

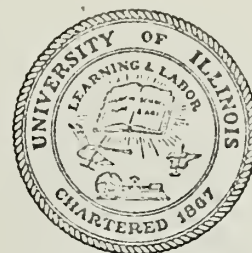
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7 CIVIL ENGINEERING STUDIES

SANITARY ENGINEERING SERIES NO. 27



THE FATE OF ZINC IN A SMALL STREAM

Metz Reference Room
Civil Engineering Department
E206 C. E. Building
University of Illinois
Urbana, Illinois 61801

By
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Supported by
DIVISION OF BIOLOGY AND MEDICINE
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DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
JUNE, 1965

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ABSTRACT

Field studies were made on the fate of zinc in a stream. A zinc chloride solution was injected over a fifty-two minute period into the Boneyard Creek at Urbana, Illinois. Samples were taken at ten minute intervals from five sampling points spaced at two hundred foot intervals for one thousand feet downstream. Zinc analyses on the samples indicated successive reduction in the zinc concentration downstream from the injection point. Following the zinc chloride addition, hydrochloric acid was added which lowered the pH slowly to 6.25 and then rapidly to 2.0. Samples taken during the addition of acid indicated that zinc was readily desorbed under acid conditions.

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I. INTRODUCTION

A. Purpose of Investigation

Radioactive zinc is discharged in low concentrations into natural water courses as a corrosion product from nuclear reactor cooling waters. Although zinc-65 is not a fission product, it is frequently found in greater abundance in aquatic organisms than any single fission product. The organisms of the fish food chain and marine shellfish are particularly affected.

Control of zinc-65 in natural waters cannot be maintained by monitoring the contaminated water because the zinc is rapidly lost from solution downstream from the influent point. Both the solubility of zinc and the adsorption of the zinc on suspended solids and bottom sediments contribute to the rapid reduction of the zinc concentration. Laboratory studies which have been conducted on the solubility of zinc and the soluble-adsorbed zinc equilibria indicate that under acid or reducing conditions zinc will return to a solution readily, thereby producing a large pulse in the soluble zinc content of a stream (11). The possibility of flood flow scour of zinc-bearing bottom sediments and transport to estuaries is also a potential hazard.

A comparison of field studies of the behavior of stable zinc with the results of laboratory tests would enable a realistic evaluation of the validity of applying tank studies of the mechanisms influencing the soluble-adsorbed zinc equilibrium. In addition, a quantitative demonstration of the sorption phenomena followed by desorption under acid conditions would be useful in corroborating previous hypothesis and demonstrating the potential hazard of sediment-adsorbed radioactive zinc.

B. Survey of Literature

1. Transport of Zinc in Natural Waters

"The dispersion mechanism is responsible for the mixing that must take place before other phenomena affecting transport, such as sorption...can occur" (12). Turbulent diffusion as opposed to molecular diffusion is by far the most important mechanism causing dispersion in streams.

Initial attempts to find a mathematical solution to turbulent diffusion problems were begun by applying Fick's Law of diffusion of chemicals with the hope that a proper coefficient could be found which described turbulent diffusion (4).

Fick's Second Law:

$$\frac{\partial c}{\partial t} = -K \left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right]$$

where

$\frac{\partial c}{\partial t}$ is the time rate of change of concentration of the diffusant at a point

K is the coefficient of diffusion at the point

$\frac{\partial^2 c}{\partial x^2}$ is the rate of change of the concentration gradient in the direction of x, etc.

Because turbulent diffusion is neither time nor spatially independent, a simple K value could not be established which agreed with observations (12).

In that turbulent flow is considered, mathematically, to be the vector addition of a mean component of velocity and a random component of velocity, the Fickian solution has been modified to incorporate this more reasonable view. For one dimension (mean velocities in the y and z direction equal zero) the equation takes the following form (6):

$$\frac{\partial c}{\partial t} = -\bar{v}_x \frac{\partial c}{\partial x} + \frac{\partial}{\partial x} (K_x \frac{\partial c}{\partial x}) + \frac{\partial}{\partial y} (K_y \frac{\partial c}{\partial y}) + \frac{\partial}{\partial z} (K_z \frac{\partial c}{\partial z})$$

where

$\frac{\partial c}{\partial t}$ is the time rate of change of concentration of the diffusant at a point

\bar{v}_x is the mean velocity in the x direction

$K_{x,y,z}$ are the eddy diffusion coefficients

$\frac{\partial c}{\partial x}$ is the concentration gradient in the x direction, etc.

Yotsukura (20) has conducted field studies on the dispersion of miscible materials in open channels. His data indicates that "the Fickian distribution is an asymptotic solution and not all properties of the Fickian solutions are satisfied in a flume test of reasonable dispersion time" (20).

Statistical turbulent diffusion theories have been developed on the basis that movements of turbulence tend to arrange the diffusant concentration into a Gaussian distribution. Taylor (12) showed experimentally and explained theoretically that initially the dispersion coefficient is time dependent and ultimately approaches a constant. This suggests that the pattern of longitudinal concentration immediately after release from a steady source is wedge shaped and then becomes parabolic later. The pattern from an instantaneous source will initially be a skew frequency, later becoming a normal frequency. From an engineering point of view, the constant coefficient is usually more important than the variable one because the physical dimensions of the stream's cross section limit the scale of the turbulent eddies, thus causing the coefficient to rapidly become constant (12). Some theoretical models for dispersion in an open channel are presented in Appendix A.

At the present there are no theories with which one can evaluate the dispersion characteristics by measurement of stream parameters (12). To apply present dispersion theory to open channel flow, one must have an evaluation of the turbulent mixing characteristics of the stream or be satisfied with less than theoretical behavior by accepting previously determined values from other rivers (See Appendix A).

2. Zinc Equilibria in Natural Waters

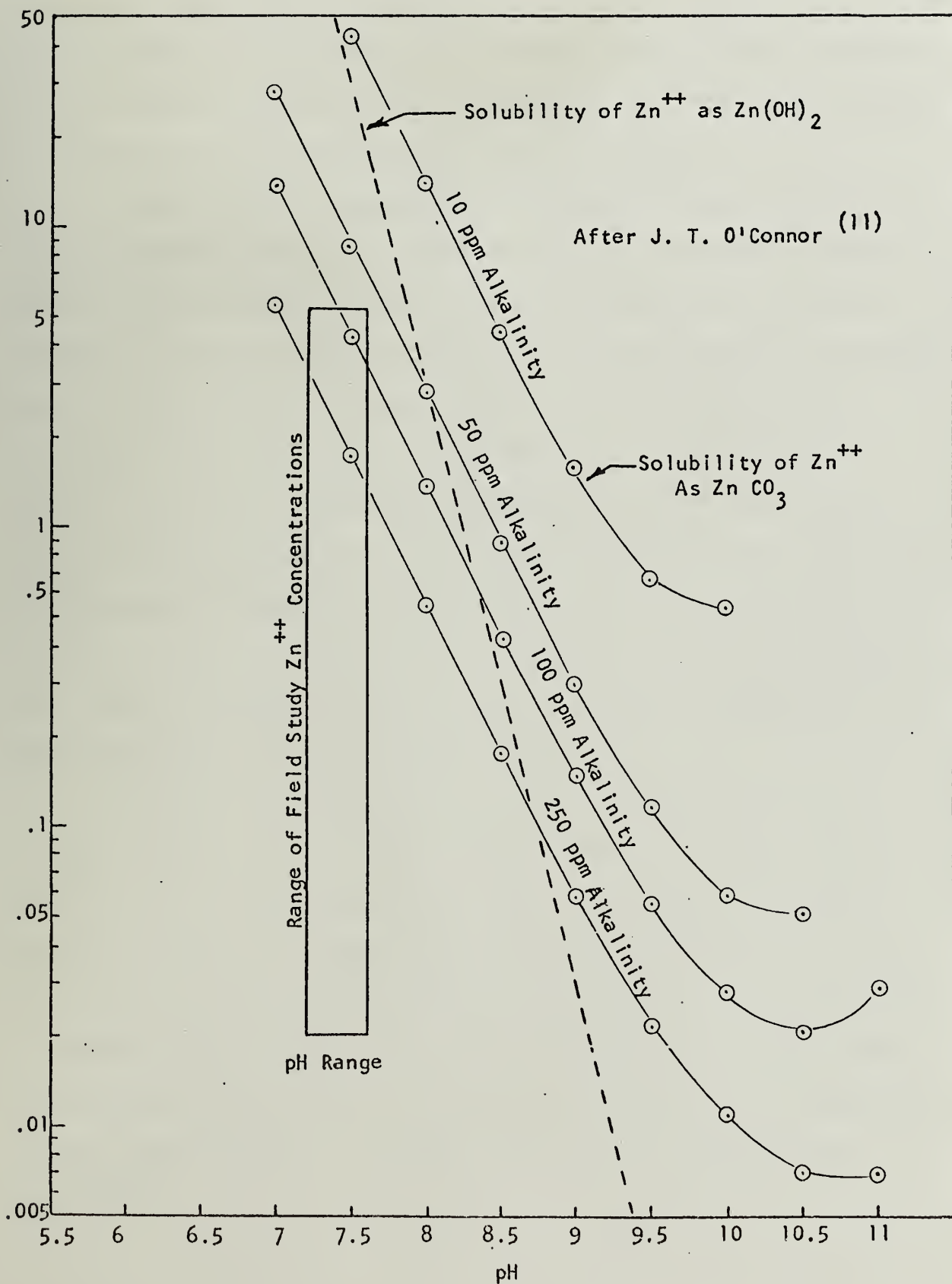
A survey to determine the fate of zinc once it is added to a stream must consider, in addition to the dispersion effects, the chemical state (solute or precipitate) and interaction with the environment.

The solubility of zinc in natural waters may be governed either by the carbonate or by the hydroxide equilibria (11). With a constant alkalinity, a one unit change in pH alters the solubility by a factor of ten (Figure 1). (The pH range encountered during the field study was 7.2 to 7.55 and the zinc concentration ranged from 0.02 mg/l to 5.03 mg/l).

Sorption, the process of taking up and holding by either adsorption or absorption or both, is of prime concern in the interaction of zinc with the environment. Although the rate of attainment of the soluble-sorbed zinc equilibrium with suspended sediment has been demonstrated to be rapid and reversible if adequate mixing is provided (10), the rate of attainment of equilibrium in unmixed or partially mixed systems, which include bottom sediments, has not been reported.

The uptake of radioactive zinc, as well as other radionuclides, by stream sediments (and suspended solids) may involve physical sorption or chemisorption. Physical sorption (characterized by small heats of

FIGURE 1: SOLUBILITY OF ZINC IN DISTILLED WATER vs. pH AND AS A FUNCTION OF ALKALINITY



adsorption, by reversibility and by rapid attainment of equilibrium (14) results from weak physical interaction of the absorbent through van der Waals forces. Chemisorption, involving strong chemical valence bonds, is important as an ion exchange phenomena where ions sorbed at the surface of the absorbate are displaced by more strongly sorbed ions of like sign.

Cation exchange replaceability is a very important aspect of ion exchange phenomena because each cation is not equally replaceable and does not have the same replacing power. Although lyotropic series have been developed for the more abundant cations, they are not universally applicable because of the influence of several variables. Since cation exchange is a stoichiometric reaction, concentration effects (law of mass action) are evident. In addition, the nature of the population of the exchange positions, the nature of the anions in the replacing solution and the nature of the clay mineral all regulate the replaceability series to some degree. Variations in temperature in the vicinity of normal stream conditions has little effect on exchange capacity. However, at elevated temperatures (125° C) appreciable effects have been reported (5).

The nature of the replacing ion and its effect on a given lyotropic series are of particular interest in relation to zinc sorption. As Grim points out, "Other things being equal, the higher the valence of the ion, the greater its replacing power and the more difficult it is to displace when already present on the clay. Hydrogen is an exception since for the most part it behaves like a divalent or trivalent ion" (5). Sayre says "This apparent contradiction is generally attributed to the explanation that the adsorbed hydrogen is actually in the form of a hydronium ion $(H_3O)^+$ " (14).

A distribution range of cation exchange capacity among the sand, silt and clay fractions of soil shows the magnitude of importance of the clay fraction.

TABLE 1
DISTRIBUTION OF CATION EXCHANGE CAPACITY (13)

	milliequivalents/100 g
Sand	0.5 to 18.9
Silt	9.6 to 25.4
Clay	20.4 to 77.6

Although ion exchange occurs with some larger grained sediments, it is usually associated with the clay fraction. The ion exchange capacity of a soil is highly dependent on the specific surface area of the soil as well as its mineralogical composition. The sorption capacity of stream sediments is roughly proportional to the surface area of the soil. The surface area is, in turn, proportional to the square of the particle diameter; thus, for a given weight of soil the total surface area of 1 micron clay particles would be one thousand times that of 1 millimeter sand particles (14).

From grain size analyses of the bottom sediments and suspended material of the Mississippi River at St. Louis, Missouri, calculations have been made of the surface area (and thus to some extent, the sorptive capacity) of suspended and bed material (14). These calculations show that the suspended material had 274 times the surface area of the bottom muds per cubic centimeter of soil. Therefore, even though the suspended materials are less dense, because of their greater surface area and exchange capacity per unit weight, they may contain the greatest proportion of absolute

exchange capacity. Utilizing Tables 2 and 3, it can be seen that any estimation of the fate of zinc must include the interacting effects of the hydrogen ion concentration and the suspended solids concentration as well as the cation exchange characteristics of suspended and bed sediments. For example, one might expect that a major portion of zinc discharged to the Colorado River would be sorbed to the suspended load while most of the sorbed zinc in the Columbia River would probably be on the bottom sediments. Qualitatively, one should expect, under these considerations, that the bottom sediments of the Boneyard Creek would sorb the greatest fraction of the zinc.

TABLE 2
FRACTION OF ZINC REMAINING IN SOLUTION
AS A FUNCTION OF pH AND SOLIDS CONCENTRATION* (10)

pH	Solids Concentration, ppm					
	15	35	78	170	476	858
6.5	.977	.950	.883	.820	.569	.370
7.0	.972	.930	.826	.691	.310	.225
7.5	.980	.895	.808	.593	.286	.181
8.0	.915	.867	.789	.568	.211	.092

*Shenandoah River water and solids, Harper's Ferry, W. Va.

TABLE 3
SOME OBSERVED RANGES OF SUSPENDED SOLIDS AND pH (16, 18)

	Avg. SS. ppm	SS. Range ppm	Avg. pH	pH Range
Delaware River	59	2 - 525	7.35	6.5 - 7.8
Mississippi River	710	100 - 3,700	---	---
Colorado River	4,120	200 - 21,900	7.7	7.4 - 8.4
Columbia River	4	0.3 - 29.2	---	---
Boneyard Creek Measurements	12.4	2.5 - 46.6	7.7	7.3 - 8.2

Attached and floating organic material, both living and dead, has a considerable effect on the reduction of the zinc concentration in streams. Plankton, for example, have been found in their natural environment

with up to 1.9 mg of sorbed zinc per gram dry weight.

3. Dispersal of Bed Sediments

Although a zinc molecule may be sorbed on bottom sediments, its location is by no means fixed. Bed materials are transported, however, at a rate which may be several orders of magnitude less than the velocity of flow. Because clay and organic coatings on sand particles tend to increase the sorptive capacity of sands to a competitive position with suspended clays (9), this phenomena has assumed an important role in the dispersion of radionuclides.

A statistical approach to the theoretical prediction of sediment dispersion has been developed on the assumption that the motion of the bed particles is a random process.

Two separate derivations (15) have been developed to yield a density function at a point (x) downstream at a time (t) after release:

$$f_t(x) = k_1 [\exp - (k_1x + k_2t)] \sum_{n=1}^{\infty} \frac{(k_1x)^{n-1}}{\Gamma(n)} \frac{(k_2t)^n}{n!}$$

which transforms to

$$f_t(x) = k_1 [\exp - (k_1x + k_2t)] (k_2t/k_1x)^{\frac{1}{2}} I_1 [2(k_1k_2xt)^{\frac{1}{2}}]$$

where

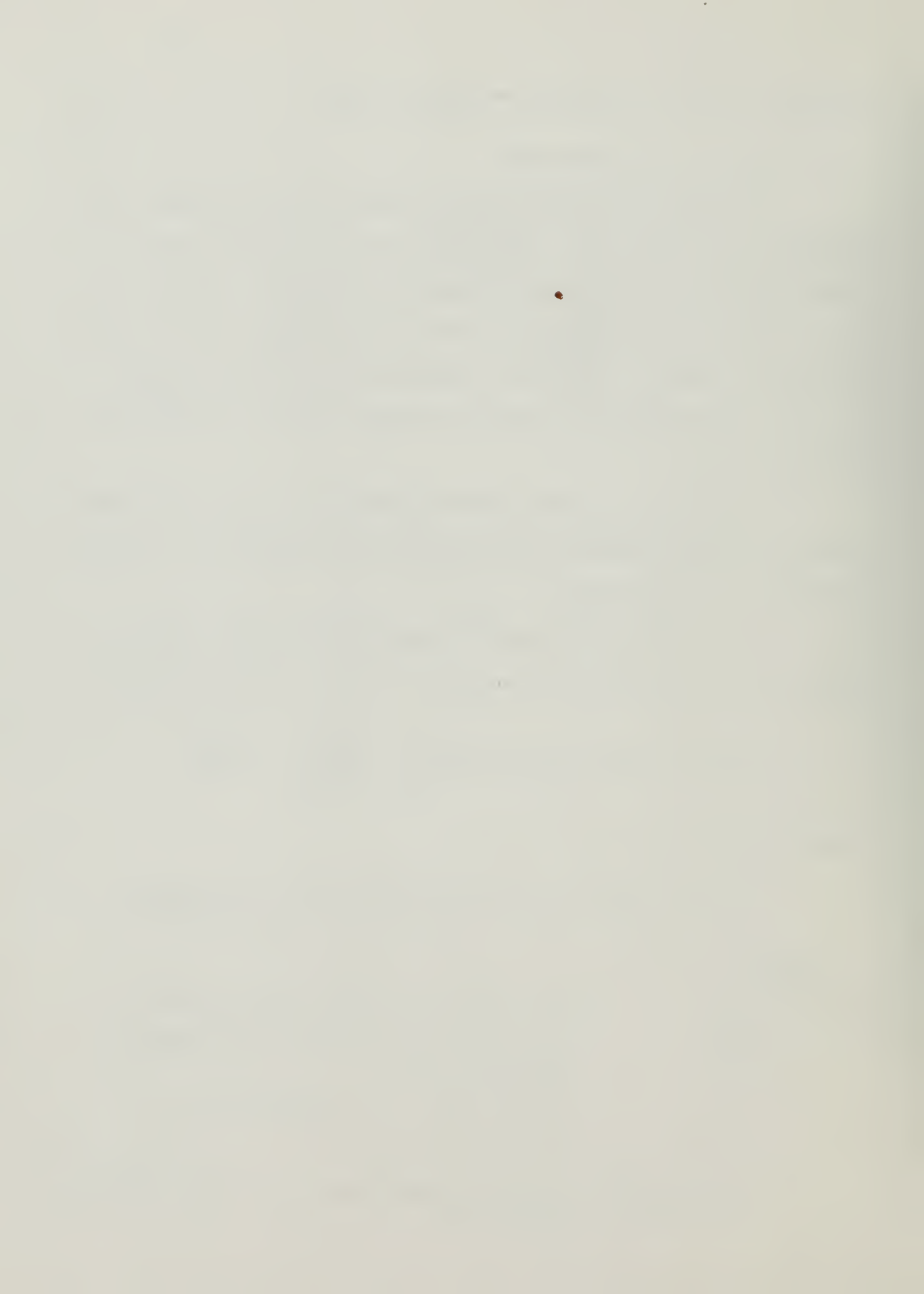
$1/k_1$ is the mean step length a particle moves

$1/k_2$ is the mean duration of the rest period between step lengths

x is the distance from release point

t is the time from release

$I_1 [2(k_1k_2xt)^{\frac{1}{2}}]$ is a modified Bessel function of the first kind of order one.



Unfortunately, the boundary conditions for which this prediction holds are not wholly realistic. The assumptions are the following: (1) the channel is straight and uniform; (2) the water and bed discharges per unit width are uniform and constant; (3) all tagged particles have identical transport properties; (4) the particles are released instantaneously from a uniform plane laterally across the channel and vertically in the bed; (5) no vertical concentration gradient of particles develops; and (6) the number of particles is large enough to approximate an infinite population, yet small enough not to disturb the existing bed material patterns (15).

Sayre and Hubbell (15) have conducted tests of this theory using sand labeled with Iridium-192. The results of the test (carried out within the boundary conditions listed) agreed very well with the predictions of the theory. In addition the test showed the striking amount of bed transport which can be accomplished in that the mean concentration moved approximately 350 feet downstream within a four day period.

The restrictions of the assumptions in this theory are not as forbidding as one might expect. Approximations for a variety of situations can be made by a variety of integrations for discharge variables (15) and by breaking the stream into reaches of some homogeneity. The major considerations left for theoretical development are mathematical models to allow for the effects of exchange of radionuclides between sediment and biota, etc.

II. EXPERIMENTAL PROCEDURES

A. The Stream Survey

The purpose of the stream survey was to make a preliminary estimate of the possibility of making a realistic evaluation of the applicability of laboratory studies of the fate of zinc to stream conditions. In addition, a quantitative demonstration of the sorption phenomena followed by desorption under acid conditions was desired in order to corroborate previous hypothesis and to demonstrate the potential hazard of sediment-adsorbed radioactive zinc.

1. Description of Test Location

The field experiment was conducted in the Boneyard Creek which flows through the University of Illinois campus at Urbana, Illinois (Figure 2). The stream derives its flow from storm sewer drainage, industrial discharges (illegal) and some ground water infiltration. As a result, flows are highly variable even on days with no precipitation (Figure 3). The relatively low flows on dry days yield a channel depth of less than eight inches at most cross sections and, thus, the creek tends to approximate the physical conditions of many rivers (Table 4).

TABLE 4
COMPARISON OF STREAM CHARACTERISTICS (12)

Stream	Location	Approx. Depth to Width Ratio	Mean Velocity ft/sec.
Colorado River	Texas	1:40	2.1
Pierce Canal	Texas	1:10	0.69
Clinch River	Tenn.	1:20	1.1 - 1.5
Chicago Ship Canal	Ill.	1:6	1.1
Ohio River	Pa.	1:30	0.29 - 0.93
Mohawk River	N.Y.	1:35	.007 - .143

FIGURE 2: STREAM STUDY SITE, UNIVERSITY OF ILLINOIS

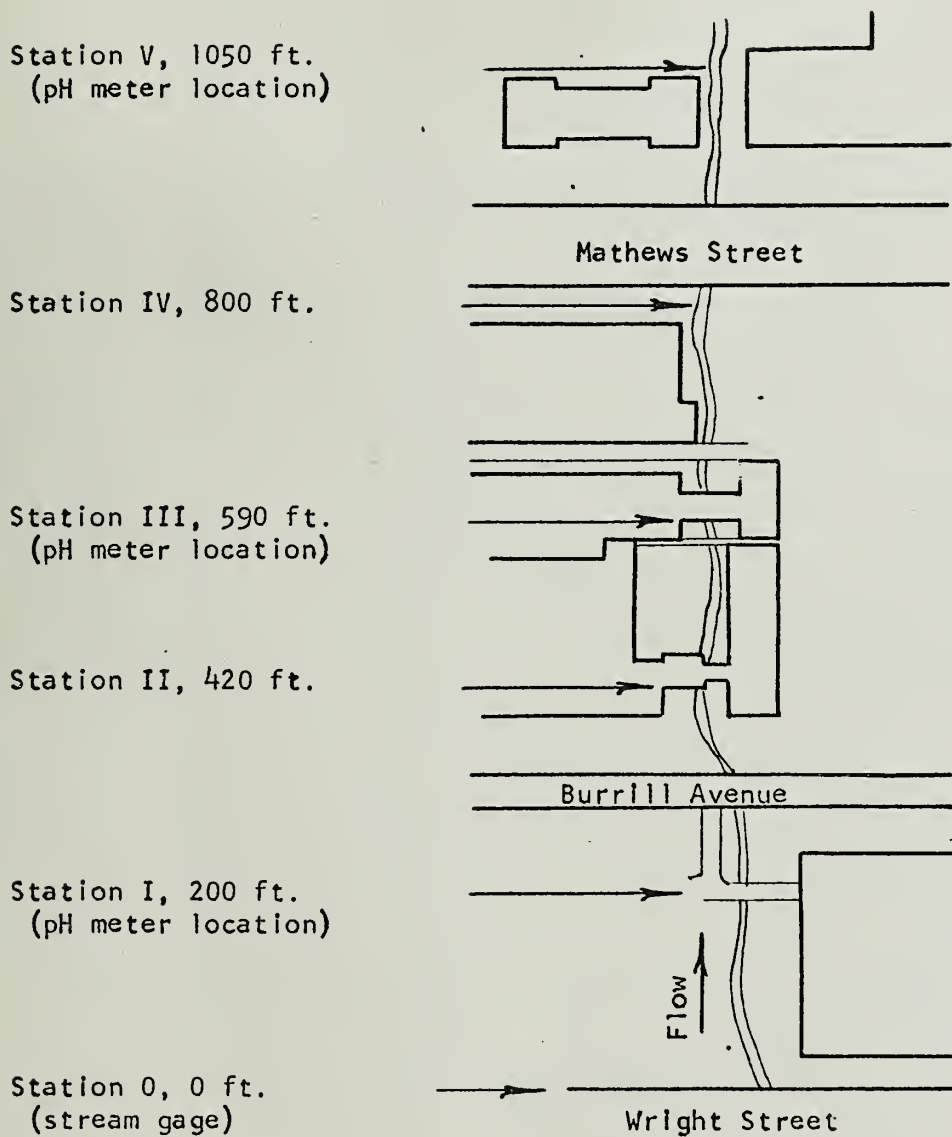
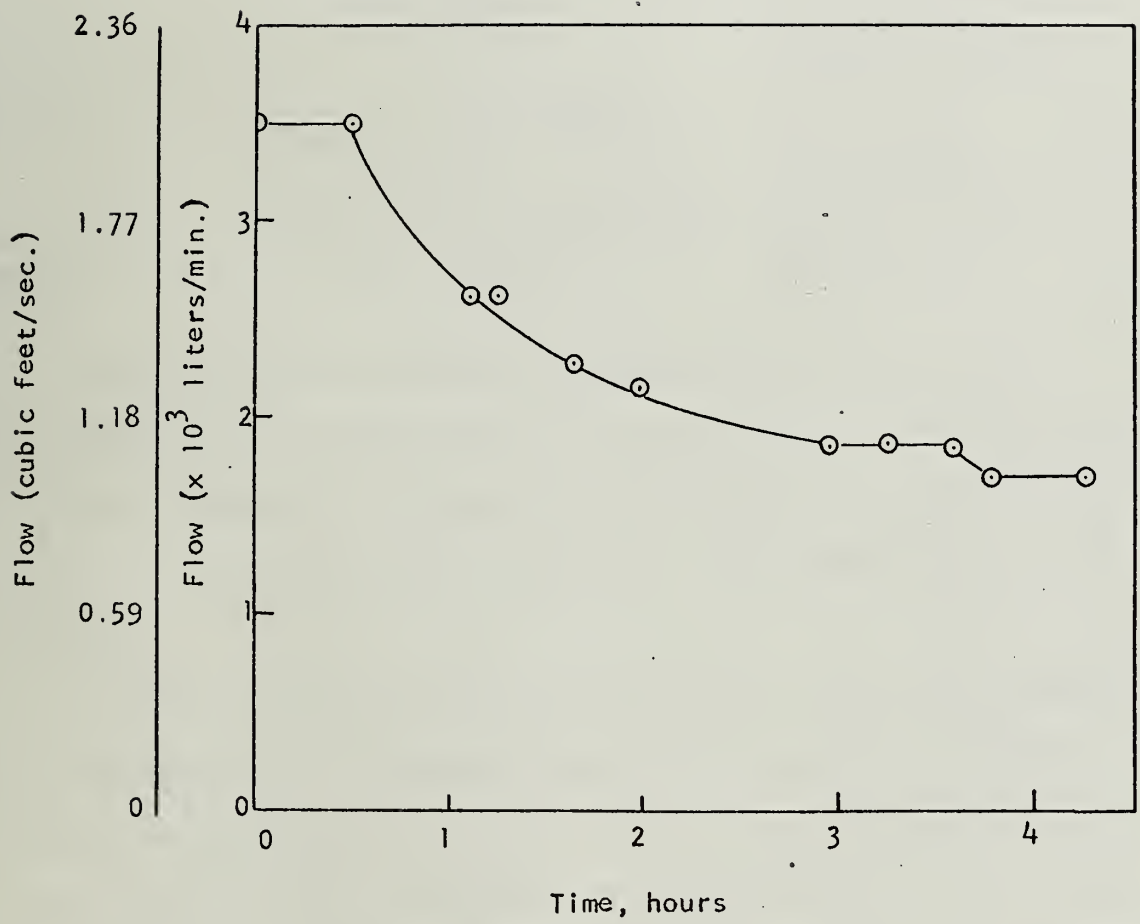


FIGURE 3: VARIATION OF FLOW



Because of the source of flow, the chemical characteristics of the Boneyard Creek are probably not as representative of most surface waters (Table 5) as the physical properties (Depth to Width--1:15; Mean Velocity--0.75 ft/sec.).

TABLE 5
PHYSICAL AND CHEMICAL CHARACTERISTICS OF BONEYARD CREEK WATER

Analysis	Range Observed	Value on Test Date
Alkalinity	126 - 210 mg/l	133 mg/l
Total hardness	---	175 mg/l as CaCO ₃
Chlorides	37.5 - 162.5 mg/l	See Figure 8
Iron	Below limits of detection	-----
pH	7.3 - 8.2	See Appendix C
Zinc	Below limits of detection	0.008 - 0.03 mg/l
Suspended solids	2.5 - 46.6 mg/l	9.4 mg/l
Temperature	25° C - 29° C	25° C - 29° C

Visual observations of the distribution of fluorescein dye at various points along the stream were used as the criteria for selecting this reach. It was observed that the dye had spread evenly to the full width of the channel one hundred feet downstream from the point where the zinc was to be injected.

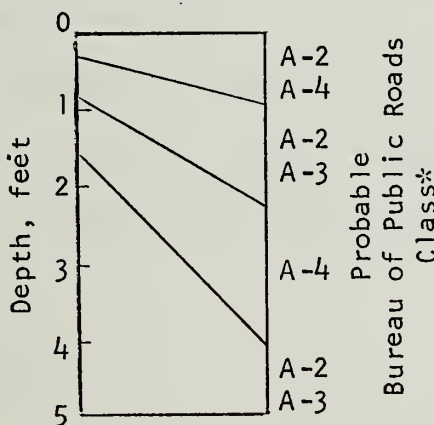
Geologically, this area was covered by both the Illinois glacier and the Wisconsin glacier. In general the extensive deposits of boulder clay left by the Wisconsin glacier are covered by loessial deposits ranging up to eight feet in depth. The pedology of the stream bed, however, varies radically from the general terrain. Excluding the street washings (ranging from cinders to an observed tooth), the bed material of the Boneyard Creek appears to fit the soil group classified by Hopkins (7) as mixed loam from small stream bottoms (Table 6) and the engineering soil group classification of Thornburn (17) and Washer (20), engineering group CH (Figure 4),

from observations of the physical properties and a grain size analysis (Table 7 and Figure 5).

TABLE 6
CHARACTERISTICS OF A MIXED LOAM (7)

Surface soil	depth - 0-6 inches
	color - black to brown loam
	texture - varying from a silt loam to a sandy loam
Gross analysis	organic carbon 3.09%
	nitrogen .28%
	phosphorous .08%
	potassium 2.08%
	magnesium .88%
	calcium 1.71%

FIGURE 4: CHARACTERISTICS OF SOIL GROUP CH (17, 20)



Topographical Expression: Nearly level to moderately rolling

Slopes: 0-2%

Parent Material: Water or sometimes windlaid sands

Surface Material:

Color: Brown to dark grayish brown

Texture: Sandy loam

Physical Condition: Very friable to loose

* BPR Class A-2 Sieve Analysis: % passing

2.00 mm	> 50
0.42 mm	> 51
0.074 mm	< 35

TABLE 7
BONEYARD CREEK BED SEDIMENT GRAIN SIZE ANALYSIS*

Hydrometer analysis:		Sieve analysis:	
% Remaining in suspension	Diameter, mm	Sieve size, mm	% passing
9.3	.035	4.699	78.0
8.3	.0249	2.000	66.0
7.3	.0176	.420	35.2
6.3	.0125	.177	9.7
5.8	.0090	.149	9.3
5.5	.0064	.074	7.7
5.4	.0045		
5.05	.0024		
4.96	.0013		
4.8	.0009		

*After Modified ASTM procedure of Bauer and Thornburn (2)

2. Measurements and Sampling Methods

Flow measurements were obtained by constructing an earth dam with a plywood core and sharp crested rectangular spillway at Station 0 (Figure 2). Calculations for flows (Figure 3) were based on the following formula (18):

$$Q = C_w \frac{2}{3} (2g)^{\frac{1}{2}} H^{3/2} L$$

where

Q is the flow rate

$$C_w = 0.605 = 0.08 H/P$$

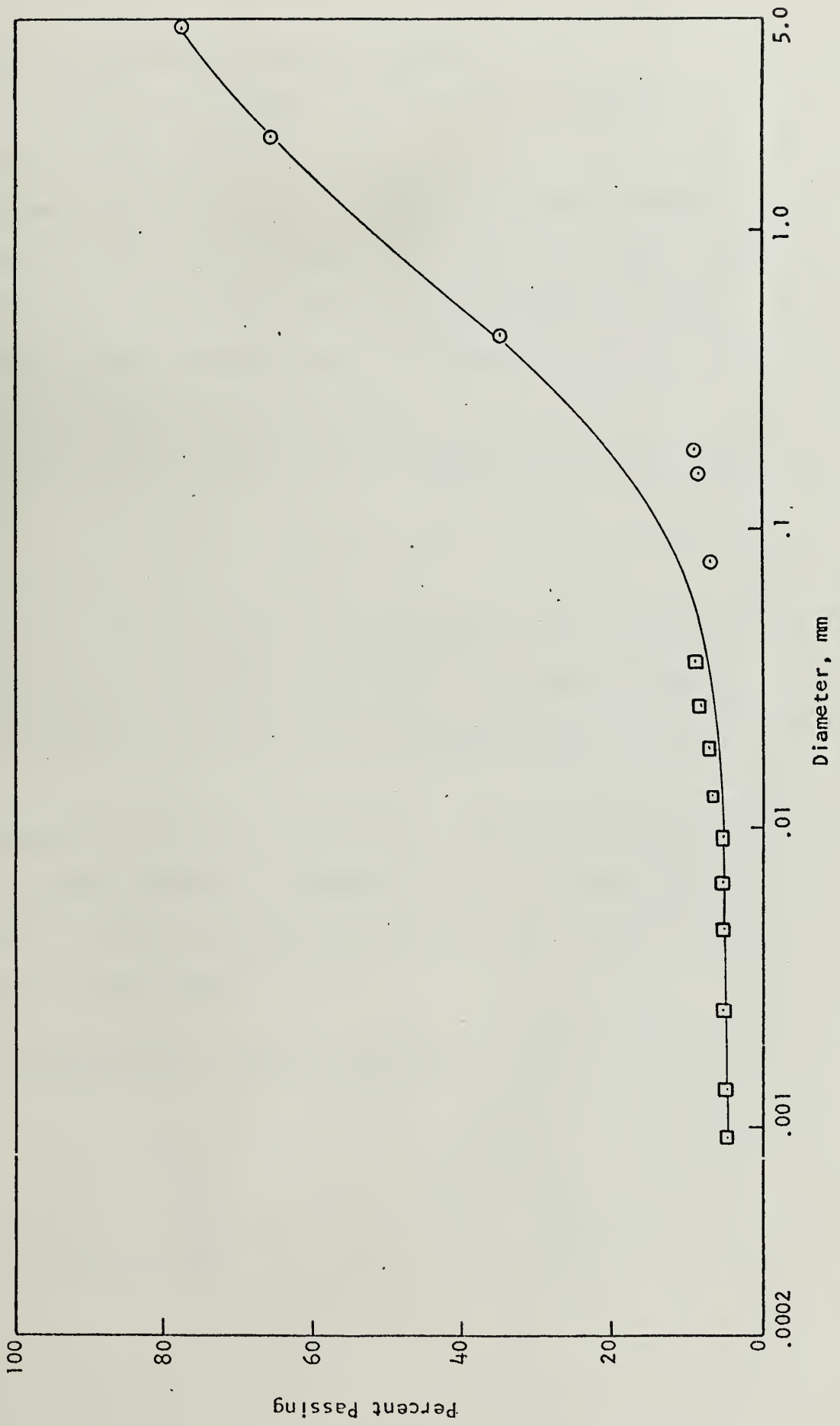
g is the acceleration due to gravity (32.2 ft/sec²)

H is the head

L is the length of the weir

P is the depth from the weir crest to the floor of the reservoir

FIGURE 5: GRAIN SIZE DISTRIBUTION CURVE



Temperature readings were taken at the weir.

Three pH meters were located at alternate sampling stations (Figure 2) to monitor pH variations.

Zinc samples were collected at Stations II through V, at mid-stream, in sixteen ounce bottles and sealed with plastic screw caps. The samples at Station I were collected in plastic counting tubes and sealed with metal caps. (It was discovered during the analysis of these samples that rust from the caps had contaminated them).

The sodium chloride samples were all collected in plastic tubes, left unsealed.

3. Test Procedure

The field test was carried out in three steps corresponding to the addition of the sodium chloride, zinc chloride and hydrochloric acid solutions. All of the chemicals were added as solutions over a measured time period.

Extended injections of the chemicals as opposed to instantaneous injections allowed some measure of compensation for the dilution effects of lateral dispersion (Figure 6) although the physical properties of the Boneyard Creek minimize these effects.

FIGURE 6: DILUTION EFFECTS OF LATERAL DISPERSION



If the sampling interval is set such that samples are taken at significantly shorter intervals than the interval of the extended injection and the injection interval is at least as long as the longest travel time between any two sampling stations, then the error from missing the peak concentration may be eliminated. For example, if two stations, five minutes in travel time apart, sampled at five minute intervals from a seven minute injection, each station would take a minimum of one sample from the peak concentration (Figure 7) or a maximum of two (Figure 8).

FIGURE 7: MINIMUM OF ONE PEAK SAMPLE

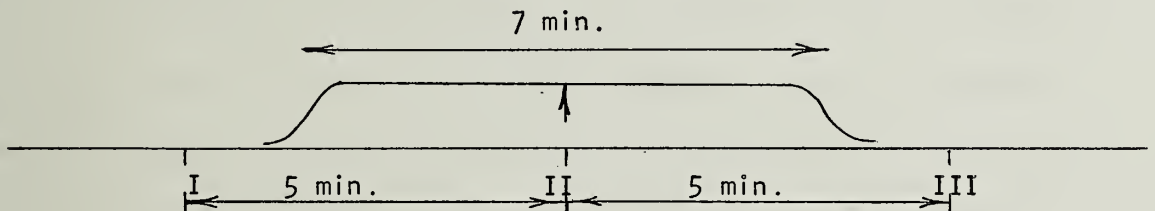
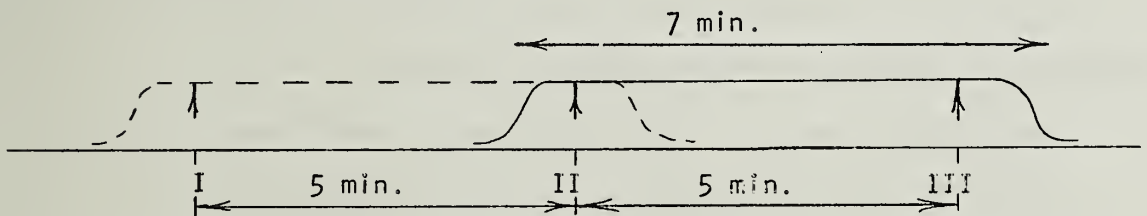


FIGURE 8: MAXIMUM OF TWO PEAK SAMPLES



The first solution, sodium chloride, was added over a period of seven minutes in order to determine the flow time between stations and the dilution which occurred because of the various discharges into the stream between sampling points. Samples were taken at all stations at five minute intervals for a thirty minute period.

After completion of the sodium chloride samples, zinc chloride was added to the Creek over a period of fifty-two minutes and samples were taken at ten minute intervals.

After an hour's delay to allow the unadsorbed zinc to wash out of the system, muriatic acid (technical grade hydrochloric acid) was added for forty-five minutes at a controlled rate of about one liter per minute followed by an accidental high rate release of unknown rate for about eight minutes. Samples were taken over an eighty minute period at ten minute intervals.

B. Analyses of Samples

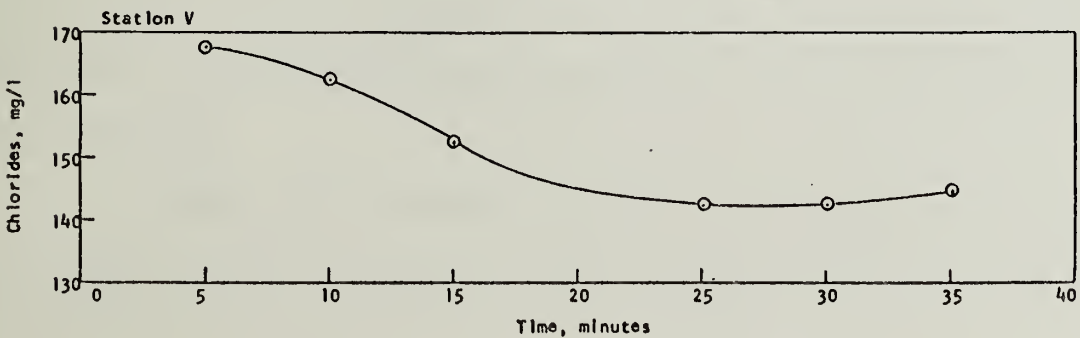
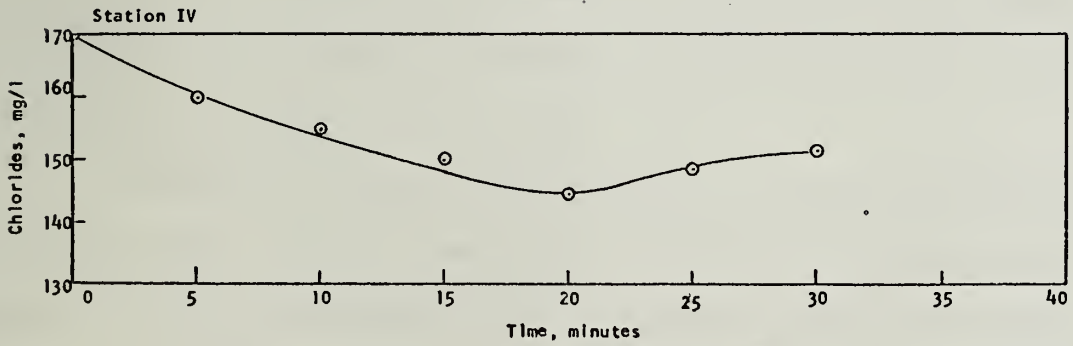
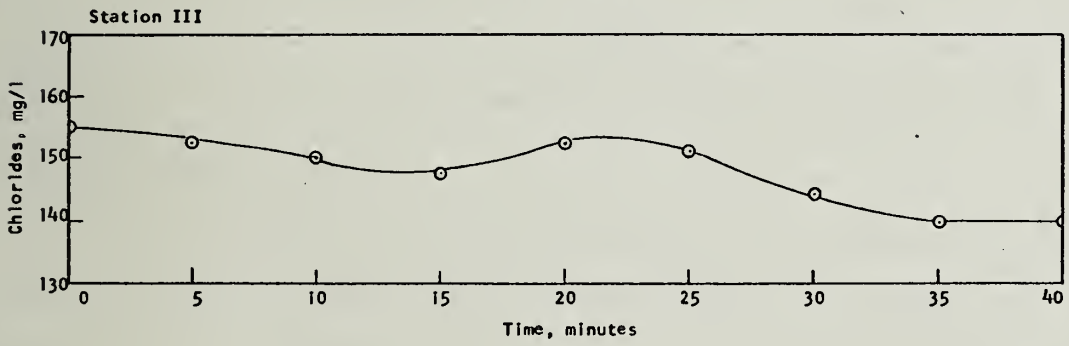
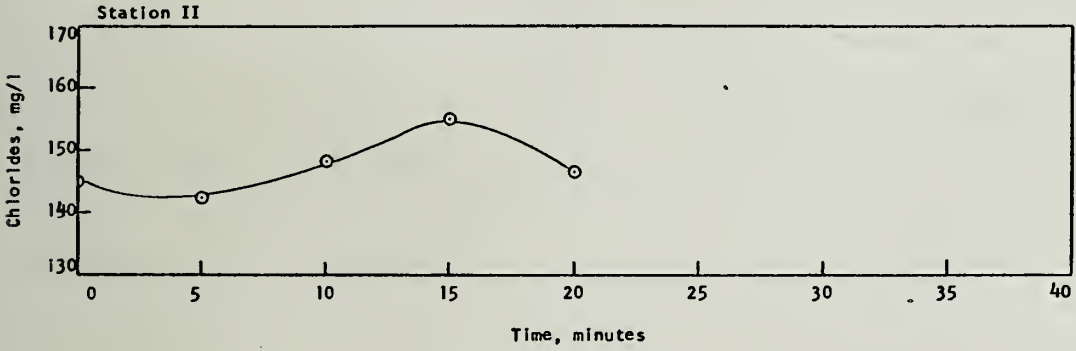
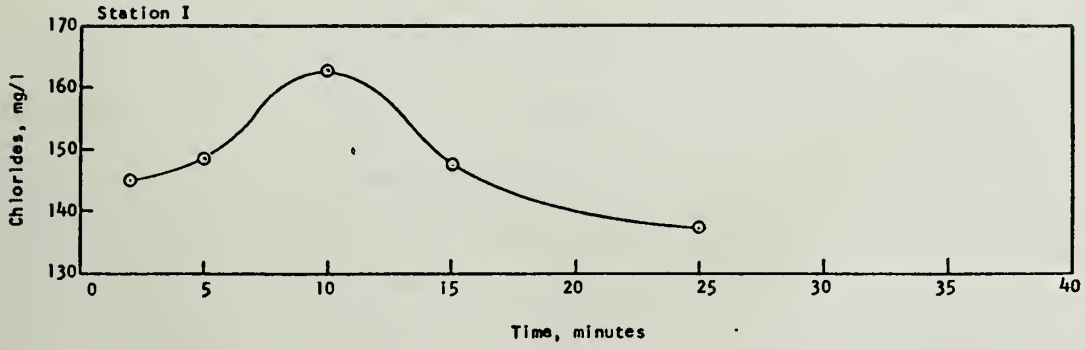
1. Sodium Chloride Tracer Samples

The first group of samples were analysed for chlorides by the "Mercuric Nitrate Method" (1). The results of these analyses are shown graphically in Figure 9. From this data two corrections were calculated to apply to the results of the zinc analysis. The reduction in the peak of the chloride concentration as it passed downstream was taken as a measure of the dilution caused by infiltration and various discharges between stations. The time between peaks at sequential stations was taken as an indication of the travel time between stations and thus allowed an estimation of the time that a sample should have been taken in order to sample an identical volume of water at each station. Tabulation of each of these corrections and the methods by which they were obtained are presented in Appendix B.

2. Zinc Removed from Solution

The samples taken during the addition of the zinc chloride were analysed for total zinc by a modification of the "Mixed Color Method" (1) outlined in Appendix D. Because analysis of filtered samples and acidified, non-filtered samples showed that precipitation of zinc was occurring in the sample bottles, these samples were acidified prior to analysis. This method,

FIGURE 9: CHLORIDE TRACER SURVEY



therefore, gives an indication of all of the zinc not sorbed on the bottom sediments. However, it does not imply that all of this zinc was in solution at the time the sample was taken.

3. Zinc desorption Samples

Samples, taken while muriatic acid (HCl) was being added to the stream, were analysed for zinc by the modified "Mixed Color Method." No adsorption or precipitation of zinc was observed in the sample bottles from spot check acidification and analysis.

C. Laboratory Investigations

1. Measurement of Sorptive Capacity

Two attempts were made to estimate the sorptive capacity of the Boneyard Creek sediments under natural conditions using stable zinc labeled with radioactive zinc-65.

In the first test 10.8 milligrams of zinc labeled with zinc-65 tracer were added to two liters of Boneyard Creek water and 1.3 grams dry weight of soil. The pH was maintained at 7.3, the pH of the stream, with hydrochloric acid and sodium carbonate. At this pH and zinc concentration no precipitation should have occurred.

Because of the high exchange capacity of suspended sediments, it was felt that it might be advisable to remove the suspended matter to observe the sorptive capacity of the bottom sediments. In the second test, the water was filtered through a 0.45 micron pore size membrane filter. This pore size (0.00045 mm) should remove all of the clay fraction (less than 0.004 mm).

Samples were taken and filtered into a counting tube (plastic, test tube with metal screw cap) after a ten minute time period was allowed

for the system to come to equilibrium. The zinc-65 tagged samples were counted in a well-type scintillation counter containing a thallium-activated, sodium iodide crystal which has a counting efficiency for zinc-65 of about 23 per cent. The reduction in radioactive count (and correspondingly the stable zinc in solution) was taken as a measure of the sorptive capacity of the sediment under stream conditions.

With the data available it was concluded that by taking the difference between the values of the sorptive capacity from the first and second test, a measure of the sorptive capacity of the suspended materials could also be obtained.

III. RESULTS AND DISCUSSION

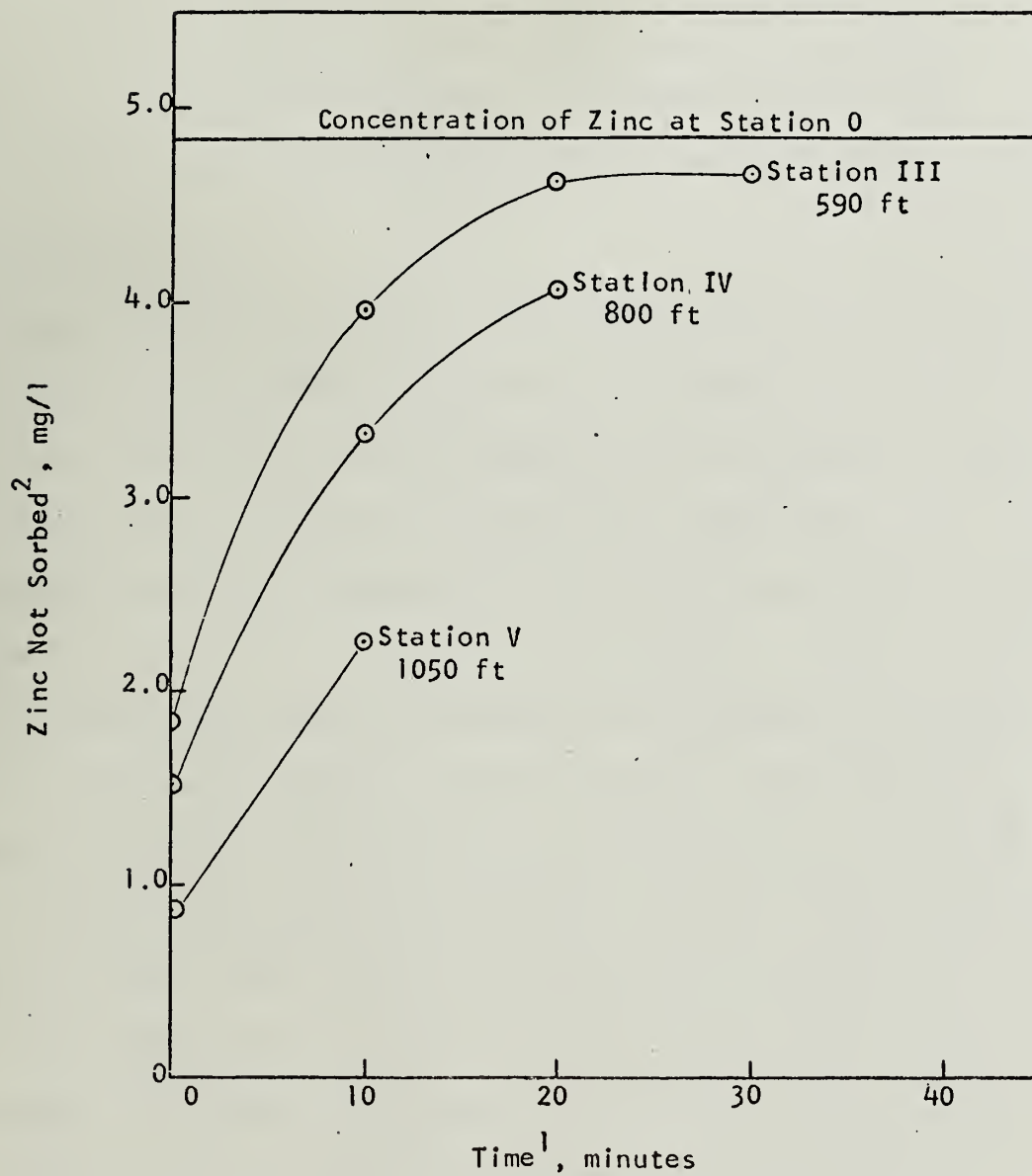
A. Zinc Sorption

Figure 10 represents the zinc not sorbed on the stream bed. The time indicated on the abscissa is the time from the beginning of the addition of zinc chloride at Station 0. Each datum from a station downstream has been corrected for flow variations (Figure 4) and dilution, and translated, in time sequence, by the methods described in Appendix B, to a correlated time at Station 0. Therefore, each sample time indicated refers to one slug as it passes from station to station. Tabulations of the data are presented in Appendix C.

Figure 10 indicates that sorption occurred between stations to various degrees. Because of the high concentration of zinc used, the sorptive capacity of the stream bed was being approached at two of the sampling points at the termination of the test.

Considering the factors of transport and equilibrium of zinc in a stream, several features of this system can be elucidated. The fact that only a relatively small surface area of stream bed was required to achieve a considerable reduction in zinc concentration implies that the role of longitudinal dispersion in reducing the concentration is much less important than lateral and vertical dispersion. A second implication is that dispersion equations using constant dispersion coefficients are of little or no value in large rivers because the time required to establish zero correlation (when the diffusing substance exceeds the Lagrangian eddy size) is usually long enough to cause greater reductions from sorption than occur from dispersion. Because of the possibility of exceeding the sorptive capacity

FIGURE 10: ZINC NOT SORBED ON STREAM BED



¹Time corrected for time of flow between stations

²Zinc concentration corrected for variation in flow and dilution between stations

of the bed sediment either by high concentrations (as approached in this case) or by prolonged exposure or because of a low sorptive capacity sediment, knowledge of zinc dispersion cannot be totally disregarded in considering the behavior of zinc in a stream.

It was not possible to check estimates of total bed sorptive capacity against the data obtained because of the precipitation which occurred at the high concentration of zinc used for the field study.

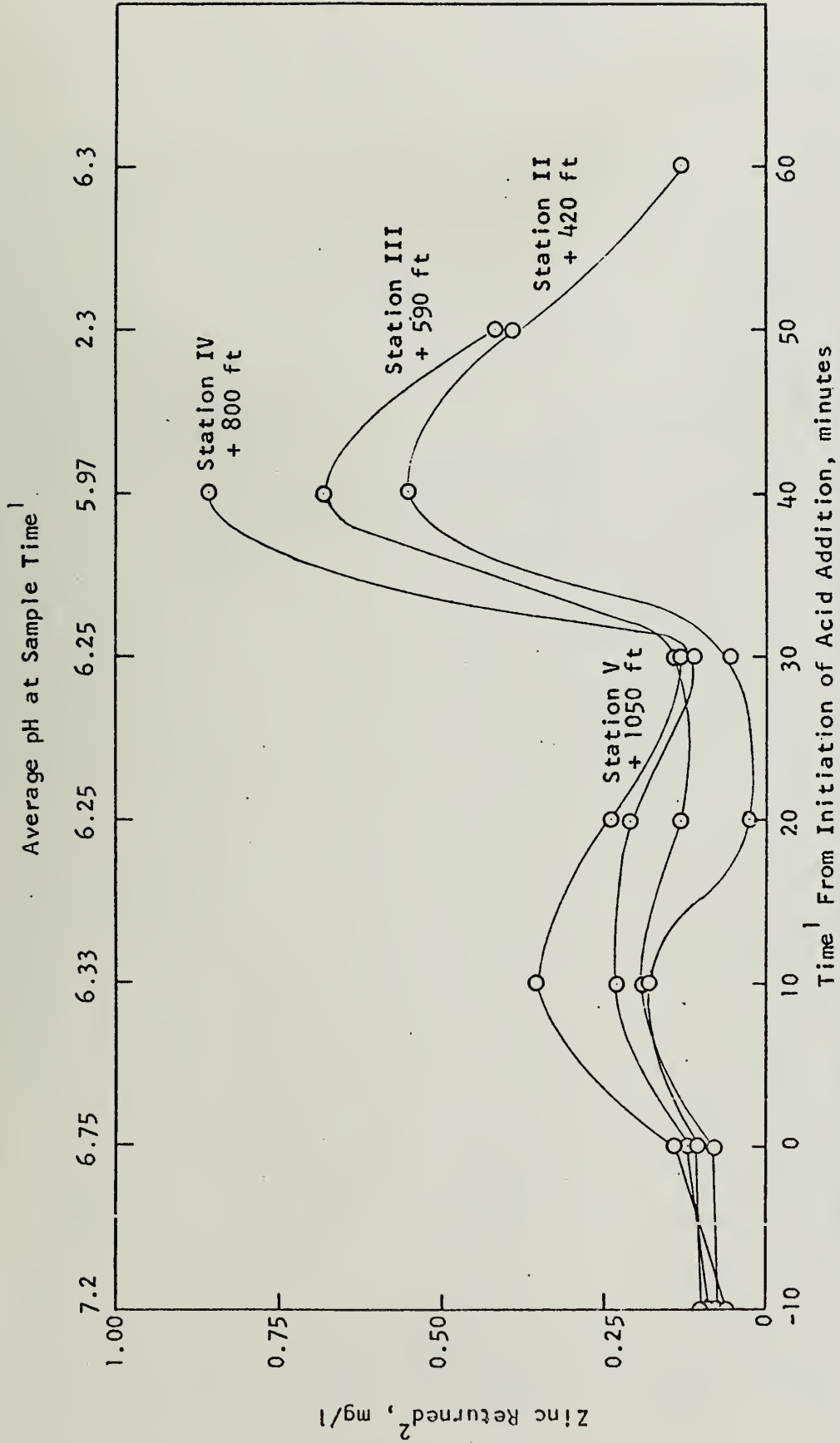
B. Zinc Desorption

Laboratory studies which have been conducted on the solubility of zinc and the soluble-adsorbed zinc equilibria indicate that under acid conditions zinc will return to solution readily, thereby producing a large pulse in the soluble zinc content of a stream (11). From Figure 11, it can be seen that the effect of a decrease in pH was to increase the zinc concentration.

The base line concentration (approximately 0.09 mg/l at -10 and 0 minutes) is above the normal base line of 0.03 mg/l. This increase is possibly the result of the effects of the law of mass action on cation exchange (5). Since a steep concentration gradient was used during sorption of the zinc, one might expect that the soluble-adsorbed zinc equilibria would shift toward the soluble side of the equilibrium with the cessation of large soluble zinc concentrations resulting from zinc chloride additions.

The desorption curves exhibit two peaks. The first peak is probably the result of desorption of zinc. The second peak is possibly the result of two phenomena, zinc desorption and the dissolving of a zinc precipitate. The zinc concentrations used and the pH range encountered in

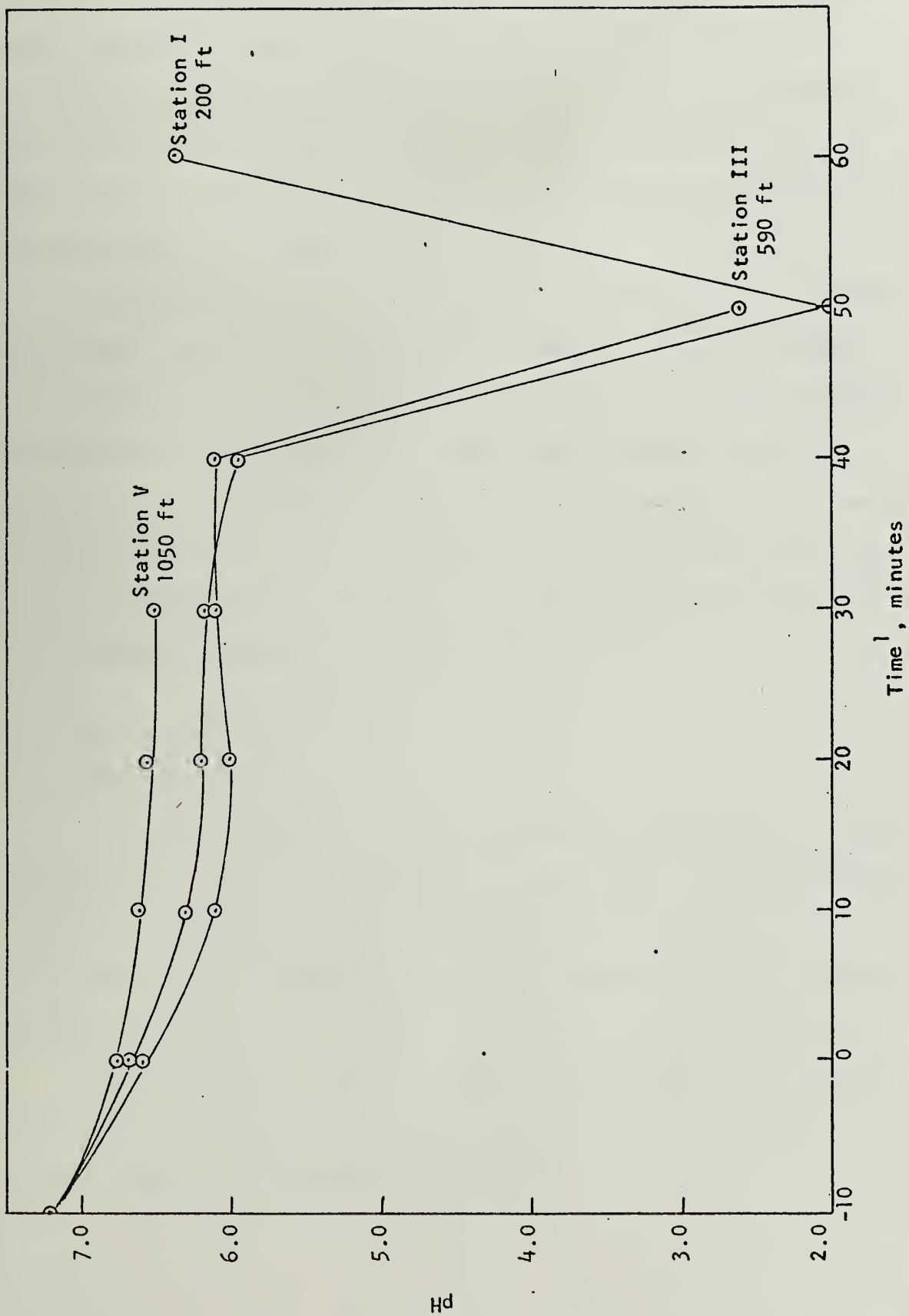
FIGURE 11: ZINC RETURNED TO SOLUTION



¹Time corrected for time of flow between stations

²Zinc concentration corrected for variation in flow and dilution between stations

FIGURE 12: VARIATION OF pH WITH ACID ADDITION



Corrected for time of flow between stations

the stream exceeded the solubility of zinc (See Figure 1). Once a precipitate of zinc has formed, a pH below 6 must be reached before it becomes soluble, whereupon it comes rapidly into solution ⁽¹⁰⁾. The large pulse at 40 minutes could then possibly be attributed to this rapid dissolving of the precipitate and subsequent releases at lower pH values would then be related to the time dependence of this reaction and not the effects of an increased hydrogen ion concentration.

Attempts to develop a mass balance of the amount of zinc sorbed and the amount returned to solution proved somewhat crude, but, however, still enlightening. Working with the data from Station III, it was found that approximately 74.7 grams of zinc were removed from the stream. A total of 27.5 grams was returned to the stream after the addition of acid. Even considering the fact that the decrease in flow left some zinc on the banks, only a percentage of the sorbed zinc seems to be readily returned to solution under acid conditions of short duration.

C. Laboratory Investigations

1. Sorptive Capacity

The sorptive capacity of the combination of suspended solids and bed sediment was found to be 0.786 mg of zinc per gram of bottom sediment plus 5 mg/l of suspended material (2.41 mEqiv per 100 grams of soil).

The sorptive capacity of the bottom sediment alone was found to be 0.502 mg of zinc per gram of soil (1.53 mEqiv per 100 grams of soil).

The difference of sorptive capacity suggests that the suspended materials can sorb up to 28.4 mg of zinc per gram of suspended matter (86.8 mEqiv per 100 grams of suspended material)..

Both the sorptive capacity of the soil and the sorptive capacity of the suspended matter fall within reported values. Values from 0.5 to 18.9 milliequivalents of cation exchange capacity per hundred grams of sand have been reported by Reynolds (13). Sayre (14) has reported values from 3 to 125 milliequivalents of cation exchange capacity per hundred grams of clay.

Although this technique of determining the proportion of sorption associated with the suspended and bed materials appears valid, the data were insufficient to make any correlation with the results of the stream survey. In addition the implications of these results alone are of considerable doubt from a statistical point of view. Further investigations designed to correlate the results of laboratory and field tests would be of value.

IV. CONCLUSIONS

The dispersion of zinc cannot accurately be predicted with dispersion equations using time independent coefficients alone. Because of the rapidity with which zinc is removed from solution, a mathematical model, including a mathematical sink to account for sorption, must consider time dependent dispersion in three planes.

Any long term appraisal of the final disposition of zinc must account for the movement of suspended matter and bed sediments as well as zinc equilibria. Field investigations to separate the effects of adsorption on the bottom sediments and on the suspended material would be useful.

Indications from the stream survey were that zinc would be returned to solution slowly from bottom sediments which had sorbed a high quantity of zinc if the zinc additions were terminated. In addition zinc can be returned to solution rapidly when the pH is lowered from 7.2 to 6.33 and from 6.25 to 5.97. Under acid conditions of short duration less than half of the zinc removed from solution is returned to solution. Further studies using lower concentrations of zinc to eliminate precipitation may result in more accurate and, perhaps, quantitative evaluation of adsorption alone.

The hypothesis of the potential hazard of a pulse release of sediment adsorbed radioactive zinc under acid conditions was substantiated by the results of the Boneyard Creek survey.

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APPENDIX A
DISPERSION CALCULATIONS

Diachishin (3) has presented the following three expressions for predicting the concentration of a material which does not react with its environs (such as a dye):

For one dimension dispersion, instantaneous injection

$$C = \frac{M}{A(4\pi D_x t)^{\frac{1}{2}}} \exp \left[- \frac{(x-Ut)^2}{4D_x t} \right]$$

For two dimensional dispersion, instantaneous injection

$$C = \frac{M}{4\pi z t (D_x D_y)^{\frac{1}{2}}} \exp \left[- \left(\frac{(x-Ut)^2}{4D_x t} + \frac{(y-Vt)^2}{4D_y t} \right) \right]$$

For three dimensional dispersion, instantaneous injection

$$C = \frac{M}{2\pi^{3/2} t^{3/2} (8D_x D_y D_z)^{\frac{1}{2}}} \exp \left[- \left(\frac{(x-Ut)^2}{4D_x t} + \frac{(y-Vt)^2}{4D_y t} + \frac{(z-Wt)^2}{4D_z t} \right) \right]$$

where

- C is the concentration of diffusant per unit volume
- M is the total mass of the diffusant
- A is the cross sectional area of the stream
- t is time
- x, y, z are the distances from the point of origin along Cartesian coordinates to any point
- D_x, D_y, D_z are the dispersion coefficients
- U, V, W are the mean velocities in x, y and z directions respectively

An empirical relationship has been developed to evaluate the longitudinal dispersion coefficient (12)

$$D_x = 0.8 \exp(0.034 U \sqrt{A})$$

This relationship seems to fit the data available fairly well; however, large discrepancies exist in some irregular cases. No work has developed a comparable advance in solving for D_y or D_z .

Rough calculations using data available for the Boneyard Creek reveal a value for D_x of $0.86 \text{ ft}^2/\text{sec}$. This says that concentration occurs as can be seen from the sample calculation below.

Assume

$$M = 1000 \text{ mg}$$

$$A = 8 \text{ ft}^2$$

$$D_x = 0.86 \text{ ft}^2/\text{sec} \text{ or } 51.5 \text{ ft}^2/\text{min}$$

$$t = 22.2 \text{ mins}$$

$$x = 1000 \text{ ft}$$

$$U = .75 \text{ ft/sec} \text{ or } 45 \text{ ft/min}$$

$$C_x = \frac{M}{A(4\pi D_x t)^{\frac{1}{2}}} \exp \left[-\frac{(x-Ut)^2}{4D_x t} \right]$$

$$C_x = \frac{(1000)}{8[4\pi(51.5)(22.2)]^{\frac{1}{2}}} \exp \left[-\frac{[(1000) - (45)(22.2)]^2}{4(.86)(30)} \right]$$

$$C_x = 3.3 \text{ mg/ft}^3$$

while at the influent point

$$C_o = \frac{1000 \text{ mg/min}}{45 \text{ ft/min} \times 8 \text{ ft}^2} = 2.78 \text{ mg/ft}^3$$

The empirical formula for D_x is, therefore, not applicable for the Boneyard Creek. Thus, even though the ratios of the dimensions of the stream resemble those of rivers, the absolute values of the dimensions render generalizations of dispersion coefficients invalid. Furthermore, one would expect then, that the dimensions of the stream limit longitudinal dispersion in short distances to a negligible value.

Time independent dispersion coefficients have been applied with success to small rivers ($A = 5000 \text{ ft}^2$) at distances greater than five hundred feet from the influent point (12). However, at shorter distances time dependent coefficients must be used.

APPENDIX B
CORRECTION CALCULATIONS

A. Correction for Dilution

1. Sample Calculation Station 0 to I

No influent pipes were in operation in this reach, therefore, the correction for dilution was unity (1.00).

2. Sample Calculation Station I to II

The peak concentration of chloride (Figure 9) at Station I was 162.5 mg/l and the peak at Station II was 155 mg/l.

The dilution was then

$$\frac{155 \text{ mg/l}}{162.5 \text{ mg/l}} = 0.957$$

The dilution correction was then

$$\frac{1.000}{0.957} = 1.045$$

The sample concentrations at Station II can then be corrected for dilution by multiplying by the factor 1.045, assuming that no chloride was added in the dilution water.

3. Tabulation of Dilution Corrections

Station I	1.000
Station II	1.045
Station III	1.062
Station IV	1.07
Station V	1.085

B. Correction for Flow Variation

Because of the constantly changing flow (Figure 3), it was necessary to compute a correction factor for each sample time in order that the data

could be considered on a concentration basis. If this was not done, low quantities of zinc released at low flows would have greater weight than high quantities at high flows.

The correction factor was taken as a fraction: the flow at a sample station with respect to the flow at time zero. The flow at the sample station was chosen from the time-correlation procedure described in C.

The correction factor for a sample taken at Station I ten minutes after the inception of zinc chloride addition would be one because the flows were equal. However, a sample taken at Station I twenty minutes after time zero would have to be multiplied by the factor 0.938 ($2420 \text{ l/min} \div 2580 \text{ l/min} = 0.938$).

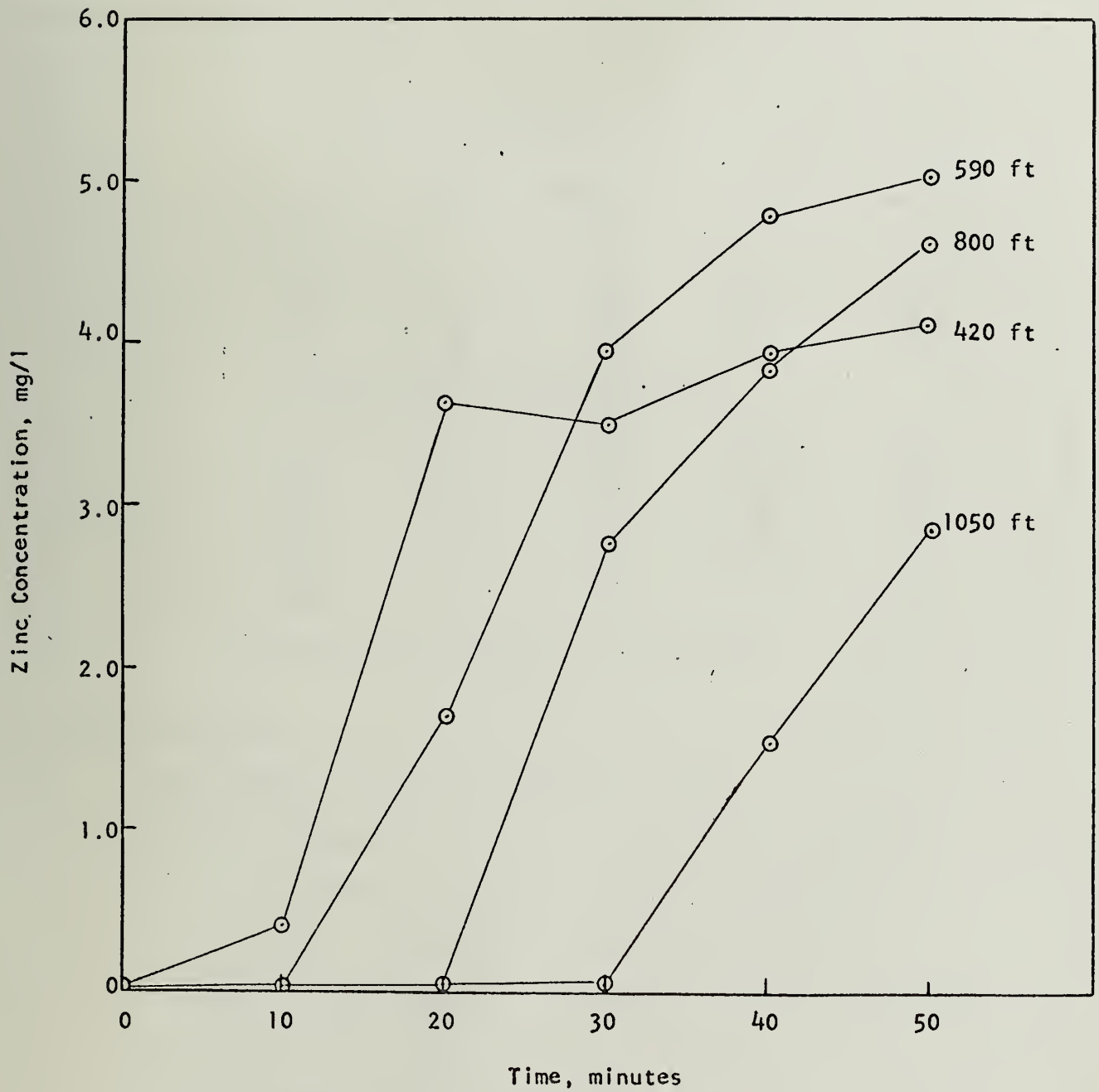
C. Correction for Travel Time

From the time required for the peak concentration of chlorides to travel from one station to the next, one can determine at what instant a sample should have been taken in order to have taken samples from the same volume of water as it passed down the stream. For example, the peak chloride concentration reached Station I ten minutes after the inception of the injection of the sodium chloride solution. Thus, a sample taken at Station I ten minutes after the inception of the addition of zinc would correspond to sampling the same volume of water that was at Station 0 at time zero.

To adjust the data as described above, the raw data was plotted in Figure 13 and values for the correlated data points were selected according to Table 8 and the correction factors for dilution and flow variation were applied.

Zinc desorption data were correlated as above using the variation in pH as the tracer instead of the results of the sodium chloride tracer.

FIGURE 13: RAW DATA, ZINC NOT SORBED ON STREAM BED



Because the flow decreased considerably and the velocity was correspondingly altered during this phase of the test, the travel time between stations corresponded to the sampling time interval and no plot was required to select time correlated data points.

TABLE 8
TIME CORRELATION OF DATA

Station Number						
0	I	II	III	IV	V	
0	10	15	20	25	35	
10	20	25	30	35	45	
20	30	35	40	45	55	
30	40	45	50	--	--	
40	Corresponding samples not taken					
50	Cessation of ZnCl ₂ addition					
0	10	20	30	40	50	
10	20	30	40	50	60	
20	30	40	50	60	70	
30	40	50	60	70	80	
40	50	60	70	80	--	
50	60	70	80	--	--	
60	70	80	--	--	--	

Cessation of HCl addition at 53 minutes

D. Sample Calculation

Data: Station II dilution correction 1.045

Required: The amount of zinc returned to solution at time corresponding to 30 minutes at Station 0.

1. Correlation time 50 minutes (from table above)

Sample concentration from Appendix C, column a - 0.060 mg/l

2. Correction for dilution

$$0.060 \times 1.045 = 0.0626 \text{ mg/l}$$

3. Correction for flow variation

Flow at time zero - 1880 l/min

Flow at time 30 min - 1760 l/min

$$0.0626 \text{ mg/l} \times \frac{1760}{1880} = 0.0586 \text{ or } 0.059 \text{ mg/l}$$

APPENDIX C
DATA

CHLORIDE TRACER CONCENTRATIONS

Time ¹	Station Number				
	I mg/l	II mg/l	III mg/l	IV mg/l	V mg/l
5	145 ²	145	155	170	172.5
10	148.3	142.5	152.5	160	167.5
15	162.5	148.3	150	155	162.5
20	145.8	155.0	147.5	150	152.5
25	137.5	146.7	152.5	145	150
30			151.7	148.3	142.5
35			144.2	151.7	142.5
40			140		143.3

¹Time following addition of chloride tracer

²At 2 minutes

TABULATION OF FLOWS AND pH

Time ¹	Flow, l/min	pH		
		I	Station Number III	V
0	2580	7.4	7.70	7.5
10	2420	7.3	7.65	7.5
20	2320	7.2	7.55	7.4
30	2240	7.25	7.42	7.35
40	2180	7.4	7.50	7.3
50	2120	---	7.46	7.35

Time ²	Flow, l/min	pH		
		I	III	V
0	1880	7.2	7.3	7.38
10	1830	6.6	7.22	7.32
20	1800	6.1	7.2	7.3
30	1760	6.0	6.7	7.3
40	1730	6.1	6.3	7.2
50	1720	6.1	6.2	6.75
60	1700	2.0	6.15	6.6
70	1700	6.35	5.85	6.55
80	1700	6.9	2.60	6.5

¹In minutes from initial injection of $ZnCl_2$

²In minutes from initial injection of HCl

Metz Reference Room
 Civil Engineering Department
 B106 C. E. Building
 University of Illinois
 Urbana, Illinois 61801

ZINC NOT SORBED ON STREAM BED

Time ¹	Station Number									
	I		II		III		IV		V	
	a ²	b ²	a	b	a	b	a	b	a	b
0	3.028		0.028	2.19	0.027	1.82	0.020	1.52	0.025	0.87
10	2.278		0.433	3.51	0.008	3.96	0.049	3.31	0.019	2.24
20	1.928		3.645	3.52	1.710	4.61	0.018	4.05	0.080	----
30	3.103		3.518	3.68	3.977	4.65	2.790	----	0.051	----
40	1.753		3.962	----	4.809	----	3.844	----	1.538	----
50	1.803		4.165	----	5.029	----	4.629	----	2.843	----

¹Time following addition of ZnCl₂

²a - raw data; b - data corrected for dilution, variation in flow and travel between stations

ZINC RETURNED TO SOLUTION

Time ¹	Station Number									
	I		II		III		IV		V	
	a ²	b ²	a	b	a	b	a	b	a	b
0	0.090		0.113	0.107	0.103	0.086	0.043	0.115	0.264	0.139
10	0.120		0.100	0.178	0.048	0.187	0.143	0.229	0.210	0.356
20	0.225		0.103	0.024	0.076	0.137	0.068	0.216	0.088	0.222
30	0.095		0.175	0.059	0.081	0.145	0.098	0.109	0.085	0.137
40	0.105		0.024	0.550	0.182	0.680	0.108	0.861	0.073	----
50	0.570		0.060	0.398	0.135	0.429	0.220	----	0.128	----
60	0.520		0.571	0.132	0.146	----	0.211	----	0.338	----
70	0.064		0.415	----	0.695	----	0.109	----	0.214	----
80	0.037		0.140	----	0.441	----	0.876	----	0.135	----

¹Time following addition of HCl

²a - raw data; b - data corrected for dilution, variation in flow and travel between stations

APPENDIX D
PROCEDURE FOR TOTAL ZINC ANALYSIS

1. Sample solution should contain between 1 μg and 15 μg of Zn in a volume of 10 ml.
2. Place sample in a 125-ml Squibb separatory funnel and bring the volume to 10 ml with Zn free water.
3. Add 5.0 ml of acetate buffer (equal volumes 2 N acetate solution and 1 + 7 acetic acid).
4. Add 1.0 ml of sodium thiosulfate solution (25 g \cdot $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 100 ml H_2O).
5. Mix.
6. Add 10 ml dithizone (II) solution (See Reference 1, p. 267).
7. Stopper and shake vigorously for 2 minutes.
8. Allow the layers to separate and allow the lower layer to run into a 25 ml volumetric flask.
9. Repeat 6 through 8 with an additional 10 ml of dithizone (II).
10. Repeat 6 through 8 with an additional 5 ml of dithizone (II).
11. Bring the volume of the sample to 25 ml with dithizone (II) and mix.
12. Set DU Spectrophotometer at wave length = 510 $\text{m}\mu$.
13. Measure and record absorbance.

