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AN EXPERIMENTAL STUDY OF THE FRESHWATER ZINC CYCLE

by
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INTRODUCTION

Zinc is generally recognized to be an essential micronutrient for the growth and development of both plants (Arnon, 1958) and animals (Underwood, 1958), thus there is a priori evidence for its occurrence in all natural waters which support living organisms. The zinc in lakes may be divided into two fractions, that present in liquid phases such as the open waters and that present in or on solid materials such as the seston and the bottom sediments. In the liquid phases this element may be present as a hydrated ion, a complexed ion, or associated with soluble organic compounds. In the solid phases zinc may form part of an inorganic precipitate, occupy a space in the crystal lattice structure of clays, be held as an exchangeable ion by either organic or inorganic exchange complexes, or be present in living organisms as a functional component of the metabolic systems. The zinc cycle may be thought of as the flux of zinc between the different phases superimposed upon the movements of the phases themselves. For example, both the uptake of a zinc ion from solution by a clay particle and the movement of that particle as it settles to become a part of the bottom sediments would be included.

It is the purpose of this study to consider the first

part of this cycle, namely the distribution of zinc between various liquid and solid phases of lakes and some of the factors which affect this distribution. Specific consideration will be given to planktonic algae, organic detritus, bottom sediments, natural lake seston, and a limited number of aquatic animals. This information will be utilized to deduce a general outline of the freshwater zinc cycle.

LITERATURE REVIEW

Information on the zinc content of natural water is limited. Morita (1955) used a dithiozone extraction technique on samples of the surface waters of ten Japanese lakes and ponds and found a range in zinc concentration of 1.3 to 18 µg/l with an average of 7.7 µg/l. Braidech and Emery (1935), using a semiquantitative spectrographic technique, analyzed the water supplies of various United States cities. If one includes only the surface waters sampled, the range is 5 to 300 µg/l with a mean of 56 µg/l. The manner of sampling is not specified and these values may include contamination from pipes used to transport the water to the treatment plants. The highest value for a lake is that of 650 µg/l reported by Kemmerer, Bovard, and Boorman (1923) for Bear Lake, Idaho, using an unspecified technique. It should be noted that they used a brass water sampler and that in a more recent study of the lake an average of 14 determinations with the dithiozone method gave a value of 20 µg/l (McConnell, Clark, and Sigler, 1957), indicating that the early value may have been in error. In a series of spectrographic analyses of 50 rivers in the United States (U.S. Department of Health, Education and Welfare, 1959) the authors found with one exception that no zinc could be detected. Their

limits of sensitivity ranged from 1000 to 200 µg/l. By way of comparison, the zinc content of the oceans has been given as 5 µg/l (Sverdrup, Johnson and Fleming, 1942), whereas Chipman, Rice and Price (1958) found an average of 10.6 µg/l for the coastal waters of the Atlantic and the Gulf of Mexico.

Whether the reported values represent total zinc or just that in solution is not indicated in most cases. The importance of this distinction will be shown later. In general the average value for fresh waters seems to lie between 5 and 100 µg/l.

The zinc ion can react with water in the following manner:

$$Zn^{++} + H_2O \rightleftharpoons ZnOH^{+} + H^{+} \rightleftharpoons Zn(OH)_2\downarrow + H^{+}$$

If we consider the first step in the hydrolysis, the following mass action expression can be written:

$$\frac{[ZnOH^{+}]\,[H^{+}]}{[Zn^{++}]} = k = 2.65 \times 10^{-6}$$

The value of the equilibrium constant taken from Kolthoff and Kameda (1931) is applied on the assumption that activities are equal to concentrations and thus represents an approximation. The proportion of the total zinc in the form of the respective ions has been calculated from this relationship for various values of pH (Table 1). It can be seen that below a pH of about 8 the $ZnOH^{+}$ ion is of little significance and the Zn^{++} ion represents almost

the entire quantity of ionic zinc. At higher pH values the $ZnOH^+$ ion assumes a greater quantitative importance.

Table 1. Proportions of Zn^{++} and $ZnOH^+$ in waters with various pH values.

pH	Per Cent of Total Zinc in Solution	
	Zn^{++}	$ZnOH^+$
4	99.9	2.51×10^{-4}
5	99.9	2.51×10^{-3}
6	99.9	2.51×10^{-2}
7	99.7	2.51×10^{-1}
8	97.5	2.51
9	79.9	20.1
10	28.5	71.5
11	3.8	97.2
12	0.4	99.6

The solubility product for zinc hydroxide may be formulated as follows:

$$[Zn^{++}] \cdot [OH^-]^2 = k_{sp} = 10^{-16}$$

The value of the solubility product was taken from the calculated values of Barton and Bethke (1960) with consideration being given to the influence of the ionic strength of average lake waters. Using this value, calculations were made of the amount of zinc which would be

in equilibrium with solid zinc hydroxide in waters of varying pH. From Table 2 it can be seen that in most lakes this precipitate will not be formed. It follows from this that the bizincate ($HZnO_2^-$) and zincate ($ZnO_2^=$) ions which are formed by the dissociation of zinc hydroxide (Fulton and Swinehart, 1954) will not be of importance in lakes.

Table 2. Concentration of dissolved zinc in equilibrium with $Zn(OH)_2$.

pH	Zinc Concentration in µg/l
6	6.5×10^7
7	6.5×10^5
8	6.5×10^3
9	6.5×10
10	6.5×10^{-1}

The only other inorganic precipitate considered to be of potential importance is that of zinc sulfide. As Hutchinson (1957) has pointed out, this will be formed only under reducing conditions such as might be found in an oxygen depleted hypolimnion or within the sediments. By assuming that the water is in equilibrium with ferrous sulfide, he showed that the amount of zinc in equilibrium with zinc sulfide at a pH of 3 is 0.25 µg/l and that for each unit increase in pH this value will decrease by a factor of about ten. On this basis one would expect zinc

sulfide to be a strong factor in the retention of zinc by reduced sediments.

Zinc may also adsorb on or coprecipitate with other compounds in lakes. Jurinak and Bauer (1956) measured the adsorption of zinc on precipitates of calcium carbonate. This is commonly found in alkaline lakes as marl. Similarly, Kolthoff and Overholser (1939) found that zinc was both coprecipitated with and adsorbed on precipitated ferric oxide. This precipitate is of common occurrence in lakes, and its ability to function as an adsorbent in the sediments is well known (Mortimer, 1941-42).

As a cation, zinc can react with clay particles in two different manners. It may occupy a position within the crystal lattice structure of the clay mineral (Elgabaly, 1950), or it may be attached to a negatively charged site on the surface (Kelly, 1948). In the former case the zinc is considered to be unexchangeable since it is not freely transferred to solution, while in the latter case it is considered to be exchangeable since it is in dynamic equilibrium with the ions in solution. When the laws of mass action are applied, the proportion of exchange sites occupied by a given species of ion is found to be dependent upon the relative concentration of that ion in solution and the energy with which it is bound to the exchange sites. In general the cations with higher valencies are bound most tightly; however, the hydrogen ion may occupy a variable position depending upon the particular

clay. A general series representing relative affinities for different ions starting with the highest is given by Millar and Turk (1951) as $H^+ > Sr^{++} > Ca^{++} > Mg^{++} > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+$. This series is not necessarily followed in all instances and depends in part upon the particular clay and the concentrations used (Kelly, 1948). The fact that one species of ion can replace another as its concentration is increased gives rise to the term ion exchange which is used to describe this specialized case of adsorption.

Ion exchange reactions have also been used to characterize many of the reactions between cations in solution and both living and dead organic materials. The organic materials in soils have long been known to possess an ion exchange capacity (Broadstreet and Ott, 1957), and this phenomenon has been demonstrated for such organisms as bacteria (McCalla, 1940a,b), yeasts (Rothstein, 1955), unicellular algae (Scott, 1944), marine benthic algae (Wassermann, 1949), higher aquatic plants (McGeorge, 1932), plant roots (Broyer and Overstreet, 1940), and isolated frog skin (Huf, 1955).

Of particular interest in the field of limnology are the ion exchange properties of Sphagnum moss (Skene, 1915), which are thought to be important in the production of bog waters with characteristically low values of pH and total dissolved solids (Ruttner, 1953). River-borne silts have been shown to exhibit ion exchange properties (Kurin and Islan, 1956) as have lake sediments (Mortimer, 1941-42;

Ohle, 1955). It is thus to be expected that ion exchange reactions might play an important role in the cycle of zinc in lakes.

In the case of living organisms one must also consider that zinc is present as an essential component of the living protoplasm. Zinc, unlike elements such as carbon or nitrogen which form structural components in the living cell, is associated with enzymes which regulate cellular metabolism. A distinction is often made between metal-proteins, in which zinc is non-specifically bound and easily removed by dissociation, and the metaloenzymes, in which the zinc is specifically bound into the matrix of the protein and is not easily removed (Hoch and Vallee, 1958). In the latter category, the following enzymes have been identified: carbonic anhydrase, alcohol dehydrogenase, glutamic dehydrogenase, and lactic dehydrogenase.

Two mechanisms of uptake by living materials are thus indicated, namely the non-specific adsorption or ion exchange reactions and the specific utilization of zinc in the synthesis of certain enzymes. By comparing the uptake of living and non-living materials, an attempt will be made to determine the quantitative importance of each.

MATERIALS AND METHODS

A major part of the experimental work involved the addition of high specific activity zinc-65 to suspensions of planktonic algae, detritus, deepwater sediments, and natural lake seston and the subsequent determination of the distribution of the added zinc between the liquid and solid phases. Some of the variables involved were the types of materials, the concentration of zinc added, the chemical composition of the medium, and the time of sampling.

The zinc-65 was obtained from the Oak Ridge National Laboratory as $ZnCl_2$ in HCl solution. This was diluted to obtain a tracer solution with a concentration of 88.9 µg/ml and an activity of about 10 µc/ml. In any given experiment the amount of tracer solution added to 100 ml of suspension ranged from 0.05 to 1.0 ml, which yielded a total zinc concentration of from 45 to 889 µg/l. It was assumed that these amounts of zinc would exceed those already in solution, so that the specific activity of the zinc in the experimental bottles would be the same as that of the tracer solution.

Radioassay for the zinc-65 was accomplished by means of a well scintillation crystal linked with an integrating scaler. The counting samples consisted either of 2 ml of

liquid or a membrane filter upon which the radioactive materials had been filtered. It was found empirically that both types of samples could be counted with equal efficiency. A standard sample of zinc-65, prepared from the same tracer solution, was counted each time the counter was used to correct for radioactive decay and variations in counter performance. The length of time the samples were counted was adjusted to give a minimum standard deviation of 5%. The standard deviation was calculated according to the method given by Kamen (1957). An exception to this procedure was made in the experiment with Daphnia pulex. In this case the animals were counted with a Geiger-Muller tube and the results expressed as counts per minute.

With the exception of the experiments with Ankistrodesmus sp. and Daphnia pulex de Geer in which Ann Arbor tap water was used, the liquid medium consisted either of natural lake water or a synthetic solution. The composition of the artificial lake water is given in Table 3. This was made up to correspond to the average river waters of the world with respect to the ratios of the major ions (Clarke, 1924). The total salinity was 100 ppm, the total alkalinity (APHA, AWWA, WPCF, 1960) 69.8 ppm as $CaCO_3$, and the pH about 8.1. It was found that the dissolution of the $CaCO_3$ was facilitated by saturating the solution with CO_2. When it was dissolved the excess gas could be removed by aeration, leaving a clear solution.

Table 3. Composition of artificial lake water.

Compound	Milliequivalents per liter	Milligrams per liter
K_2SO_4	0.064	5.58
NaCl	0.190	11.11
NaOH	0.105	4.20
H_2SO_4	0.247	12.11
$CaCO_3$	1.193	59.71
$MgCO_3$	0.327	13.79

Measurements of algal uptake were conducted using Golenkinia paucispina West and West, a spherical green alga bearing numerous needle-like setae of approximately the same length as the cell diameter (10 μ). An essentially unialgal stock of this alga was maintained for several months in aerated tap water and provided a convenient source of supply. On the day prior to an experiment an aliquot of the suspension was filtered on Reeve Angel No. 202 filter paper and the cells were resuspended in the artificial lake water. They were allowed 24 hours to equilibrate with the new medium. This suspension was added in 100 ml aliquots to a series of 125 ml reagent bottles (Pyrex) and another 100 ml sample was filtered on a membrane filter (Millipore, AA) for subsequent cell counts. In some experiments different amounts of labeled zinc were added to each bottle, while in others the same amount

of zinc was added to each bottle (178 µg/l but the chemical composition of the water was changed. This might involve the addition of NaOH or H_2SO_4 in order to change the pH or the addition of $CaCl_2$, $MgCl_2$, NaCl, or KCl to alter the concentrations of the major cations. The bottles were placed in the dark at room temperature (24-25° C.) and remained there for the duration of the experiment, except for occasional periods of shaking for the purpose of keeping the cells in suspension.

Except for those experiments in which uptake was measured as a function of time and the cultures were sampled at periodic intervals, the experiments were terminated at the end of 24 hours, for it was found that equilibrium was substantially complete at that time. The samples consisted of a 2 ml aliquot of the suspension which was used to estimate the total zinc content and a 90 ml aliquot portion which was filtered on a membrane filter with a pore size of about 1 µ (Millipore AA) and used to estimate the amount of zinc associated with the suspended materials.

Variations in the above procedure included the use of cells which had been suspended in 10% formalin overnight before resuspension in the artificial water and experiments conducted at 8° C.

In order to approximate the autochthonous detrital materials originating from the decay of higher aquatic vegetation, an artificial detritus was prepared by placing

well-washed specimens of Elodea canadensis Michx. Ceratophyllum demersum Linnaeus, and Potomogeton Richardsonii (Benn.) Rydb. in a polyethelyne container with tap water and allowing them to remain at room temperature for 22 days. At the end of that time the larger materials were removed by filtration through a fine mesh screen and the finer materials were concentrated on No. 202 filter paper. A portion of the latter material was suspended in the artificial lake water and the rest was placed in a 10% formalin solution to kill the bacterial flora. This formalin treated material was also resuspended in artificial lake water and both suspensions were used in a manner analogous to that used for the Golenkinia suspensions.

A black, anaerobic mud was collected with an Ekman dredge from a depression in Whitmore Lake, Livingston Co., Michigan and was stored in a polyethelyne bucket at 4° C. The organic content of the oven dry material, as estimated by loss on ignition at 600° C., was 37%. The water content of the wet mud as determined from oven dried samples at 97° C. was found to be 93.9% of the wet weight. A weighed portion of the wet mud (1.019 g) was added to 3 liters of artificial lake water to make a suspension with a sediment concentration of 20.7 mg/l on an oven dry basis. The suspension was allowed to sit for 18 days, so that the sediment material can probably be considered as oxidized. This material was used to determine the effects of pH and concentration on uptake in the manner previously described

for the algae. However, the zinc content of the water was determined directly by allowing the sediments to settle to the bottom of the bottles, and the supernatent liquid was sampled directly.

In order to relate the experiments on these artificial systems to conditions prevailing in nature, surface waters were collected from four local lakes between March 20 and March 27, 1961. These waters, with their suspended materials, were treated in the manner previously described for the artificial systems with pH and zinc concentration as the experimental variables. In this case, however, the experiments were conducted at 8° C. in order to approximate the environmental temperature. Determinations were also made of the total alkalinity and pH of the waters. Surface water samples were also collected from Little Silver Lake, Livingston Co., Michigan, on several dates in the spring of 1961; and between May 1 and May 4, 1961, similar samples were collected from 20 lakes in the vicinity of Ann Arbor, Michigan. Duplicate 100 ml samples of water from each lake and 0.2 ml of the tracer solution were added to each of two 125 ml bottles. They were placed in the dark at 8° C. for 24 hours, at which time they were sampled for zinc distribution.

Two types of experiments were conducted to assess the role of zooplankton organisms in the cycling of zinc in the open waters. In the first, adult individuals of Daphnia pulex were added to a culture of Ankistrodesmus

in one flask and to membrane-filtered water in another. The same amount of tracer solution was then added to each culture. At periodic intervals five animals were removed from each container, each group placed on a single planchet and their radioactivity was determined with a Geiger-Muller counter. At 24 hours a group of Daphnia were removed from the culture containing the Ankistrodesmus and placed in a fresh culture of algae without the zinc-65. The animals were removed 22 hours later and assayed for radioactivity. In the second experiment 50 adult Daphnia magna Straus were added to a 500 ml suspension of Golenkinia which had been labeled with zinc 24 hours before. In this case periodic samples were taken to follow the distribution of zinc in the water and the suspended materials exclusive of the animals. At the end of 48 hours 20 adults were removed and assayed for radioactivity while still alive. They were then placed in another, non-radioactive, algal culture and left of 46 hours, at which time 19 were removed and counted.

Two series of experiments were conducted to determine the extent of zinc uptake by non-suspended sediments. On July 27, 1961, water was collected from the oxygen-depleted hypolimnion of South Fishtail Bay, Douglas Lake, Cheboygan Co., Michigan, and used to fill a one liter glass-stoppered bottle (care being taken to avoid the introduction of air bubbles). A core sampler was used to collect a sample of the black anaerobic mud found in the bay, and this was added to the water sample to make a thick

slurry. Portions of this slurry were added to six 4 oz screw-cap bottles. Three were left open to the air and three were capped, without air bubbles. A similar procedure was followed with the water and sediments from Bryant's Bog, which was also anaerobic in the deeper waters. These sediments were dark brown in color and of a fibrous nature. After seven days an oxidized microzone was observed on the mud surfaces of the bottles without caps, indicating aerobic conditions. Next, 0.2 ml of tracer solution was added to each bottle and subsequent samples were taken of the supernatent water at the ends of six and eight days. The water removed from the anaerobic bottles was replaced to prevent the formation of an air bubble. No oxidized zone was observed in these bottles during the course of the experiment, indicating that the bottle caps excluded atmospheric oxygen.

In the second series of experiments a layer of sediments from Whitmore Lake was placed in each of fourteen 8 oz glass bottles. One hundred milliliters of artificial lake water were added to each bottle. Two weeks later an oxidized microzone was observed on the mud surfaces. The bottles were paired and 0.1 ml of tracer solution was added to each of the first pair. Bottles in the second pair each received 0.2 ml and successive increments were added to the remaining pairs, thus the bottles of the seventh pair each received 0.7 ml of tracer solution. They were left in the dark at room temperature (24-26° C.) and 2 ml

samples of the supernatent liquid were taken periodically for radioassay.

In order to measure the depth of penetration of zinc into the sediments, a 600 ml Pyrex beaker was filled with Whitmore Lake sediments to a depth of about 2.5 cm and 300 ml of artificial lake water were added. After one day, 0.6 ml of tracer solution was added and five days later the supernatent water was removed. The sediments were allowed six days to become partially air dried. As a result of shrinkage the sediment depth had decreased from 2.5 cm to 1 cm. The sediment could then be removed from the beaker in one piece without breaking. Ten randomly selected cores of approximately one cm^2 were cut from the sediment block and sectioned transversly into four sections each with a thickness of 2.5 mm. These were assayed for radioactivity in the same manner as the previous samples.

Two other beakers were set up at the same time in order to test the effect of burrowing benthic animals on the penetration of zinc in the sediments. Into each of these systems were placed five nymphs of the mayfly, Ephemera simulans Walker, ranging in length from one to two centimeters. During the course of the experiment, they were observed to form burrows in the soft sediment and to draw currents of water through them. After the surface water had been removed and the sediments had started to dry, the animals came to the surface and were recovered for radioassay without disturbing the sediments. Five

sediment cores were taken from each beaker and treated in the manner described above.

RESULTS

ZINC UPTAKE AS A FUNCTION OF TIME

The uptake of zinc with time for a variety of materials is summarized in Figures 1 through 4. It can be seen that the typical curve is characterized by a rapid initial uptake which continually decreases to approach a horizontal asymptote. The individual points were calculated as percentages of the estimated equilibrium value. In subsequent experiments equilibrium was considered to have been obtained at the end of 24 hours. As a relative measure of the rate of uptake, the time required for the amount of zinc taken up to reach 70% of the equilibrium value was determined graphically and is presented in Table 4. The shortest time (55 minutes) applied to living Golenkinia cells at 26° C. while the longest (155 minutes) was found for the Whitmore Lake sediments. It is of interest to note the similarity between the uptake curves and rates for both formalin killed and living cells of Golenkinia. This is considered to be evidence for a non-metabolic reaction. Attention is also drawn to Figure 4 which illustrates that under conditions of illumination the cells of Ankistrodesmus continue to take up zinc when the darkened culture had already reached equilibrium. This aspect will be treated in the general discussion of the nature of

zinc uptake.

Table 4. Time required for zinc uptake to reach 70% of the equilibrium value for Whitmore Lake sediments and two species of algae.

Material used	Time in minutes
Whitmore sediments 26° C.	155
Ankistrodesmus 26° C. (living)	100
Golenkinia 26° C. (living)	55
Golenkinia 8° C. (living)	130
Golenkinia 26° C. (formalin killed)	70

Attempts were made to analyze the kinetics of the reaction in terms of a first order reaction as was done in the case of phosphorus uptake by Hayes, McCarter, and Cameron (1952). Plots of the logarithm of the difference between the equilibrium value and the amount taken up at any time against time resulted in curves which were concave upward, indicating that the reaction was more involved than a simple exchange. It was found that if the uptake was plotted against the logarithm of the time interval after the addition of the tracer, the resulting curves appear to be linear, at least for the earlier part of the reaction. These plots are presented in Figure 5 using the same data used in the previous figures. It should be noted that the vertical scale has been shifted in order to

accommodate all of the curves without overlapping. This procedure alters the apparent intercept but leaves the slope the same. This type of plot represents the Elovich Law (Laidler, 1954) which has found previous application in studies of chemisorption. The theoretical basis of this law will be considered later.

ZINC UPTAKE AS A FUNCTION OF CONCENTRATION

The relationship between zinc uptake and the concentration of zinc in solution is summarized in Figures 6 through 10. The two factors are obviously correlated, and when plotted on logarithmic scales the relationship appears to be linear. This corresponds to the Freundlich isotherm (Freundlich, 1926) which has found wide usage for the expression of data on adsorption in many different types of systems. The mathematical relationship is given by:

$$x = mkc^n$$

where x is the amount of zinc uptake, c is the concentration of zinc in solution, m is the mass of the adsorbent, and k and n are constants for a particular system at a constant temperature. The units used in this study are micrograms for x and micrograms per liter for c. The constant k is relative and will depend upon the units used and, as will be shown later, upon the chemical composition of the water. In this study k is expressed as $l^n/mg.\mu g^{n-1}$. The constant n, however, is independent of the units used and appears to

be a function of the material employed. In the case of the Whitmore Lake sediments m is taken as milligrams, oven dry weight, while for the Golenkinia cells m is also taken as milligrams on the assumption that one cubic millimeter of the cell volume, as calculated from microscopic measurements and cell counts, is equivalent to one milligram wet weight. In the other experiments m was held constant but not determined and represents the mass of material contained in one liter of the suspension. It is thus convenient to work with the value mk which is expressed as $1^{n-1}/\mu g^{n-1}$. This value can be applied directly to the Freundlich equation to predict zinc uptake when the zinc concentration is specified.

On the assumption that the Freundlich equation best represents the data, the lines in the figures were calculated using the least squares method on the logarithms of the experimental values. The appropriate constants are presented in Table 5. The values for the exponent n range from 0.33 to 0.80 with a median of 0.62. The remaining seven fall between 0.58 and 0.72. The similarity found between the values for different materials suggests that a single equation might be used to describe the distribution of zinc between solid and liquid phases in lakes.

When the individual curves are considered, it is noted that the formalin killed Golenkinia followed the same type of relationship as did the living cells, the exponent n being 0.62 and 0.60 respectively. The calculated value of

mk for the formalin killed Golenkinia ($0.0530\ l^{n-1}/\mu g^{n-1}$) was higher than that for the living cells ($0.0174\ l^{n-1}/\mu g^{n-1}$).

Table 5. Calculated constants for the Freundlich isotherms used to relate zinc uptake to concentration for several natural and artificial systems.

Material	Water	mk ($l^{n-1}/\mu g^{n-1}$)	n
Golenkinia (living)	Artificial	0.0174[a]	0.60
Golenkinia (formalin killed)	Artificial	0.0530[a]	0.62
Detritus (untreated)	Artificial	2.51[b]	0.61
Detritus (formalin treated)	Artificial	0.409[b]	0.58
Whitmore Lake Sediments	Artificial	0.0308[a]	0.80
Pickerel Lake Seston	Natural	3.44[c]	0.33
Little Silver Lake Seston	Natural	0.186[c]	0.71
Bass Lake Seston	Natural	0.723[c]	0.72
Lauff's Bog Seston	Natural	0.0706[c]	0.63

[a] m is equal to 1 mg.

[b] m was not determined.

[c] m represents the mass of seston in one liter of lake water.

On the one hand, errors in cell counts or changes in cell diameters may be responsible for this difference while on

the other hand the formalin may have modified the chemical characteristics of the cells; or the respiratory activities of the living cells may have changed the pH of the solution sufficiently to alter the equilibrium.

In the case of the formalin treated and untreated detritus similar exponents were again found (0.58 and 0.61 respectively) indicating that uptake was not a function of bacterial activity. In this case the quantity of material in suspension was visibly different for the untreated and formalin treated materials, so that no comparison can be made of their respective adsorptive capacities.

The uptake of zinc by lake seston shown in Figures 9 and 10 appears to follow the same type of relationship in spite of differences in pH and total alkalinity as given in Table 8. An exception is found in the results from Pickerel Lake with an exponent of 0.33. This may be due to an unequal distribution of larger detrital particles, although no substantiating evidence can be given in support.

ZINC UPTAKE AS A FUNCTION OF pH

The analysis of the data on the influence of pH on uptake was complicated by the fact that the same amount of zinc was added to each bottle. This meant that if a given change in pH acted to reduce uptake, the concentration of zinc in solution would be correspondingly increased and thus tend to offset the change. In like manner if the extent of uptake were increased by a given pH change, the

concentration in solution would be decreased and tend to offset the change.. In order to avoid this difficulty, the Freundlich equation was transformed by dividing both sides by c^n to give:

$$x/c^n = mk$$

Thus the calculated value of mk, as obtained by dividing the uptake by the concentration raised to the appropriate power, provides an estimate of uptake independent of the concentration in solution. Actually, in any given experiment, the variation in c was small, so that errors in the determination of the exponent n would have little effect.

Figures 11 through 13 summarize the results of experiments with live Golenkinia, untreated detritus, Whitmore Lake sediments and natural lake seston. It will be noted that uptake increases with rising pH values and that by plotting mk on a log scale against pH on a linear scale an apparent linear relationship is found for pH values less than 8. With the data in that range, the straight lines shown in the figures were calculated by least squares. The general equation for these lines is:

$$\text{Log } mk = s \cdot pH + \text{Log } K$$

where s and K are constants. Since by definition $pH = -\text{Log } [H^+]$, we can substitute in the above equation to get:

$$\text{Log } mk = -s \cdot \text{Log } [H^+] + \text{Log } K$$

and by taking antilogarithms arrive at:

$$mk = K \cdot [H^+]^{-s}$$

The constant s is a dimensionless exponent which expresses the degree to which changes in the hydrogen ion concentration will affect zinc uptake. The calculated values for this constant are presented in Table 6. They are found to range from 0.38 to 0.66 with a median value of 0.49.

Table 6. Calculated values of the exponent s in the relationship expressed by $mk = K \cdot [H^+]^{-s}$ for several different materials.

Material	s
Golenkinia (living)	0.49
Detritus (untreated)	0.66
Whitmore Lake Sediments	0.41
Little Silver Lake Seston	0.38
Bass Lake Seston	0.43
Lauff's Bog Seston	0.55
Pickerel Lake Seston	0.63

Above a pH of about 8 the points tend to fall above the calculated lines as shown in Figures 13, 14, and 15. This may indicate the adsorption of the $ZnOH^+$ ion in

addition to the Zn^{++} ion. It was previously shown that the proportion of $ZnOH^{+}$ ions starts to become significant in this pH range and the uptake of this ion by clays has been demonstrated in other studies (Elgabaly and Jenny, 1943). It might be noted that zinc differs from strontium in that its uptake tends to fall off at a pH of about 9 (Rhodes, 1957).

THE INFLUENCE OF OTHER CATIONS ON ZINC UPTAKE

A few experiments were conducted on the effects of other cations on zinc uptake using only live Golenkinia. In every case increases in the concentrations of other cations decreased the uptake of zinc. The data were treated quantitatively in the same manner as were those in the pH experiments. The concentrations of the ions under investigation were calculated as the sums of the original concentrations in the artificial water and the amounts added. These were expressed as negative logarithms in a manner analogous to that applied to the hydrogen ion. These data are summarized in Figures 16 and 17, and lines were calculated on the assumption of a linear relationship between mk and pCa, pMg, pNa, and pK. It can be seen that the equations for these lines are analogous to those calculated to express the relationship between mk and the hydrogen ion concentration. Thus the slopes are dimensionless exponents which express the degree to which the respective cations can reduce zinc uptake. These values are

presented in Table 7 and range from 0.34 for calcium to 0.05 for sodium. These are all less than the comparable values found for the hydrogen ion. The general order of $Ca^{++} > Mg^{++} > Na^{+} > K^{+}$ is in agreement with the findings of McCalla (1940b) for bacteria and Rothstein (1955) for yeasts with the exception of Na^{+} and K^{+} whose positions were reversed.

Table 7. The influence of Ca^{++}, Mg^{++}, K^{+}, and Na^{+} on the uptake of zinc by Golenkinia as expressed by the slopes of the lines relating Log mk to pCa, pMg, pK, and pNa.

Ion	Slope (Dimensionless)
Ca^{++}	0.34
Mg^{++}	0.15
K^{+}	0.04
Na^{+}	0.05

ZINC UPTAKE BY NATURAL LAKE SESTON

From the forgoing results it can be seen that zinc uptake is dependent upon the amount and kind of suspended material, the concentration of zinc in solution and the concentrations of other cations. In order to apply the information gained from these experiments to natural lakes it was felt that the value of mk provided the most useful parameter, since it accounts for all of the factors and in a sense represents the capacity for zinc uptake. Values of mk were thus calculated for the surface water samples

of each lake investigated. This was accomplished by dividing the micrograms of zinc adsorbed by the suspended material in one liter of lake water by the concentration of zinc in solution in micrograms per liter raised to the -0.6 power. The values for the 20 lakes sampled between May 1 and 4, 1961 are presented in Table 8 with the determinations of pH and total alkalinity. It might be noted that the water sample from First Sister Lake, which had the maximum value, was visibly turbid due to the runoff from a nearby road and that it was possible to filter only 50 ml before the membrane filter was clogged. With the other samples 100 ml could be easily filtered. If this value is excluded from the series, the mean value is 0.451 while the median is 0.447. It can be seen from Table 9 that the values of mk in Little Silver Lake show an increasing trend from March 20 to June 5 when the sampling was terminated. This could be due to increases in the standing crops of phytoplankton. It is doubtful if the spring bloom was sampled in this series.

ZINC UPTAKE BY ZOOPLANKTON

The uptake of zinc-65 by Daphnia pulex in the presence and absence of particulate materials is illustrated in Figure 18. It can be seen that in the filtered water little zinc was concentrated, while those animals grazing on the algae had taken up measurable amounts. The animals moved from the labeled algal culture to an unlabeled culture

Table 8. Total alkalinity, pH, and capacity for zinc uptake (expressed as a calculated value for mk) for the surface waters of 20 lakes in the vicinity of Ann Arbor, Michigan. (May 1-4, 1961)

Lake	$(1^{n-1}{}^{mk}/_{\mu g^{n-1}})$	Total Alkalinity (ppm $CaCO_3$)	pH
First Sister Lake (T.2S.,R.5E.,S.25)	2.21	97	8.4
Wolf Lake (T.1N.,R.5E.,S.13)	0.979	157	8.5
Reed Lake (T.1N.,R.5E.,S.10)	0.705	123	8.3
Bishop Lake (T.1N.,R.5E.,S.3)	0.612	132	8.3
Long Lake (T.1N.,R.5E.,S.9)	0.600	178	8.5
Appleton Lake (T.1N.,R.5E.,S.3)	0.594	194	8.4
Whitmore Lake (T.1S.,R.6E.,S.5)	0.492	119	8.4
North Lake (T.1S.,R.4E.,S.18)	0.483	110	8.4
Big Portage Lake (T.1S.,R.4E.,S.1)	0.454	184	8.4
Little Portage Lake (T.1S.,R.4E.,S.2)	0.448	184	8.3
Zukey Lake (T.1N.,R.5E.,S.22)	0.447	178	8.4
Winans Lake (T.1N.,R.5E.,S.13)	0.410	146	8.5
Bass Lake (T.1N.,R.5E.,S.21)	0.408	172	8.4
Buck Lake (T.1N.,R5E.,S.23)	0.381	101	8.3
Little Appleton Lake (T.1N.,R.5E.,S.3)	0.372	198	8.4

Table 8. Continued

Lake	$(l^{n-1}/\mu g^{mk_{n-1}})$	Total Alkalinity (ppm $CaCO_3$)	pH
Pond near Pickeral Lk. (T.1S.,R.4E.,S.8)	0.368	187	8.2
Little Silver Lake (T.1N.,R.5E.,S.36)	0.310	101	8.3
Blind Lake (T.1S.,R.5E.,S.12)	0.270	163	8.4
Pickerel Lake (T.1S.,R.4E.,S.8)	0.190	190	8.2
Lauff's Bog (T.1S.,R.5E.,S.28)	0.052	7	5.9

Table 9. Values of mk for Little Silver Lake on several dates in the spring of 1961.

Date	$(l^{n-1}/\mu g^{mk_{n-1}})$
March 20	0.166
April 3	0.172
April 25	0.208
May 2	0.310
May 16	0.449
June 5	0.465

dropped in activity from 20.6 to 4.4 c/m per animal in the 24 hour period, indicating that at least a part of the activity detected in the animals was due to the gut contents.

In the experiment with Daphnia magna in which the

concentration of zinc in the particulate and solution phases was followed, it was found that there was a decrease in the zinc associated with the particulate matter and a corresponding increase in the soluble zinc. This information is presented in Table 10. It was hypothesized that this was due to a reduction in the quantity of particulate materials as a result of the grazing activities of the Daphnia. In order to test the validity of this theory, the density of particulate matter was considered to be directly proportional to the calculated values of mk on the assumption that other conditions were remaining constant. When the logarithms of the mk values are plotted as a function of time, a linear relation is found for the first 30 hours which is in agreement with previous findings on the exponential nature of zooplankton grazing. The rate constant was 0.00714 per hour, so that with a population of 100 adults per liter the calculated rate of removal of particulate materials would be 1.7 ml swept clear per animal per day. This is well within the grazing capacity of zooplankton organisms.

At the end of 48 hours it was found that the total zinc associated with 100 animals was 0.26 µg, and after 46 more hours in a clean solution this had dropped to 0.043 µg. Since the total zinc concentration was 75 µg/l, it can be seen that there was little concentration by the animals themselves and that a large part of the zinc found was apparently associated with the gut contents. This agrees with the findings of Chipman (1958) who worked with marine

copepods.

Table 10. The effect of Daphnia magna on the distribution of zinc between water and suspended Golenkinia cells.

Time Hours	Zinc in particulate matter µg/l	Zinc in Solution µg/l
0[a]	31.8	39.6
4.0	26.8	40.3
22.0	17.2	56.5
26.5	17.1	58.0
28.5	15.8	67.6
47.0	14.8	62.0

[a] Time at which animals were introduced into previously labeled suspension of Golenkinia.

By way of summary, it was found that the two species of zooplankters tested do not significantly concentrate zinc and that their main influence of the zinc cycle will be to alter or reduce the amount of particulate matter through their grazing activities.

ZINC UPTAKE BY SEDIMENTS

The amount of zinc taken up by anaerobic and aerobic sediments from Douglas Lake and Bryant's Bog was calculated as the difference between the amount of zinc originally added and the amount found in the water at the end of eight days. These results are expressed as percentages in

Table 11. Uptake by the aerobic sediments ranged from 77.3 to 84.9% and that for the anaerobic sediments from 15.3 to 27.9%. The differences between the two sediments are negligible in comparison with the differences between oxidized and reduced sediments.

Table 11. Zinc uptake by lake sediments in artificial sediment-water systems.

Sediment Source	Percentage Uptake after 8 Days	
	Aerobic	Anaerobic
Bryant's Bog	84.0	27.9
	79.4	18.6
	77.3	[a]
Douglas Lake	84.8	19.4
	84.9	15.3
	83.6	19.8

a Gas bubble formation caused sediments to float to surface.

The data for each of the 14 Whitmore Lake sediment-water systems were converted to percentages of the amount of zinc initially added to the water. These values were averaged and plotted against the square root of time in Figure 20. This particular time scale was chosen because it conveniently covered the range of values while maintaining the general shape of the curve. The curve is characterized by a rapid initial uptake, with a loss of

60% of the added zinc from the water in the first 24 hours. The rate continually diminishes until at the end of 537 hours only about 4% of the added zinc remained in the water.

The rate of loss of zinc from the water is probably a function of the rates of diffusion and turbulent transfer in the water, the rate of reaction with the sediments, and the rate of penetration into the sediments themselves. The latter factor was complicated by the non-linearity of the adsorption isotherm found to apply to these sediments. The significant finding of this experiment is that as zinc is carried to the bottom waters by sedimentation of organic particles it tends to be transferred to the sediments as these materials are decomposed.

The depths to which zinc will penetrate the Whitmore Lake sediments are indicated in Table 12. In the case of undisturbed sediments the majority of the zinc was recovered within the first 2.5 mm of the dried sediments, which would correspond to roughly 6 mm in the wet material. This is in agreement with the experience of Zicker, Berger, and Hasler (1956), who found that phosphorus was unable to diffuse out of lake muds when covered by as little as one fourth inch of the sediments. When the mayfly nymphs were present the distribution was more irregular as indicated by the large standard deviations, and the mean values tended to approach a uniform distribution. This is undoubtedly due to the fact that the nymphs constructed

burrows in the sediments through which currents of water were drawn. Since the depth of the burrows was limited by the bottom of the container, the maximum depth of mixing cannot be predicted.

Table 12. Relative amounts of zinc penetrating to different depths in Whitmore Lake sediments in the presence and absence of nymphs of the mayfly Ephemera simulans.

Depth[a] mm	Per Cent of Total Zinc	
	Mayflies Present	Mayflies Absent
0.0-2.5	40.2 ± 20.0[b]	91.8 ± 2.53
2.5-5.0	16.2 ± 7.52	4.0 ± 1.05
5.0-7.5	23.7 ± 17.1	2.2 ± 0.51
7.5-10.0	19.6 ± 11.3	2.2 ± 1.00

[a] Depths represent those in partially dried sediment and should be multiplied by a factor of about 2 in order to represent the in situ depths.

[b] Represents the standard deviation calculated from a sample of 10.

The area of the mud surfaces was 55 cm^2 and, since 53 μg of zinc were added to each beaker, the concentration of zinc was 9636 $\mu g/m^2$. The mean zinc content per animal including gut contents was 0.096 μg. Since there were five animals per beaker or about 900 per square meter, the total zinc content in the animal population was 86 $\mu g/m^2$ or 0.9% of the total. It can thus be inferred that these animals function mainly to mix the zinc in the sediments, and that their ability to concentrate the metal is not significant.

DISCUSSION

THE NATURE OF ZINC UPTAKE

It was previously indicated that two distinct types of mechanisms may be operating in the uptake of zinc by particulate materials in lakes, namely ion exchange or adsorption reactions and biological utilization through the synthesis of zinc-containing enzymes. From these data it would appear that the former reaction is of greater importance, since the killed cells of Golenkinia behaved in a manner similar to living cells with respect to the kinetics of uptake and in their response to increases in the zinc concentration of the solution. That living cells take up zinc as a direct response to the concentration in solution would indicate that this is a "luxury" consumption above their immediate metabolic needs. Although the continuously increasing uptake by illuminated cells of Ankistrodesmus might appear to represent a metabolically linked uptake mechanism, it seems possible that this is merely a secondary reaction brought about by a rising pH in response to the photosynthetic withdrawal of CO_2. The correlations found between zinc uptake and oxygen production by marine benthic algae (Bachmann and Odum, 1960) are probably due to the same cause.

Indirect evidence for an adsorptive type reaction may

be derived from the Elovich equation which was found to be in agreement with the empirical uptake curve found. Its application to a wide range of chemisorption data has been demonstrated by Taylor and Thorn (1952) who put forth the following theoretical interpretation. In differential form the equation may be expressed as follows:

$$dx/dt = ae^{-bx}$$

where x represents the amount of material adsorbed and a and b are constants. The fact that the equation applies during a period prior to equilibrium in which the concentration in solution may undergo large changes, suggests that of the two reactants, the ions in solution and the exchange sites, it is the mass action of the latter which determines the instantaneous rate. The mass action of the ions in solution determines only the initial rate given by a. It follows from this that the reaction is limited by the availability of sites until it nears completion and that the sites are eliminated in an exponential manner.

An alternate interpretation is given by Porter and Tompkins (1953) who assume that there are several different types of sites with different energies of adsorption, and that these sites follow a continuous distribution function with respect to their energies. The limiting step in the reaction is considered to involve the migration of adsorbed atoms from sites with low energy to those with higher energies.

The Freundlich equation, which was found to represent

best the equilibrium uptake, was likewise first derived as an empirical expression for various adsorption reactions. It has found application in limnologically related studies to describe the uptake of Ca^{++}, Mn^{++}, Sr^{++}, Fe^{++}, Cu^{++}, and Zn^{++} by Chlorella (Knauss and Porter, 1954), the uptake of phosphorus and copper by Chesapeake Bay solids (Carrit and Goodgal, 1954), the uptake of phosphorus by lake sediments (Olsen, 1958), and the uptake of zinc by ferric hydroxide (Kolthoff and Overholser, 1939).

The theoretical significance of the Freundlich equation is as yet somewhat uncertain. If uptake occurred on only one type of site and there were no interaction between the adsorbed ions, one would expect the Langmuir equation to apply. This can be expressed as:

$$x/m = \frac{ac}{b + c}$$

where x/m is uptake per unit mass, c is the concentration in solution and a and b are constants. Sips (1948, 1950) has approached the problem by assuming that the former assumption does not hold and has found that the Freundlich isotherm can be approximated by assuming an exponential distribution of sites without any interaction between the adsorbed cations. Since this assumption still lacks convincing proof, the Freundlich isotherm is best considered to be semi-empirical. Thus the Elovich and Freundlich equations do not provide a theoretical basis for explaining the mechanism of zinc uptake, but by analogy with other

types of adsorption reactions they do tend to support the ion exchange type reaction proposed. The concept is further supported by the fact that in each case in which the concentration of other cations was increased the relative uptake of zinc was decreased in a regular manner. This could be due to competition between cations for the available adsorption sites.

In the preceding section the following relations were demonstrated for living Golenkinia cells:

$$k \propto [H^+]^{-0.5}, \quad k \propto [Ca^{++}]^{-0.3}, \quad k \propto [Mg^{++}]^{-0.15}, \quad K \propto [Na^+]^{-0.05},$$
$$\text{and } k \propto [K^+]^{-0.04},$$

where k is the constant in the Freundlich equation. These proportions can be combined and an equals sign introduced by adding a new constant K' so that:

$$k = k' \cdot [H^+]^{-0.5} \cdot [Ca^{++}]^{-0.3} \cdot [Mg^{++}]^{-0.15} \cdot [Na^+]^{-0.05} \cdot [K^+]^{-0.04}$$

Since it was shown that k is equal to 0.0174 when $[H^+]$ is 7.94×10^{-7}M, $[Ca^{++}]$ is 2.39×10^{-3}M, $[Mg^{++}]$ is 6.54×10^{-4}M, $[Na^+]$ is 2.95×10^{-4}M and $[K^+]$ is 6.4×10^{-5}M; the numerical value of k' as calculated from the above equation is 3.11×10^{-9} $l^{n-1.04} M^{1.04}/mg\ \mu g^{n-1}$. From the Freundlich equation:

$$x = mkc^{0.6}$$

we can substitute k' for k to get:

$$x = mk'c^{0.6}[H^+]^{-0.5}\ [Ca^{++}]^{-0.3}[Mg^{++}]^{-0.15}\ [Na^+]^{-0.05}[K^+]^{-0.04}$$

In order to be consistent x and c can be converted into molar units by dividing each by 65×10^3, and a new constant k'' is defined as $k'(65 \times 10^6)^{-0.4}$ thus:

$$\overline{Zn} = mk'' [Zn^{++}]^{0.6}[H^+]^{-0.5}[Ca^{++}]^{-0.3}[Mg^{++}]^{-0.15}[Na^+]^{-0.05}[K^+]^{-0.04}$$

where $\overline{Zn}$ represents the amount of zinc taken up in moles and the symbols in brackets represent the concentrations of the respective ions in solution. If the value of mass is expressed in milligrams and all other concentrations in moles, the constant k'' has the numerical value of 2.33×10^{-12} $K^{-144}/mg.l^{0.44}$. This value is considered to be applicable only to the live cells of Golenkinia used in these experiments, since there is no indication that uptake by different materials is a function of their mass alone. For example, if a surface reaction is involved, the surface to volume ratio would be of decisive importance. On the other hand, the similarity between the values found for the exponent of the zinc and hydrogen ion concentrations when different materials are considered suggest that the exponents are approximations of the constants which would be applicable to a wide range of materials. The exponents for the other cations are based on only a few samples. However, they follow in the expected order and probably represent relative orders of magnitude.

THEORETICAL ZINC DISTRIBUTION IN LAKES

The empirical relations developed in the preceding

sections provide a means for estimating the distribution of zinc between solid and liquid phases in lakes under a wide variety of conditions. The Freundlich isotherm was used to calculate the percentage distribution of zinc as a function of the constant mk. It can be seen in Figure 21 that a family of curves is the result. Each curve approaches 100% adsorption as the value of total zinc approaches zero, so that the absolute value of mk is of little importance below about 1 µg/l. As the total zinc concentration increases to values above approximately 10 µg/l, the percentage uptake becomes largely a function of the value of mk and relatively independent of the total concentration.

Since the value of mk is a function of the mass and type of material in suspension as well as the chemical composition of the water, it is difficult to calculate from the parameters usually measured in limnological studies. In this case, however, it was determined directly so that an estimate can be made of the zinc distribution in the lakes studied. If the total zinc concentration ranged between 10 and 100 µg/l and 0.5 is used as an average value for mk in these lakes, the per cent of the total zinc in the particulate fractions will range from 10 to 18%. If the value of mk is increased by a factor of 10, say during the spring plankton bloom, the per cent in the solid phase would range from 55 to 79%. On the other hand, If the total zinc concentration was below 10 µg/l, the uptake

would be difficult to predict due to the steepness of the curves.

The validity of these curves is suggested by the findings of Chipman et al. (1958) who found with sea water which had a zinc concentration of about 10 µg/l that a non-illuminated culture of Nitzschia cells (43×10^7 cells/l) removed 87% of the carrier-free zinc-65 added.

On the basis of the factors shown to affect the value of mk it can be seen that if the total zinc content is kept constant, the per cent uptake will increase with increasing pH and increasing quantities of suspended materials. Alternately, the per cent uptake will decrease with increasing concentrations of other cations.

THE CYCLE OF ZINC IN LAKES

A hypothetical outline of the freshwater zinc cycle is presented in Figure 22. The main source of supply will involve the tributary waters, although Morita (1955) has found the zinc content of rain and snow at Nagoya, Japan to range from 2.5 to 12 µg/l. Under the pH conditions prevailing in most lakes the soluble zinc will be found in the open waters as the zinc ion. In accordance with the equilibrium principles already established, it is to be expected that a portion of the zinc will be adsorbed by organic and inorganic particles suspended in the water, as well as by the higher aquatic plants and the bottom sediments. A portion of the zinc adsorbed by the phyto-

plankton will be transferred through the food chains by direct feeding, although the amount actually retained by the higher trophic levels is not expected to be large in relation to the total amount of zinc in the lake. This last step has been directly demonstrated in nature, where trace amounts of Zn^{65} introduced into the Columbia River by the Hanford reactor have been followed through both aquatic and terrestrial food chains (Davis, 1958; Perkins, Nielsen, Roesch, and McCall, 1961).

Through the action of sedimentary processes, some of the particulate materials will be carried to the sediments and will take with them their adsorbed zinc. This scavenging process is thought to be instrumental in the removal of rare metals from the oceans (Goldberg, 1953; Krauskopf, 1956) and has been directly demonstrated as a mechanism for the transport of phosphorus to the hypolimnion of Linsley Pond by Hutchinson and Bowen (1950).

In a stratified lake it would be expected that a portion of the zinc would be released in the hypolimnion before it reached the sediments. This could be a result of the decomposition of organic adsorbents or a shift in the equilibrium due to a lowered pH resulting from trophogenic processes. Indeed, Morita (1956) did find increases in the zinc content with depth in stratified lakes and, if one considers copper to be similar to zinc in its chemistry, the hypolimnetic enrichment in this metal found by Riley (1939) in Connecticut lakes can also be considered as support for this hypothesis.

If the lake is highly alkaline, the precipitation of calcium carbonate due to the photosynthetic activities of the phytoplankton will provide another means of transporting zinc to the sediments. In like manner the precipitation of ferric oxide at the end of periods of stagnation will provide an additional source of scavenging particles.

Under oxidizing conditions it would appear that the greater part of the zinc reaching the sediments would not be available for release to the open waters. Uptake and recycling by rooted aquatic plants and benthic organisms would seem to be of minor quantitative importance, and the precipitation of highly insoluble zinc sulfide below the surface oxidized layer would appear to preclude its release to the water. Furthermore, when zinc was added to the water overlying the Whitmore Lake sediments, there was a very strong uptake by the mud surface, a result which is not surprising in view of the proven adsorptive capacity of these sediments when in suspension. That this process of accumulation has been acting in the oceans over geological time is supported by the relatively high contents of zinc in sedimentary rocks (Rankama and Sahama, 1950) and the calculated removal of a large fraction of the zinc added to the oceans through the erosion of the continents (Krauskopf, 1956).

Under reducing conditions there may be some release of the zinc from the sediments. This was indicated by the lower affinity for zinc found when oxidized and re-

duced sediments were compared and is in agreement with the findings of Mortimer (1941-42) on the release of cations by reduced sediments. This is thought to be a consequence of the reduction of ferric ions and the resulting dissolution of ferric oxide which is an important adsorbent in the sediments of lakes. Clearly more work is needed on this phase of the problem in order to assess the quantitative significance of this release.

The actual zinc content in the waters of a lake will thus represent a balance between the rate of supply from the drainage basin, the rate of transport to the sediments and rooted aquatic plants, the rate of release from the plants and reduced sediments and the rate of removal by the outlet. In all probability this equilibrium will be constantly shifting in response to variations in these factors as the seasonal sequences proceed. If we make the reasonable assumption of a net transport into the sediments, the lake will then represent a trap for zinc so that the outflow will be less than the inflow into the system.

It should be pointed out that this description is largely based upon deductions from a limited set of laboratory experiments and as such should be considered only a first approximation of the natural cycle. As further studies are made, other factors will undoubtedly be uncovered which will modify the conclusions reached in this paper. Some specific factors not covered are the importance of the soluble organic chelators shown to be

produced by microorganisms (Fogg and Westlake, 1955) and the inorganic complexes of zinc (Bjerrum, 1941) which might alter the equilibrium relations. A specific example of the latter would be the formation of complexes with ammonia which are known to reduce the adsorption of zinc by ferric hydroxide (Kolthoff and Overholser, 1939) and could be of some importance in the release of zinc from sediments. Finally, field studies are needed both to test the hypotheses put forth in this paper and to provide quantitative information on the rates of cycling in lakes.

SUMMARY

1. Trace amounts of zinc are probably to be found in all lakes which support living organisms. The purpose of this study was to determine quantitatively some of the factors which affect the distribution of zinc between the water and various solid materials in lakes, and to use this information to formulate a hypothetical outline of the freshwater zinc cycle.

2. From published chemical constants it was concluded that dissolved zinc would be present mainly as the zinc ion and that zinc hydroxide would be of minor importance in most lakes. Zinc sulfide was considered to be of potential importance as a factor preventing the release of the zinc ion from reduced muds.

3. The ion exchange reactions of clays, silts, and both living and dead organic materials were pointed out as factors of potential importance in the zinc cycle. The metabolic role of zinc was briefly summarized.

4. Zinc-65 was used as a tracer to measure the uptake of zinc by suspensions of Golenkinia paucispina, organic detritus, lake sediments, and natural lake seston. It was also used to follow zinc uptake by Daphnia pulex and Daphnia magna in relation to the presence of suspended materials. Artificial mud-water systems were used to measure zinc

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uptake by lake sediments and to determine the influence of numphs of the mayfly Ephemera simulans on its penetration into such sediments.

5. All of the suspended materials tested were able to take up zinc regardless of whether they were living or dead. The uptake curves could be approximated by the Elovich equation, which states that the instantaneous rate of uptake is an exponential function of the amount already taken up. The theoretical basis of this equation is discussed.

6. The amount of zinc taken up at equilibrium was related to the amount of zinc in solution by the Freundlich equation: $x = mkc^n$ where x is the amount taken up, c is the concentration in solution, m is the mass of adsorbent, and k and n are constants. The values of n were found to be similar for a wide variety of materials tested.

7. If the amount of zinc in solution remained constant, the zinc uptake was a linear function of the hydrogen ion concentration raised to a negative fractional power. Values of this exponent were calculated for various materials and found to be similar. For live Golenkinia the following empirical equation was proposed to express zinc uptake as a function of the chemical composition of the solution:

$$\overline{Zn} = mk''[Zn^{++}]^{0.6}[H^+]^{-0.5}[Ca^{++}]^{-0.3}[Mg^{++}]^{-0.15}[Na^+]^{-0.05}[K^+]^{-0.04}$$

where $\overline{Zn}$ represents the amount of zinc uptake, m the mass of cells, k'' a constant and the symbols in brackets con-

centrations of the respective ions in solution.

8. Due to the facts that zinc uptake follows the Elovich and Freundlich equations which also apply to various types of adsorption reactions and that increases in the concentrations of other cations reduces zinc uptake, the mechanism involved is thought to be a type of ion exchange.

9. Daphnia pulex and Daphnia magna did not accumulate significant fractions of the zinc in solution and lost much of what was taken up when placed in a fresh medium. By removing organic materials from suspension, they act to increase the percentage of zinc in the liquid phase.

10. Oxidized sediments took up about 95% of the zinc added to the water above them, whereas less was taken up by reduced sediments. About 90% of the zinc taken up by such sediments did not penetrate beyond the first 6 mm from the mud surface. When nymphs of the mayfly Ephemera simulans were present, the zinc was mixed into the sediments and approached a uniform distribution. These nymphs did not accumulate a significant fraction of the added zinc.

11. Using the Freundlich equation, theoretical curves were derived to predict the zinc distribution between liquid and solid phases in lakes as a function of the total zinc content and the mass of the suspended material present. The percentage of the total zinc adsorbed by the suspended materials in the surface waters of 20 lakes sampled between May 1 and 4, 1961, was estimated to lie between 10 and 18%.

12. A theoretical outline of the freshwater zinc cycle was presented which was characterized by exchanges between dissoved zinc and various organic and inorganic suspended materials as well as rooted aquatic plants and bottom sediments. The transfer of zinc to the bottom through the sedimentation of adsorbents and the probability of subsequent release are discussed. A net transfer to the sediments is proposed so that the inflow of zinc into a lake should be greater than the outflow. The formation of ammonia complexes and organic chelates are suggested as possible factors which may alter the scheme presented.

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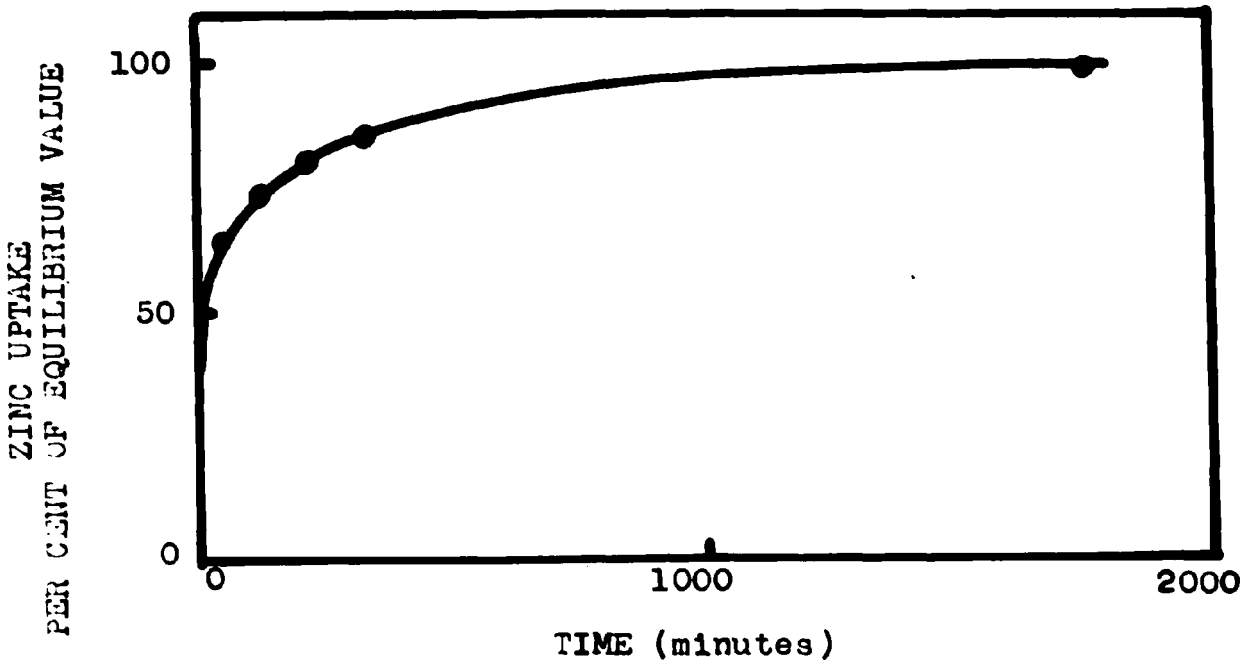


Figure 1. Zinc uptake by formalin killed Golenkinia as a function of time.

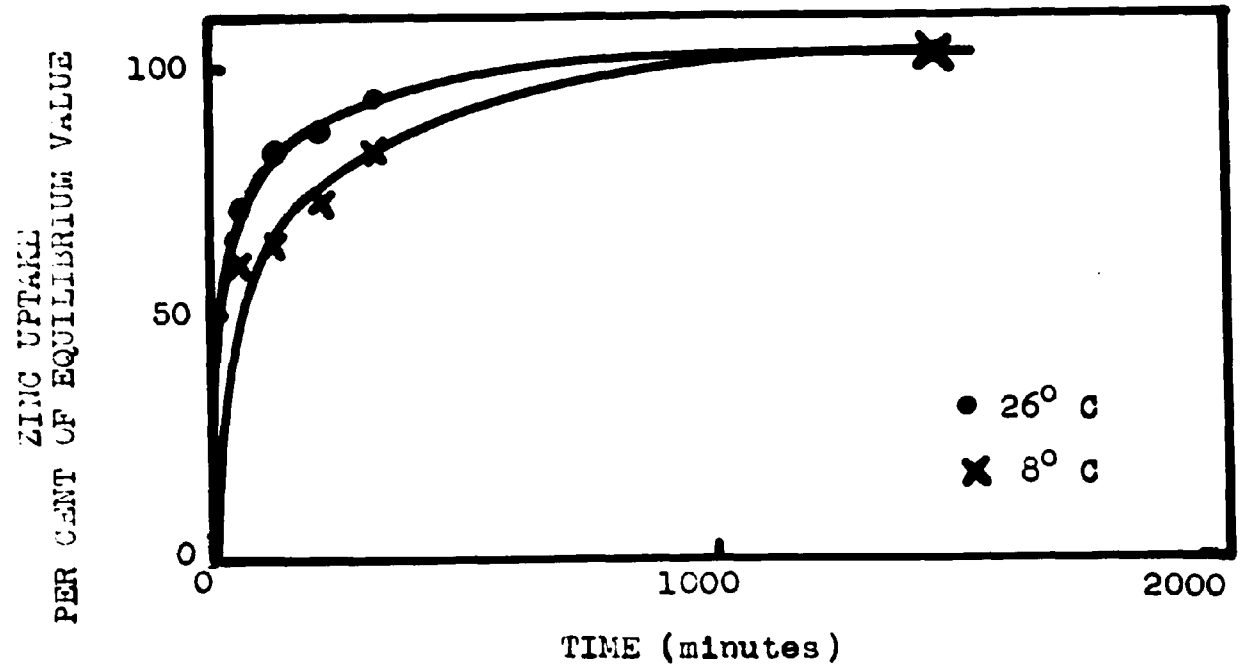


Figure 2. Zinc uptake by living cells of Golenkinia at 8°C. and 26° C. as functions of time.

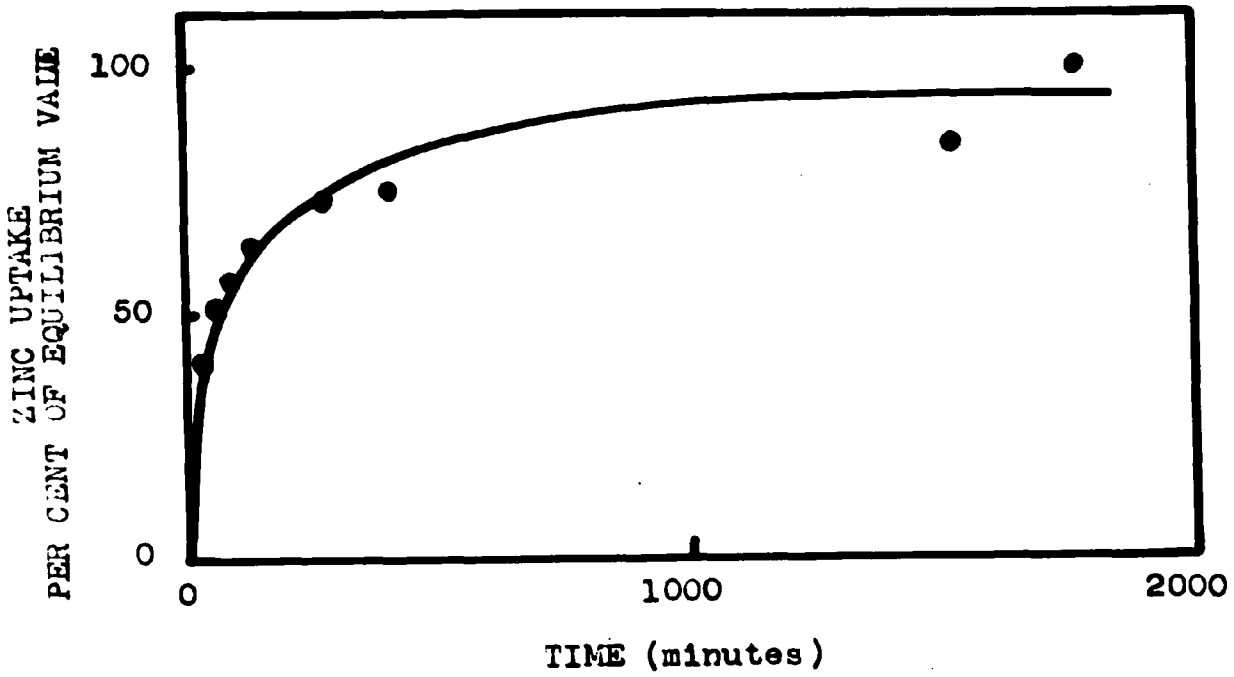


Figure 3. Zinc uptake by suspended Whitmore Lake sediments as a function of time.

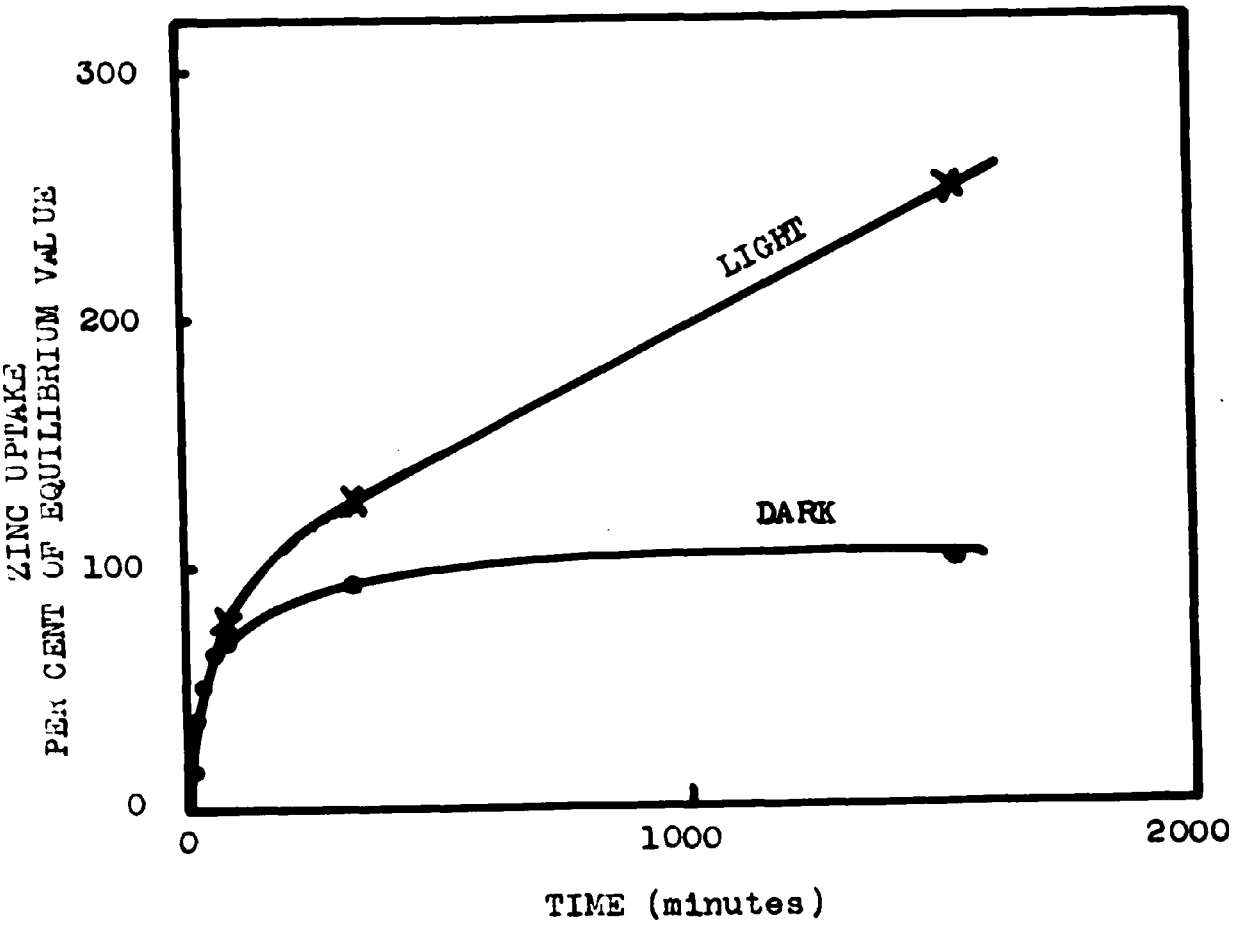


Figure 4. Zinc uptake by Ankistrodesmus as a function of time. At 50 minutes a portion of the culture was placed in the light while the rest remained in the dark.

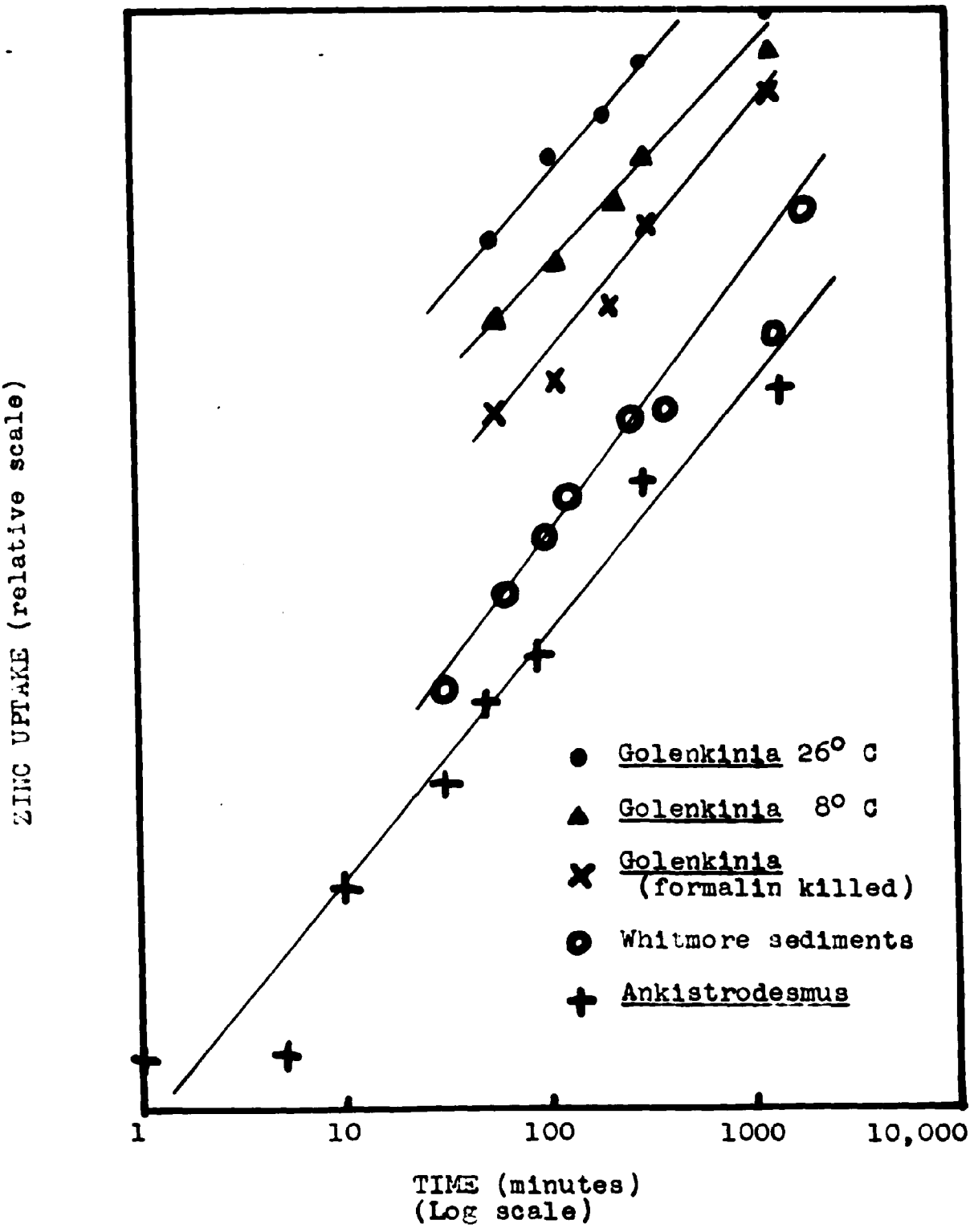


Figure 5. Zinc uptake by Golenkinia, Whitmore Lake sediments and Ankistrodesmus as functions of Log time.

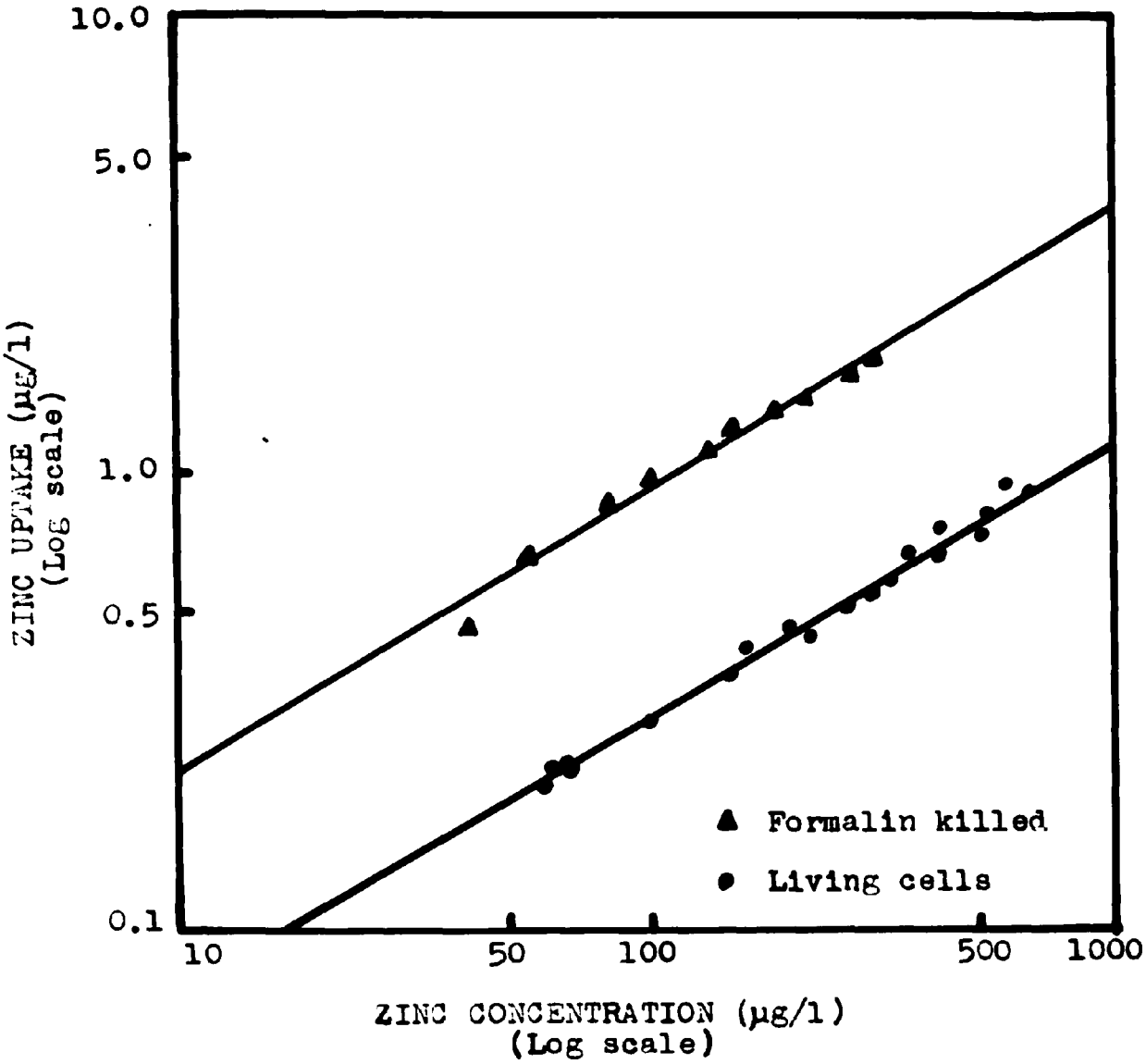


Figure 6. Zinc uptake by living and formalin killed cells of Golenkinia as functions of the concentration of zinc in solution.

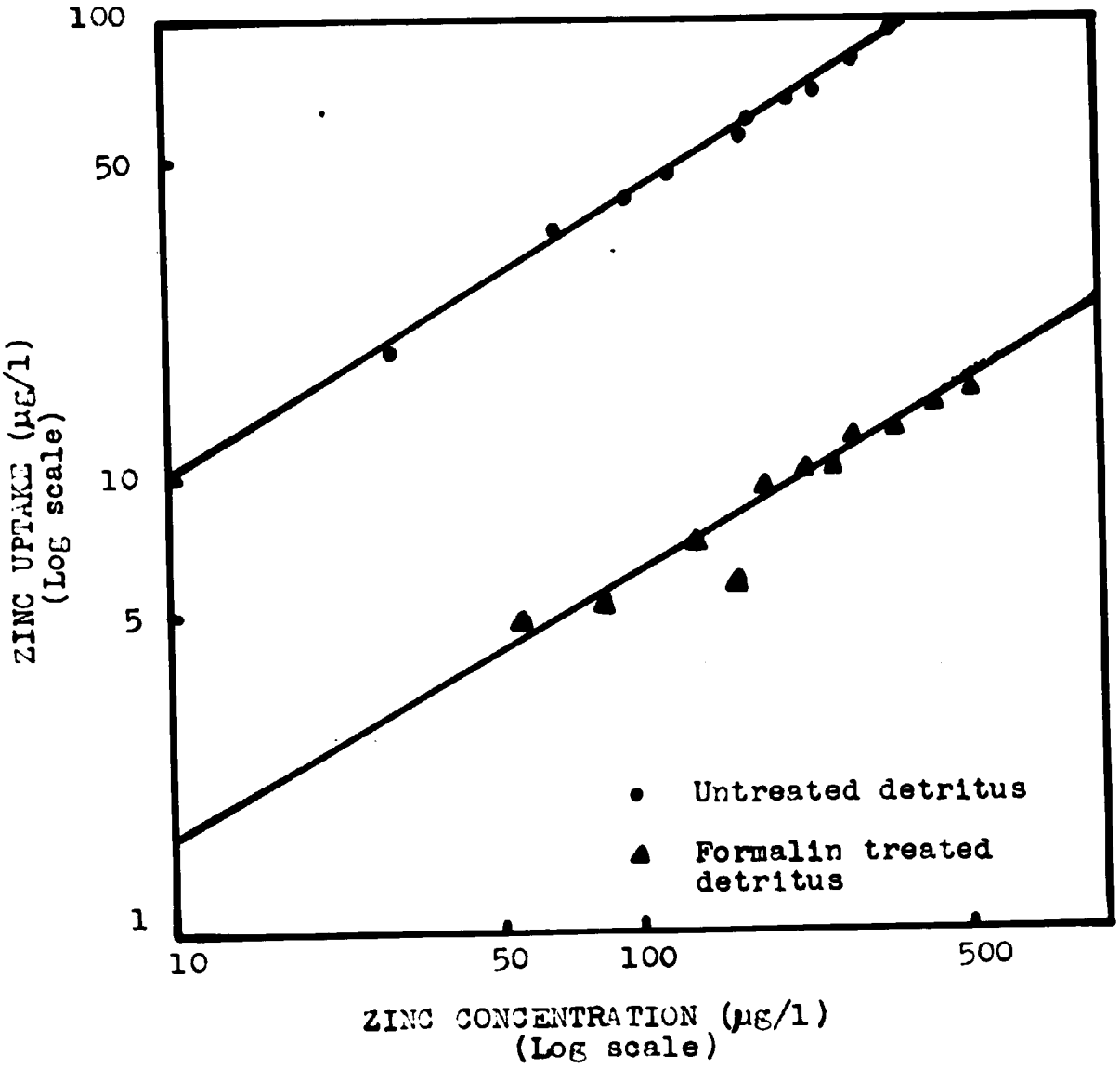


Figure 7. Zinc uptake by untreated and formalin treated detritus as functions of the concentration of zinc in solution.

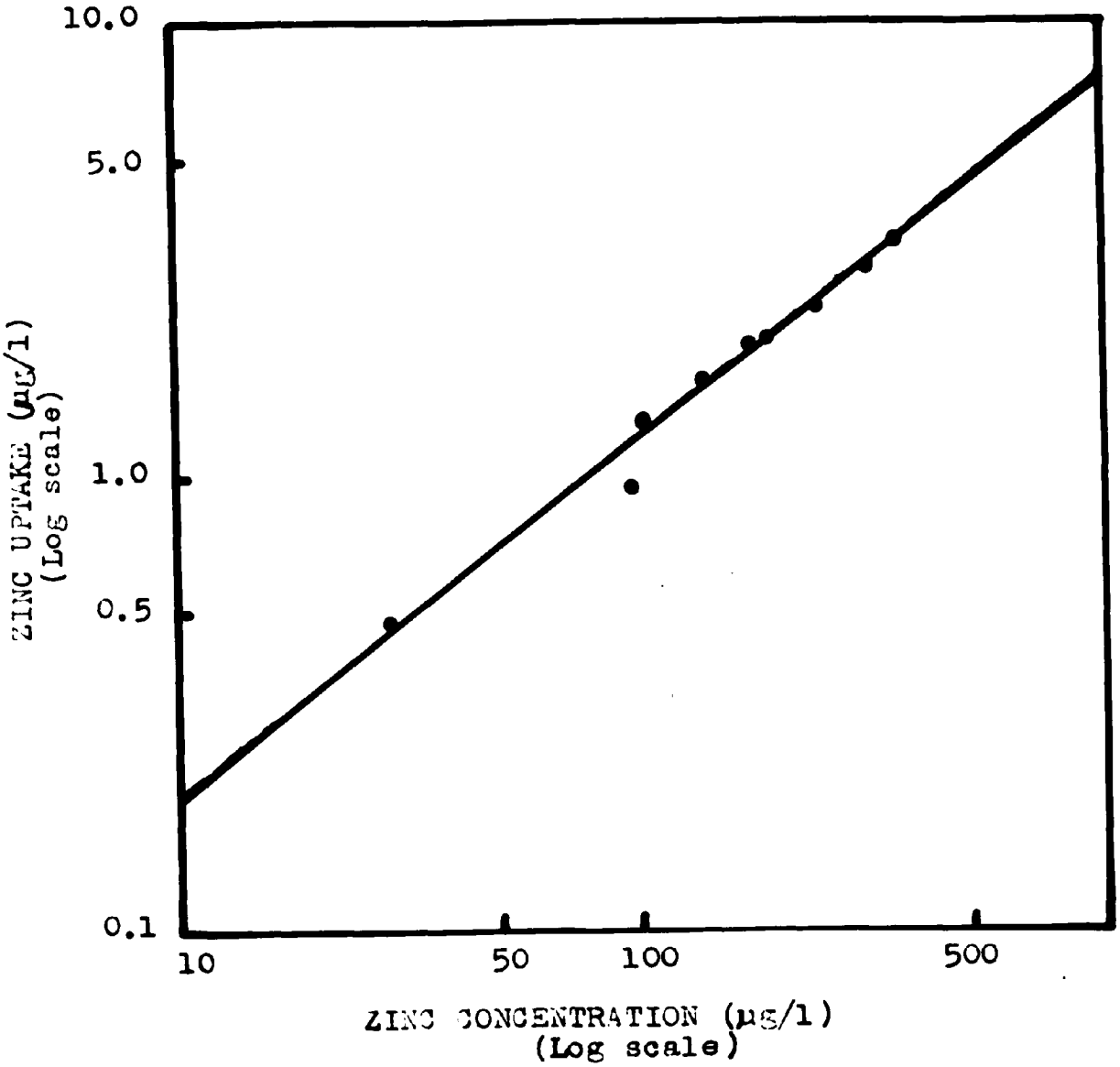


Figure 8. Zinc uptake by Whitmore Lake sediments as a function of the concentration of zinc in solution.

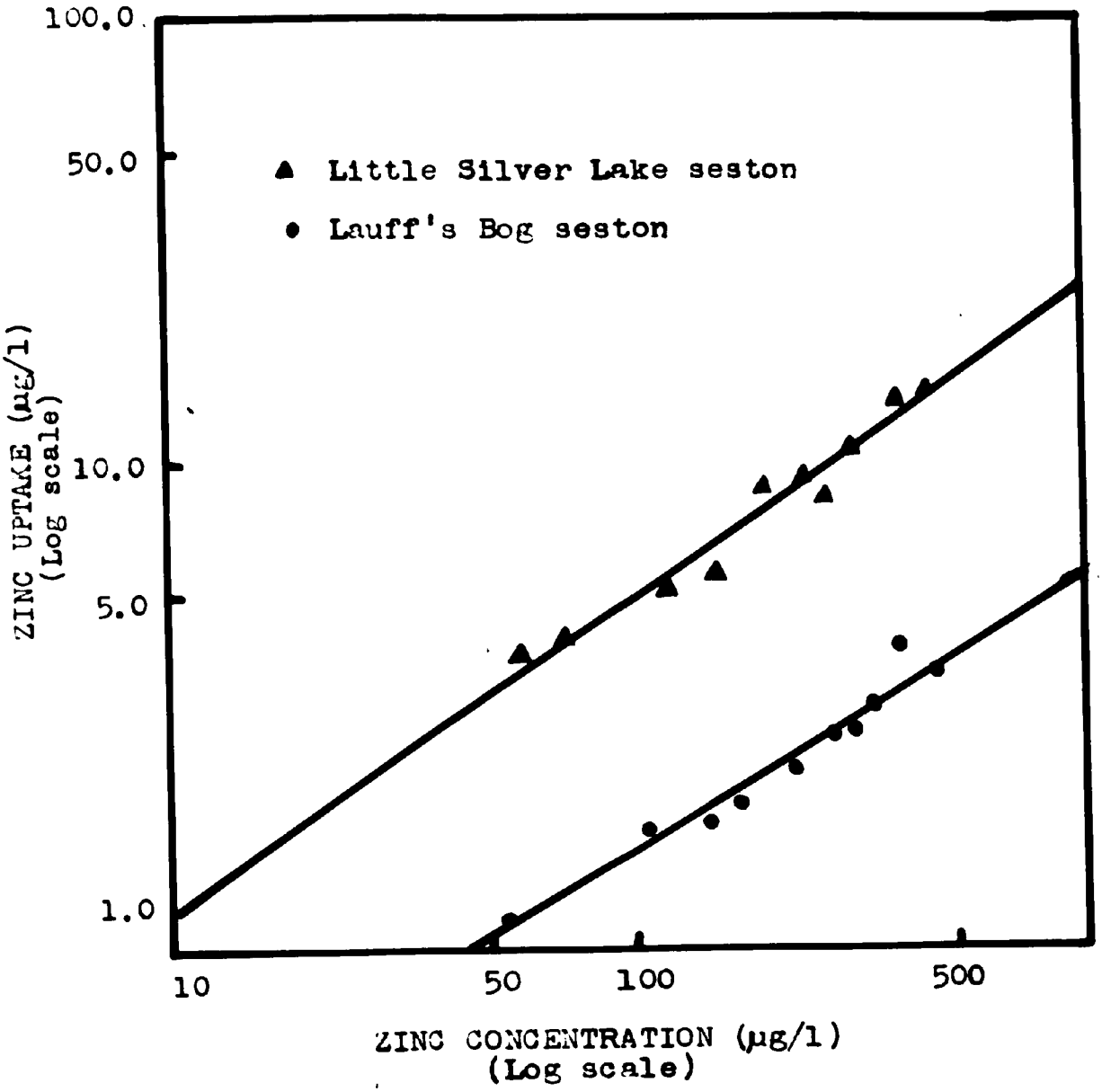


Figure 9. Zinc uptake by the seston of Little Silver Lake and Lauff's Bog as functions of the concentration of zinc in solution.

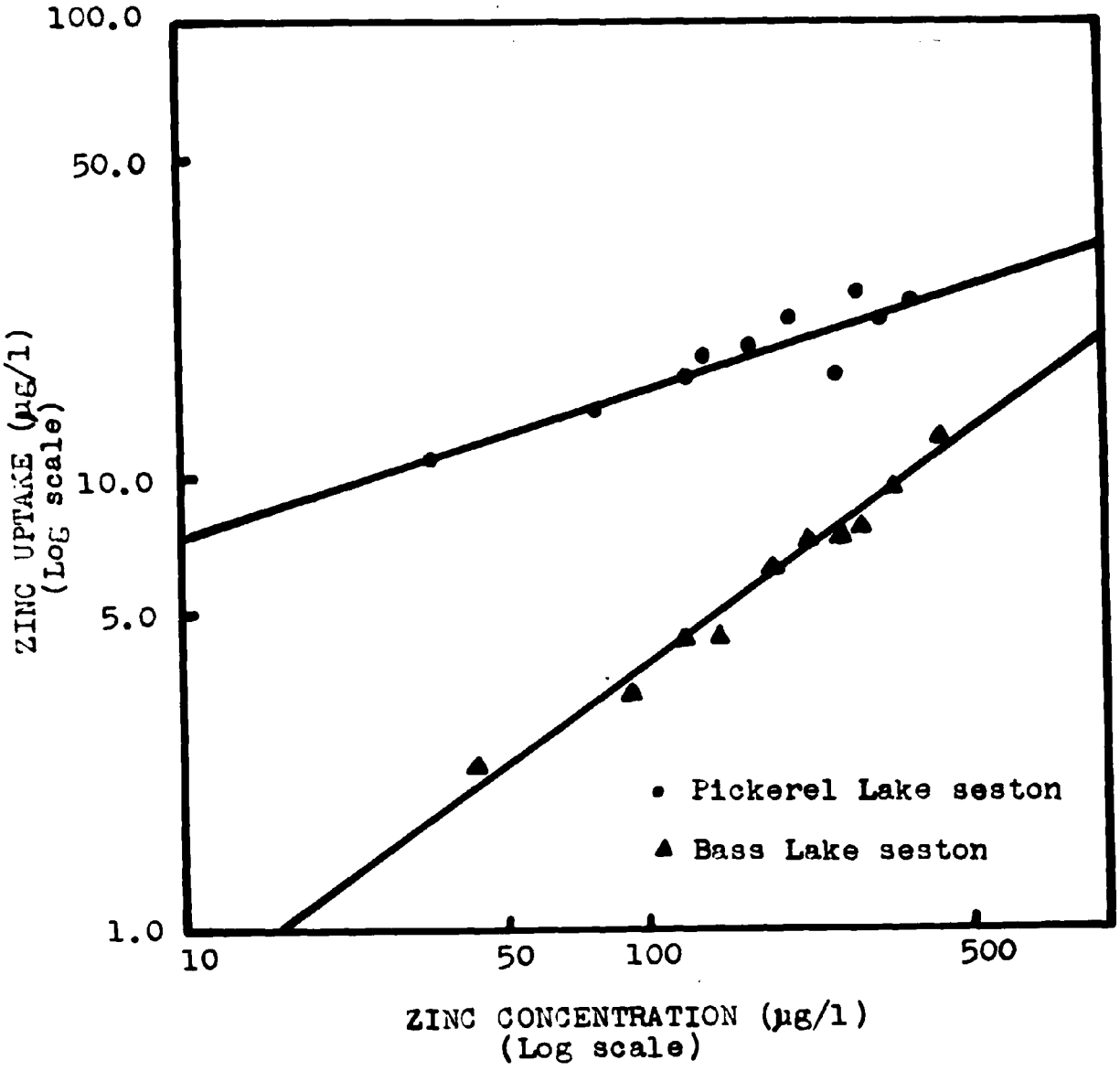


Figure 10. Zinc uptake by the seston of Pickerel Lake and Bass Lake as functions of the concentration of zinc in solution.

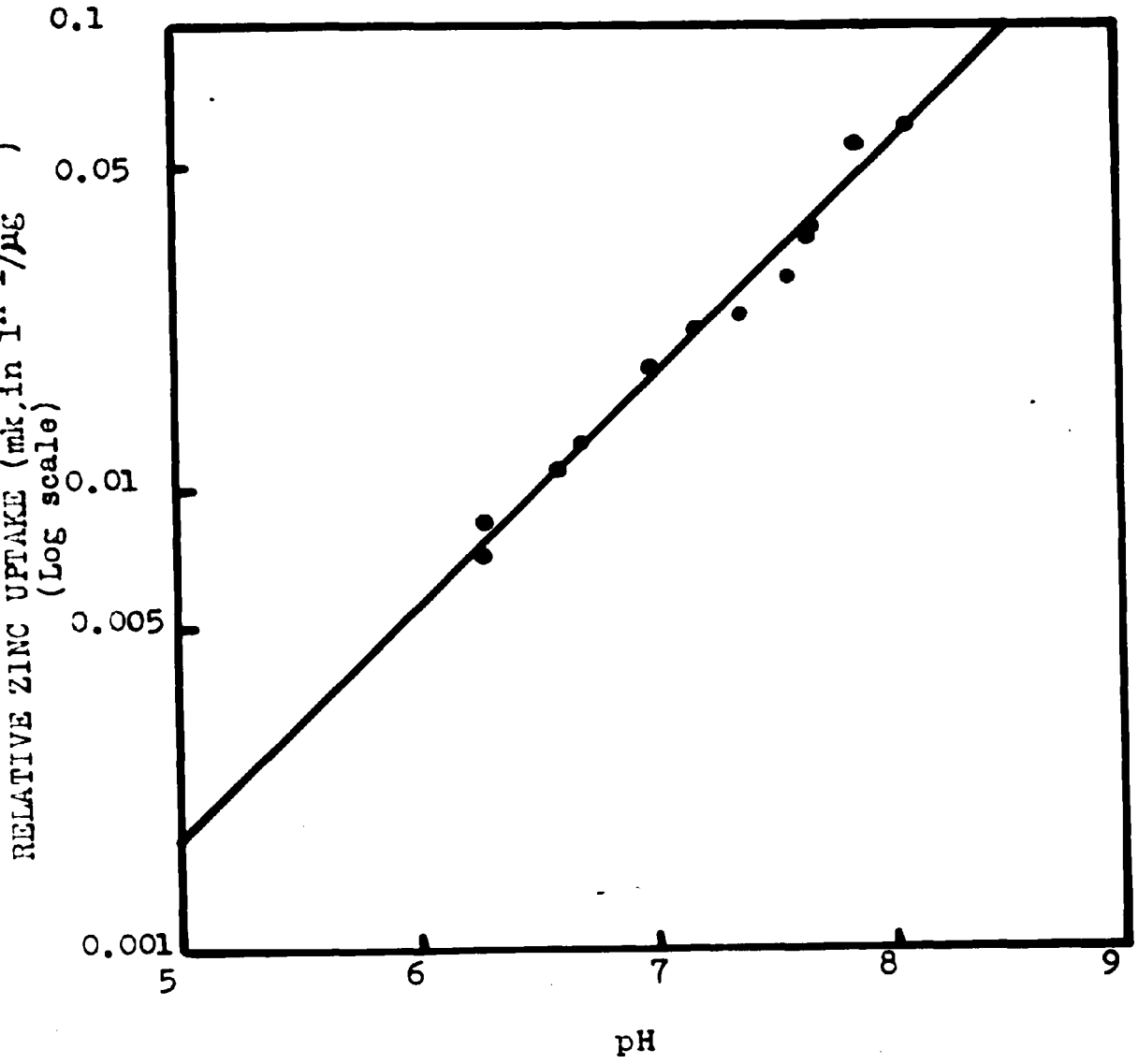


Figure 11. Relative zinc uptake by living cells of Golenkinia as a function of pH.

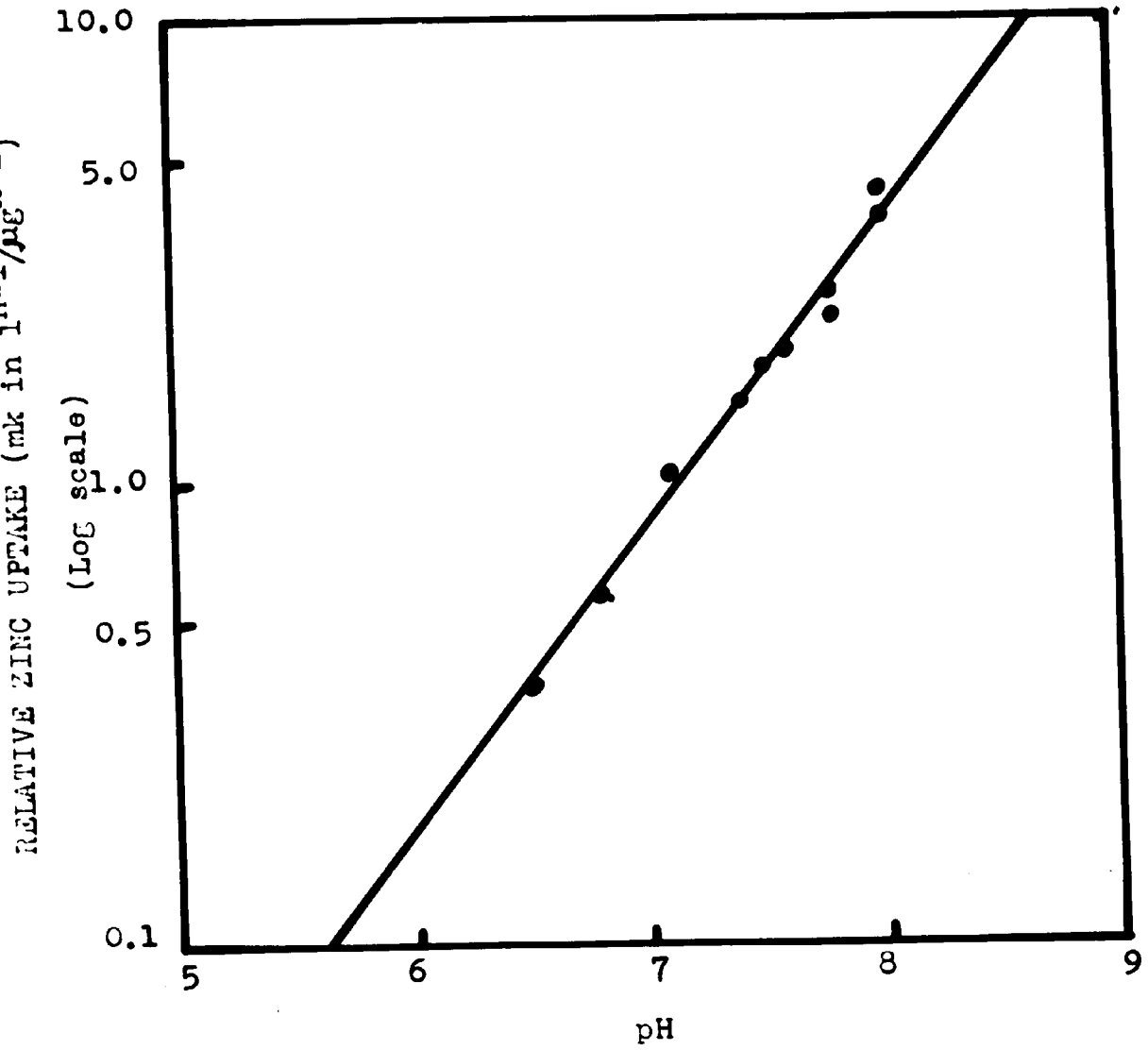


Figure 12. Relative zinc uptake by untreated detritus as a function of pH.

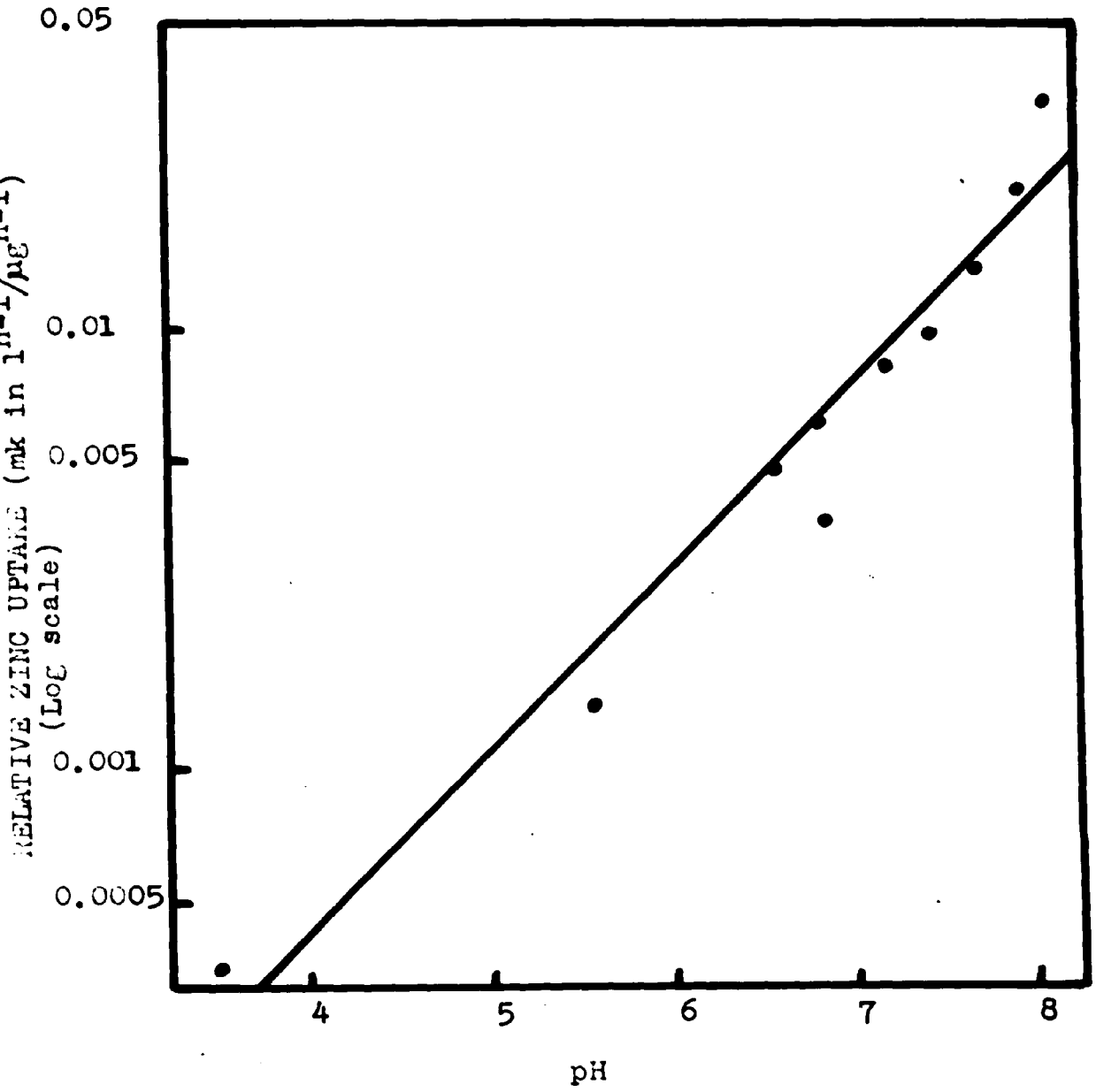


Figure 13. Relative zinc uptake by Whitmore Lake sediments as a function of pH.

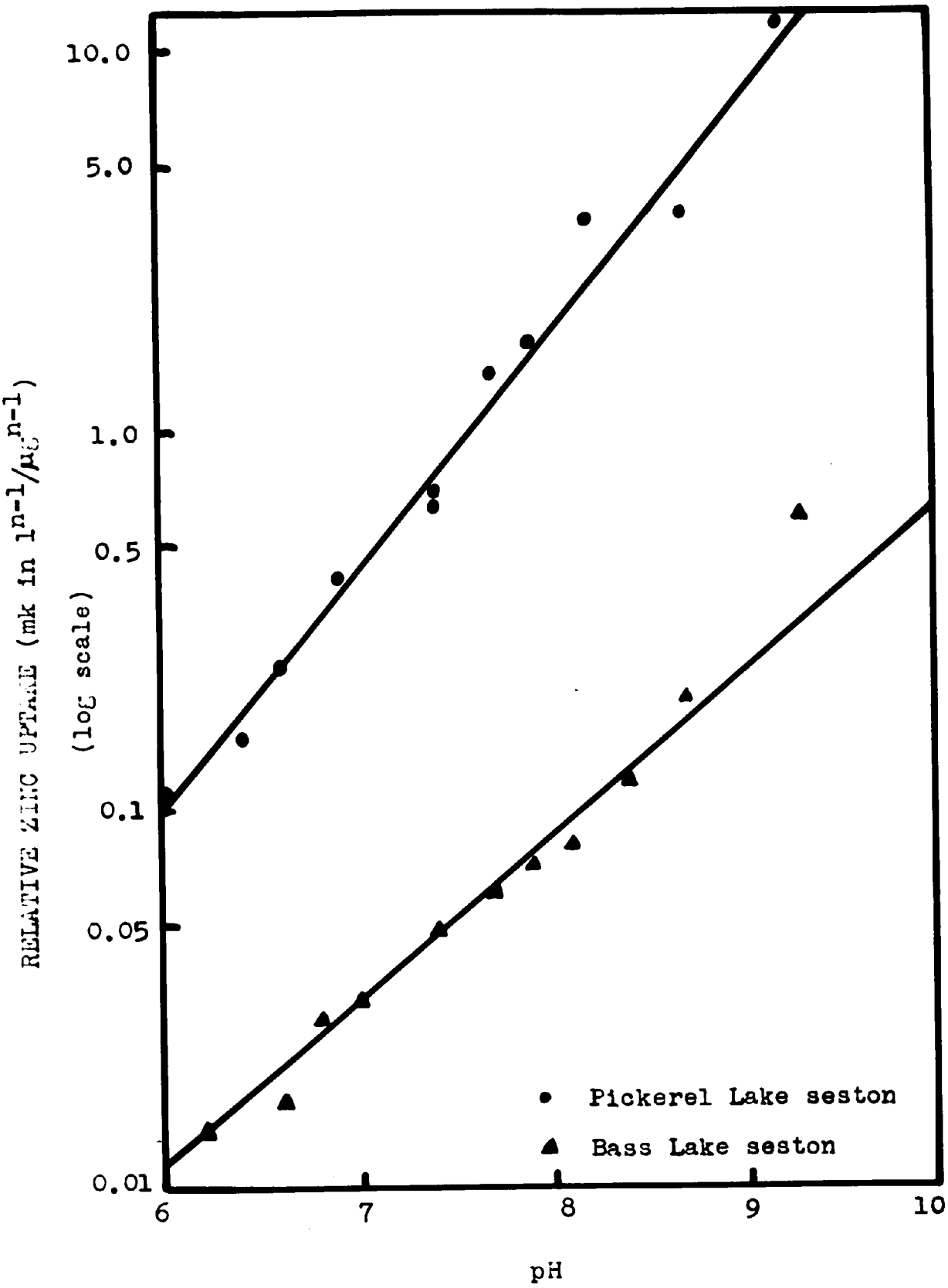


Figure 14. Relative zinc uptake by seston from Pickerel and Bass Lakes as functions of pH.

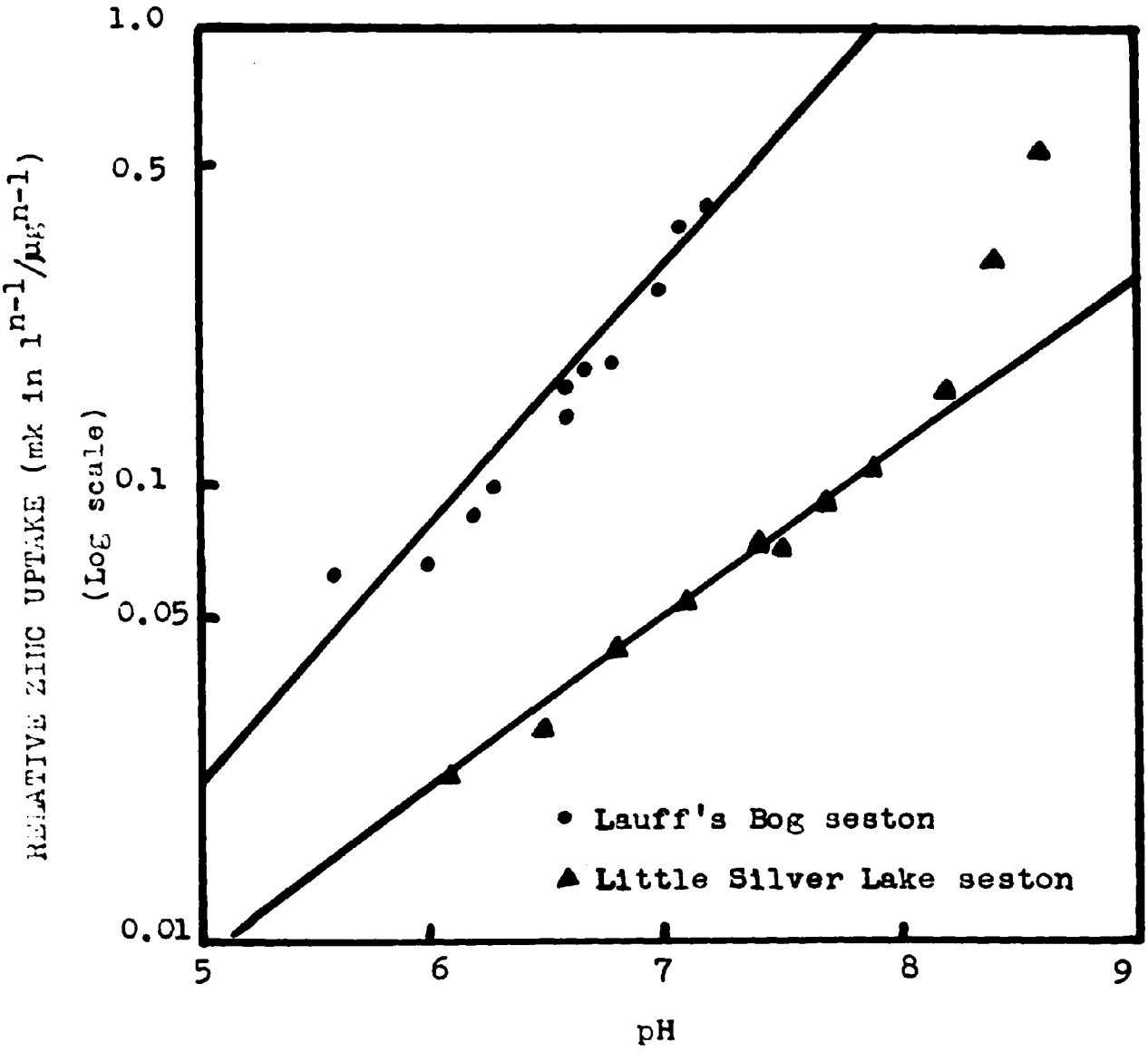


Figure 15. Relative zinc uptake by seston from Lauff's Bog and Little Silver Lake as functions of pH.

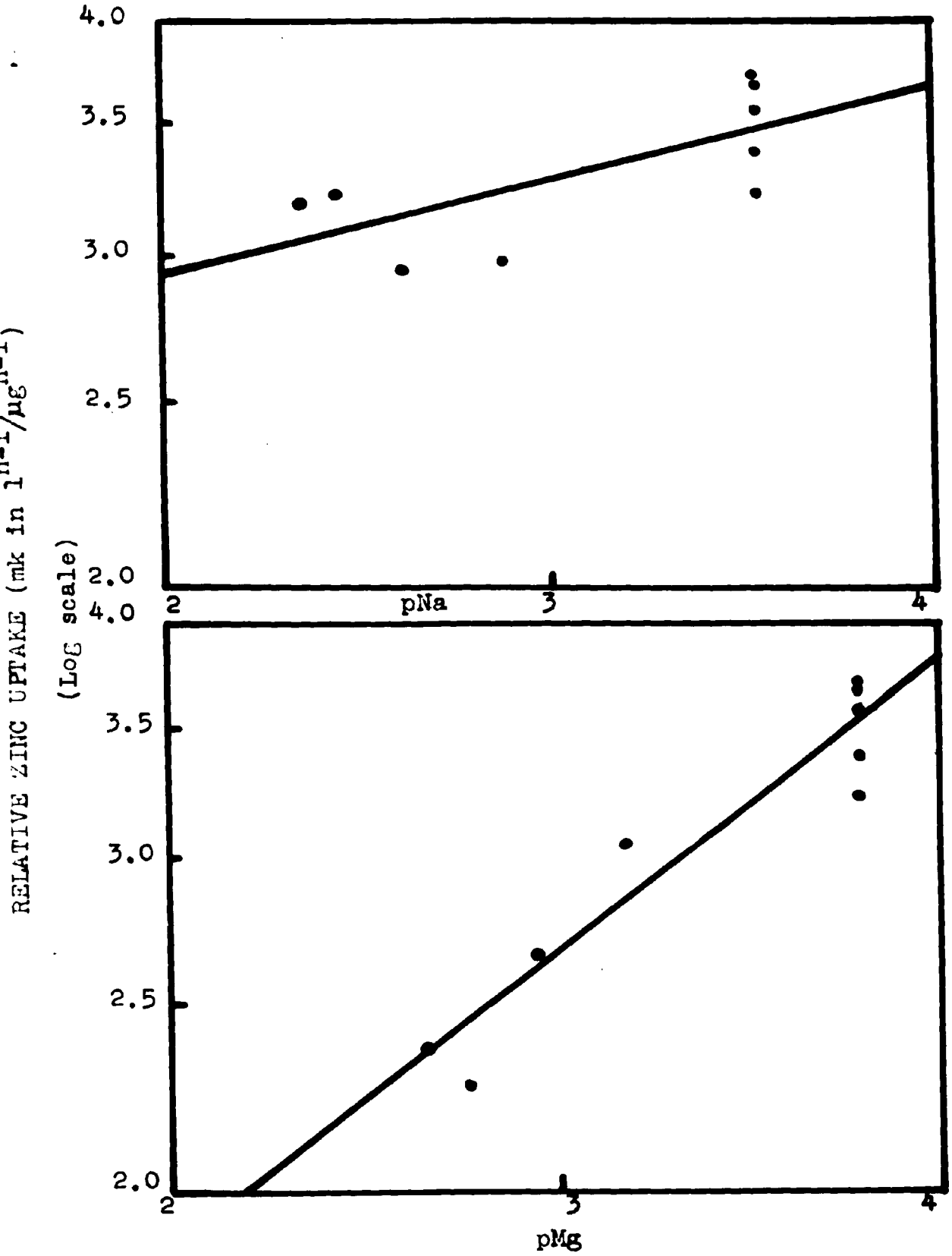


Figure 16. Relative zinc uptake by Golenkinia as a function of pNa and pMg.

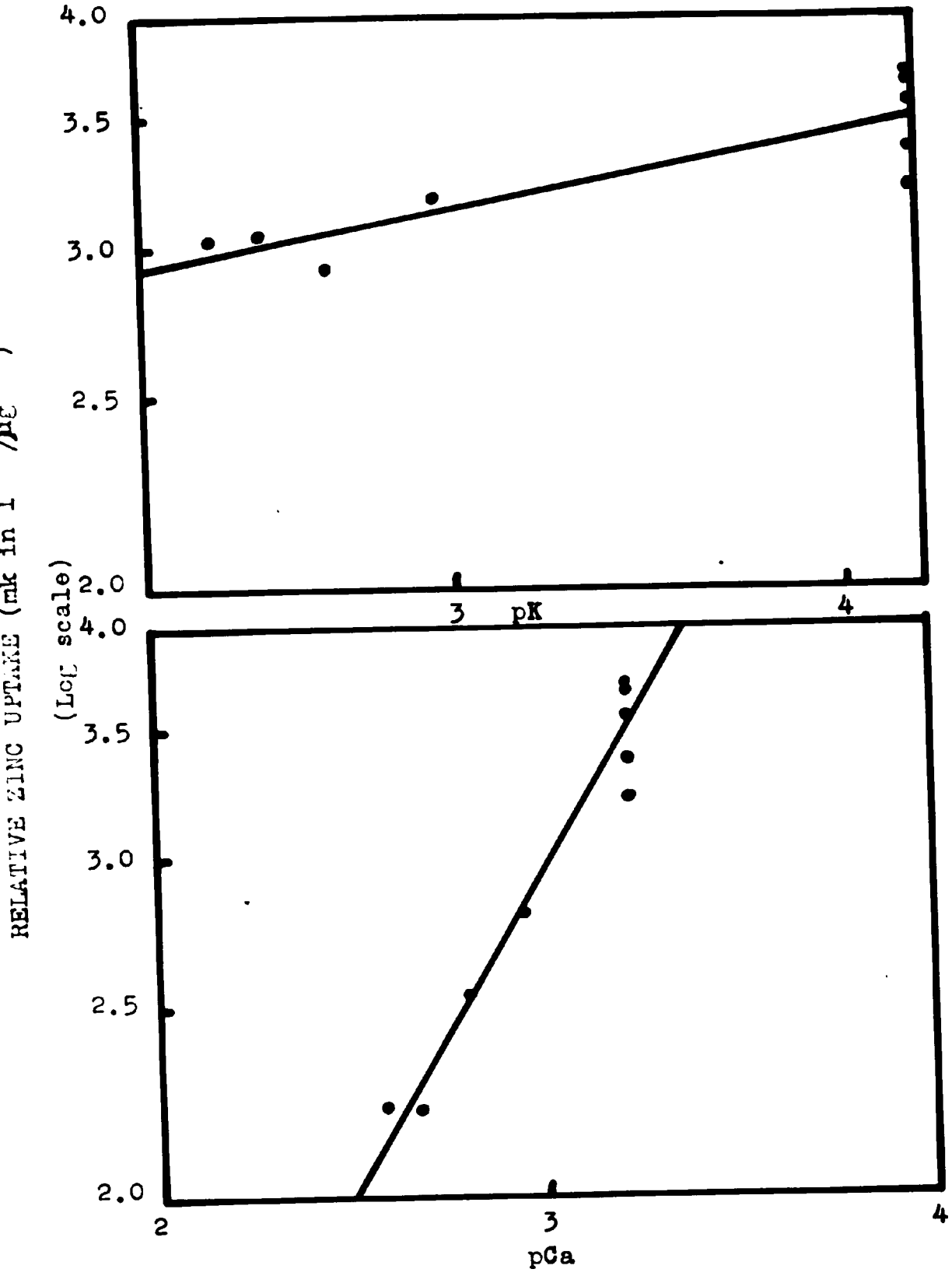


Figure 17. Relative zinc uptake by Golenkinia as a function of pK and pCa.

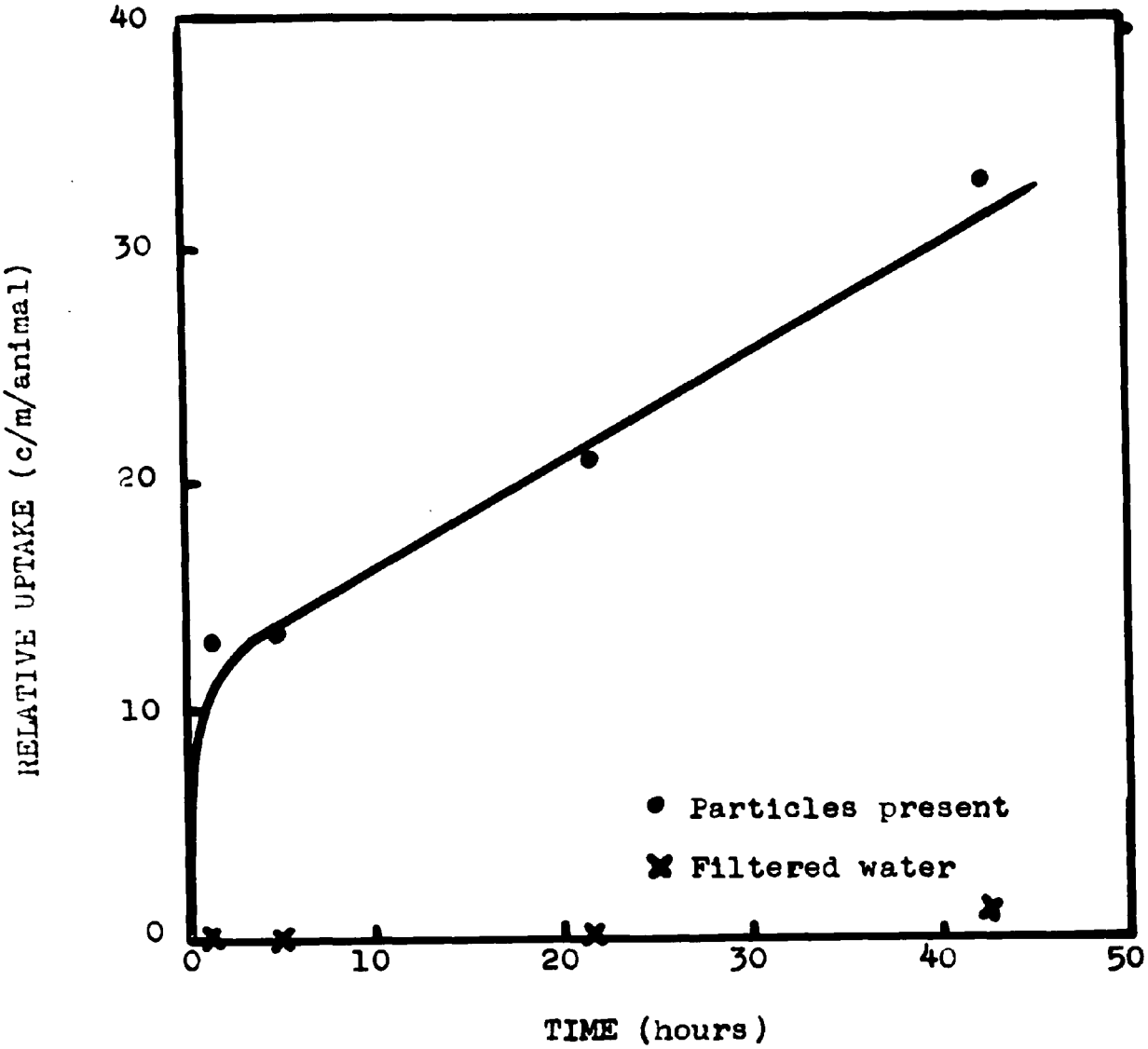


Figure 18. Uptake of Zn^{65} by adult Daphnia pulex in the presence and absence of particulate materials as functions of time.

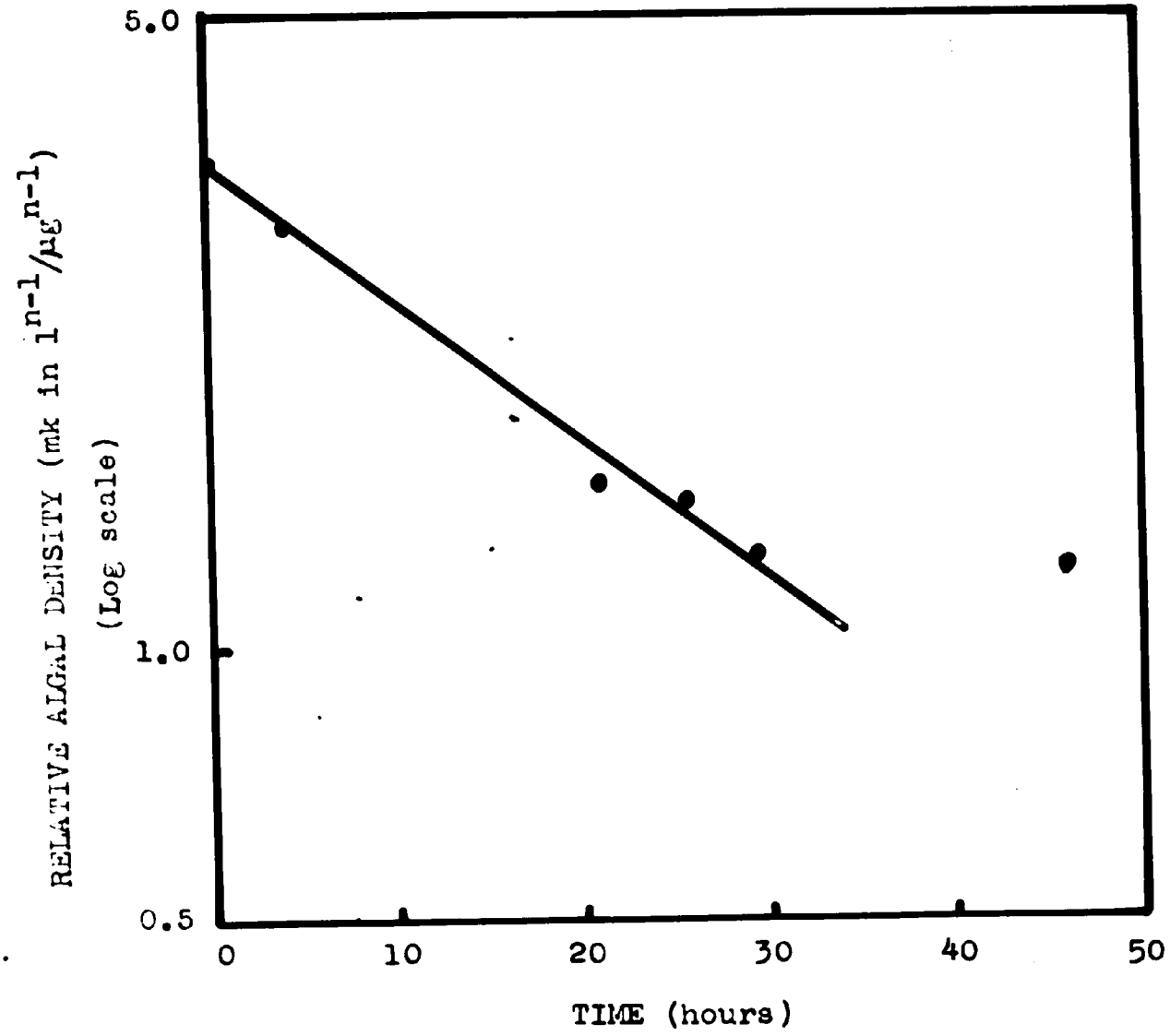


Figure 19. The apparent density of Golenkinia cells as calculated from zinc distribution as a function of time in the presence of Daphnia magna.

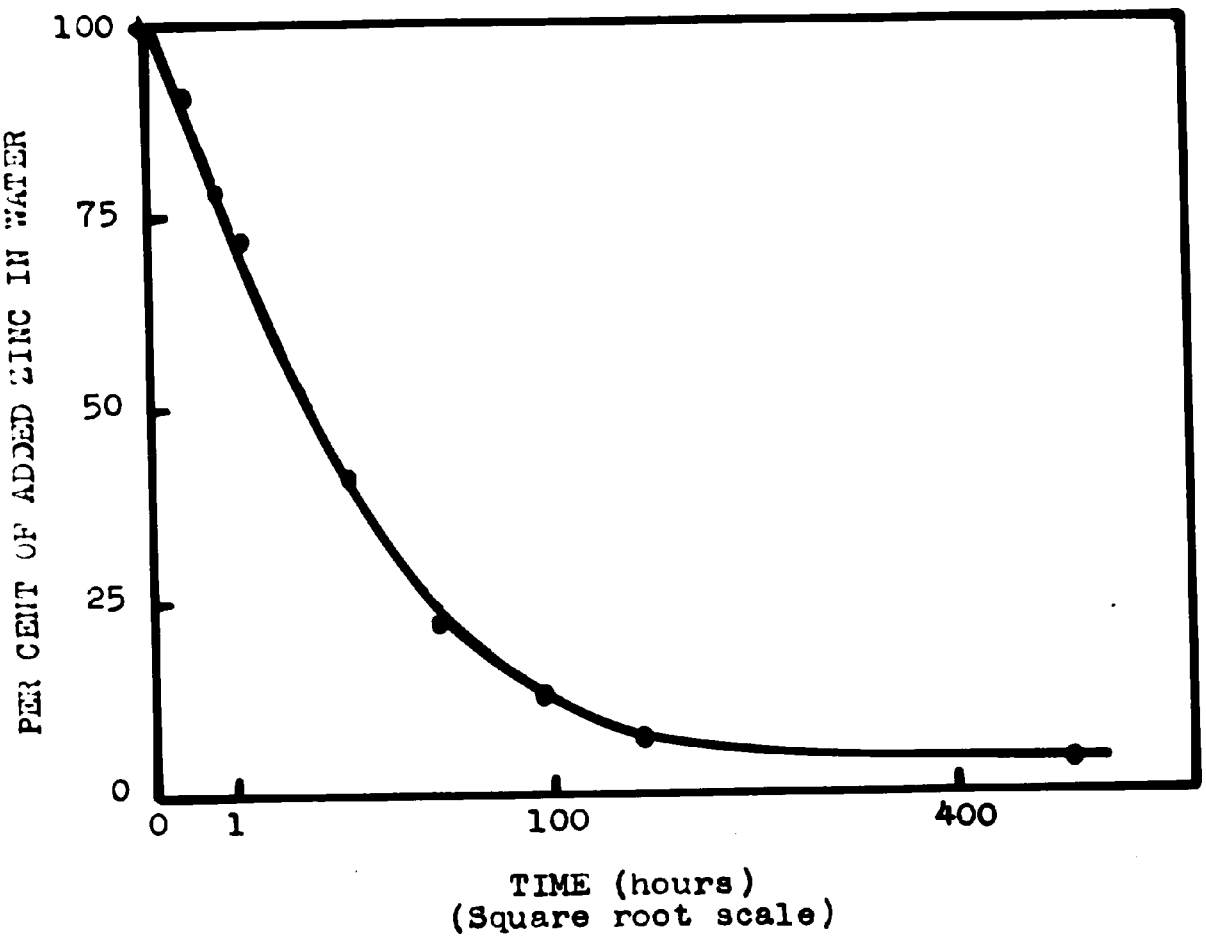


Figure 20. Percentage of added zinc remaining in water overlying Whitmore Lake sediments as a function of the square root of time.

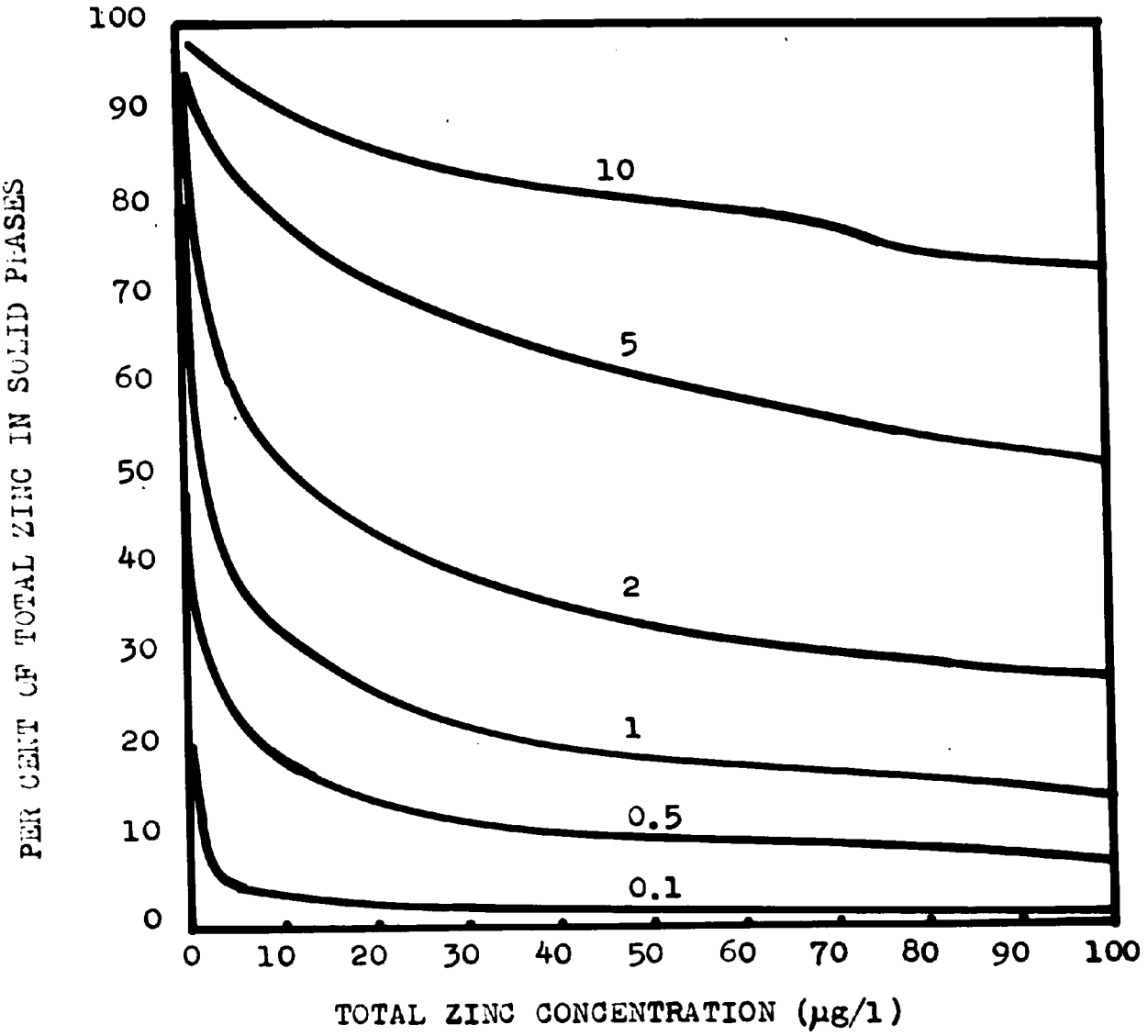


Figure 21. Theoretical curves showing the distribution of zinc between solid and liquid phases as a function of the total zinc concentration and the constant mk. The number above each line represents the value of mk from which the line was calculated.

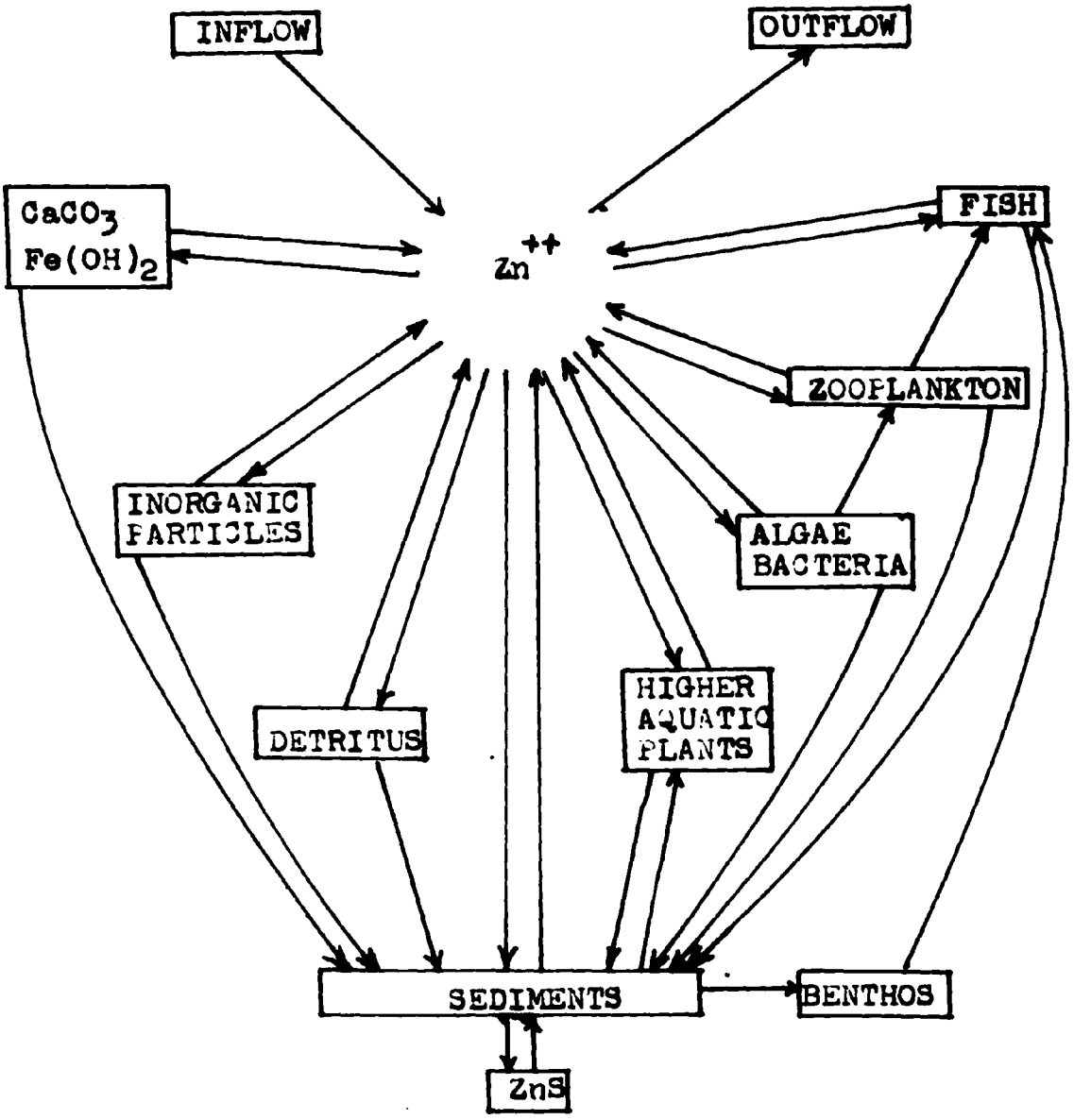


Figure 22. Theoretical outline of the freshwater zinc cycle.