system and recontouring efforts within the lake were begun in January 1986 and were completed in October 1986. During the construction period, the lake was maintained in a drained condition so that the majority of the required earth work could be conducted under dry conditions. At the completion of the earth work and stormsewer modifications in October, the lake was allowed to

TABLE 3-8
 PHYSICAL CHARACTERISTICS OF
 LAKE ELLA BEFORE AND AFTER RESTORATION

| PARAMETER | BEFORE RESTORATION | AFTER RESTORATION |
|---|------------------------|------------------------|
| Surface Area | 5.38 hectare | 4.77 hectare |
| | 13.3 acres | 11.8 acres |
| Volume | 113,000 m ³ | 82,500 m ³ |
| | 86,461 ft ³ | 63,124 ft ³ |
| Mean Depth | 2.10 m | 2.0 m |
| | 6.9 ft | 6.6 ft |
| Maximum Depth | 2.7 m | 4.0 m |
| | 8.9 ft | 13.1 ft |
| Length of Shoreline | 983 m | 1094 m |
| | 3224 ft | 3588 ft |
| Mean Water Elevation Above Sea Level | 48.0 m | 47.4 m |
| | 157.4 ft | 155.5 ft |

refill naturally with stormwater. By January 1987, the lake had refilled to the design normal water level.

In February 1987, a whole-lake surface treatment of alum was conducted to clarify the water column prior to start-up of the injection system. This whole-lake addition of alum involved a surface application of approximately 6,500 liters (2000 gallons) of alum with careful monitoring of the lake pH so that a final whole-lake pH no lower than 6.5 was achieved at the end of the application process. The alum injection system was then placed on automatic operation and the performance of the system was observed and fine tuned for a period of several months.

When the alum injection system became operational in January 1987, the metering pumps were set to inject alum at a dose of 20 mg/l as Al_2O_3 . During the period from January to June 1987, the operation of the system was carefully observed, and a number of adjustments and repairs were made to both electrical and mechanical components of the system. In addition, a number of operational problems were observed with the system which required corrective action. A summary of major operational problems experienced with the Lake Ella alum injection system is given in Table 3-9.

Shortly after initial start-up of the system in January 1987, an underground sonic meter cable was cut and shorted out by a work crew, causing the alum feed pumps to pump continuously, and approximately 2000 gallons of alum were pumped into the lake over a very short period of time. This incident reduced the average lake pH to approximately 3.8 on this occasion. Time limiters were installed on each injection pump so that a maximum pumping period of one hour is allowed before the pumps are automatically shut-off. The transmitted signal from the flow meters must return to zero before the pumps are automatically reset and able to pump again. These time limiters essentially eliminate the possibility of over-pumping alum into the lake due to faulty system components.

TABLE 3-9

OPERATIONAL EXPERIENCE AT LAKE ELLA¹

| DATE | OPERATIONAL PROBLEM |
|---------------------------|---|
| January 1987 | <p>A sonic meter was cut and shorted out, causing one of the pumps to pump the entire contents of the storage tank into the lake. The solution was to place a timer on the pumps that would limit how long a pump would operate continuously.</p> <p>It is recommended that alum tanks be filled with water for first few months of operation to test system.</p> |
| February 1987 | Sonic meters were signaling pumps to come on when stormsewer flow was not occurring. |
| December 1987 | Lightning hit one of the sonic meters. Pump has to be turned on and off manually. |
| August 1988 | All sonic meters hit by lightning and sent off for repairs. Additional lightning protection added to the system. |
| February 1989 | Some of the sonic meters are not working. Service technician called to perform repairs. |
| February to December 1989 | No reports. |
| January 1990 | Systems 5 and 6 down. Pump control panels hit by lightning. Sensitivity adjusted on others. Control panels returned for repairs to factory. Spare parts ordered for future use. |
| February 1990 | Systems not very sensitive at low flows. Service technician called to investigate cause. |
| July 1990 | Fuses blown in two sonic meters. Easily replaced. |

1. Based upon operational records maintained by William M. Bishop Engineers.

Additional problems also occurred with the sonic meters during this initial start-up period which frequently were signalling the feed pumps to come on when stormwater was not flowing through the system. These problems required numerous sensitivity adjustments and additional fine-tuning of the injection process. Many of the operational problems listed in Table 3-9 are a result of the effects of lightning on the sensitive electronic equipment within the system. Both the sonic meter circuitry and the pump control panels appear to be extremely sensitive to lightning surges. Several levels of lightning protection have been added to the system since 1987, and many of the initial problems resulting from lightning seem to have been resolved.

Reliable operation of the system began in approximately July of 1987. At this time, the system was still operating at a treatment dose of 20 mg/l. During the period from July through December 1987, the lake exhibited excellent water quality characteristics with the exception of pH which exhibited a mean value of approximately 5.5 with fluctuations ranging from 4.55 to 6.27.

Beginning in January 1988, the alum treatment dose was gradually decreased to 10 mg/l as Al_2O_3 . This reduction in treatment dose resulted in an immediate improvement in lake pH, and produced consistent average pH levels in excess of 6.0 on all measurement dates. The system has continued to be operated at a dose of 10 mg/l since January 1988.

Chemical Requirements

The annual runoff volume which receives alum treatment as it enters Lake Ella is approximately 342 ac-ft. This runoff volume represents approximately 95% of the total annual runoff inputs to Lake Ella. The annual alum requirement to treat the runoff volume at a feed rate of 10 mg/l is approximately 10,077 gallons/year or about 2.2 tanker truck loads of 4500 gallons each. The alum storage tank is designed to hold

22,700 liters (6000 gallons) which is in excess of a 90-day supply for average rain conditions during the wettest month of the year, July. Estimated annual chemical costs for alum, based on a current volume contract price of \$0.50/gallon, including transportation, is approximately \$5039. A summary of chemical requirements for alum injection at Lake Ella is given in Table 3-10 for a range of alum treatment doses.

TABLE 3-10

**SUMMARY OF CHEMICAL REQUIREMENTS FOR
ALUM INJECTION OF STORMWATER AT LAKE ELLA**

| PARAMETER | ALUM DOSE (mg/l as Al ₂ O ₃) | | | |
|--|---|---------|---------|---------|
| | 10 mg/l | 15 mg/l | 20 mg/l | 25 mg/l |
| Chemical Requirements ¹ (gallons/year) | 10,077 | 15,116 | 20,154 | 25,193 |
| Chemical Requirements per Inch of Rain ² (gallons/inch of rain) | 168 | 252 | 336 | 420 |
| Ratio of Alum to Runoff (%) | 0.0090 | 0.0136 | 0.0181 | 0.0226 |
| Annual Chemical Costs ³ (\$) | 5,039 | 7,558 | 10,077 | 12,597 |
| Tanker Loads per Year ⁴ | 2.2 | 3.4 | 4.5 | 5.6 |
| Average Time Between Tanker Loads (months) | 5.4 | 3.6 | 2.7 | 2.1 |

1. Based upon total alum treatment of 95 percent of annual runoff inputs to Lake Ella - equal to 342 ac-ft per year
2. Based on an annual rainfall of 60 inches/year
3. Based on a cost of \$0.50/gallon for alum, including transportation costs
4. Based on a tanker volume of 4,500 gallons

CHAPTER 4

FIELD AND LABORATORY PROCEDURES

Field and laboratory investigations were conducted from October 1988 through December 1990 to evaluate the pollutant removal efficiency and water quality impacts of the Lake Ella alum injection system. Research efforts were divided into five primary tasks: (1) evaluation of long-term water quality characteristics within Lake Ella following installation of the alum stormwater treatment system; (2) sediment studies designed to investigate floc accumulation and the effects of floc on the stability and chemical characteristics of lake sediments; (3) disposal and toxicity studies designed to provide information on potential problems associated with the ultimate disposal of the accumulated alum floc; (4) rate experiments designed to examine the rate of changes in aluminum speciation during coagulation processes; and (5) bioassay studies designed to examine the long-term and short-term effects of alum coagulation and alum floc on fish test species.

Although water quality monitoring efforts were not conducted as a part of the research described in this report, a discussion of water quality conditions within Lake Ella is provided in later sections to enable a more thorough understanding of the overall operation and efficiency of the alum injection process. As a result, a brief discussion of water quality monitoring procedures is provided in this section.

Water Quality Monitoring

Routine water quality monitoring efforts were begun in Lake Ella in February 1987 by personnel from Environmental Research & Design, Inc. following the initial

start-up of the alum injection system. Water quality monitoring was conducted on a biweekly basis for the first six months of system operation, extending from February to July 1987. Water quality samples were then collected on a monthly basis from August to December 1987. Beginning in January 1988, water quality samples were collected on a bimonthly basis which extended through December 1988. Quarterly water quality monitoring was initiated in January 1989. Beginning in January 1990, all water quality monitoring and sample analyses were conducted by the City of Tallahassee wastewater laboratory.

Water quality monitoring was conducted at four fixed locations in Lake Ella as indicated in Figure 4-1. All samples were collected using a 2.4 liter clear acrylic Kemmerer water sampler. Samples were collected at each monitoring location as vertical depth composite samples with equal portions collected from the 0-1 m layer, the 1-2 m layer, and the 2-3 m layer, if available. Physical-chemical profiles of temperature, pH, dissolved oxygen, conductivity and redox potential were also performed at each monitoring location using a Hydrolab Surveyor II water quality monitor. Readings were collected immediately beneath the water surface and at 0.5 m intervals extending to the bottom sediments. Secchi disk transparencies were also recorded at each sampling location.

Upon return to the laboratory, water samples were analyzed by ERD for the parameters listed in Table 4-1 using the indicated analytical methods. From January 1987 to December 1989, all water quality samples were analyzed jointly by both Environmental Research & Design, Inc. and the City of Tallahassee Wastewater Laboratory. Beginning in January 1990, water quality analyses were conducted only by the City of Tallahassee Wastewater Laboratory.

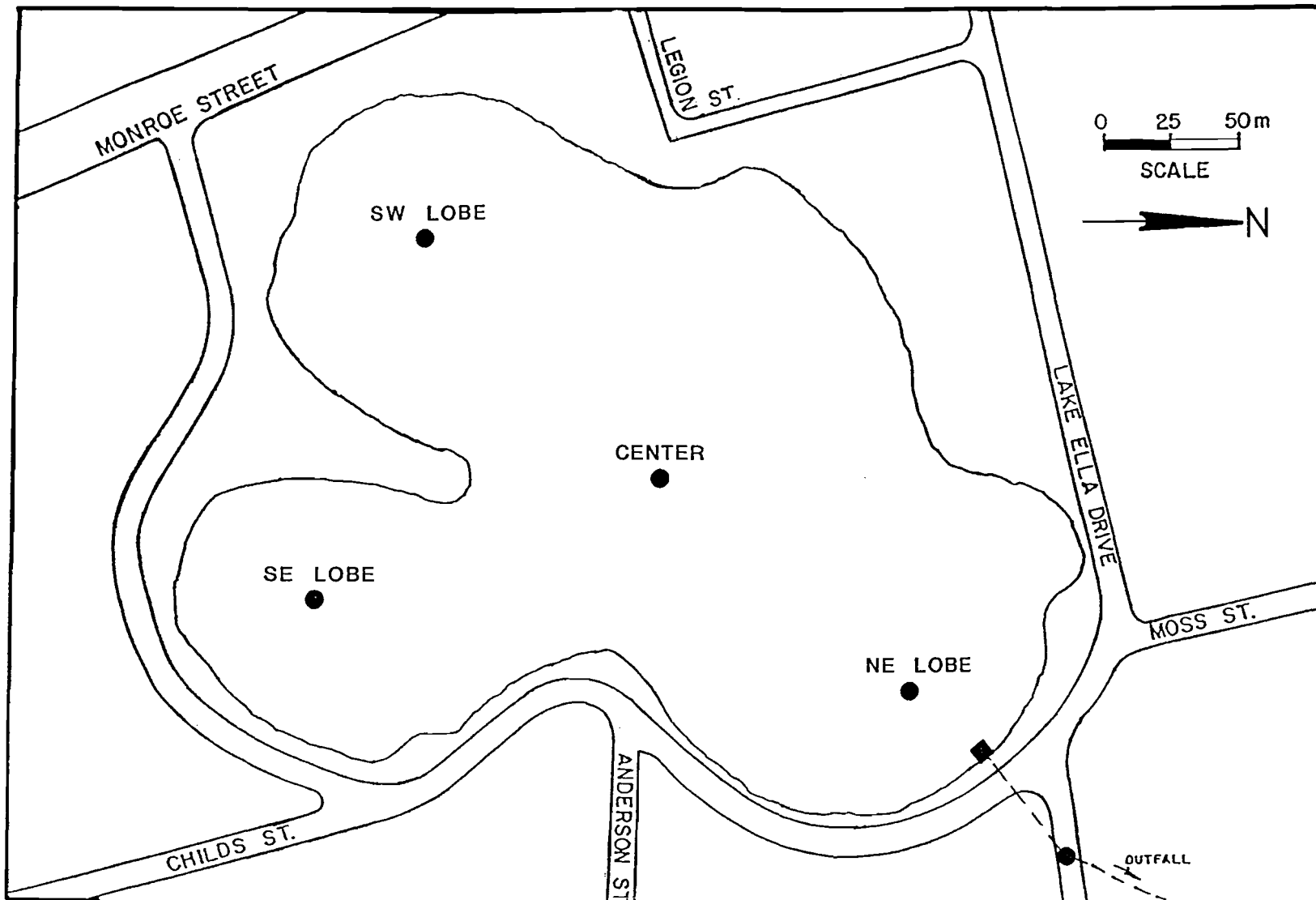


Figure 4-1. Sample Locations for Water Quality and Sediment Sampling in Lake Ella.

TABLE 4-1

ANALYTICAL METHODS USED FOR LAKE ELLA STUDY

| PARAMETER | ANALYTICAL METHOD |
|------------------------------|--------------------------------------|
| Alkalinity | EPA-83 ¹ , Sec. 310.1 |
| Ammonia | SM-16 ² , Sec. 417C |
| Nitrite + Nitrate | EPA-83, Sec. 353.3 |
| Dissolved Organic Nitrogen | EPA-83, Sec. 351.2 (filtered sample) |
| Particulate Organic Nitrogen | EPA-83, Sec. 351.2 |
| Total Nitrogen | By Addition |
| Dissolved Orthophosphorus | EPA-83, Sec. 365.2 |
| Total Phosphorus | SM-16, Sec. 424C,F |
| Turbidity | EPA-83, Sec. 180.1 |
| Total Suspended Solids | EPA-83, Sec. 160.2 |
| Volatile Suspended Solids | EPA-83, Sec. 160.4 |
| Total Dissolved Solids | EPA-83, Sec. 160.1 |
| Volatile Dissolved Solids | EPA-83, Sec. 160.4 |
| Sulfate | EPA-83, Sec. 375.4 |
| Chlorophyll-a | SM-16, Sec. 1002G |
| Total and Dissolved Aluminum | EPA-83, Sec. 202.1 |
| Total and Dissolved Cadmium | EPA-83, Sec. 213.1 |
| Total and Dissolved Chromium | EPA-83, Sec. 218.1 |
| Total and Dissolved Copper | EPA-83, Sec. 220.1 |
| Total and Dissolved Iron | EPA-83, Sec. 236.1 |
| Total and Dissolved Lead | EPA-83, Sec. 239.1 |
| Total and Dissolved Nickel | EPA-83, Sec. 249.1 |
| Total and Dissolved Zinc | EPA-83, Sec. 289.1 |

1. Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised March 1983.
2. Standard Methods for the Examination of Water and Wastewater, 16th ed., 1985.

Sediment Studies

Sediment studies were divided into five tasks designed to investigate the accumulation, migration and stability of the sediment floc layers. Each of these tasks is described in the following sections.

Benthic Survey

Benthic surveys were conducted in Lake Ella on three separate occasions. The first survey was conducted on November 29, 1985, immediately prior to the lake drawdown conducted as part of the lake restoration construction activities. The second benthic survey was conducted on January 16, 1987, after the lake had refilled following installation of the alum injection system and prior to start-up of the alum treatment process. The final benthic survey was conducted on May 25, 1990, after approximately three years of operation of the alum injection system.

On each collection date, benthic samples were collected from a minimum of eight randomly selected locations within Lake Ella using a 15 cm x 15 cm stainless steel Eckman dredge. Triplicate dredge samples were collected at each location, washed free of silt and debris in the field, and combined to form a single composite of each site for further laboratory analyses. In general, all benthic analyses were completed within 72 hours of sample collection.

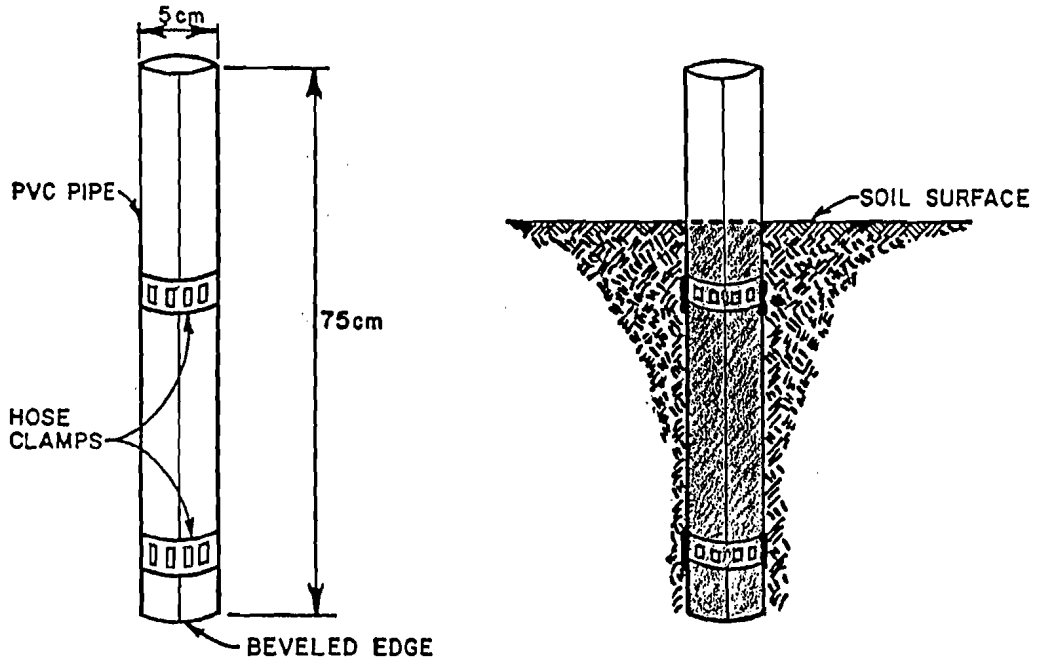
Sediment Metal Accumulation and Migration

Sediment core samples were collected from Lake Ella on two separate occasions. The first set of sediment cores were collected on February 21, 1987, coinciding with the start-up of the alum injection system. The second set of core samples were collected on November 11, 1988, after approximately two years of operation of the alum injection system.

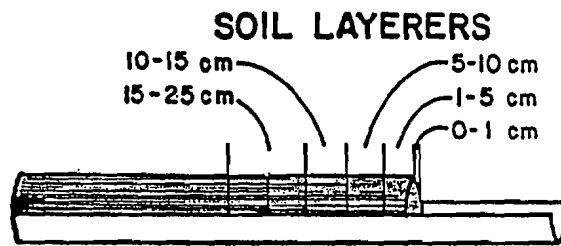
Sediment core samples were collected at four locations within the lake which coincided with the four water quality monitoring locations indicated in Figure 4-1. Sediment cores were collected using a non-metallic split-spoon type core collection device. The collection device consisted of a 5 cm (2 in) diameter split acrylic pipe, approximately 75 cm in length, with a beveled edge on one end for ease in sediment penetration. A schematic of the split-spoon sediment core sampler is given in Figure 4-2. A pair of hose clamps are used to hold the split-spoon sampler in place as it is inserted into the sediments. In some locations, the collection tube could be pushed into the sediments by hand, while at other locations a rubber hammer was used. The sediment removal technique consisted of inserting the sample collection device into the sediments to a depth of approximately 40 cm and then removing it using an upward twisting motion.

Upon retrieval of each core sample, visual observations of surface floc accumulations were made prior to opening and sectioning the core sample. Core samples were then divided into the following layers for analysis: 0-1 cm, 1-5 cm, 5-10 cm, 10-15 cm and 15-25 cm. Three replicate core samples were collected at each location and combined by layer to form a composite sample for each location and depth layer. A total of 20 sediment samples were created on each sample date by collection of five depth layers at the four lake sites.

Upon return to the laboratory, sediment samples were analyzed for moisture content, organic content, total P, total N, soluble Al, and total Zn, Cu, Fe, Pb, and Al. Details of laboratory methods and quality control procedures for sediment analyses are given in the FDER approved Quality Assurance Plan for Environmental Research & Design, Inc.



SAMPLER PUSHED INTO SOIL



CORE SAMPLE AFTER COLLECTION WITH TOP OF SPLIT-SPOON REMOVED

Figure 4-2. Schematic of the Sediment Core Collection Device.

Chemical Speciation of Sediment Cores

Each of the pre-modification and post-modification sediment samples (40 total samples) was carried through a series of chemical speciation extractions which identified five fractions of phosphorus and heavy metal associations in sediments:

1. Soluble - Metal ions contained in water which are trapped in interstitial pore spaces or loosely bound to sediment matter.
2. Exchangeable - Ions which are specifically adsorbed and are ion exchangeable.
3. Bound to Carbonates - Metal ions which are associated with sediment carbonates as a precipitate or coprecipitate.
4. Bound to Iron and Manganese Oxides - Metal species attached or adsorbed onto iron or manganese oxides.
5. Bound to Organic Matter - Metals which are bound by adsorption or complexation to various forms of organic matter such as living organisms, detritus, and coatings on mineral particles.

After a critical evaluation of the available literature, a modification of the chemical extraction steps proposed by Tessler et al. (1979) was adopted. This procedure was used successfully by Harper (1985) to examine the chemical speciation of heavy metals in the sediments of a detention pond receiving highway runoff. All sediment samples were initially air dried and finely ground by passage through a 600 micron plastic mesh to remove extraneous material. A minimum of three finely ground 2 gram samples from each composite core layer was taken through the speciation steps. All extractions were conducted in 50 ml polypropylene centrifuge tubes to minimize losses of solid material. Details of the extraction procedure are given in the following sections. Extracted samples were then analyzed for zinc, copper, iron, aluminum, lead and total phosphorus.

Soluble

A 2 gram sample of finely ground sediment (weighed to the nearest 0.1 mg) was placed in a 50-ml polypropylene centrifuge tube with 16 ml of distilled/deionized water. The mixture was agitated continuously for one hour at room temperature (25°C). Following extraction, the mixture was centrifuged at 3000 rpm for 30 minutes. The supernatant was carefully decanted and prepared for metal analysis.

Exchangeable

The sediment residue remaining after the above process was extracted at room temperature (20°C) with 16 ml of 1 M MgCl₂ (pH 7.0) with continuous agitation for one hour. The supernatant was removed with a pipet and placed in an acid-washed glass flask. The sediment residue was washed with 16 ml of distilled/deionized water by constant agitation for five minutes. After centrifugation for 30 minutes at 3000 rpm, the wash water supernatant was decanted off and added to the original extracted supernatant. The volume of rinse water was kept to a minimum to avoid excessive solubilization of solid material, particularly organic matter. The wash water was added to the original extraction solution since heavy metals present in the wash water theoretically represent an amount which was released during extraction but not poured off with the extraction solution. This process was conducted for each of the three replicate extractions with all extraction and wash solutions combined into a single flask for final analysis.

Bound to Carbonates

The sediment residue from above was extracted with 16 ml of 1 M NaOAc (pH 5.0) with continuous agitation at room temperature (20°C) for five hours. Following extraction, the mixture was centrifuged at 3000 rpm for 30 minutes. The supernatant

was removed for analysis and the residue washed with 16 ml of distilled/deionized water as before. Wash waters were added to the original extracted supernatant as described previously. This process was conducted for each of the three replicate extractions with all extractions and wash solutions combined into a single flask for final analysis.

Bound to Fe-Mn Oxides

The residue from above was extracted with 40 ml of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (V/V) acetic acid for six hours at 96°C with occasional agitation. After centrifugation at 3000 rpm for 30 minutes, the supernatant was removed for analysis, and the residue was washed with 16 ml of distilled/deionized water. Wash waters were added to the original extracted supernatant as described previously. This process was conducted for each of the three replicate extractions with all extraction and wash solutions combined into a single flask for final analysis.

Bound to Organic Matter

To the residue from above were added 6 ml of 0.02 M HNO_3 and 10 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3 . The mixture was heated to 85°C for two hours with occasional agitation. A second 6 ml aliquot of 30% H_2O_2 (adjusted to pH 2 with HNO_3) was then added and the sample was heated again to 85°C for three hours with intermittent agitation. After cooling, 10 ml of 3.2 M NH_4OAc in 20% HNO_3 (V/V) were added, and the sample was diluted to 40 ml and agitated continuously for 30 minutes. The addition of NH_4OAc is designed to prevent adsorption of extracted metals onto the oxidized sediment. After centrifugation at 3000 rpm for 30 minutes, the supernatant was decanted for analysis and the residue washed with 16 ml of distilled/deionized water as before.

Fractionation of Sediment Phosphorus/Aluminum

A fractionation procedure for inorganic soil phosphate was conducted on both the pre- and post-modification sediment samples for each location and depth layer, comprising a total of 40 sediment samples. The modified Chang and Jackson procedure, as proposed by Peterson and Corey (1966), was used for phosphorus fractionation. This procedure divides phosphorus associations into aluminum phosphate, iron phosphate, reductant soluble phosphate and calcium phosphate bondings. This analysis was used to provide a comparison of changes in phosphorus sediment bonding and stability as a result of alum floc accumulation.

The Influence of pH and Redox Potential on the Stability of Phosphorus and Heavy Metals in Alum Treated Sediments

The effects of changes in pH and redox potential on the release of phosphorus and heavy metal in alum treated sediments were investigated in a series of experiments conducted using an incubation system which allowed regulation of pH and automatic control of redox potential at a pre-selected value. A two-liter, four-neck, flat bottom reaction kettle was used to contain sediment suspensions under selected environmental conditions. A schematic of the apparatus used for incubating sediment suspensions is shown in Figure 4-3. As indicated in this figure, the flask was fitted with a platinum electrode, a glass electrode for measurement of pH, a calomel half-cell, glass inlet tubes for air and nitrogen, an outlet tube for discharge of excess gases, and a sample port for adding acids or bases during pH adjustments or for sampling sediments at the completion of incubation. A water trap was placed at the end of the outlet tube to prevent atmospheric oxygen diffusion into the suspension.

The alum sediment mixture used in the incubation studies was collected on May 25, 1990 as a composite grab sample from a deep area of Lake Ella near the

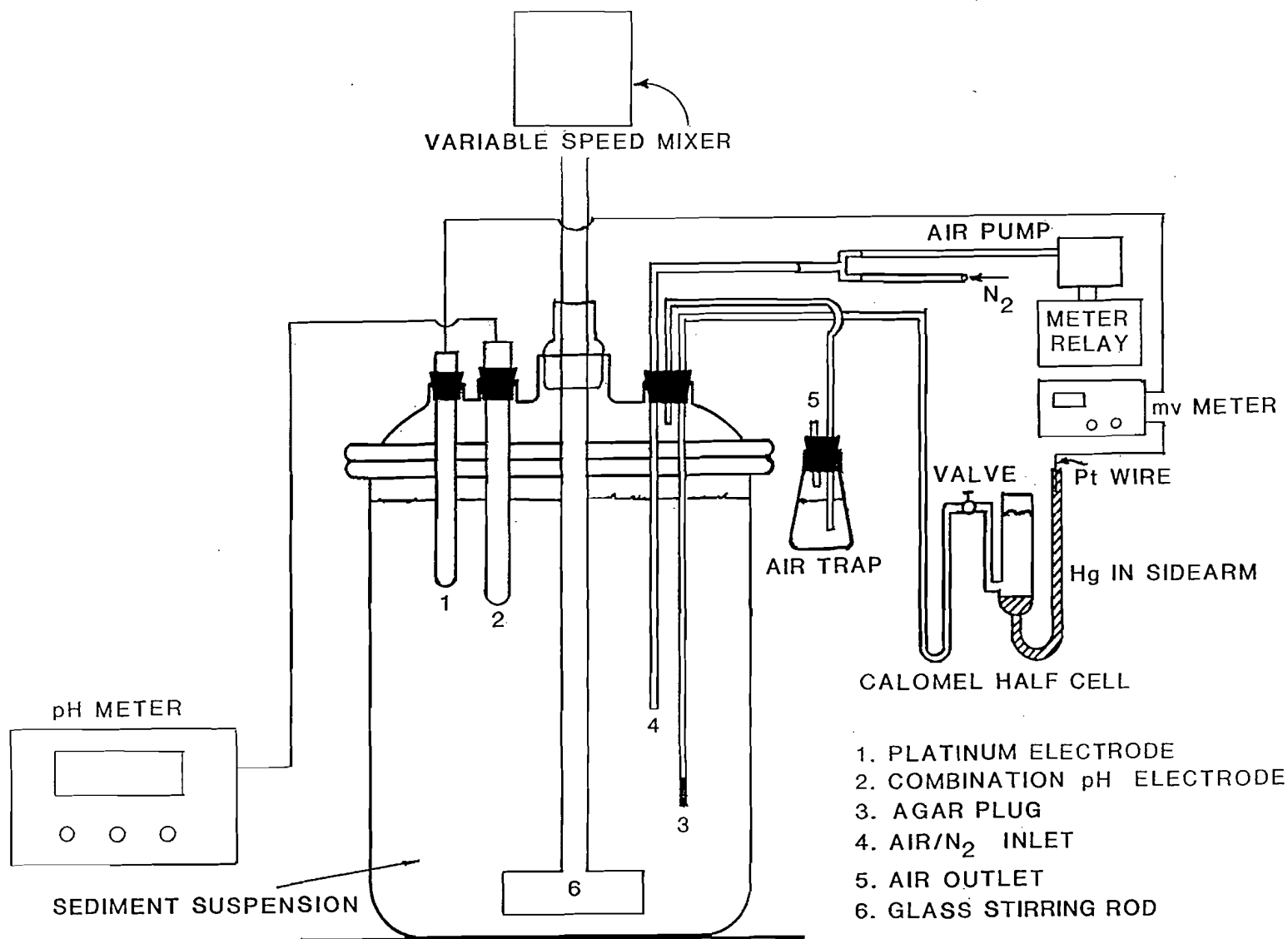


Figure 4-3. Schematic of the Incubation Apparatus Used for pH and Redox Studies.

outfall discharge line. This area of the lake was contoured during the restoration efforts as a sump area for collection of excess alum floc and is designed to contain the largest accumulations of floc material found within Lake Ella. A total of 20 liters of sediment material was collected using a stainless steel Eckman dredge and stored in a large polyethylene container which was covered with approximately 25 cm of lake water. This composite sample of alum floc and sediment material was used for all incubation studies. Sediments were initially mixed by vigorous stirring prior to sample collection for a particular incubation test to insure a homogeneous sample. Moisture content and organic content were determined on the mixed sample used in each incubation experiment.

To begin each experiment, approximately 1800 ml of mixed sediment slurry were placed in the acid-washed reaction kettle. The reaction vessel was closed and the suspension stirred with an external glass stirring rod to maintain the slurry in suspension throughout the incubation period. After stirring was begun, the redox potential was slowly adjusted to the desired level. For highly oxidized redox potentials, several days were often required to achieve the desired redox levels. Reduced conditions were generally obtained more quickly. The suspension pH was adjusted as necessary. Each experiment conducted at a specified pH level included four redox potentials ranging from highly oxidized to highly reduced: +400 mv, +200 mv, 0 mv and -200 mv. Incubation studies were conducted at natural pH levels, which resulted in pH values in the range of 6.8 to 7.0, and also at pH values of 6.0 and 5.0.

Redox potential was measured using a Corning platinum inlay electrode connected to a Corning Model 120 pH and millivolt meter. A separate saturated calomel reference electrode was used to complete the cell. A platinum wire was inserted into the side arm of the calomel electrode containing mercury and connected to the reference side of the meter. The calomel electrode was connected to the sediment

suspension with a saturated potassium chloride-agar salt bridge. A meter relay was constructed and connected to the terminals used for measurement of redox potential. The purpose of the relay was to monitor redox potential and activate a small aquarium pump which would provide a small stream of air to the reaction vessel when the redox potential of the suspension dropped below the desired level. The desired level for activation of the pump could be set internally in the relay so that any desired redox potential could be selected. The purpose of the air pump was to provide oxygen to offset the natural tendency for isolated sediments to become more reduced with time. The airflow from the pump was regulated with a flow meter at 5 ml/min. to allow slow oxidation of the suspension during the aeration cycle. When the suspension was again oxidized to the proper level, the meter relay automatically switched off the aerator.

In studies requiring a highly reduced environment, nitrogen gas was added to the suspension to remove excess oxygen. For incubations conducted at less than 100 mv (Eh), a continuous stream of nitrogen gas was bubbled through the sediment suspension at a rate of 5 ml/min. Nitrogen gas was effective in purging excess oxygen from the system due to small leaks and prevented a buildup of gaseous decomposition products such as carbon dioxide. Removal of excess CO₂ was necessary to prevent undesirable changes in metal carbonate chemistry.

Suspension pH was adjusted to the proper level initially and then readjusted when the pH changed by ± 0.1 unit. Adjustments were made using 30% Suprapur hydrochloric acid or 12 N sodium hydroxide through the serum cap located in the center rubber stopper. The pH was measured continuously on an Orion Model 920 pH meter using a Ross epoxy combination pH electrode. Virtually no drift was measured in pH calibration even in suspension which were maintained in a highly reduced state for 30 days or more. Adjustments to the calibration were less than 0.05 units in all experiments with several requiring no adjustments at all. During incubation of suspensions, the temperature was maintained at 25°C $\pm 1^{\circ}$.

The incubation apparatus performed remarkably well throughout the entire experimental period. Once the calomel electrodes with the agar tips had become equilibrated, they produced an extremely trouble-free continuous reference cell for redox potential. The agar plugs on the calomel electrodes never required replacement and provided a quick response which was similar to a pre-manufactured calomel electrode.

At the termination of an incubation period, a 200 ml sample of circulating sediment suspension was withdrawn from the reaction vessel using a siphon into a sealed 250 ml polycarbonate bottle. In studies conducted under reducing conditions, the presence of free oxygen in the extracted sample could cause changes in redox potential that would result in immediate oxidation of metal ions to insoluble forms. To minimize potential oxidation of extracted sediments, all sample preparation procedures and filtration of reduced suspensions were conducted under a nitrogen purged atmosphere. Each of the sample collection bottles were modified by sealing a serum cap into a hole drilled in each bottle cap to permit transfer of extracted samples to and from the bottle without oxygen contamination. The sealed bottle was purged with nitrogen prior to adding an aliquot of reduced suspension.

The bottle containing the sediment suspension was then centrifuged for 30 minutes at 3000 rpm. The supernatant was removed using the apparatus shown in Figure 4-4. A syringe connected to a low pressure nitrogen source was inserted through the serum cap. A polyethylene pipet connected to a covered filtration funnel was inserted into the air space above the liquid. A vacuum was applied to the filtration flask which displaced the air in the flask by pulling nitrogen into the system. After purging for several minutes, the suction tube was pushed into the supernatant which was then drawn into the filter. The supernatant was filtered into a polycarbonate receiving flask containing 3 ml of redistilled nitric acid. After filtration, 150 ml of the

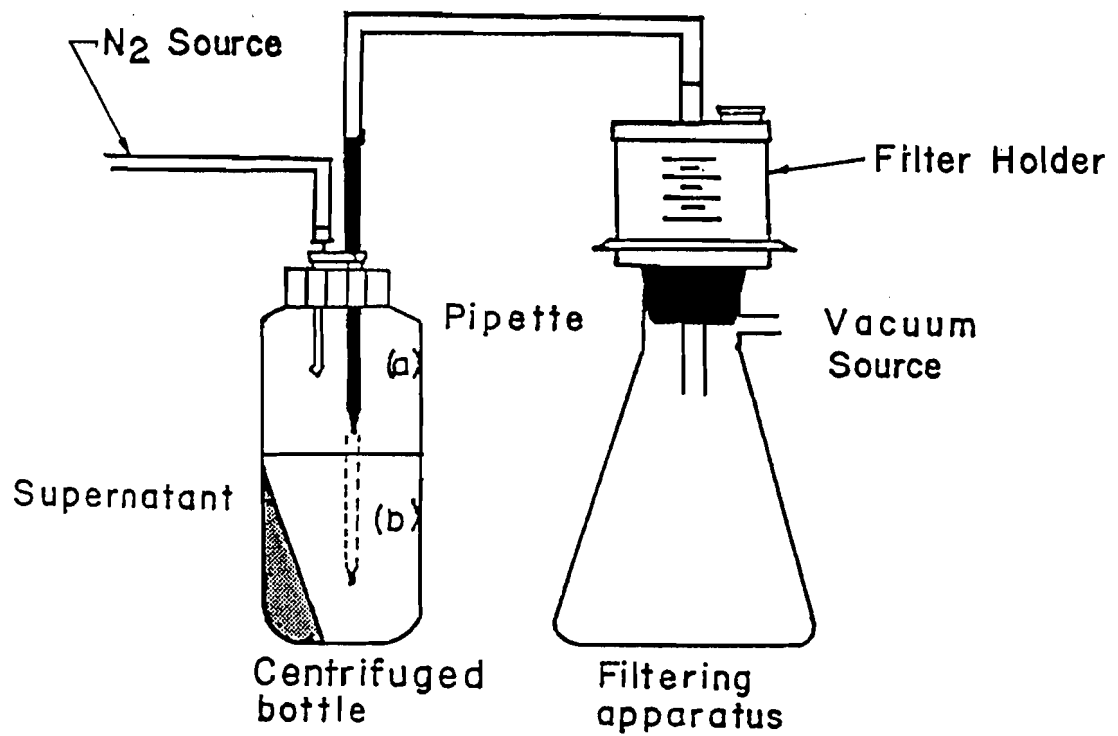


Figure 4-4. Apparatus for Filtering Supernatant Solutions Under a Nitrogen Atmosphere: (1) Pipette in N₂ Purge Position and (b) Pipette in Filtering Position.

acidified sample was digested and analyzed for phosphorus, aluminum, iron, zinc, copper and lead.

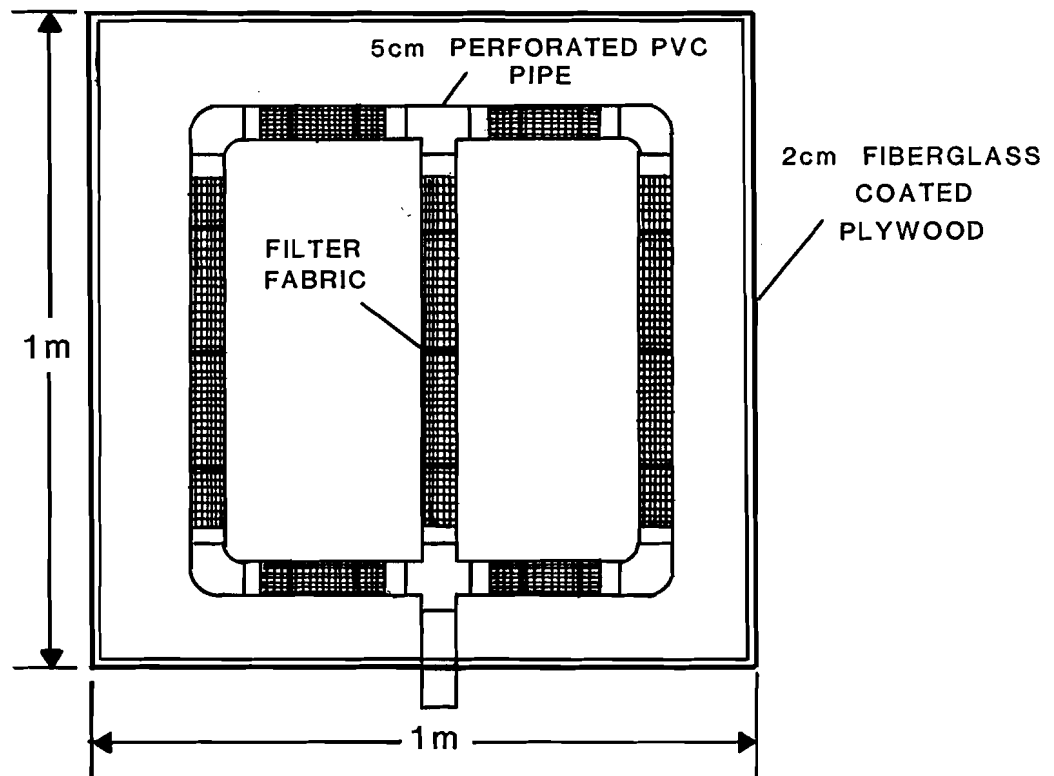
Sediment Disposal and Toxicity Studies

A series of investigations were conducted to provide information on potential problems associated with ultimate disposal of the accumulated alum floc. These studies required a relatively large volume of alum floc particularly for tasks related to evaluation of drying characteristics of the sludge. Since floc accumulations in Lake Ella were too thin to allow collection of an adequate volume of pure sludge, alum sludge was produced by coagulation of urban stormwater and collection of the residual sludge.

Bulk stormwater was collected during eight storm events from an urbanized watershed in Orlando. The stormwater from each event was returned to the laboratory and treated with a selected alum dose and allowed to settle for a minimum of 24 hours. A total of five alum doses were tested on the stormwater to evaluate floc production at different coagulant doses. Stormwater was coagulated at alum doses of 10, 15, 20, 25 and 30 mg/l as Al_2O_3 . In some cases, sodium aluminate was also added as an additional coagulant and buffering agent to prevent reductions in pH below values of 6.0-6.5. At the end of 24 hours, the treated stormwater supernatant was siphoned off and saved for subsequent bioassay studies. The settled floc layers were combined in a large storage tank until the desired sludge volume of approximately 175 liters was obtained. The production of this volume of sludge required the coagulation of approximately 7,000 liters (1850 gallons) of stormwater.

Following collection of the required sludge volume, the alum sludge was placed on a sand drying bed and allowed to dewater. A schematic of the drying bed used in these investigations is given in Figure 4-5. The drying bed was constructed from

PLAN VIEW



FRONT VIEW

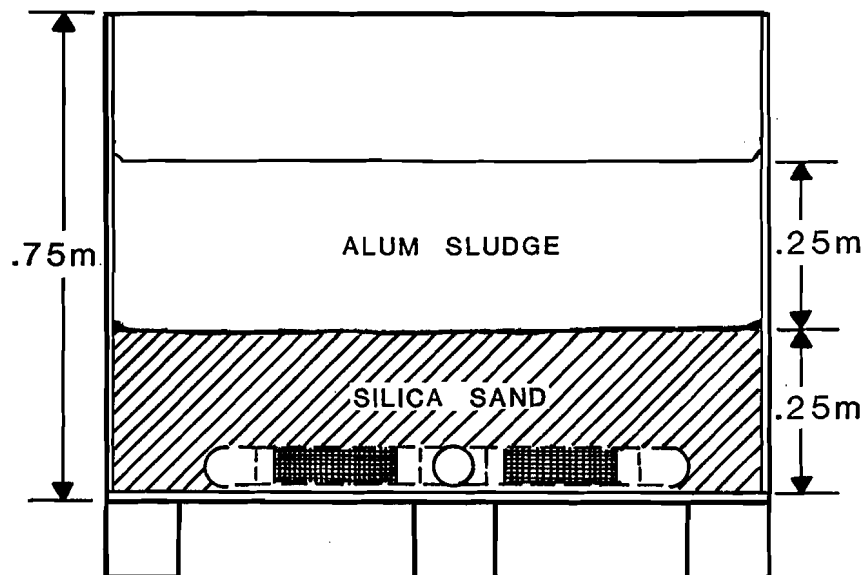


Figure 4-5. Drying Bed Used for Evaluation of Sludge Characteristics.

fiberglass reinforced plywood with a surface area of 1 m x 1 m and a depth of 0.75 meters. An underdrain system was constructed on the bottom of the filter using a perforated 5 cm (2 in) PVC pipe covered with filter fabric. A 0.25 m layer of silica sand was placed over the perforated pipe. The sludge was applied directly to the surface of the sand, and the outflow through the underdrain was collected on a continuous basis as long as flow was present. Physical characteristics of the sludge were observed during the drying period.

After the sludge had dried, it was collected, ground up into a fine powder, and analyzed for the standard sludge parameters of total nitrogen, total phosphorus, potassium, cadmium, copper, lead, nickel, zinc, iron, aluminum and pH as specified in Chapter 17-7 of the Florida Administrative Code. These analyses were conducted to allow comparison of the characteristics of alum sludge with typical wastewater treatment sludges and the associated disposal methods. Dried sludge samples were also carried through a standard EP Toxicity Test to provide further information on potential disposal methods and problems.

Rate Experiments

A series of laboratory investigations were conducted to examine the rate of changes in aluminum speciation during the coagulation process. Raw stormwater samples were collected during rain events from an urbanized watershed in Orlando for use in these investigations. Upon return to the laboratory, stormwater samples were coagulated with alum at doses of 10, 20, 30, 40 and 50 mg/l as Al_2O_3 . The post-treatment pH of each sample was maintained at a level of 6.0-6.5. In some cases, this required the addition of sodium aluminate as a buffering agent.

The appropriate amount of alum and/or sodium aluminate to achieve a specific dose at a pH level of 6.0-6.5 was determined initially for each raw stormwater sample

prior to initiation of the rate experiment. A new 1000 ml raw stormwater sample was placed in a 1.5 liter polycarbonate beaker and mixed rapidly with a large stirring bar. The appropriate amounts of alum and/or sodium aluminate were added simultaneously to the stormwater. The rapid mix process was continued for 60 seconds, after which agitation was stopped completely. This process was intended to simulate the addition of alum and/or sodium aluminate to a stormsewer line during a storm event where the alum and stormsewer flow would mix within the stormsewer as a result of turbulent conditions finally discharging into a quiescent receiving water body.

After introduction of the alum and/or sodium aluminate coagulants, small aliquots of the treatment mixture were rapidly removed at predetermined time intervals of 10, 20, 30, 45 and 60 seconds and 2.5, 5 and 10 minutes. Each aliquot was filtered immediately through a 0.45 micron filter using a syringe-type apparatus, and analyzed for soluble monomeric aluminum concentrations using the pyrocatechol violet method of Dougan and Wilson (1974). These experiments were designed to provide information on the length of time which elevated aluminum concentrations may exist in the treated runoff flow following initial coagulant addition.

Biotoxicity Testing

Two separate types of bioassay experiments were conducted to examine the potential toxicity of alum treated runoff on selected species of fish. The first series of experiments were conducted as long-term bioassay tests using *Gambusia sp.* as the test organisms. A second set of tests was conducted using fathead minnows (*Pimephales promelas*) in the standard EPA seven-day chronic larval survival and growth test. Each of these procedures is described in the following section.

Fathead Minnow Toxicity Test

A Seven-Day Fathead Minnow (*Pimephales promelas*) Chronic Larval Survival and Growth Test (EPA/600/4-89/001) was performed to assess the chronic biotoxicity of alum treated stormwater. Test organisms, a few hours old, were obtained from a commercial vendor for use in the test. A summary of test conditions is given in Table 4-2.

Urban stormwater was collected from an Orlando urban watershed during a storm event. Fifteen liters of raw stormwater were placed into five 20-liter polyethylene containers. The raw stormwater treatment contained untreated stormwater, while the other four samples were treated with a combination of alum and sodium aluminate to achieve a total coagulant dose of 20 mg/l as Al_2O_3 at final pH values of 6.0, 6.5, 7.0 and 7.5. Alum treatment to pH levels of 6.0 and 6.5 required the addition of only alum, while the pH 7.0 and 7.5 treatments required both alum and sodium aluminate. The treated stormwater was mixed rapidly for one minute immediately after dosing and allowed to settle for approximately one hour. After settling, the supernatant from the raw stormwater and each treatment was carefully syphoned into separate containers. Care was taken to avoid including any floc material or solids that had settled on the bottom of the containers. The siphoned water was stored at 4°C and used for the remainder of the experiment. A control test water was also used which consisted of dilution water formulated in the laboratory as described in the EPA procedure.

One-liter nalgene beakers were used as sample chambers with four replicates for each test concentration listed in Table 4-2. Each sample chamber was filled with one liter of the respective test water for a total of 24 sample chambers. Fifteen fathead minnow larvae less than 24 hours old were placed into each sample container. All tests were conducted according to the procedure described in EPA Method 1000.0 (EPA/600/4-89/001).

TABLE 4-2

**SUMMARY OF TOXICITY TEST CONDITIONS FOR THE FATHEAD MINNOW
(*PIMEPHALES PROMELAS*) SEVEN-DAY LARVAL SURVIVAL AND GROWTH TEST**

| PARAMETER | CONDITIONS |
|--|--|
| Test Type | Static renewal |
| Temperature (°C) | 25 ± 1°C |
| Light Quality | Ambient laboratory illumination |
| Light Intensity | 100 ft-candles |
| Photoperiod | 16 h light, 8 h darkness |
| Test Chamber Size | 1.5 liter |
| Test Solution Volume | 1000 ml/replicate |
| Renewal of Test Concentrations | Daily |
| Age of Test Organisms | Newly hatched larvae less than 24 hours old |
| No. Larvae per Test Chamber | 15 |
| No. Replicate Chambers per Concentration | 4 |
| No. Larvae per Concentration | 60 |
| Feeding Regime | Feed 0.1 ml newly hatched (less than 24 hrs old) brine shrimp nauplii 3 times/day at 4-hr intervals. Sufficient larvae were added to provide an excess. Larvae were not fed during the final 12 hrs of test. |
| Cleaning | Siphoned daily, immediately before test solution renewal |
| Aeration | None, except when DO concentration falls below 40% saturation. Rate of aeration adjusted to approximately 100 bubbles/minute. |
| Dilution Water | Moderately hard synthetic water prepared using distilled/deionized water and reagent grade chemicals. |
| Test Concentrations | <ol style="list-style-type: none"> 1. Control 2. Raw Stormwater 3. pH 6.0 4. pH 6.5 5. pH 7.0 6. pH 7.5 |
| Test Duration | 7 days |
| Endpoints | Survival and growth (weight) |
| Test Acceptability | 80% or greater survival in controls; average dry weight of surviving controls equals or exceeds 0.25 mg. |

The test solutions were cleaned daily by siphoning uneaten and dead brine shrimp and other material from the bottom of the test chambers. Approximately 150 ml of test solution were siphoned from each test chamber during this process. This water was collected and composited for each treatment, filtered and used for daily chemical analyses. The test chambers were then carefully refilled with the appropriate test water which had been equilibrated to room temperature. Daily measurements of temperature, initial and final dissolved oxygen, and initial and final pH were conducted in each of the 24 test chambers on a daily basis. Measurements of alkalinity, hardness, conductivity, sulfate and monomeric aluminum were conducted in a composite sample formed by combining equal aliquots from each of the four containers for a particular test condition. Monomeric aluminum concentrations were determined according to the pyrocatechol violet method of Dougan and Wilson (1974).

The test was terminated after seven days and the surviving larvae in each test chamber were counted and prepared for dry weight determination. The surviving minnows were preserved in 70 percent ethanol. Immediately prior to dry weight analysis, each group of larvae were rinsed with distilled water and transferred to a tared weighing boat and dried for two hours at 100°C. Immediately upon removal from the oven, the weighing boats were placed into a desiccator, cooled to room temperature and weighed to the nearest 0.1 milligram.

Long-Term Biotoxicity Tests

Long-term bioassay investigations were conducted over a period of 60 days using *Gambusia sp.* as test organisms. All bioassay experiments were conducted in 40-liter all-glass test chambers. A total of four test chambers were used. One test chamber contained moderately hard dilution water only and served as the control, another test chamber received periodic additions of untreated raw stormwater, and the

remaining two test chambers received periodic additions of coagulated stormwater runoff at alum doses of 15 and 25 mg/l. A summary of experimental test chamber designations and initial test conditions is given in Table 4-3.

At the beginning of the study, each test chamber was filled with approximately 30 liters of moderately hard dilution water from an oligotrophic lake in Orlando. Approximately 60 *Gambusia sp.* fish were added to each of the four test chambers and allowed to acclimate to the new environment for a period of 24 hours. Following the 24-hour acclimation period, the testing protocol outlined in Table 4-3 was begun. Fifty percent of the water within each test chamber was siphoned off and replaced with either dilution water, raw stormwater or alum treated stormwater as indicated in Table 4-3. Fresh dilution water and raw stormwater were collected approximately once each week. If not used immediately, the water was stored at 4°C until needed. All test waters were allowed to equilibrate to room temperature prior to use.

Alum treated waters were added to the 15 mg/l and 25 mg/l chambers in a manner which simulated the introduction of alum treated runoff into a receiving water body. First, 15 liters of water was siphoned off from each chamber and discarded. Two 15-liter aliquots of raw stormwater were placed in large polyethylene containers. An alum dose of 15 mg/l was added to one container, while a dose of 25 mg/l was added to the other. Each container was vigorously mixed for approximately 60 seconds and poured directly into the appropriate test chamber. All coagulation and flocculation processes occurred inside the test chambers, and the alum floc settled on the bottom of the test chambers. Care was taken not to remove any settled floc during the siphon processes which occurred every third day. As a result, test organisms were subjected to the combined effects of periodic coagulation processes as well as continuous contact with alum floc.

TABLE 4-3
 SUMMARY OF EXPERIMENTAL TEST CONDITIONS
 USED IN LONG-TERM BIOASSAY EXPERIMENTS

| CHAMBER DESIGNATION | INITIAL CONDITIONS | TEST CONDITIONS |
|---------------------|---|---|
| 1 - Control | Contained 30 liters of moderately hard dilution water from an oligotrophic lake filtered through a 0.45 micron filter | Approximately 15 liters siphoned off every third day and replaced with fresh dilution water |
| 2 - Raw Stormwater | Contained 30 liters of moderately hard dilution water from an oligotrophic lake filtered through a 0.45 micron filter | Approximately 15 liters siphoned off every third day and replaced with raw stormwater from an urban watershed |
| 3 - 15 mg/l Alum | Contained 30 liters of moderately hard dilution water from an oligotrophic lake filtered through a 0.45 micron filter | Approximately 15 liters siphoned off every third day and replaced with raw stormwater treated with 15 mg/l alum |
| 4 - 25 mg/l Alum | Contained 30 liters of moderately hard dilution water from an oligotrophic lake filtered through a 0.45 micron filter | Approximately 15 liters siphoned off every third day and replaced with raw stormwater treated with 25 mg/l alum |

Test conditions and protocol were maintained for a period of approximately 60 days. Each test chamber was aerated continuously at a rate of approximately 20 ml/min. to ensure adequate oxygen levels. Measurements of pH and dissolved aluminum concentrations were conducted in each test chamber approximately 30 minutes after addition of test waters. Fish mortality was recorded on a daily basis throughout the 60-day test period.

Analytical Methods

In general, the analytical procedures listed in Table 4-1 were used for all analyses conducted as a part of this research. The only exception to these procedures involved the analysis of dissolved aluminum concentrations. When it was desired to measure the total dissolved aluminum content of a test sample, then the method listed in Table 4-1 was used. However, in some test instances, it was more useful and meaningful to evaluate the concentration of dissolved monomeric aluminum species such as Al^{+3} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_4^-$, etc. In surface waters without significant organic stain, monomeric forms of aluminum generally constitute more than 95 percent of the total dissolved aluminum species present. For these analyses, the pyrocatechol violet method of Dougan and Wilson (1974) was used. This method is specific for monomeric aluminum species and has a minimum detection limit of less than 5 $\mu\text{g}/\text{l}$. This method is also less sensitive to interferences from fluoride and polyphosphates than the more common Eriochrome cyanine R method.

CHAPTER 5

RESULTS AND DISCUSSION

Field monitoring, sample collection and laboratory analyses were conducted from October 1988 to December 1990 to evaluate the performance and effectiveness of the Lake Ella alum stormwater treatment system. A discussion of experimental results from each of these tasks is given in the following sections.

Water Quality Characteristics of Lake Ella Following Alum Treatment of Stormwater

As indicated previously, water quality monitoring was not part of the research efforts funded in this project. However, to provide a comprehensive picture of the overall performance of the Lake Ella alum injection system, a summary of water quality characteristics in Lake Ella after introduction of the alum treatment process is given briefly in this section. All sample collection and laboratory analyses described in the following pages were conducted by personnel from Environmental Research & Design.

As indicated in the previous section, reliable operation of the alum treatment system at a dose of 10 mg/l began in January 1988. Operation of the system at this treatment dose produced consistent average pH levels in excess of 6.0 on all measurement dates. Operation of the system at a dose of 10 mg/l has continued since January 1988.

A summary of water quality characteristics in Lake Ella from January 1988 to May 1990 with alum treatment of stormwater at a dose of 10 mg/l is given in Table 5-1. Information provided for pH, specific conductivity and dissolved oxygen in Table

TABLE 5-1

SUMMARY OF WATER QUALITY CHARACTERISTICS
IN LAKE ELLA FROM 1/88 TO 5/90 WITH ALUM
TREATMENT OF STORMWATER AT A DOSE OF 10 mg/l

| PARAMETER | UNITS | MEAN VALUE ¹ | RANGE OF VALUES |
|----------------------|-------------------------|-------------------------|------------------|
| pH | s.u. | 6.43 | 6.01-7.12 |
| Spec. Conductivity | $\mu\text{S}/\text{cm}$ | 118 | 92-145 |
| Diss. O ₂ | mg/l | 7.4 | 5.4-10.1 |
| Alkalinity | mg/l | 11.0 | 1.8-27.0 |
| NH ₃ -N | $\mu\text{g}/\text{l}$ | 14 | < 10-32 |
| NO ₃ -N | $\mu\text{g}/\text{l}$ | 43 | < 10-347 |
| Diss. Organic N | $\mu\text{g}/\text{l}$ | 197 | 50-399 |
| Part. Organic N | $\mu\text{g}/\text{l}$ | 163 | 56-343 |
| Total N | $\mu\text{g}/\text{l}$ | 417 | 126-653 |
| Ortho-P | $\mu\text{g}/\text{l}$ | 2 | < 2-5 |
| Diss. Organic P | $\mu\text{g}/\text{l}$ | 13 | 4-21 |
| Particulate P | $\mu\text{g}/\text{l}$ | 12 | < 2-30 |
| Total P | $\mu\text{g}/\text{l}$ | 26 | 11-45 |
| Cl | mg/l | 19 | 14-22 |
| SO ₄ | mg/l | 33 | 11-52 |
| BOD | mg/l | 3.0 | 1.0-5.2 |
| Color | Pt-Co | 13 | 0.5-22 |
| Chlorophyll-a | mg/m ³ | 5.1 | 1.5-12.2 |
| T.D.S. | mg/l | 77 | 37-107 |
| V.D.S. | mg/l | 16 | 2-30 |
| Turbidity | NTU | 2.5 | 0.8-6.0 |
| S.S. | mg/l | 3.6 | 1.1-9.0 |
| V.S.S. | mg/l | 2.4 | 0.7-6.2 |
| Secchi Disk | m | > 2.2 | 1.4-2.9 (bottom) |

1. n = 11 samples

5-1 is based upon field measurements collected within Lake Ella at each of the four monitoring locations. Field measurements were collected at the water surface and at 0.5 m intervals extending to the bottom sediments. Mean values were calculated for each field parameter to form a water column average value for each of the four sample locations. These four values were then averaged to obtain a whole-lake mean value for each field parameter on each sample collection date. Summary statistics for pH, specific conductivity and dissolved oxygen listed in Table 5-1 are based upon these whole-lake average values. Measurements of Secchi disk depth presented in Table 5-1 are based upon whole-lake mean values formed by averaging individual measurements collected at each of the four sample locations on a particular sample collection date. Values for laboratory measured parameters listed in Table 5-1 are based upon whole-lake average values from vertical depth composite samples collected at each of the four sample locations on a specific sample collection date as described in Chapter 4.

As seen in Table 5-1, operation of the alum stormwater treatment system at a dose of 10 mg/l resulted in a mean pH value of approximately 6.43 with a range of values from 6.01 to 7.12. This range of fluctuation in pH level is relatively small for a lake system and is also within the area of minimum aluminum solubility as presented in Figure 2-2. Measured pH values were relatively uniform within the water column on all measurement dates. In fact, no indication of thermal or chemical stratification was observed within the lake in any field measurement.

Measured values of specific conductivity were also found to be relatively uniform within the water column with a mean whole-lake average of 118 $\mu\text{S}/\text{cm}$ and a range of values from 92 to 145 $\mu\text{S}/\text{cm}$. Total dissolved solids within the water column were also relatively low with a mean of only 77 mg/l. Measurements of dissolved oxygen were relatively uniform through the water column with an average value of 7.4 mg/l. The minimum average whole-lake dissolved oxygen concentration was 5.4 mg/l.

which exceeds the minimum criterion of 5 mg/l for Class III surface waters listed in Chapter 17-302 of the Florida Administrative Code. No evidence of dissolved oxygen stratification was observed on any field measurement date. In general, differences in dissolved oxygen concentrations from the water surface to the bottom were less than 1 mg/l. Oxygen demand within the water column was low as evidenced by a BOD value of only 3 mg/l.

Alum treatment of stormwater runoff in Lake Ella at a dose of 10 mg/l (as Al_2O_3) resulted in a mean alkalinity of 11.0 mg/l with a range of 1.8 to 27.0 mg/l. These alkalinity values are relatively low and result from two factors. First, Lake Ella has a history of low alkalinity levels with pre-alum treatment levels ranging approximately 20-30 mg/l. Second, stormwater inputs entering Lake Ella, as measured during 1986, were also found to have relatively low alkalinity levels in the range of 40-50 mg/l. Treatment of water with alum consumes alkalinity at a rate of approximately 3 mg/l alkalinity for every 1 mg/l (as Al_2O_3) of alum used. Coagulation of runoff containing an alkalinity level of 40-50 mg/l at an alum dose of 10 mg/l should result in a treated water with an alkalinity of approximately 10-20 mg/l which is similar to levels measured within Lake Ella.

In general, concentrations of all measured nitrogen species were extremely low within Lake Ella during 1988 and 1990. Mean concentrations of ammonia and nitrate averaged only 14 and 43 $\mu\text{g/l}$, respectively, and constituted only 14% of the total nitrogen species found within the lake. Mean concentrations of both nitrate and ammonia were equal to or less than minimum concentration levels necessary for nutrient uptake by most algal species. Organic nitrogen represented the dominant nitrogen form within Lake Ella with approximately equal contributions between dissolved and particulate forms.

As seen in Table 5-1, concentrations of all measured phosphorus species were also extremely low within Lake Ella. The mean orthophosphorus concentration within

the lake was approximately 2 $\mu\text{g}/\text{l}$ which is a level near or below minimum concentrations necessary for algal uptake. The dominant phosphorus forms were dissolved organic phosphorus and particulate phosphorus, constituting 92% of the mean total phosphorus value of 26 $\mu\text{g}/\text{l}$.

Measured concentrations of chlorophyll-a within Lake Ella exhibited a range of values from 1.5 to 12.2 mg/m^3 with a mean of 5.1 mg/m^3 . A mean chlorophyll level of 5.1 mg/m^3 is generally considered to indicate oligotrophic conditions. This low level of algal production is also evident in the relatively low values for turbidity and suspended solids found within Lake Ella. Water clarity within the lake, as indicated by measurements of Secchi disk depth, was excellent on all measurement dates with a mean Secchi disk depth in excess of 2.2 m. This mean value underestimates water clarity to some degree since Secchi disk depths exceeded the water column depth on many measurement dates. Measured values of turbidity and suspended solids were extremely low with mean values of 2.5 NTU and 3.6 mg/l , respectively.

A comparison of water quality characteristics in Lake Ella before and after initiation of the alum injection system is given in Table 5-2. Post-treatment water quality data for Lake Ella provided in this table is based upon alum stormwater treatment at a dose of 10 mg/l from January 1988 to May 1990. With the exception of specific conductivity, alum treatment of stormwater resulted in significant improvements in water column concentrations of virtually all measured parameters when compared to mean chemical characteristics existing in Lake Ella prior to the alum injection process. Historical concentrations of turbidity were reduced by 89%, ammonia by 95%, nitrate by 14%, organic nitrogen by 77%, total nitrogen by 78%, orthophosphorus by 91%, total phosphorus by 89%, chlorophyll-a by 97% and BOD by 93%. Secchi disk measurements increased more than 340% from a value of less than 0.5 m to a mean in excess of 2.2 m at all locations.

TABLE 5-2

COMPARISON OF WATER QUALITY CHARACTERISTICS
OF LAKE ELLA BEFORE AND AFTER INITIATION OF ALUM STORMWATER TREATMENT

| PARAMETER | UNITS | MEAN CHEMICAL CHARACTERISTICS PRIOR TO ALUM TREATMENT (1974-85) ¹ | MEAN CHEMICAL CHARACTERISTICS WITH ALUM TREATMENT (1/88-5/90) ² | PERCENT CHANGE (%) |
|--------------------------------------|-------------------|--|--|--------------------|
| pH | s.u. | 7.41 | 6.43 | -13 |
| Spec. Conductivity | $\mu\text{S/cm}$ | 91 | 118 | +30 |
| Dissolved O ₂ | mg/l | 3.5 (1 m) | 7.4 | +111 |
| Alkalinity | mg/l | 25.3 | 11.0 | -57 |
| Turbidity | NTU | 22 | 2.5 | -89 |
| NH ₃ -N | $\mu\text{g/l}$ | 276 | 14 | -95 |
| NO ₂ + NO ₃ -N | $\mu\text{g/l}$ | 50 | 43 | -14 |
| Organic N | $\mu\text{g/l}$ | 1550 | 360 | -77 |
| Total N | $\mu\text{g/l}$ | 1876 | 417 | -78 |
| Ortho-P | $\mu\text{g/l}$ | 23 | 2 | -91 |
| Total P | $\mu\text{g/l}$ | 232 | 26 | -89 |
| SO ₄ ⁻² | mg/l | - | 33 | - |
| Chlorophyll-a | mg/m ³ | 180 | 5.1 | -97 |
| BOD | mg/l | 41 | 3.0 | -93 |
| Secchi Disk Depth | m | <0.5 | >2.2 | +340 |

1. n = 15 samples

2. n = 11 samples at an alum dose of 10 mg/l as Al₂O₃ during the period from January 1988 to May 1990

Measured concentrations of sulfate ions within Lake Ella averaged 33 mg/l after initiation of alum stormwater treatment. Although pre-treatment measurements of sulfate concentrations within Lake Ella are not available, the post-treatment value of 33 mg/l represents an increase in sulfate levels within the lake since sulfate ions are released as a part of the dissolution process for aluminum sulfate (alum). Sulfate ions generally exhibit conservative behavior under oxidized conditions. No toxic effects are known from sulfate concentrations at this relatively low level. Increases in concentrations of sulfate ions are largely responsible for the slight increase in specific conductivity from 91 $\mu\text{S}/\text{cm}$ prior to alum treatment to a mean of 118 $\mu\text{S}/\text{cm}$ following alum treatment.

Substantial improvements were achieved in dissolved oxygen conditions within Lake Ella following initiation of alum stormwater treatment. Field measurements of dissolved oxygen conducted within Lake Ella prior to initiation of the alum treatment system were conducted primarily at a depth of 1 m below the water surface. The mean dissolved oxygen value during the period from 1984 to 1985 at this depth was approximately 3.5 mg/l. Sporadic dissolved oxygen measurements conducted at depths greater than 1 m indicated levels of dissolved oxygen near zero on virtually all measurement dates. Following start-up of the alum treatment system, dissolved oxygen conditions within Lake Ella improved dramatically to a whole-lake average value of approximately 7.4 mg/l during 1988-90. Whole-lake average dissolved oxygen levels exceeded 5 mg/l on all measurement dates during the period from January 1988 to May 1990.

Visually, the water column appeared to be exceptionally clear during this period, and no evidence was observed of filamentous algal growth in areas along the shoreline. However, in response to improved conditions of water clarity, the growth of rooted macrophytes such as slender spikerush, water lilies and numerous other species,

increased rapidly. All of these species entered the lake naturally since no littoral zone planting was conducted as part of the restoration efforts. This growth first appeared in 1987 as small patches within the shallow areas near the shoreline. By spring of 1990, this growth had extended to all shoreline areas and many of the deeper areas within the lake. Grass carp were introduced in 1990 at a stocking rate of approximately 5 fish/acre in an attempt to achieve long-term control of the rooted macrophytes within the lake. Routine mechanical harvesting is also being considered by the City of Tallahassee.

A comparison of physical-chemical profiles collected in Lake Ella on November 29, 1985 prior to start-up of the alum injection system with measurements collected on September 5, 1987 after introduction of the alum injection system is given in Figure 5-1. These profiles represent typical physical-chemical conditions within Lake Ella before and after alum treatment of stormwater. As seen in Figure 5-1, post-treatment levels of dissolved oxygen are greater than pre-treatment dissolved oxygen levels at all measured depths. In addition, post-treatment dissolved oxygen levels are virtually uniform throughout the water column, while significant reductions in dissolved oxygen are observed at lower depths under pre-treatment conditions. A slight reduction in pH within the water column was observed following alum treatment of stormwater, with post-treatment values ranging from approximately 6.2 at the surface to a value near 6.0 at a depth of 3 m.

A comparison of fluctuations in pH, phosphorus, dissolved oxygen and chlorophyll-a in Lake Ella from July 1987 to May 1990 is given in Figure 5-2. Measured concentrations of dissolved orthophosphorus have remained relatively constant, with no measured values exceeding 5 $\mu\text{g/l}$ on any measurement date. A larger fluctuation has been observed in measured concentrations of total phosphorus, however, with values ranging from 11 to 45 $\mu\text{g/l}$. Whole-lake average values for

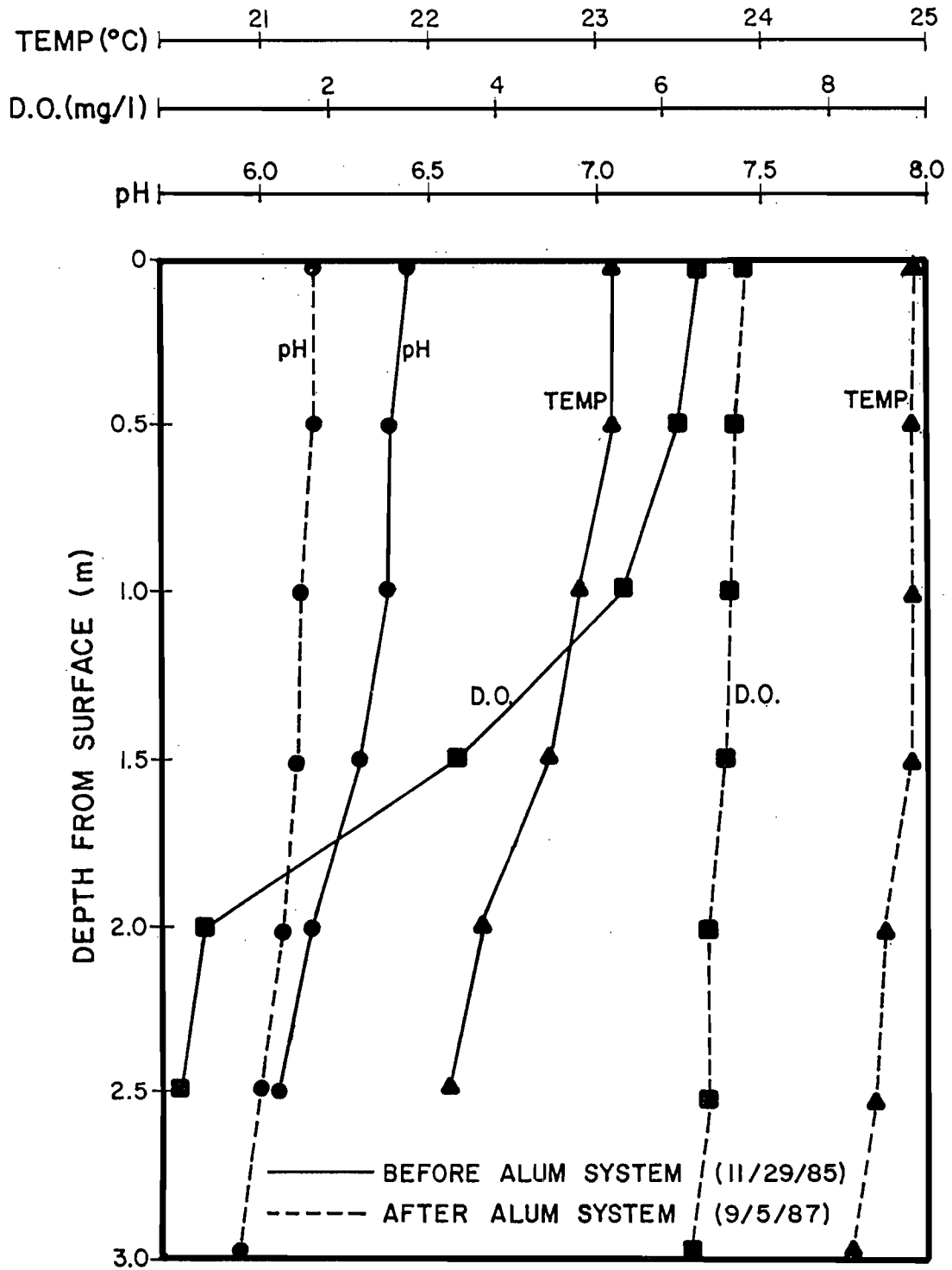


Figure 5-1. Comparison of Pre-Treatment and Post-Treatment Physical-Chemical Profiles in Lake Ella.

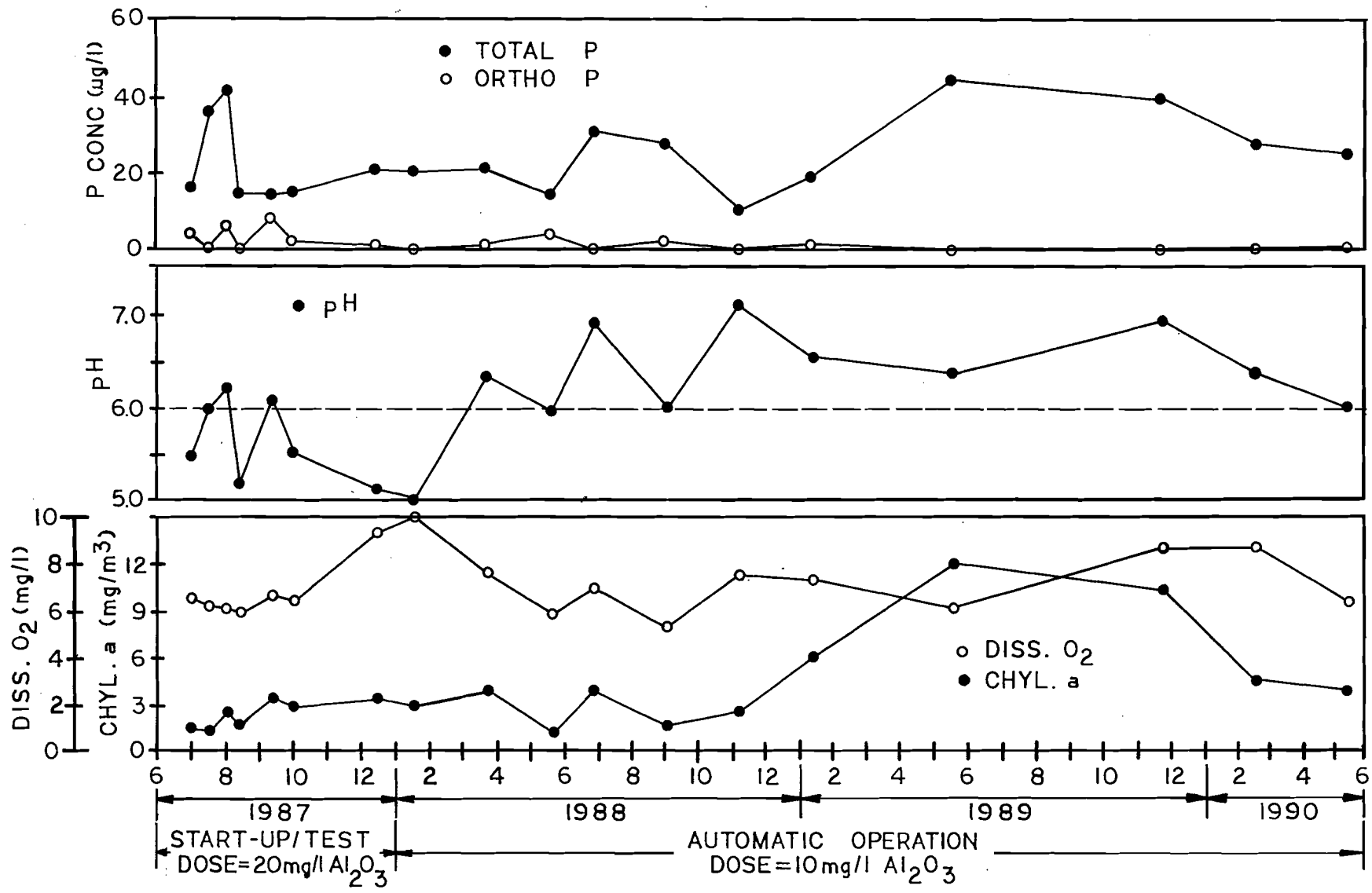


Figure 5-2. Fluctuations in pH, Phosphorus, Dissolved Oxygen and Chlorophyll-a in Lake Ella from 6/87 to 5/90.

dissolved oxygen have also exhibited minor fluctuations with measured values near saturation levels on most monitoring dates. With the exceptions of sampling events conducted in May and November of 1989, measured concentrations of chlorophyll-a have been relatively stable within Lake Ella, with overall values ranging from 1.5 to 12.2 mg/m³.

As indicated previously, an alum dose of 20 mg/l was used at Lake Ella during the initial start-up and testing phase which extended through December of 1987. During this time, pH levels within Lake Ella were frequently depressed below a value of 6.0. In response to these periodic conditions of low pH, the alum dose was reduced to 10 mg/l beginning in January of 1988. This reduction in alum dose immediately improved pH conditions within the lake, resulting in pH values at or above a level of 6.0 for the remainder of the monitoring period.

A summary of measured concentrations of heavy metals in Lake Ella during alum treatment of stormwater at a dose of 10 mg/l from January 1988 to May 1990 is given in Table 5-3. Measured concentrations of all heavy metals were extremely low within Lake Ella with mean concentrations of cadmium and chromium less than 1 µg/l and mean concentrations of copper and lead less than 5 µg/l. Concentrations of all heavy metals were found to be substantially less than the State of Florida Class III criteria for recreational surface waters.

Measured concentrations of aluminum in Lake Ella from January 1988 to May 1990 with alum stormwater treatment at a dose of 10 mg/l were also found to be extremely low. The average dissolved aluminum concentration was found to be 44 µg/l, with a range of values from 6 to 108 µg/l. Total aluminum concentrations averaged 189 µg/l, with a range of values from 38 to 610 µg/l.

Fluctuations in concentrations of dissolved and total aluminum in Lake Ella from June 1987 to May 1990 are shown in Figure 5-3. Concentrations of both total

TABLE 5-3

CONCENTRATIONS OF HEAVY METALS
IN LAKE ELLA FROM 1/88 TO 5/90 WITH ALUM
TREATMENT OF STORMWATER AT A DOSE OF 10 mg/l

| HEAVY METAL | | UNITS OF MEASUREMENT | MEAN VALUE ¹ | RANGE OF VALUES | STATE OF FLORIDA CLASS III CRITERIA ² |
|-------------|-------|----------------------|-------------------------|-----------------|--|
| Aluminum | Diss. | µg/l | 44 | 6-108 | - |
| | Total | µg/l | 193 | 38-610 | None |
| Cadmium | Diss. | µg/l | 0.16 | <0.1-0.40 | - |
| | Total | µg/l | 0.17 | <0.1-0.50 | 0.8 |
| Copper | Diss. | µg/l | 2.6 | 0.1-12 | - |
| | Total | µg/l | 2.8 | 0.1-12 | 30 |
| Chromium | Diss. | µg/l | 0.22 | 0.0-0.7 | - |
| | Total | µg/l | 0.53 | 0.0-1.8 | 50 |
| Iron | Diss. | µg/l | 25 | 2-64 | - |
| | Total | µg/l | 129 | 26-410 | 1000 |
| Lead | Diss. | µg/l | 1.6 | 0.1-4.1 | - |
| | Total | µg/l | 2.8 | 0.1-4.5 | 30 |
| Zinc | Diss. | µg/l | 12.4 | 0.0-44 | - |
| | Total | µg/l | 12.8 | 0.0-45 | 30 |

1. n = 11 samples

2. Chapter 17-302 Florida Administrative Code

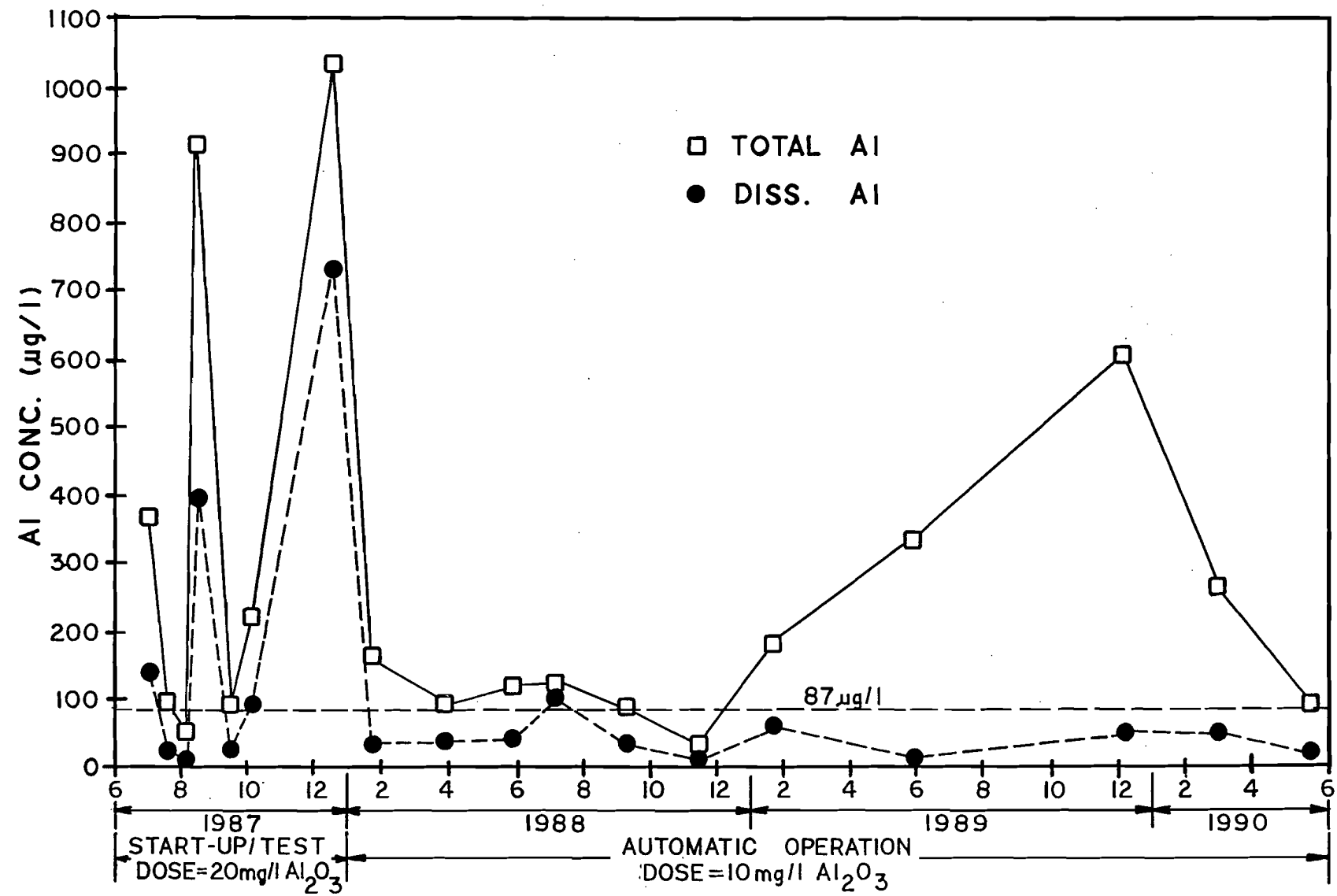


Figure 5-3. Fluctuations in Aluminum Concentrations in Lake Ella from 6/87 to 5/90.

and dissolved aluminum were extremely variable during the start-up and testing period from June through December of 1987 using an alum dose of 20 mg/l. As indicated previously, several operational problems were encountered during this period which resulted in excess addition of alum to the lake with a resulting decrease in whole-lake pH values. The two spikes in the data sets, occurring in August and December 1987, can be attributed to these malfunctions. However, other fluctuations in dissolved aluminum concentrations were caused when the initial alum dose of 20 mg/l consumed excessive amounts of alkalinity from the poorly buffered stormwater inputs entering the lake. On these occasions, pH levels within the lake would decrease with a corresponding increase in concentrations of dissolved aluminum. When the alum dose was reduced to 10 mg/l in January 1988, pH levels stabilized within the lake at values between 6 and 7 with a corresponding decrease in concentrations of dissolved aluminum. Only one of the eleven measurements taken within the lake at a treatment dose of 10 mg/l exceeded the U.S. EPA recommended level of 87 $\mu\text{g/l}$ for dissolved aluminum.

It should be emphasized that the relationships shown in Figure 5-3 are site-specific for the Lake Ella system only. Reductions in pH values caused by various alum doses are site-specific and depend upon the buffering capacity of the particular stormwater stream and receiving waterbody. Although an alum dose of 20 mg/l was found to result in unacceptable pH fluctuation within Lake Ella, many lake systems could easily accept this dose or a higher dose and experience no problems in pH.

Relationships between pH and dissolved aluminum concentrations in Lake Ella from June 1987 to May 1990 is given in Figure 5-4. Water column concentrations of dissolved aluminum appear to be highly correlated with pH levels within the lake. Relatively high levels of both dissolved and total aluminum were observed when pH levels dropped in the range of 5.0 to 5.5. At whole-lake pH values of 6.0 or above,

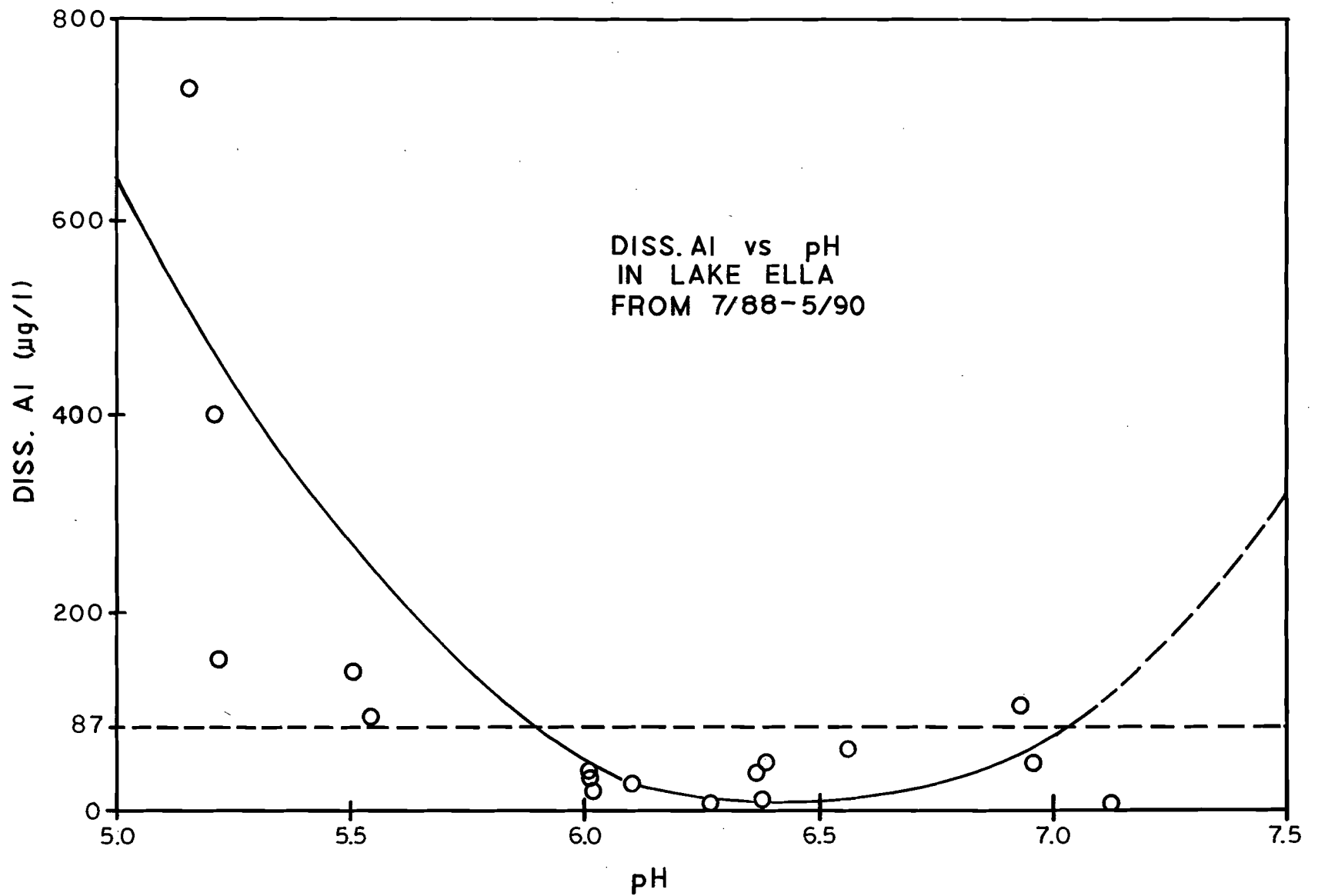


Figure 5-4. Relationships Between pH and Dissolved Aluminum Levels in Lake Ella from 7/88 to 5/90.

measured aluminum concentrations for both dissolved and total forms remained at relatively low values.

A best-fit second-order polynomial equation was developed for the relation between pH and dissolved aluminum using a SAS regression procedure. This best-fit regression line is indicated in Figure 5-4. Based upon this relationship, dissolved aluminum levels within the lake reach equilibrium concentrations less than the U.S. EPA recommended maximum dissolved aluminum criterion of $87 \mu\text{g/l}$ when the pH is between approximately 5.9 and 7.0. pH levels less than approximately 5.9 or greater than 7.0 within Lake Ella while receiving alum stormwater treatment will result in aluminum concentrations which may slightly exceed the $87 \mu\text{g/l}$ criterion. This relationship is similar in shape and pH range to the equilibrium diagram for hydroxo-aluminum complexes presented in Figure 2-2. This relationship clearly demonstrates that dissolved aluminum levels within an alum treated waterbody are determined primarily by chemical solubility limitations. As long as mean pH levels within the treated system are maintained within the range of 6.0 to 7.0, aluminum concentrations will remain within an acceptable range.

A comparison of pre- and post-modification trophic states in Lake Ella is given in Table 5-4. As indicated previously, alum treatment of stormwater runoff decreased mean concentrations of total phosphorus from 0.232 mg/l to 0.026 mg/l , mean chlorophyll levels from 180 mg/m^3 to 5.1 mg/m^3 and increased mean Secchi disk depth from less than 0.5 to greater than 2.0 m.

Trophic state indices were calculated for pre- and post-modification conditions based upon the Florida Trophic State Index proposed by Brezonik (1984) which was developed specifically for Florida lakes. The empirical equations for calculating the Florida Trophic State Index are as follows for phosphorus limited lakes:

TABLE 5-4

COMPARISON OF PRE- AND POST-MODIFICATION
TROPIC STATES IN LAKE ELLA

| PARAMETER | PRE-MODIFICATION CONDITION | POST-MODIFICATION CONDITION |
|---|-------------------------------|--------------------------------|
| Mean P Concentration (mg/l) | 0.232 | 0.026 |
| Mean Chlorophyll-a (mg/m ³) | 180 | 5.1 |
| Mean Secchi Disk (m) | <0.5 | >2.2 |
| Florida TSI Value Based On: | | |
| a. Total P | 104.7 | 53.1 |
| b. Chlorophyll-a | 91.6 | 40.3 |
| c. Average | 98.2 | 46.7 |

$$\begin{aligned} \text{TSI (Chl-a)} &= 16.8 + 14.4 (\text{Chl-a}) && (\text{mg/m}^3) \\ \text{TSI (SD)} &= 60.0 - 30.0 \ln (\text{SD}) && (\text{m}) \\ \text{TSI (TP)} &= 23.6 \ln (\text{TP}) - 23.8 && (\mu\text{g/l}) \\ \text{TSI (Avg)} &= 1/3 [\text{TSI (Chl-a)} + \text{TSI (SD)} + \text{TSI (TP)}] \end{aligned}$$

Average trophic state values less than 50 indicate oligotrophic conditions, values between 50 and 60 indicate mesotrophic conditions, and values from 61 to 70 indicate eutrophic conditions.

Trophic state indices for Lake Ella were calculated for pre- and post-treatment conditions using the pre- and post-water quality characteristics listed in Table 5-2. Under pre-modification conditions, Lake Ella exhibited a Florida Trophic State Index value for total phosphorus of approximately 104.7 and a value of 91.6 for chlorophyll-a. The average pre-modification trophic state index of 98.2 is well into the hypereutrophic category. Under post-modification conditions, trophic state indices within Lake Ella decreased sharply. The post-modification trophic state index for total phosphorus and chlorophyll-a were 53.1 and 40.3, respectively, for an average of 46.7. This value places Lake Ella under post-modification conditions in the oligotrophic category. Based upon trophic state indices, construction of the alum stormwater treatment system at Lake Ella has improved water quality conditions from hypereutrophic to oligotrophic.

Benthic Survey

As indicated previously, benthic surveys were conducted in Lake Ella on three separate occasions. One survey was conducted on November 29, 1985, immediately prior to the initiation of the draining and construction activities for installation of the alum stormwater treatment system. The second benthic survey was conducted on

January 16, 1987, at the completion of construction of the alum stormwater system after the lake had been totally refilled for a period of approximately three to four months. The final benthic survey was conducted on May 25, 1990, after approximately three years of operation of the alum stormwater treatment system.

The initial benthic survey conducted on November 29, 1985, prior to any dredging or restoration activities, did not produce any viable organisms at any of the eight monitoring locations within Lake Ella. It appears that the accumulated sediment and debris contributed by stormwater runoff over a period of many years exhibited toxic effects within the sediments which inhibited the colonization of benthic organisms within the lake.

Similarly, the benthic survey conducted on January 16, 1987 also did not produce viable benthic organisms at any of the eight monitoring locations. This survey was conducted following the dredging and recontouring activities within Lake Ella after the lake had been allowed to refill for approximately three to four months. Although much of the accumulated toxic material had been removed, it appears that benthic communities had not had sufficient time to recolonize the lake. It should be noted, however, that approximately four of the eight monitoring locations were in areas of the lake which were not completely drained during the drawdown and construction activities. These areas were unaffected by construction and recontouring activities within the lake. Therefore, the lack of benthic organisms on this date cannot be attributed solely to the dredging and recontouring activities since some of the monitoring locations remained in an undisturbed condition.

The results of the benthic survey conducted in Lake Ella on May 25, 1990 are given in Table 5-5. On this date, benthic organisms were encountered at six of the eight sampling locations within the lake. Benthic organisms were not found near the center of the northeast lobe or near the boat ramp. As seen in Figure 3-4, the center of

TABLE 5-5
RESULTS OF BENTHIC SURVEY
CONDUCTED IN LAKE ELLA ON MAY 25, 1990

| SAMPLE SITE | SITE DESCRIPTION | ORGANISMS/m ² | | |
|--------------|---------------------------------|--------------------------|---------|-------|
| | | <i>TUBIFEX sp.</i> | LEECHES | TOTAL |
| 1 | Center of S.E. Lobe | 14 | 14 | 43 |
| 2 | S.E. Lobe Near end of Peninsula | 14 | 14 | 28 |
| 3 | Near Outfall | 57 | 0 | 57 |
| 4 | Center of N.E. Lobe | 0 | 0 | 0 |
| 5 | Center of Lake | 29 | 129 | 158 |
| 6 | Near Boat Ramp | 0 | 0 | 0 |
| 7 | Near Fountain | 129 | 14 | 143 |
| 8 | Center of S.W. Lobe | 86 | 28 | 114 |
| Lake Average | | 41 | 14 | 55 |

the northeast lobe receives accumulations of alum floc from two injection points. However, the sample collected near the boat ramp was located between two outfall pipes extending into the lake where accumulations of alum floc would not be expected. Therefore, factors other than floc accumulations may be responsible for the lack of benthic species at these two locations. Only two species of benthic organisms, tubifex worms and leeches, were found at any location. On an average basis, a total of 55 benthic organisms per square meter were found within the lake.

Although the population densities listed in Table 5-5 appear to be relatively small, the existence of these populations after three years of continuous alum applications within Lake Ella indicates that, at least for the species found, the existence of alum precipitate within the sediments is not incompatible with the environmental requirements of these species. The fact that both of the benthic organisms found in Lake Ella are typical polluted water-type organisms is not surprising since Lake Ella is basically a large regional stormwater management facility which receives an average of approximately 47,000 kg of suspended solids, 122 kg of zinc and 13 kg of lead each year, the majority of which ends up deposited in the sediments. A comparison of the three benthic surveys conducted in Lake Ella from 1985-1990 is given in Table 5-6.

Metal Accumulation and Migration

Sediment core samples were collected at four locations within Lake Ella, as described previously, to evaluate metal accumulation and migration as a result of the alum treatment process. Sediment core samples were collected at the same locations as the water quality monitoring stations indicated in Figure 4-1. An initial set of core samples was collected on February 21, 1987, coinciding with the start-up of the alum treatment process. The second set of core samples were collected on November 11, 1988, after almost two years of operation of the alum stormwater treatment system.

TABLE 5-6

COMPARISON OF BENTHIC SURVEYS
 CONDUCTED IN LAKE ELLA FROM 1985-1990

| DATE | LAKE CONDITION | AVERAGE NO. OF ORGANISMS/m ² | | |
|----------|--|---|---------|-------|
| | | <i>TUBIFEX sp.</i> | LEECHES | TOTAL |
| 11/29/85 | Immediately prior to lake drawdown | 0 | 0 | 0 |
| 1/16/87 | Following dredging, after lake had refilled for 3-4 months | 0 | 0 | 0 |
| 5/25/90 | After 2½ years of alum system operation | 41 | 14 | 55 |

General characteristics of pre-treatment sediment core samples collected in Lake Ella on February 21, 1987 are given in Table 5-7. In general, measured values for moisture content, organic content and total phosphorus are highest in the surface layers and decreased rapidly with increasing sediment depth. A similar trend is also observed at some locations for nitrogen concentrations in the sediments, although reductions in nitrogen concentration with increasing depth are less than those observed with the other parameters. Relatively high values for moisture content and organic content are found in the southwest lobe, southeast lobe and northeast lobe, with much smaller values at the center location. Much of this difference may be due to the fact that the center of the southwest lobe, southeast lobe and northeast lobe remained wet during the Lake Ella drawdown and were not subjected to dredging activities. On the other hand, approximately 2-3 ft. of excess muck material was removed from the center lobe. Mean values of sediment pH appear to be greatest at the surface and decrease with increasing sediment depth.

General characteristics of sediment cores collected in Lake Ella on November 11, 1988 are presented in Table 5-8. As observed with the February 21, 1987 sample set, sediment concentrations of moisture content, organic content, phosphorus and nitrogen are greatest in the surface layers and decrease with increasing sediment depth. A similar trend is also observed for sediment pH.

A comparison of mean characteristics of sediments in Lake Ella before and after alum treatment of stormwater, based upon mean values from the four sediment collection sites, is given in Table 5-9 and in Figure 5-5 for sediment concentrations of nitrogen and phosphorus. It appears that sediment concentrations of moisture content, organic content and phosphorus are greater in core samples collected on the 1988 date than those collected on the 1987 date. For moisture and organic content, it appears that the extent of these elevated sediment concentrations is limited to the top 10-15 cm of

TABLE 5-7
 GENERAL CHARACTERISTICS OF SEDIMENT
 CORE SAMPLES COLLECTED IN LAKE ELLA ON 2/21/87
 (Before Alum Treatment of Stormwater)

| LOCATION | DEPTH LAYER (cm) | SEDIMENT CHARACTERISTICS | | | NUTRIENT CONCENTRATIONS ($\mu\text{g/g}$ dry weight) | |
|------------|------------------|--------------------------|----------------------|---------------------|---|------|
| | | pH | MOISTURE CONTENT (%) | ORGANIC CONTENT (%) | P | N |
| S.W. Lobe | 0-1 | 5.34 | 82.9 | 17.9 | 2121 | 6476 |
| | 1-5 | 5.65 | 65.1 | 13.0 | 1428 | 3962 |
| | 5-10 | 5.47 | 55.9 | 7.9 | 855 | 2821 |
| | 10-15 | 5.40 | 47.9 | 6.5 | 709 | 1287 |
| | 15-25 | 5.35 | 46.0 | 6.3 | 810 | 1183 |
| Center | 0-1 | 6.22 | 36.1 | 9.9 | 679 | 1488 |
| | 1-5 | 6.11 | 36.7 | 8.4 | 570 | 1478 |
| | 5-10 | 6.01 | 29.0 | 9.7 | 545 | 1114 |
| | 10-15 | 5.87 | 25.4 | 9.9 | 491 | 1004 |
| | 15-25 | 5.73 | 21.1 | 7.5 | 411 | 636 |
| S.E. Lobe | 0-1 | 6.17 | 70.9 | 23.4 | 909 | 2660 |
| | 1-5 | 6.05 | 47.9 | 21.6 | 794 | 1889 |
| | 5-10 | 5.96 | 23.8 | 18.7 | 703 | 1467 |
| | 10-15 | 5.87 | 28.2 | 12.4 | 627 | 1085 |
| | 15-25 | 5.76 | 23.4 | 12.1 | 575 | 716 |
| N.E. Lobe | 0-1 | 6.35 | 61.6 | 11.1 | 1595 | 1328 |
| | 1-5 | 6.19 | 39.1 | 10.0 | 1167 | 1365 |
| | 5-10 | 6.01 | 38.9 | 7.6 | 1163 | 1263 |
| | 10-15 | 5.90 | 39.7 | 6.6 | 1032 | 991 |
| | 15-25 | 5.82 | 32.2 | 4.7 | 1001 | 881 |
| Mean Value | 0-1 | 6.02 | 62.9 | 15.6 | 1359 | 2988 |
| | 1-5 | 6.00 | 47.2 | 13.3 | 990 | 2174 |
| | 5-10 | 5.86 | 39.2 | 11.0 | 816 | 1666 |
| | 10-15 | 5.76 | 35.3 | 8.9 | 715 | 1092 |
| | 15-25 | 5.67 | 30.7 | 7.7 | 699 | 855 |

TABLE 5-8
 GENERAL CHARACTERISTICS OF SEDIMENT
 CORE SAMPLES COLLECTED IN LAKE ELLA ON 11/11/88
 (After Alum Treatment of Stormwater)

| LOCATION | DEPTH LAYER (cm) | SEDIMENT CHARACTERISTICS | | | NUTRIENT CONCENTRATIONS ($\mu\text{g/g}$ dry weight) | |
|------------|------------------|--------------------------|----------------------|---------------------|---|------|
| | | pH | MOISTURE CONTENT (%) | ORGANIC CONTENT (%) | P | N |
| S.W. Lobe | 0-1 | 5.67 | 78.6 | 29.7 | 1965 | 5238 |
| | 1-5 | 5.50 | 75.4 | 28.3 | 1691 | 4866 |
| | 5-10 | 5.48 | 71.1 | 24.5 | 1591 | 3262 |
| | 10-15 | 5.42 | 65.0 | 22.6 | 1238 | 2470 |
| | 15-25 | 5.39 | 60.1 | 19.5 | 1359 | 2335 |
| Center | 0-1 | 5.75 | 68.9 | 17.6 | 876 | 1999 |
| | 1-5 | 5.94 | 38.5 | 7.6 | 641 | 815 |
| | 5-10 | 5.90 | 25.5 | 6.5 | 634 | 649 |
| | 10-15 | 5.86 | 21.6 | 6.1 | 563 | 779 |
| | 15-25 | 5.81 | 30.3 | 8.2 | 550 | 725 |
| S.E. Lobe | 0-1 | 6.33 | 80.5 | 17.4 | 1344 | 2990 |
| | 1-5 | 5.83 | 34.9 | 6.1 | 678 | 1336 |
| | 5-10 | 5.75 | 25.1 | 5.0 | 684 | 1265 |
| | 10-15 | 5.62 | 20.3 | 5.1 | 674 | 871 |
| | 15-25 | 5.60 | 19.0 | 5.3 | 382 | 560 |
| N.E. Lobe | 0-1 | 6.11 | 87.3 | 22.5 | 1767 | 3435 |
| | 1-5 | 5.90 | 58.4 | 13.6 | 1225 | 838 |
| | 5-10 | 5.85 | 50.6 | 11.7 | 870 | 265 |
| | 10-15 | 5.76 | 38.6 | 9.7 | 787 | 267 |
| | 15-25 | 5.70 | 29.4 | 7.1 | 778 | 259 |
| Mean Value | 0-1 | 5.97 | 78.8 | 21.8 | 1488 | 3416 |
| | 1-5 | 5.79 | 51.8 | 13.9 | 1059 | 1964 |
| | 5-10 | 5.75 | 43.1 | 11.9 | 945 | 1360 |
| | 10-15 | 5.67 | 36.4 | 10.9 | 816 | 1097 |
| | 15-25 | 5.63 | 34.7 | 10.0 | 767 | 970 |

TABLE 5-9

SUMMARY OF MEAN CHARACTERISTICS OF SEDIMENTS IN
LAKE ELLA BEFORE AND AFTER ALUM TREATMENT OF STORMWATER

| SAMPLE | DEPTH LAYER (cm) | SEDIMENT CHARACTERISTICS | | | NUTRIENT CONCENTRATIONS ($\mu\text{g/g}$ dry weight) | |
|----------|------------------|--------------------------|----------------------|---------------------|---|------|
| | | pH | MOISTURE CONTENT (%) | ORGANIC CONTENT (%) | P | N |
| 2/21/87 | 0-1 | 6.02 | 62.9 | 15.6 | 1359 | 2988 |
| | 1-5 | 6.00 | 47.2 | 13.3 | 990 | 2174 |
| | 5-10 | 5.80 | 39.2 | 11.0 | 816 | 1666 |
| | 10-15 | 5.76 | 35.3 | 8.9 | 715 | 1092 |
| | 15-25 | 5.67 | 30.7 | 7.7 | 699 | 855 |
| 11/11/88 | 0-1 | 5.97 | 78.8 | 21.8 | 1488 | 3416 |
| | 1-5 | 5.79 | 51.8 | 13.9 | 1059 | 1964 |
| | 5-10 | 5.75 | 43.1 | 11.9 | 945 | 1360 |
| | 10-15 | 5.67 | 36.4 | 10.9 | 816 | 1097 |
| | 15-25 | 5.63 | 34.7 | 10.0 | 767 | 970 |

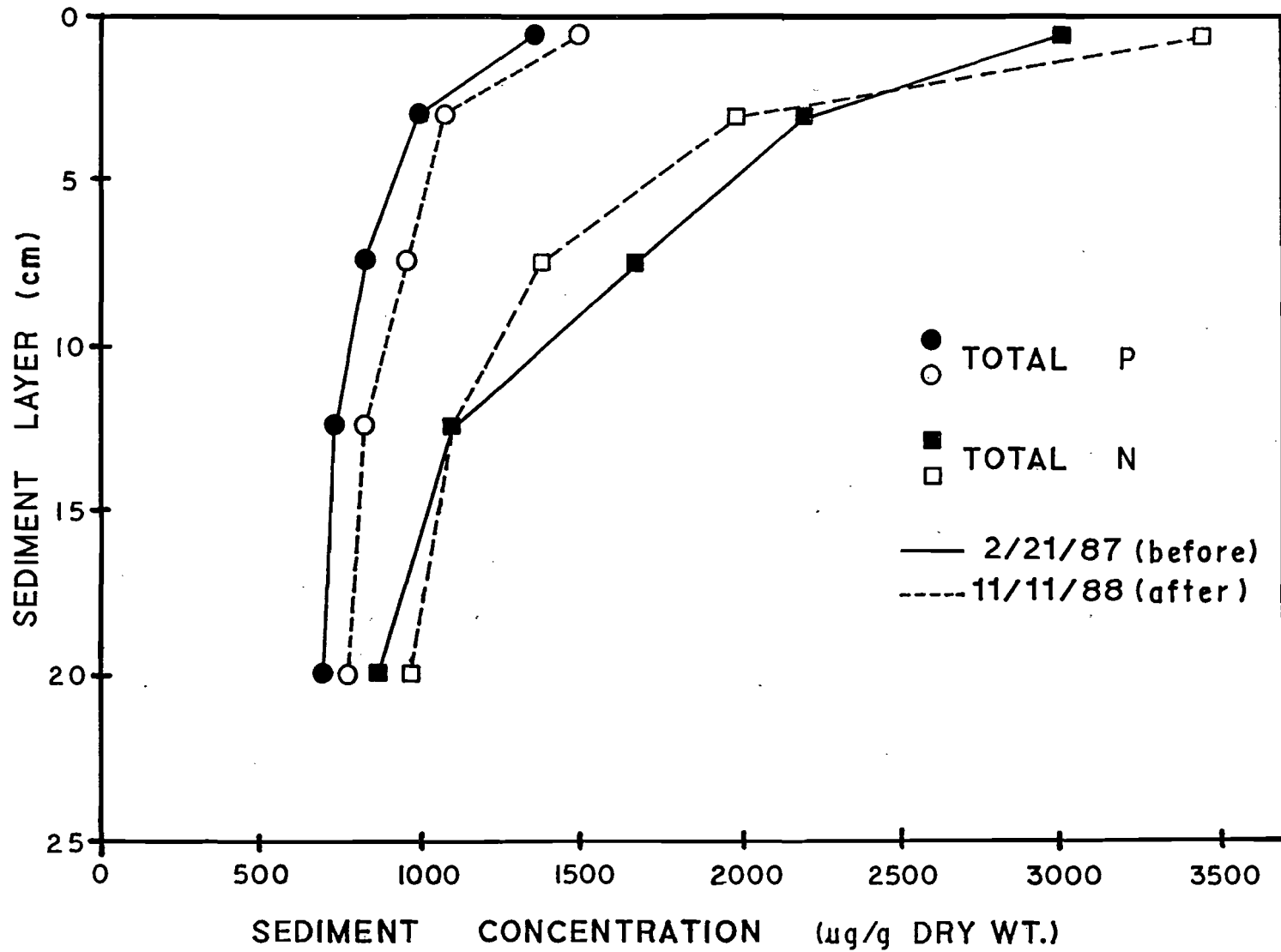


Figure 5-5. Comparison of Sediment Concentrations of Nitrogen and Phosphorus in Lake Ella Based on Core Samples Collected on 2/21/87 and 11/11/88.

the sediments. Sediment concentrations of these parameters below a depth of 15 cm are relatively similar between the two collection dates.

As seen in Table 5-9, mean sediment concentrations of total phosphorus are slightly greater at all measured sediment depths in sample cores collected in November 1988 compared with pre-treatment sediment cores collected in February 1987. In contrast, sediment concentrations of total nitrogen are slightly higher in the 0-1 cm layer for post-treatment sediments, while lower concentrations are observed in post-treated sediments at lower sediment depths. Decreases in concentration with increasing sediment depth appear to be more pronounced for total nitrogen than for total phosphorus. However, regardless of the sediment concentrations depicted in Figure 5-5, there appears to be little difference in sediment retention characteristics of either total nitrogen or total phosphorus between the two sample collection dates. The general sediment pattern of highest concentrations near the sediment surface with decreasing concentrations at lower layers appears to be virtually identical in sediment samples collected on each of the two dates. It appears that the introduction of alum into the sediments has not altered the accumulation or sediment retention characteristics of either nitrogen or phosphorus.

As seen in Table 5-9, sediment pH values appear to be slightly less in the post-treatment sediments than measured in pre-treatment sediments. These decreases in sediment pH values range from approximately 0.5 to 0.20 pH units, depending upon the particular sediment layer. Differences in sediment pH appear to diminish in the 15-25 cm layer with approximately equal sediment pH values in this layer for both pre- and post-sediment conditions. As seen in Tables 5-7 and 5-8, pH values in the 0-1 cm layer actually increased in post-treatment sediments core samples collected in the southwest and southeast lobes of Lake Ella. This finding is particularly significant since the southwest lobe receives inputs of alum sludge from a large stormsewer system

and the southeast lobe receives inputs from two treated stormsewer systems. It appears that introduction of alum floc into Lake Ella sediments is not having an appreciable effect on pH conditions within the lake sediments.

Sediment concentrations of heavy metals in core samples collected in Lake Ella on February 21, 1987 are given in Table 5-10. Substantial variability appears to exist on this collection date between sediment metal concentrations at each of the four monitoring locations. Metal concentrations in core samples collected within the southwest lobe, the southeast lobe and the northeast lobe appear to be somewhat greater for most parameters than those measured in the center of the lake. There also appears to be a tendency for sediment metal concentrations to decrease with increasing sediment depth. This trend is particularly evident in the mean values for each of the four locations listed at the bottom of Table 5-10 and is most apparent for sediment concentrations of lead and zinc and less apparent for aluminum, copper and iron.

Heavy metal concentrations in core samples collected in Lake Ella on November 11, 1988 are presented in Table 5-11. Several differences are apparent in the post-treatment sediment metal concentrations presented in Table 5-11 compared with the pre-treatment sediment metal concentrations presented in Table 5-10. First, the extreme variability in sediment concentrations of copper and iron between sample locations is substantially less in the post-treatment sediments than in pre-treatment sediments, particularly in the 0-1 cm layer. Much of this may be due to a natural repositioning of sediments within the lake following the dredging and recontouring operations. Second, sediment concentrations of aluminum increase slightly at all locations within the lake in the 0-1 cm layer. Aluminum concentrations in layers beneath the 0-1 cm layer are relatively similar between the two collection dates. Finally, an interesting trend appears to have developed for sediment concentration of lead with sediment lead concentrations peaking at three of the four sample locations within the 1-5 cm layer rather than in the surface 0-1 cm layer.

TABLE 5-10

**SEDIMENT METAL CONCENTRATIONS IN CORE
SAMPLES COLLECTED IN LAKE ELLA ON 2/21/87
(Before Alum Treatment of Stormwater)**

| LOCATION | DEPTH LAYER (cm) | SEDIMENT CONCENTRATION ($\mu\text{g/g}$ dry weight) | | | | |
|-------------|------------------|--|----|--------|-----|-----|
| | | Al | Cu | Fe | Pb | Zn |
| S.W. Lobe | 0-1 | 86,469 | 51 | 26,979 | 517 | 103 |
| | 1-5 | 86,966 | 25 | 28,809 | 463 | 139 |
| | 5-10 | 81,264 | 57 | 28,101 | 691 | 57 |
| | 10-15 | 83,161 | 49 | 28,691 | 676 | 27 |
| | 15-25 | 79,541 | 24 | 24,128 | 350 | 20 |
| Center | 0-1 | 42,903 | 14 | 13,302 | 226 | 108 |
| | 1-5 | 43,467 | 14 | 10,968 | 258 | 88 |
| | 5-10 | 45,800 | 12 | 8,117 | 170 | 47 |
| | 10-15 | 40,026 | 14 | 9,790 | 119 | 54 |
| | 15-25 | 36,942 | 11 | 7,258 | 149 | 13 |
| S.E. Lobe | 0-1 | 66,070 | 43 | 16,116 | 280 | 105 |
| | 1-5 | 53,499 | 12 | 8,761 | 118 | 63 |
| | 5-10 | 47,663 | 12 | 6,714 | 106 | 34 |
| | 10-15 | 53,461 | 7 | 6,112 | 84 | 26 |
| | 15-25 | 75,296 | 5 | 6,803 | 47 | 20 |
| N.E. Lobe | 0-1 | 71,799 | 17 | 13,785 | 131 | 127 |
| | 1-5 | 71,161 | 11 | 10,308 | 101 | 97 |
| | 5-10 | 75,098 | 8 | 14,803 | 135 | 69 |
| | 10-15 | 74,244 | 8 | 15,022 | 160 | 56 |
| | 15-25 | 70,260 | 8 | 10,883 | 113 | 47 |
| Mean Values | 0-1 | 66,810 | 31 | 17,521 | 289 | 111 |
| | 1-5 | 63,773 | 16 | 14,712 | 233 | 97 |
| | 5-10 | 62,456 | 22 | 14,434 | 276 | 52 |
| | 10-15 | 62,723 | 20 | 14,904 | 260 | 41 |
| | 15-25 | 65,510 | 12 | 12,268 | 165 | 25 |

TABLE 5-11

SEDIMENT METAL CONCENTRATIONS IN CORE
 SAMPLES COLLECTED IN LAKE ELLA ON 11/11/88
 (After Alum Treatment of Stormwater)

| LOCATION | DEPTH LAYER (cm) | SEDIMENT CONCENTRATION ($\mu\text{g/g}$ dry weight) | | | | |
|-------------|------------------------|--|----|--------|-----|-----|
| | | Al | Cu | Fe | Pb | Zn |
| S.W. Lobe | 0-1 | 89,596 | 97 | 19,560 | 168 | 132 |
| | 1-5 | 76,451 | 35 | 16,124 | 478 | 57 |
| | 5-10 | 65,653 | 27 | 14,149 | 267 | 69 |
| | 10-15 | 63,641 | 12 | 7,628 | 148 | 56 |
| | 15-25 | 56,416 | 10 | 6,578 | 85 | 13 |
| Center | 0-1 | 45,545 | 78 | 12,713 | 354 | 134 |
| | 1-5 | 43,570 | 15 | 9,317 | 244 | 84 |
| | 5-10 | 37,536 | 13 | 8,494 | 175 | 21 |
| | 10-15 | 36,674 | 13 | 7,732 | 143 | 21 |
| | 15-25 | 44,866 | 12 | 8,997 | 149 | 13 |
| S.E. Lobe | 0-1 | 69,116 | 43 | 17,881 | 50 | 135 |
| | 1-5 | 67,221 | 7 | 14,665 | 196 | 103 |
| | 5-10 | 62,554 | 5 | 7,200 | 31 | 91 |
| | 10-15 | 64,488 | 9 | 6,280 | 19 | 74 |
| | 15-25 | 73,370 | 7 | 8,104 | 26 | 38 |
| N.E. Lobe | 0-1 | 82,532 | 33 | 20,097 | 538 | 109 |
| | 1-5 | 77,695 | 59 | 20,541 | 638 | 76 |
| | 5-10 | 77,278 | 40 | 22,330 | 689 | 62 |
| | 10-15 | 74,918 | 25 | 20,550 | 424 | 55 |
| | 15-25 | 71,196 | 21 | 23,402 | 248 | 55 |
| Mean Values | 0-1 | 71,697 | 63 | 17,563 | 278 | 128 |
| | 1-5 | 66,234 | 29 | 15,162 | 389 | 80 |
| | 5-10 | 60,755 | 22 | 13,043 | 291 | 61 |
| | 10-15 | 59,930 | 15 | 10,548 | 184 | 52 |
| | 15-25 | 61,462 | 13 | 11,770 | 127 | 30 |

A comparison of mean heavy metal concentrations for all sample locations in pre-treatment and post-treatment sediment core samples is given in Table 5-12 and in Figure 5-6 for zinc, lead and copper. Sediment concentrations of aluminum, copper and zinc appear to have increased slightly in the upper sediment layers between the two collection dates. In contrast, sediment concentrations of iron appear to be relatively unchanged between the two collection dates. For those elements which exhibited increased concentrations, the increased concentrations are limited to sediment depths of 5 cm or less. Increased levels of aluminum and copper appear to extend to the 5 cm depth layer, while increased levels of zinc extend only approximately 1 cm deep.

Sediment concentrations of lead in the 0-1 cm layer are relatively unchanged between the two collection dates. However, sediment lead concentrations increase substantially in the 1-5 cm layer, while concentrations decrease somewhat in the 10-15 and 15-25 cm layers. This trend is not observed for any of the other measured heavy metals. There is no apparent physical or chemical explanation for this unusual phenomenon, if in fact that attenuation patterns presented in Figure 5-6 are accurate representations of lead concentrations within Lake Ella. This situation deserves further investigation.

It is interesting to note that sediment concentrations of aluminum increase by only 7.3% in the 0-1 cm layer and 3.9% in the 1-5 cm layer during the approximately two-year period between collection of the core samples. These increased aluminum concentrations within the sediments do not appear to extend below a depth of 5 cm. Aluminum concentrations measured in soil layers below a depth of 5 cm are virtually identical between the two collection dates. These measurements provide evidence that the alum floc produced during the treatment of stormwater runoff is accumulating within the sediments of Lake Ella to depths of 5 cm or less.

TABLE 5-12

COMPARISON OF MEAN HEAVY METAL
CONCENTRATIONS IN SEDIMENTS FROM LAKE ELLA
BEFORE AND AFTER ALUM TREATMENT OF STORMWATER

| SAMPLE | DEPTH LAYER (cm) | SEDIMENT CONCENTRATION ($\mu\text{g/l}$ dry weight) | | | | |
|----------|------------------------|--|----|--------|-----|-----|
| | | Al | Cu | Fe | Pb | Zn |
| 2/21/87 | 0-1 | 66,810 | 31 | 17,521 | 289 | 111 |
| | 1-5 | 63,773 | 16 | 14,712 | 233 | 97 |
| | 5-10 | 62,456 | 22 | 14,434 | 276 | 52 |
| | 10-15 | 62,723 | 20 | 14,904 | 260 | 41 |
| | 15-25 | 55,510 | 12 | 12,268 | 165 | 25 |
| 11/11/88 | 0-1 | 71,697 | 63 | 17,563 | 278 | 128 |
| | 1-5 | 66,234 | 29 | 15,162 | 389 | 80 |
| | 5-10 | 60,755 | 22 | 13,043 | 291 | 61 |
| | 10-15 | 59,930 | 15 | 10,548 | 184 | 52 |
| | 15-25 | 61,462 | 13 | 11,770 | 127 | 30 |

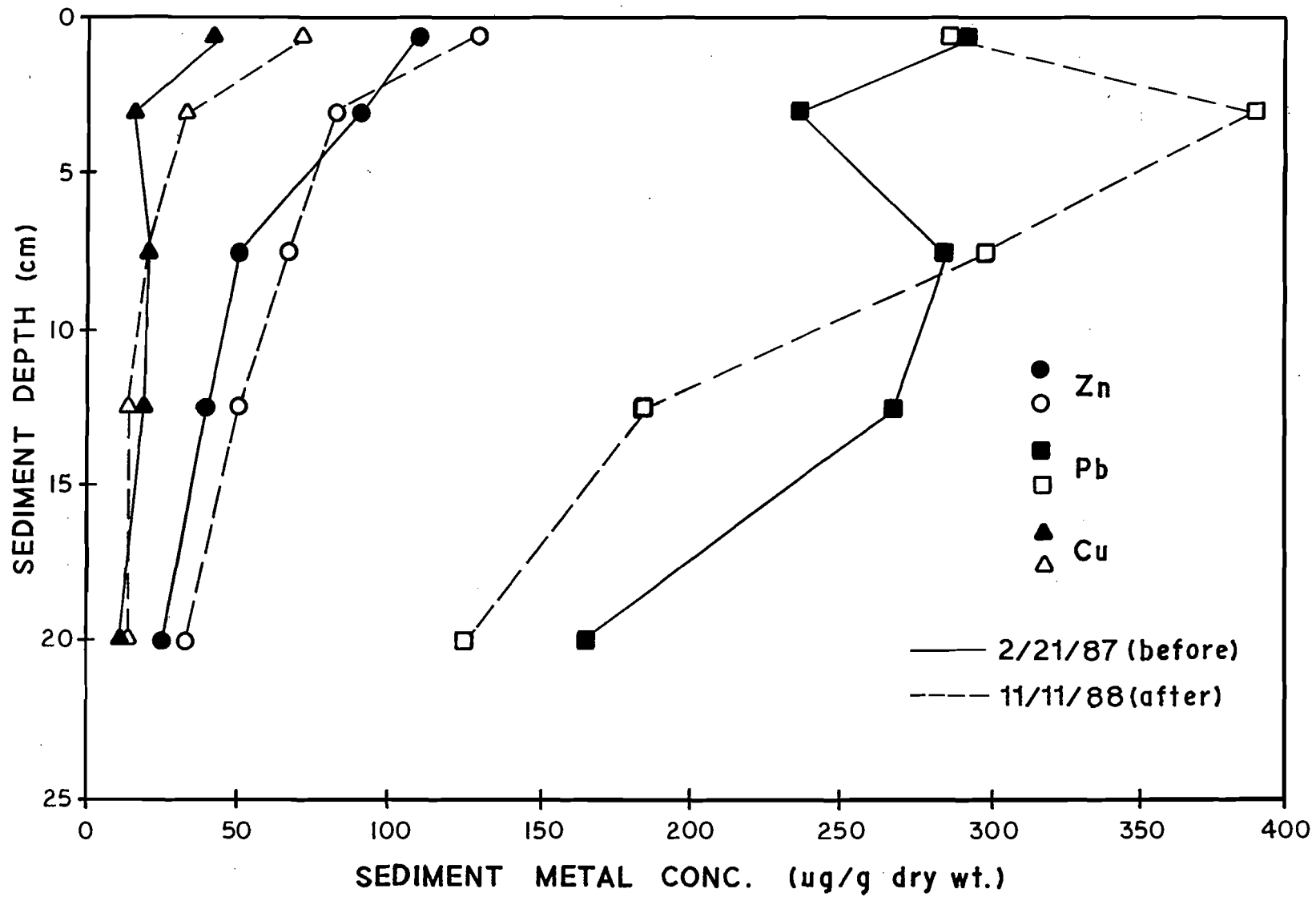


Figure 5-6. Comparison of Pre-Treatment and Post-Treatment Sediment Concentrations of Zinc, Lead and Copper in Lake Ella.

A comparison of sediment concentrations of aluminum at the four sample locations in pre- and post-treatment sediments in Lake Ella is given in Figure 5-7. Sediment profiles of aluminum at the center sediment location appear relatively unchanged in pre- and post-treatment sediments. Little change is also apparent in sediment concentrations in the southwest lobe. However, increased sediment concentrations of aluminum are evident in the southeast and northeast lobes, particularly in the upper sediment layers. The northeast lobe, located near the lake outfall, was contoured as a sump area during the dredging process for accumulation of alum floc deposits. Increases in sediment aluminum concentrations suggest that the area is functioning as a sediment sump as designed. Sediment accumulations are greatest in the southeast lobe, which is a shallow isolated area with two inflow points receiving alum treatment. Alum floc produced within this lobe from treatment of stormwater runoff is apparently remaining within the lobe and is not migrating toward the outfall sump. The adjacent southwest lobe, which receives alum treated runoff through a large 42-inch stormsewer, does not show the measurable increases observed in the southeast lobe. Floc produced within the southwest lobe is apparently migrating out of this area toward the outfall sump.

A comparison of sediment concentrations of zinc at the four sample locations in pre- and post-treatment sediments is given in Figure 5-8. Although fluctuations in the data are apparent, sediment zinc concentrations in the southwest lobe, center and northeast lobe areas appear relatively unchanged in pre- and post-treatment conditions. However, as observed for aluminum, sediment concentrations of zinc have increased substantially in the southeast lobe under post-treatment conditions. These increased zinc concentrations are presumably due to the removal of runoff related zinc inputs by the alum floc with subsequent settling into the sediments.

A comparison of pre- and post-treatment sediment concentrations of copper is given in Figure 5-9. It is apparent that post-treatment sediments appear to accumulate

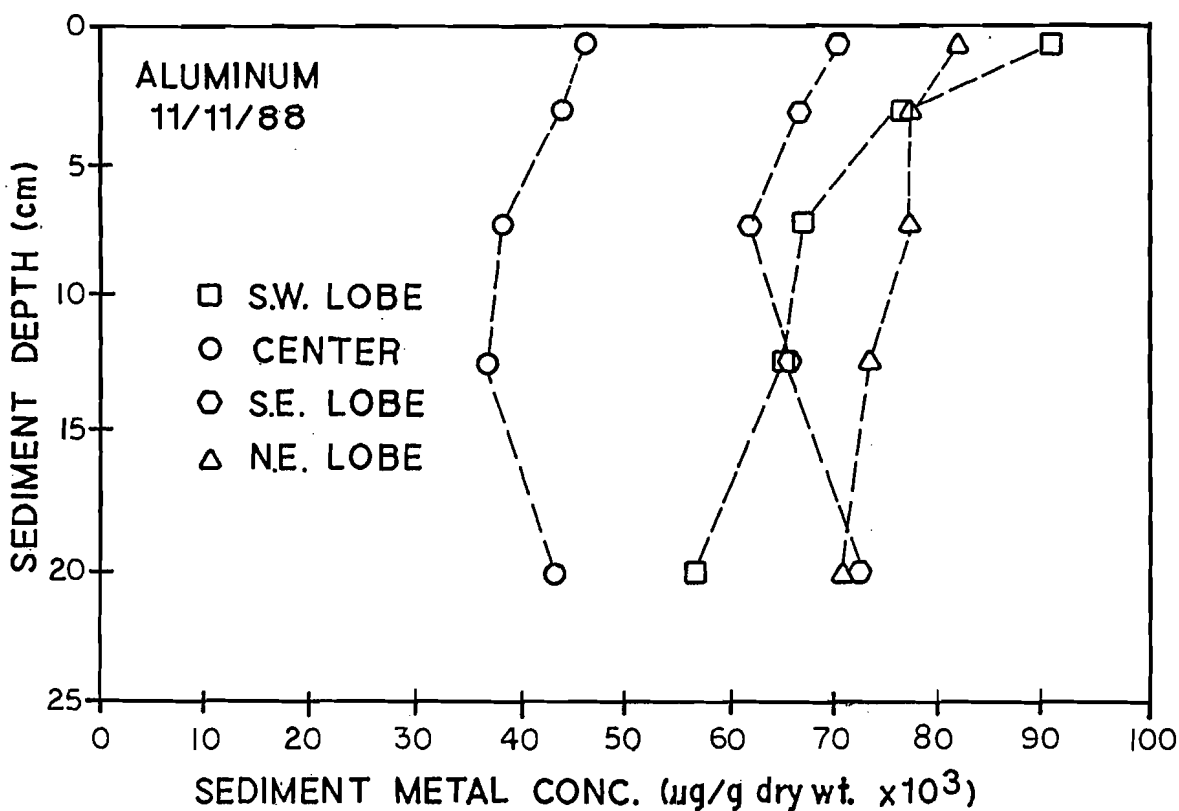
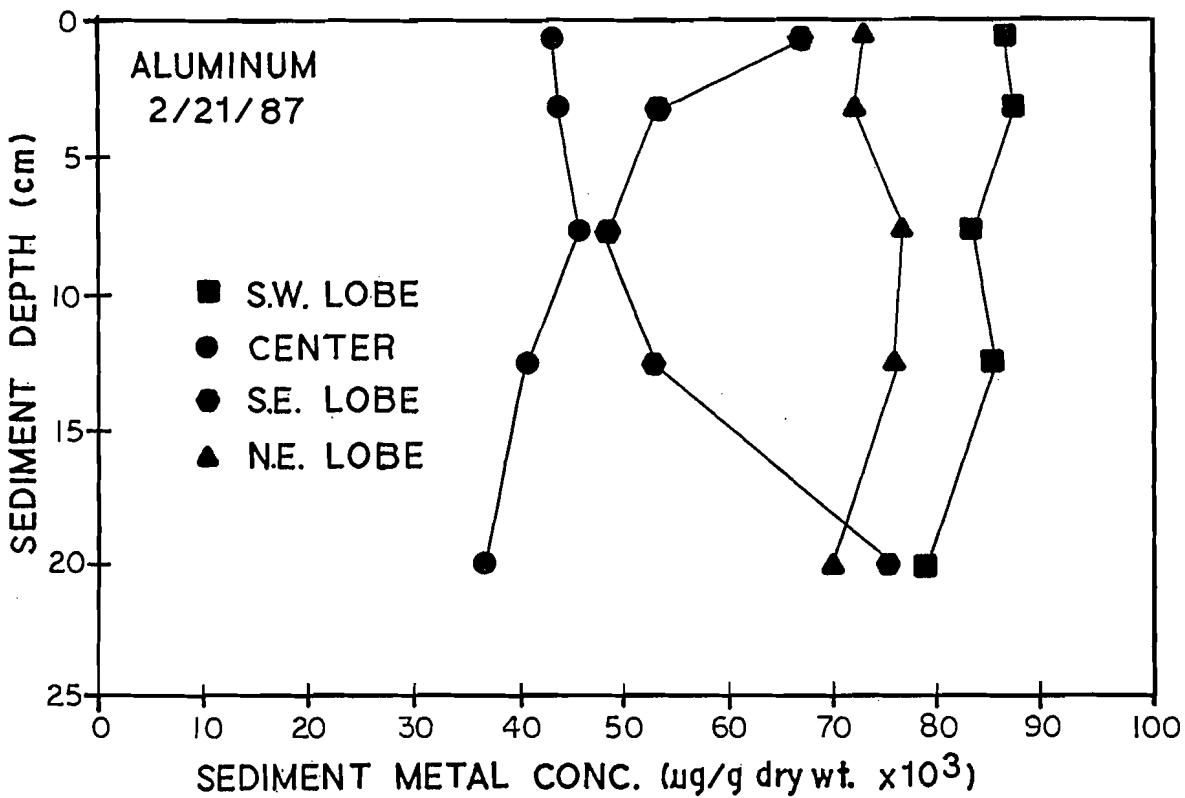


Figure 5-7. Comparison of Sediment Concentrations of Aluminum at the Four Sample Locations in Pre- and Post-Treatment Sediments in Lake Ella.

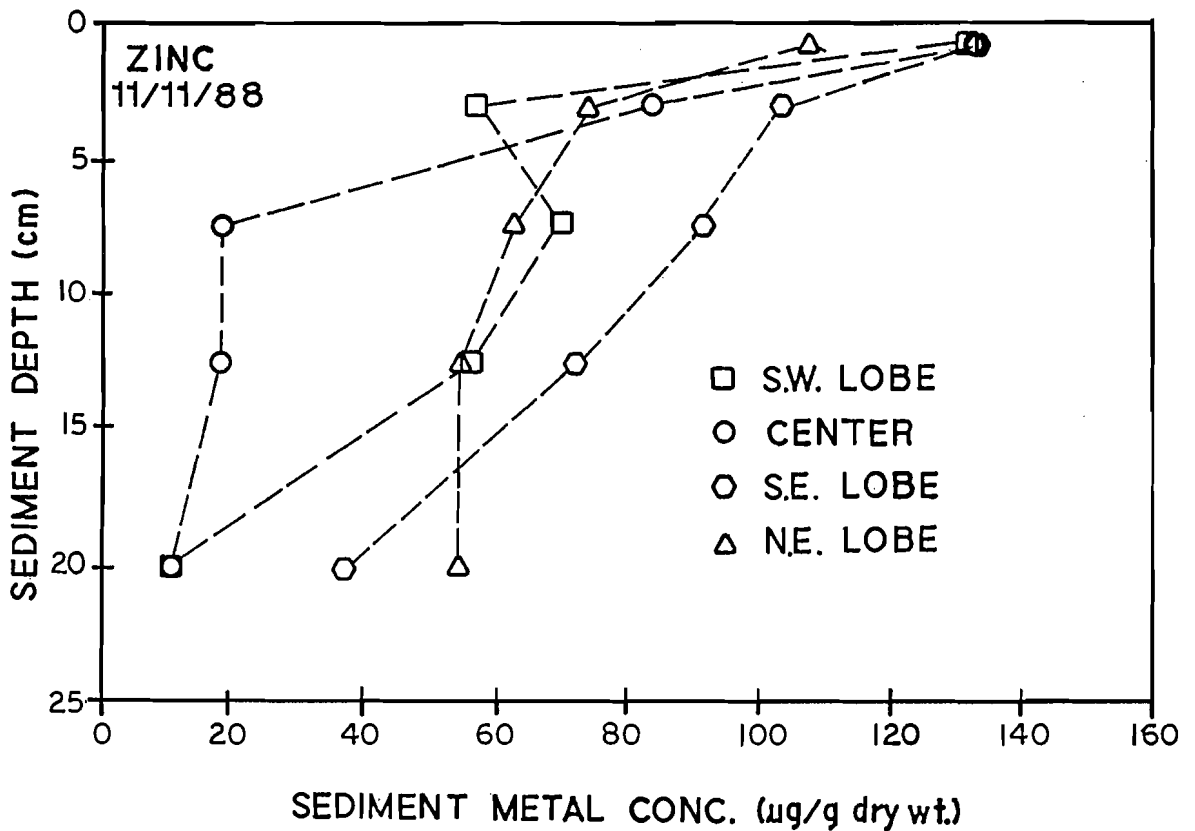
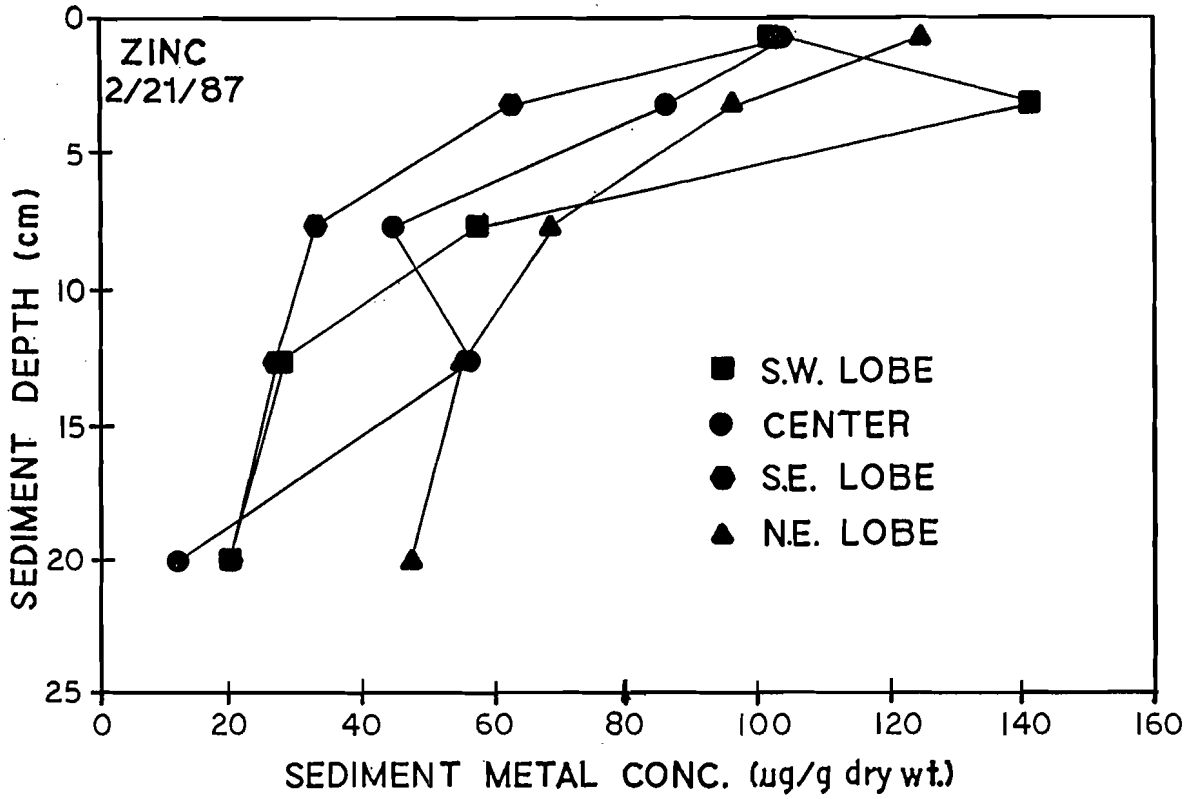


Figure 5-8. Comparison of Sediment Concentrations of Zinc at the Four Sample Locations in Pre- and Post-Treatment Sediments in Lake Ella.

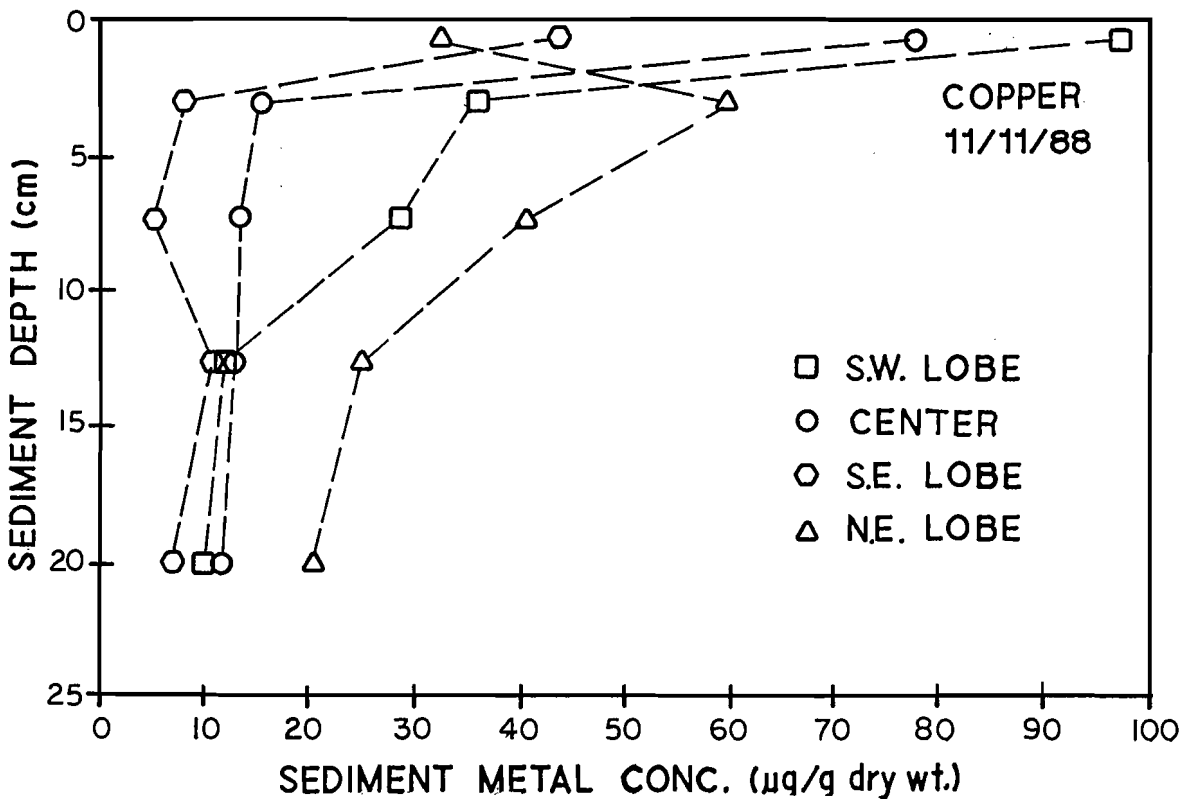
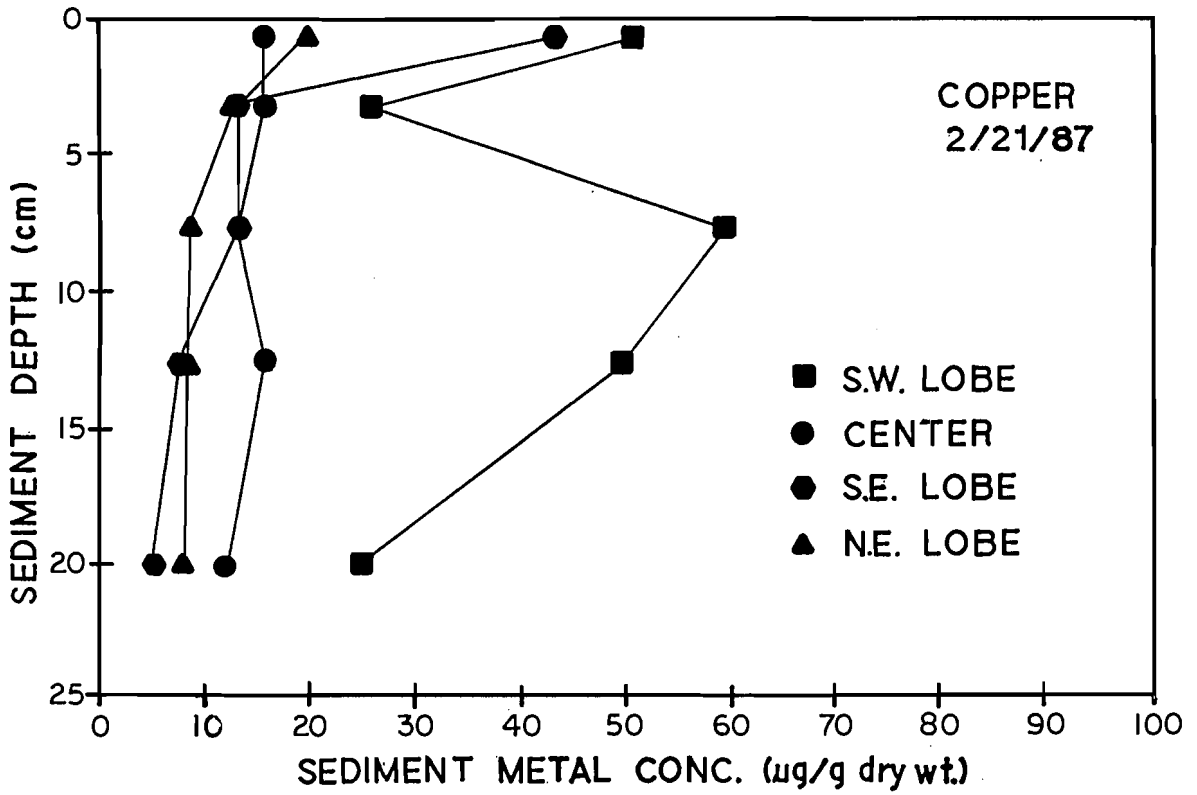


Figure 5-9. Comparison of Sediment Concentrations of Copper at the Four Sample Locations in Pre- and Post-Treatment Sediments in Lake Ella.

copper to a higher degree in the 0-1 cm layer than was observed for the pre-treatment sediments, particularly for the center and southwest portions of the lake. An increase in sediment copper concentrations is observed in the northeast lobe, presumably a result of settling and accumulation of copper bound to alum precipitate within this area. Sediment copper concentrations below a depth of 1 cm appear to be relatively similar in pre- and post-treatment areas with the exception of the northeast lobe.

A comparison of sediment concentrations of lead at the four sample locations in pre- and post-treatment sediments is given in Figure 5-10. Sediment concentrations of lead also show increased levels at the northeast lobe near the outfall sump. As discussed previously, sediment lead concentrations appear to peak in the 1-5 cm layer rather than the 0-1 cm layer in post-treatment sediments. This trend is apparent at two of the four sample locations in pre-treatment sediments, although it is more pronounced in the post-treatment condition.

Sediment concentrations of all measured heavy metals appear to have been affected by inputs from the alum stormwater treatment system. Sediment concentrations of aluminum, copper, zinc and lead have increased substantially in the northeast lobe of the lake which was designed as a settling area for the alum floc. Sediment concentrations of heavy metals in the center of the lake as well as the southwest lobe have been affected to a lesser degree. In contrast, the southeast lobe, which is an isolated area receiving inputs of alum treated stormwater from two separate locations, has exhibited increases in sediment concentrations of aluminum and other heavy metals.

It should be noted that increases in sediment metal content are naturally occurring phenomena in surface water bodies receiving inputs of stormwater runoff. Accumulation of heavy metals in the sediments of Lake Ella would have occurred whether or not the stormwater treatment system was constructed. However, as

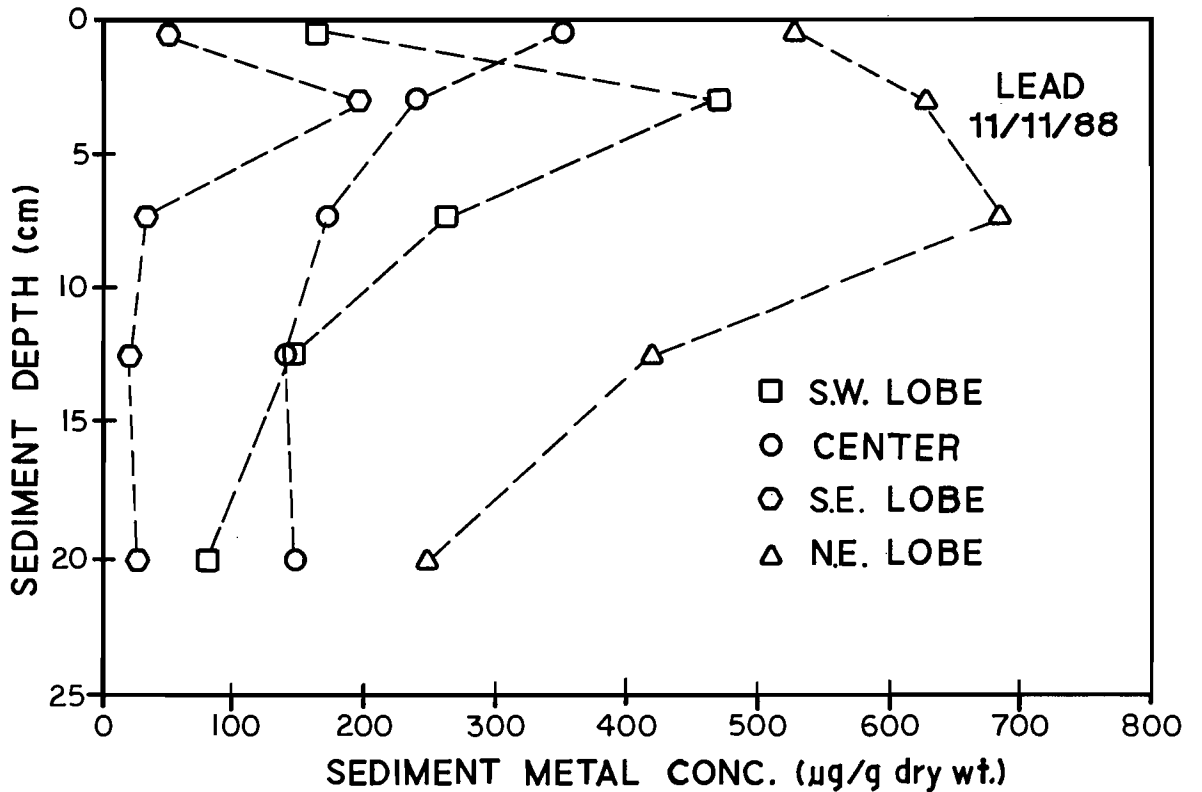
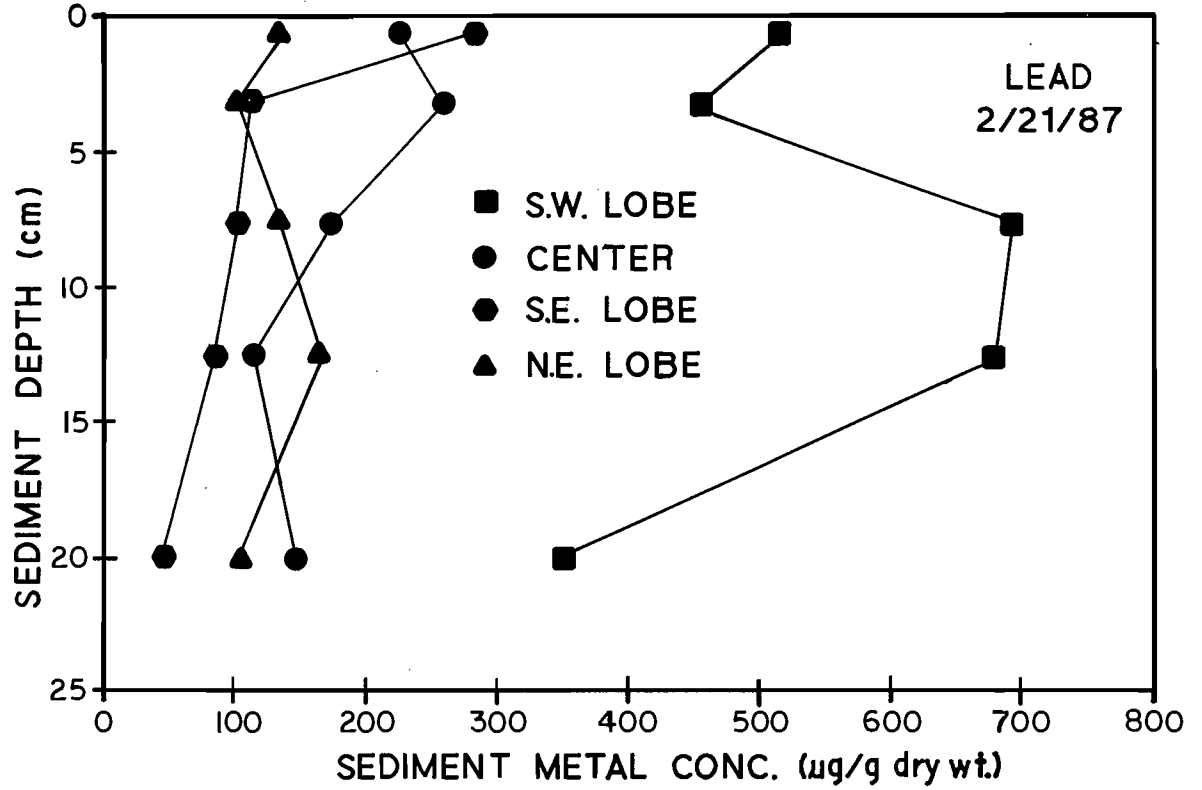


Figure 5-10. Comparison of Sediment Concentrations of Lead at the Four Sample Locations in Pre- and Post-Treatment Sediments in Lake Ella.

discussed in a previous section, alum has been shown to be extremely effective in removing both dissolved and particulate heavy metal inputs by adsorbing or enmeshing these heavy metals into the alum precipitate with a subsequent settling into the bottom sediments. Since this process is substantially more effective than the removal processes which existed within Lake Ella prior to installation of the alum stormwater treatment system, the accumulation rate of heavy metals within the sediments of the lake may increase under post-treatment conditions at a rate in excess of that observed during pre-treatment conditions.

Speciation of Heavy Metals and Phosphorus in Lake Ella Sediments

Composite sediment samples were formed by layer for each of the two collection dates by combining equal amounts of sediment material from each layer at each of the four sampling locations. These composite sediment samples were processed through a series of chemical extraction steps to identify and quantify sediment-metal associations with the following five fractions: (1) soluble metal ions in the interstitial spaces between soil particles; (2) metals bound to sediments through exchange reactions; (3) metals bound with precipitates of iron and manganese oxides; (4) metals bound as precipitates with carbonates; and (5) metals bound in associations with organic matter. It is generally believed that the stability of metal-sediment associations increases in the following order: soluble < exchangeable < bound to carbonates < bound to iron and manganese oxides < bound to organic matter.

A summary of sediment speciation of heavy metals and phosphorus in composite core samples collected in Lake Ella on February 21, 1987 is given in Table 5-13. Relatively little of the measured heavy metals and phosphorus is released from the sediments in a soluble ionic form. Exchange fractions for each of the heavy metals and phosphorus are also extremely low with values in most cases less than those observed

TABLE 5-13

**SEDIMENT SPECIATION OF HEAVY METALS AND PHOSPHORUS
IN COMPOSITE CORE SAMPLES COLLECTED IN LAKE ELLA ON 2/21/87
(Before Alum Treatment of Stormwater)**

| SPECIATION FRACTION | SEDIMENT LAYER (cm) | SEDIMENT RELEASE ($\mu\text{g/g}$ dry sediment) | | | | | |
|---------------------|---------------------|--|------|------|-----|------|-----|
| | | Al | Cu | Fe | Pb | Zn | P |
| Soluble | 0-1 | 59 | 1.3 | 16 | 9.5 | 0.5 | <1 |
| | 1-5 | 25 | 0.1 | 3 | 0.9 | 0.2 | 4 |
| | 5-10 | 80 | <0.1 | 5 | 1.0 | 0.1 | 7 |
| | 10-15 | 120 | <0.1 | 10 | 0.6 | <0.1 | 8 |
| | 15-25 | 25 | 0.3 | 2 | 0.2 | 0.3 | 10 |
| Exchange | 0-1 | 2.2 | 0.2 | 3 | 1.0 | 0.3 | 2 |
| | 1-5 | 7.3 | 0.1 | 3 | 1.0 | 0.1 | 2 |
| | 5-10 | 3.3 | <0.1 | 8 | 2.9 | <0.1 | 1 |
| | 10-15 | 2.6 | <0.1 | 2 | 0.1 | <0.1 | 2 |
| | 15-25 | 2.0 | <0.1 | 2 | 1.1 | <0.1 | 2 |
| Carbonate | 0-1 | 54 | 0.1 | 15 | 19 | 0.4 | 1 |
| | 1-5 | 46 | <0.1 | 34 | 57 | 0.5 | 8 |
| | 5-10 | 35 | <0.1 | 24 | 66 | 0.3 | 2 |
| | 10-15 | 51 | <0.1 | 20 | 43 | 0.2 | 8 |
| | 15-25 | 22 | <0.1 | 21 | 31 | 0.2 | 6 |
| Fe/Mn | 0-1 | 1280 | 1.5 | 1975 | 28 | 6.5 | 187 |
| | 1-5 | 2379 | 1.4 | 2199 | 102 | 4.2 | 115 |
| | 5-10 | 2344 | 1.5 | 2339 | 121 | 2.9 | 128 |
| | 10-15 | 1961 | 1.2 | 2298 | 100 | 2.9 | 102 |
| | 15-25 | 1620 | 1.0 | 2314 | 42 | 2.5 | 83 |
| Organic | 0-1 | 1837 | 9.1 | 138 | 8.4 | 4.2 | 958 |
| | 1-5 | 2158 | 6.7 | 157 | 8.0 | 1.6 | 879 |
| | 5-10 | 1596 | 5.6 | 133 | 6.5 | 1.0 | 496 |
| | 10-15 | 1894 | 2.8 | 83 | 1.8 | 0.9 | 511 |
| | 15-25 | 1447 | 2.8 | 83 | 3.7 | 0.5 | 309 |

for the soluble metal fractions. Carbonate metal associations are similar for most metals to soluble metal associations. However, sediment carbonate associations for lead appear to be substantially greater than either exchange or soluble fractions.

The majority of metal and phosphorus sediment associations appear to be with Fe/Mn oxides and organic material. Virtually all of the measured heavy metals and phosphorus exhibit sediment fractions several orders of magnitude greater with Fe/Mn and organic associations than with soluble, exchange or carbonate fractions. Aluminum is equally associated with Fe/Mn oxides and organic material as the primary bonding mechanisms for this metal in the sediments. Copper and phosphorus are primarily associated with stable organic associations in the sediments. On the other hand, iron, lead and zinc are bound primarily to Fe/Mn oxide associations.

A summary of sediment speciation of heavy metals and phosphorus in composite core samples collected in Lake Ella on November 11, 1988 is presented in Table 5-14. Sediment speciation schemes represented in this table appear to be relatively similar to those measured in February 1987.

A comparison of sediment speciation of heavy metals and phosphorus in the top 25 cm of Lake Ella sediments under pre- and post-treatment conditions is given in Table 5-15. Soluble fractions of aluminum, copper, zinc and phosphorus decrease substantially in post-treatment sediments compared with pre-treatment sediments. In contrast, soluble fractions of iron and lead appear to increase slightly in post-treatment sediments. Increased associations with exchange fractions in post-treatment sediments is observed for copper, iron and lead, while exchange fractions of aluminum, zinc and phosphorus remain relatively unchanged. Although slight changes are observed in sediment speciation for the various extracted fractions between pre- and post-treatment sediments, the dominant bonding mechanism for heavy metals in the sediments remained unchanged between pre- and post-treatment conditions. Associations with Fe/Mn oxides represented the dominant bonding mechanism for aluminum, iron, lead

TABLE 5-14

**SEDIMENT SPECIATION OF HEAVY METALS AND PHOSPHORUS
IN COMPOSITE CORE SAMPLES COLLECTED IN LAKE ELLA ON 11/11/88
(After Alum Treatment of Stormwater)**

| SPECIATION FRACTION | SEDIMENT LAYER (cm) | SEDIMENT RELEASE ($\mu\text{g/g}$ dry sediment) | | | | | |
|---------------------|---------------------|--|------|------|-----|------|------|
| | | Al | Cu | Fe | Pb | Zn | P |
| Soluble | 0-1 | 82 | <0.1 | 5 | 4.5 | 0.4 | <1 |
| | 1-5 | 22 | <0.1 | 20 | 0.3 | 0.3 | 1 |
| | 5-10 | 27 | <0.1 | 32 | 1.1 | <0.1 | <1 |
| | 10-15 | 49 | <0.1 | 49 | 1.1 | <0.1 | 1 |
| | 15-25 | 42 | <0.1 | 47 | 0.4 | <0.1 | 2 |
| Exchange | 0-1 | 3.0 | 0.2 | 6 | 0.5 | 0.3 | 1 |
| | 1-5 | 2.4 | <0.1 | 11 | 1.5 | 0.2 | 1 |
| | 5-10 | 2.8 | 0.1 | 16 | 2.7 | <0.1 | 1 |
| | 10-15 | 3.9 | 0.1 | 13 | 2.3 | <0.1 | 1 |
| | 15-25 | 2.4 | <0.1 | 7 | 0.3 | <0.1 | 1 |
| Carbonate | 0-1 | 220 | 0.5 | 83 | 22 | 0.6 | 5 |
| | 1-5 | 56 | 0.1 | 58 | 37 | 0.5 | 5 |
| | 5-10 | 64 | <0.1 | 72 | 41 | 0.5 | 6 |
| | 10-15 | 64 | <0.1 | 59 | 28 | 0.4 | 5 |
| | 15-25 | 53 | 0.1 | 27 | 8.2 | 0.2 | 6 |
| Fe/Mn | 0-1 | 4191 | 3.3 | 1735 | 39 | 8.4 | 132 |
| | 1-5 | 1542 | 1.5 | 2372 | 61 | 6.3 | 106 |
| | 5-10 | 2343 | 0.7 | 2319 | 65 | 3.6 | 108 |
| | 10-15 | 1958 | 0.6 | 2175 | 54 | 2.8 | 110 |
| | 15-25 | 1252 | 0.3 | 1452 | 16 | 2.8 | 69 |
| Organic | 0-1 | 1566 | 15.8 | 178 | 4.2 | 3.7 | 369 |
| | 1-5 | 2231 | 8.4 | 248 | 2.2 | 2.0 | 762 |
| | 5-10 | 2557 | 5.0 | 252 | 4.9 | 2.1 | 1535 |
| | 10-15 | 1620 | 2.3 | 133 | 1.5 | 1.0 | 335 |
| | 15-25 | 1205 | 1.0 | 71 | 0.2 | 0.8 | 344 |

TABLE 5-15

COMPARISON OF SEDIMENT SPECIATION OF
HEAVY METALS AND PHOSPHORUS IN THE TOP 25 cm
OF LAKE ELLA BEFORE AND AFTER ALUM TREATMENT OF STORMWATER

| SPECIATION FRACTION | PERCENT OF TOTAL METAL EXTRACTED | | | | | |
|--------------------------------|----------------------------------|------|------|------|------|------|
| | Al | Cu | Fe | Pb | Zn | P |
| PRIOR TO ALUM TREATMENT | | | | | | |
| Soluble | 1.5 | 3.6 | 0.2 | 0.7 | 4.4 | 1.2 |
| Exchange | 0.1 | 1.1 | 0.1 | 1.0 | 1.5 | 0.3 |
| Carbonate | 1.0 | 0.9 | 1.0 | 34.1 | 5.9 | 0.9 |
| Fe/Mn | 52.0 | 21.2 | 94.3 | 60.6 | 66.6 | 16.8 |
| Organic | 45.4 | 73.2 | 4.4 | 3.6 | 21.6 | 80.8 |
| AFTER ALUM TREATMENT | | | | | | |
| Soluble | 1.1 | 1.0 | 1.8 | 1.2 | 1.8 | 0.1 |
| Exchange | 0.1 | 1.6 | 0.5 | 2.0 | 1.5 | 0.1 |
| Carbonate | 1.8 | 2.0 | 2.3 | 34.4 | 6.4 | 0.4 |
| Fe/Mn | 49.1 | 15.6 | 88.4 | 59.7 | 65.6 | 6.0 |
| Organic | 48.0 | 79.8 | 7.0 | 2.7 | 24.7 | 93.4 |

and zinc under both pre- and post-treatment conditions. It is interesting to note that the decreased association with soluble fractions observed for many of the measured heavy metals under post-treatment conditions is accompanied by an increase in associations with organic matter for many of the same heavy metals. This change in speciation indicates a shift in bonding mechanisms from less stable soluble associations to more stable organic sediment associations, indicating that metal associations with post-treatment sediments may be more stable than associations found under pre-treatment sediments. However, although slight increases or decreases in certain speciation fractions may be present for individual metal or phosphorus species, the dominant bonding mechanisms retaining each of these heavy metals and phosphorus into the sediments remains unchanged after introduction of the alum stormwater treatment system.

The relatively high association of aluminum with organic matter in both pre- and post-treatment sediments is interesting since aluminum is relatively insignificant in terms of biological mechanisms which would incorporate aluminum into organic associations. High associations with organic matter are expected for metals such as copper and phosphorus which are important in biological processes. The most likely explanation for aluminum associations with organic matter is that organic matter is sorbed onto the surface of aluminum particles as it settles through the water column toward the sediments. Once organic matter is bound to aluminum, it is apparently maintained in a relatively stable state.

Fractionation of Sediment Phosphorus

Fractionation of inorganic soil phosphate was conducted on both pre- and post-alum treatment sediment samples for each of the four sample locations and each of the five sediment depth layers. The modified Chang and Jackson procedure was used

which divides phosphorus associations into aluminum phosphate, iron phosphate, reductant soluble phosphate and calcium phosphate bonding mechanisms.

A summary of sediment phosphorus associations in sediment core samples collected in Lake Ella on February 21, 1987 is given in Table 5-16. In these pre-alum treatment sediments, concentrations of soluble phosphorus appear to be relatively low. The dominant inorganic phosphate fraction is aluminum phosphate, although large proportions of iron phosphate, reductant soluble phosphorus and calcium phosphate are also found. There appears to be little variation in the data presented in Table 5-16 between the four sample stations. No dominant trend of increasing or decreasing phosphorus associations is apparent with increasing sediment depth. The only exception to this generality appears to occur in the southwest lobe where concentrations of aluminum phosphate, iron phosphate, reductant soluble phosphorus and calcium phosphate are substantially higher than values measured at the other stations.

A summary of sediment phosphorus associations in sediment core samples collected in Lake Ella on November 11, 1988 is given in Table 5-17. Concentrations of soluble phosphorus appear to be extremely low in sediments collected on this date. The dominant phosphorus fractions are aluminum phosphate, reductant soluble phosphorus and calcium phosphate. The importance of iron phosphate as a bonding mechanism for phosphorus has been decreased substantially in these post-treatment sediments over the values observed in the pre-treatment sediments.

A comparison of sediment phosphorus associations in Lake Ella before and after alum treatment of stormwater is given in Table 5-18. Concentrations of soluble phosphorus in sediments appear to be substantially lower in the post-treatment sediments than those observed in the pre-treatment sediments. Sediment associations with aluminum phosphate appear to be relatively similar between the two dates. On the

TABLE 5-16

SEDIMENT PHOSPHORUS ASSOCIATIONS IN SEDIMENT
CORE SAMPLES COLLECTED IN LAKE ELLA ON 2/21/87
(Before Alum Treatment of Stormwater)

| STATION | SEDIMENT LAYER (cm) | SEDIMENT P CONCENTRATION ($\mu\text{g/g}$ dry sediment) | | | | |
|-----------|---------------------|--|--------------------|----------------|---------------------|-------------------|
| | | SOLUBLE P | ALUMINUM PHOSPHATE | IRON PHOSPHATE | REDUCTANT SOLUBLE P | CALCIUM PHOSPHATE |
| N.E. Lobe | 0-1 | 3.1 | 144 | 82.2 | 94.6 | 85.9 |
| | 1-5 | 4.7 | 156 | 79.6 | 102 | 88.8 |
| | 5-10 | 2.9 | 159 | 85.2 | 135 | 59.0 |
| | 10-15 | 2.7 | 148 | 97.4 | 140 | 88.5 |
| | 15-25 | 2.0 | 175 | 79.6 | 110 | 44.2 |
| S.E. Lobe | 0-1 | 3.8 | 119 | 72.6 | 85.7 | 79.5 |
| | 1-5 | 4.2 | 158 | 56.3 | 79.2 | 73.8 |
| | 5-10 | 3.7 | 166 | 59.3 | 70.8 | 36.9 |
| | 10-15 | 2.9 | 132 | 59.1 | 62.3 | 36.3 |
| | 15-25 | 3.8 | 144 | 37.2 | 65.6 | 28.2 |
| Center | 0-1 | 2.8 | 157 | 77.0 | 139 | 95.6 |
| | 1-5 | 3.9 | 157 | 66.0 | 273 | 79.3 |
| | 5-10 | 3.1 | 168 | 70.2 | 85.4 | 60.8 |
| | 10-15 | 5.4 | 147 | 70.9 | 75.6 | 55.1 |
| | 15-25 | 2.8 | 169 | 53.8 | 78.5 | 62.4 |
| S.W. Lobe | 0-1 | 3.2 | 191 | 120 | 254 | 133 |
| | 1-5 | 3.4 | 171 | 58.9 | 251 | 135 |
| | 5-10 | 3.0 | 209 | 83.6 | 198 | 141 |
| | 10-15 | 3.7 | 176 | 105 | 310 | 180 |
| | 15-25 | 3.7 | 151 | 73.0 | 374 | 213 |

TABLE 5-17

SEDIMENT PHOSPHORUS ASSOCIATIONS IN SEDIMENT
CORE SAMPLES COLLECTED IN LAKE ELLA ON 11/11/88
(After Alum Treatment of Stormwater)

| STATION | SEDIMENT LAYER (cm) | SEDIMENT P CONCENTRATION ($\mu\text{g/g}$ dry sediment) | | | | |
|-----------|---------------------|--|--------------------|----------------|---------------------|-------------------|
| | | SOLUBLE P | ALUMINUM PHOSPHATE | IRON PHOSPHATE | REDUCTANT SOLUBLE P | CALCIUM PHOSPHATE |
| N.E. Lobe | 0-1 | 1.4 | 193 | 19.1 | 224 | 312 |
| | 1-5 | 1.4 | 215 | 34.4 | 109 | 101 |
| | 5-10 | 2.2 | 182 | 31.7 | 125 | 94.0 |
| | 10-15 | 2.2 | 170 | 32.3 | 92.3 | 74.9 |
| | 15-25 | 1.7 | 164 | 23.2 | 39.3 | 55.0 |
| S.E. Lobe | 0-1 | 1.9 | 182 | 29.7 | 98.5 | 90.1 |
| | 1-5 | 1.2 | 157 | 7.5 | 40.3 | 54.2 |
| | 5-10 | 1.2 | 159 | 4.2 | 24.3 | 48.6 |
| | 10-15 | 1.6 | 166 | 35.7 | 22.1 | 44.8 |
| | 15-25 | 1.8 | 120 | 42.3 | 46.0 | 51.1 |
| Center | 0-1 | 3.1 | 121 | 7.5 | 113 | 77.2 |
| | 1-5 | 2.1 | 166 | 16.1 | 91.3 | 56.5 |
| | 5-10 | 2.5 | 128 | 15.4 | 68.7 | 39.5 |
| | 10-15 | 2.6 | 130 | 19.5 | 66.9 | 39.5 |
| | 15-25 | 2.6 | 130 | 17.1 | 91.1 | 72.1 |
| S.W. Lobe | 0-1 | 2.6 | 110 | 33.0 | 199 | 118 |
| | 1-5 | 2.4 | 151 | 22.5 | 159 | 62.3 |
| | 5-10 | 2.7 | 157 | 31.2 | 162 | 90.8 |
| | 10-15 | 2.4 | 160 | 21.2 | 200 | 86.4 |
| | 15-25 | 1.9 | 151 | 21.3 | 247 | 130 |

TABLE 5-18

COMPARISON OF SEDIMENT PHOSPHORUS ASSOCIATIONS IN
LAKE ELLA BEFORE AND AFTER ALUM TREATMENT OF STORMWATER

| COLLECTION DATE | SEDIMENT LAYER (cm) | SEDIMENT P CONCENTRATION ($\mu\text{g/g}$ dry sediment) | | | | |
|-----------------|---------------------|--|--------------------|----------------|---------------------|-------------------|
| | | SOLUBLE P | ALUMINUM PHOSPHATE | IRON PHOSPHATE | REDUCTANT SOLUBLE P | CALCIUM PHOSPHATE |
| 2/21/87 | 0-1 | 3.2 | 153 | 88.0 | 143 | 98.5 |
| | 1-5 | 4.1 | 161 | 65.2 | 176 | 94.2 |
| | 5-10 | 3.2 | 157 | 74.6 | 122 | 74.4 |
| | 10-15 | 3.7 | 151 | 83.1 | 147 | 90.0 |
| | 15-25 | 3.1 | 141 | 60.9 | 157 | 87.0 |
| 11/11/88 | 0-1 | 2.3 | 152 | 22.3 | 109 | 149 |
| | 1-5 | 1.8 | 172 | 20.1 | 99.9 | 68.5 |
| | 5-10 | 2.2 | 176 | 20.6 | 95.0 | 68.2 |
| | 10-15 | 2.2 | 157 | 27.2 | 95.3 | 61.4 |
| | 15-25 | 2.0 | 160 | 26.0 | 106 | 77.1 |

other hand, substantial reductions in phosphorus associations with iron phosphate are observed in the post-treatment sediments. Reductions in phosphorus associations as calcium phosphate and as reductant soluble phosphorus are also observed in the post-treatment sediments, although not to the extent exhibited by reductions in iron phosphate.

A comparison of pre- and post-treatment phosphorus fractions in Lake Ella is presented graphically in Figure 5-11. This figure presents post-treatment phosphorus associations as a fraction of pre-treatment concentrations for soluble, aluminum phosphate and iron phosphate associations. Overall, phosphorus associations with iron in the post-treatment sediments have been reduced to approximately 30% of the values found prior to alum treatment. Iron-bound phosphorus associations were reduced to approximately 25% of pre-treatment concentrations in the 0-1 cm layer, 31% in the 1-5 cm layer and 28% in the 5-10 cm layer. The sediment profile for iron-phosphorus associations presented in Figure 5-11 suggests that the effects of aluminum floc within the sediments has altered sediment phosphorus association as deep as 15-25 cm within the sediment, although changes in sediment fractions were most apparent in the top 10 cm of sediments.

In contrast, phosphorus associations with aluminum increased within the sediments. Aluminum-phosphorus associations increased by 7% in the 1-5 cm layer, 12% in the 5-10 cm layer, 4% in the 10-15 cm layer and 14% in the 15-25 cm layer. The reduction in iron-phosphorus associations, combined with this increase in aluminum-phosphorus associations, suggests that phosphorus associations in post-treatment sediments are substantially more stable than phosphorus associations in pre-treatment sediments. Aluminum-phosphorus associations are virtually immune to changes in redox potential and pH which can cause iron-phosphorus associations to break apart with a subsequent release of phosphorus in a soluble form. The conversion

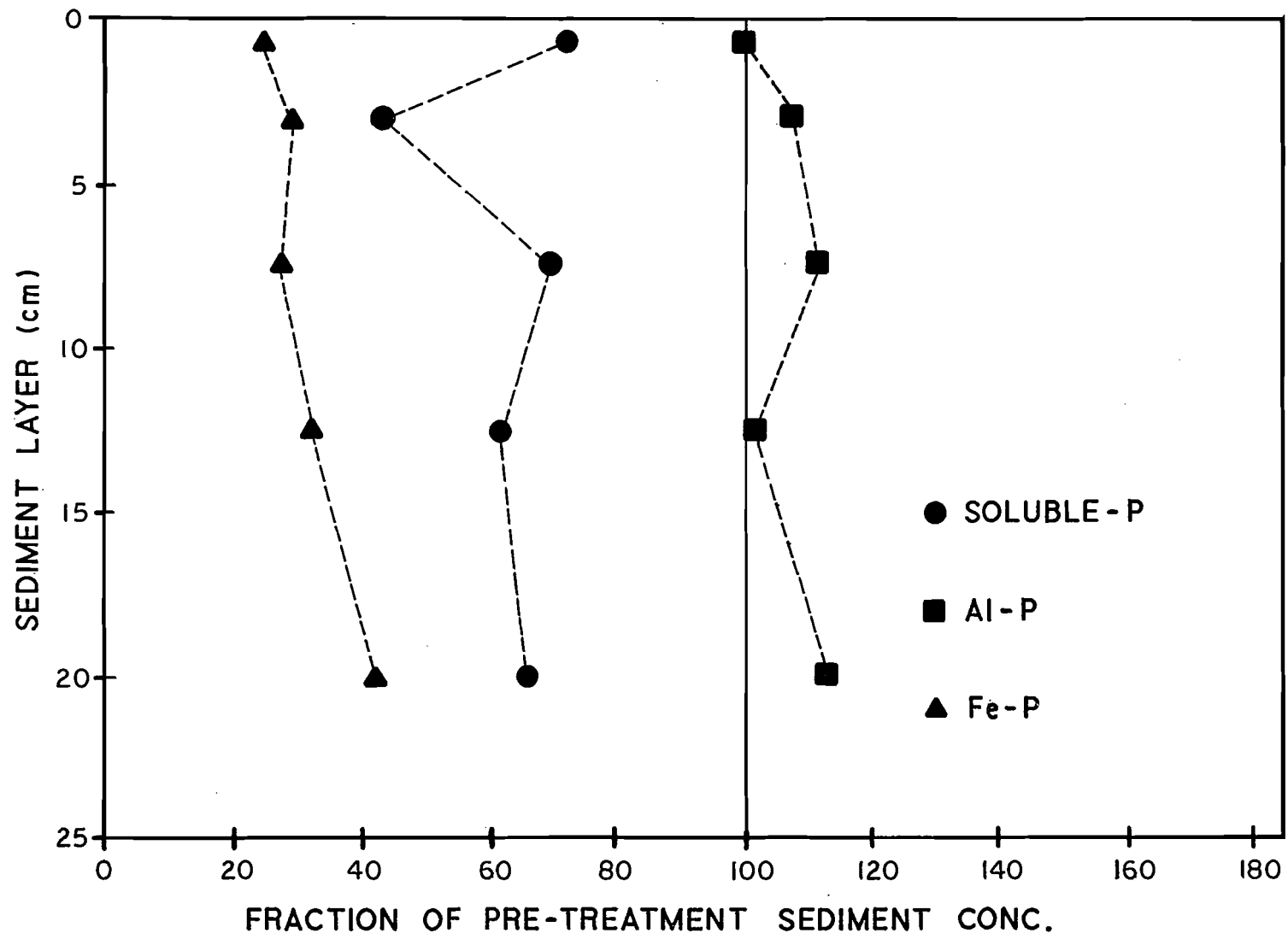


Figure 5-11. Comparison of Pre- and Post-Treatment Phosphorus Fractions in Lake Ella.

to aluminum phosphate forms indicates that the probability of phosphorus being released from post-treatment sediments has been substantially reduced compared with pre-treatment sediments.

Phosphorus associations as soluble phosphorus have been reduced to only 60% of the values found in the pre-treatment sediments, while reductant soluble phosphorus has been reduced to only 70% of the pre-existing values. The only phosphorus fractionation which exhibited an increase was the aluminum phosphate fraction. These substantial reductions in soluble phosphorus within the sediments are due primarily to the conversion of phosphorus bonding from one dominated by iron associations to one dominated by relatively inert aluminum associations.

A comparison of total sediment phosphorus released during fractionation procedures from each of the five sediment fractions is given in Table 5-19. Prior to alum treatment of runoff into Lake Ella, an average of 468.2 $\mu\text{g/g}$ phosphorus was released within the top 25 cm from each of the five extraction procedures. Following alum treatment of stormwater in Lake Ella, an average of 374.6 $\mu\text{g/g}$ phosphorus was released within the same top 25 cm in spite of a slight accumulation in phosphorus levels within the sediments from the pre-treatment collection date to the post-treatment collection date. In addition to providing substantial reductions in the amount of soluble phosphorus and iron phosphate bonds present within the Lake Ella sediments, the application of alum to the sediments has reduced the total amount of phosphorus which can be extracted from the sediments using the rather vigorous extraction techniques of the modified Chang and Jackson procedure. Not only has the introduction of alum created a reduction in the less stable phosphorus associations within the sediments, it has also resulted in an overall reduction in the total amount of phosphorus available to be released from the sediments. The phosphorus remaining in the sediments at Lake Ella appears to be substantially less available and more tightly bound following the alum treatment system than existed in sediments before introduction of this system.

TABLE 5-19

COMPARISON OF TOTAL SEDIMENT
PHOSPHORUS RELEASE DURING FRACTIONATION
PROCEDURES BEFORE AND AFTER ALUM TREATMENT OF STORMWATER

| COLLECTION DATE | SEDIMENT LAYER (cm) | TOTAL P RELEASED ($\mu\text{g/g}$ dry sediment) |
|---|---------------------|---|
| 2/21/87 (Before Alum Treatment of Stormwater) | 0-1 | 485.7 |
| | 1-5 | 500.5 |
| | 5-10 | 431.2 |
| | 10-15 | 474.8 |
| | 15-25 | 449.0 |
| | Avg. | 468.2 |
| 11/11/88 (After Alum Treatment of Stormwater) | 0-1 | 434.6 |
| | 1-5 | 362.3 |
| | 5-10 | 362.0 |
| | 10-15 | 343.1 |
| | 15-25 | 371.1 |
| | Avg. | 374.6 |

**Influence of pH and Redox Potential on the
Stability of Heavy Metals in Alum Treated Sediments**

A series of experiments were conducted to evaluate the influence of pH and redox potential on the stability of heavy metals in alum treated sediments. Sediments for use in these experiments were formed as a 50-50 mixture of alum treated sediments collected from the sump area in the northeast lobe of Lake Ella and pure alum sludge formed from coagulation of stormwater runoff from an urbanized watershed in Orlando. Three separate experiments were conducted at redox potentials of -200 mv (highly reduced), 0 mv (reduced), +200 mv (slightly reduced) and +400 mv (oxidized) and at pH conditions of natural pH (approximately 7.0), 6.0 and 5.0.

A summary of the release of heavy metals and phosphorus from Lake Ella alum sludge under various redox potentials at natural pH values is given in Table 5-20. The initial sediment pH value at the start of the incubation period after the sediment slurry had reached equilibrium was approximately 7.1. As the sediments were purged with nitrogen and the sediment redox value began to decrease toward the first desired setting of -200 mv, a general slow decrease in pH value was observed. By the time the redox potential reached equilibrium at -200 mv, the suspension pH had stabilized at a value of approximately 6.9. This general pH value was maintained as the sediment suspension was oxidized to higher values of redox potential, with equilibrium pH values of 6.87 at 0 mv, 6.85 at 200 mv and 7.07 at 400 mv.

Release of heavy metals and phosphorus from Lake Ella alum sludge is extremely low at all values of redox potential at natural pH values. With the exception of iron, the release of heavy metals and phosphorus is substantially less than 1 $\mu\text{g/g}$ of dry sediment material contained within the incubation apparatus. With the exception of iron, each of the tested heavy metals and phosphorus appear to be relatively immune to the effects of redox potential since few differences are observed in release rates from the sediments under reduced or oxidized conditions for these metal species. On the

TABLE 5-20

RELEASE OF HEAVY METALS AND PHOSPHORUS FROM LAKE ELLA
ALUM SLUDGE UNDER VARIOUS REDOX POTENTIALS AND pH VALUES

| REDOX POTENTIAL (mv) | SLURRY pH | HEAVY METALS RELEASED ($\mu\text{g/g}$ dry sediment) | | | | | | | | |
|----------------------------|--------------------|---|------|------|-------|------|-------|------|-------|------|
| | | P | Al | Cd | Cu | Cr | Fe | Ni | Pb | Zn |
| -200 | Natural pH 6.91 | 0.01 | 0.91 | 0.02 | 0.05 | 0.14 | 10.34 | 0.08 | 0.04 | 0.02 |
| 0 | 6.87 | 0.02 | 0.80 | 0.02 | 0.05 | 0.17 | 5.51 | 0.14 | 0.04 | 0.03 |
| +200 | 6.85 | 0.02 | 0.85 | 0.03 | 0.03 | 0.10 | 0.24 | 0.13 | 0.05 | 0.02 |
| +400 | 7.07 | 0.07 | 0.49 | 0.03 | <0.01 | 0.09 | 0.13 | 0.14 | 0.01 | 0.12 |
| -200 | 6.00 | 0.09 | 0.03 | 0.05 | 0.04 | 0.08 | 173 | 0.05 | <0.02 | 0.12 |
| 0 | 6.00 | 0.07 | 0.09 | 0.05 | 0.02 | 0.09 | 151 | 0.09 | <0.02 | 0.15 |
| +200 | 6.00 | 0.05 | 0.11 | 0.05 | 0.03 | 0.08 | 21 | 0.06 | 0.02 | 0.12 |
| +400 | 6.00 | 0.04 | 0.03 | 0.04 | 0.04 | 0.08 | 0.06 | 0.06 | 0.07 | 0.09 |
| -200 | 5.00 | 0.07 | 4.83 | 0.06 | <0.02 | 0.08 | 664 | 0.07 | <0.02 | 0.19 |
| 0 | 5.00 | 0.05 | 6.54 | 0.06 | 0.05 | 0.08 | 529 | 0.07 | 0.02 | 0.11 |
| +200 | 5.00 | 0.08 | 5.87 | 0.07 | 0.06 | 0.08 | 569 | 0.08 | 0.22 | 0.10 |
| +400 | 5.00 | 0.15 | 6.49 | 0.09 | 0.02 | 0.08 | 4.05 | 0.11 | 0.34 | 0.09 |

other hand, iron is released at substantially greater amounts under reduced and slightly reduced conditions, but is released at a very small degree under oxidized conditions.

The release of heavy metals and phosphorus from Lake Ella alum sludge at a pH of 6.0 under various redox potentials is also given in Table 5-20. With the exception of iron, the release of heavy metals and phosphorus at a pH of 6.0 under redox conditions ranging from highly reduced to oxidized is substantially less than 1 $\mu\text{g/g}$ of dry sediment material contained within the incubation apparatus. The release of iron is substantially lower under reduced conditions at a redox potential of -200 mv than under oxidized conditions at a redox potential of 400 mv. A slight tendency for increased release under reduced conditions is also observed for phosphorus and zinc, although release rates are extremely small, even under reduced conditions. With the exception of iron, all of the tested heavy metals and phosphorus appear to be relatively immune to the effects of redox potential at a pH of 6.0. The release of phosphorus, iron and zinc appear to increase somewhat at a pH level of 6.0 compared to natural pH values of approximately 7.0, while the sediment release of aluminum, copper, chromium, nickel and lead appear to decrease slightly at a pH of 6.0.

A summary of the release of heavy metals and phosphorus in Lake Ella alum sludge under various redox potentials at a pH of 5.0 is given near the bottom of Table 5-20. Sediment release of phosphorus, cadmium, copper, chromium, nickel and zinc at a pH level of 5.0 appear to be similar to that observed at other pH levels. However, increases in sediment release of aluminum and iron are observed at this pH level. The release of iron is substantially greater under reduced conditions than under oxidized conditions, while no relationship with redox potential is observed for releases of aluminum. Even at this pH level, the release of phosphorus, cadmium, copper, chromium, nickel, lead and zinc is substantially less than 1 $\mu\text{g/g}$ of sediment material. Even though aluminum release is observed at this pH level, the release rates are still

extremely small, ranging from 4-7 μg aluminum/g dry sediment weight. Overall, sediment metal associations appear to remain relatively stable in alum treated sediments under all redox conditions at a pH level of 5.0.

The data presented in Table 5-20 presents strong evidence that all of the heavy metals tested, with the possible exception of iron, are extremely stable and bound in tight associations with the sediments and the alum sludge. Almost without exception, the release rates presented in Table 5-20 are substantially less than release rates for the same metal species reported by Harper (1985) using a similar incubation apparatus to incubate sediments under similar conditions from a detention pond receiving highway runoff. This pond, located along Interstate-4 north of Orlando, had been receiving highway runoff for approximately 8-10 years at the time of collection of sediments for use in incubation experiments. Sediments were incubated under redox potentials similar to those used for Lake Ella and at pH values of 5.0 and 6.5.

A comparison of sediment release of aluminum under various conditions of pH and redox potential in Lake Ella and in the highway detention pond is given in Figure 5-12. Release of aluminum from Lake Ella sediments is extremely small under all conditions of redox potential at pH values of 6.0 and 7.0. An increase in the release of aluminum is observed from Lake Ella sediments at a pH of 5.0. However, the release of aluminum from Lake Ella sediments under all conditions of redox potential and pH is substantially lower than the release of aluminum from sediments collected within the detention pond receiving highway runoff. This comparison suggests that, even though Lake Ella is receiving periodic inputs of alum floc, the stability of aluminum within the sediments has increased. It is interesting to note that in both Lake Ella and in the highway pond aluminum release from the sediments appears to be lower under reduced conditions than under oxidized conditions.

A comparison of sediment release of copper under various conditions of pH and redox potential in Lake Ella and in the highway detention pond is given in Figure 5-13.

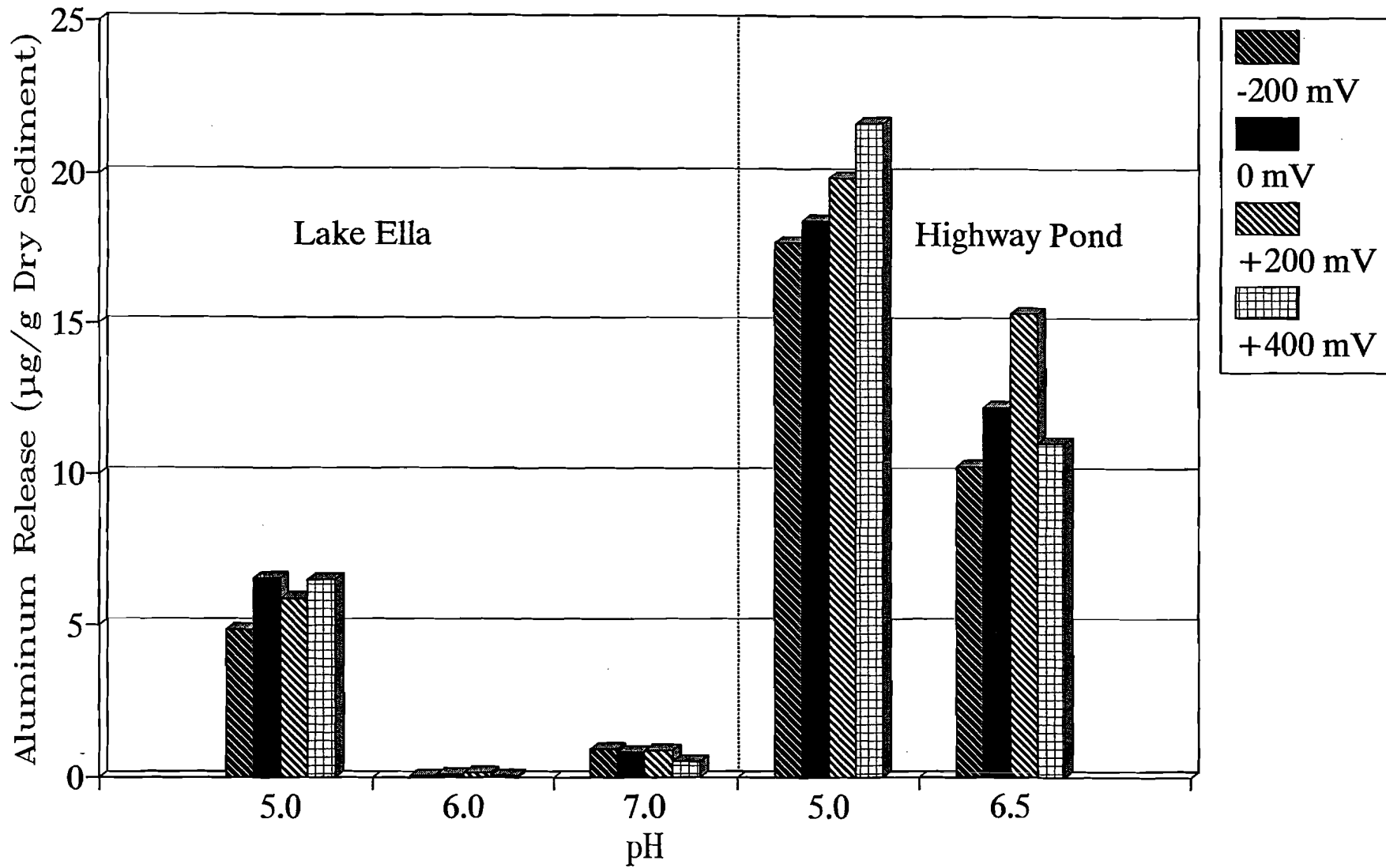


Figure 5-12. Comparison of Sediment Release of Aluminum Under Various Conditions of pH and Redox Potential in Lake Ella and in a Highway Detention Pond.

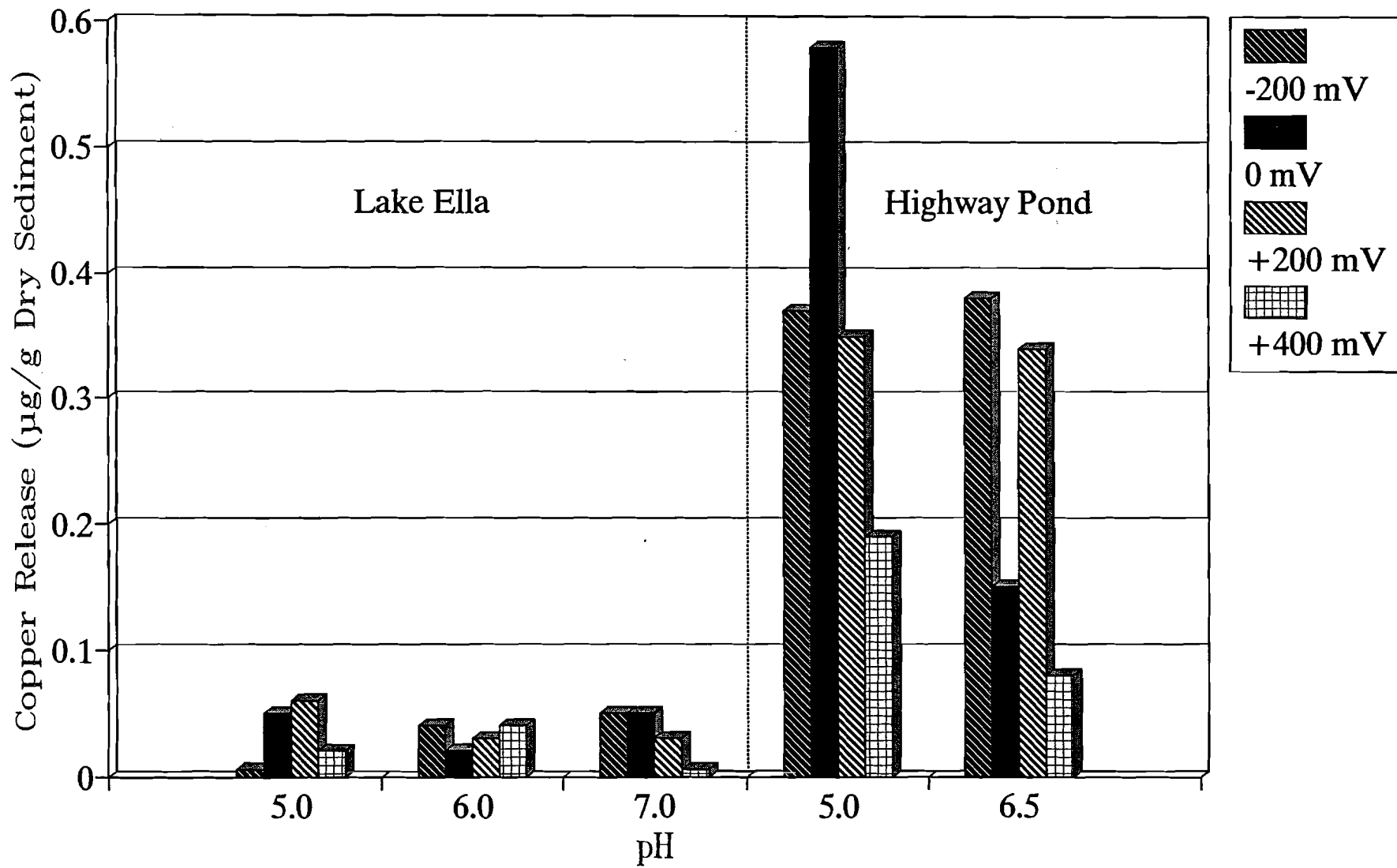


Figure 5-13. Comparison of Sediment Release of Copper Under Various Conditions of pH and Redox Potential in Lake Ella and in a Highway Detention Pond.

The release of copper from Lake Ella sediments averages less than 0.12 $\mu\text{g/g}$ dry sediments for each of the three tested pH values. However, copper release from sediments within the highway detention pond are substantially greater than those found within the sediments of Lake Ella. Continuous accumulation of alum floc within Lake Ella has apparently increased the ability of the sediments to retain copper compared with sediments existing within the highway pond.

A comparison of sediment release of lead under various conditions of pH and redox potential in Lake Ella and in the highway detention pond is given in Figure 5-14. Release of lead within Lake Ella is extremely small compared with that found within the highway pond. Similar to the results for copper, the accumulation of alum floc within the sediments is apparently increasing the ability of the sediments to retain lead compared with those found within the highway pond.

A comparison of sediment release of iron under various conditions of pH and redox potential is presented in Figure 5-15. Contrary to the results obtained for copper, lead and zinc, the release of iron from Lake Ella sediments was substantially greater than found within the highway pond particularly at a pH level of 5.0. Sediment release of iron at a pH value of approximately 7.0 was relatively similar between the two sediments.

The presence of alum floc within the sediments of Lake Ella appears to substantially enhance the ability of the sediment to retain both heavy metals and phosphorus compared with sediments from a highway detention pond which did not receive alum treatment. Release of copper, zinc, lead, nickel, chromium and cadmium from Lake Ella sediments under redox conditions ranging from highly reduced to oxidized and at pH levels ranging from 5.0 to 7.0 was found to be extremely small, indicating stable sediment associations under a wide range of environmental conditions.

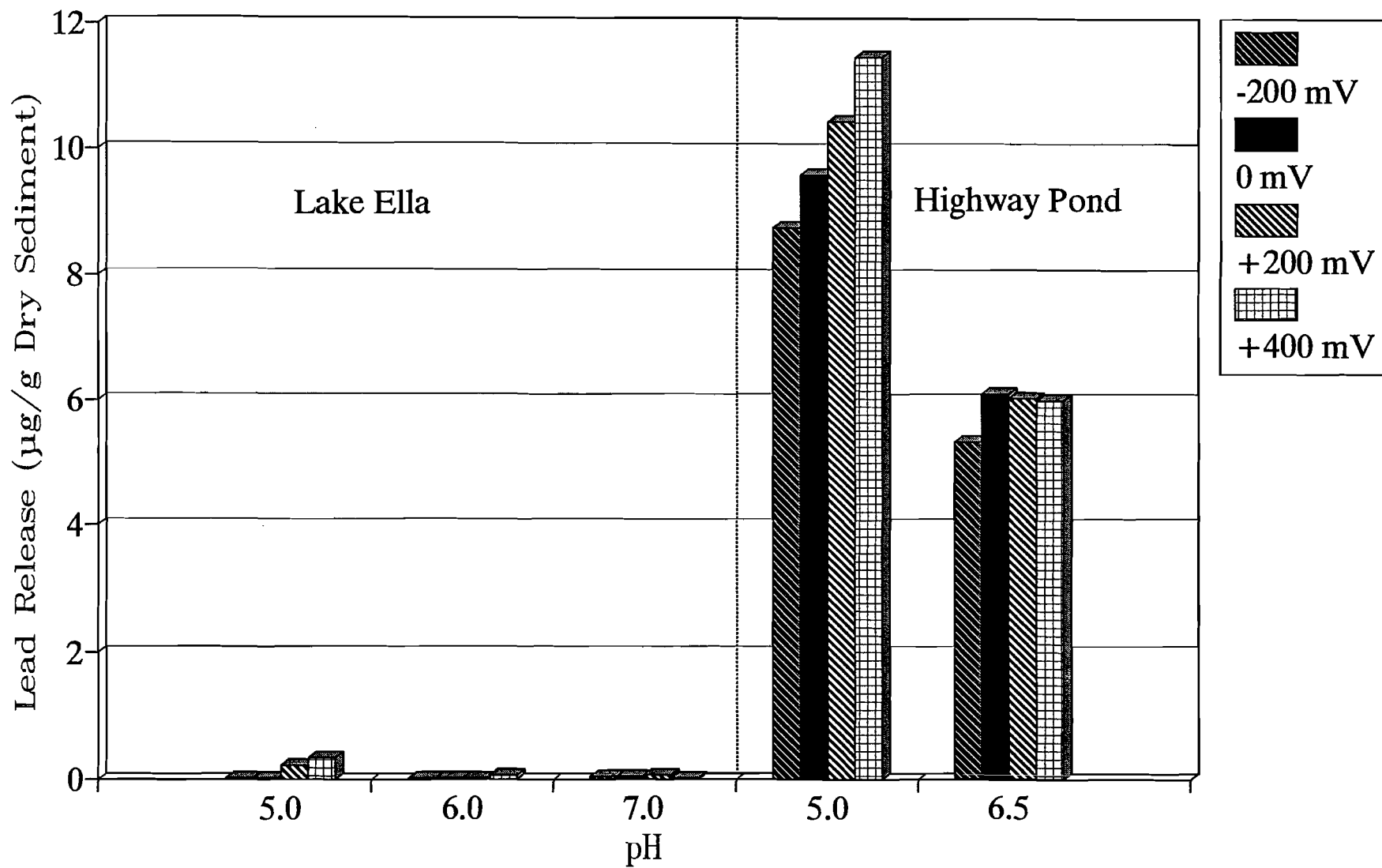


Figure 5-14. Comparison of Sediment Release of Lead Under Various Conditions of pH and Redox Potential in Lake Ella and in a Highway Detention Pond.

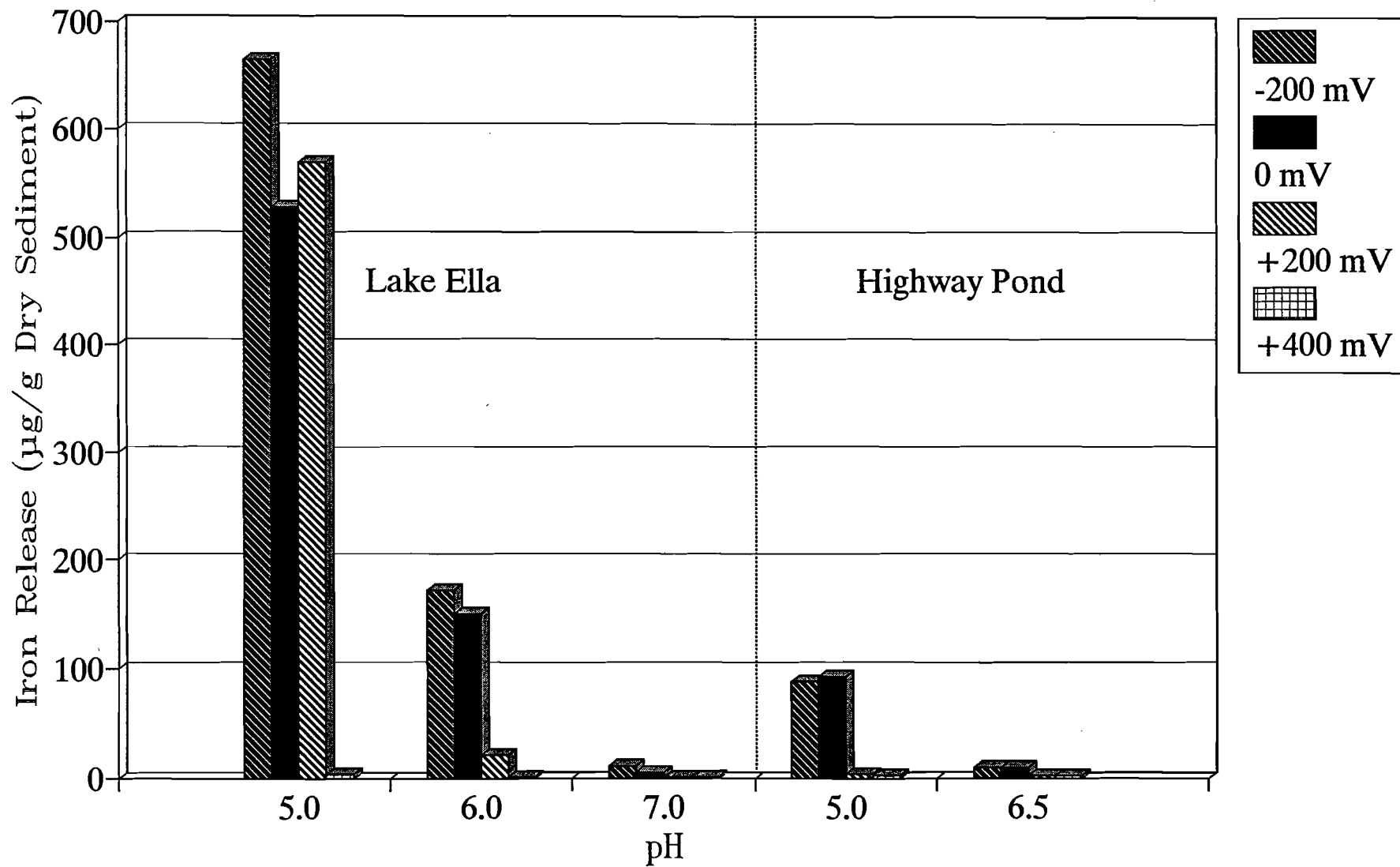


Figure 5-15. Comparison of Sediment Release of Iron Under Various Conditions of pH and Redox Potential in Lake Ella and in a Highway Detention Pond.

Estimates of Floc Accumulation

Estimates of floc accumulation in Lake Ella were conducted at each of the four sample locations used for collection of water quality samples on May 25, 1990. Floc depths were estimated using a 5-cm diameter clear acrylic core tube which was penetrated into the sediments to a depth of approximately 0.5 m. The core sample was retrieved intact, and the depth of the surface floc layer was measured and recorded for each location. Triplicate core samples were collected at each location and the results were averaged to form an estimate of the floc layer depth for each sample location.

Estimates of alum floc accumulation in Lake Ella at each of the four sample locations is given in Table 5-21. Visible grayish-white surface floc layers were found at three of the four sample locations. At these locations, the surface floc layer exists as discrete floc particles rather than a smooth uniform layer. Some of the floc at each location had penetrated to lower layers within the sediments and was visible, extending down to a depth of approximately 5 cm in virtually all of the core samples collected. It is obvious that a portion of the floc material is mixing with the existing sediment material within the lake rather than accumulating as a distinct surface layer. No visible floc layer was found in the northeast lobe, located near the outfall, even though this layer was designed as a sump for floc material, and core samples collected at this location indicated the highest levels of aluminum content within the lake. The sediment material at this location was observed to be very fine and soupy in texture. It is likely that the floc material penetrated into the sediments rather than accumulating as a distinct layer at the surface.

Distinct surface deposits of floc material appears to be greatest in the southwest and southeast lobes of the lake. Each of these areas contains stormwater outfalls which receive alum treatment. Center portions of the lake contain the least amounts of accumulated floc with an average floc depth of approximately 1 cm. Much of the floc

TABLE 5-21
MEASUREMENTS OF ALUM FLOC ACCUMULATION
IN LAKE ELLA BASED ON CORE SAMPLES
COLLECTED ON MAY 25, 1990

| LOCATION | FLOC LAYER DEPTH ¹ (cm) |
|----------|---------------------------------------|
| SW Lobe | 1.33 |
| SE Lobe | 2.0 |
| Center | 1.0 |
| NE Lobe | No visible floc layer |

1. Average of triplicate core samples at each location collected in clear acrylic core tubes.

produced within the lake may bypass the area as it migrates slowly toward the sump area near the outfall.

The average accumulation of floc material at the three locations where a visible floc layer was observed is approximately 1.4 cm. These core samples were collected after the alum system had been in operation for approximately 3 years. This corresponds to an average accumulation rate of approximately 0.5 cm/yr. This measured accumulation rate is approximately half of the accumulation rate which was originally estimated for Lake Ella based upon laboratory jar tests conducted during the design of the alum treatment system. The remainder of the floc material is apparently being mixed into, and becoming a part of, the existing sediments within the lake. This theory is supported by the fact that concentrations of soluble phosphorus and iron-bound phosphorus were reduced substantially within the sediments of the lake to depths extending into the 15-25 cm layer, presumably as a result of binding with aluminum. Although floc material could be visually seen extending to depths of 5 cm within the sediments, the results of the phosphorus fractionation indicates that migrations may extend to deeper depths. Based upon an average accumulation rate of approximately 0.5 cm/yr, as long as 25-30 years may be required to accumulate a 6-inch (15 cm) layer of alum floc within Lake Ella.

A separate experiment was conducted to evaluate the rate of consolidation of alum floc once deposited into lake sediments. Stormwater runoff was collected from an urban watershed in Orlando and treated in the laboratory at an alum dose of 88 mg/l as Al_2O_3 . This relatively high dose was achieved using a combination of alum and sodium aluminate to achieve a final pH of approximately 6.5. The alum floc was allowed to settle, and measurements of floc depth were recorded for a period of 18 days.

A summary of consolidation patterns of the alum floc with time is given in Figure 5-16. Consolidation of the alum floc is relatively rapid over the first 2-3 days

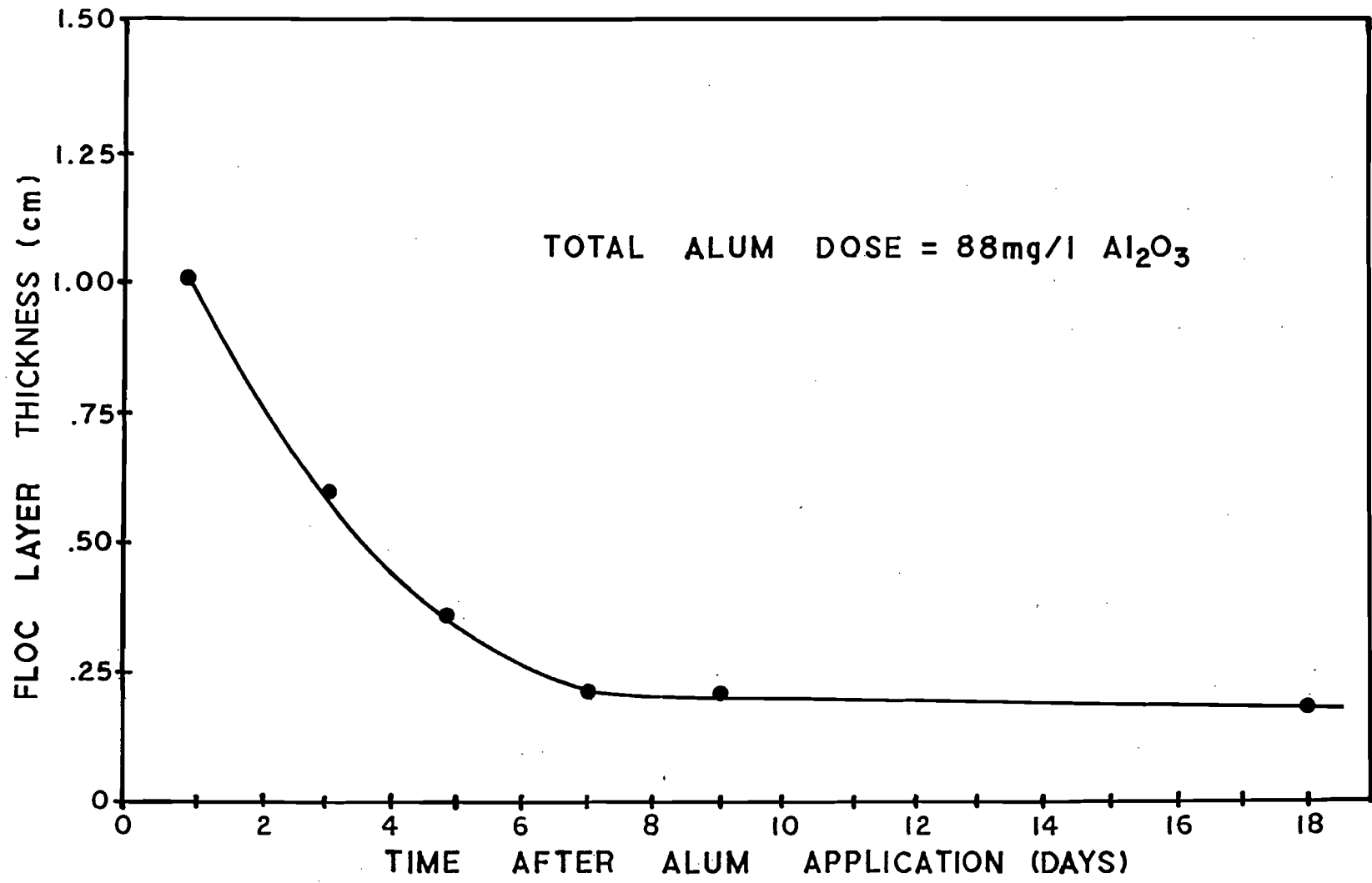


Figure 5-16. Typical Consolidation of Alum Floc with Time After Stormwater Treatment.

but slows substantially after that time. Consolidation appears to approach a maximum value after approximately 7 days, although consolidation continued throughout the 18-day duration of the experiment. Had this experiment been conducted for a longer period of time, an additional small amount of consolidation may have been recorded.

Sludge Production

Investigations were conducted to evaluate alum sludge production at various alum treatment doses. As described previously, a large volume of alum sludge was produced by coagulation of approximately 7000 liters (1850 gallons) of stormwater collected from an urban watershed in Orlando. Stormwater samples were treated with a variety of alum doses including 10, 15, 20, 25 and 30 mg/l to evaluate sludge production at typical stormwater treatment dosage rates.

A summary of the maximum anticipated production of alum sludge from alum treatment of stormwater at the five treatment doses listed previously is given in Table 5-22. The anticipated sludge volumes listed in this table are based upon a minimum settling time of 30 days. Collected sludge volumes appear to approach maximum consolidation after this period of time. However, it is likely that a small degree of additional consolidation will occur within the alum sludge at time periods in excess of 30 days.

As seen in Table 5-22, sludge production, even at a relatively high alum dose of 30 mg/l, represents a relatively small portion of the treated flow. It should also be noted that the volume of sludge produced is not linear with increasing alum dose. For example, an alum dose of 15 mg/l produces a sludge volume of 2.0 m³/1000 m³ of stormwater treated. An alum dose of 30 mg/l produces an alum sludge volume of 6.9 m³/1000 m³ of treated stormwater rather than a value of 4.0 m³ as may be expected by simply doubling the sludge production achieved at 15 mg/l.

TABLE 5-22

MAXIMUM ANTICIPATED PRODUCTION OF ALUM SLUDGE
FROM ALUM TREATMENT OF STORMWATER AT VARIOUS DOSES

| ALUM DOSE (mg/l) | SLUDGE PRODUCTION ¹ | | |
|------------------|--------------------------------|---------------------------------|-------------------------------------|
| | AS % OF TREATED FLOW | PER 1000 m ³ TREATED | PER 10 ⁶ GALLONS TREATED |
| 10 | 0.16 | 1.6 m ³ | 214 ft ³ |
| 15 | 0.20 | 2.0 m ³ | 268 ft ³ |
| 20 | 0.28 | 2.8 m ³ | 374 ft ³ |
| 25 | 0.40 | 4.0 m ³ | 535 ft ³ |
| 30 | 0.69 | 6.9 m ³ | 922 ft ³ |

1. Based on a minimum settling time of 30 days.

The relationship between alum sludge production and alum treatment dose is shown in Figure 5-17. This relationship appears to be exponential in nature rather than linear. There are several possible explanations for this non-linear relationship. First, the formation and production of alum floc is more complete at higher alum doses than at lower alum doses. This trend has been observed on numerous occasions in laboratory studies and can also be observed in measurements of turbidity and suspended solids conducted on runoff samples treated with alum at various treatment doses. Floc produced at smaller doses is often very fine in nature and resistant to settling, whereas floc produced at larger doses is often larger and settles rapidly. The more complete production of alum sludge at higher doses is also observed in measurements of aluminum concentrations which are frequently lower with alum treatment at high doses than in alum treated water at lower doses.

A second explanation for the non-linear relationship between floc production and alum dose is related to the efficiency of pollutant removal achieved at various doses of alum. Removal of suspended solids and turbidity increases with increasing alum dose. As a result, higher alum doses not only contain larger quantities of floc but also include particulate matter present in stormwater samples which may have been removed from solution and precipitated along with the alum floc.

The values listed in Table 5-22 which relate sludge production to various doses of alum should be viewed as "maximum" anticipated sludge production volumes when evaluating sludge accumulation within a waterbody receiving alum stormwater treatment. As indicated previously, much of the accumulated sediment material mixes with the existing sediments and does not accumulate as a distinct separate surface layer of alum floc. Actual observed sludge production within a waterbody receiving alum treatment would generally be 50% or less of the values listed in Table 5-22. However, these values are useful as worst case estimates for purposes of evaluating potential effects on future stormwater alum treatment systems.

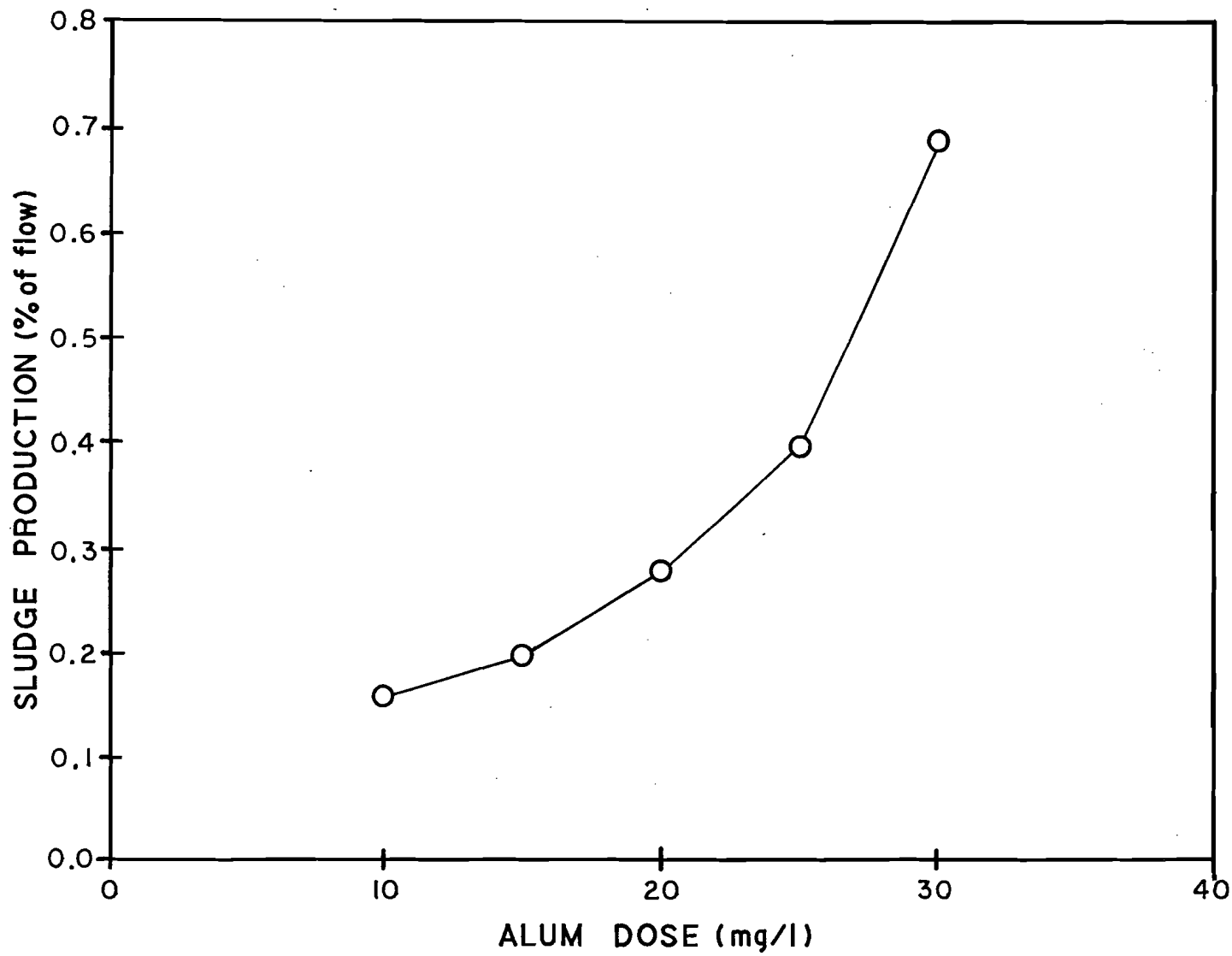


Figure 5-17. Relationship Between Alum Sludge Production and Alum Treatment Dose.

Sludge Disposal

After evaluation of anticipated sludge production volumes, each of the sludge samples was combined together to form a single composite sludge sample for use in drying and leachate investigations. As described previously, this composite sludge sample was poured onto a drying bed and the characteristics of the leachate monitored continuously at the discharge point for the underdrain from the sand filter.

A summary of chemical characteristics of alum sludge leachate collected at the filter discharge is given in Table 5-23. Alum sludge leachate was found to have a mean pH value of 6.37 with a relatively low alkalinity of 37 mg/l. Measured concentrations of both total nitrogen and total phosphorus are relatively low and similar in value to concentrations normally found in stormwater runoff. Total nitrogen is comprised approximately equally of ammonia, nitrate and particulate organic nitrogen. Measured total phosphorus is comprised primarily of particulate phosphorus, with a relatively small concentration of dissolved orthophosphorus. The leachate was also found to be extremely low in both BOD and color.

Alum sludge leachate was also found to have extremely low levels of aluminum, with a mean concentration of only 23 $\mu\text{g/l}$ for dissolved aluminum and 141 $\mu\text{g/l}$ for total aluminum. Extremely low levels of all measured heavy metals are found in the leachate flow. Measured concentrations of all heavy metals are substantially less than surface water standards for Class III waters as specified in Chapter 17-302 of the Florida Administrative Code.

After collection of the alum sludge leachate, the sludge layer was allowed to dry naturally in an outdoor location. Initial phases of the drying process were characterized by a general shrinking of the sludge material, particularly near the walls of the filter box. As the surface sludge layers began to dry, cracks began to develop within the sludge which extended throughout the sludge column at the completion of drying. The

TABLE 5-23

CHEMICAL CHARACTERISTICS OF
ALUM SLUDGE LEACHATE

| PARAMETER | UNITS | CONC. | CHAPTER 17-3 F.A.C. CLASS III SURFACE WATER STANDARDS |
|--------------------|-----------------|-------|---|
| pH | s.u. | 6.37 | - |
| Alkalinity | mg/l | 37 | ≥ 20 mg/l |
| NH ₃ -N | $\mu\text{g/l}$ | 306 | - |
| NO _x -N | $\mu\text{g/l}$ | 404 | - |
| Diss. Organic N | $\mu\text{g/l}$ | 91 | - |
| Part. Organic N | $\mu\text{g/l}$ | 405 | - |
| Total N | $\mu\text{g/l}$ | 1207 | - |
| Diss. Ortho-P | $\mu\text{g/l}$ | 24 | - |
| Diss. Organic P | $\mu\text{g/l}$ | 35 | - |
| Part. P | $\mu\text{g/l}$ | 77 | - |
| Total P | $\mu\text{g/l}$ | 136 | - |
| Color | Co-Pt | 18 | - |
| BOD | mg/l | 1.7 | - |
| Total Diss. Al | $\mu\text{g/l}$ | 23 | - |
| Total Part. Al | $\mu\text{g/l}$ | 118 | - |
| Total Al | $\mu\text{g/l}$ | 141 | - |
| Total Cd | $\mu\text{g/l}$ | <1 | ≤ 0.8 |
| Total Cu | $\mu\text{g/l}$ | 9 | ≤ 30 |
| Total Cr | $\mu\text{g/l}$ | 2 | ≤ 50 |
| Total Fe | $\mu\text{g/l}$ | 40 | ≤ 1000 |
| Total Ni | $\mu\text{g/l}$ | 11 | ≤ 100 |
| Total Pb | $\mu\text{g/l}$ | 15 | ≤ 30 |
| Total Zn | $\mu\text{g/l}$ | 10 | ≤ 30 |

final dried sludge depth was approximately 40% of the initial sludge depth placed in the drying box.

After the alum sludge had dried completely, a composite sample of sludge was collected for analysis of typical wastewater sludge parameters to evaluate potential methods for disposal of alum sludge. Chemical characteristics of the alum sludge are given in Table 5-24 and compared with typical wastewater criteria for Grade 1 domestic wastewater sludge as outlined in Chapter 17-7 of the Florida Administrative Code. Alum sludge was found to have relatively low values of nitrogen, phosphorus and potassium, as well as each of the measured heavy metals. Concentrations of measured heavy metals were found to be substantially less than the maximum allowable values for disposal of the sludge as a Grade 1 wastewater sludge.

Based upon this analysis, dried alum sludge could potentially be disposed of in a manner similar to that used for Grade 1 wastewater sludge. A Grade 1 sludge may be applied to sod farms, pasturelands, forests, highway shoulders and medians, nurseries, land reclamation projects and soil use for growing human food chain crops. Grade 1 sludges may also be used on playgrounds, parks, golf courses, lawns, hospital grounds or other areas with unrestricted public access where frequent human contact is likely to occur.

Although the characteristics of alum sludge allow it to be placed on sod farms, pastureland and nurseries, alum sludge would probably not make a good agricultural soil material. First, concentrations of nitrogen, potassium and phosphorus are extremely low in the alum sludge. Second, even though phosphorus is present within the sludge other research efforts as well as those described in this report indicate that the phosphorus is tightly bound to aluminum and is largely unavailable for release and uptake by plant species. Although this may be undesirable in agricultural applications, these sediment characteristics may be a benefit in lake systems for limiting the growth

TABLE 5-24
 CHARACTERISTICS OF THE ALUM
 SLUDGE USED FOR DISPOSAL STUDIES

| SLUDGE PARAMETER | UNITS | MEASURED VALUE | CH. 17-7 SLUDGE CRITERIA - GRADE I ¹ |
|---------------------|------------------|-------------------|---|
| Total N | % dry weight | 0.28 | none |
| Total P | % dry weight | 0.18 | none |
| Total K | % dry weight | 0.09 | none |
| Cd | mg/kg dry weight | 2.2 | ≤30 |
| Cu | mg/kg dry weight | 26 | ≤900 |
| Pb | mg/kg dry weight | 41 | ≤1000 |
| Ni | mg/kg dry weight | 13 | ≤100 |
| Zn | mg/kg dry weight | 39 | ≤1800 |
| pH | s.u. | 6.8 | none |

1. Criteria for land application of Grade 1 if the following conditions are met:
 - a. Application is limited to sod farms, pasturelands, forests, highway shoulders and medians, plant nursery use, land reclamation projects and soil used for growing human food chain crops (excluding rootcrops, leafy vegetables, tobacco, and vegetables to be eaten raw).
 - b. Use on playgrounds, parks, golf courses, lawns, hospital grounds, or other unrestricted public access areas where frequent human contact is likely to occur is restricted to processed domestic sludge and composted domestic sludge.

of aquatic vegetation in deeper portions of the lake after improvements in water clarity resulting from the alum treatments.

Rate Experiments

Laboratory experiments were conducted to examine the rate of changes in aluminum speciation during the coagulation process. The primary purpose of these studies was to determine the length of time which potentially toxic Al^{+3} species exist within a stormwater stream following addition of liquid alum or sodium aluminate. This information is useful in the design of alum injection systems since it provides an estimate of the necessary length of time required for mixing within the stormsewer system after addition of the alum before the treated water can be released into surface waters.

Changes in concentrations of monomeric dissolved aluminum as a function of time after addition of alum to stormwater runoff collected on March 27, 1989 are presented in Figure 5-18. For this experiment, alum doses of 10, 20, 30, 40 and 50 mg/l as Al_2O_3 were tested. Each chemical addition was conducted using alum in combination with sodium aluminate so that the solution pH did not drop below a value of 6.0 after addition of the coagulant.

As seen in Figure 5-18, concentrations of monomeric dissolved aluminum decrease rapidly after the introduction of alum into the test water. After approximately 20-30 seconds, dissolved aluminum concentrations are reduced below the initial aluminum concentration of 198 $\mu\text{g/l}$. After approximately 60 seconds, all coagulant doses, with the exception of 10 mg/l, reach monomeric dissolved aluminum concentrations of approximately 50-100 $\mu\text{g/l}$. Although monomeric dissolved aluminum had been converted into alum floc at this time, the floc was microscopic and not visible with the unaided eye. Aluminum concentrations continued to decrease

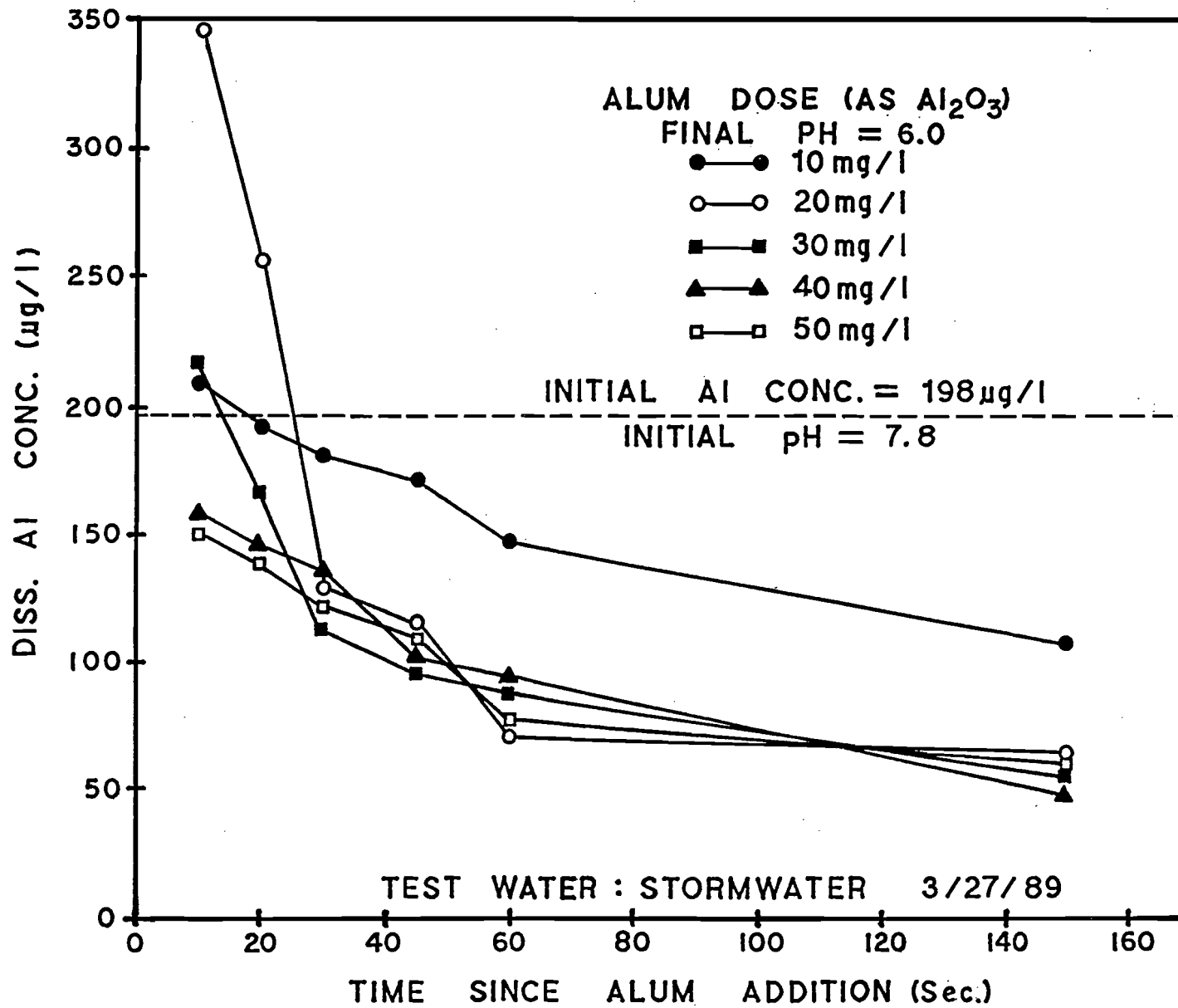


Figure 5-18. Changes in Concentrations of Monomeric Dissolved Aluminum with Time After Addition of Alum to Stormwater Runoff Collected on 3/27/89.

slowly after 60 seconds, reaching an equilibrium value of approximately 50 $\mu\text{g}/\text{l}$ after 2-3 minutes.

Changes in concentrations of monomeric dissolved aluminum with time after addition of alum to stormwater runoff collected on April 4, 1989 are indicated in Figure 5-19. Results obtained during this experiment are similar to those obtained in the March 27th experiment. Concentrations of dissolved monomeric aluminum decrease rapidly after addition to the stormwater flow, reaching levels below initial levels in the stormwater after approximately 20-30 seconds. With only the exception of the 30 mg/l dose, concentrations appear to level off at approximately 100 $\mu\text{g}/\text{l}$ after 1 minute, reaching final values between 50-100 $\mu\text{g}/\text{l}$ after 2-3 minutes.

The results presented in Figures 5-18 and 5-19 suggest that a minimum mixing period of approximately 60 seconds within the stormsewer lines after the addition of alum is sufficient to allow dissolved concentrations of monomeric aluminum to decrease below approximately 100 $\mu\text{g}/\text{l}$. It appears that a safe design parameter for use in designing alum injection systems would be to evaluate the time of travel through the stormsewer line and adjust the point of addition of alum into the stormwater flow so that a minimum travel time of 60 seconds is achieved for treated storm events.

Bioassay and Toxicity Testing

Two separate types of bioassay experiments were conducted to evaluate the potential toxicity of alum treated runoff on selected species of fish. The first series of experiments were conducted using fathead minnows (*Pimephales promelas*) in the standard EPA Seven-Day Chronic Larval Survival and Growth Test. A second set of experiments were conducted as long-term bioassay tests using *Gambusia sp.* as test organisms. The results of each of these experiments are described in the following sections.

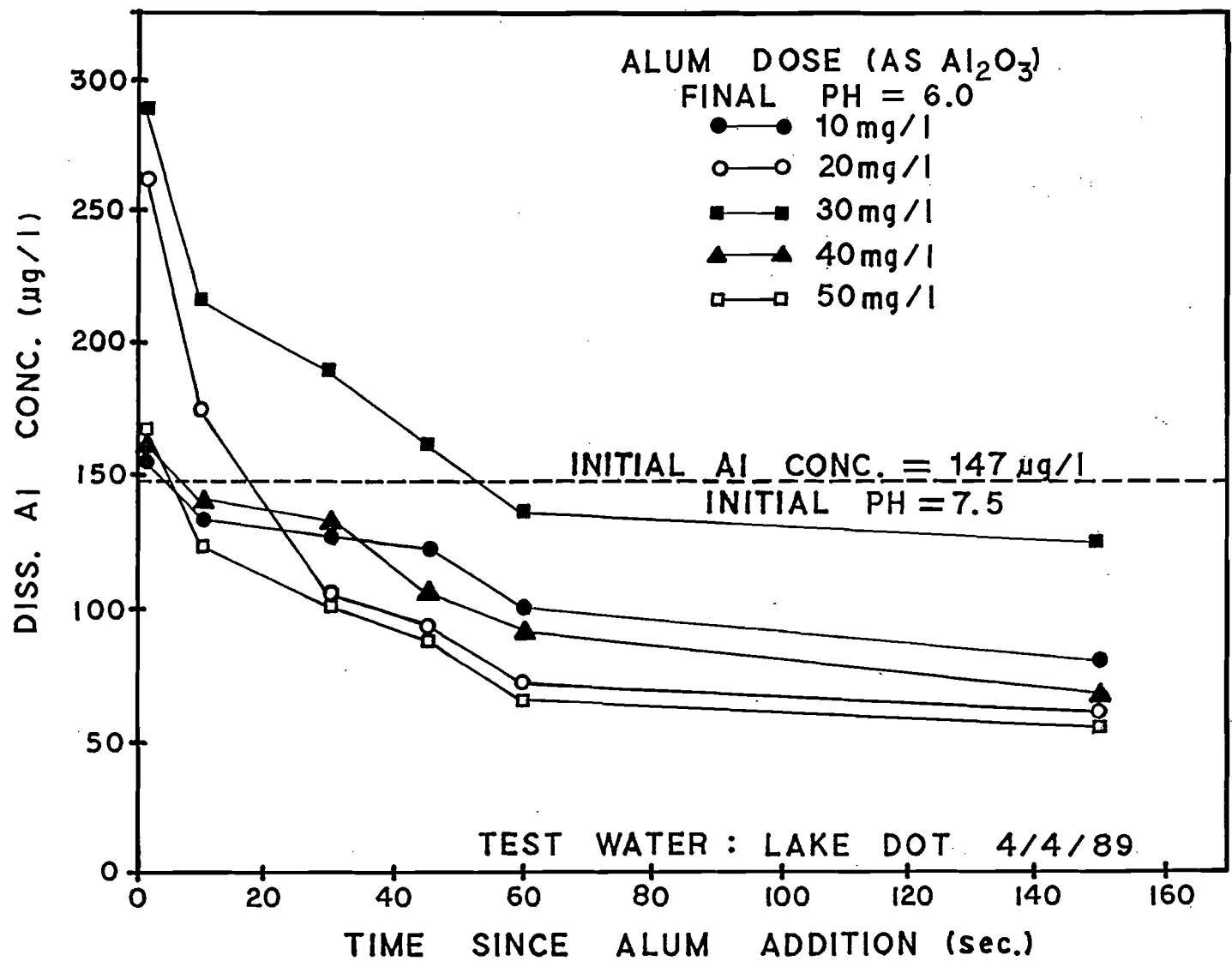


Figure 5-19. Changes in Concentrations of Monomeric Dissolved Aluminum with Time After Addition of Alum to Stormwater Runoff Collected on 4/4/89.

Fathead Minnow Toxicity Tests

A Seven-Day Fathead Minnow (*Pimephales promelas*) Chronic Larval Survival and Growth Test (EPA/600/4-89/001) was performed to assess the chronic biotoxicity of alum treated stormwater. Test organisms, a few hours old, were obtained from a commercial vendor for use in the test. The test was conducted as a static renewal test with test solutions renewed every 24 hours. A summary of test chambers used in this experimentation is given below:

1. Control: Consisting of dilution water made according to the EPA procedure listed previously.
2. Raw Stormwater: Raw stormwater collected from an urban Orlando watershed.
3. pH 6.0: Stormwater which had been treated with alum to achieve a final pH of 6.0.
4. pH 6.5: Stormwater which had been treated with alum to achieve a final pH of 6.5.
5. pH 7.0: Stormwater which had been treated with alum to achieve a final pH of 7.0
6. pH 7.5: Stormwater which had been treated with alum to achieve a final pH of 7.5.

The test was conducted for a total of seven days as described in the EPA procedure.

A summary of routine chemical and physical measurements conducted within the test chambers during the Fathead Minnow Survival and Growth Test is given in Table 5-25. Measurements of temperature, initial and final dissolved oxygen, and initial and final pH were conducted in each of the 24 test beakers daily for the 7-day duration of the experiments. Values in Table 5-25 represent an average of these measurements collected in the four test beakers for a particular test treatment. Measurements of alkalinity, hardness, conductivity, sulfate and dissolved aluminum were conducted on a single composite sample formed from equal aliquots of test waters collected from each of the four test chambers on a daily basis.

TABLE 5-25

**ROUTINE CHEMICAL AND PHYSICAL MEASUREMENTS CONDUCTED
DURING THE FATHEAD MINNOW LARVAL SURVIVAL AND GROWTH TEST**

| TEST CHAMBERS | PARAMETER | DAY | | | | | | |
|-----------------------------------|----------------------|------|------|------|------|------|------|------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Control | Temp. (°C) | 24.9 | 24.8 | 24.0 | 24.0 | 24.8 | 24.0 | 24.5 |
| | D.O. (mg/l): Initial | 6.2 | 7.0 | 5.0 | 5.5 | 7.2 | 6.6 | 6.4 |
| | Final | 7.6 | 7.0 | 6.2 | 6.9 | 8.1 | 7.9 | -- |
| | pH: Initial | 6.63 | 6.73 | 6.68 | 6.69 | 6.86 | 6.86 | 6.81 |
| | Final | 6.59 | 6.50 | 6.55 | 6.68 | 6.98 | 6.94 | -- |
| | Alkalinity (mg/l) | 15 | 16 | 14 | 15 | 15 | 16 | 17 |
| | Hardness (mg/l) | 71 | 82 | 77 | 69 | 76 | 76 | 80 |
| | Conductivity (µS/cm) | 302 | 302 | 312 | 313 | 315 | 325 | 330 |
| Sulfate (mg/l) | 41 | 61 | 64 | 65 | 63 | 64 | 65 | |
| Diss. Al (µg/l) | 9 | 13 | 12 | 9 | 10 | 9 | 13 | |
| Raw Stormwater | Temp. (°C) | 24.9 | 24.8 | 24.0 | 24.0 | 24.8 | 24.0 | 24.9 |
| | D.O. (mg/l): Initial | 5.9 | 3.0 | 7.8 | 7.0 | 8.2 | 6.7 | 5.9 |
| | Final | 6.1 | 8.2 | 8.1 | 8.0 | 8.2 | 8.0 | -- |
| | pH: Initial | 7.01 | 7.36 | 7.88 | 8.12 | 8.38 | 7.98 | 7.87 |
| | Final | 7.19 | 8.06 | 7.93 | 8.12 | 8.31 | 8.03 | -- |
| | Alkalinity (mg/l) | 86 | 99 | 110 | 121 | 132 | 140 | 155 |
| | Hardness (mg/l) | 151 | 146 | 155 | 171 | 159 | 148 | 161 |
| | Conductivity (µS/cm) | 325 | 333 | 354 | 363 | 365 | 385 | 395 |
| Sulfate (mg/l) | 63 | 38 | 38 | 37 | 33 | 31 | 32 | |
| Diss. Al (µg/l) | 25 | 34 | 36 | 37 | 26 | 25 | 26 | |
| Alum Treated Stormwater at pH 6.0 | Temp. (°C) | 24.9 | 24.4 | 24.8 | 24.0 | 24.8 | 24.0 | 24.9 |
| | D.O. (mg/l): Initial | 7.2 | 6.6 | 6.0 | 6.2 | 7.6 | 7.4 | 7.2 |
| | Final | 7.4 | 6.8 | 6.9 | 6.6 | 7.5 | 7.6 | 7.3 |
| | pH: Initial | 6.10 | 6.08 | 6.06 | 6.11 | 6.09 | 6.10 | 6.14 |
| | Final | 6.06 | 6.02 | 6.03 | 6.02 | 6.04 | 6.03 | 6.02 |
| | Alkalinity (mg/l) | 30 | 31 | 30 | 32 | 30 | 29 | 28 |
| | Hardness (mg/l) | 136 | 135 | 141 | 138 | 137 | 138 | 136 |
| | Conductivity (µS/cm) | 346 | 350 | 348 | 349 | 356 | 351 | 353 |
| Sulfate (mg/l) | 66 | 83 | 88 | 90 | 94 | 97 | 98 | |
| Diss. Al (µg/l) | 20 | 21 | 18 | 17 | 19 | 20 | 22 | |

TABLE 5-25 -- CONTINUED

| TEST CHAMBERS | PARAMETER | DAY | | | | | | |
|-----------------------------------|-------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|------------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Alum Treated Stormwater at pH 6.5 | Temp. (°C) | 24.9 | 24.8 | 24.8 | 24.0 | 24.8 | 24.0 | 24.9 |
| | D.O. (mg/l): Initial Final | 6.5 8.0 | 6.7 7.1 | 5.0 5.4 | 6.2 7.2 | 7.0 8.1 | 6.2 7.8 | 5.9 -- |
| | pH: Initial Final | 6.68 6.72 | 6.57 6.61 | 6.58 6.52 | 6.47 6.60 | 6.51 6.49 | 6.59 6.66 | 6.60 -- |
| | Alkalinity (mg/l) | 44 | 42 | 41 | 43 | 37 | 33 | 33 |
| | Hardness (mg/l) | 137 | 137 | 139 | 140 | 144 | 141 | 138 |
| | Conductivity (µS/cm) | 351 | 366 | 393 | 401 | 414 | 433 | 446 |
| | Sulfate (mg/l) | 76 | 102 | 111 | 115 | 125 | 127 | 140 |
| | Diss. Al (µg/l) | 22 | 36 | 22 | 25 | 34 | 26 | 17 |
| Alum Treated Stormwater at pH 7.0 | Temp. (°C) | 24.9 | 23.8 | 24.9 | 24.0 | 24.8 | 24.0 | 24.9 |
| | D.O. (mg/l): Initial Final | 6.5 7.9 | 6.5 6.8 | 5.8 5.4 | 6.1 7.4 | 7.1 8.1 | 7.0 7.9 | 7.2 -- |
| | pH: Initial Final | 7.19 7.16 | 7.05 7.04 | 7.08 7.13 | 7.05 7.10 | 7.08 7.11 | 7.08 7.03 | 7.07 -- |
| | Alkalinity (mg/l) | 65 | 72 | 74 | 71 | 73 | 60 | 61 |
| | Hardness (mg/l) | 145 | 143 | 142 | 135 | 146 | 136 | 143 |
| | Conductivity (µS/cm) | 338 | 344 | 386 | 394 | 407 | 430 | 433 |
| | Sulfate (mg/l) | 57 | 69 | 86 | 87 | 104 | 113 | 106 |
| | Diss. Al (µg/l) | 56 | 79 | 63 | 67 | 70 | 64 | 69 |
| Alum Treated Stormwater at pH 7.5 | Temp. (°C) | 24.9 | 23.8 | 24.9 | 24.0 | 24.0 | 24.0 | 24.9 |
| | D.O. (mg/l): Initial Final | 6.5 7.9 | 5.8 6.4 | 5.9 6.4 | 6.3 7.4 | 6.8 8.1 | 6.8 7.7 | 7.1 -- |
| | pH: Initial Final | 7.32 7.36 | 7.89 7.41 | 7.49 7.34 | 7.57 7.76 | 7.76 7.74 | 7.73 7.86 | 7.85 -- |
| | Alkalinity (mg/l) | 73 | 84 | 94 | 98 | 101 | 102 | 102 |
| | Hardness (mg/l) | 135 | 137 | 138 | 144 | 145 | 145 | 141 |
| | Conductivity (µS/cm) | 352 | 365 | 406 | 409 | 415 | 435 | 434 |
| | Sulfate (mg/l) | 56 | 64 | 73 | 75 | 68 | 78 | 79 |
| | Diss. Al (µg/l) | 87 | 118 | 106 | 119 | 140 | 128 | 169 |

Mean dissolved oxygen levels within the control test chambers were in excess of 5 mg/l on all measurement dates. Measured values of pH ranged from 6.5 to 6.98. Alkalinity within the control chambers is relatively low with values of approximately 15 mg/l. Measured values of hardness are also relatively low with an average of approximately 76 mg/l throughout the 7-day period. Measured concentrations of alkalinity and hardness within the control test chambers are somewhat lower than values measured within the raw stormwater and the alum treated stormwater. In contrast, the mean values for conductivity of 314 $\mu\text{S}/\text{cm}$ and of 60 mg/l for sulfate are similar to those measured within the other test chambers. Concentrations of dissolved aluminum within the control chamber are relatively low with an average value of approximately 11 $\mu\text{g}/\text{l}$.

Concentrations of dissolved oxygen within the raw stormwater samples remained at adequate levels with the exception of day 2 when concentrations decreased to 3.0 mg/l. Measurements of pH began at approximately 7.0 at the beginning of the test but increased steadily throughout the test period with a final value of approximately 8.0. Measured concentrations of alkalinity, hardness and conductivity appear to increase steadily over the 7-day test period with mean values of 120 mg/l for alkalinity, 156 mg/l for hardness and 360 $\mu\text{S}/\text{cm}$ for conductivity. The average value for dissolved aluminum is approximately 30 $\mu\text{g}/\text{l}$.

Dissolved oxygen concentrations within alum treated test chambers maintained levels greater than 5.0 in all of the test chambers throughout the 7-day test period. In general, pH conditions within each of the test chambers is maintained relatively close to the desired pH level for each of the four pH levels tested. As expected, measurements of alkalinity increase with increasing pH values with a mean alkalinity of 30 mg/l for the stormwater treated at pH 6.0, 39 mg/l for the stormwater treated at pH 6.5, 68 mg/l for the stormwater treated at pH 7.0 and 93 mg/l for the stormwater treated at pH

7.5. Measurements of hardness within each of the alum treated test chambers are relatively similar with an average of approximately 135-145 mg/l. Measurements of conductivity are also similar at each of the four tested pH values with a mean of approximately 350-370 $\mu\text{S}/\text{cm}$.

Sulfate concentrations average 88 mg/l at pH 6.0, 114 mg/l at pH 6.5, but decrease to 89 mg/l at pH 7.0 and 70 mg/l at pH 7.5. The reduction in sulfate levels at pH values of 7.0 and 7.5 result from the use of sodium aluminate, which does not contribute sulfate to the water column, as part of the total alum dose to achieve these higher pH levels. Concentrations of dissolved aluminum average 20 $\mu\text{g}/\text{l}$ at pH 6.0, 26 $\mu\text{g}/\text{l}$ at pH 6.5, 67 $\mu\text{g}/\text{l}$ at pH 7.0 and 124 $\mu\text{g}/\text{l}$ at pH 7.5.

Survival data for the Fathead Minnow Larval Survival and Growth Test is presented in Table 5-26. Survival data is presented for each of the four replicate test containers at each test condition along with data for the control and raw stormwater. Average values for the four replicates are also provided. In general, the number of survivors in a particular test series are relatively uniform between the four replicate containers on most of the measurement dates. However, variations in survivors are evident when mortalities began to occur within the test chambers. However, by the end of the 7-day test period, mortality levels are relatively similar between the four replicate containers.

Survival results for the Fathead Minnow Larval Survival and Growth Test are summarized in Figure 5-20. Survival percentages for alum treated stormwater at a pH of 6.0 and 6.5 are similar to that obtained within the control with a final survival in excess of 95%. Mortalities began to be observed in stormwater runoff treated at a pH level of 7.0 with an ultimate survival percentage of approximately 57% at the end of seven days. However, even though mortalities were observed at a pH of 7.0, these mortalities were less than that observed within the raw stormwater which exhibited a

TABLE 5-26

**SURVIVAL DATA FOR FATHEAD MINNOW
LARVAL SURVIVAL AND GROWTH TEST**

| TEST | REP. NO. | NO. OF SURVIVORS | | | | | | | |
|--------------------------|----------|------------------|------|------|------|------|------|------|------|
| | | INITIAL | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Raw Stormwater | 1 | 15 | 15 | 15 | 15 | 15 | 9 | 3 | 3 |
| | 2 | 15 | 14* | 14 | 14 | 14 | 14 | 6 | 3 |
| | 3 | 15 | 15 | 15 | 14 | 14 | 9 | 8 | 4 |
| | 4 | 15 | 15 | 15 | 15 | 15 | 12 | 7 | 2 |
| | Avg. | 15.0 | 14.8 | 14.8 | 14.5 | 14.5 | 11.0 | 6.7 | 3.0 |
| Control | 1 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| | 2 | 15 | 15 | 15 | 15 | 15 | 14 | 13 | 13 |
| | 3 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| | 4 | 15 | 15 | 15 | 15 | 14 | 14 | 14 | 14 |
| | Avg. | 15.0 | 15.0 | 15.0 | 15.0 | 14.8 | 14.5 | 14.3 | 14.3 |
| Alum Treated pH = 6.0 | 1 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| | 2 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| | 3 | 15 | 15 | 15 | 15 | 15 | 14 | 14 | 14 |
| | 4 | 15 | 15 | 15 | 15 | 15 | 15 | 14 | 14 |
| | Avg. | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 14.8 | 14.5 | 14.5 |
| Alum Treated pH = 6.5 | 1 | 15 | 15 | 15 | 15 | 14 | 14 | 14 | 14 |
| | 2 | 15 | 15 | 15 | 15 | 14 | 14 | 14 | 14 |
| | 3 | 15 | 15 | 15 | 15 | 14 | 14 | 14 | 14 |
| | 4 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| | Avg. | 15.0 | 15.0 | 15.0 | 15.0 | 14.3 | 14.3 | 14.3 | 14.3 |
| Alum Treated pH = 7.0 | 1 | 15 | 15 | 15 | 15 | 14 | 14 | 14 | 14 |
| | 2 | 15 | 15 | 15 | 15 | 13 | 9 | 9 | 8 |
| | 3 | 15 | 15 | 15 | 15 | 10 | 9 | 8 | 6 |
| | 4 | 15 | 15 | 15 | 15 | 9 | 7 | 6 | 6 |
| | Avg. | 15.0 | 15.0 | 15.0 | 15.0 | 11.5 | 9.8 | 9.3 | 8.5 |
| Alum Treated pH = 7.5 | 1 | 15 | 15 | 15 | 15 | 5 | 3 | 3 | 3 |
| | 2 | 15 | 15 | 15 | 15 | 11 | 6 | 3 | 3 |
| | 3 | 15 | 14 | 14 | 9 | 8 | 6 | 3 | 2 |
| | 4 | 15 | 15 | 15 | 15 | 11 | 3 | 2 | 2 |
| | Avg. | 15.0 | 14.8 | 14.8 | 13.5 | 8.8 | 4.5 | 2.8 | 2.5 |

* Crushed while cleaning

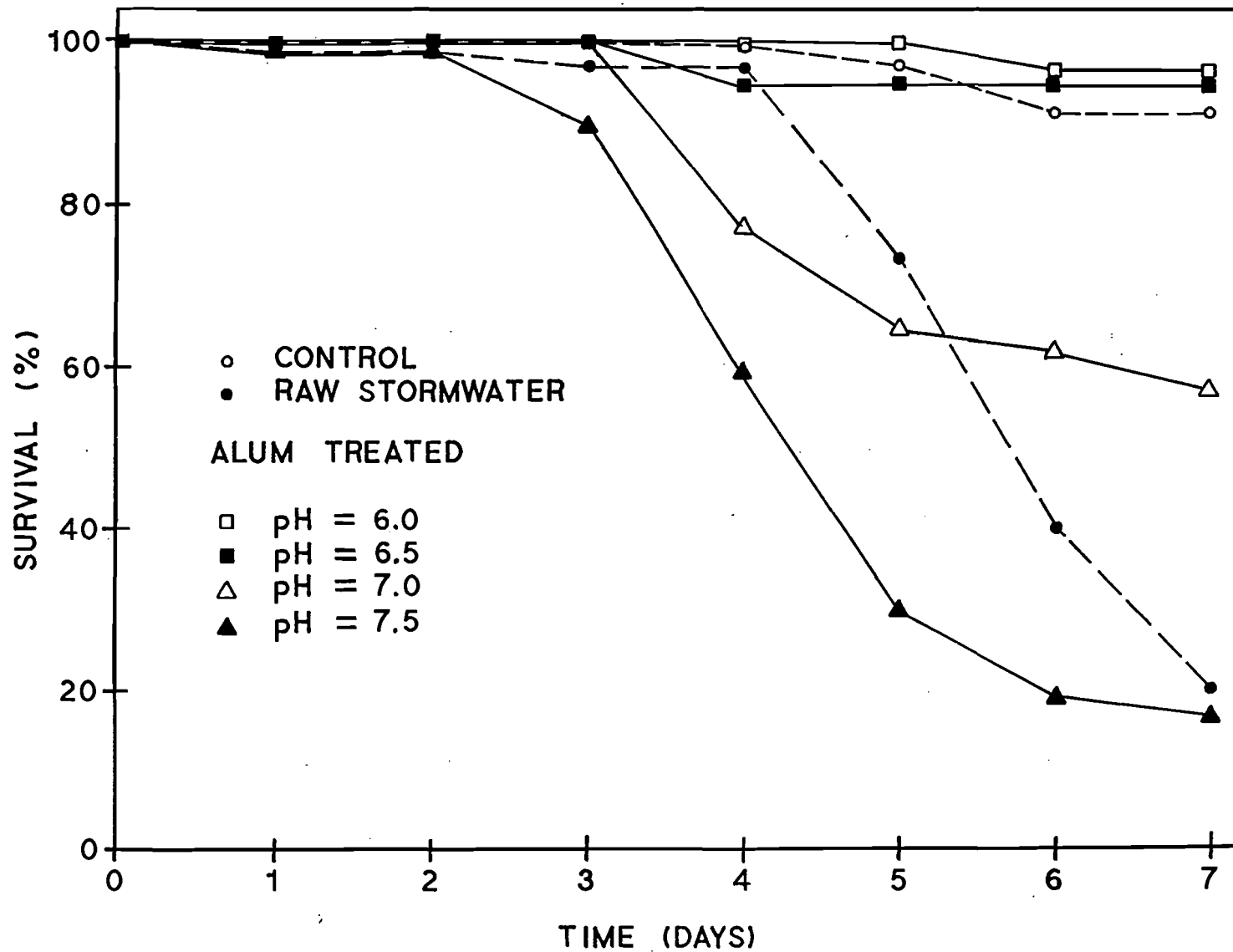


Figure 5-20. Survival Results for the Fathead Minnow Larval Survival and Growth Test.

survival of only 20% at the end of the 7-day test period. The rate of mortality in stormwater treated with alum at a pH of 7.5 is similar to that observed in raw stormwater.

The information presented in Figure 5-20 suggests that there is no chronic toxicity associated with alum treated stormwater when pH levels of 6.0 and 6.5 are maintained. Chronic biotoxicity increases at a pH of 7.0, but is less than the toxicity of the raw stormwater itself. As a result, alum stormwater treatment systems should be designed to maintain pH levels at values between 6.0 and 7.0, preferably in the range of 6.0-6.5. The relatively large mortality found at a pH level of 7.5 indicates that alum stormwater treatment should not be conducted at this pH level.

Final larval weight data for the Fathead Minnow Larval Survival and Growth Test is presented in Table 5-27. Test larvae exposed to alum treated runoff at a pH of 6.0 produced the greatest mean dry weight per organism, 0.5377 mg. Mean dry larval weights were slightly lower at other pH values with the lowest larval weight obtained at a pH of 7.5. Mean larval weight within the raw stormwater samples was found to be 0.4271 mg which is slightly less than that obtained within the alum treated containers. Larvae maintained within the control chambers experienced substantially less growth weight than found in either the raw stormwater or the alum treated stormwater with a mean dry larval weight of only 0.2625 mg per organism. This value is slightly above the minimum of 0.25 mg necessary for test acceptability as outlined in Table 4-2. It is obvious that alum treatment of stormwater runoff did not affect the viability of the test organisms in the alum treated chambers.

The relationship between survival of fathead minnows and dissolved aluminum levels measured in the short-term biotoxicity tests is given in Figure 5-21. Survival data was obtained for the fathead minnow survival tests from Table 5-26 for each of the test chambers over the 7-day period and combined with concentrations of dissolved

TABLE 5-27

FINAL LARVAL WEIGHT DATA FOR THE FATHEAD
MINNOW LARVAL SURVIVAL AND GROWTH TEST

| TEST CHAMBER | MEAN DRY WEIGHT OF LARVAE (mg) |
|----------------|-----------------------------------|
| Control | 0.2625 |
| Raw Stormwater | 0.4271 |
| pH 6.0 | 0.5377 |
| pH 6.5 | 0.4891 |
| pH 7.0 | 0.5261 |
| pH 7.5 | 0.4667 |

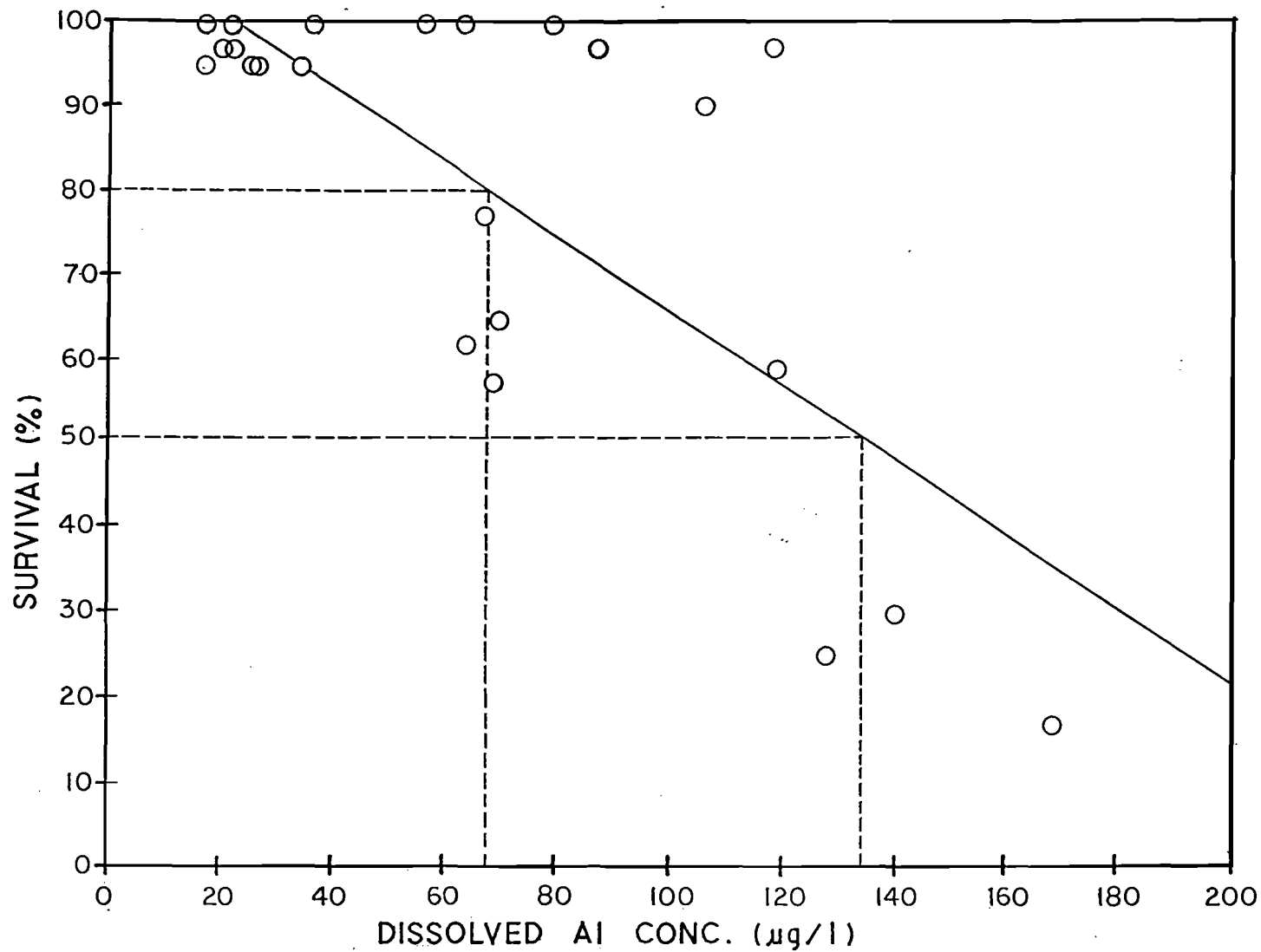


Figure 5-21. Relationship Between Survival of Fathead Minnows and Dissolved Aluminum Levels in Short-Term Chronic Biotoxicity Tests.

aluminum provided in Table 5-25 for each of the test chambers over the same 7-day period. These points are plotted in Figure 5-21. A "best-fit" regression line is shown on the diagram for this relationship.

The information provided in Figure 5-21 shows a clear relationship between aluminum concentrations and larval survival with a high degree of survival at low aluminum concentrations and low survival rates at higher aluminum concentrations. Based upon this relationship, a 50% survival rate occurs at an aluminum level of approximately 136 $\mu\text{g/l}$. An 80% survival rate corresponds to a dissolved aluminum concentration of approximately 66 $\mu\text{g/l}$ which is near the recommended water quality criterion of 87 $\mu\text{g/l}$ established by the U.S. EPA. It is interesting to note that average dissolved aluminum levels within Lake Ella during alum stormwater treatment at a dose of 10 mg/l resulted in an average dissolved aluminum concentration of approximately 44 $\mu\text{g/l}$ which corresponds to a survival rate of approximately 90% for fathead minnow species.

Long-Term Biototoxicity Tests

Long-term bioassay investigations were conducted over a period of 60 days using *Gambusia sp.* as test organisms. A total of four test chambers were used containing moderately hard dilution water as a control, untreated raw stormwater, stormwater coagulated at an alum dose of 15 mg/l and stormwater coagulated at an alum dose of 25 mg/l. Approximately 50% of the water contained within each test chamber was removed every third day and replaced with the appropriate control, raw stormwater or alum treated water. All coagulation and flocculation processes were allowed to occur inside the test chambers and the alum floc accumulated on the bottom of each test chamber. Test organisms were subjected to the combined effects of periodic coagulation processes as well as continuous contact with alum floc.

Measured values of pH and dissolved aluminum in long-term bioassay experiments are given in Table 5-28. pH values in the control and raw stormwater appear to decrease steadily over the 60-day test period, beginning at a pH of approximately 8.0 and ending at pH values between 7.2 and 7.4. pH values in alum treated test chambers maintained average values of approximately 7.4. Concentrations of dissolved aluminum in the control and raw stormwater chambers averaged less than 10 $\mu\text{g/l}$ over the 60-day test period. Average aluminum concentrations of 30 and 34 $\mu\text{g/l}$ were measured within test chamber receiving alum treated stormwater runoff at doses of 15 and 25 mg/l, respectively.

The results of long-term bioassay experiments using *Gambusia sp.* are given in Figure 5-22. Survival rates of *Gambusia sp.* within the raw stormwater as well as stormwater treated with alum at 15 and 25 mg/l exceeds 90% over the 60-day test period. In contrast, mortalities are observed within the control test chamber beginning after about 30 days. It is apparent that the continued exposure to alum from the combined effects of periodic coagulation processes as well as continuous contact with alum floc was not toxic to the *Gambusia sp.* over the 60-day test period. These results are particularly interesting since *Gambusia* are common inhabitants of polluted lakes and stormwater management systems where the use of alum for treatment of stormwater would seem appropriate.

TABLE 5-28

MEASURED VALUES OF pH AND DISSOLVED ALUMINUM IN LONG-TERM BIOASSAY EXPERIMENTS

| DAY | pH VALUES | | | | DISSOLVED Al ($\mu\text{g/l}$) | | | |
|-------------|-----------|----------------|--------------|--------------|----------------------------------|----------------|--------------|--------------|
| | CONTROL | RAW STORMWATER | 15 mg/l ALUM | 25 mg/l ALUM | CONTROL | RAW STORMWATER | 15 mg/l ALUM | 25 mg/l ALUM |
| 0 | 8.01 | 7.97 | 7.26 | 7.15 | - | - | - | - |
| 6 | 7.91 | 7.81 | 7.99 | 8.01 | 3 | 8 | 101 | 161 |
| 12 | 7.46 | 7.71 | 7.59 | 7.65 | 6 | 9 | 21 | 54 |
| 18 | 7.31 | 7.61 | 7.67 | 7.77 | 3 | 9 | 97 | 98 |
| 24 | 7.51 | 7.51 | 7.52 | 7.62 | 4 | 5 | 19 | 30 |
| 30 | 7.32 | 7.59 | 7.37 | 7.33 | 27 | 8 | 34 | 65 |
| 36 | 7.58 | 7.48 | 7.35 | 7.32 | 27 | 12 | 18 | 25 |
| 42 | 7.50 | 7.60 | 7.35 | 7.32 | 4 | 4 | 9 | 9 |
| 48 | 7.33 | 7.35 | 7.24 | 7.25 | 1 | 5 | 8 | 25 |
| 54 | 7.44 | 7.01 | 7.02 | 7.04 | 2 | 4 | 9 | 9 |
| 60 | 7.36 | 7.17 | 7.16 | 7.13 | 2 | 5 | 13 | 12 |
| Avg. Values | 7.52 | 7.53 | 7.41 | 7.42 | 7.2 | 6.3 | 30 | 44 |

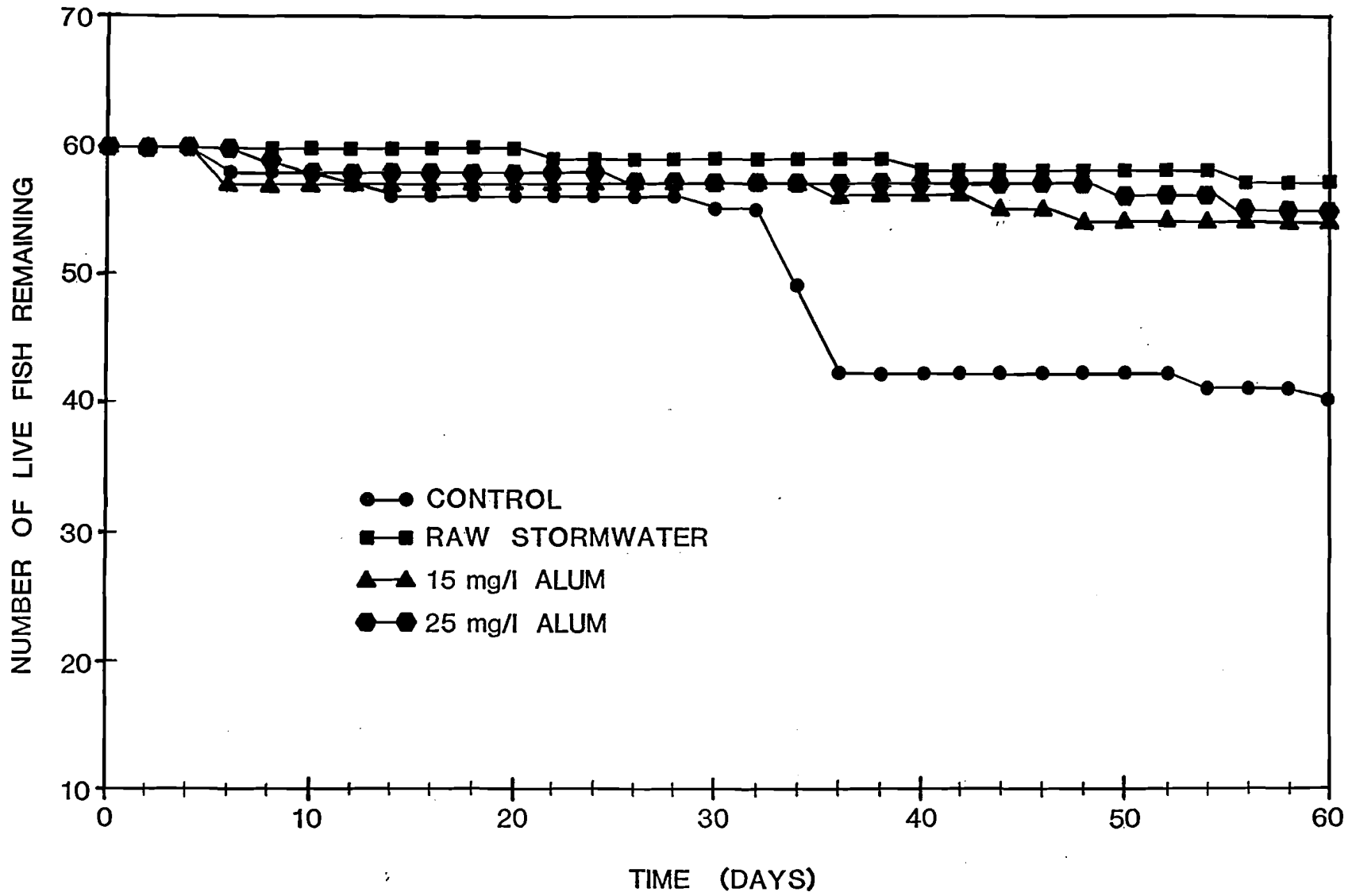


Figure 5-22. Results of Long-Term Bioassay Experiments Using *Gambusia sp.*

CHAPTER 6

SUMMARY AND CONCLUSIONS

Summary

Historical Characteristics of Lake Ella

Lake Ella is a small 5.3 ha (13.29 ac) land-locked lake located in Tallahassee, Florida which receives large quantities of stormwater runoff from a highly urbanized 63.7 ha (157.2 ac) watershed. As a result of continual stormwater loadings, algal productivity in Lake Ella increased substantially during the 1970s and early 1980s. Algal blooms were a frequent and often persistent occurrence. Build-up of flocculant sediment matter increased rapidly, and large masses of algae could be seen floating along the shoreline. Measurements of dissolved oxygen in Lake Ella often indicated super-saturated concentrations near the surface which declined rapidly with increasing depth. At depths below 2 m, dissolved oxygen levels were typically less than 1 mg/l. During the period from 1974-1985, sporadic measurements of water quality in Lake Ella indicated high levels of turbidity, total phosphorus, BOD and extremely high levels of chlorophyll-a. Secchi disk transparency was generally less than 0.5 m on all measurement dates.

Stormwater inputs into Lake Ella during 1984 were found to contain high levels of total nitrogen, comprised primarily of nitrate and organic nitrogen. Concentrations of total phosphorus and orthophosphorus in stormwater inputs were found to be extremely high with a mean total phosphorus concentration of 750 $\mu\text{g/l}$ and orthophosphorus concentration of 490 $\mu\text{g/l}$. Measured values for BOD and suspended solids averaged 25.5 mg/l and 111 mg/l, respectively.

After a detailed watershed analysis and evaluation of restoration alternatives, it was decided that conventional stormwater management techniques such as retention ponds, detention ponds, filtration systems or underground exfiltration systems were not feasible within the Lake Ella watershed due to limitations of available space and soil characteristics. A pilot study was conducted to evaluate the feasibility of using alum to treat stormwater runoff entering Lake Ella. Alum treatment of stormwater in laboratory testing was found to reduce concentrations of total nitrogen by 47%, total phosphorus by 91%, BOD by 42% and suspended solids by 85%. Total coliform and fecal coliform bacteria were reduced by 94% and 91%, respectively.

Description of the Alum Injection System

Based upon the impressive removal efficiencies for stormwater pollutants obtained in laboratory studies using alum, an alum stormwater treatment system was designed for Lake Ella using sonic flow meters and variable speed injection pumps to automatically inject liquid alum into the stormsewer lines upstream of the lake at a flow-proportioned rate. Mixing of the alum and stormwater occurs within the stormsewer line, and the floc produced settles on the lake bottom providing an added benefit of nutrient inactivation in the sediments. Several of the smaller individual stormsewer lines were combined and connected together to consolidate points of discharge into the lake from 18 inlets to 10 inlets. Six of these 10 inlet points, representing 95% of the annual runoff inputs into Lake Ella, were equipped with points of alum injection. The alum is injected into the stormwater flow approximately 30-150 m upstream of the point of discharge into the lake to allow adequate time for mixing of the alum and stormwater flow. Pumps and control devices for the injection system are housed in an above-ground structure with an adjacent 22,700 liter alum storage tank.

Capital construction costs for the alum injection system were approximately \$200,400. Almost 50% of this cost was for the alum injection pumps themselves which cost approximately \$15,000 each. This capital cost is approximately \$3,141/ha (\$1,270/ac) of watershed area treated. In general, the capital costs involved in constructing an alum injection system are relatively independent of watershed size and depend primarily on the number of outfall locations treated.

The alum treatment system for Lake Ella treats approximately 342 ac-ft of runoff each year, representing approximately 95% of the total annual runoff inputs to Lake Ella. This treatment at an alum dose of 10 mg/l requires approximately 10,077 gallons/year of alum at an average annual cost of approximately \$5,039.

In addition to installation of an alum stormwater treatment system, a substantial dredging and recontouring process was also conducted at Lake Ella which removed approximately 38,260 m³ (50,000 yd³) of accumulated sand debris and muck from the bottom of Lake Ella. These activities required draining the lake which exposed approximately 70% of the lake bottom. A peninsula was added to the lake which connected an existing island to the shoreline. This peninsula reduced the surface area of the lake from 5.38 ha (13.3 ac) to 4.77 ha (11.8 ac) which decreased the volume of the lake by approximately 27%.

Construction of the alum injection system and recontouring efforts within Lake Ella were begun in January 1986 and were completed in October 1986. At the completion of work efforts in October, the lake was allowed to refill naturally with stormwater.

The alum stormwater treatment system became operational in January 1987 with the metering pumps set to inject alum at a dose of 20 mg/l as Al₂O₃. Several operational problems were observed during the initial start-up period, some of which caused excess alum to be pumped into the lake, reducing pH levels to unacceptable

levels. Time limiters were installed on the injection pump to limit the amount of time the pumps could operate before being automatically shut off. Reliable operation of the system at a treatment dose of 20 mg/l began in July 1987. During the period from July to December 1987, the lake exhibited excellent water quality characteristics with the exception of pH which fluctuated in value from 4.55 to 6.27. Beginning in January 1988, the alum treatment dose was decreased to 10 mg/l as Al_2O_3 . This reduction in treatment dose resulted in an immediate improvement in lake pH, and produced consistent average pH levels in excess of 6.0 on all measurement dates. The system has continued to be operated at a dose of 10 mg/l since January 1988.

Water Quality Characteristics of Lake Ella Following Alum Treatment of Stormwater

Operation of the alum stormwater treatment system during the period from January 1988 to May 1990 at a dose of 10 mg/l resulted in a mean pH value of approximately 6.43 with a range of values from 6.01-7.12. No indication of thermal or chemical stratification was observed within the lake on any field measurement date. Measurements of dissolved oxygen averaged 7.4 mg/l with a minimum level of 5.4 mg/l. Differences in dissolved oxygen concentrations from the water surface to the bottom were less than 1 mg/l. Measured values of alkalinity within Lake Ella were relatively low with a mean of 11.0 mg/l.

Measured concentrations of nitrogen species were extremely low within Lake Ella from 1988 to 1990 which mean concentrations of ammonia and nitrate averaging only 14 $\mu\text{g/l}$ and 43 $\mu\text{g/l}$, respectively. Measured concentrations of all phosphorus species were also extremely low within Lake Ella. The mean orthophosphorus concentration within the lake was approximately 2 $\mu\text{g/l}$ which is a level near or below minimum concentrations necessary for algal uptake. The dominant phosphorus forms within Lake Ella were dissolved organic phosphorus and particulate phosphorus,

constituting 92% of the mean total phosphorus value of 26 $\mu\text{g}/\text{l}$. Measured concentrations of chlorophyll-a exhibited a range of values from 1.5 mg/m^3 to 12.2 mg/m^3 with a mean of 5.1 mg/m^3 . Water clarity within the lake was excellent on all measurement dates with a mean Secchi disk depth in excess of 2.2 m.

Alum treatment of stormwater entering Lake Ella at a dose of 10 mg/l from January 1988 to May 1990 reduced historical concentrations of turbidity by 89%, ammonia by 95%, nitrate by 14%, organic nitrogen by 77%, total nitrogen by 78%, orthophosphorus by 91%, total phosphorus by 89%, chlorophyll-a by 97% and BOD by 93%. Secchi disk measurement increased more than 340% from a value of less than 0.5 m to a mean in excess of 2.2 m at all sample locations. However, in response to improved conditions of water clarity, the growth of rooted macrophytes has increased rapidly within the lake. This growth first appeared in 1987, but by the spring of 1990 had extended to all shoreline areas and many of the deeper areas within the lake. Grass carp were introduced in 1990 in an attempt to achieve long-term control of rooted macrophytes within the lake.

Measured concentrations of all heavy metals are extremely low within Lake Ella, with mean concentrations of cadmium and chromium less than 1 $\mu\text{g}/\text{l}$ and mean concentrations of copper and lead less than 5 $\mu\text{g}/\text{l}$. Concentrations of all heavy metals were found to be substantially less than the State of Florida Class III criteria for recreational surface waters. Measured concentrations of aluminum within Lake Ella with alum stormwater treatment at a dose of 10 mg/l are also low, with an average dissolved aluminum concentration of 44 $\mu\text{g}/\text{l}$ and a range of values from 6 $\mu\text{g}/\text{l}$ to 108 $\mu\text{g}/\text{l}$. Water column concentrations of dissolved aluminum appear to be highly correlated with pH levels within the lake. Dissolved aluminum levels within Lake Ella remained below the U.S. EPA recommended criterion of 87 $\mu\text{g}/\text{l}$ for dissolved aluminum when pH values remained between approximately 5.9 and 7.0. Dissolved

aluminum concentrations at pH values less than 5.9 and in excess of 7.0 were found to be greater than the 87 $\mu\text{g/l}$ criterion.

Alum treatment of stormwater runoff in Lake Ella resulted in a dramatic alteration of the trophic state conditions within the lake. Under pre-modification conditions, Lake Ella exhibited a Florida Trophic State Index value for total phosphorus of approximately 105 and a value of 92 for chlorophyll-a, indicating hypereutrophic conditions. Under post-modification conditions, trophic state indices for total phosphorus and chlorophyll-a were reduced to 53 and 40, respectively, indicating oligotrophic conditions within the lake.

Effects of Alum Stormwater Treatment on Benthic Populations

Benthic surveys were conducted in Lake Ella on three separate occasions: (1) immediately prior to initiation of the draining and construction activities for installation of the alum stormwater treatment system; (2) at the completion of construction of the alum stormwater treatment system after the lake had been refilled for approximately 3-4 months; and (3) after approximately three years of operation of the alum stormwater treatment system. Benthic surveys conducted prior to construction activities and at the completion of construction activities after the lake had refilled did not indicate the presence of any viable organisms at any of the eight monitoring locations within the lake. The benthic survey conducted after three years of alum treatment system operation indicated viable organisms of *Tubifex sp.* and leeches at six of the eight monitoring locations within the lake, although at relatively low population densities. The existence of these populations after three years of continuous alum applications to Lake Ella indicates that, at least for the species found, the existence of alum precipitate within the sediments is not incompatible with the environmental requirements of these species.

Accumulation and Migration of Heavy Metals in Lake Ella Sediments

Sediment core samples were collected at four locations within Lake Ella to evaluate metal accumulation and migration as a result of the alum treatment process. An initial set of core samples was collected on February 21, 1987, coinciding with the start-up of the alum treatment system. A second set of core samples was collected on November 11, 1988, after almost two years of operation of the alum stormwater treatment system. Sediment concentrations of moisture content, organic content and phosphorus are greater in core samples collected on the 1988 date than those collected on the 1987 date. For moisture and organic content, increased sediment concentrations are limited to the top 10-15 cm with concentrations below this depth relatively similar between the two collection dates.

There appears to be little difference in sediment retention characteristics of either total nitrogen or total phosphorus between pre- and post-treatment sediment cores. The general pattern of highest concentrations near the sediment surface and decreasing concentrations at lower sediment depths appears to be virtually identical in sediment samples collected on each of the two dates. Introduction of alum into the sediment has not substantially altered the accumulation or sediment retention characteristics of either nitrogen or phosphorus.

Measured values of sediment pH were found to be slightly less in post-treatment sediments than in pre-treatment sediments. Decreases in sediment pH values ranged from approximately 0.5 to 0.20 pH units, depending upon the particular sediment layer. Differences in sediment pH appear to diminish in the 15-25 cm layer with approximately equal sediment pH values in this layer for both pre- and post-treatment conditions. Sediment pH levels in the 0-1 cm layer increased slightly in areas of Lake Ella which exhibited the highest accumulation of alum floc.

Sediment concentrations of aluminum, copper and zinc appear to increase slightly in the upper sediment layer in post-treatment sediment core samples. In contrast, sediment concentrations of iron appear to be relatively unchanged between the two collection dates. For those elements which exhibited increased concentrations in post-treatment sediments, the increased concentration levels are limited to sediment depths of 5 cm or less. Increased sediment concentrations of zinc extended only 1 cm deep. Sediment concentrations of lead were relatively unchanged between the two collection dates.

Sediment concentrations of aluminum increased by 7.3% in the 0-1 cm layer and 3.9% in the 1-5 cm layer during the two-year period between collection of core samples. Measured increases in aluminum sediment concentrations do not appear to extend below a depth of 5 cm. This pattern suggests that alum floc produced during the treatment of stormwater runoff is accumulating within the sediments of Lake Ella to depths of 5 cm or less. Increases in sediment aluminum concentrations within the northeast lobe, which was contoured as a sump area for accumulation of alum floc deposits, suggests that the area is functioning as a sediment sump as designed. Sediment concentrations of copper, zinc and lead have increased in this region of the lake, while concentrations of heavy metals in the center of the lake are relatively similar in pre- and post-treatment sediments. Since alum is extremely effective in removing both dissolved and particulate forms of heavy metal inputs in stormwater runoff, the deposition of heavy metals into the sediments of Lake Ella may be greater as a result of the alum treatment system than under pre-treatment conditions.

Speciation of Heavy Metals and Phosphorus in Lake Ella Sediments

A speciation procedure was conducted on composite sediment samples from pre-and post-treatment sediments to identify and quantify sediment metal associations

with the following five fractions: (1) soluble ions; (2) metals bound through exchange reactions; (3) metals bound with precipitates of iron and manganese oxide; (4) metals bound as precipitates with carbonates; and (5) metals bound in associations with organic matter. It is generally believed that the stability of metal sediment associations increases in the following order: soluble < exchangeable < bound to carbonate < bound to Fe/Mn oxide < bound to organic matter.

Soluble fractions of aluminum, copper, zinc and phosphorus were found to decrease substantially in post-treatment sediments compared with pre-treatment sediments. In contrast, soluble fractions of iron and lead were found to increase slightly in post-treatment sediments. Increased associations with exchange fractions in post-treatment sediments is observed for copper, iron and lead, while exchange fractions of aluminum, zinc and phosphorus remained relatively unchanged. Nevertheless, the dominant bonding mechanism for heavy metals in the sediments remains unchanged between pre- and post-treatment conditions. Associations with Fe/Mn oxides represents the dominant bonding mechanism for aluminum, iron, lead and zinc under both pre- and post-treatment conditions. Decreased associations with soluble fractions observed for many of the heavy metals under post-treatment conditions is accompanied by an increase in associations with organic matter for many of the same heavy metals. This change in speciation indicates a shift in bonding mechanism from less stable soluble associations to more stable organic sediment associations. This suggests that metal associations with post-treatment sediments may be more stable than associations found under pre-treatment sediments.

Speciation of Sediment Phosphorus

Fractionation of inorganic soil phosphate was conducted on both pre- and post-alum treatment sediment samples for each of the four sample locations and each of

the five sediment depth layers using the modified Chang and Jackson speciation procedure which divides phosphorus associations into soluble, aluminum phosphate, iron phosphate, reductant soluble phosphate, and calcium phosphate bonding mechanisms.

Concentrations of soluble phosphorus in post-treatment sediments was found to be lower than that observed in pre-treatment sediments. Substantial reductions in phosphorus associations with iron phosphate were also observed in post-treatment sediments, while slight increases were observed in the degree of associations with aluminum phosphate. Evaluation of changes in phosphorus speciation with increasing sediment depth indicates that the effects of alum floc within the sediment has altered sediment phosphorus associations as deep as 15-25 cm within the sediments, although alterations in sediment phosphorus fractions are most apparent in the top 10 cm of the sediments.

The reduction in soluble phosphorus associations and iron phosphorus associations, combined with an increase in aluminum phosphorus association, suggests that phosphorus associations in post-treatment sediment are substantially more stable than phosphorus associations in pre-treatment sediments. These alterations in phosphorus speciation suggest that phosphorus is much less likely to be released from post-treatment sediments under either oxidized or reduced conditions than that which occurs with pre-treatment sediments. Post-treatment phosphorus in the sediments of Lake Ella appears to be substantially less available and more tightly bound following installation of the alum treatment system than existed within the sediments before introduction of this system.

Influence of pH and Redox Potential on the Stability of Heavy Metals in Alum Treated Sediments

A series of experiments were conducted to evaluate the influence of pH and redox potential on the stability of heavy metals in alum treated sediments. Three separate experiments were conducted at redox potentials of -200 mv (highly reduced), 0 mv (reduced), +200 mv (slightly reduced) and +400 mv (oxidized) and at pH conditions ranging from 5.0 to 7.0. With the exception of iron, the release of heavy metals in phosphorus from Lake Ella alum sludge was extremely low at all values of redox potential, ranging from highly reduced to oxidized and at pH values ranging from 5.0 to 7.0. The release of phosphorus, cadmium, copper, chromium, nickel, lead and zinc is substantially less than 1 $\mu\text{g/g}$ of sediment material under this wide range of environmental conditions. The release of aluminum is less than 1 $\mu\text{g/g}$ of sediment material at pH values of 6.0 and 7.0, but increases to approximately 4-7 $\mu\text{g/g}$ at a pH value of 5.0.

The results of these incubation experiments presents strong evidence that each of the heavy metals tested, with the possible exception of iron, are extremely stable and bound in tight associations with the sediments and the alum sludge. Almost without exception, release rates measured during these experiments using alum sludge are substantially less than the release rates for the same metal species reported by Harper (1985) using a similar incubation apparatus to incubate sediments under similar conditions from a detention pond receiving highway runoff. This pond, located along I-4 north of Orlando, had been receiving highway runoff for approximately 8-10 years at the time of collection of sediments for use in incubation experiments. This comparison suggests that, even though Lake Ella is receiving periodic inputs of alum floc, the stability of aluminum and heavy metals within the sediments has increased. The presence of alum floc within the sediments of Lake Ella appears to substantially enhance the ability of the sediments to retain both heavy metals and phosphorus

compared with sediments from a highway detention pond which does not receive alum treatment. The release of copper, zinc, lead, nickel, chromium and cadmium from Lake Ella sediments under redox conditions ranging from highly reduced to oxidized and at pH levels ranging from 5.0 to 7.0 was found to be extremely small, indicating stable sediment associations under a wide range of environmental conditions.

Estimates of Floc Accumulation in Lake Ella

Estimates of floc accumulation in Lake Ella were conducted on May 25, 1990 at each of the four sample locations used for collection of water quality samples. Visible grayish-white surface floc layers were found at three of the four sample locations, with the surface floc layer comprised of discrete floc particles rather than a smooth uniform layer. Penetration of the floc into the pre-existing sediments was visible, extending down to a depth of approximately 5 cm, in virtually all core samples collected. This suggests that the floc material is mixing with the existing material within the lake rather than accumulating as a distinct surface layer. No visible floc layer was found in the northeast lobe, designed as a sump for floc material, although core samples collected at this location indicated the highest levels of aluminum content within the lake. Apparently, the sediment material at this location, which is very fine and soupy in texture, allows the alum precipitate to penetrate into the sediments rather than accumulating as a distinct surface layer.

The average floc accumulation at the three locations where visible surface layers was observed is approximately 1.4 cm over the three-year operational period. This corresponds to an average accumulation rate of 0.5 cm/yr which is approximate half of the accumulation rate which was originally estimated for Lake Ella based upon laboratory jar tests conducted during the design of the alum treatment system. Mixing of the floc layer with the existing sediment is apparently responsible for the decreased

accumulation rate of a surface alum layer. Based upon an average accumulation rate of approximately 0.5 cm/yr, as long as 25-30 years may be required to accumulate a 15 cm layer of alum floc within Lake Ella.

Sludge Production

Investigations were conducted to evaluate the production of alum sludge at various alum treatment doses by coagulation of urban stormwater collected from a watershed in Orlando. Stormwater samples were treated with a variety of alum doses including 10, 15, 20, 25 and 30 mg/l as Al_2O_3 to evaluate sludge production at typical stormwater treatment dosage rates. Sludge production constitutes a relatively small portion of the treated runoff flow with a sludge volume of approximately 0.2% at an alum dose of 15 mg/l. Sludge production increases to approximately 0.69% at an alum dose of 30 mg/l in a non-linear relationship. More complete production of alum sludge and corresponding greater removal efficiencies for suspended solids and turbidity are responsible for the non-linear relationship between floc production and treatment dose. However, due to the mixing of alum floc with existing sediments, the actual observed sludge production within a waterbody receiving alum treatment would be substantially less than the relationships generated during these laboratory studies.

Sludge Disposal

Sludge drying and leachate investigations were conducted to evaluate potential disposal methods which could be used for ultimate disposal of the alum sludge. Composite sludge samples were placed onto a drying bed and the characteristics of the leachate were monitored continuously at the filter underdrain. Alum sludge leachate was found to be approximately neutral in pH with low levels of both total nitrogen and total phosphorus. Concentrations of aluminum within the leachate are extremely low

with a mean dissolved aluminum concentration of 23 $\mu\text{g}/\text{l}$. Low levels of all heavy metals are also found in the leachate flow with concentrations substantially less than surface water standards for Class III waters.

Dried alum sludge was found to have chemical characteristics similar to that of a Grade 1 domestic wastewater sludge with relatively low values of nitrogen, phosphorus and potassium as well as heavy metals. Based upon this analysis, dried alum sludge could potentially be disposed of on sod farms, pasturelands, forests, highway shoulders, nurseries and land reclamation projects. Although regulatory restrictions allow the use of alum sludge in agricultural and sod farm applications, alum sludge would probably not make a good agricultural soil material due to the fact that phosphorus is tightly bound to aluminum is largely unavailable by release and uptake by plant species. This characteristic may be a benefit in lake systems for limiting the growth of aquatic vegetation in deeper portions of the lake after improvements in water clarity resulting from the alum treatment process.

Rate Experiments

Laboratory experiments were conducted to examine the rate of changes in aluminum speciation during the coagulation process. Upon addition of alum to stormwater runoff, monomeric aluminum species quickly incorporate into a microscopic precipitate form of aluminum hydroxide. After approximately 60 seconds, dissolved monomeric aluminum concentrations are reduced to approximately 50-100 $\mu\text{g}/\text{l}$. It appears that a safe design parameter for use in evaluating alum injection systems is to design the point of addition of alum into the stormwater flow so that a minimum travel time of 60 seconds can be achieved prior to discharge into the receiving waterbody. This length of time will allow adequate mixing of the alum and stormwater flow and reduce dissolved aluminum concentrations to non-toxic levels.

Bioassay and Toxicity Testing

Short-term and long-term bioassay experiments were conducted to evaluate the potential toxicity of alum treated runoff on selected species of fish. The first series of experiments were conducted using fathead minnows (*Pimephales promelas*) in the standard EPA Seven-Day Chronic Larval Survival and Growth Test. A second set of experiments were conducted as long-term bioassay tests using *Gambusia sp.* as test organisms.

No chronic toxicity was found with alum treated stormwater in short-term fathead minnow tests at pH levels of 6.0 and 6.5. Chronic biotoxicity was found to increase at a pH level of 7.0, but toxicity of the alum treated runoff was substantially less than the raw stormwater itself. Mortalities increased substantially in alum treated runoff at a pH level of 7.5, presumably due to increased dissolved aluminum concentrations at this level. These results suggest that alum stormwater treatment systems should be designed to maintain pH levels in the treated flow at values between 6.0 and 7.0, preferably in the range of 6.0 to 6.5.

A clear relationship was observed between aluminum concentrations and fathead minnow larval survival with good survival rates at low aluminum concentrations and low survival rates at higher aluminum concentrations. An 80% survival rate in these experiments corresponds to a dissolved aluminum concentration of approximately 66 $\mu\text{g/l}$ which is near the recommended water quality criterion of 87 $\mu\text{g/l}$ established by the U.S. EPA.

Long-term bioassay experiments using *Gambusia sp.* were conducted using four test chambers designated as: (1) control; (2) untreated raw stormwater; and stormwater coagulated at alum dose rates of (3) 15 and (4) 25 mg/l. In test chambers receiving alum treatment, all coagulation and flocculation processes were allowed to occur inside the test chambers with the alum floc accumulating on the bottom of the chamber. Test

organisms were subjected to the combined effects of periodic coagulation processes as well as continuous contact with alum floc.

Survival rates of *Gambusia sp.* within the raw stormwater as well as stormwater treated with alum at 15 and 25 mg/l exceeded 90% over the 60-day test period. Continued exposure to alum from the combined effects of periodic coagulation processes as well as continuous contact with alum floc was not toxic to *Gambusia sp.* over the 60-day test period.

Conclusions

From the results obtained in these investigations, the following specific conclusions were reached:

1. Operation of the Lake Ella stormwater treatment system at a dose of 10 mg/l resulted in stable pH levels within the lake with a mean of approximately 6.43 and a range of values from 6.01-7.12. No indication of thermal or chemical stratification was observed within the lake in field measurements on any measurement date. Measurements of dissolved oxygen were relatively uniform through the water column with an average value of 7.4 mg/l and a minimum of 5.4 mg/l.

2. Operation of the alum stormwater treatment system resulted in extremely low levels of total nitrogen, total phosphorus and chlorophyll-a within Lake Ella. Water clarity within the lake averaged more than 2.2 m. Historical concentrations of turbidity within Lake Ella were reduced by 89%, ammonia by 95%, nitrate by 14%, organic nitrogen by 77%, total nitrogen by 78%, orthophosphorus by 91%, total phosphorus by 89%, chlorophyll-a by 97% and BOD by 93%. Secchi disk measurements increased more than 340%. Calculations of Florida Trophic State Indices for pre- and post-treatment conditions within Lake Ella indicate a change in trophic state from hypereutrophic to oligotrophic conditions.

3. Measured concentrations of all heavy metals are extremely low within Lake Ella with mean concentrations of cadmium and chromium less than 1 $\mu\text{g/l}$ and mean concentrations of copper and lead less than 5 $\mu\text{g/l}$. Concentrations of all heavy metals are substantially less than the State of Florida Class III criteria for recreational waters.

4. Measured concentrations of aluminum in Lake Ella with alum stormwater treatment at a dose of 10 mg/l are extremely low. The average dissolved aluminum concentration within the lake is 44 $\mu\text{g/l}$ with a range of values from 6-108 $\mu\text{g/l}$. A strong relationship appears to exist between concentrations of dissolved aluminum and pH levels within the lake. Average lake pH values between 5.9 and 7.0 resulted in dissolved aluminum concentrations less than the EPA recommended criterion of 87 $\mu\text{g/l}$. Increases in dissolved aluminum concentrations were observed at pH values below and above this range.

5. A benthic survey conducted after three years of alum system operation found viable organisms of *Tubifex sp.* and leeches at six of the eight sampling locations within the lake. No viable benthic organisms were found in surveys conducted prior to dredging and restoration activities as well as a benthic survey conducted immediately prior to start-up of the alum treatment system.

6. Slight increases were observed in sediment concentrations of total phosphorus, total nitrogen, and heavy metals in post-treatment sediments compared with pre-treatment sediments. Increased sediment concentrations of heavy metals appear to be limited to sediment depths of 5 cm or less. Patterns of sediment metal concentrations suggests that inputs of alum sludge are having no effect on overall patterns of accumulation or sediment retention for either heavy metals or phosphorus.

7. Inputs of alum sludge into the sediments have resulted in decreases in sediment pH ranging from approximately 0.5 to 0.20 pH units with an average

post-treatment sediment pH value in the 0-1 cm layer of approximately 5.97. Differences in sediment pH appear to diminish in the 15-25 cm layer with approximately equal sediment pH values in this layer for both pre- and post-treatment conditions.

8. Sediment concentrations of aluminum have increased by only 7.3% in the 0-1 cm layer and 3.9% in the 1-5 cm layer during the two-year operation of the alum treatment system. Increased aluminum concentrations within the sediments do not appear to extend below a depth of 5 cm.

9. With the exceptions of iron and lead, heavy metals and phosphorus were found to have decreased associations with soluble fractions accompanied by an increase in associations with organic matter in post-treatment sediments compared with pre-treatment sediments. This change in speciation indicates a shift in bonding mechanism for these metals from less stable soluble associations to more stable organic sediment associations. These results suggest that metal associations with post-treatment sediments may be more stable than associations found under pre-treatment conditions.

10. Phosphorus associations as soluble phosphorus and iron phosphate are substantially reduced in post-treatment sediments along with a corresponding increase in bonding with aluminum phosphate within the sediments. Phosphorus associations in post-treatment sediments appear to be more stable than in pre-treatment sediments as a result of transformation from soluble and iron phosphate forms to one dominated by aluminum phosphate forms.

11. With the exception of iron, the release of phosphorus and heavy metals from alum treated sediments was found to be less than 1 $\mu\text{g/g}$ of dry sediment under redox conditions ranging from highly reduced to oxidized and at pH levels from 5.0 to 7.0 in laboratory incubation experiments. These release rates are substantially less than those observed in a similar series of experiments using sediments collected from a

highway detention pond. The introduction of alum into the sediments has apparently increased the bonding of heavy metals and phosphorus within the sediments over that exhibited by non-alum treated sediments.

12. Aluminum appears to be tightly bound in alum treated sediments under both reduced and oxidized conditions and at pH levels ranging from 5.0 to 7.0. The release of aluminum from alum treated sediments appears to be relatively unaffected by changes in redox potential within the sediment.

13. A portion of the alum floc deposited onto the sediment surface appears to be mixing with the existing sediment to a depth of approximately 5 cm. The remainder of the alum floc is apparently accumulating as a surface layer at a rate of approximately 0.5 cm/yr within Lake Ella. This measured accumulation rate is approximately half of the rate estimated in laboratory jar tests.

14. The production of alum sludge at a treatment dose of 10 mg/l constitutes less than 0.2% of the treated runoff volume. The relationship between sludge production and alum dose is non-linear due to a more complete production of alum floc and removal of particulate matter at higher treatment doses.

15. Leachate from alum sludge is characterized by extremely low levels of nitrogen, phosphorus and heavy metals, including aluminum. Chemical characteristics of dried alum sludge are similar to Grade 1 domestic wastewater sludge which can be disposed of in areas with unrestricted public access.

16. After addition of alum to a wastewater flow, dissolved aluminum ions are rapidly incorporated into microscopic aluminum hydroxide precipitate. After approximately 60 seconds, monomeric dissolved aluminum concentrations are reduced to values of approximately 50-100 $\mu\text{g/l}$.

17. No chronic toxicity was observed to fathead minnows with alum treated stormwater runoff when pH levels of 6.0 and 6.5 are maintained. Chronic biotoxicity increases at a pH of 7.0 but is less toxic than the raw stormwater itself.

18. Continued exposure to alum from the combined effects of periodic coagulation processes as well as continuous contact with alum floc was not toxic to *Gambusia sp.* over a 60-day test period.

REFERENCES

- Baker, J.P., and C.L. Schofield. 1982. Aluminum toxicity to fish in acidic waters. Water Air Soil Pollut., 18, 289-309.
- Bartlett, R.J., and D.L. Riego. 1972. Effect of chelation on the toxicity of aluminum. Plant Soil, 37, 419-423.
- Benjamin, M.M., and J.O. Leckie. 1980. Adsorption of metals at oxide interfaces: Effects of the concentrations of adsorbate and competing metals. In R.A. Baker (Ed.), Contaminants and Sediments, Vol. 2. Ann Arbor, MI: Ann Arbor Science.
- Bertsch, P.M. 1989. Aqueous polynuclear aluminum species. In G. Sposito (Ed.), The Environmental Chemistry of Aluminum, pp. 85-117. Boca Raton, FL: CRC Press, Inc.
- Biesinger, K.E., and G.M. Christensen. 1972. Effects of various metals on survival, growth, reproduction and metabolism of *Daphnia magna*. J. Fish. Res. Board Can., 29, 1691-1700.
- Bloom, P.R. 1983. The kinetics of gibbsite dissolution in nitric acid. Soil Sci. Soc. Am. J., 47, 164-168.
- Bohn, H.L., B.L. McNeal, and G.A. O'Connor. 1985. Soil Chemistry, 2nd ed. New York: Wiley-Interscience.
- Bolan, N.S., N.J. Barrow, and A.M. Posner. 1985. Describing the effect of time on sorption of phosphate by iron and aluminum hydroxides. J. Soil Sci., 36, 187.
- Booth, C.E., D.G. McDonald, B.P. Simons, and C.M. Wood. 1988. Effects of aluminum and low pH on net ion fluxes and ion balance in the brook trout (*Salvelinus fontinalis*). Can J. Fish. Aquat. Sci., 45 (9), 1563-1574.
- Boyd, C.E. 1979. Aluminum sulfate (alum) for precipitating clay turbidity from fish ponds. Trans. Am. Fish. Soc., 108, 307-313.
- Brooke, L. 1985. University of Wisconsin-Superior, Superior, WI. (Memorandum to C. Stephan, US EPA, Duluth, MN, July 25).
- Brown, D.J.A. 1983. The effect of calcium and aluminum concentrations on the survival of brown trout (*Salmo trutta*) at low pH. Bull. Environ. Contam. Toxicol., 30, 582-587.

- Buckler, D.R., P.M. Mehrle, L. Cleveland, and F.J. Dwyer. 1989. Manuscript. Influence of pH on the toxicity of aluminum and other inorganic contaminants to east coast striped bass. Columbia National Fisheries Research Laboratory, Columbia, MO.
- Buergel, P.M., and R.A. Soltero. 1983. The distribution and accumulation of aluminum in rainbow trout following whole-lake alum treatment. J. Freshwater Ecol., 2, 37-44.
- Bulson, P.C., D.L. Johnstone, H.L. Gibbons, and W.H. Funk. 1984. Removal and inactivation of bacteria during alum treatment of a lake. Appl. Environ. Microbiol., 48 (2), 425-430.
- Burrows, W.C. 1977. Aquatic aluminum: chemistry, toxicology, and environmental prevalence. CRC Crit. Rev. Environ. Control. 7, 167-216.
- Call, D.J. 1984. University of Wisconsin-Superior, Superior, WI. (Memorandum to C. Stephan, U.S. EPA, Duluth, MN, November 27). In F. Grostomski, The Toxicity of Aluminum to Aquatic Species in the United States, EPA.
- Chang, S.C., and M.L. Jackson. 1957. Fractionation of soil phosphorus. Soil Sci., 84, 133-144.
- Chen, Y.S.R., J.N. Butler and W. Stumm. 1973. Kinetic study of phosphate reaction with aluminum oxide and kaolinite. Environ. Sci. Technol., 7, 327.
- Cleveland, L., E.E. Little, R.H. Wiedmeyer, and D.R. Buckler. 1989. Chronic no-observed-effect concentrations of aluminum for brook trout exposed in low-calcium, dilute acidic water. In T.E. Lewis (Ed.), Environmental Chemistry and Toxicology of Aluminum, pp. 229-246. Chelsea, MI: Lewis Publishers, Inc.
- Cooke, G.D., and R.H. Kennedy. 1981. Precipitation and Inactivation of Phosphorus as a Lake Restoration Technique, EPA-600/3-81-012.
- Cooke, G.D., E.B. Welch, S.A. Peterson, and P.R. Newroth. 1986. Lake and Reservoir Restoration. Stoneham, MA: Butterworth Publishers.
- Davis, J.A. and J.D. Hem. 1989. The surface chemistry of aluminum oxides and hydroxides. In G. Sposito (Ed.), The Environmental Chemistry of Aluminum, pp. 185-219. Boca Raton, FL: CRC Press, Inc.
- Davis J.A. and J.O. Leckie. 1980. Surface ionization and complexation at the oxide/water interface. III. adsorption of anions. J. Colloid. Interface Sci., 74, 32.
- Decker, C. and R. Menendez. 1974. Acute toxicity of iron and aluminum to brook trout. Proc. W. Va. Acad. Sci., 46, 159-167.
- Detrich, D., and C. Schlatter. 1989. Aluminum toxicity to rainbow trout at low pH. Aquatic Toxicology, 15 (3), 197-212.

- Dominie, D.R., II. 1980. Hypolimnetic aluminum treatment of softwater Annabessacook Lake. In Restoration of Lakes and Inland Waters, pp. 417-423. EPA-440/5-81-010.
- Driscoll, C.T., J. Baker, J. Bisogni, and C. Schofield. 1980. Effects of aluminum speciation on fish in dilute, acidified waters. Nature (Lond.), 284, 161-164.
- Dugger, D.L., J.H. Stanton, B.N. Irby, B.L. McConnel, W.W. Cummings and R.W. Maatman. 1964. The exchange of twenty metal ions with weakly acidic silanol group of silica gel. J. Phys. Chem., 68, 757.
- Eisenreich, S.J., D.E. Armstrong, and R.F. Harris. 1977. A Chemical Investigation of Phosphorus Removal in Lakes by Aluminum Hydroxide. Tech. Rept. 77-02. Madison, WI: Water Resources Center, University of Wisconsin.
- Everhart, W.H., and R.A. Freeman. 1973. Effects of Chemical Variations in Aquatic Environments, Vol. II. Toxic Effects of Aqueous Aluminum to Rainbow Trout. EPA-R3-73-011b.
- Fiat, D. and R.E. Connick. 1968. Oxygen-17 magnetic resonance studies of ion solution. The hydration of aluminum (III) and gallium (III) ions. J. Amer. Chem. Soc., 90, 608-615.
- Foy, C.D. 1974. Effects of aluminum on plant growth. In E.W. Carson (Ed.), The Plant Root and its Environment, pp. 601-642. Charlottesville, VA: University Press of Virginia.
- Garrison, P.J., and D.J. Knauer. 1984. Long-term evaluation of three alum treated lakes. In Lake and Reservoir Management, pp. 513-517. EPA 440/5-84-001.
- Gasperino, A.F., M.A. Beckwith, G.R. Keizur, R.A. Soltero, D.G. Nichols, and J.M. Mires. 1980. Medical Lake improvement project: Success story. In Restoration of Lakes and Inland Waters, pp. 424-428. EPA-440/5-81-010.
- Gunn, J.M., and D.L.G. Noakes. 1987. Latent effects of pulse exposure to aluminum and low pH on size, ionic composition, and feeding efficiency of lake trout (*Salvelinus namaycush*) alevins. Can. J. Fish. Aquat. Sci., 44, 1418-1424.
- Hall, R.J., C.T. Driscoll, G.E. Likens and J.M. Pratt. 1985. Physical, chemical and biological consequences of episodic aluminum additions to a stream. Limnol. Oceanogr., 30, 212-220.
- Harper, H.H. 1985. Fate of Heavy Metals in Stormwater Management Systems. Ph.D. Dissertation, University of Central Florida, Orlando, FL.
- Harper, H.H., Y.A. Yousef, and M.P. Wanielista. 1979. Fate of heavy metals in stormwater management systems. In Proceedings of the Third Annual Conference: Lake and Reservoir Management. EPA 440/5/84-001.
- Hartwell, B.L., and F.R. Pember. 1918. The presence of aluminum as a reason for the difference in the effect of so-called acid soil on barley and rye. Soil Sci., 6 (4), 259-279.

- Havas, M. 1985. Aluminum bioaccumulation and toxicity to *Daphnia magna* in soft water at low pH. Can. J. Fish. Aquat. Sci., 42, 1741-1748.
- Helliwell, S., G.E. Batley, T.M. Florence, and B.G. Lumsden. 1983. Speciation and toxicity of aluminum in a model fresh water. Environ. Technol. Lett., 4, 141-144.
- Hem, J.D. 1986. Geochemistry and aqueous chemistry of aluminum. In J.W. Coburn and A.C. Alfrey (Eds.), Kidney International, p. 29. New York: Springer-Verlag.
- Hem, J.D. and C.E. Roberson. 1967. Form and stability of aluminum hydroxide complexes in dilute solutions. U.S. Geol. Surv. Water-Supply Pap., 1927-A.
- Hingston, F.L., A.M. Posner, and J.P. Quirk. 1971. Competitive adsorption of negatively charged ligands on oxide surfaces. Discuss. Faraday. Soc., 52, 334.
- Hingston, F.L., A.M. Posner, and J.P. Quirk. 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. J. Soil Sci., 23, 177.
- Hingston, F.L., A.M. Posner, and J.P. Quirk. 1974. Anion adsorption by goethite and gibbsite. II. Description of anions from hydrous surfaces. J. Soil Sci., 25, 16.
- Hsu, P.H. 1988. Aluminum hydroxides and oxyhydroxides. In J.B. Dixon and S.B. Weed (Eds.), Minerals in Soil Environments, 2nd ed. Madison, WI: Soil Science Society of America.
- Hsu, P.H., and T.F. Bates. 1964. Formation of X-ray amorphous and crystalline aluminum hydroxides. Mineral Mag., 33, 749.
- Huang, C.P. 1975. Adsorption of phosphate at the hydrous - Al₂O₃ electrolyte interface. J. Colloid Interface Sci., 53, 178.
- Huang, C.P., and W. Stumm. 1973. Specific adsorption of cations on hydrous gamma-Al₂O₃. J. Colloid. Interface Sci., 43, 409.
- Hue, N.V., G.R. Craddock, and F. Adams. 1986. Effects of organic acids on aluminum toxicity in subsoils. Soil Sci. Soc. Am. J., 50, 28-34.
- Hutchison, J.R., and J.B. Sprague. 1986. Toxicity of trace metal mixtures to American flagfish (*Jordanella floridae*) in soft, acidic water and implications for cultural acidification. Can. J. Fish. Aquat. Sci., 43, 647-655.
- Jernelov, A. 1970. Phosphate Reduction in Lakes by Precipitation with Aluminum Sulfate. 5th International Water Pollution Research Conference. New York: Pergamon Press.
- Johnson, N.M., C.T. Driscoll, J.S. Eaton, G.E. Likens, and W.H. McDowell. 1981. "Acid rain" dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. Geochim. Cosmochim. Acta., 45, 1421-1437.

- Kane, D.A., and C.F. Rabeni. 1987. Water Res., 21, 633.
- Kennedy, R.H. 1978. Nutrient Inactivation with Aluminum Sulfate as a Lake Reclamation Technique. Ph.D. Dissertation, Kent State University, Kent, OH.
- Kimball, G. Manuscript. The effects of lesser known metals and one organic to fathead minnows (*Pimephales promelas*) and *Daphnia magna*. University of Minnesota, St. Paul, MN.
- Kurbatov, M.H., G.B. Wood, and J.D. Kurbatov. 1951. Isothermal adsorption of cobalt from dilute solutions. J. Phys. Chem., 55, 1170.
- Kyle, J.H., A.M. Posner, and J.P. Quirk. 1975. Kinetics of isotopic exchange of phosphate adsorbed on gibbsite. J. Soil Sci., 26, 32.
- Lamb, D.S., and G.C. Bailey. 1981. Acute and chronic effects of alum to midge larvae (*Diptera; Chironomidas*). Bull. Environ. Contam. Toxicol., 27, 59-67.
- Lijlema, L. 1980. Interaction of orthophosphate with Iron (III) and aluminum hydroxides. Environ. Sci. Technol., 14, 537.
- Lind, C.J., and J.D. Hem. 1975. Effects of organic solutes on chemical reactions of aluminum. U.S. Geol. Surv. Water-Supply Pap. 1827-G.
- Maetz, J. 1974. Aspects of adaptation to hypo-osmotic and hyper-osmotic environments. In D.C. Malins and J.R. Sargent (Eds.), Biochemical and Biophysical Perspectives in Marine Biology, Vol. 1, p. 143.
- Malley, D.F., and K. Donkersloot. 1988. Effects on ionic composition of blood and tissues of *Anodonta grandis grandis* (*Bivalvia*) of the addition aluminum and acid to a lake. Arch. Environ. Contam. Toxicology, 17 (4), 479-491.
- Malte, H., and R.E. Weber. 1988. Respiratory stress in rainbow trout dying from aluminum exposures in soft, acid water with or without added sodium chloride. Fish Physiol. Biochem., 5 (4), 249-256.
- McCauley, D.J., L.T. Brooke, D.J. Call, and C.A. Lindberg. 1986. Acute and chronic toxicity of aluminum to *Ceriodaphnia dubia* at various pH's. University of Wisconsin-Superior, Superior, WI.
- McCormick, J.H., K.M. Jensen, and L.E. Anderson. 1989. Chronic effects of low pH and elevated aluminum on survival, maturation, spawning and embryo-larval development of the fathead minnow in soft water. Water Air and Soil Pollution, 43, 293-307.
- McDonald, D.G. 1983. J. Exp. Biol., 102, 123.
- Messenger, A.S. 1975. Climate, time and organisms in relation to podzol development in Michigan sands. II. Relationships between chemical element concentrations in mature tree foliage and upper humic horizons. Soil Sci. Soc. Am. J., 39, 698-702.

- Messenger, A.S., J.R. Kline, and D. Wildrotter. 1978. Aluminum biocycling as a factor in soil change. Plant Soil, 49, 703-709.
- Moffett, M.R. 1979. Changes in the microcrustacean communities of East and West Twin Lakes, Ohio, following lake restoration. Master's Thesis, Kent State University, Kent, OH.
- Muniz, I.P., and H. Leivestad. 1980. Toxic effects of aluminum on brown trout (*Salmo trutta*, L.). In Proceedings of the International Conference on the Ecological Impact of Acid Precipitation, pp. 268-269. SNSF Project Report, Oslo, Norway.
- Narf, R.P. 1978. An Evaluation of Past Aluminum Sulfate Lake Treatments: Present Sediment Aluminum Concentrations and Benthic Insect Communities. Madison, WI: Department of Natural Resources.
- Neville, C.M. 1985. Physiological response to juvenile rainbow trout, *Salmo gairdneri*, to acid and aluminum - Prediction of field responses from laboratory data. Can. J. Fish. Aquat. Sci., 42, 2004-2019.
- Parker, D.B., and B.A. McKeown. 1987. Comp. Biochem. Physiol., 87A, 267.
- Pavan, M.A., F.T. Bingham, and P.F. Pratt. 1982. Toxicity of aluminum to coffee in Ultisols and Oxisols amended with CaCO₃, MgCO₃, and CaSO₄·2H₂O. Soil Sci. Soc. Am. J., 46, 1201-1207.
- Peterson, G.W., and R.B. Corey. 1966. A modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphates. Soil Sci. Soc. Amer. Proc., 30, 563-565.
- Peterson, S.A., W.D. Sanville, F.S. Stay, and C.F. Powers. 1974. Nutrient Inactivation as a Lake Restoration Procedure. Laboratory investigations. EPA-660/3-74-032. Springfield, VA: National Technical Information Service.
- Ramamoorthy S. 1988. Effect of pH on speciation and toxicity of aluminum to rainbow trout (*Salmo gairdneri*). Can. J. Fish. Aquat. Sci., 45, 634-642.
- Rao, V.N.R. and S.K. Subramanian. 1982. Metal toxicity tests on growth of some diatoms. Acta. Bot. Indica., 10, 274-281.
- Reader, J.P., T.R. Dalziel, and R. Morris. 1988. Growth, mineral uptake and skeletal calcium deposition in brown trout, *Salmo trutta* L., yolk-sac fry exposed to aluminum and manganese in soft acid water. J. Fish. Biol., 32 (4), 607-624.
- Roberson, C.E., and J.D. Hem. 1967. Solubility of aluminum in the presence of hydroxide, fluoride, and sulfate. U.S. Geol. Surv. Water-Supply Pap., 1827-C.
- Ruby, S.M., J. Aczel, and G.R. Craig. 1977. Water Res., 11, 757.
- Saddler, K., and S. Lynam. 1988. The influence of calcium on aluminum induced changes in the growth rate and mortality of brown trout, *Salmo trutta* L. J. Fish. Biol., 33 (2), 171-179.

- Schindler, D.W. 1974. Eutrophication and recovery in experimental lakes: Implications for lake management. Science, 184, 897-899.
- Schindler, P.W. 1981. Surface complexes at oxide-water interfaces. In M.A. Anderson and A.J. Rubin (Eds.), Adsorption of Inorganics at Solid-Liquid Interfaces. Ann Arbor, MI: Ann Arbor Science.
- Schitzer, M., and S.I.M. Skinner. 1963a. Organic-metallic interactions in soils. II. Reactions between forms of iron and aluminum and organic matter of a podzol Bh horizon. Soil Sci., 96, 181-186.
- Schitzer, M., and S.I.M. Skinner. 1963b. Organic-metallic interactions in soils. I. Reactions between a number of metal ions and the organic matter of podzol Bh horizon. Soil Sci., 96, 86-93.
- Schofield, C.L., and J.R. Trojnar. 1980. Aluminum toxicity to brook trout (*Salvelinus fontinalis*) in acidified waters. Environ. Sci. Res., 17, 341-366.
- Soltero, R.A., D.G. Nichols, A.F. Gasperino, and M.A. Beckwith. 1981. Lake restoration: Medical Lake, Washington. J. Freshwater Ecol., 1, 155-165.
- Stanley, R.A. 1974. Toxicity of heavy metals and salts to Eurasian watermilfoil (*Myriophyllum spicatum* L.). Arch. Environ. Contam. Toxicol., 2, 331-341.
- Stol, R.J., A.K. Van Helden, and P.L. DeBruyn. 1976. Hydrolysis-precipitation studies of aluminum (III) solutions. II. A kinetic study and model. J. Colloid Interface Sci., 57, 115.
- Stumm, W., and J.J. Morgan. 1970. Aquatic Chemistry. New York: Wiley-Interscience.
- Tam, W.H., L. Birkett, R. Makaran, P.D. Payson, D.K. Whitney, and C.K. Yu. 1987. Can. J. Fish. Aquat. Sci., 44, 630.
- Tessler, A., P.G. Campbell, and M. Bisson. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem., 51, 844-851.
- Ulrich, B., R. Mayer, and P. K. Khanna. 1980. Chemical changes due to acid precipitation in a Loess-derived soil in Central Europe. Soil Sci., 130 (4), 193-199.
- U.S. Environmental Protection Agency. 1988. Ambient Water Quality Criteria for Aluminum. EPA-440/5-86-008.
- Wood, J.M. 1985. Effects of acidification on the mobility of metals and metalloids: An overview. Environ. Health Perspect., 63, 115-119.
- Woodward, D.F., A.M. Farag, M.E. Mueller, E.E. Little, and F.A. Vertucci. 1989. Sensitivity of endemic Snake River cutthroat trout to acidity and elevated aluminum. Trans. Am. Fish. Soc., 118 (6), 630-643.

Wright, R.F., and E. Snekvik. 1978. Verh. Int. Ver. Limnol., 20, 765.

Youson, J.H., and C.M. Neville. 1987. Deposition of aluminum in the gill epithelium of rainbow trout (*Salmo gairdneri Richardson*) subjected to sublethal concentrations of the metal. Can. J. Zool., 65, 647-656.