ZINC DISTRIBUTION IN A SMALL STREAM RECEIVING TREATED TEXTILE WASTEWATER

BY

JONATHAN CHARLES, HAY,

Thesis submitted to the Graduate Faculty of the Virginia

Polytechnic Institute and State University in partial

fulfillment of the requirements for the degree of

MASTER OF SCIENCE

ΙN

ENVIRONMENTAL SCIENCES AND ENGINEERING

P.H. King, Chairman

R.C. Hoehn

September, 1977

Blacksburg, Virginia

LD 5655 1855 1977 H385 C.2

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to the Virginia

State Water Control Board for granting him educational leave to
complete his Masters Thesis. Without the cooperation of Mr. Art

Sullard, Dye Superintendent, and other personnel from Virginia

Crafts, Inc., this study could not have been conducted. The author
greatly appreciates the assistance of his committee chairman, Dr. Paul

H. King, and other members of his committee, Dr. Robert C. Hoehn
and Dr. Gregory D. Boardman, in the preparation of this thesis.

Tom Ragland and Barbara Thompson deserve special thanks for their
assistance in running TOC and AAS analyses. The author wishes
to thank Karen Felschow, his typist, and Jeffrey Lighthiser for
his assistance in the preparation of graphs. The author expresses
appreciation to his family for their support and encouragement
over the past year.

The Environmental Protection Agency has provided support for this research in the form of a Traineeship Grant to the author.

TABLE OF CONTENTS

<u>P</u>	age
ACKNOWLEDGEMENTS	i
LIST OF TABLES	vi
LIST OF FIGURES	iii
I. INTRODUCTION	1
II. LITERATURE REVIEW	3
Sources of Zinc to Natural Waters	3 3 6
Aqueous Forms of Zinc	10
Environmental Factors Affecting the Interactions and Distribution of Zinc	13 13 15
Aqueous Chemistry of Zinc and Other Heavy Metals	17 17 17 18 20 24
Organic Compounds as a Control Mechanism for Heavy Metals	26 26 26 31
Hydrous Oxides as a Control Mechanism for Heavy Metals	32 32 33 34

TABLE OF CONTENTS (con't.)

		Page
Importance of Particle Size and Grain Chemistry		35 36 36
Distribution of Zinc and Other Heavy Metals in Natural Waters		38
Summary		41
II. MATERIALS AND METHODS		42
Site Description		42
Sampling Station Locations. Station 1 Station 2 Station 3 Station 4 Station 5 Station 6 Station 7 Station 8	· · · · · · · · · · · · · · · · · · ·	43 43 46 46 46 47 47 48 48
Field Procedures		48
Field Laboratory Procedures		50 50 51
Virginia Tech Lab Procedures	• •	52 52
Total Zinc	· ·	52 53 53 53 54 55

TABLE OF CONTENTS (con't.)

		Page
IV.	RESULTS	56
	Results of Water Quality Determinations Effluent Water Quality	56 56 58
	Results of Suspended, Dissolved, and Total Zinc Analyses	64 68 68
	Results of Sediment Determinations for Zinc and Percent Loss on Ignition	71 71 71 77
	Relationship of Zinc Concentrations to Water Quality	77
٧.	DISCUSSION	84
	Sources of Zinc to Ash Camp Creek	84 84 86 89
	Distribution and Partitioning of Zinc	
	in Ash Camp Creek	90
	Ash Camp Creek	90
	Ash Camp Creek	94
	The 5.2 to 8.2 km Segment of Ash Camp Creek	95
VI.	CONCLUSIONS	97
VII.	SUMMARY	99
VIII.	LITERATURE CITED	101

TABLE OF CONTENTS (con't.)

																Page
IX.	APPENDIX.		•	•		•	•	•			•					108
VIT	A								• .				•			122
ABS	TRACT															

LIST OF TABLES

<u>Table</u>		Page
1	Summary of Physical and Chemical Characteristics of Stream and Effluent Water Samples	57
2	Summary of Mean Concentrations of Dissolved, Particulate, and Total Zn in Stream and Effluent Water Samples	65
3	Relationships of Zinc in the Water Column: Ratios of Dissolved, Suspended and Total Zinc	67
4	Summary of Zn Concentrations and Percent Loss on Ignition Data for the Sediments of Ash Camp Creek	72
5	Relationship of Zinc in the Water Column to Zinc in the Sediments: Ratios of Dissolved, Suspended, Total Water Column, and Zinc in the Sediments	74
A 1	Field pH Data for Stream and Effluent Water Samples	109
A 2	Field Temperature (Temp) and Dissolved Oxygen (D.O.) Data for Stream and Effluent Water Samples	110
A 3	Field Conductivity Data for Stream and Effluent Water Samples	111
A 4	Alkalinity Data for Stream and Effluent Water Samples	112
A 5	Calcium (Ca) and Total (Tot) Hardness (EDTA) Data for Stream and Effluent Water Samples	113
A 6	Total Suspended Solids (TSS) Data for Stream and Effluent Water Samples	113
A 7	Volatile Suspended Solids (VSS) Data for	115

LIST OF TABLES (con't.)

<u>Table</u>		Page
A 8	Total Organic Carbon (TOC) Data for Stream and Effluent Water Samples	116
A 9	Total Zinc (Zn) Data for Stream and Effluent Water Samples	117
A 10	Dissolved Zinc (Zn) Data for Stream and Effluent Water Samples	118
A 11	Suspended Zinc (Zn) Data for Stream and Effluent Water Samples	119
A 12	Data for Zinc in the Upper 5 cm. of Stream Sediments	120
A 13	Data for Percent (%) Loss on Ignition for Stream Sediments	121

LIST OF FIGURES

<u>Figure</u>		Page
1	Map of Study Area Showing Ash Camp Creek and Sampling Station Locations	44
2	Enlargement of a Portion of Figure 1 Showing Stations 1-6 and Discharges from Va. Crafts and the Keysville STP	45
3	Relationship of (A) Mean Dissolved Oxygen and (B) Mean Temperature to Distance Downstream on Ash Camp Creek	59
4	Relationships of (A) Mean Total Suspended (TSS), (B) Mean Conductivity, and (C) Volatile Suspended Solids (VSS) to Distance Downstream on Ash Camp Creek	60
5	Relationships of (A) Mean pH, (B) Mean Calcium (Ca) Hardness (EDTA), (C) Mean Alkalinity, (D) Mean Magnesium (Mg) Hardness (EDTA) to Distance Downstream on Ash Camp Creek	61
6	Relationship of Mean Total Organic Carbon (TOC) to Distance Downstream on Ash Camp Creek	62
7	Relationships of (A) Mean Dissolved Zinc, (B) Mean Total Zinc, and (C) Mean Suspended Zinc to Distance Downstream on Ash Camp Creek	66
8	Various Ratios of (A) Mean Dissolved Zinc to Mean Suspended Zinc, (B) Mean Dissolved Zinc to Total Zinc, and (C) Mean Suspended Zinc to Total Zinc vs. Distance Downstream on Ash Camp Creek	70
9	Relationships of (A) Mean Percent Loss on Ignition and (B) Mean Zinc in the Sediments to Distance Downstream on Ash Camp Creek	73
10	Comparison of the Concentrations of (A) Mean Zinc in Sediments, (B) Mean Suspended Zinc, and (C) Mean Dissolved Zinc at Various Sampling Stations	75

LIST OF FIGURES (con't.)

<u>Figure</u>		Page
11	Various Ratios of (A) Mean Dissolved Zinc, (B) Mean Suspended Zinc, and (C) Mean Total Zinc to Mean Zinc in the Sediments vs. Distance Downstream on Ash Camp Creek	76
12	Mean Dissolved Zinc as a Function of Mean Conductivity in Effluent and Water Samples	78
13	Mean Suspended Zinc as a Function of (A) Mean Total Suspended Solids (TSS), and (B) Mean Volatile Suspended Solids (VSS)	80
14	Mean Total Zinc as a Function of Mean Alkalinity	81
15	Mean Total Zinc as a Function of (A) Mean Total Hardness (EDTA), and (B) Mean Calcium Hardness (EDTA)	82
16	Mean Total Zinc as a Function of Mean Total Organic Carbon (TOC)	83
17	Mean Zinc in Sediments as a Function of Mean Percent Loss on Ignition	83

I. INTRODUCTION

Heavy metal pollution of the biosphere has been the focus of considerable research interest to environmental scientists and engineers in recent years. The ubiquitous use of zinc in industrial applications has greatly increased the rate of introduction of this heavy metal pollutant into the Nation's waters and has raised questions concerning its possible impact on aquatic systems.

Zinc is an essential and beneficial element in animal and plant metabolism. The daily adult human intake averages 0 to 15 mg. A deficiency may lead to retardation (1). For domestic water supplies, the concentration of zinc should be below 5 mg/l because higher concentrations can impart a bitter and astringent taste to water (1). Toxic concentrations of zinc compounds can cause adverse changes in the morphology and physiology of fish. The toxicity of the metal to aquatic organisms is affected by several environmental factors, including hardness, dissolved oxygen, and temperature and is species dependent (1). E.P.A. (1) has recommended that "0.01 of the 96-hour $LC_{\overline{50}}$ as determined through a bioassay using a sensitive resident species" be utilized to determine toxic level of zinc for fresh water aquatic life. The toxic level for zinc established by the Virginia State Water Control Board is 0.01 mg/l.

Ash Camp Creek, which has its headwaters near the Town of Keysville, Virginia, traverses in a southwesterly direction through pastureland and forestland of Charlotte County for about 12 kilometers before reaching its confluence with Roanoke Creek, a tributary to the Roanoke River. The stream receives near its headwaters an industrial

wastewater discharge from Virginia Crafts, Inc. (Va. Crafts), a domestic sewage discharge from Town of Keysville sewage treatment plant, and urban runoff from The Town of Keysville. The industry, which manufactures tufted bath rugs and bath sets, discharges an industrial wastewater effluent, which is treated by means of an aerated lagoon and sedimentation, that contains color and concentration of zinc in excess of one part per million. According to King (2), the major in-plant source of zinc in the discharge is a latex backing accelerator.

The results of a Virginia State Water Control Board study conducted in October of 1975 showed that the industrial effluent was adversely affecting water quality and macrobenthic populations in Ash Camp Creek along an eight kilometer segment below the point of discharge (3). The cause of decline in macrobenthic populations was attributed to organic overloading from Va. Craft's effluent. Zinc levels of .22 mg/l were also noted 8 km below the discharge point (3). The company is currently under a State Water Control Board Consent Order to upgrade its treatment facilities to reduce zinc levels and color in the effluent.

It was the purpose of the study described herein to define the distribution and partitioning of zinc among the suspended and dissolved fractions of the water column and in the sediments of Ash Camp Creek and to relate the foregoing information to various water quality parameters. The results of the study should be useful for assessing the water quality effects of the discharge and for evaluating the fate of zinc in an aquatic system.

II. LITERATURE REVIEW

In the following section, a review of pertinent literature on the properties, chemistry, regulation and control, and distribution of zinc in the aquatic environment is provided. The information contained in the literature has been grouped under several subsections. The subsections, in order of discussion, are as follows: Sources of Zinc to Natural Waters, Aqueous Forms of Zinc, Environmental Factors Affecting the Interactions and Distribution of Zinc, Aqueous Chemistry of Zinc and Other Heavy Metals, Organic Compounds as a Control Mechanism for Heavy Metals, Hydrous Oxides as a Control Mechanism for Heavy Metals, Importance of Particle Size and Grain Chemistry, and Distribution of Zinc and Other Heavy Metals in Natural Waters.

Sources of Zinc to Natural Waters

The sources of zinc and other heavy metals which are released to the aquatic environment may be either natural or man influenced. The effect of man's activities has been to accelerate the flux of heavy metals at specific points into the biogeochemical cycle (4).

Natural Sources

Natural sources of the element include: soils and rocks and precipitation and fallout.

Soils and rocks constitute the most important natural source of heavy metals to the aquatic environment. The average concentration of zinc in the earth's crust is 40 ppm (5). The amount of zinc and transition metals in an aquatic system reflects the rock type and

mineral content of geological formations in the drainage basin. Depending on the formation process, various rock types will vary as to the concentration of zinc and other elements. Williams et. al. (6) cite data from Turekian and Wedepohl (7), which give the following concentrations (mg/kg) of zinc in various rock types: for plutonic rocks, ultramatic, 50; Basaltic, 105; plagiclase, 60; orthoclase, 39; syenite, 132; and for sedimentary rock, shale, 95; sandstone, 16; and carbonate, 20. As pointed out by Williams et. al., streams situated in limestone areas will pick up more metals than would lakes located in a limestone basin because the erosion forces of the stream promote the movement of rock and associated metals into the stream. and Wagner (8) observed that the extractable amounts of Zn, Pb, and Cu in sediments of the Buffalo River, Arkansas, paralleled the rise and fall of extractable Ca plus Mg in the sediments, which indicates that the close association of the metals with their favorite rock host. dolomite. As indicated previously, shale contains larger amounts of zinc and other heavy metals than other sedimentary rocks. Shale should, according to Steele and Wagner (8) make the following two contributions to the metal content of sediments:

- Fine particles of shale or clay from shale, could be in the sediments;
- 2) Groundwater could have a higher concentration of dissolved metals due to contact with the shale. When the ferrous iron precipitates as hydrous ferric oxide on stream sediments, other dissolved metals are settled by coprecipitation and sorption.

Pita and Hyne (9) showed the effect of a lead-zinc mineralized area on the heavy metal content of the sediments in downstream reservoirs on the Neosho River near Joplin, Missouri. They found that the reservoir sediments selectively concentrated zinc over lead and that Zn was selectively weathered and transported from the source area.

Biogenic sediments (those formed by living organisms) exhibit a selective enrichment of most transition elements. As pointed out by Holmes <u>et. al.</u> (10), there is a natural enrichment of Zn in oil, asphalt, and coal and their ash. For example, coal may contain 500 mg/kg of zinc and its ash as much as 10,000 mg/kg (5).

Soils and clay minerals often exhibit enrichment of zinc and other transition metals (6). It has been found that soils containing high organic fractions and/or hydrous oxides of iron, manganese and titanium will bind significant quantities of metals. Data from Allaway (11) cited by Williams et. al. (6) indicate that the typical concentration of zinc found in soils ranges from 10-300 mg/kg.

Precipitation and fallout constitute the second most important source of trace transition elements in aquatic systems. The metalladed material contained in precipitation and fallout is introduced into the air from both natural sources (i.e., dust from volcanic eruptions, dust from erosion and weathering of rocks, smoke from forest fires) and man's activities (i.e., combustion of fossil fuels, and manufacture of steel and other metals) (6). Williams <u>et. al.</u> (6) present data giving typical concentrations ($\mu g/m^3$ of air) of zinc in air particles

as follows: urban air, 0.7; rural - suburban air, 0.05; and oceanic air, 0.0025.

Man Influenced Sources

"Pollution contamination" is the third principal source of trace elements to the aquatic environment. This source is associated with the direct discharge of treated and untreated effluents from agricultural, municipal, residential or industrial establishments and from the disturbance of drainage basin with concomitant contaminated runoff to a waterbody (6). It is this source of contamination with which this study is primarily concerned.

Leckie and James (4) point out that there are few reliable data available relative to the quantities of trace metals entering the aquatic environment via domestic and industrial waste effluents. Trace metals (Pb, Zn, Cd and Cu) can be found in domestic wastewaters in the mg/l range (4). Among the factors which determine the amounts of trace metals in domestic sewage are: water usage, quantity and types of food eaten, time of year, economic status, and the prevalence of garbage grinders (6). As mentioned earlier, the daily adult human intake of zinc averages from 0 to 15 mg (1). Not all of the zinc consumed by humans is retained by the body; the excess is passed off in excrement and ends up reaching the aquatic environment where the water carriage system of waste disposal is employed (6).

The zinc content of the effluent of a treatment plant discharging to the Back River, Maryland was 280 mg/l (12). Chen et. al.

(13) give the following zinc data for the Hyperion Treatment Plant, Los Angeles: primary effluent, 430 μ g/l; secondary effluent, 104 μ g/l; and final effluent, 195-460 μ g/l (all composite samples). The studies of Papakostidis et. al. (14) indicate that the concentration of zinc and other heavy metals in the Saronikos Gulf (near Athens, Greece) in an area contaminated from the discharge of an untreated domestic and industrial wastewater was 8-200 times greater than in the surrounding uncontaminated sediments. Typical concentrations of zinc in the contaminated study area ranged from 45-1800 mg/kg. Helz (12) gives data which show a sharp decrease in trace metal concentrations of a river below an outfall as compared to that in the sewage effluent prior to discharge. Zinc, for example, dropped from 280 ppb in the effluent to about 9 ppb in the river (from dilution).

Because of variations with type of industry and specific operations within the industry, a representative concentration of metals in effluents from industries is difficult to determine (6). The quantities of water used as well as types of processes employing the water can influence the concentration of metals in the effluent. For example, the concentration of heavy metals may even be higher when water conservation is practiced (6). Zinc has an ubiquitous association with industrialization. The types of industries which discharge zinc in wastewater effluents include: general industrial and mining, plating, fertilizer, paper products, and fibers (15).

Almost 3,000,000 short tons of recoverable zinc are mined each year

in the world. The United States mines about 500,000 tons per year (1).

Few studies are available which provide information concerning the specific effects of metals in industrial discharges into aquatic systems. Holmes <u>et. al.</u> (10) found concentrations of zinc in harbor sediments of Corpus Christi Harbor (Texas), which receives a discharge from zinc smelting industries, as high as 11,000 ppm. The data from Papakostidis <u>et. al.</u> (14) was cited earlier.

Allen et. al. (16) described the contribution of dyes to the metal content of textile mill effluents. Among the sources of metals in the dyes are: water from which dyes are prepared, raw materials (acids, alkalis, organic intermediates, etc.), and catalysts. Some dyes which are prepared as a double salt containing zinc may contain a zinc concentration of about 3%. Basic and direct dyes contain about 32 ppm of zinc whereas fiber reactive and vat dyes contain about 4 ppm. Heavy metals are also employed to improve light fastness and wash fastness on certain fabric/dye combinations and are used as catalysts in the application of wash-wear, durable press and water repellant finishes. A dilution of about 10,000 fold is provided by process water so that metal contaminants emanating from dyes appear at levels of a few parts per billion or less in the textile mill effluent (16).

Another source of pollution contamination of trace metals is the agricultural activities of man (6). Trace elements play an essential role in the nutritional needs of plants and animals.

According to the data of Allway (11) cited by Williams (6), the normal concentration of zinc in plants varies from 15-200 mg/kg. The excreta of animals, that have consumed plants, are a source of metal contamination for aquatic systems. Irrigation water and fertilizers (which have been shown to contain significant quantities of chromium, copper, iron, manganese, nickel and zinc) are two additional agricultural sources (6).

The runoff from highways and streets can also introduce significant amounts of metals into waterbodies. As pointed out by Williams et. al. (6), the metal content of runoff depends upon the following factors: street cleaning techniques of city or town, the activities on the street, and the land use on the area adjoining the street. Williams et. al. (6) cite other investigators (17) who determined the following concentrations of zinc for various road types: a city street, 400 mg/kg; a rural road, 70 mg/kg; and a highway, 190 mg/kg. Pitt and Amy (17) compared the metal loading from road surface runoff to normal sanitary sewage for a typical city of 100,000 people during one hour with a rainfall of .1 inches and found that the load of zinc to stream from street runoff was 140 lbs/hr compared to .84 lbs/hr, during the same period, for sanitary sewage.

Two additional sources of trace metals in drainage are mining and land clearing. Mining exposes large amounts of waste metal contaminated rock to accelerated weathering conditions (10). Acid mine drainage typically contains concentrations of Zn, Cd, Be,

Cu, Ni and Co at levels higher than those found in normal streams. The mean concentration of these metals is 3.5 mg/l (16). Because land clearing increases the erosion potential of an area, it can promote the movement of metals to the aquatic environment (6).

Aqueous Forms of Zinc

Numerous authors have investigated the forms of zinc and other heavy metals in wastewater effluents and aquatic systems.

Metals in natural waters may be suspended, colloidal, or soluble. Suspended particles are larger than 100 m_{μ} in size and soluble particles less than 1 m_{μ} but less than 100 m_{μ} . The colloidal particles are greater than 1 m_{μ} but less than 100 m_{μ} (6).

According to Williams et. al. (6) suspended and colloidal particles may be characterized as individual and/or mixed metals in the form of hydroxides, oxides, silicates, sulfides, or other compounds or may include clay, silica, or organic matter to which metals are attached by complexation, adsorption, or ion exchange. The soluble metals can consist of ions, simple or complex, or unionized organo-metallic chelates or complexes (6). The concentration and distribution of the various forms of a metal are regulated by various potential interactions (physical, chemical, and biological reactions) that take place within the waterbody (6).

Helz <u>et. al</u>. (12) studied the behavior of heavy metals discharged from a wastewater treatment plant into an estuarine environment. They determined that a significant portion of each trace metal in the effluent was associated with particulates. The concentration

of zinc in dissolved solids was 50 μ g/l as compared to 280 μ g/l associated with particulates. As mentioned previously, Chen et. al. (13) analyzed trace elements in effluents of different treatment processes of the Hyperion Treatment Plant, Los Angeles. Most of the Cd, Ci, Cu, Hg, Zn, and Fe in the primary effluent was associated with particulate matter. Because of its low suspended solids content, secondary effluent contained mainly dissolved trace metals; in fact, zinc and cadmium exhibited markedly more solubility in secondary effluent than primary effluent. Other data (13) showed that the primary effluent was the dominant source of suspended particulates and trace metals in the final effluent, and that, even through secondary treatment removed 90 to 95% suspended solids, it removed less than 40 to 60% of the total and less than 40% of dissolved Cd, Ni, Pb, Zn, and The highest fraction of trace metals in wastewater was in the size range 0.2 to $0.8\,\mu$, excepting zinc which exhibited highest concentrations in the 8-44u size range. The concentration of zinc associated with particulate matter was given as follows: primary effluent, 3200 mg/kg, secondary effluent, 2700 mg/kg; and final effluent, 2700 mq/kq (13).

Williams <u>et. al.</u> (6) present typical metal concentrations for various regions of the Hudson River. In two of the regions (3 and 4), where large municipal aid industrial discharges have occurred, there is a pronounced increase in dissolved zinc (from 4.3 to $15.8~\mu g/1$) and an increase in suspended zinc (from 0. to $3.7~\mu g/1$). Increases in hardness, alkalinity and pH also occur in these regions (6).

Perhac (18) determined that almost all solid matter in two streams in northeast Tennessee occurred in the dissolved state and that only small amounts occurred as coarse particulates and only traces as colloids (under 1%). For most metals, excepting zinc and Mn, the highest concentration was found in the colloids (50-1840 ppm for zinc); the lowest concentration was in the dissolved solids (42-141 ppm for zinc). The zinc concentration in the coarse particulates was also high, ranging from 228 to 2480 ppm. As pointed out in the study (18), although the colloids are most concentrated with heavy metals, the greatest quantity of each metal occurs in the dissolved state because dissolved solids comprise most of the total solids in water. The following distribution percentages were given for zinc: dissolved solids 53 - 92%; coarse particulates, 7.3 - 46%; and colloidal particulates, 0.4 to 2.4%.

Two other findings of Perhac's study are worth noting.

First, a stream draining a non-carbonate area generally has a lower percentage of metal in solution than does a stream draining carbonate rock (90% of metals were dissolved). Second, colloids, which account for less than 1% of particulates in stream if present in sufficient quantities, can carry considerable quantities of an element which, otherwise, would have a low solubility in water.

The work of Pita and Hyne (6) also confirmed that most zinc in water occurs in the dissolved state, existing as either an ionic solution and/or as organo-metallic complexes (heavy metals exhibit a higher solubility in the aqueous system as organo-metallic complexes).

DeGroot and Allerson (19) determined that the characteristics of suspended matter can be an important factor determining transport capability of a stream for metals. For the Rhine River, metals supplied to the stream by industrial waste adhered to solids in decreasing contents in the following order: suspended matter, original mud (main component settling in shallow areas), and erosion mud. The distribution of solid substances in the environment diminishes in the same order (i.e., erosion mud is deposited locally on river plains, whereas part of the suspended matter moves very far). In sum, those solid substances which are most contaminated are transported the farthest and given the most widespread distribution in the aquatic environment (19).

Environmental Factors Affecting the Interactions and Distribution of Zinc

Several environmental factors, e.g., Eh and pH, water depth, flow intensity and duration, and algae blooms may affect the interactions and distribution of heavy metals in the aquatic environment.

pH and Eh

Both pH and Eh can exert control over the distribution of metal species by regulating the potential interactions (complexation, sorption, dissolution, precipitation) that occur in an aqueous environment. Since hydrogen can effect adsorption and ion exchange by competing for active sites or by changing the degree of protolysis of the sorbing material, pH can exert regulation over the attachment

of metals to insoluble carriers (6). The pH exerts control over the solubility. For example, the precipitation of CaCo₃ through an increase in pH can remove metals like Zn and Cu through adsorption and coprecipitation (6). A change in pH of natural waters can change the degree of complexation of a metal in solution since many complexing agents are weak acids or bases (6).

O'Connor et. al. (20) plotted zinc concentrations of Chesapeake Bay tributaries against pH. They found that zinc levels of more alkaline streams are markedly lower than those of neutral streams. They attributed this decrease in zinc concentration with increasing pH to increased adsorption on river silts at higher pH's. Their hypothesis was confirmed by laboratory experiments (20).

Oxidation-reduction potential, Eh, exerts a similar effect on certain heavy metals and may actually effect pH changes (6). Changing redox environments can affect trace metals in two ways:

(1) by direct changes in the oxidation state of the metal ion, and/or (2) by causing redox changes in available or competing ligands or chelates (4). Iron and manganese are most affected by Eh changes. Lower redox potentials favor the Fe²⁺ and Mn²⁺ valence states that are more soluble than the oxidized states (6).

Gorham and Swaine (21) carried out investigations of oxidized surface muds, reduced subsurface muds and glacial clays collected from lakes in England. They discovered that the oxidate crusts exhibited a strong enrichment of Mn, Fe, Ba, Sr, Pb, and Bn. Accumulation of Zn in the oxidate crust was attributed to the marked

sorptive properties of ferromanganese minerals which scavenge trace metals (21). The importance of these minerals is subject of a later subsection.

The distribution of zinc and cadmium in waters of Corpus Christi Harbor is explained in terms of Eh (10). During the summer Zn and Cd are increased in the oxidized surface water because of industrial effluents: Zinc exists in the ionic state (Zn⁺²) and Cd exists as CdCl⁺. Below surface waters, where anoxic conditions exist, zinc and cadmium react with sulfide ions and are precipitated. The precipitation process is accelerated as the redox boundry rises. Because of the above reaction, a metal-rich oxidized surface layer, metal poor reduced lower layer, and metal sulfide-rich sediment are created. During the winter, the flow of oxygen rich water into previously stagnant areas results in the desorption of precipitated metals (10).

Other Factors

Delfino et. al. (22) have suggested that water depth may be a factor controlling the distribution of trace metals in surface sediments. Surface sediment samples from various areas of Lake Mendota, Wisconsin exhibited a high positive statistical correlation between concentrations of Mn, Fe, and P concentrations in the sample and depth from which the sample was collected (22).

Flow intensity and duration may also influence the trace metal content of aquatic systems. In citing the work of Durum and Hofty (23),

Andelman (24) points out that certain metals (Fe, Al, Mn, and Ti) which readily precipitate in natural waters to form hydroxides as particulates or colloids may be dissolved from certain suspended minerals under the turbulent conditions of high flow. The process is facilitated by complex formations with organic material leached from decaying vegetation; in addition, under conditions of high flow the concentration of metals would be higher than solubility and redox relationships might permit (24).

Silker (25) observed that zinc and cobalt concentrations followed the Columbia River flow curve closely and attained a maximum concentration during the higher river flow in June. Andelman (24) explains that if the stream load of a metal is proportional to flow, a continuous leaching process is involved as ground and surface waters pass over soils and minerals. On the other hand, if the concentration decreases with flow, a relatively constant source of load of trace elements is involved, which is diluted as the flow increases.

Algae blooms have been cited as a possible mechanism for removal of zinc in an estuarine environment. According to Helz et. al. (12), algae bloom occurring during the day could raise the pH above 9.0 and induce the rapid, inorganic deposition of trace metal hydroxides, carbonates, or phosphate. The increased pH could also result in greater removal by sorption on organic and inorganic particulates.

Aqueous Chemistry of Zinc and Other Heavy Metals

A consideration of the aqueous chemistry (properties, hydrolyses, complexation, sorption and ion exchange and solubility) of zinc and other heavy metals is provided in the following discussion.

Important Chemical Properties

The chemical properties of zinc have been reviewed by Lingane (26). Some of the more important properties are listed as follows:

- 1. In forms compounds only in the +2 oxidation state,
- 2. The aquo zinc ion is a very weak acid $(K=2.45 \times 10^{-10})$,
- 3. Zinc forms complexes with a variety of ligands. It has a coordination number of 4.

Hydrolysis Reactions

In solution environments, metal cations are hydrated to form aquo complexes (27). The heavy metals, Zn, Cd, Hg, Pb, belong to a group of oxyphilic and sulfophilic elements that undergo hydrolysis reactions at lower pH values than alkali and alkaline earth ions and display multiple hydrolyses at pH values encountered in the environment (28). Many of the divalent metals, eg., Cu^{2+} , Pb^{2+} Ni^{2+} , Co^{2+} and Zn^{2+} hydrolyze in the range of pH of natural environment according to the reaction

$$K_1 = \frac{[MOH (n-1)^+][H^+]}{[M^{N+}]}$$
 which expressed logarithmically yields.

$$pK_{1} = -\log \frac{[MOH (n-1)+]}{[M^{n+1}]} + pH$$

Hydrolysis may proceed further through a stepwise loss of coordinated water (4).

Hahne and Kroontje (28) showed that Zn (II) forms $M(OH)_3^-$ and $M(OH)_4^{2-}$ complexes under highly alkaline conditions at pH's higher than normally encountered in the environment. At pH 6-7, all Zn (II) is present as divalent ionic form (assuming no other reactions). $Zn(OH)_2$ forms at pH ranges of 7 to 12. Based on intrinsic solubilities, the authors estimated that up to 160 ppm of Zn (II) could exist as soluble $Zn(OH)_2$; precipitation would occur when the metal ion concentration exceeds its intrinsic solubility (28).

Complexation

The complexation of metals by inorganic ligands plays a significant role in the control of trace metals by influencing solubility, sorption on suspended matter and bottom sediments, and uptake by biota (24). As pointed out by Chau et. al. (20), complexation reactions are highly pH dependent. Dissociation complexes occur at low pH's due to competition of hydrogen ions for the ligands and; therefore, complex formation is favored at higher pH's.

A number of natural and synthetic inorganic complexing agents other than solvent water, which may react with metal ions, are present in natural waters. Among the important inorganic complexing agents are Cl^- , $\text{S64}^=$, HC0^-_3 , F^- , and sulfide and phosphate species (4).

Most inorganic ligands are present in natural waters at concentrations higher than the concentration of trace metals they tend to complex. Further, each metal ion will exhibit a speciatation dependent on the stability of the hydrolysis products and tendency of metal to form complexes with inorganic ligands (4). Depending on the metal concentration and ligand concentration, a number of insoluble complex ions and insoluble phases may result from reactions of metals with inorganic ligands. The distribution of metals between solid and aqueous phases can be affected by the formation of insoluble ligand complexes, (4), as will be noted later in this discussion.

Stumm (27) has maintained that metal ions in natural waters are not complexed by ligands other than $\rm H_2O$ or $\rm OH^-$ because most bases indigenous to natural waters are unidentate ligands which form less stable complexes than multidentate ligands, especially in dilute solutions. In addition, he has maintained that in natural waters the concentration of ligands and affinity of ligands for metal ions with the exception of $\rm H_2O$ and $\rm OH^-$ are usually sufficiently small (27).

Chlorides like hydroxyl and hydrogen ions are found in all natural waters and should be regarded, according to Hahne and Kroontje, (28) as "one of the most mobile and persistent complexing agents with retard to heavy metals" The chloride ion concentration determines the degree of complexation and differentiates metals in accordance with their affinity for such complex formations. Experimental data indicate that the formation of ZnCl⁺ begins at a chloride concentration

of 354 mg/l and peaks at 10,000 ppm. Whereas ZnCl₃-, and ZnCl₄-2 complexes predominate above 35,000 ppm; Zn (OH)₂ was found to predominate over Zn(II)-Cl complexes at chloride concentrations less than 89,000 ppm (28). Further, for various Zn (II), Cd (II) and Pb (II), a 3 to 39 fold increase in solubility was noted, depending on type of precipitate encountered at chloride concentrations of 35,460 ppm (28). Williams, et. al. (6) cite data which indicate that as chlorosity is increased, a greater proportion of manganese becomes dissolved rather than suspended.

In natural waters there are also a large number of natural and synthetic organic substances with which metal species may complex. Among organic ligards are: natural degradation products of plant and animal tissue (amino and humic acids), organic species derived from chemicals applied by man (detergents, cleaning agents, NTA, EDTA, pesticides, ionic and nonionic surfactants) (4). The term metallo-organic is applied to structural configurations in which organic matter is bonded to a metal (4). A subsequent subsection is devoted to role of organic matter in trace metal regulation.

Sorption and Ion Exchange

Sorption and ion exchange of trace metals can occur onto particle surfaces as well as into the particle's structure. Both processes are varied and complex and influenced by a variety of environmental factors (24).

Adsorption has been shown to increase abruptly in the pH range where hydrolyses products become a significant fraction of

the aqueous metal ion (4). As explained by Leckie and James (4), for each metal there exists a critical pH range, often less than one pH unit wide over which the amount of metal adsorbed increases from almost zero to almost complete removal from the solution. If the adsorbing substrate possesses a negative surface charge, there is generally a reversal of surface charge at particle water interface from - to + when the pH is suitable for high adsorption densities and hydrolysis. The zeta potential of the solid is little effected by the free aquo species (4). With a change in zeta potential, there is change in observed stability of colloidal dispersions which is indicated by a rapid coagulation and setting when zeta potential decreases to a low magnitude (4).

Leckie and James (4) demonstrated the above principles by illustrating the adsorptive behavior of Co (II) on a variety of oxide minerals. The results showed that at low pH the percentage of adsorption is low, but when the pH is increased to allow hydrolysis to become significant, the percentage adsorption increased from 0 to 100% (4).

Huang et. al. (30) found that the adsorption of zinc, lead, and copper increased on hydrous oxides and soils in the pH range 5 to 6. As the pH was increased further, chemical precipitation became a dominant mechanism in removal. When the pH decreased below the above range, the adsorption of copper and zinc declined appreciably (30).

In addition to pH, the amount of adsorption is dependent on: temperature, salinity, time of standing, amount and physical state of the adsorbent, and the concentration of adsorbed ions (31). Slowey and Hood (31) found that the efficiency of removal of metal in seawater was related to the steady-state concentration and the rate of supply

According to Leckie and James (4), complexing ligands affect adsorption in at least two ways:

- By competing with OH⁻ in the coordination of metal low, thereby, repressing the formation of hydro complexes;
- 2) By forming a second suite of adsorbing complexes.

Huang et. al. (30) observed a more pronounced adsorption of heavy metal ions in the presence of anions. Anions were found to enhance heavy metal precipitation at low pH values, at which adsorption is not likely to occur in their absence. Phosphate ions were under most circumstances less effective than organic compounds in promoting adsorption (30). The sequence of effectiveness of compounds in enhancing adsorption was given as follows: humic acid > nitrilotriacetate > glycine > tartrate > phosphate (30).

In a lab study (49) where zinc was adsorbed on montomoorillinite (clay) from 2 ppm solution, some 99 percent of the ion was removed within a few hours. Several other adsorbents were evaluated; including, ferric oxide, manganese dioxide, apatite, clay, plankton, and peat moss. Manganese dioxide was found to be the best adsorbent followed by ferric oxide (31). A separate subsection is devoted to the discussion of these two compounds. According to Slowey and Hood (31), adsorption provides the most satisfactory explanation for the observed concentrations of rare metal ions in seawater. Unlike precipitation processes, adsorption processes are cumulative; irregardless of how low the concentration of an ion may be, the addition of fresh adsorbent will reduce it further (31).

Leckie and James (4) discuss three models for adsorption of metals: the ion exchange model, adsorption in the electric double layer model, and the general model for the adsorption of hydrolyzable metal ions. Sorption of trace elements onto sorping minerals can occur without ion exchange as a result of coulombic interactions with the surface and its electrical double layer (24). Because most particles in water are negatively charged, charged trace cations or colloidal trace elements can be held at the negatively charged surface of such colloidal or particulate mineral or other material.

Changes in freshwater calcium concentrations effect adsorption. Waters with a larger calcium concentration would have a higher concentration of dissolved trace elements because of the inhibition of their exchange sites onto minerals (24). The work of Masironi (32) cited by Andelman (24) indicates positive correlations between trace elements and calcium concentration. Other alkali metal ions, Ma and Ki would have a similar but smaller effect because they are univalent (24).

Solubility Considerations

The concentration of heavy metal in an aqueous system is controlled in part by "congruent and incongruent solubility states of various oxides, carbonates, sulfates, and sulfides (30)." Important factors controlling the solubility of mineral phases are: the pH of the solution, type and concentration of inorganic and organic ligands and chelating agents, the oxidation state of the mineral components, and the redox environment of the system (4). Microbial activity in the sediment which changes an aerobic environment to an anaerobic one will also solubilize heavy metals (30).

Huang et. al. (30) present data which show that at a pH of 5 and total carbonate and sulfur concentration of 10^{-3} mole/l each, the concentration of free lead, zinc and cadmium is controlled by the solubilities of PbSO₄, CuO, $Zn_4(OH)_6SO_4$ and $Cd_4(OH)_6SO_4$ in aerobic conditions and of PbS, CuS, CdS, and ZnS in anaerobic conditions, respectively (the effect of chelation was not considered).

The solubility of zinc in distilled water is governed by zinc hydroxide or zinc carbonate equilibrium. Zinc salts which precipitate from supersaturated solutions are reported to be a mixture of carbonate and hydroxide (20). The precipitation of $Zn(OH)_2$ (from 0.01M zinc ion) does not occur until the pH is above 5.80 (26). According to O'Conner (20), the concentrations of zinc found in natural waters are below the solubility limitations imposed by carbonate and hydroxide equilibria. According to Lingane (26), the solubility of $Zn(OH)_2$ can be increased by increasing the concentration of both NH_4^+ and NH_3 .

Because heavy metal sulfides are rather insoluble, the reaction of metal ion with sulfide can be an important mechanism whereby trace metals are removed from the aqueous phase. The two crystalline forms of ZnS (sphalerite and nurtzite) have solubility products of 10^{-24} and 10^{-22} , respectively (26). Highly organic sediments can contain large quantities of reduced material especially sulfides (4). E.P.A. (33) cites the work of Biggs (34) who gives the order of solubilities of divalent sulfides as Hg < Cu < Pb < Cd < Ni < Zn. E.P.A. (33) investigated the concentration of trace elements in Baltimore Harbor sediments to determine if the least soluble sulfides showed the highest ratios. The results compared favorably with the expected order except for zinc, which apparently was present in forms other than sulfide (33).

As noted by Jonasson and Timperly (35), any metal sulfides in muds in tidal areas are subject to dissolution when they come into contact with freshly oxygenated tidal waters. The authors (35) observed intense mobilization processes in small lakes when water levels dropped sufficiently to leave bottom silts and muds in an oxidizing rather than a reducing environment. They (35) proposed that direct competition between sulfide and organic ligands controls heavy metals in sediments.

Lawrence and McCarty (36) demonstrated that the presence or addition of sulfide to a digestor containing heavy metals resulted in the formation of extremely insoluble metal sulfides. They (36)

found that most heavy metals could be precipitated and rendered nontoxic in the presence of equivalent concentrations of sulfide.

Slowey and Hood (31) cite sulfide precipitation as a possible mechanism for reducing the concentration of 13 elements to values within or lower than ranges found in sea water.

Organic Compounds as a Control Mechanism for Heavy Metals

The role of organic matter in the control of heavy metal distribution has been the center of much research over recent years.

Importance of Organic Matter

As pointed out by Rashid and Leonard (37), organic compounds constitute only 2-3% of the sediment and are present in concentrations rarely in excess of 20 mg/l in natural waters, yet they play a significant role in the controlling the solubility, mobility, concentration and accumulation of metal. The group of organic complexing agents, found in natural waters, which have received greatest research attention are humic compounds.

Humic Substances

Schnitzer (38) provides an excellent review of the chemical and physical properties of humic compounds. Among the most widely occurring compounds on the earth's surface, humic compounds have the following characteristics: they are acidic, partially aromatic, chemically complex substances of molecules ranging from a few hundred

to several thousand in molecular weight. They lack specific chemical and physical characteristics associated with non-humic compounds (carbohydrates, peptides, amino acids, etc.), and they exhibit appreciable exchange capacity due primarily to carboxyl and phenolic groups and complex metal ions. The bulk of the organic matter in soils and possibly in waters is comprised of humic compounds. Based on solubility, three groups of humic compounds are distinguished: fulvic acid (acid and alkali soluble), humic acid (alkali soluble) and humin (insoluble in alkali and acid). Fulvic acid, which can comprise 25 to 75% of the organic matter in soils and is composed of as much as 60% functional groups (carboxyls, hydroxyls and carbonyls), is considered by Schnitzer (38) to play a dominant role in controlling the supply and availability of metals in soils and waters.

Rashid and Leonard (37) conducted studies to determine the effect of humic substances on the solubility of various metals from their insoluble salts and on the precipitation behavior of these metals as carbonates, hydroxides, and sulfides. Significant findings include the following:

- For carbonate salts, each gram of humic acid solubilized from 54 to 250 mg of metal (134.0 mg/l of zinc) and even larger quantities were dissolved by acid hydrolysate of humic acid;
- 2) Humic acid prevents the precipitation of metals as carbonate salts and metal sulfides; 13 to 26 times more metal ions was required to cause precipitation.
- Reactions of humic acid and metals involve chelation and complexation of various functional groups; the

products of the reactions are stable and soluble organo-metallo complexes.

It is the complexes described in 3 above which account for the large quantities of metals solubilized from insoluble metal carbonates and sulfides. Complexed metal ions remain in solution unavailable for precipitation as sulfides, hydroxides, and carbonates. In the environment, they could be transported considerable distances (37).

Pillai et. al. (39) found that trace elements present in humic and fulvic acids form an integral part of the structure of these compounds. Bivalent elements form cationic and non-cationic complexes while tri and tetravalent ions formed mainly non-cationic complexes with humic substances. They observed the following order of stability for organo-metallic complexes: Al > Fe > Cu > Mn> Co > mg > Zn > Ca. Their data suggest that fulvic acid can better solubilize metallic elements from their salts than humic acid (39).

Schnitzer and Skinner (40) give the following orders of stability of complexes formed between a soil fulvic acid and metal ions: at pH 3; $Cu^{++} > Fe^{++} > Pb^{++} > Co^{++} > Ca^{++} > Zn^{++} > Mn^{++} > Mg^{++}$; and at pH 5; $Cu^{++} > Pb^{++} > Fe^{++} > Ni^{++} > Mn^{++} \approx Co^{++} > Ca^{++} > Zn^{++} > Mg^{++}$.

The experiments of Khanna and Stevenson (41) demonstrated the formation of stable metal complexes with metals bound primarily by acidic groupings, probably carboxyls. Schnitzer and Skinner (40) also provide evidence for the formation of electrovalent

bonds between negatively charged carboxyl groups of organic-matter and positive charged metals. The results of the foregoing investigators showed no evidence for the participation of phenolic hydroxyl groups in the organo-metallic reactions.

Ong and Bisque (42) showed that the functional groups of humic substances dissociate in water forming polyelectrolytes. Experiments with coagulation of humic colloids by different electrolytes showed agreement with the Shulze-Hardy rule that trivalent ions are more effective in coagulating humic matter than divalent ions and that divalent ions are more effective than monovalent ions.

Rashid (43) tested a number of humic acids isolated from marine sediments (collected from oxidizing acid reducing environments) and noted that there were differences in the amount of metal ions complexed which may be attributed to chemical characteristics of the humic acids, differences in ionic radius, the structure of ionic shells, and of polarization of metal ions. By the use of desorption studies, he determined the binding strength of humic acids and metal ions. The results suggest that within the same valence the degree of binding of metal ions varied widely. His studies showed that under experimental conditions the binding strengths of Co, Mn, Mi and Zn appeared weak, but with aging of sediments with geologic time, the bonding strengths became stronger (43).

Adsorption studies by Rashid (43) indicated the following order of adsorption for metals by peat: Cu > Ni > Co > Zn > Mn.

In was found to be the predominant metal on the peat.

The work of Leland <u>et. al.</u> (44) suggests that fulvic acids, which have a higher number of functional groups than do humic acids and lower molecular weights, have greater mobility in the aquatic environment and, therefore, are of greater importance in the transport of metals.

DeGroot and Allerson (19) determined that the mobilization of metals fixed to suspended matter which occurred downstream of tidal area of certain rivers was caused by the decomposition of organic matter in the sediments from the fresh water tidal area and release of decomposition products which formed organo-metallic complexes with metals from the suspended matter. The authors isolated fulvic acid and humic acid from organic matter of the tidal freshwater regions of the Ems and Rhine. The fulvic acid fraction was determined to be mainly responsible for the mobilization process. They distinguished three groups of fulvic acids based on M.W. and determined that only groups having M.W. of 1,000 to 10,000 had chelating properties. By comparison of fulvic acid fractions, they found that the Ems had a greater mobilizing capacity than the Rhine. They also point out that because of a lack of organic matter and decomposition in the fresh water tidal region of tropical rivers that there should be no mobilization of heavy metals in suspended matter in such rivers as they flow from a freshwater tidal region into the sea (19).

Other Organic Substances

Lerman and Childs (46) investigated two organic compounds, NTA and citrate, which can be found in natural waters affected by industrial societies, and found that the two compounds could modify the existing distributions of ionic species in waters. The investigators determined that the two compounds form strong complexes with metals such as Cu, Pb, Fe, Ni, Co, and Zn and weaker complexes with Ca and Mg. The authors proposed that the role of equilibrium exchange and adsorption mechanisms by sediment particles in regulating the rise in concentration of a complexing agent introduced from outside of the waterbody is to slow down the rate of approach to steady state, without affecting the steady state concentration value (45).

Effect of Organic Matter on Trace Metal Distribution

Several investigators have found strong positive correlations between concentrations of organic matter and trace metals. Bakir-Blocker et. al. (46) demonstrated that organic rich mud from the East and West portion of Grand Traverse Bay, Lake Michigan contained more zinc and other metals than silty surface sediment. Trace element acid organic carbon content of the surface sediment were strongly correlated with the mean grain size of the sediment. Results of the study also showed that surface sediments from "low energy environments" of deposition contained higher concentrations of trace elements and organic matter than "higher energy environments" of the bay which are not conducive to preserving organic matter in sediments or accumulating trace elements (46).

Investigations by Loring (47) of the distribution of zinc, copper, and lead in the sediments of Saguenay Fjord, Norway, showed strong correlations of non-detrital (acid soluble) Zn, Cu, and Pb with mud and organic matter. Other findings suggest that the amounts of Zn, Cu, and Pb in the non-detrital fraction may depend not only on the quantity of organic matter, but also on the type, as it is characterized by its C/N ratio. The affinity of elements for organic matter was in the order Zn > Cu > Pb (47).

The work of Duce et. al.. (48) demonstrated that the concentration of metals was enriched in the surface microlayer of Narragansett Bay (Rhode Island) water relative to the bulk of the water 20 centimeters below the surface. The metal enrichment was found in the particulate and organic fractions but not in the inorganic fraction. A lipoid material was abundant in the microlayer (48).

Hydrous Oxides as a Control Mechanism for Heavy Metals

The role of hydrous oxides of iron and manganese in metal regulation in aquatic systems has received the consideration of several investigators.

Importance of Hydrous Oxides

According to Jenne (49), hydrous oxides of Mn and Fe furnish a principle control on the fixation of Co, Cu, and Zn in soils, clays, and sediments. Because the oxides occur as coatings on silicate material rather than as discrete well-crystallized minerals, these substances

can exert chemical control in excess of their total concentration.

In fact, Jenne (49) maintains that most of sorption of heavy metals by clays and soils could be because of manganese oxide coatings present in minor amounts.

Factors Controlling Hydrous Oxides

Important factors controlling the availability of hydrous oxides occluded heavy metal include the following (49):

- Aqueous concentration of metal in question;
- 2) Aqueous concentration of other heavy metals;
- 3) pH, Eh;
- 4) Amount and strength of organic chelates, and inorganic complex ion formers present in solution.

Of the above factors, pH and Eh are deemed the most important. If conditions of pH and/or Eh are such that hydrous oxides and occluded heavy metals undergo partial dissolution, organic matter would then play a direct role in control of heavy metal availability, especially in highly organic soils and sediments. Changes in pH control heavy metal fixation and availability on oxides by affecting the competitive exchange of hydrogen with heavy metals on hydrous oxides and by dissolution-precipitation and oxidation of hydrous manganese and iron oxides (49).

Morgan and Stumm (50) determined that the z.p.c. (zero point of change) for colloidal hydrous MnO_2 was about 2.8. At pH values above the z.p.c., OH^- ions bind to the hydrous oxide surface or cause dissociation of H^+ ions from surface OH groups. With increasing pH,

the charge (portion of charge due to OH and H^+) becomes more negative. The cation exchange capacity of hydrous oxides increases with increasing pH (increasing negative charge). In addition, the affinity of MnO_2 for H^+ and multivalent cations is larger than that for alkali ions. The concentration of the cations also affects the charge characteristics and colloidal stability of hydrous oxides. Polyvalent cations were found to reduce the charge and decrease colloidal stability. The MnO_2 dispersion exhibited a higher sorption capacity for Mn^{+2} , Zn^{+2} than for Mg^{+2} and Ca^{+2} , likely, because the former ions are hydrolyzable to a greater extent (50).

Distribution and Mode of Occurrence

In the southeastern U.S. black coatings of Fe-Mn oxides are found developed on outcrops and boulders in streams. In a study of these coatings in streams of Georgia, Carpenter et. al. (51) observed that the coatings occurred at the interface between oxidic and reducing waters. Both the dissolved oxygen and carbon content of the bottom sediment, therefore, play a role in controlling the position of the interface at any point in time. Jenne (49) has found that Mn oxides precipitate at Eh values above +200 mv. A dissolution of the precipitate occurred with a lowering of the Eh.

The period of growth for the coatings was observed to be from April to November. The thickness and abundance of the coatings declined in the winter. The authors (51) have proposed that a decrease in both

Eh and pH because of the creation of anoxic conditions which have

resulted from the accumulation of leaves over the stream bottom caused the dissolution of the black coatings during the winter months. The principal source of dissolved manganese for coatings was groundwater (51).

Turekian and Scott (52) found that aged iron and manganese oxides are not good cation absorbers for normal stream concentration of trace elements, but that fresh precipitates of iron oxide (hydroxide) either in the soil profiles or as a result of an acid industrial waste being neutralized act as an excellent metal scavenger.

Duchart <u>et. al.</u> (53) determined that the distribution of zinc and other elements in sediment pore spaces was the result of burial and consequent reduction of Mn and Fe oxide films or layers in rapidly accumulating sediments.

Perhac's study (18) found that free iron oxides can occur on disseminated particles and as coatings on other minerals, especially on clays and quartz. Minor amounts can also occur with organic matter. He attributed the association with free iron oxides rather than surface adsorption as the major factor controlling the fixation and availability of trace metals.

Importance of Particle Size and Grain Chemistry

Particle size and grain chemistry are important parameters determining the distribution of metals in a stream sediment.

Particle Size Considerations

Sediments can be classified in particle size groups as follows: clay 0.004 mm; silt; 0.004-0.062 mm; fine sand, 0.062-0.5 mm; medium sand, 0.05-2.0 mm; and coarse sand, > 2.0 mm (54).

Metallic concentration is affected by particle size and surface area as demonstrated by the work of Oliver (54) and Slate (55).

The average metal concentration in mg/kg of silt samples was

Fe, 17,440; Zn, 88; Pb 33; Hg, 0.22; Cu, 25; Ni, 29, Co, 15; Mn, 189; Cr, 27. In medium size samples, the (mg/kg) concentration was Pb, 5; Hg, 15; Zn, 24; Cu, 9; Ni, 10; Co, 6; Fe, 4,300; Mn, 63; and Ci, 9. Slatt (55) demonstrated that the average concentration of trace metals increases systematically from muddy sand to sandy mud to mud in the sediments of Conception Bay, Newfoundland. E.P.A. (33) found that two stations in Baltimore Harbor with high sand (90%) had the lowest concentration of metals.

Clay Minerals

Because of a high surface area per unit weight and adsorption capacity, clays are excellent scavengers of trace metals (33). In fact, the concentration of metals in soils and sediments can be related to clay content. Zinc concentrations in sediments were found to follow the order: clay > silt > organic matter > sand (56).

A complex set of physiochemical conditions determine the reactivity of clays with dissolved constituents (57). These are listed as follows:

- 1) Origin of clays;
- 2) Size and shape (size not to exceed 2μ);
- Structure.

Factors governing the selective characteristics of clays for different cations are: valence, hydrated ionic radius, electronegativity, and free energy of formation (44). The ion exchange properties of clays are similiar to cation exchange resins, excepting the fact that charge characteristics of clays originate from isomorphous replacements and broken edges of crystal surfaces (44). Adsorption on clays results because of unbalanced forces on the interface which arise as a result of broken bonds at the surface, lattice defects, and from isomorphous substitution within the lattice. Because adsorption depends on the strength of surface energy of solid, adsorption is most efficient at high values of total surface energy. The large surface energy of clays makes them good sorbents. Adsorption of metals on clays can be explained in terms of the electrical double layer concept (57).

Leland <u>et. al.</u> (44) cite data from Tiller and Hodgson (58) which indicate for cobalt and zinc (with similar reactivities) the following order of reactivity for unground clay minerals: hechlorite > vermiculite > nontronite > montmorillonite > halloysite > kaolinite. Grinding was found to have a serious effect on the reactivity for cobalt and zinc. For ground minerals the order becomes: musconite > phlogopite > talc > brotite > vermiculite > pyrophylitte. The effect of grinding is to cause an increase in the surface areas of clay minerals and formation of broken crystal edges (58).

Complexing agents may alter the affinity of clay minerals for different cations. For this reason, the relative roles in retention and transport of trace elements must be evaluated with caution (43).

It should be noted that even though fine grained sediment fractions may contain higher concentrations of metal that most of the total element may be in the coarse fraction in those sediments where the coarse grained particles predominate. Perhac (18) noted that 60.2 percent of total zinc was in the $>100\mu$ fraction of bottom sediment.

Distribution of Zinc and Other Heavy Metals in Natural Waters

Several studies have been performed to define the distribution and transport mechanisms of zinc and other heavy metals in aquatic systems. Some of these are discussed below.

Turekian and Scott (52) showed that eastern U.S. streams were higher in metal concentrations than western U.S. streams.

Durum and Hoffty (23) cite data which indicate that the range of zinc in large rivers of North America varies from 0 to 215 ppb.

E.P.A. (33) compared the concentration levels of heavy metals found in Baltimore Harbor to another highly industrialized harbor the Elizabeth River, to the Chesapeake Bay, and to the James River. The zinc concentrations (avg.= 880 mg/kg) in the Baltimore Harbor sediments were 2-3 times the levels (avg. = 350 mg/kg) found in the south branch of the Elizabeth River. The James River sediments contained the

least amount of zinc (avg. = 131 mg/kg) with the average values of the James very similar to the open Bay (13).

Holmes et. al. (10) showed that spatial and temporal variations in zinc and cadmium occur in marine estuarine systems. During the summer, dissolved Zn and Cd ranged from a high of 480 to 78 ppb, respectively, in Corpus Christi Harbor to a low of 6 ppb and 3 ppb, respectively, in Corpus Christi Bay. During the winter, zinc ranged from 182-4 ppb and cadmium from 10 to less than 2 ppb.

Duke <u>et. al.</u> (59) studied the movement and distribution of Zinc 65 in water, sediments, and macrobiota of two experimental estuarine ponds. The result of their experiments indicate that sediments serve as a major reservoir of zinc in the estuarine environment and that the exchange of zinc between the sediment and water dominated the cycling of this element and controlled its distribution in the ponds.

In his investigations of the distribution of trace metals in Poole Harbor, Poole Town, England, Boyden (60) determined that several trace metals, especially Cd, nickel and Zn fluctuated widely in the waters of a restricted region of the Harbor. Elevated tissue levels in shellfish and algae collected from the area were in contrast to low levels in the sediments (60).

Mills and Oglesby (61) reported that levels of soluble Pb,
Cd, Zn, Cu, and Ca were low in Lake Cayuka, New York, in comparison
to the major rivers of the U. S. as well as below drinking water standards.

It was proposed that much of the trace elements in the tributary stream sediments likely end up as deltaic and lacustrine deposits (61).

The sediments of Sorfjord in west Norway were studied (62). A fall off in sediment metal concentrations for zinc was noted as the distance from area of discharge from a zinc smelting plant increased. This decrease was attributed to dilution by metal-poor natural sediments (62).

Gibbs (63) determined the amount of metals transported by each of five chemical mechanisms of transport in rivers. These mechanisms included:

- la) Dissolving or ionic species and inorganic
 associations;
- 1b) Complexing with organic molecules in solution;
- 2) Adsorption on solids;
- 3) Precipitation and coprecipitation on solids
 (metallic coatings);
- 4) Incorporation in solid biological materials;
- 5) Incorporation in crystalline structures.

He found that incorporation into crystalline structure of sediments is the major mechanism. This mechanism is controlled by crystalline material carried by the river. The materials composition is determined by the composition of rocks of the drainage basin. The major transport mechanisms for iron were metallic coatings and crystalline particles (63).

Summary

It is evident from the foregoing discussion that a complex array of physical, chemical, as well as biological factors interact to regulate the concentration and distribution of zinc and other heavy metals in the water column (among the suspended, dissolved and colloidal fractions) and in the sediments of natural waters. The concentration and distribution of a heavy metal in an aquatic system are affected not only by the nature and characteristics of the source of the metal but, even more importantly, by the chemical, physical and biological conditions, i.e., water quality of the receiving stream.

The information presented in this section should provide a basis for evaluating and explaining the experimental data concerning the concentration of zinc in the dissolved and suspended fractions of the water column and in the sediments of Ash Camp Creek downstream of the discharge from Va. Crafts. In view of the literature, the reader should be mindful that no single factor (chemical, physical, and/or biological) will be responsible for controlling the concentration and distribution of zinc among dissolved and suspended solids and the sediments of Ash Camp Creek.

III. MATERIALS AND METHODS

The study reported in this thesis was performed over a four week period during June 1977. Samples were collected on June 9, 16, 23, 28, and 29.

In the following section, a description of Ash Camp Creek and location of sampling stations as well as an outline of various field and laboratory procedures employed in the study are provided.

Site Description

The headwaters of Ash Camp Creek stem from the discharge of two stormwater drainage pipes from the Town of Keysville, Virginia. Below the stormwater drainage pipe, the stream meanders through a wooded area for approximately 200 meters (m.) before reaching its confluence with the industrial wastewater discharge from Virginia Crafts, Inc. (Va. Crafts). The segment of stream (just described) upstream of the discharge point is intermittent inflow. Wastewater treatment of the industrial effluent, which contains substantial color and is contaminated with zinc, is accomplished by an aerated lagoon and sedimentation followed by post aeration using an aeration ladder. During the study period, the discharge was in excess of 100,000 gallons per day.

Below the Va. Craft's discharge, the stream flows for about 150 m. before simultaneous confluence with a domestic sewage discharge from the Town of Keysville and the flow from a small unnamed tributary. The domestic sewage is treated by primary settling,

biological filtration through a trickling filter, and post chlorination within the discharge pipe. During the study period, the flow from the effluent pipe was about 25-35% of the flow in Ash Camp Creek upstream of the discharge point.

Downstream from the treated sewage discharge, Ash Camp

Creek traverses through pastureland and forestland for another

approximately 11.5 kilometers (km.), joining with many smaller tributaries along its length, before reaching its confluence with Roanoke

Creek, a tributary to the Roanoke River.

Much of the streambed of Ash Camp Creek is rocky, consisting of shale outcroppings (64). The stream aquatic habitat is comprised of both riffles and pools. A series of beaver dams along the course of the stream has created several small impoundments, which likely function as sedimentation basins.

Sampling Station Locations

Eight sampling stations were established at various locations along Ash Camp Creek and at major discharge points. The stations, which are indicated in Figures 1 and 2, are described as follows:

Station 1

This was the upstream control station and was located in a pool area approximately 20 m. upstream from the point of discharge from Va. Crafts. Flow at this station was intermittent. Highest flows were observed during wet weather (June 9 and June 23). The sources of flow in streams above this station consist of stormwater

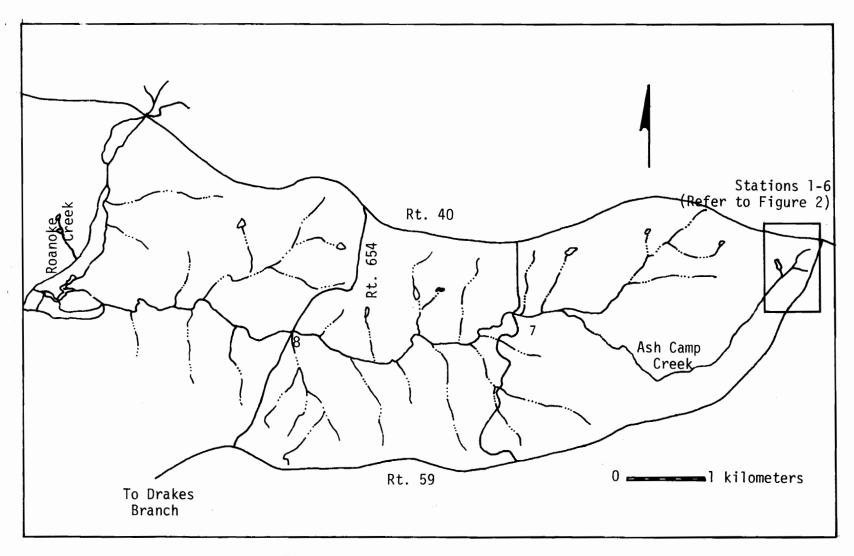


FIGURE 1. Map of Study Area Showing Ash Camp Creek and Sampling Station Locations Numbers Indicate Stream Sampling Station Locations

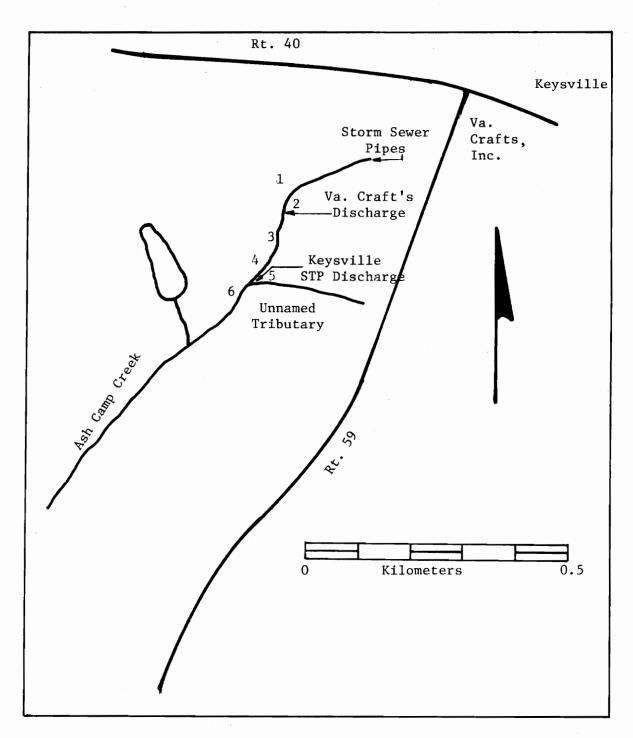


FIGURE 2. Enlargement of a Portion of Figure 1 Showing Stations 1-6 and Discharges from Va. Crafts and the Keysville STP Numbers Indicate the Location of Stream Sampling Locations

from the Town of Keysville and runoff from forestland and from Va. Craft's parking lot. An oily sheen was observed floating on the surface of the water on the June 16 sampling date and an aromatic petroleum odor in the water (and/or sediments) was noted on all sampling dates. The substrate consisted largely of gravel and sand with smaller amounts of finer sediments.

Station 2

This station was located at the end of the aeration ladder from Va. Craft's wastewater treatment facility. Access to this station as well as to stations 1, 3, and 4 is gained through a gate from Va. Craft's wastewater treatment facility. The wastewater was generally yellow-brown colored and foamed somewhat as it entered Ash Camp Creek.

Station 3

Station 3 was located approximately 50 m. below the discharge from Va. Crafts and just upstream of the point where Ash Camp Creek flows through a concrete culvert. The station can be most easily reached by following the creek from Virginia Craft's discharge to a point 4 m. upstream from the concrete culvert. The stream bed was scoured at this site and consisted of primarily gravel and sand with smaller amounts of finer sediment.

Station 4

Station 4 was situated about 70 m. upstream from the Keysville Sewage Treatment Plant discharge and about 80 m. downstream from

the Va. Craft's discharge. The station can be most easily reached from the access road to the Keysville Sewage Treatment Plant.

Scouring was also evident at this location, but deposits of sand, gravel (but less gravel than at Station 3), and finer sediments were present close to stream banks. Water color was yellow-brown at this station, as it was at Station 3.

Station 5

Station 5 was located at the end of the effluent pipe from the Keysville Sewage Treatment Plant. The pipe discharges about 150 m downstream from the point of discharge from the Va. Craft's effluent. High chlorine residuals were observed (as evidenced by pungent odor and burning of eyes) on the June 23, 28, and 29 sampling dates. A small unnamed tributary joins with flow of the sewage treatment plant at the point of confluence with Ash Camp Creek.

Station 6

Station 6 was located near a sludge bank which is formed in a pool about 40 meters downstream from the sewage treatment plant discharge. Septic conditions were noted at this station, indicated by characteristic odor of hydrogen sulfide gas and a black color. The substrate was very fine and watery consisting of primarily organic matter with lesser amounts of salt, clay, silt, and fine sand. No gravel was present.

Station 7

Station 7 was located approximately 5 km. below the discharge point from Va. Crafts on the upstream side of a beaver dam impoundment. Access is gained by hiking through the woods in westerly direction from the south approach to the Continental Can Bridge. The beaver dam impoundment measures about 5 meters across at the dam and is perhaps 2 m in maximum depth. The substrate consisted of mostly fine grained silts, clays, fine sands, and plant debris (i.e., fragments of leaves and twigs). The impounded water had a characteristic greenish brown tinge.

Station 8

This was the farthest downstream station in the study, located about 8 km. below Virginia Craft's discharge on the upstream side of the Route 654 bridge. The stream was free flowing at this point. A small beaver dam was observed obstructing flow upstream from this station. Sand, silt, and clays comprised the substrate. There was little or no gravel present. No unusual color was noted.

Field Procedures

Four water samples were collected from each of the above described stations on each of the five sampling dates. All water samples, except those from Station 7, were collected from the surface. Samples from Station 7 were taken from about 0.5 m. below the surface. The water samples are described as follows:

- Sample 1 (Zn water sample) was collected in a polyethylene container (65); subsamples from this collection were later processed for dissolved zinc, suspended zinc, and total zinc.
- 2) Sample 2 (water quality sample) was collected in a polypropylene container; subsamples were later processed for solids, alkalinity, and hardness determinations.
- 3) Sample 3 (TOC sample) was collected in a brown amber bottle for TOC analysis.
- 4) Sample 4 (field test sample) was collected in a standard B.O.D. bottle and was subjected to field tests for temperature, D.O., pH, and conductivity, in that order.

Two sediment cores, which were collected from all stations except 2 and 5, were obtained by forcing Phlegar plastic core tubes (60 cm long by 3.4 cm in diameter) into the streambed. The tube ends were sealed with polystyrene stoppers (No. 10). Collection methods were as described by Namminga and Wilhm (66). Cores were collected on all sampling dates except June 28.

Immediately after all samples for a given station had been collected, field tests for temperature, D.O., pH, and conductivity were run. The following field instruments were utilized to perform the above tests: A YSI Model 54A Oxygen Meter (Yellow Springs Instrument Company), a Photovolt Model 126 pH Meter (Photovolt Corporation), and a Barnstead Model Pm-70CB Conductivity Bridge (Barnstead Sybron Corporation). All instruments were calibrated and operated in accordance with the particular manufacturer's instructions. After completion of the above tests, the water sample (field test sample) used for the field tests was discarded.

The other three samples (1-3) were placed in a polystyrene ice chest, pending transport to the laboratory. With regard to the core tubes, excess water above the sediment was siphoned off through Tygon tubing before firmly sealing the tubes. The tubes were then frozen in the field in dry ice freezer boxes which were constructed by cutting holes in the lids of reagent acid boxes. Due to a shortage of dry ice, it was not possible to freeze in the field the cores collected on June 29 sampling date. These samples were returned to the laboratory in Blacksburg and then frozen with dry ice.

Field Laboratory Procedures

A temporary field laboratory, which was established in the Va. Craft's wastewater treatment facility laboratory building, was used to perform various chemical tests and filtrations prior to transport of the samples to the VPI & SU Sanitary Engineering Laboratory (Tech lab) in Blacksburg. Samples from the field were returned to the field laboratory within 1 to 2 hours of collection.

Procedures for Water Quality Determinations (Samples 2 and 3)

Upon reaching the lab, T.O.C. samples were immediately removed from ice chests and acidified with concentrated HCl (67).

A portion of water from water quality sample was transferred to a Gooch crucible, that had been prepared in accordance with Standard Methods (67) and was filtered. Two replicate Gooch crucibles were employed for each of the 8 water samples. After filtration, the

crucibles were placed in a dessicator to await further processing for suspended solids and volatile suspended solids.

Alkalinity and hardness (Total and Ca) were also determined on subsamples from the water quality sample for each sampling location, again, in accordance with procedures prescribed by <u>Standard Methods</u> (67). A methyl purple indicator was employed for alkalinity titrations. Standard TitraVer was used as the titrant in the EDTA Titrimetric Procedure (67) for hardness.

Due to the length of time involved in processing zinc samples (Sample 1) it was possible to run many of the above tests concurrently with the zinc procedures described below.

Procedures for Zinc Water Samples

Processing for dissolved, suspended, and total zinc proceeded as follows.

The samples for zinc analysis were removed from the ice chests. For dissolved and suspended zinc, a portion of the Zn water sample was transferred, using a volumetric transfer pipette (50 ml), to a membrane filter apparatus containing a .45 μ membrane filter and a vacuum was applied. The filtrate, which was collected for dissolved zinc analyses, was emptied into a polyethylene container and acidified with 1:1 HNO $_3$ (68). The residue and filter membrane were placed in a beaker (and covered with Parafilm) and saved for subsequent suspended zinc analysis.

For each sample, two filter runs were conducted. Filter runs required 5 to 45 minutes each, depending on sampling site

location. Between each filtration, the membrane filter apparatus was acid washed and rinsed. After completion of the filtrations, the remaining water sample, which would be later analyzed for total zinc, was acidified with 1:1 HNO_3 (68).

Virginia Tech Lab Procedures

Procedures for Water Quality Determinations

Upon return to the Tech lab, Gooch crucibles were processed for determination of suspended solids and volatile suspended solids (67). Total organic carbon (TOC) samples were analyzed by an Dohrman Envirotech Total Organic Carbon Analyzer.

Procedures for Dissolved, Suspended and Total Zinc

Procedures for analysis of suspended, dissolved, and total zinc were completed as follows:

Suspended Zinc

The two replicate filter membranes and residues from each zinc water sample were processed for suspended zinc pursuant to the methods of E.P.A. (68) with the exception that the dried residue remaining at completion of acid refluxing was acidified with concentrated ${\rm HNO_3}$ as recommended by <u>Standard Methods</u> (69). Dilution of samples was required prior to analysis by Atomic Absorption Spectrophotometry (AAS).

Dissolved Zinc

These samples required no additional processing except dilution prior to atomic absorption analysis.

Total Zinc

For the total zinc determination, three replicate subsamples (usually 50 ml) were taken from the zinc water sample for each station and processed according to the methods of E.P.A. (68). Again, the dried residue remaining at the end of the reflux was acidified with concentrated HNO_3 , as recommended by Standard Methods (69).

In the digestion procedures for suspended and total zinc, Lindberg and Corning Hot Plates were employed. All the above samples were stored in polyethylene containers (65) following processing.

Procedures for Zinc in Sediments

Core samples were removed from freezer boxes and placed in the laboratory freezer until further processing could be performed. Processing of core samples for zinc involved the following procedures:

- Cores were thawed slightly using hot water and exuded after removal of stoppers by forcing a pipe into one end.
- 2) The upper 5 cm section of two cores collected from same sampling location on same date were placed in a crucible, thus providing a composite sample for each location.
- 3) The crucibles were placed in a drying oven at 103°C for 48 hours (6). They were then placed in a desicator to cool.

- 4) The dried and cooled sediments were ground with a mortar and pestle just enough to break up dried clumps of mud (70) and then sieved through a .25 mm polyethylene sieve.
- 5) The fines were collected and put in a drying oven at 103°C for at least 1 hour and then cooled in a desicator.
- 6) A dried and cooled portion (about 2.5 grams) of the fines for each sample was placed in a 300 ml C.O.D. flask, 50 ml of 0.5N HCl was added, the flask was stoppered, and then placed on a shaker for 12 hours.

Step 6 of the above procedures is a modification of methods described by Agemian and Chau (71) and Namminga and Wilhm (66).

Upon completion of the above procedures, the samples were filtered, diluted and analyzed by AAS.

An oven dried portion of the sieved sediment from each station was ignited at 550°C for 12 hours to obtain percent loss on ignition.

General Procedures for Zinc

All filtrations for any of the above procedures for zinc were made using glass fiber filters as recommended by Burrell (15). Glassware was kept scrupulously clean by washing with detergent and tap water, rinsing with 1:1 HNO3, tap water, 1:1 HCl, tap water, and finally distilled-deionized water (68). Blank corrections were made for all samples: total, dissolved, suspended, and sediment. Distilled-deionized water was used where necessary, in all metal processing procedures.

Sensitivity of the Zinc Analysis

According to Perkin Elmer (72), the sensitivity in atomic adsorption is "the concentration of an element (usually expressed in μ g/ml for aqueous solution) which will produce a signal of 1% A (0.0044 absorbance units)." For the standard conditions prescribed by Perkin Elmer, the sensitivity of the analysis for zinc is 0.018 μ g/ml Zn for 1% absorption. Perkin Elmer points out that a standard which contains 0.5 μ g/ml will give an absorbance reading of about 0.012 absorbance units (about 25%) (72).

IV. RESULTS

Water quality data, as well as zinc and sediment data collected for the various sampling stations during the course of the study, are listed in Appendix Tables A 1 through A 13. The data have been grouped in the Appendix Tables in the following sequence: Table A 1, pH; Table A 2, temperature and dissolved oxygen; Table A 3, conductivity; Table A 4, alkalinity; Table A 5, total and magnesium hardness (EDTA); Table A 6, total suspended solids; Table A 7, volatile suspended solids; Table A 8, total organic carbon; Table A 9, total zinc; Table A 10, dissolved zinc: Table A 11, suspended zinc; Table A 12, zinc in the sediments; and Table A 13, percent loss on ignition for the sediments. The data for a particular sampling station in each of the above Appendix Tables have been averaged and the averages (means), are summarized in Tables 1, 2, and 4. The data are further compared, analyzed, and/or correlated in Tables 3 and 5 and in Figures 3-17 which will be the subject of the following discussion.

Results of Water Quality Determinations

Table 1 provides a summary of the physical and chemical characteristics of stream and effluent water samples.

Effluent Water Quality

The effluent quality of the discharges from Va. Crafts and the Keysville Sewage treatment plant (STP) can be determined by evaluating the mean water quality parameters determined for Stations 2 and 5. A comparison of the data among various parameters for the

Table 1. Summary of Physical and Chemical Characteristics of Stream and Effluent Water Samples

Physical	Characte	ristics	(means)	Chemical Characteristics (means)						
Sampling Station	Temp °C	Suspend Total mg/l	ed Solids Volatile mg/l	D.O. mg/l		Conductivity µmhos/cm	Total Alkalinity as CaCO ₃ mg/l	Hardness (E Total mg/l	DTA)* Ca mg/l	TOC mg/1
1	20.0	23.2	7.7	5.8	8.7	35	44	93	89	17.6
2	25.8	60.8	35.8	7.2	7.2	121	41	81	74	83.8
3	25.8	51.7	33.0	6.9	7.4	120	44	82	73	75.2
4	26.2	45.8	32.0	5.8	7.0	120	42	76	72	75.1
5	23.4	64.3	40.7	5.7	6.4	51	55	61	56	60.7
6	26.5	45.6	31.0	5.2	7.1	105	49	76	67	81.0
7	23.6	6.7	3.8	7.4	7.2	40	41	65	59	35.3
8	24.4	13.9	4.4	6.0	7.5	23	42	53	46	16.5

^{*}Hardness as CacO₃

two effluents shows that mean values for dissolved oxygen, temperature, pH, conductivity, total and calcium hardness (EDTA) and total organic carbon are higher in the industrial effluent. The greatest discrepancies are noted in dissolved oxygen, conductivity, total and calcium hardness, and total organic carbon. For the foregoing parameters, the following mean values in Va. Crafts' effluent were determined: dissolved oxygen, 7.2 mg/l; conductivity, 121 µmhos/cm; total hardness, (EDTA), 81 mg/l as $CaCO_3$; calcium hardness (EDTA), 74 mg/l as $CaCO_3$; and total organic carbon, 83.8 mg/l. In contrast, mean values for the Keysville STP effluent samples are: dissolved oxygen, 5.7 mg/l, conductivity 51 μ mhos/cm, total hardness (EDTA) 61 mg/l as $CaCO_3$; calcium hardness (EDTA), 56 mg/l as $CaCO_3$; and total organic carbon, 51 mg/l. The sewage effluent was slightly higher in alkalinity, 55 mg/l as $CaCO_3$, and lower in pH, 6.4, compared to the Va. Craft's effluent which had mean alkalinity and pH values of 41 mg/l and 7.2, respectively. On the June 23 sampling date, the STP effluent contained no alkalinity and its pH was 4.6.

Water Quality Effects of Discharges

The effect of the two discharges, particularly the Va.

Crafts discharge, on water quality in Ash Camp Creek is evident, as shown in Table 1 and Figures 3-6.

Below the point of discharge from Va. Crafts (Stations 3 and 4) there is a marked increase in temperature, suspended solids (total and volatile), dissolved oxygen, conductivity and total organic

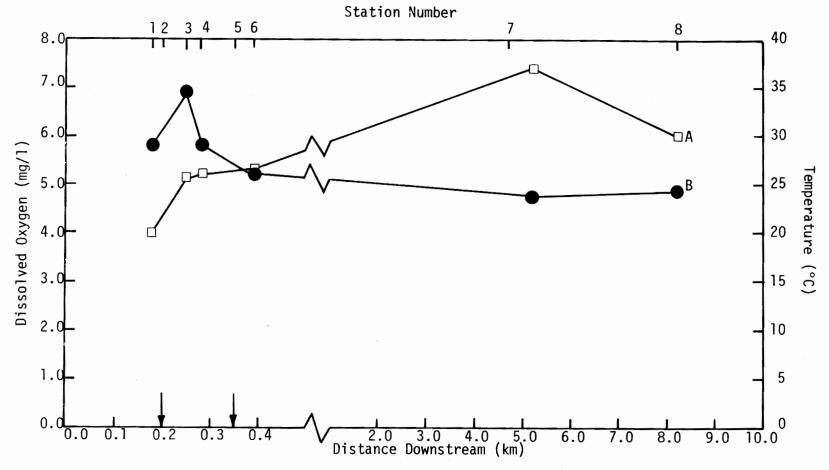


FIGURE 3. Relationship of (A) Mean Dissolved Oxygen and (B) Mean Temperature to Distance Downstream on Ash Camp Creek

Station Number

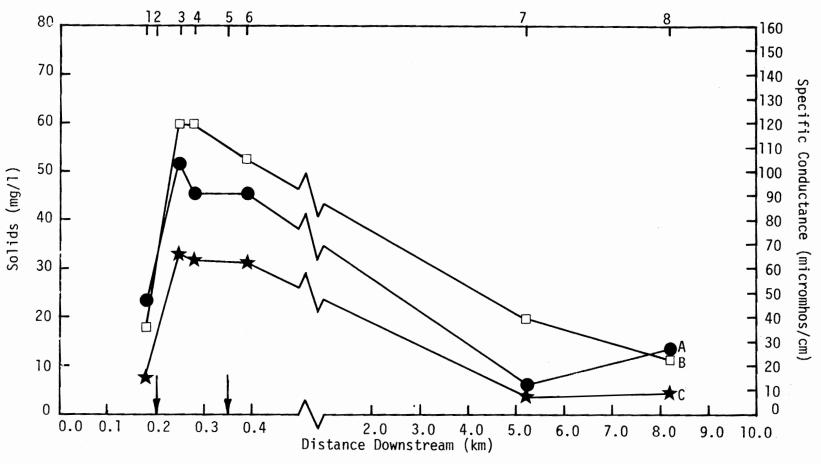


FIGURE 4. Relationships of (A) Mean Total Suspended (TSS), (B) Mean Conductivity, and (C) Volatile Suspended Solids (VSS) to Distance Downstream on Ash Camp Creek

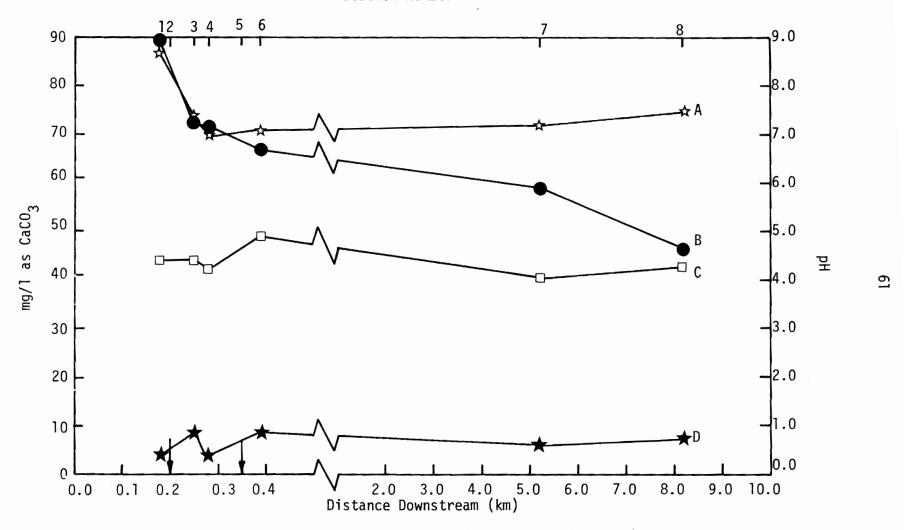


FIGURE 5. Relationships of (A) Mean pH, (B) Mean Calcium (Ca) Hardness (EDTA), (C) Mean Alkalinity, (D) Mean Magnesium (Mg) Hardness (EDTA) to Distance Downstream on Ash Camp Creek

Station Number

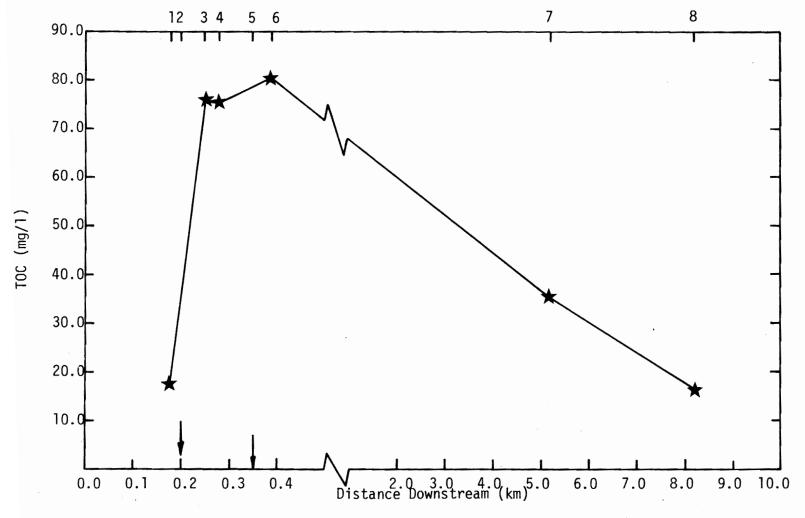


FIGURE 6. Relationship of Mean Total Organic Carbon (TOC) to Distance Downstream on Ash Camp Creek

carbon. A slight decrease in pH form 8.7 at Station 1 to 7.4 at Station 3 also occurs downstream from the point of discharge. Between Stations 3 and 4 (both downstream of Va. Crafts but upstream of the Keysville STP) gradual decreases in suspended solids (total and volatile), dissolved oxygen, pH, hardness (total and calcium) and alkalinity occur. The other parameters remained relatively constant.

Data collected from Station 6, which is located near a sludge bank just downstream from the Keysville STP, show that domestic sewage discharge does not modify (as per the parameters analyzed) the existing water quality in the stream (which has been established by the Va. Crafts discharge). A comparison of water quality data between Stations 4 and 6 indicates that the only parameters affected by the discharge are: alkalinity which increases from 42 to 49 mg/l as ${\rm CaCO}_3$, dissolved oxygen which falls from 5.8 to 5.2 mg/l, and conductivity which drops slightly from 120 to ${\rm 105~\mu mhos/cm}$. The other parameters are not significantly affected by the domestic sewage discharge. It should be pointed out that Ash Camp Creek also receives the flow of an unnamed tributary at the point of discharge from the sewage treatment plant. The water quality effects of this flow are inseparable from the effects of Keysville sewage treatment plant.

Pronounced decreases in several of the water quality parameters occur downstream from the sewage treatment plant discharge, as noted in Figures 3-5. For example, total suspended solids, volatile suspended solids, conductivity, total hardness (EDTA), calcium

hardness (EDTA), and total organic carbon decreases from 45.6 mg/l, 31.0 mg/l, $105 \text{ }\mu\text{nhos/cm}$, 75 mg/l as CaCO_3 , 67 mg/l as CaCO_3 , and 81 mg/l, respectively, at Station 6 (40 m. below sewage outfall) to 13.9 mg/l, 4.4 mg/l, $23 \text{ }\mu\text{mho/cm}$, 53, mg/l as CaCO_3 , 46 mg/l as CaCO_3 and 16.5 mg/l, respectively, at Station 8 (7.8 km downstream). The decrease in total suspended solids, volatile suspended solids, conductivity, and total organic carbon is most dramatic from Stations 6 to 7. The dissolved oxygen reaches a maximum, 7.4 mg/l at Station 7 before declining to 6.0 mg/l at Station 8. Temperature and pH remain at almost constant levels between Stations 6 and 8.

Results of Suspended, Dissolved and Total Zinc Analyses

In Table 2, the mean concentrations of total, dissolved, and suspended zinc in stream and effluent water samples are listed. These values have been plotted against distance downstream from the headwaters of Ash Camp Creek in Figure 7 and the ratios of dissolved and suspended zinc to each other and to total zinc (sum of dissolved and suspended) are given in Table 3. It should be noted from Table 2 that the sum of suspended and dissolved zinc values do not always equal the total zinc value for a particular station. For this reason, it was necessary to calculate the ratios of dissolved and suspended to total zinc based on comparisons between dissolved and suspended zinc values to a total value which represented the sum of the dissolved and suspended fractions.

Table 2. Summary of Concentrations of Dissolved, Particulate, and Total Zn in Stream and Effluent Water Samples

Dissolved mg/l				Suspended, mg/l			Total ^a , mg/l		
Station Number	No. Samples	mean	max ^b	No. Samples with detectable amounts	mean	ma x b	No. Samples with detectable amounts	mean	max ^b
1	6/10	≤ 0.34	0.80	9/10	≤ 0.45	0.98	5/15	<u>≤</u> 1.10	5.00
2	10/10	0.84	2.25	10/10	1.02	1.70	15/15	1.91	3.10
3	10/10	0.91	2.40	8/10	≤ 0.84	2.10	15/15	1.79	2.90
4	10/10	1.28	2.40	9/10	≤ 0.95	2.10	15/15	1.71	3.60
5	3/10	≤ 0.63	2.85	10/10	0.38	0.80	11/15	0.53	1.90
6	8/10	≤ 0.80	1.90	9/10	≤ 1.05	2.30	15/15	1.14	2.50
7	5/10	≤ 0.58	2.40	10/10	0.35	0.90	4/15	≤0.19	1.70
8	2/10	≤ 0.34	1.80	8/10	≤ 0.24	0.80	5/15	≤0.31	1.50

 $^{^{\}mathrm{a}}$ This value represents results of a separate analysis; not the sum of dissolved and suspended fractions

^bDoes not include apparently contaminated samples (likely contaminated by glassware)

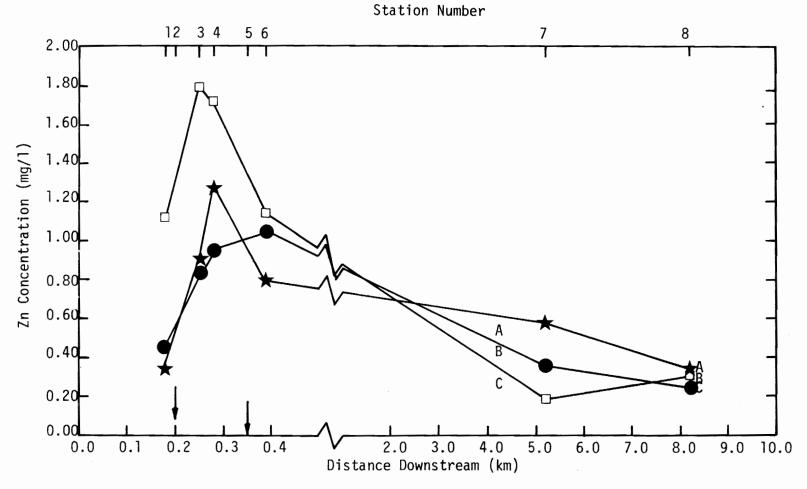


FIGURE 7. Relationships of (A) Mean Dissolved Zinc, (B) Mean Total Zinc, and (C) Mean Suspended Zinc to Distance Downstream on Ash Camp Creek

Table 3. Relationships of Zn in the Water Column: Ratios of Dissolved, Suspended, and Total Zinc

	Mean Conce	ntration		Ratios				
Sampling Station	Dissolved mg/l	Suspended mg/l	Total ^a mg/l	<u>Dissolved</u> Suspended	<u>Dissolved</u> Total	Suspended Total		
1	≤ 0.34	≤ 0.45	≤ 0.79	≤ 0.76	≤ 0.43	≤ 0.57		
2	0.84	1.02	1.86	0.82	0.45	0.55		
3	0.91	≤ 0.84	≤ 1.75	≥ 1.08	≤ 0.52	≤ 0.48		
4	1.28	≤ 0.95	≤ 2.23	≥ 1.35	≤ 0.57	≤ 0.43		
5	≤ 0.63	0.38	≤ 1.01	≤ 1.65	≤ 0.62	≤ 0.38		
6	≤ 0.80	≤ 1.05	≤ 1.85	≤ 0.76	≤ 0.43	≤ 0.57		
7	≤ 0.58	0.35	≤ 0.93	≤ 0.60	≤ 0.62	≤ 0.38		
8	≤ 0.34	≤ 0.24	≤ 0.58	≤ 1.40	≤ 0.59	≤ 0.41		

^aRepresents the sum of dissolved and suspended

Zinc in the Discharges

A comparison of effluent samples (Stations 2 and 5) shows that dissolved, suspended, and total zinc values of 0.84, 1.02, and 1.19 mg/l, respectively, for the Va. Crafts effluent and \leq 0.63, 0.38, and \leq 0.53 mg/l, respectively, for Keysville STP effluent. As shown in Table 3, the ratios of dissolved to suspended zinc were 0.82 and \leq 0.65 mg/l for the Va. Crafts and Keysville STP effluents, respectively. A greater amount of zinc was suspended (ratios of suspended to total Zn of 0.55) in the Va. Crafts effluent than in Keysville STP effluent (ratio of \leq 0.38). The dissolved zinc comprised about 46% of total zinc in the industrial effluent and 67% of total Zinc of the domestic sewage effluent.

Zinc Concentrations in the Stream

The control station upstream from Va. Crafts was found to contain zinc as determined by dissolved, suspended, and total analyses. The mean total zinc was ≤ 1.10 mg/l. The maximum total zinc value, 5.00 mg/l, was recorded for this station. High zinc concentrations are most likely the result of urban runoff because highest values were recorded during periods of wet weather, June 9 and 16. Most of the zinc at Station 1 was in the suspended form.

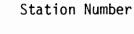
As a result of the Va. Craft's discharge, the zinc content of the stream was increased to almost 1.80 mg/l of total zinc. The discharge increased the dissolved zinc content of the stream by about 9%, as noted by a comparison of data between Stations 1 and 3.

Between Stations 3 and 4, there was a decrease in the proportion of suspended zinc as indicated by an increase in the ratio of dissolved to suspended from ≥ 1.08 (Station 3) to ≥ 1.35 and a change in ratio of suspended to total zinc from ≤ 0.48 to ≤ 0.43 . The above changes are reflected in shift of slope of the graph shown in Figure 8. Note also in Figure 8 the rather random pattern of the plots of dissolved to total and suspended to total zinc. This pattern suggests that changes in the partitioning of zinc between dissolved and particulate fractions may be occurring in this stream segment.

Downstream from the sewage treatment plant (Station 6), a decrease in dissolved zinc (ratio of dissolved to total falls from ≤ 0.57 at Station 4 to ≤ 0.43 at Station 6) and an increase in suspended zinc (ratio increases from ≤ 0.43 to ≤ 0.57) should be noted. A decline in total zinc from 1.71 mg/l (Station 4) to 1.14 mg/l (Station 5) is indicated in Figure 7. The sewage effluent and flow from the unnamed tributary apparently function to dilute zinc concentrations and to change the partitioning pattern.

As illustrated in Figure 7, below Station 6, rapid decreases in dissolved, suspended, and total zinc occur. Dissolved and suspended zinc fall from ≤ 0.80 and ≤ 1.05 mg/l, respectively, to ≤ 0.34 and ≤ 0.24 mg/l, respectively, at Station 8. Total zinc dropped to ≤ 0.19 mg/l at Station 7 and then increased slightly to ≤ 0.31 mg/l at Station 8.

Referring to Table 3, note that as flow proceeds farther downstream, changes in the ratio of dissolved to total zinc and sus-



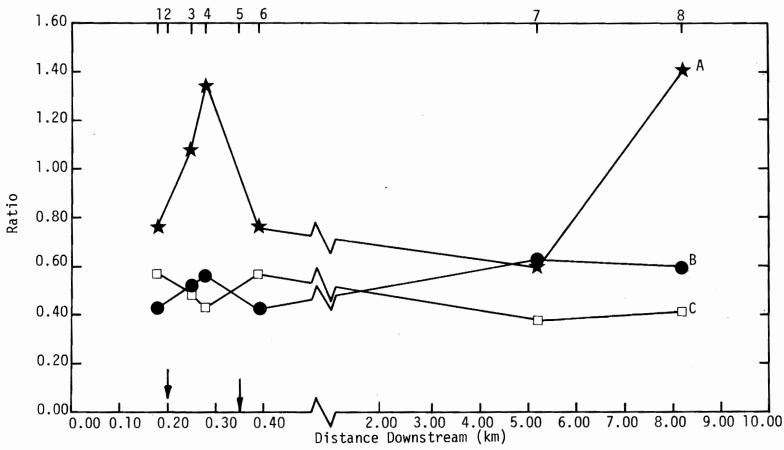


FIGURE 8. Various Ratios of (A) Mean Dissolved Zinc to
Mean Suspended Zinc, (B) Mean Dissolved Zinc to Total Zinc, and
(C) Mean Suspended Zinc to Total Zinc vs. Distance Downstream on Ash Camp Creek

pended to total zinc occur. The dissolved to total zinc ratio increases from ≤ 0.43 to ≤ 0.59 and the suspended to total zinc ratio decreases from ≤ 0.57 to ≤ 0.41 between Stations 6 and 8. The dissolved to suspended ratio increases from ≤ 0.76 to ≤ 1.40 , likely, as a consequence of a decline in proportion of suspended zinc.

Results of Sediment Determinations for Zinc and Percent Loss on Ignition

Table 4 presents a summary of mean zinc concentrations and mean percent loss on ignition data for the sediments of Ash Camp Creek. These values are plotted in Figure 9.

Zinc in the Sediments

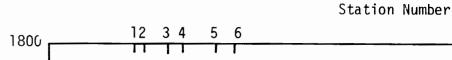
A mean zinc concentration of 307 mg/kg was found in the sediments of the upstream control station (Station 1). The highest mean concentration, 1038 mg/kg. was found at Station 4 about 80 m downstream from the Va. Craft's discharge. Below the sewage treatment plant, a mean zinc level of 627 mg/kg was determined. Zinc in the sediments dropped to a minimum value (31 mg/1) at Station 7 before increasing slightly (to 49 mg/1) at Station 8.

Ratios of Water Column to Sediment Zinc Values

A comparison of the concentrations of zinc as suspended, dissolved, and total zinc in the water column to zinc in the sediments is given in Table 5 and Figures 10 and 11. As shown in Figure 10, where the highest zinc concentrations in the sediments occurred

Table 4. Summary of Zinc Concentrations and Percent Loss on Ignition Data for the Sediments of Ash Camp Creek

	Zn in the Sediments m				
Station Number	No. Samples with detectable amounts	Mean Max		Mean % Loss on Ignition	
1	8/8	307	602	4.58	
3	8/8	550	726	4.05	
4	8/8	1038	1505	3.72	
6	8/8	627	766	8.00	
7	8/8	31	43	1.70	
8	8/8	49	103	2.12	



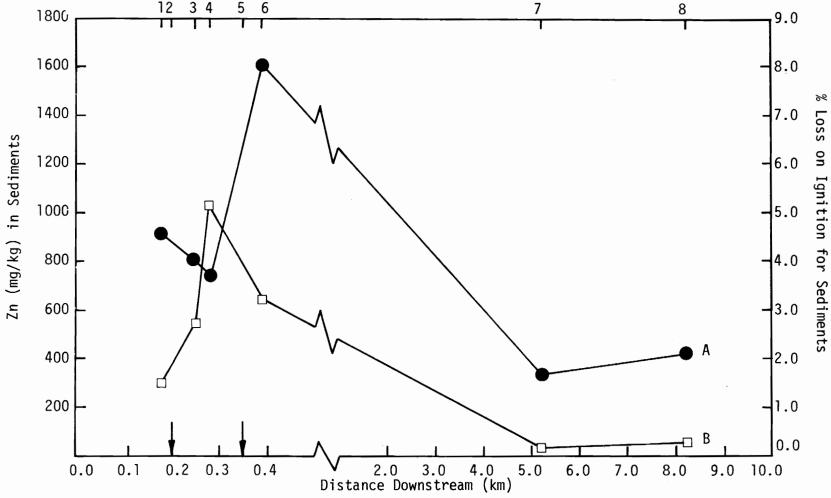


FIGURE 9. RELATIONSHIPS OF (A) Mean Percent Loss on Ignition and (B) Mean Zinc in the Sediments to Distance Downstream on Ash Camp Creek

Table 5. Relationships of Zinc in the Water Column to Zinc in the Sediments: Ratios of Dissolved, Suspended, Total Water Column, and Zinc in Sediments

							•	
	Mean Concentration ^a				Ratios of Mean Concentrations			
Station Number	Dissolved mg/l	Suspended mg/l	Total ^b mg/l	Sediments mg/l	Dissolved Sediments	Suspended Sediments	Total Water Column Sediments	
1	≤ 0.34	≤ 0.45	≤1.10	307	≤ 0.001	<u>≤</u> 0.0015	≤ 0.0036	
2	0.84	1.02	1.91					
3	0.91	≤ 0.84	1.79	550	0.0017	≤ 0.0015	0.0033	
4	1.28	≤ 0.95	1.71	1038	0.0012	≤ 0.0009	0.0017	
5	≤ 0.63	0.38	≤0.53					
6	≤ 0.80	≤ 1.05	1.14	627	≤ 0.0013	≤ 0.0017	0.0018	
7	≤ 0.58	0.35	≤0.19	31	≤ 0.0187	0.0113	≤ 0.0061	
8	≤ 0.34	< 0.24	≤ 0.31	49	≤ 0.0069	≤ 0.0049	≤ 0.0063	

^aA mg/l and mg/kg are both equivalent to a ppm.

^bThese values are the result of separate analyses (not the sum of suspended and dissolved).

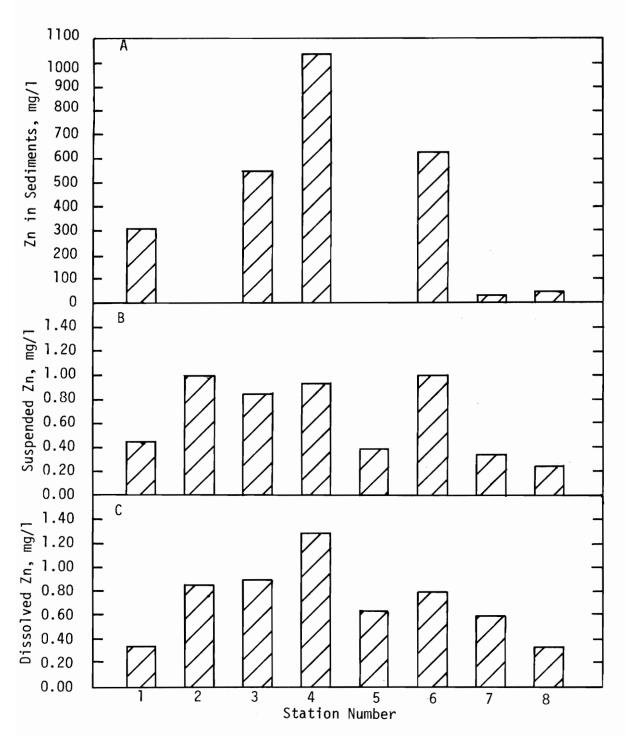


FIGURE 10. Comparison of the Concentrations of (A) Mean Zinc in Sediments, (B) Mean Suspended Zinc, and (C) Mean Dissolved Zinc at Various Sampling Stations

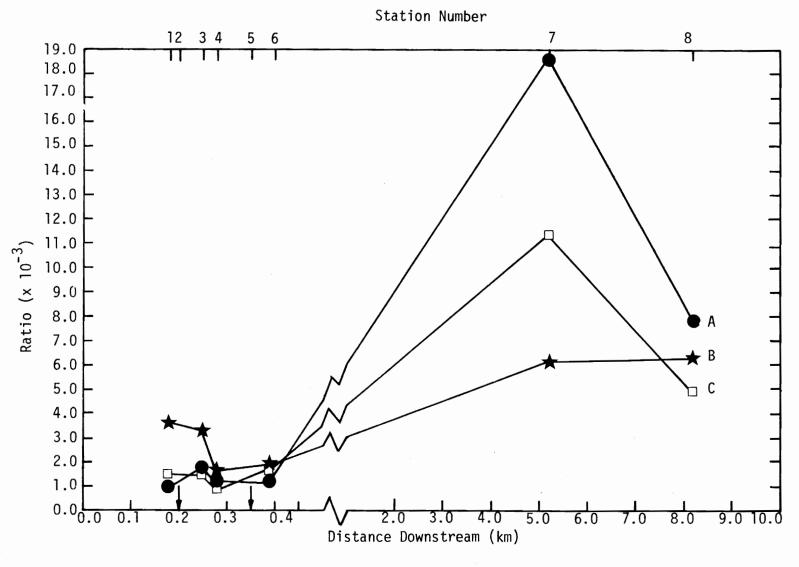


FIGURE 11. Various Ratios of (A) Mean Dissolved Zinc,
(B) Mean Suspended Zinc, and (C) Mean Total Zinc to Mean Zinc in the Sediments vs. Distance Downstream on Ash Camp Creek

(Station 4), there was a slight decrease in suspended zinc ratio and an increase in dissolved zinc ratio. As Table 5 and Figure 11 show, dissolved zinc, suspended zinc, and total zinc in the water column to zinc in the sediments ratios reached a minimum value at Station 4 and increased downstream. The highest ratios for dissolved zinc and suspended zinc to zinc in the sediments occurred at Station 7. The highest ratio of total water column zinc to zinc in the sediments occurred at Station 8. Note the sharp decline in the ratios of dissolved and suspended zinc to zinc in the sediments which occurred between Stations 7 and 8.

Percent Loss on Ignition

The highest mean percent loss on ignition (8%) was noted at Station 6 below the sewage treatment plant and the lowest, 1.7% was found at Station 7. The values for percent loss on ignition for Stations 3 and 4 did not vary significantly and the values were similar to those determined for the upstream control station.

Relationship of Zinc Concentrations to Water Quality

The relationship of dissolved, suspended, and total zinc and zinc in the sediments to various water quality parameters is illustrated in Figures 12 to 17.

As shown in Figure 12, with decreasing conductivity, dissolved zinc concentrations fall off rapidly. The relationship of total and volatile suspended solids to the concentration of suspended

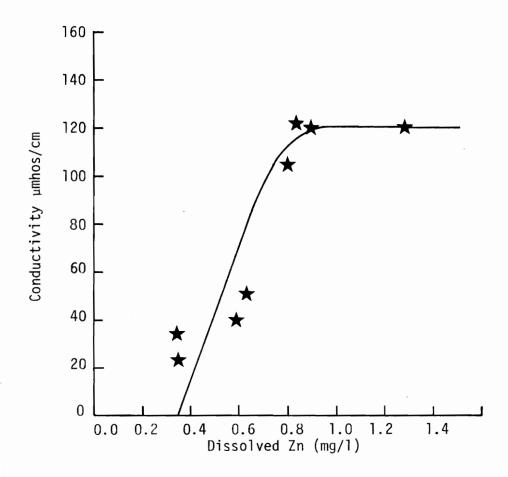


FIGURE 12. Mean Dissolved Zinc as a Function of Mean Conductivity in Effluent and Water Samples

zinc is depicted in Figure 13. An apparent straight line relationship exists between the suspended zinc concentration and both total and volatile suspended solids. The slopes of two graphs (a and b) are almost parallel, suggesting that volatile content of suspended matter may have a significant function in regulation of zinc concentrations.

As Figure 14 would suggest, slight changes in alkalinity (those measured by this study) show no apparent relationship to the concentration of total zinc. Figure 15 relates total and calcium hardness to total zinc concentrations. With decreases in total and calcium hardness, there are rapid decreases in total zinc. Because most of the total hardness of effluent and water samples is comprised of calcium, calcium rather than the various other hardness components, likely is the controlling factor in this relationship.

In Figures 16 and 17, plots of total zinc as a function of total organic carbon (TOC) and zinc in the sediments as a function of percent loss on ignition are indicated. A straight line plot is shown for Zn in the sediments as a function of percent loss on ignition (Figure 17). Total zinc concentration declines markedly with decreases in total organic carbon (Figure 16).

It should be emphasized, again, that the control of zinc distribution in Ash Camp Creek is a result of the interactions of a number of the above factors and not simply the result of any single factor.

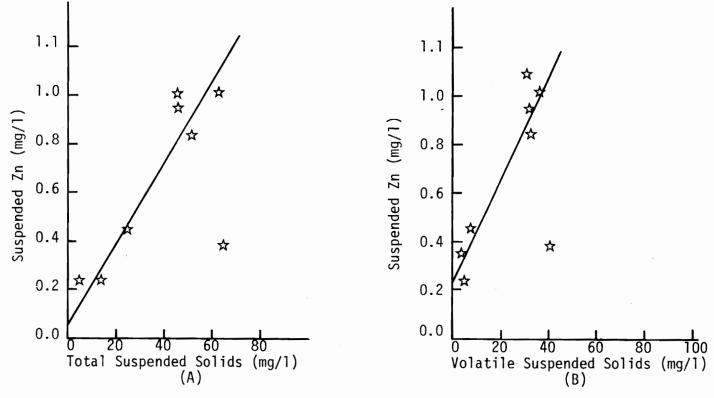


FIGURE 13. Mean Suspended Zinc as a Function of (A) Mean Total Suspended Solids (TSS), and (B) Mean Volatile Suspended Solids (VSS)

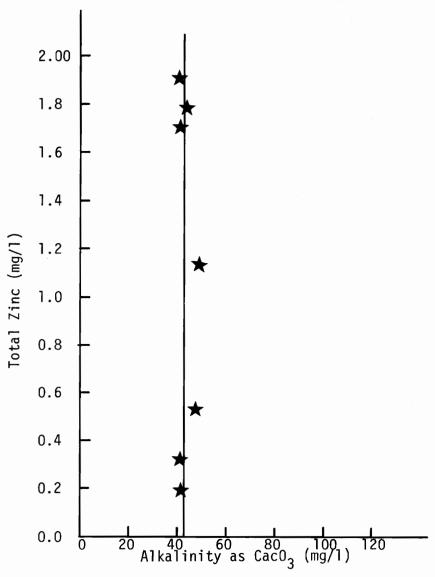


FIGURE 14. Mean Total Zinc as a Function of Mean Alkalinity

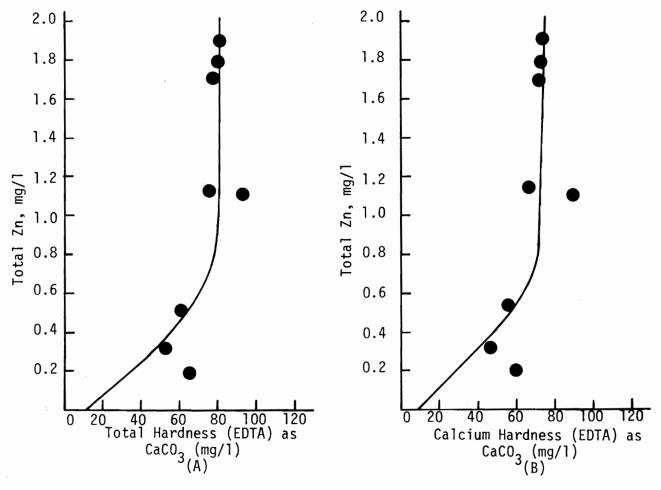


FIGURE 15. Mean Total Zinc as a Function of (A) Mean Total Hardness (EDTA), and (B) Mean Calcium Hardness (EDTA)

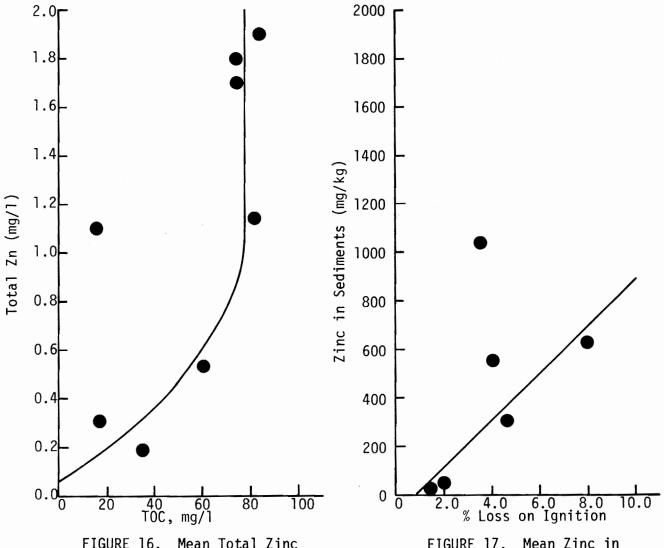


FIGURE 16. Mean Total Zinc as a Function of Mean Total Organic Carbon (TOC)

FIGURE 17. Mean Zinc in Sediments as a Function of Mean Percent Loss on Ignition

V. DISCUSSION

Sources of Zinc to Ash Camp Creek

The results show that there are three discrete sources of zinc being discharged to Ash Camp Creek: urban runoff, the effluent from Va. Crafts, and the effluent from the Keysville STP. Each of the aforementioned sources makes a variable contribution of zinc to the stream, exhibits a varying pattern of metal partitioning among dissolved and suspended fractions, and has a distinct set of chemical and physical water quality characteristics. Of the three sources, the effluent from Va. Crafts is the most important followed, in order, by the Keysville STP effluent and urban runoff. A consideration of each source is provided in the following subsections.

The Effluent from Va. Crafts

As the results indicate, the effluent from Va. Crafts is by far the major source of zinc to Ash Camp Creek. Total zinc was detected in the effluent in 15 out of 15 samples collected over the course of the study with a mean concentration being 1.91 mg/l. Based on a discharge of about 100,000 gallons per day, the load of zinc contributed to the stream is approximately 1.59 lbs/day.

Most of the zinc was associated with particulate matter (about 55%). This finding would be in agreement with the results of Helz et. al. (12) and Chau et. al. (29) who found significant amounts of zinc and other trace metals associated with particulates in domestic wastewater effluents. The form of zinc in the suspended fraction may

be as hydroxides, oxides, silicates, sulfides, and other compounds which are attached to particulates by complexation, adsorption, or ion exchange (6). According to Chen et. al. (13) wastewater particulates in the size range 0.2 to 0.8μ bear the highest concentrations of trace metals. Because $.45\mu$ membrane filters were employed in suspended zinc determinations, many of the smaller particulates ($<.45\mu$) with highest zinc concentrations likely were analyzed with the dissolved zinc fraction. Almost 50% of the suspended solids in the discharge is volatile, suggesting that much of suspended matter is composed of organic substances which are known to play an important role in transporting trace metals. The direct relationship of suspended zinc to total suspended solids and volatile suspended solids has been graphically demonstrated (Figure 13).

Dissolved zinc comprised about 45% of the total zinc in the industrial effluent. This zinc is associated, particularly, with colloids and dissolved solids. The dissolved solids content of effluent is likely an important indication of the concentration of zinc in the dissolved fraction, as indicated by Figure 12.

Studies by King (2) in 1976 showed that the insoluble fraction of zinc (suspended fraction) comprised only about 25 percent of the total zinc with the major portion being soluble (dissolved fraction). On the other hand, the current study determined that about twice as much of zinc is suspended, with the suspended and dissolved fractions comprising almost equal percentages of the total. It is possible that

insoluble zinc concentrations in the effluent have increased since the King study.

According to King (2), overall zinc removal by alum coagulation would be in the order of 25 to 40 percent assuming an insoluble fraction of 25 percent and a soluble fraction of 75 percent. He predicted that zinc removal by alum coagulation would not be sufficient to reduce effluent concentration to 1 mg/l. If the partitioning pattern of the effluent has changed to increase the fraction of insoluble zinc, higher levels of removal than previously predicted might be achieved as a result of alum coagulation (which is quite effective in removing suspended particulates). It should be kept in mind that total zinc levels determined in current study are about 1-2 mg/l lower than those that existed in the effluent at the time of the King study.

An alum coagulation color removal treatment system is to be installed in the near future. Alum along with a polymer will be employed. Part of the color is associated with colloidal material. Because of association of metals with colloids, removal of these substances, by alum coagulation, together with suspended solids, should further reduce the dissolved zinc (< .45 μ) content of the effluent.

The Effluent from the Keysville STP

The results have shown that the wastewater effluent from the Keysville STP is a source of suspended and dissolved zinc, discharged to Ash Camp Creek. The highest concentration of zinc was associated with the dissolved fraction (mean \leq 0.63 mg/l); however, there is a degree of uncertainty associated with this mean because detectable concentrations

were noted for only 3 out of 10 dissolved zinc samples. Suspended concentrations (mean = 0.38 mg/l) were detected in 10 out of 10 samples. For this reason, a greater degree of certainty should be placed in the mean of suspended zinc analyses. Subtracting the suspended zinc mean from the mean for total zinc (\leq 0.53) gives a value for dissolved zinc of about 0.15 mg/l. The fact that most of the zinc in likely in suspended form is in the agreement with other investigators (13).

It should be pointed out that the mean total zinc value $(\leq 0.53 \text{ mg/l})$ is somewhat higher than the 0.10 mg/l value reported for secondary effluent from the City of Los Angeles (13) and 0.28 mg/l value reported for effluent from City of Baltimore (12). Dilution is likely to play a dominant role in lowering concentrations of zinc in larger collection systems, such as those serving Los Angeles and Baltimore.

One of the contributors to the Keysville wastewater collection system is the Keysville laundrymat. It is likely that many laundry products (i.e., phosphate detergents, bleaches, softeners) may contribute zinc to the collection system. One problem with a smaller collection system such as Keysville is that a single discharge contaminated with zinc may not receive sufficient dilution to lower the zinc level to trace concentrations.

It was noted over the course of the study that the trickling filter at Keysville was not operating properly due to a defective mercury seal associated with the distributor arm. Repairs were accomplished during late June. During the repair period, primary

treated sewage was bypassed around the filter and highly chlorinated prior to discharge. Mean total suspended solids were quite high for the study period (about 64 mg/l) probably as a consequence of the bypassing procedure. A high, mean suspended zinc level value may be a consequence of high total suspended solids in the inadequately treated effluent. The relationship of suspended solids to suspended zinc has been previously explained. If the influent wastewater had been properly treated by the trickling filter, one would anticipate that attachment of inorganic and organic suspended particulates to filter media would have likely reduced the suspended particulates, and consequently, the suspended zinc concentration in the effluent. Because of biotic uptake and sorption, dissolved zinc concentrations might also have been reduced.

Because of a high volatile suspended solids (total suspended solids was 60% volatile) and high total organic carbon content much of the zinc (dissolved and suspended) is probably associated with the carbonaceous constituents of the effluent. A lower dissolved solids content (lower conductivity) sewage than for industrial effluent may be the reason why there is a smaller percentage of metal associated with the dissolved fraction of the treated sewage.

The reduction of the total suspended solids content of the effluent to the secondary treatment requirement of 30 mg/l would reduce total suspended solids by about half. A reduction in the solids concentration should bring about a concomittant reduction in zinc. Proper

operation of the trickling filter should reduce dissolved zinc through sorption and biological uptake within the slime growths and suspended zinc through the various mechanisms associated with filtration.

Urban Runoff

As was indicated in the literature review, a significant source of trace metals to aquatic systems is from urban drainage.

The storm sewer pipes which empty into the headwaters of Ash Camp Creek receive drainage from a residential area, a highway, a service station, a car wash, and other undetermined areas. Parking lot runoff from Va. Crafts also enters the stream at its headwaters.

As was mentioned previously, petroleum products (oil, gasoline, etc.) contain zinc and other trace metals. Runoff from streets and parking lots and drainage from a gas station and car wash would be highly contaminated with petroleum products and, consequently, with zinc. The evidence for petroleum in Ash Camp Creek was indicated by an oily slick as well as an aromatic petroleum odor observed at Station 1 during the study.

Urban runoff, as a source of zinc, is confirmed by the fact that water column zinc concentrations were detected only on days of wet weather (June 9 and June 23). Most of the zinc in the water column was suspended (about 57%), which might indicate that zinc in runoff from Keysville is associated primarily with suspended particulates. Chen $\underline{\epsilon t}$. al. (13) reported that silt in runoff from an urbanized area may contain 3,000 - 8,000 ppm. of zinc. During dry weather flow, the stream at Station 1 becomes a small pool. The

quiescent conditions of the pool likely promote sedimentation of suspended solids and associated trace metals which enter the stream in urban runoff.

The mean percent loss on ignition for sediments at Station 1 was about 4.6, the second highest of all sampling stations. It is possible that zinc in urban runoff may be associated with suspended organic matter.

Because the urban runoff source of zinc to Ash Camp Creek is dependent on rainfall in the drainage basin and street cleaning practices, this source would be variable and the load of zinc (lbs/day) although high during wet weather would probably be low at other times.

Distribution and Partitioning of Zinc in Ash Camp Creek

The discussion that follows will consider separately three segments of Ash Camp Creek: the upper 0.4 km segment, the 0.4 to 5.2 km segment, and the 5.2 to 8.2 km segment. Each of these segments exhibits a particular pattern of distribution and partitioning of zinc in the water column and sediments and has a unique set of physical and chemical water quality characteristics associated with it.

The Upper 0.4 km Segment of Ash Camp Creek

The results indicate that the major influence on water quality of Ash Camp Creek, especially in the first 0.4 km, is the Va. Craft's discharge. The discharge significantly affects the suspended solids (total and volatile), dissolved oxygen, pH, conductivity, total organic carbon, and the zinc content of the stream. The water quality

effects of discharges from stormwater pipes are most pronounced during wet weather but are normally overshadowed by effects of the Va. Craft's discharge.

During periods of intermittent inflow, the segment of stream between Stations 1 and 4 is comprised about 99% of Va. Craft's effluent. This stream segment is, therefore, normally atypical of a streams of higher flow where dilution would play a major role in reducing trace metal concentrations as flow proceeds downstream. Concentrations are, therefore, likely reduced by variations in hydraulic conditions along this segment which promote sedimentation of suspended particles and associated zinc.

Between Stations 3 and 4 the flow passes through several bends and obstructions as well as through a concrete culvert. A reduction in flow velocity likely occurs between these two stations.

A reduction in stream velocity would promote a settling of suspended particulates to the sediment. The lower the velocity, the smaller the size of suspended particles that would settle.

There is a 25% decrease in total suspended solids between the discharge and Station 4. Volatile suspended solids and total organic carbon do not decrease appreciably between the discharge and Station 4. The means for percent loss on ignition for the sediments of Stations 3 and 4 do not differ significantly from the mean of Station 1. The data would suggest that a more rapid deposition of inorganic suspended particles than volatile suspended particles may be occurring in the stream segment between the point of discharge and Station 4.

The mean ratio of dissolved to suspended zinc increases from about 1.1 at Station 8 to 1.4 at Station 4, suggesting a possible decline in suspended zinc concentration between the two stations.

There is a slight increase in dissolved zinc which could account for the increase in the above ratio. There is also a reduction of total zinc from Stations 3 to 4. The ratio of total zinc in the water column to zinc in the sediments declines by almost 50% between Stations 3 and 4, which suggests that the increases in sediment concentrations may be caused by sedimentation from the water column.

Because the conductivity is constant from the point of discharge to Station 4, it is likely that dissolved solids are not precipitating within this stream segment. For this reason, dissolved zinc is not likely being deposited on the streambed along this segment.

In sum, the high sediment concentrations at Station 4 have been caused probably by sedimentation of inorganic particles in response to a reduced flow velocity at the station. The inorganic particles may have zinc complexes attached by sorption or contain surface coatings of hydrous oxides of iron and manganese to which the zinc is bound. An analysis of sediments for iron and manganese might confirm the existence of the hydrous oxide coatings.

Between Stations 4 and 6, the stream receives flow from the Keysville STP and an unnamed tributary. There is a reduction of 33% in total zinc concentration and 38% in dissolved zinc concentration whereas the concentration of suspended zinc increases slightly. A drop in conductivity occurs between Stations 4 and 6 and there is a 100% increase in the organic content of the sediments.

The reduction in conductivity suggests that either dilution of dissolved solids or that the complexation, precipitation, and/or sorption processes may be functioning to reduce dissolved solids and associated zinc. Complexation of zinc with organic and inorganic ligands contained in sewage effluent seems likely. The high sediment concentration of zinc and high organic matter content may be related, as was shown in Figure 17.

Probably the most important means of removal of zinc at Station 6 is sulfide precipitation. Sulfide is generally found in large quantities in highly organic sediments. The reaction of dissolved zinc with sulfide would form a relatively insoluble precipitate. [Log of K (25°C) is 25.15]. It should be pointed out that the mean dissolved oxygen, 5.4 mg/l, determined for this station indicated the existence of aerobic conditions. The dissolved oxygen, however, was measured at the surface; below—the surface near the mud-water interface, where sulfide precipitation likely occurs, conditions were likely anaerobic (reducing). The presence of sulfide was confirmed by the characteristic odor of hydrogen sulfide gas given off from the sludge bank at Station 6. The source of the sulfide is most likely the effluent from the domestic sewage treatment plant.

A slight increase in the percentage of dissolved zinc was noted at Station 6. This result might suggest inorganic zinc complexes might be forming which render suspended zinc compounds

soluble and facilitate downstream transport of the metal. The sewage treatment plant may discharge high concentrations of inorganic ligands (Cl $^-$, HCO $_3$ $^-$, PO $_4$ $^-$) which promote the mobilization of insoluble zinc compounds.

Soluble organic compounds that are the byproducts (simple sugars, organic acids, peptides, humic compounds) of sewage treatment and biological activity in the sludge bank might also act to complex suspended zinc, rendering it more soluble (increasing percentage of dissolved zinc) and, thereby, facilitating zinc transport to downstream areas.

The 0.4 to 5.2 km Segment of Ash Camp Creek

Below Station 6, as Figure 1 illustrates, Ash Camp Creek receives the discharge from several small tributaries, many of which exhibit intermittent flow during the summer. According to the State Water Control Board (64), Ash Camp Creek would be intermittent for 2 to 5 kilometers without the discharges from Va. Crafts and the Keysville STP. Any flow contributions from tributaries would likely function to dilute stream zinc concentrations. The dilution should be greater during rainy periods and during late fall, winter, and spring when tributary inflow is greater.

Along the 0.4 to 5.2 km segment of Ash Camp Creek, several beaver dams have been constructed. The impoundments associated with the dams provide quiescent settling areas that promote sedimentation of suspended metals. These areas also serve as "mixing basins" which allow contact of dissolved zinc with complexing agents (probably humic

substances and other organic compounds) that are released as decomposition products within the surrounding forestland and washed into stream in runoff. Trace metals such as zinc can attach to organic compounds and promote coagulation and settling in accordance with the Schulze Hardy rule.

Total zinc concentrations decline by 83% from Stations 6 to 7. Dissolved zinc drops by 28% and suspended zinc by 67%. There is a reduction of total suspended solids of 85% and volatile suspended solids of 88%. Because dilution is minimal from Station 6 to 7, the above data would seem to suggest that sedimentation may be playing a key role in reducing the suspended zinc concentrations.

The fact that conductivity decreases by 62% between Stations 6 and 7 indicates that complexation and precipitation processes may be functioning to remove dissolved solids and complexed zinc.

Although a decline in TOC of 56% and in suspended volatile solids of 58% is noted, at Station 7, there is no dramatic increase in organic carbon in sediments as indicated by mean percent loss on ignition. It seems probable that carbon compounds with complexed zinc may be settling out upstream of Station 7.

The 5.2 to 8.2 km Segment of Ash Camp Creek

Between Stations 7 and 8, inflow from tributaries becomes greater.

According to the State Water Control Board (64), below 5 kilometers

(Station 7) Ash Camp Creek is typical of any stream with permanent flow.

Dilution, therefore, becomes a more important factor in reducing the concentrations of various water quality components. In this segment because of dilution, a 50% decrease in conductivity and total organic

carbon occur, but there is a slight increase in total suspended solids (volatile solids do not change). It is possible that tributaries might be introducing an additional suspended solids load, thereby, increasing the suspended solids concentration of Ash Camp Creek.

The carbon content of the sediments (as indicated by percent loss on ignition) does not differ between Stations 7 and 8. Carbon compounds which are settling out in the sediments are possibly being diluted with low carbon inorganic sedimentary material.

Dilution is likely responsible for the decline in suspended and dissolved zinc concentrations between Stations 7 and 8. At Station 8, most of the zinc is in the dissolved fraction with a lesser amount in the suspended fraction. The ratio of dissolved zinc to total zinc is much greater than the ratio of suspended zinc to total zinc. The above data also suggest that suspended zinc has declined more than dissolved zinc because of sedimentation which affects preferentially the suspended fraction.

The concentration of zinc in the sediments is higher at Station 8, although not significantly different from that at Station 7. It is possible that zinc compounds or complexes may be adsorping to inorganic stream constituents (clays, silts, etc.) which are carried downstream and deposited in the vicinity of Station 8 during periods of high flow. Ferrous and manganese oxide coatings on inorganic silts, clays, and fine sands may play an important role in scavenging dissolved and complexed zinc from the water column. A black coating, possibly, of hydrous oxides of manganese and iron, on the sediments was noted downstream from Station 8.

VI. CONCLUSIONS

The following conclusions can be derived from the results of this study:

- The major source of zinc to Ash Camp Creek is the Va. Crafts discharge followed, in order, by the Keysville STP, and urban runoff. The contribution from urban runoff appears only to be important during wet weather when rainfall washes zinc and other pollutants from streets, paved surfaces, and other areas of the watershed into the stream.
- 2. The measured zinc levels in Ash Camp Creek below the Va. Crafts outfall exceed the toxic level (.01 mg/l) established by the Virginia State Water Control Board for aquatic life in Ash Camp Creek. During wet weather, the toxic level is exceeded at Station 1 upstream of the point of discharge. Levels of zinc in the Keysville sewage treatment plant effluent also exceed the toxic level.
- 3. There is a definite partitioning pattern of zinc in effluent and stream water samples. Ratios of dissolved to suspended zinc varied from about 0.60 to 1.35. Ratios of dissolved to total zinc and suspended to total zinc varied from about 0.43 to 0.62 and from 0.38 to 0.57, respectively. Changes in the above ratios appear to be related to the sedimentation of suspended zinc onto stream sediments.
- 4. Direct correlations between suspended zinc and total suspended solids and suspended zinc and volatile suspended solids appear to exist in effluent and stream water samples. The above relationship would suggest that (a) the zinc content of the effluents and the stream may be influenced by the suspended solids concentration, and (b) the amount of suspended organic matter may be an important factor determining the zinc concentration.
- 5. Of the chemical and physical factors in Ash Camp Creek which affect the distribution and partitioning of zinc, sedimentation, dilution, sulfide precipitation, and adsorption on inorganic sediment particles may play a dominant role. The high sediment concentrations of zinc (over 1,000 mg/kg) 80 m downstream from the

Va. Craft's discharge seem to be the result of sedimentation of suspended zinc in response to decreased flow velocity. Sulfide precipitation is possibly an important mechanism for zinc removal in the sludge bank area below the sewage outfall. Beaver dam impoundments in the segment of Ash Camp Creek between the Keysville STP outfall area and 4.8 km downstream facilate sedimentation by providing quiescent conditions for the settling of suspended zinc and other suspended pollutants. Downstream of Station 7 (4.9 km below STP outfall) where Ash Camp Creek becomes a permanent type stream, dilution, sedimentation, and adsorption to inorganic sediment particles appear to function in reducing zinc concentrations.

VII. SUMMARY

It was the purpose of this study to determine the distribution and partitioning of zinc in a small stream, Ash Camp Creek, which receives a treated textile wastewater, domestic sewage, and urban runoff. Water samples were collected and analyzed to determine the physical and chemical water quality characteristics and the distribution and partitioning of zinc among dissolved and suspended fractions of the water column. Several core samples were obtained and analyzed to determine zinc concentrations in the sediments.

The results indicate that the major source of zinc is the treated textile waste followed, in order, by sewage discharge, and urban runoff. Water samples analyzed for each of the sources exhibited a pronounced partitioning of zinc among the dissolved and suspended fractions and showed distinct physical and chemical water quality characteristics. Urban runoff was only important as a zinc source during wet weather.

In the upper 0.4 km segment of Ash Camp Creek; water quality is most influenced by the physical and chemical characteristics of the industrial discharge. Partitioning of zinc was evident along this segment and sediment concentrations ranged from 300 to 1000 ppm. In the region downstream of the industrial discharge, hydraulic conditions, e.g., reduced stream velocity, which are dependent on the discharge rate of treated textile wastewater seem to affect the sedimentation of zinc to the streambed.

The discharge from the sewage treatment plant and flow of a small tributary which empties into Ash Camp Creek at the point of discharge from the STP have a moderating effect on the water quality of Ash Camp Creek, functioning to slightly dilute concentrations of pollutants (contributed by treated textile wastewater). Sulfide precipitation may be a major mechanism by which zinc is removed from solution in the sludge area downstream from the sewage discharge. Mobilization of zinc from this region may be facilitated by complexation with organic and inorganic ligands released as decomposition products from sludge bank and by-products of domestic wastewater treatment or as components of sewage effluent.

The stream receives flow from only a few permanent type tributaries in the region from the sewage outfall to 5.2 km downstream. Beaver dams and other obstructions along this segment act to create quiescent settling areas for the deposition of suspended zinc.

In the region from 5.2 to 8.2 km downstream, the stream receives the flow of permanent type tributaries which act to dilute zinc and other pollutant concentrations. Zinc is also likely removed in this region by sorption onto inorganic particles of the sediments. Water quality is greatly improved 8 kilometers below the point of discharge of the treated textile waste.

Correlations between various water quality parameters and either suspended, dissolved, and/or total zinc were demonstrated.

VIII. LITERATURE CITED

- 1. U. S. Environmental Protection Agency (E.P.A.), "Quality Criteria for Water," Washington, D.C. (1976).
- 2. King, P. H., "Feasibility of Reduced Zinc Discharge, Virginia Crafts, Inc., Keysville, Virginia." Blacksburg, Virginia (1976).
- 3. Pitchford, R. W., "Ash Camp Creek, Roanoke River Basin, Charlotte County (BS75-033), "Bureau of Surveillance and Field Studies, Division of Ecological Studies, State Water Control Board, Richmond, Virginia (1976).
- 4. Leckie, J. O., and R. O. James, "Control Mechanisms for Trace Metals in Natural Waters." In Aqueous--Environmental Chemistry of Metals. Alan J. Rubin, Ed., Ann Arbor Science Publishers, Inc., Ann Arbon, Michigan (1974).
- 5. Krejci-Graf, K., "Trace Elements in Sediments, Oils, and Allied Substances." Encyclopedia of Geochemistry and Environ-mental Sciences, R. W. Fairbridge, Editor, Van Nostrand-Reinhold, New York, 1201 (1972).
- 6. Williams, S. L., et. al., "Sources and Distribution of Trace Metals in Aquatic Systems." <u>In Aqueous Environmental Chemistry of Metals</u>, Alan J. Rubin, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan (1974).
- 7. Turekian, K. K., and K. W. Wedepohl, <u>Bull. Geol. Soc. Am</u>. <u>72</u>, 175 (1961).
- 8. Steele, K. F. and G. H. Wagner, "Trace Metal Relationships in Bottom Sediments of Fresh Water Stream--The Buffalo River, Arkansas." Jour. of Sed. Petrology, 45, 310 (1975).
- 9. Pita. F. W., and N. J. Hyne, "The Depositional Environment of Zinc, Lead, and Cadmium in Reservoir Sediments." <u>Water</u> Research, 9, 701 (1975).
- 10. Holmes, C. W., et. al., "Migration and Redistribution of Zn and Cd in Marine Estuarine System." Env. Sci and Tech., 8, 255 (1974).
- 11. Allaway, W. H., Advan. Agron., 20, 234 (1968).

- Helz, G. R., et. al. "Behavior of Mn, Fe, Cu, Zn, Cd, and Pb Discharged From A Wastewater Treatment Plant into an Estuarine Environment." Water Research, 9, 631 (1975).
- 13. Chen, K. Y. et. al., "Trace Metals in Wastewater Effluents."

 Jour. Water Poll. Control Fed., 46, 2663 (1974).
- 14. Papakostidis, G., et. al., "Heavy Metals in Sediments from the Athens Sewage Outfall Area." Marine Poll. Bull., 6, 136 (1975).
- 15. Burrell, D. C., Atomic Spectrometric Analysis of Heavy-metal Pollutants in Water, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan (1974).
- 16. Allen, W. E., et. al., "The Contribution of Dyes to the Metal Content of Textile Mill Effluents." <u>Textile Chem.</u> Colorist, 4, 275 (1972).
- 17. Pitt, R. E. and G. Amy. <u>Environmental Protection Technology</u>
 <u>Series</u>, E.P.A.--R-73-283, U. S. Government Printing Office,
 Washington, D. C. (1973).
- 18. Perhac, R. M., <u>Water Transport of Heavy Metals in Solution and</u>
 By Different Sizes of Particulate Solids, National Technical
 Information Service, Washington, D.C. (1974).
- 19. DeGroot, A. J., and E. Allersman, "Field Observations on the Transport of Heavy Metals in Sediments." <u>In Heavy Metals in the Aquatic Environment</u>, P. A. Krenke., Ed., Permagon Press, New York, 85 (1975).
- 20. O'Conner, J. T., <u>et. al.</u>, "Zinc Concentrations in Rivers of the Chesapeake Bay Region." <u>Journ. Amer. Water Works Assoc.</u>, 56, 280 (1964).
- 21. Gorham, E., and D. J. Swaine, "The Influence of Oxidizing and Reducing Conditions upon the Distribution of some Elements in Lake Sediments." <u>Limnology and Oceanography</u>, 10, 268 (1965).
- 22. Delfino, J. J., et. al., "Distribution of Mn, Fe, P, Mg, K, Na, and Ca in the Surface Sediments of Lake Mendota, Wisconsin." Environ. Sci. and Tech., 3, 1189 (1969).
- 23. Durum, W. H. and J. Hoffty, "Implications of the Minor Element Content of Some Major Streams of the World." Geochim. Cosmochim Acta, 27, 1 (1963).

- 24. Andelman, J. B., "Incidence, Variability and Controlling Factors For Trace Elements in Natural, Fresh Waters."

 In Trace Metal and Metal-Organic Interactions in Natural Waters, P.C. Singer, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, (1973).
- 25. Silker, W. B., "Variations in Elemental Concentrations in the Columbia River." Limnol. Oceanog., 9, 540 (1964).
- 26. Lingane, J. J., <u>Analytical Chemistry of Metallic Elements</u>, Reinhold Publishing Corporation, New York (1966).
- 27. Stumm, W., "Metal Ions in Aqueous Solutions." <u>In Principles</u> and Applications of Water Chemistry, S. D. Forest and J. V. Hunter, eds., John Wiley and Sons, Inc., (1967).
- 28. Hahne, H. C. and W. Kroontje, "Significance of pH and Chloride Concentration on Behavior of Heavy Metal Pollutants:

 Mercury (II), Cadmium (II), Zinc (II), and Lead (II)."

 Journ. Environ. Quality, 2, 444 (1973).
- 29. Chau, Y. K., et. al., "Determination of the Apparent Complexing of Lake Waters." <u>Journ. Fish. Res. Board Can.</u>, <u>31</u>, 1515. (1974).
- 30. Huang, C. P., et. al., "Interfacial Reactions and Fate of Heavy Metals in Soil-Water Systems." <u>Journ. Water</u> Poll. Control Fed., 49, 745 (1977).
- Slowey, J. F. and D. W. Hood, "Copper, Manganese and Zinc Concentrations in Gulf of Mexico Waters." Geochim. Cosmochim, Acta, 35, 121 (1971).
- 32. Masironi, R., "Cardiovascular Mortality in Relation to Radioactivity and Hardness of Local Water Supplies in the U.S.A." Bull. World Health Org., 43, 687 (1970).
- 33. U. S. Environmental Protection Agency (E.P.A.) "Distribution of Metals in Baltimore Harbor Sediments," Report No. E.P.A. 70903/9-74-012, Philadelphia, Pennsylvania (1974).
- 34. Biggs, R. B., "Trace Metal Concentration in Sediments of Baltimore Harbor at Dundalk Marine Terminal," Chesapeake Biological Laboratory, Report No. 68-97 (1968).
- 35. Jonasson, I. R. and M. H. Timperly, "Discussion of Field Observations on the Transport of Heavy Metals in Sediments (A. J. DeGroot and E. Allersman)." <u>In Heavy Metals in the Aquatic Environment</u>, P. A. Kernkel, ed., Permagon Press, New York (1975).

- 36. Lawrence, A. W., and P. L. McCarty, "The Role of Sulfide in Preventing Heavy Metal Toxicity in Anaerobic Treatment."

 Journ. Water Poll. Control Fed., 37, 392 (1965).
- 37. Rashid, M. A., and J. D. Leonard, "Modifications in the Solubility and Precipitation Behavior of Various Metals As a Result of Their Interaction with Sedimentary Rock." Chemical Geology 11, 89 (1973).
- 38. Leland, H. W., et. al., "Factors Affecting The Distribution of Lead and Other Trace Elements in the Sediments of Sourthern Lake Michigan." In Trace Metals and Metal-Organic Interactions in Natural Waters, P. C. Singer, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan (1973).
- 39. Lerman, A., and C. W. Childs, "Metal-Organic Complexes in Natural Waters: Control of Distribution by Thermodynamic, Kinetic and Physical Factors." <u>In Trace Metals and Metal-Organic Interactions in Natural Waters</u>, P. C. Singer, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan (1973).
- Bakir-Blocker, A., et. al., "Trace-Element and Organic Carbon Content of Surface Sediment from Grand Traverse Bay, Lake Michigan." Geol. Society of America Bull., 86 1358 (1975).
- 41. Loring, D. H., "The Distribution and Partition of Zinc, Copper, and Lead in the Sediments of Saguenay Fjord." <u>Can. Journ. Earth Sci.</u>, 13, 960 (1976).
- 42. Duce, R. A., et. al., Enrichment of Heavy Metals and Organic Compounds in the Surface Microlayer of Narragansett Bay, Rhode Island," Science, 176, 161 (1972).
- 43. Schnitzer, M., "Metal-Organic Interactions in Soils and Waters."

 In Organic Compounds in Aquatic Environments, D. S. Faust
 and J. R. Hunter, eds., Marcel Dekker, New York, (1971).
- 44. Pillai, T. N. W., <u>et. al</u>. "Organic Materials in the Marine Environment and Associated Metallic Elements." <u>Current Science</u>, 4, 75 (1971).
- 45. Schnitzer, M. and S. I. M. Skinner, "Organo-Metallic Interactions in Soils: Stability Constants of Pb++__, Ni++__, MN++__, Co++__, Ca++__, and Mg++__ Fulvic Acid Complexes," Soil Science, 103, 247 (1967).

- 46. Khanna, S. D. and F. J. Stevenson, "Metallo-Organic Complexes in Soils: I. Potentiometric Titration of Some Soil Organic Matter Isolates in the Presence of Transition Metals." Soil Science, 93, 298 (1962).
- 47. Ong, H. L., and R. E. Bisque, "Coagulation of Humic Colloids by Metal Ions." Soil Science, 106, 220 (1968).
- 48. Rashid, M. A., Adsorption of Metals on Sedimentary and Peat Humic Acids." <u>Chemical Geology</u>, 13, 115 (1974).
- 49. Jenne, E. A., "Controls on Mn, Fe, Co, Ni, Cu, and Zn Concentrations in Soils and Water: the Significant Role of Hydrous Mn and Fe Oxides." <u>In Trace Inorganics in Water</u>, R. F. Gould, ed., American Chem. Society, Washington, D. C. (1967).
- 50. Morgan, J. J. and W. Stumm, "Colloid-Chemical Properties of Manganese Dioxide." <u>Jour. of Colloid Science</u>, <u>19</u>, 347 (1964).
- 51. Carpenter, R. H., et. al., "Fe-Mn Oxide in Stream Sediment Geochemical Surveys." <u>Journ. of Geochem. Exploration</u>, 4, 349 (1975).
- 52. Turekian, K. K., and M. R. Scott, "Concentrations of Cr, Ag, Mo, Ni, Co, and Mn in Suspended Materials in Streams." Environ. Sci. Technol., 1, 940 (1967).
- 53. Duchart, P., et. al., "Distribution of Trace Elements in the Pore Waters of Shallow Water Marine Sediments." <u>Limnology</u> and Oceanography, 18, 605 (1973).
- 54. Oliver, B. G., "Heavy Metal Levels of Ottawa and Riddeau River Sediments." Environ. Sci. Technol., 7, 135 (1973).
- 55. Slatt, R. M., "Geochemistry of Bottom Sediments, Conception Bay, Southeastern Newfoundland." Can. Journ. Earth Sci., 11, 768 (1974).
- 56. Maxfeld, J. M., et. al., "Heavy Metal Pollution in the Sediments of the Coeur D'Alene River Delta." Environ. Poll., 7, 1 (1974).
- 57. Wayman, C. H., "Adsorption on Clay Mineral Surfaces." <u>In Principles and Applications of Water Chemistry</u>, S. D. Faust and J. V. Hunter, eds., John Wiley and Sons, Inc., New York (1967).

- 58. Tiller, K. G., and J. F. Hodgson, "The Specific Sorption of Cobalt and Zinc by Layer Silicates." Clay and Clay Minerals, 9, 393 (1962).
- 59. Duke, T. W., et. al., "Cycling of Trace Elements in the Estuarine Environment I. Movement and Distribution of Zinc 65 and Stable Zinc in Experimental Ponds." Chesapeake Science, 7, 9 (1966).
- 60. Boyden, C. R., "Distribution of Some Trace Metals in Poole Harbour, Dorsett." Marine Poll. Bull., 6, 180 (1975).
- 61. Mills, E. L., and R. T. Oglesby, "Lead, Cd, Zn, Cu, and Co in Streams and Lake Waters of Cayuga Lake Basin, New York." Environ. Sci. Technol., 8, 243 (1974).
- 62. Skei, J. M., et. al., "The Distribution of Heavy Metals in Sediments of Sorfjord, West Norway," <u>Water, Air, and Soil Poll.</u>, 1 452 (1972).
- 63. Gibbs, R. J., "Mechanisms of Trace Metal Transport in Rivers." Science, 180, 71 (1973).
- 64. State Water Control Board. Memorandum entitled "Evaluation of a Potential Mixing Zone for Ash Camp Creek." February 28, 1977.
- 65. Struempler, A. W., "Adsorption Characteristics of Silver, Lead, Cadmium, Zinc and Nickel on Borosilicate glass, Polytehylene and Polypropylene Container Survices." Analytical Chemistry, 45, 225 (1973).
- 66. Namminga, H. and J. Wilhm, "Heavy Metals in Water Sediments and Chironomids." <u>Journ. Water Poll. Control Fed.</u>, 49, 1725 (1977).
- 67. "Standard Methods for the Examination of Water and Wastewater." 13th Ed., Amer. Pub. Health Assn., New York, N.Y. (1971).
- 68. U. S. Environmental Protection Agency (E.P.A.). Methods for Chemical Analysis of Water and Wastes. Report No. 625/6-74-003 (1974).
- 69. "Standard Methods for the Examination of Water and Wastewater." 14th Ed., Amer. Pub. Health Assn., New York, N. Y. (1976).
- 70. Anderson, J., "A Study of the Digestion of Sediment By the HNO₃-H₂SO4 and the HNO₃-HCI Procedures." <u>Atomic Adsorption</u> Newsletter, 13, 31 (1974).

- 71. Agemian, H., and A. S. Y. Chau, "Evaluation of Extraction Techniques for the Determination of Metals in Aquatic Sediments." <u>The Analyst</u>, <u>101</u>, 761 (1976).
- 72. Perkin Elmer, <u>Analytical Methods for Atomic Spectrophotometry</u> "Cookbook" <u>Supplement</u>, Norwalk, Connecticut (1976).

IX. APPENDIX

Table A 1. Field pH Data for Stream and Effluent Water Samples

Sampling Date	Station Number												
		2	3	4	5	6	7	8					
6/9/77	8.2	7.0	6.4	6.0	6.5	6.8	6.8	7.5					
6/16/77	9.3	6.8	6.8	7.0	7.1	7.2	7.3	7.3					
6/22/77	8.8	8.2	7.8	7.2	4.6*	6.5	6.7	7.1					
6/28/77	8.7	6.9	7.6	7.3	7.0	7.2	7.7	7.7					
6/29/77	8.6	7.3	8.2	7.7	6.7	8.0	7.4	7.7					
Average	8.7	7.2	7.4	7.0	6.4	7.1	7.2	7.5					

^{*}Measured in lab at Va. Crafts

Table A 2. Field Temperature (Temp) and Dissolved Oxygen (D.O.) Data for Stream and Effluent Water Samples (Temp Values in °C and D.O. Values in mg/l)

Sampling Date		,			S	tatio				F						
	Temp	D.O.		2 D.O.	Temp	3 D.O.	Temp	4 D.O.		5 D.O.		6 D.O.	Temp	D.O.	Temp	8 D.O.
6/9/77	17	7.0	20	7.2	21	7.5	20	7.0	20	5.1	20	7.3	20	8.0	19	7.6
6/16/77	19	7.2	26	6.6	25	5.2	26	5.4	22	6.2	26	4.6	22	7.0	25	5.5
6/23/77	19	*	26	*	26	*	26	*	21	*	24	*	19	*	20	*
6/28/77	22	5.6	28	6.7	28	6.6	30	6.7	27	6.7	33	5.1	29	7.0	30	3.6
6/29/77	24	3.3	29	8.5	29	8.2	29	4.2	27	4.6	30	3.9	28	7.6	28	7.1
Average	20.2	5.8	25.8	7.2	25.8	6.9	26.2	5.8	23.4	5.7	26.5	5.2	23.6	7.4	24.4	6.0

*D.O. meter not functioning properly

Table A 3. Field Conductivity Data for Stream and Effluent Water Samples (All Values in $\mu mho/cm)$

Sampling	Station Number												
Date	1	2	3	4	5	6	7	8					
6/9/77	8.04x10 ^{-3*}	130.00	123.00	126.00	46.3	111.80	36.00	14.20					
6/16/77	40.80	120.00	127.00	126.00	48.00	103.00	44.80	28.00					
6/23/77	13.60	113.00	106.00	103.00	48.00	96.00	47.70	21.70					
6/28/77	46.60	117.00	117.00	124.00	62.00	106.00	26.00	26.00					
6/29/77	39.80	123.00	125.00	120.00	51.00	109.00	45.00	23.00					
Average	35.20	120.50	119.60	119.80	51.06	105.16	39.90	22.58					

^{*}Error in measurement; value not averaged

Table 4 A. Alkalinity Data for Stream and Effluent Water Samples (All Values in mg/l as ${\rm CaCO}_3$)

Date			Statio	n Number			-	
	. 1	2	3	4	5	6	7	8
6/9/77	18.0	20.0	20.0	17.0	78.0	37.0	40.0	43.0
6/16/77	61.0	22.0	40.0	37.0	46.0	51.0	45.0	40.0
6/23/77	18.0	51.0	51.0	50.0	*	51.0	39.0	42.0
6/28/77	57.0	55.0	54.0	52.0	74.0	51.0	37.0	44.0
6/29/77	65.0	55.0	56.0	55.0	22.0	55.0	42.0	43.0
Average	43.8	40.6	44.2	42.2	55.0	49.0	40.6	42.4

^{*}No Alkalinity present

Table A 5. Calcium (Ca) and Total (TOT) Harndess (EDTA) Data for Stream and Effluent Water Samples (All Values in mg/l as $CacO_3$)

		Station Number														
i	1		- 2	2		3	4	1		5		6		7	- {	3
Sampling Date	Tot	Ca	Tot	Ca	Tot	Ca	Tot	Ca	Tot	Ca	Tot	Ca	Tot	Ca	Tot	Ca
6/9/77	26.0	22.0	80.0	72.0	80.0	70.0	74.0	64.0	66.0	62.0	82.0	68.0	68.0	60.0	44.0	36.0
6/16/77	130.0	128.0	84.0	70.0	82.0	68.0	76.0	74.0	42.0	34.0	72.0	64.0	60.0	58.0	60.0	50.0
6/23/77	40.0	38.0	74.0	70.0	72.0	70.0	74.0	72.0	64.0	*	76.0	66.0	74.0	70.0	60.0	58.0
6/28/77	148.0	144.0	90.0	84.0	94.0	84.0	80.0	78.0	70.0	64.0	72.0	66.0	58.0	48.0	50.0	46.0
6/29/77	120.0	114.0	78.0	76.0	80.0	72.0	76.0	72.0	64.0	62.0	76.0	70.0	64.0	58.0	52.0	42.0
Average	92.8	89.2	81.2	74.4	81.6	72.8	76.0	72.0	61.2	55.5	75.6	68.8	68.4	58.8	53.2	46.4

^{*}Interference

Table A 6. Total Suspended Solids (TSS) Data for Stream and Effluent Water Samples (All Values in mg/l)

Sampling Date			Sta	țion Numbe	er			
	1	2	3	4	5	6	7	8
6/9/77 (1) (2)	55.0 35.0	14.6 31.0	36.7 53.3	30.0 30.0	45.2 60.0	24.0 20.0	1.5	4.0 3.0
6/16/77 (1) (2)	10.0	71.6 65.0	52.0 48.0	76.0 50.0	33.0 10.0	20.0 44.0	9.0	16.0 17.3
6/23/77 (1) (2)	45.3 40.0	76.0	70.0 74.0	62.0 56.0	84.3 82.0	70.0 78.0	8.0 8.8	7.6 11.6
6/28/77 (1) (2)	10.8 10.4	66.7 70.0	14.5 78.2	56.0 32.0	100.0	68.0 34.0	14.0 3.2	21.5 15.5
6/29/77 (1) (2)	8.4 6.8	66.0 86.0	44.0 46.0	20.0 46.0		86.0 12.0	5.5 3.5	13.3 28.7
Average	23.2	60.8	51.7	45.8	64.3	45.6	6.7	13.9

Table A 7. Volatile Suspended Solids (VSS) Data for Stream and Effluent Water Samples (All Values in mg/l)

Sampling Date			Stat	tion Number	r	,		
	1	2	3	4	5	6	7	8
6/9/77 (1) (2)	14.0 4.0	13.3 28.0	28.3 28.3	21.6 12.9	41.9 46.0	22.0		2.5 2.0
6/16/77 (1) (2)	6.8	51.7 53.3	52.0 36.0	52.0 36.0	31.0 10.0	10.0 34.0	 5.5	6.7 8.7
6/23/77 (1) (2)	20.6 18.7	60.0	52.0 52.0	48.0 40.0	74.2 70.0	42.0 60.0	4.8 5.0	1.2 4.8
6/28/77 (1) (2)	1.6	26.0	23.5 41.8	22.0	40.0 52.0	42.0 14.0	2.0	2.5 2.5
6/29/77 (1) (2)	1.2	36.0 18.0	4.0 12.0	 24.0	1.3	24.0	1.5	1.3 11.3
Average	7.7	35.8	33.0	32.0	40.7	31.0	3.8	4.4

]

Table A 8. Total Organic Carbon (TOC) Data for Stream and Effluent Water Samples (All Values in mg/l)

Sampling Date	Station Number												
	1	2	3	4	5	6	7	8					
6/9/77	18.3	73.0	63.5	68.4	84.0	100.3	65.0	37.0					
6/16/77	26.0	80.2	76.0	76.4	50.6	65.8	23.1	11.0					
6/23/77	27.4	79.4	69.1	69.7	72.6	92.3	23.0	10.8					
6/28/77	8.4	102.5	85.0	75.4	24.4	67.0	18.6	7.1					
6/29/77	7.8	83.7	82.6	85.4	71.8	79.4	46.7	56.9*					
Average	17.6	83.8	75.2	75.1	60.7	81.0	35.3	16.5					

^{*}Error in analysis; not averaged

Table A 9. Total Zinc (Zn) Data for Stream and Effluent Water Samples (All Values in mg/l)

_				Station Numl	oer			
	1 1	2	3	4	5	6	7	8
6/9/77 (1) (2) (3)	5.00 4.60 ≤0.01	2.00 5.30 3.10	4.60 6.80 2.90	8.00* 5.40 3.60	5.90 3.80 0.60	6.00 16.40 2.50	0.60 1.70 0.40	1.50 0.90 ≤ 0.01
6/16/77 (1) (2) (3)	≤ 0.01 ≤ 0.01 ≤ 0.01	2.10 2.00 2.10	1.70 2.00 1.70	3.60 1.30 1.40	1.90 4.60* 1.10	1.90 1.30 1.40	≤ 0.01 ≤ 0.01 ≤ 0.01	≤ 0.01 ≤ 0.01 0.80
6/23/77 (1) (2) (3)	0.50 2.40 3.90	1.90 2.40 1.60	2.30 1.90 1.10	0.80 1.20 1.60	.060 ≤ 0.01 ≤ 0.01	1.50 0.90 1.80	<pre></pre>	≤ 0.01 ≤ 0.01 ≤ 0.01
6/28/77 (1) (2) (3)	≤ 0.01 ≤ 0.01 ≤ 0.01	1.80 1.60 2.60	0.90 1.20 0.90	1.10 0.90 2.50	0.80 0.80 ≤ 0.01	0.40 0.90 0.30	0.10 ≤ 0.01 ≤ 0.01	0.45 0.85 ≤ 0.01
6/29/77 (1) (2) (3)	≤ 0.01 ≤ 0.01 ≤ 0.01	1.40 1.40 0.72	0.90 1.30 1.60	1.30 0.40 2.50	0.20 ≤ 0.01 0.30	0.70 0.60 0.60	≤ 0.01 ≤ 0.01 ≤ 0.01	< 0.01 < 0.01 ≤ 0.01
Average	≤ 1.10	1.91	1.79	1.71	≤ 0.53	1.14	≤ 0.19	≤ 0.31

^{*}Apparently contaminated; value not averaged

Table A 10. Dissolved Zinc (Zn) Data for Stream and Effluent Water Samples (All Values as mg/1)

Sampling Date				Station Nu	umber			
	1	2	3	4	5	6	7	8
6/9/77 (1) (2)	≤ 0.01 ≤ 0.01	1.60	1.20 2.40	2.40 1.70	≤ 0.01 ≤ 0.01	1.90 1.10	0.08 <u><</u> 0.01	≤ 0.01 ≤ 0.01
6/16/77 (1) (2)	0.45 0.80	1.25 2.25	1.30 1.60	2.25 2.30	2.85 2.40	1.65 4.10	2.40 1.10	1.50 1.80
6/23/77 (1) (2)	0.65 0.65	0.70 1.00	0.80 0.95	0.40 1.75	1.00 < 0.01	0.15 0.70	1.20 0.95	≤ 0.01 ≤ 0.01
6/28/77 (1) (2)	≤ 0.01 ≤ 0.01	0.30 0.25	0.15 0.30	0.50 0.20	≤ 0.01 ≤ 0.01	0.80 0.85	≤ 0.01 ≤ 0.01	< 0.01 ≤ 0.01
6/29/77 (1) (2)	0.05 0.80	0.10 0.15	0.10 0.30	0.95 0.30	≤ 0.01 ≤ 0.01	≤ 0.01 ≤ 0.01	≤ 0.01 ≤ 0.01	≤ 0.01 ≤ 0.01
Average	≤ 0.34	0.84	0.91	1.28	≤ 0.63	≤ 0.80	≤ 0.58	≤ 0.34

^{*} Apparently contaminated, value not averaged

Table A 11. Suspended Zinc (Zn) Data for Stream and Effluent Water Samples (All Values in mg/l)

Sampling Date				Station No	umber			
	1	2	3	4	5	6	7	8
6/9/77 (1) (2)	0.60 0.98	0.82 0.46	0.75 0.79	0.49 0.71	0.55 0.55	1.00 0.71	0.21 0.11	0.12 0.19
6/16/77 (1) (2)	0.05 0.40	0.90 2.80*	2.10 1.40	2.10 1.30	0.50 4.00*	1.00	0.90 0.10	2.50* ≤ 0.01
6/23/77 (1) (2)	0.32 0.52	0.70 1.30	≤ 0.01 0.50	0.60 0.60	0.24 0.16	< 0.01 ≤ 1.10	0.06 0.06	0.12 0.08
6/23/77 (1) (2)	0.30 0.62	0.90 1.30	1.20	1.60 1.40	0.20 0.80	2.30 1.50	0.80 0.70	1.65* 0.60
6/29/77 (1) (2)	0.70 0.01	1.10	≤ 0.01 0.20	0.70 ≤ 0.01	0.05 0.35	0.40 0.60	0.20 1.50	≤ 0.01 0.80
Average	0.45	1.02	≤ 0.84	≤ 0.95	0.38	≤ 1.05	0.35	≤ 0.24

^{*}Apparently contaminated; value not averaged

Table A 12. Data for Zinc in the Upper 5 cm of Stream Sediments (All Values in mg/kg)

ampling Date			Station Number	r		
	1	3	4	6	7	8
6/9/77 (1) (2)	604.94 296.49	345.62 315.71	943.92 910.17	514.73 766.07	27.71 15.73	70.87 23.71
6/16/77 (1) (2)	325.10 292.59	542.13 496.50	709.01 701.55	692.52 490.86	23.52 43.39	27.76 27.96
6/23/77 (1) (2)	282.03 222.20	647.82 661.30	1045.08 991.63	660.85 740.81	39.57 27.77	102.63 51.82
6/29/77 (1) (2)	207.63 226.56	725.95 661.72	1504.47 1494.06	476.68 674.71	31.83 35.71	43.75 43.75
Average	307.19	549.59	1037.49	627.15	30.65	49.03

Table A 13. Data For Percent (%) Loss on Ignition for Stream Sediments (All Values in %)

Sampling Date	Station Number					
	1	3	4	6	7	8
6/9/77	4.38	4.42	3.39	9.58	1.93	1.77
6/16/77	5.13	4.20	4.00	7.35	1.02	1.65
6/23/77	4.50	3.68	3.36	9.28	2.03	2.48
6/29/77	4.30	3.89	4.12	5.77	1.82	2.58
Average	4.58	4.05	3.72	8.00	1.70	2.12

ATIV

Jonathan C. Hay was born in Pasadena, California on January 27, 1951. He attended elementary school in Whittier, California, before moving with his parents to Richmond, Virginia in 1960. After attending elementary school for three years in Richmond, he returned with his family to California for completion of his elementary education. In 1964, he and his family returned to Richmond where they have since resided. Jonathan was graduated from John Randolph Tucker High School in May 1969. He attended Virginia Tech for a year before transferring to the University of Richmond. He graduated Magna Cum Laude receiving a Bachelor of Science Degree in Biology. Jonathan was elected to Phi Beta Kappa, Beta Beta Biological Honor Society, Gamma Sigma Epsilon Chemical Honor Society. During 1973 to 1976 he worked as a Pollution Control Specialist for the Bureau of Enforcement, State Water Control Board and attended graduate school part-time at Virginia Commonwealth University. From 1976-1977, he attended VPI & SU under an E.P.A. Traineeship Grant, where he completed the requirements for a Master of Science Degree in Environmental Sciences and Engineering. Jonathan plans to work for the County of Los Angeles Sanitation Districts.

Jonathan's father is a Welding Engineer, now retired from Reynolds Metals Company, and his mother is a homemaker. He has three sisters and one brother.

Josiathan C. Hay

ZINC DISTRIBUTION IN A SMALL STREAM RECEIVING TREATED TEXTILE WASTEWATER

by

Jonathan C. Hay
(Abstract)

Effluent samples for a treated textile wastewater and treated domestic sewage wastewater and water and sediment samples for an 8.2 km region of Ash Camp Creek near Keysville, Virginia, were collected in June, 1977. Effluent and stream water samples were analyzed for various water quality parameters and for suspended, dissolved, and total zinc. Sediment samples were analyzed for zinc and percent loss on ignition. The treated textile wastewater was the major source of zinc to the The effluent and stream water samples exhibited a marked partitioning of zinc among the dissolved and suspended fractions of the water column. The ratios of mean dissolved to mean suspended zinc ranged from about 0.76 to about 1.40. The ratios of mean dissolved to total zinc and mean suspended to total zinc ranged from about 0.42 to 0.62 and from about 0.38 to 0.57, respectively. Anomalously high zinc concentrations were found in the sediments 0.80 m downstream from the point of discharge of the treated textile wastewater and appeared to be caused by sedimentation of suspended zinc induced by a reduction in stream velocity. The domestic discharge together with flow from a small unnamed tributary had a moderating effect on the water quality of the stream functioning to dilute stream pollutant load. Sulfide

precipitation appeared to be an important mechanism by which zinc was concentrated in the sediments 40 m below the domestic sewage discharge. Zinc concentrations declined further downstream likely as a result of such factors as dilution, sedimentation, and sorption by inorganic sediment particles.