Title

The Potential for Acid-Precipitation Damage to Lakes of the Sierra Nevada, California

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THE POTENTIAL FOR ACID-PRECIPITATION DAMAGE TO LAKES OF THE SIERRA NEVADA, CALIFORNIA

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TECHNICAL COMPLETION REPORT

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ABBREVIATED ABSTRACT

Acid precipitation has been measured in many areas of California, including the Sierra Nevada. This region is characterized by high-elevation, granite-based lakes which may be sensitive to acid inputs. Possible damage to these aquatic systems due to continued acid deposition was investigated during a program of field monitoring and laboratory microcosm experiments. During 1979-1981 Sierra lake water samples were analyzed for pH, alkalinity, and concentrations of major and minor cations. Microcosm systems, established in a controlled laboratory environment using lake water and sediments, were treated with nitric acid and then analyzed for changes in chemical and biological variables.

INTRODUCTION

Acid precipitation in the western United States is now being measured and monitoring networks are being set up to determine the nature and extent of its occurrence. In California two recent studies by McColl (1980) and Morgan and Liljestrand (1980) have documented instances of acidic deposition. It would appear that in the State the nitrate (NO_3^-) component often outweighs the sulfate ($SO_4^=$) contribution in rainfall.

One of the areas of California potentially sensitive to acidic deposition is the Sierra Nevada, located along the eastern boundary. A report on sensitive areas in North America by Galloway and Cowling (1978) identifies the Sierra as a region characterized by poorly-buffered soils and granite-based lakes. The subalpine and alpine lakes in this region share many of the characteristics of lakes adversely affected by acid deposition in other parts of the U.S. and the world (Cowling, 1980).

We chose to study selected subalpine lakes of the western slope of the Sierra to establish baseline water quality which would allow for the identification of chemical and biological changes due to acidic deposition. We then attempted to simulate the ecosystem stress of increased acidic deposition, particularly in the form of snowmelt (Johannessen and Henriksen, 1978), on these systems by performing microcosm experiments in the laboratory. In these experiments we were particularly concerned with recording changes in concentrations of micronutrients (iron, manganese) and trace elements (aluminum, cadmium, copper, lead, zinc) which might be leached from lake sediments with increasing acidification. This phenomenon is particularly important to study in light of findings by Cronan and Schofield (1979) on the importance of aluminum leaching in the Northeast which has led to toxic effects on biota in Adirondack lakes.

METHODS

Between 1979-81 we sampled 35 lakes in the Sierra Nevada, most located in subalpine basins between 1600-2600 m. Two lower elevation reservoirs were included to allow for comparison of water quality parameters. Each lake was sampled once, at three stations in the lake: shore; midlake, at the surface; and midlake, at secchi disc depth. Samples were collected and analyzed for pH (Sargent-Welch model PBX pH meter), alkalinity (by Gran titration), temperature, transparency, major and minor cations (Ca, Mg, Al, Cd, Cu, Pb, Mn, Fe, Zn) (by graphite-furnace atomic-absorption spectrophotometry, Perkin-Elmer) and biological populations (phytoplankton and zooplankton). Trace analysis was performed on filtered (0.45 μm Nucleopore) and unfiltered samples. Phytoplankton samples were collected using a 5-ml pipette and counted with a Wild microscope using Utermohl inverted-microscope techniques. Zooplankton samples were collected using a 64 μm mesh sieve and species populations were estimated from microscope counts.

Three sets of microcosms were set up in a light- and temperature-controlled facility at Lawrence Berkeley Laboratory. Whole water samples and sediments from two Sierra lakes: Tenaya Lake (2480 m) and

Mosquito Lake (2440 m) and one Bay Area reservoir, Briones (70 m), were collected and used to fill 18-liter Nalgene tanks. These microcosms were sampled weekly and the samples analyzed for pH, alkalinity/acidity, cations (Ca, Mg, Al, Cd, Cu, Fe, Pb, Mn, Zn) (total and dissolved) and populations of phytoplankton and zooplankton. The same analytical techniques were used in both field and lab.

RESULTS

Sierra lakes sampled were in the circumneutral pH range (6.0-8.0), with low alkalinities (29.0-200.0 μ eq/l). Table 1 presents data on water quality for some of these subalpine lakes. Calcium and magnesium levels were low, indicative of low-alkalinity systems. The trace element analysis indicated the presence of detectable (> 1.0 μg/l) levels of aluminum, iron and manganese. Figure 1 shows a plot of pH vs. alkalinity for 24 Sierra lakes and the two comparison reservoirs.

Of the three sets of microcosm experiments run, the Tenaya Lake experiment will be discussed here. For additional data from these experiments we refer you to Tonnessen and Harte (1980) and Tonnessen (1982).

During the Tenaya Lake experiment three replicate tanks with sediment and three without sediment were maintained as controls at a system pH of 6.3-6.5 for a 7-week period (see Figure 2). On day 1 sufficient nitric acid was added to the 3 treatments with sediment and 3 treatments without sediment to bring the system pH down to 4.0. Following this "acidification" there was little change (or buffering) in system pH.

Table 1: Water Quality of Ten Lakes of The Sierra Nevada

	ALTITUDE (m)	pH	ALKALINITY µeq/l	Ca mg/l	Mg mg/l	Al µg/l	Fe µg/l	Mn µg/l
Woods Lake	2510	6.5	178.0	1.90	0.55	11.4	16.0	3.4
Tenaya Lake	2480	6.3	29.0	0.30	0.03	21.2	4.6	4.5
Mosquito Lake	2440	6.9	62.0	0.35	0.09	18.2	50.6	4.7
Kirkwood Lake	2340	7.1	104.0	0.76	0.24	5.4	29.5	0
Angora Lake	2270	6.6	41.8	0.20	0.06	30.9	12.9	1.3
Echo Lake	2260	6.7	56.0	0.35	0.09	4.9	2.2	3.4
Huntington Lake	2120	6.6	150.0	0.58	0.12	6.1	7.3	2.7
Haven Lake	2050	6.7	87.0	0.30	0.36	26.4	3.5	1.1
Forebay Lake	2000	6.6	128.0	0.60	0.15	14.8	5.0	10.4
Fuller Lake	1630	6.6	192.0	1.50	0.42	12.7	19.2	12.0

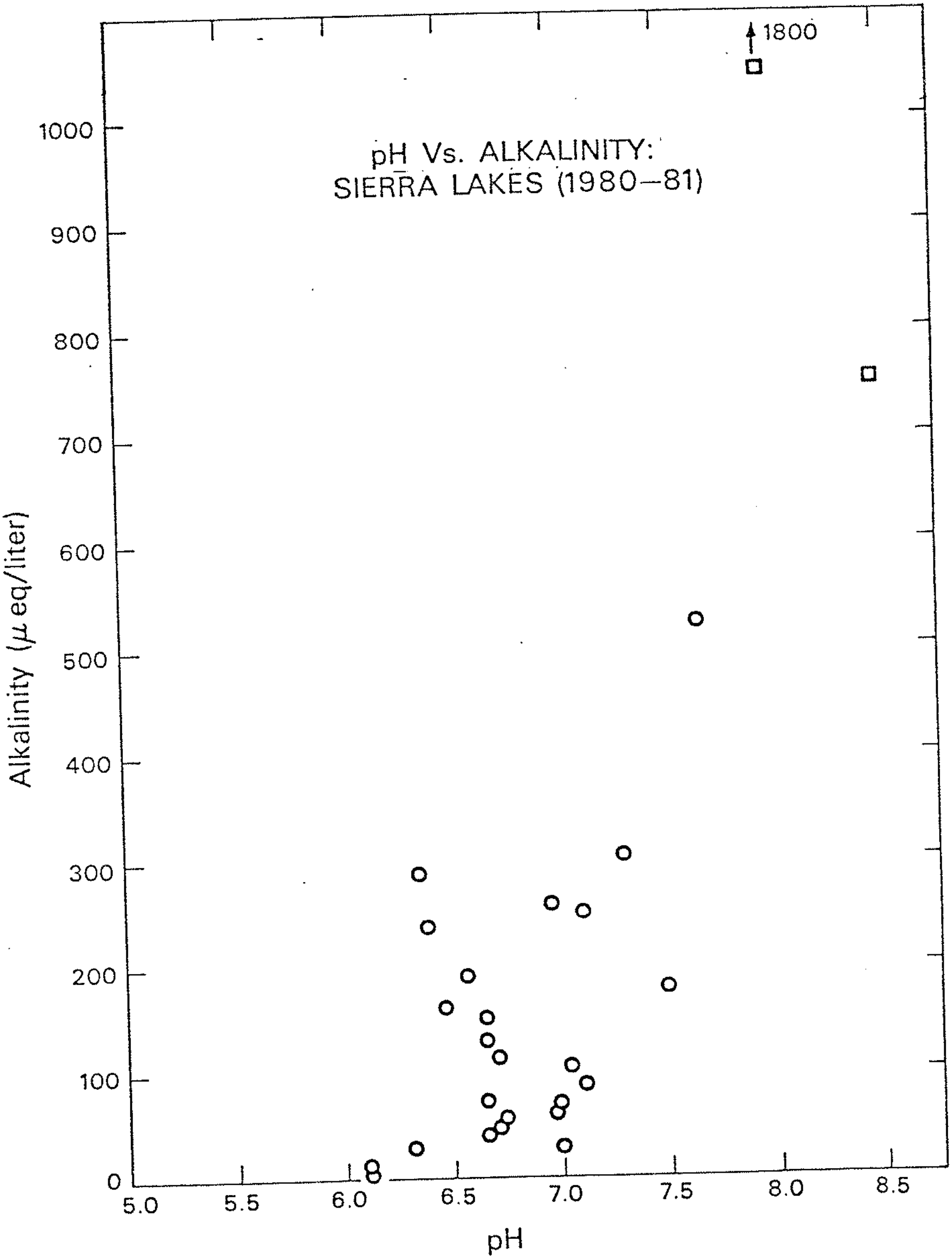

Figure 1

XBL 8111-1618

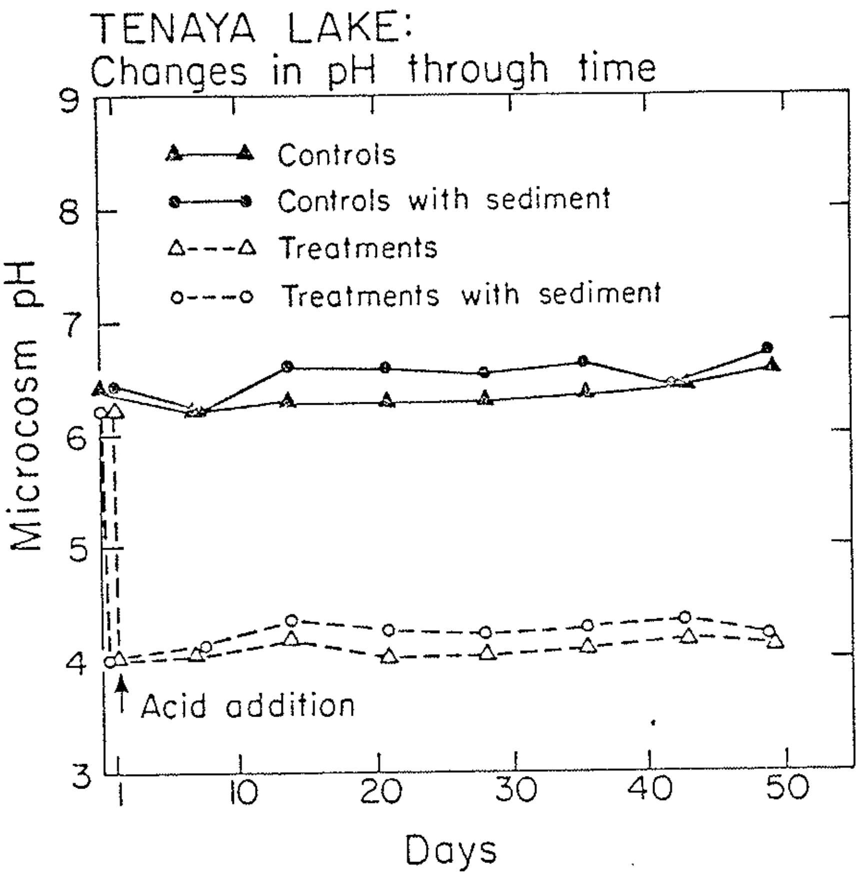

Figure 2

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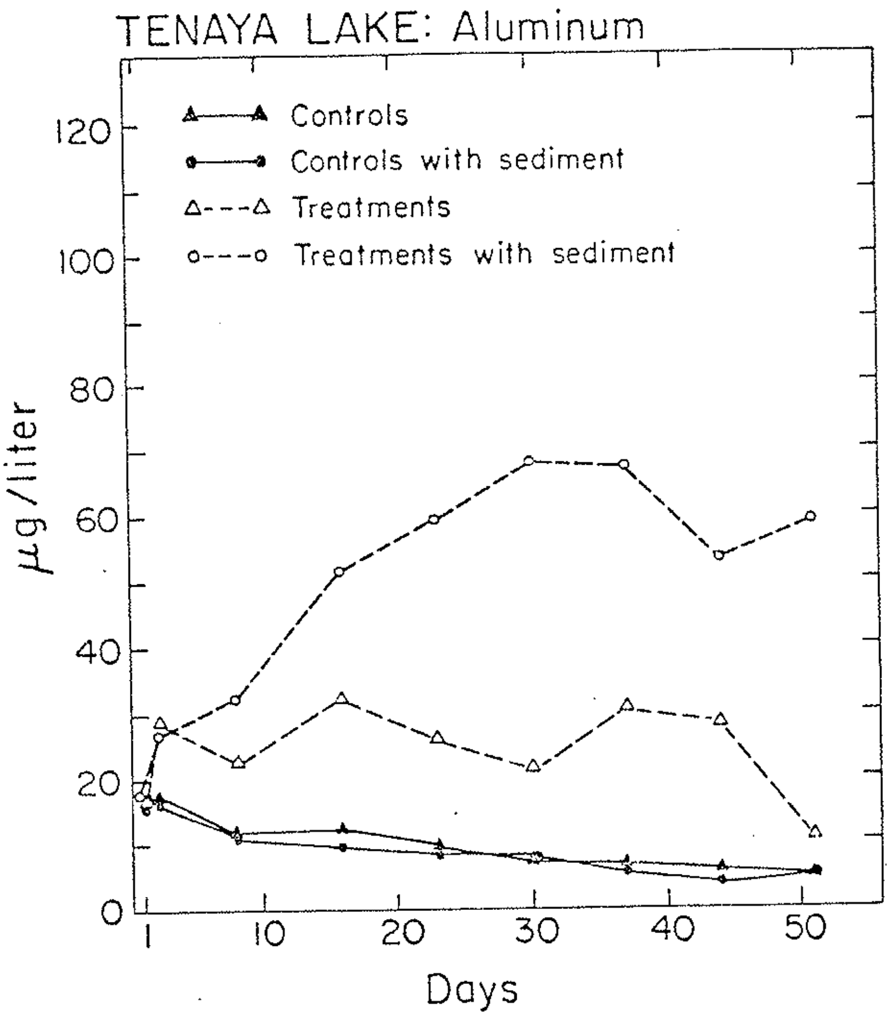
The treatments with sediment increased to a pH of 4.2 and then remained stable. The acidification of these treatments was accompanied by small increases in dissolved Ca, Mg, Mn and Fe levels. Dissolved aluminum concentrations in the treatments with sediments showed the largest increases (from 18.0 to 68.0 μg/l) (see Figure 3). Smaller increases in aluminum in the treatments without sediment reflect leaching from suspended particulates in the water column.

Among the zooplankton counted in this experiment, the largest number belonged to the group <u>Rotifera</u>. In the control systems the growth rate of this population increased from 8 individuals/liter at week 3 to 195 individuals/liter at the end of 7 weeks. The acid-treated systems supported fewer numbers of rotifers, with the largest population being recorded at week 7 in the treatments with sediment (60 individuals/liter).

Phytoplankton groups responded variably to the acid stress. In general, planktonic chlorophyte populations remained relatively unaffected by the acid treatment, while chrysophytes (particularly diatoms) were adversely affected. Cryptomonads increased significantly in the acidified systems without sediment. In all treatments a mat of filamentous green algae (including <u>Mougeotia</u> sp.) formed on the bottom of the tanks.

DISCUSSION

The field data we collected in the Sierra Nevada indicate the sensitivity of these subalpine lakes to acid deposition. The thin,



XBL 823-205 A

Figure 3

poorly-buffered soils, small watershed areas, granitic basins and low-alkalinity waters of this region indicate the potential susceptibility of these aquatic systems to acid stress. Baseline monitoring of pH, alkalinity, principal anions and cations and trace elements, such as aluminum, needs to be continued in both the subalpine and alpine systems of the Sierra to detect changes due to increasing acidification. Evidence from other parts of the world point to the early spring snowmelt period as the time of greatest vulnerability. Sampling should be carried out at this time.

Possible impacts of this acidification have been simulated in our microcosm experiments. By manipulating these laboratory systems we have attempted to predict what effects might be detected as acidification proceeds and what processes might be altered as a result of this stress. The experiments we have performed indicate the importance of littoral sediment leaching of aluminum, manganese and iron. A progressive loss of alkalinity coupled with increases in levels of these elements in the water column of Sierra lakes might be an early sign of progressive watershed acidification.

Among the plankton the identification of "indicator" species would be useful in detecting system acidification. Yan and Stokes (1978) made use of experimental enclosures in Canadian lakes and demonstrated certain systematic phytoplankton changes with increasing acidification. In a number of in situ experiments, including the whole lake acidification by Schindler (1980) in the Experimental Lakes Area of Canada, the development of an algal mat (including <u>Mougeotia</u> sp.) was characteristic of accelerating acidification in lakes.

Certain of these same systematic population changes following acid stress were also observed during our microcosm experiments. Those groups whose growth rates appeared to be stimulated by the addition of acid included dinoflagellates and cryptomonads. The diatoms experienced population decreases in the treatments. In one set of microcosms an algal mat developed, a result similar to that observed in other experiments and field observations.

These results suggest the validity of using microcosm systems to investigate changes in lake geochemical processes and to identify indicator species in sensitive systems which are currently being subjected to acid stress.

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Figure 1: pH vs. alkalinity for 26 California lakes; 0 indicates subalpine lakes, □ represents lower-elevation reservoirs.

Figure 2: Changes in microcosm pH through time in the Tenaya Lake experiment. Nitric acid was added to treatments at day 1.

Figure 3: Changes in concentrations of dissolved aluminum in microcosms during the Tenaya Lake experiment.

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ACID RAIN AND ECOLOGICAL DAMAGE: IMPLICATIONS OF SIERRA NEVADA LAKE STUDIES

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Introduction

"Acid rain" is a popular term describing precipitation—rain, snow, fog, mist, dew, dust—whose acid content has been increased by human activity. It is generally attributed to the burning of fossil fuels such as coal, oil, and natural gas, in power plants, industrial facilities, and automobiles, producing emissions of sulfur oxides and nitrogen oxides. These oxides then undergo acid-forming chemical transformations in the atmosphere, and are transported—often substantial distances from the emission sources—and deposited as "acid rain."

Acid rain was first recognized as a serious problem in the Scandinavian countries. As early as 1955, increasing acidity was being noted in southern Norway and Sweden.[1] The problem was soon widely acknowledged as fish populations in many Scandinavian lakes and streams were reduced or eradicated. Concern over acid rain in the United States began mounting in the 1960s with the loss of trout populations from sensitive Adirondack lakes of northern New York state.[2] The effect of acid rain on forests, grasslands, and croplands is now also a real concern, with the possibility of significant economic loss due to lowered productivity.[3]

Acid Precipitation in California

California was long assumed to be relatively free of acid rain. Winds blowing across the state from the Pacific Ocean are free of the industrial pollutants that blow across the northeast; there are no large, coal-fired power plants in the state; and the Central Valley and desert areas contain alkaline soils, which are a source of dust particles that could neutralize acid rain.

But two projects sponsored by the California Air Resources Board (CARB) studied the chemical composition of the state's rain, using samples collected in 1978 and 1979, demonstrating that precipitation was acidic in both northern and southern California.[4] A network of eight stations in northern California, from urban areas to the Tahoe Basin, was set up to record seasonal variations in the acidity of rain and snow. The pooled data showed an average pH of 4.9—measured on the pH scale that defines unpolluted rain as pH 5.6.[5] (On the pH scale each decrease of 1.0 represents a ten-fold increase in acidity, with the neutral point at 7.0.) Rainfall in urban areas such as Los Angeles and the Bay Area was found to be particularly acidic, the pH of some storms being as low as 2.89, about the same pH as vinegar. These results concerned CARB officials, who, in January, 1981, convened a symposium on the effects of acid precipitation.[6] It was agreed that California faces potential ecosystem damage from acid rain, including forest, fish, and agricultural crop loss. The principal sources of the acids were not positively identified, but likely candidates are the urban population centers with their automobiles, refineries, and oil-fired power plants.

The High Sierra Watersheds

Fortunately, California recognized the potential problem before its natural resources were damaged. So far,

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scientists are unsure how acid rain may affect the state's ecosystems. From observations in other parts of the world, however, we know that the small headwater lakes of the Sierra Nevada—being relatively unable to neutralize acids—are good systems to study in looking for early signs of deterioration.

Subalpine lakes on the western slope are especially susceptible because their small volumes, limited watershed areas, location in granitic basins, and thin watershed soils all contribute to a lack of buffering capacity, or ability to neutralize acid.[7] These sensitive lakes constitute an early warning system that may reflect the effects of increasing California air pollution.

A large volume of California's precipitation falls as snow on the western slope of the Sierra, as east-moving weather systems pass over California's population centers and then drop much of their precipitation. Studies of acid snowfall in Canada and Norway have noted that pollutants were concentrated in the part of the snow that melts first in the spring.[8] If that also happens in California, then the acid and associated ions may flow out in a concentrated pulse, harming the lakes and streams that receive the meltwater. The biological activity of these especially vulnerable mountain lakes could be seriously damaged by such acid pulses.

Measurement of pH alone is not likely to provide the most useful information for anticipating chemical and biological changes in the lakes. Before a significant pH drop is observed, there is a gradual loss of buffering capacity. Consequently periodic measurements of buffering capacity are particularly important. A drop in a lake's buffering capacity is an early warning of impending change in the pH and the lake's biological character. Buffering capacity can be partially renewed by natural geological and biological processes.[9] It is important to measure the rate of renewal of buffering capacity, as this provides a useful measure of the resistance of the lake and its surrounding watershed to acidification.

Our research project collected data on the sensitivity of these subalpine lakes. A brief summary of our experimental approach and results is given here. (For complete details concerning analytical techniques, sampling methods, and analysis of experimental error, the interested reader is referred to the final research report).[10]

The first step in studying selected aquatic systems of the Sierra Nevada was to record the existing chemical and biological conditions of lakes likely to be most vulnerable, thus providing a baseline estimate of the systems' health. In a controlled laboratory setting, we also studied possible changes caused by increasingly acidic precipitation. These laboratory experiments were conducted with simulated lake systems (called microcosms), to which acid was added. The resulting chemical and biological changes were then compared with the conditions of other lake microcosms used as controls, which received no acid. Observations made elsewhere suggest that lakes affected by acid rain have elevated concentrations of such elements as lead, zinc, cadmium, iron, aluminum, and manganese.[11] Large concentrations of such metals could damage water quality and biological populations. Enhanced metal concentrations may also flow downstream and endanger the health of downstream water users. Accordingly, we watched particularly for changes in levels of toxic metals in the microcosm systems receiving acid treatment.

Water-Quality Studies in the Sierra Nevada

Twenty-six lakes located at elevations of 5000 feet to 9000 feet on the western slope of the Sierra Nevada were sampled during the spring, summer, and fall of 1980 and 1981. Many are located in the subalpine zone (basins with few trees and thin soils), in national parks, national forests, and wilderness areas. As noted earlier, baseline data were obtained on pH, buffering capacity (measured by the amount of material available to neutralize acid), and on concentrations of trace metals such as aluminum, cadmium, copper, iron, lead, manganese, and zinc.[12] Calcium and magnesium, components of some of the most common natural buffering materials in lakes and soils, were also measured. Phytoplankton species (microscopic plant life) were identified and individuals counted to provide an indication of the biological state of the system.

The pH of all lakes sampled between June and October was in the neutral range, pH 6-8. Alkalinity of the Sierra lakes, or the amount of material available to neutralize acid, was very low, measured at 10 μeq/liter (micro-equivalents per liter) to 500 μeq/liter. By comparison, a well-buffered aquatic system has an alkalinity of more than 1,000 μeq/liter. These data are summarized in Figure 1 and Figure 2. Figure 3, plotting pH versus alkalinity, shows low alkalinities in Sierra lakes over a range of pH values. (Note: For comparison, data were also collected on two lower-elevation reservoirs, Briones and Isabella. These showed both high pH and alkalinity, and are represented in Figure 3 by the square symbols.)

Wide regional variations in lakewater metal concentrations were found, with relatively high levels of aluminum (40 to 250 micrograms per liter) being recorded in some Sierra lakes.[13] Aluminum is toxic at high concentrations, and is easily leached by acids into lakewater from watersheds and sediments. In areas plagued by chronic lake acidification, fish kills have been directly attributed to aluminum toxicity.[14]

The combination of near-neutral pH, low alkalinity, and availability of alumina minerals in soils and sediment, indicates that many Sierra lakes are susceptible to acid-rain damage. These characteristics are shared with lakes found to be sensitive in other parts of the world.

Our study provides a limited data base on the chemical and biological characteristics of a group of vulnerable Sierra lakes. In the future, field monitoring of selected lakes needs to be continued regularly, to watch for gradual changes in lakewater chemistry that could warn of ecosystem acidification. Especially important is monitoring of lakewater chemistry during snowmelt, when the lakes may be most vulnerable to acid stress.

Experimental Studies of Lake Acidification

When the field survey found the Sierra Nevada lakes susceptible to acid rain, we then sought to determine how acidification might affect these aquatic systems.

Although field experiments in which lakes and streams were artificially acidified have been performed elsewhere, we concluded that laboratory microcosm research, not involving damage to natural lakes, was more appropriate for studying Sierra lakes' vulnerability to acid precipitation.[15]

The microcosms used to simulate the lakes and test their probable response to acid rain were 18-liter plastic tanks, filled with water and sediment collected in the field, and maintained under controlled light and temperature conditions. By using these small replicas of the lake ecosystems, we were able to study the effect of altering acidity. Controllable variables such as temperature, light, and aeration were matched approximately to the levels observed in the actual lakes. Chemical and biological interactions in the lakewater determined the nutrient and metal concentrations, and changes in the plankton populations.

The lakes simulated included a well-buffered Bay Area reservoir (Briones), and two high-altitude, subalpine Sierra lakes (Mosquito Lake, west of Ebbetts's Pass, and Tenaya Lake in Yosemite National Park). Nitric acid (HNO_3) was added to stress the systems because of the high relative concentration of the nitrate anion in precipitation falling in California. It was assumed that it would be easier to interpret changes in a microcosm that had been subjected to increases in a single acid anion.

In each experiment, microcosms were studied under various conditions. For greater statistical reliability three replicates of each condition were set up for the Sierra lake experiments and two were set up for each condition to be studied in the Briones Reservoir experiment. Because lake sediments are sources of both potentially toxic metals and of buffering agents, microcosms were set up with and without lake sediments. Some of the microcosms were stressed with enough acid to bring the system down to pH 4, an acidified state. Following this one-time acid addition, resembling the acid stress observed in Scandinavia and the Adirondacks during snowmelt, several variables were measured weekly over a seven-weeks experimental period: (1) pH, (2) alkalinity, (3) metal concentrations in the water, and (4) phytoplankton and zooplankton (animal life of the plankton) species and numbers. To demonstrate that inadvertent metal contamination did not occur in the laboratory, distilled water controls were set up in parallel with the lake microcosms, and metal concentrations were measured weekly in these controls.

Chemical and Biological Changes

Due to the comparative lack of buffering materials in the water and sediment, the Sierra lake microcosms recovered slowly or not at all after they were treated with acid (see Figure 4, Mosquito Lake, and Figure 5, Tenaya Lake). The Mosquito Lake systems recovered slightly--the pH increased to about 5. This could be attributed to the buffering capacity of the fine-grained organic sediments. These sediments are characteristic of lower-elevation lakes in forested basins and have a greater buffering capacity than the coarse-grained gravel sediments of high-elevation lakes such as Tenaya.

Over a number of years vulnerable lakes may gradually lose the ability to buffer acid because the buffering capacity may be partially used up during the successive snowmelt acid pulses. These subtle changes in lake chemistry may not become obvious until a lake's alkalinity is exhausted, producing a sudden pH drop. Figure 6 charts the exhaustion of buffering capacity in an experiment using water and sediments from Briones Reservoir. Here, acid was added at weeks 0, 2, and 4, depressing the pH to 4 each time. In each instance the pH begins a recovery towards the baseline, but the alkalinity remains depressed (between 0 and 150 μeq/liter). Moreover, pH and alkalinity recovery is weaker following each successive acid addition.

These pH and alkalinity changes after acidification are only some of the complex chemical reactions caused by such stress. Acid can also cause the release of metals, from sediment and suspended particles. For example, Figures 7-9 summarize the levels of dissolved aluminum, iron and manganese released during the Mosquito Lake microcosm experiment.[16]

Phytoplankton and zooplankton populations responded to acid in various ways. Generally the counts of individuals and numbers of species decreased in the acid-stressed systems, although the magnitude of the effect was more pronounced on zooplankton populations than on phytoplankton populations. In some cases acid did not cause a decrease in the populations, but instead suppressed the population blooms observed in the unacidified controls. (Because nitric acid supplies the nitrate ion, a nutrient for algae, some scientists have speculated that acidification might enhance algal growth. Indeed, for one species—a filamentous green alga—a bloom was encouraged in the acidified microcosms of Tenaya Lake.)[17]

Summary of Experimental Results

In summary, these experiments have identified some of the variables that change significantly during acidification. Large decreases in pH cause significant increases of certain metals that are toxic at high concentrations. The acidified systems also exhibited significant biological effects, with some species being favored over others. By monitoring these variables in real lakes, changes in ecosystems due to acidic deposition can be identified. Admittedly in these experiments the lake microcosms were acidified suddenly, while in the field this process may take years or decades. Nevertheless, the diagnostic variables identified can help in recognizing early signs of lake damage due to acidification.

Acid-induced biological and chemical changes can progressively alter freshwater lake systems. The greatest threats to Sierra lakes are (1) loss of the already small buffering capacity, leading to chronic lake acidification, (2) toxic effects of increased acidity on organisms, and (3) indirect and synergistic toxic effects on organisms, including man, due to metals leached from watershed soils or sediment because of increasingly acid rainfall and snowmelt.

Recommendations: Monitoring, Research, and Regulation

The sensitive Sierra lakes will almost inevitably deteriorate if they are exposed to acid rain. Their chemistry and biology will change as their buffering capacity is depleted.

Changes in these sensitive systems due to acid rain may also serve as a warning of more gradual, imperceptible changes that may be taking place in other ecosystems further downstream. Accordingly, California should not defer policy decisions on acid rain until the Sierra lakes have in fact been damaged and changes have begun to be observed. More research is needed on pollution pathways, deposition, and effects, but there is already enough information to justify formulating environmental regulations to protect all of California's natural resources from acid-rain damage.

The most pressing priority is a network of precipitation sampling stations to detect variations in the pH and chemical composition of rain, snow, fog, mist, and dry deposition. Anions, principally sulfate and nitrate, and other important atmospheric constituents such as ammonium, alkaline agents, and trace metals, should be monitored on a year-round, storm-by-storm (or event) basis to identify sources of air pollutants and seasonal trends.

We can now only guess at possible sources and pathways of pollution affecting acidity of precipitation in California. Without better understanding of the atmospheric pathways of pollutant dispersal, it will be difficult to make informed policy decisions about power plant siting. We know that the mountain lakes are sensitive to acid deposition, but we do not yet know how to predict the amount of acid deposition that will reach the Sierra Nevada from fossil-fuel power plants located at alternative sites within the state. Monitoring the chemistry of precipitation provides insight into the atmospheric pathways for pollutant dispersal from existing sources, but provides little direct information about the consequences of locating new sources in areas where there are now no sources of pollution. Developing the ability to predict these consequences will require the combined research skills of atmospheric chemists and meteorologists. Such an interdisciplinary effort is currently in progress at the Lawrence Berkeley Laboratory.

Another pressing priority for California is a lake-monitoring network in the Sierra Nevada. Water quality is important because these lakes are used for recreation, fishing, and as sources of agricultural and municipal water supplies. Without monitoring, important changes in lakewater chemistry could go undetected until the lakes are damaged.

Large changes in pH, alkalinity and dissolved metals have been observed when snowmelt enters adversely affected Adirondack and Scandinavian lakes. Any monitoring scheme should emphasize the snowmelt period to see if similar changes in water chemistry occur in California. Studying snowpack chemistry may also alert us to changes in the precipitation chemistry in the Sierra Nevada where most of the precipitation falls as snow. Because acidification can cause increased toxic metal concentrations in the water, it is also important to monitor background metal levels, and to identify the major sources of toxic metals in California's waters.

Studies are needed of other biological effects of lake acidification that are likely to extend beyond damage to the plankton populations observed in the experiments described here. Microbe-mediated nutrient cycles, soil building processes, and forest and fish productivity in Sierra watersheds could also be altered and perhaps harmed by acidification.

The California Air Resources Board appears to be taking the lead in studying and regulating precursors of acid rain, such as sulfur dioxide or nitrogen oxide emitted during fossil-fuel combustion. In the future, California agencies responsible for regulating energy production and for protecting aquatic resources should cooperate in studying and regulating potential causes of acid rain. In addition to the California Air Resources Board, other agencies that might participate include the California Energy Commission, the Department of Fish and Game, and the Water Quality Control Board. Federal concern with acid rain in California prompted the National Atmospheric Disposition Program (NADP) to install a number of monitoring stations in the state. Federal and state officials should be encouraged to cooperate in expanding networks to monitor both precipitation and lakewater quality.

Despite uncertainties about acid rain and its effects in California, existing data can be used for informed regulation of fossil-fuel burning processes and for siting fossil-fuel burning facilities. For example, available evidence points to mobile sources—principally automobiles—as a major contributor to acid deposition in California, especially in the urban areas. Although the evidence has not yet been thoroughly analyzed, southern California mobile-source pollution may even be a significant contributor to acid rain in the Rocky Mountains.[18] In light of these findings, and those on the Sierra lakes' susceptibility to acid inputs, we recommend against weakening present automotive nitrogen oxide emission standards. Moreover, stricter future standards may be warranted after we learn more about atmospheric pathways and lake vulnerability.

An improved understanding of the Sierra lakes' vulnerability can help policy makers formulate siting criteria that will avoid, or at least limit, the adverse effects of fossil-fuel combustion on water supplies. The effects of acid rain will probably be most severe in high-altitude lakes with predominantly granitic bedrock and sparse vegetation, in central- and southern-Sierra regions. Accordingly, decisions about where to locate large, fossil-fuel burning facilities should be made in light of what is known about atmospheric transformation of pollutants, and the deposition and effects of acidic compounds in these sensitive regions. Meteorological information on the movement of air masses and pollutants in California can suggest where acid might be deposited, and these areas can be monitored. This information can be used in making decisions about where to build power plants or large industrial facilities. In this way, vulnerable areas could be protected from pollution.

State environmental assessment procedures do not currently require that new facilities be evaluated in terms of their potential contribution to acid rain. There is a precedent, however, for requiring specific impacts to be evaluated (e.g., impacts of projects on energy consumption). Environmental impact reporting for new refineries, and for petroleum or coal-fired electric generating plants, could thus be required to include full discussion, using the best available scientific information, of the facility's probable contribution to acid deposition, and of the possible impact the acid deposition will have on the state's sensitive ecosystems. The analyses might include information on emissions, meteorological trends, and existence of sensitive ecosystems downwind of proposed new sources. We believe that such environmental impact reporting ought to be required in California.

Conclusion

The California Legislature recognized the importance of the acid-rain problem by creating the Assembly Select Committee on Acid Precipitation to evaluate existing evidence on acid deposition and recommend legislation. In February 1982, Assembly Bill 2752 was introduced, proposing the Kapiloff Acid Deposition Act, designed to finance and implement a coordinated monitoring and research effort administered by the California Air Resources Board. This legislation was passed by the California Legislature, and signed by the Governor in September 1982. This act is a reasonable first step toward controlling acid deposition and limiting its deleterious effects. It authorizes not only monitoring and research to define the extent and nature of the problem in California, but also calls for an analysis of possible control strategies, including emission-control technologies, alternative-energy policies, and air-quality management strategies. This kind of research and analysis can lay the groundwork for effective future regulation.

Delay in regulation, after the extent of the problem is recognized, could mean loss of the valuable goods and services society derives from healthy ecosystems.[19] Many ecological effects are either irreversible or very costly to remedy. Now that we know something about the sensitivity of the Sierra aquatic systems, these data should be used in regulatory decision making. The potential for significant damage should not be ignored until damage has occurred. Even if some of the initial regulations should later prove to be too strict, it would be easier to modify regulations than to restore damaged ecosystems.

Through a reasoned consideration of (1) the best scientific information on the subject, and (2) the economic impact of possible regulations, public policy makers can attempt to formulate regulatory strategies to protect ecosystem quality. Resolution of the scientific and economic uncertainties should result in more effective policies for control of acid-rain damage.

FIGURE 1

Distribution of Sierra Lakes pH's
Measured in 1980-81 (n=26)

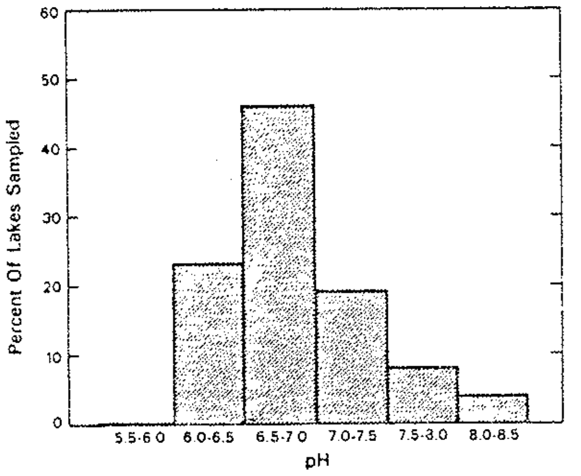


FIGURE 2

Distribution of Sierra Lakes Alkalinities
Measured in 1980-81 (n=26)

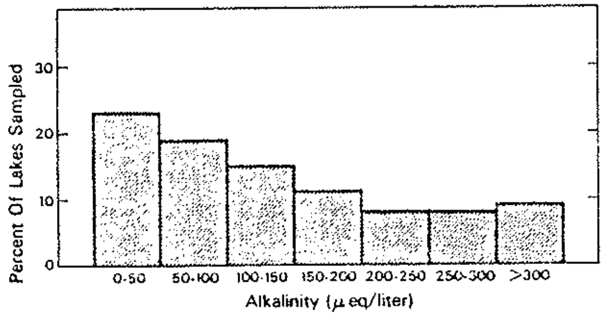
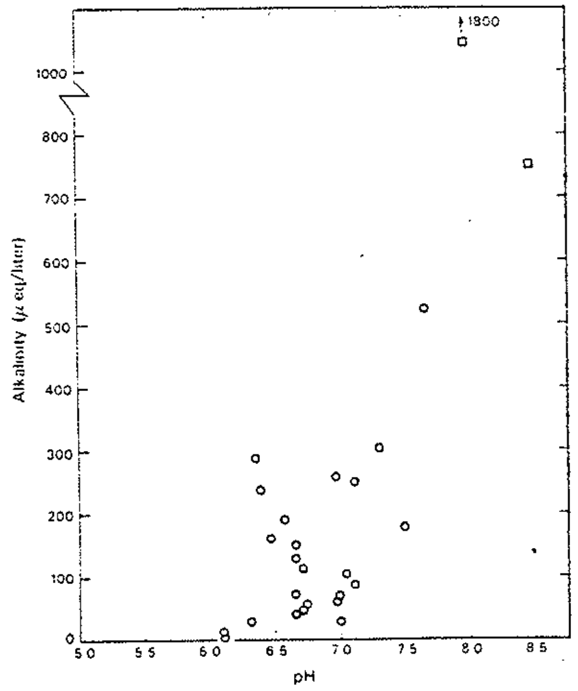


FIGURE 3

pH and Alkalinity for Sierra Lakes Measured in 1980-81 (n=26)



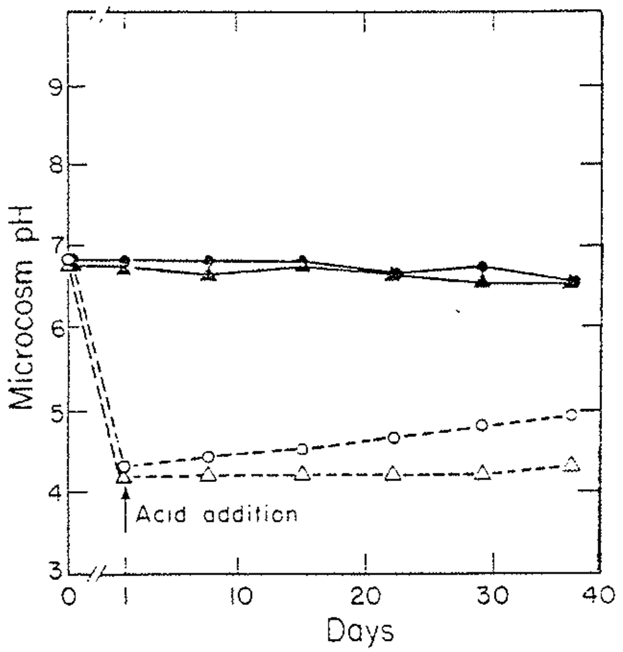
Legend:

○ = a high-elevation Sierra lake.

□ = a lower-elevation reservoir.

FIGURE 4

Changes in pH of Microcosms (simulated lake systems), the Mosquito Lake Experiment



Legend:

▲——▲ Controls

●——● Controls with sediment

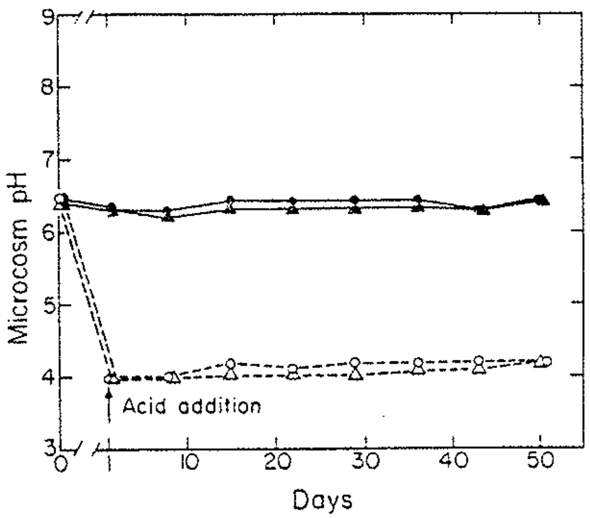
△- - -△ Treatments

○- - -○ Treatments with sediment

Note: The experiment covered five weeks.

FIGURE 5

Changes in pH of Microcosms (simulated lake systems), the Tenaya Lake Experiment



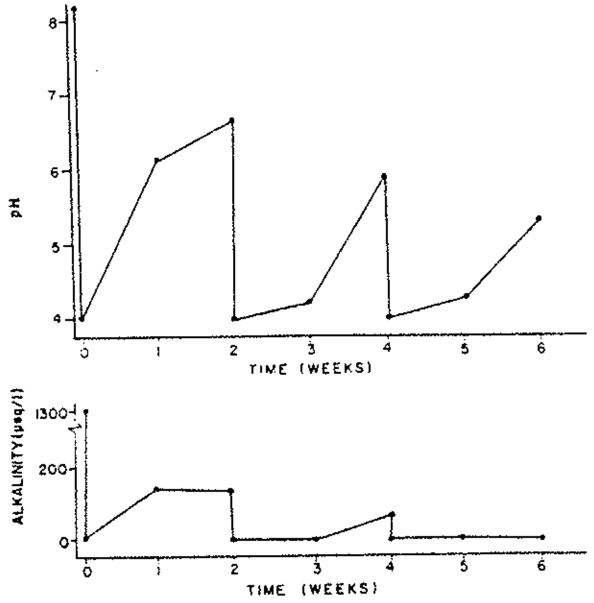
Legend:

- ▲——▲ Controls
- ●——● Controls with sediment
- △---△ Treatments
- ○---○ Treatments with sediment

Note: The experiment covered seven weeks.

FIGURE 6

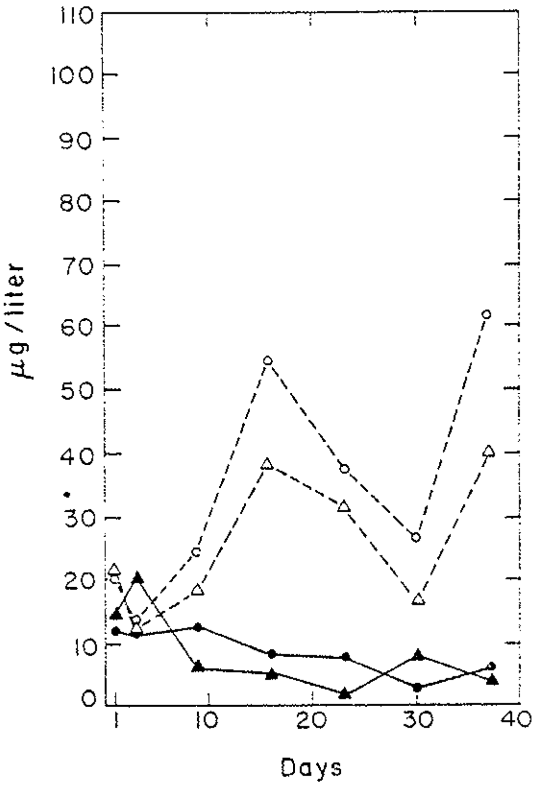
Loss of Buffering Capacity in Briones Reservoir Microcosms (simulated systems)



Notes: Acid was added at weeks 0, 2, and 4. The experiment covered six weeks.

FIGURE 7

Levels of Dissolved Aluminum Measured During the Mosquito Lake Experiment



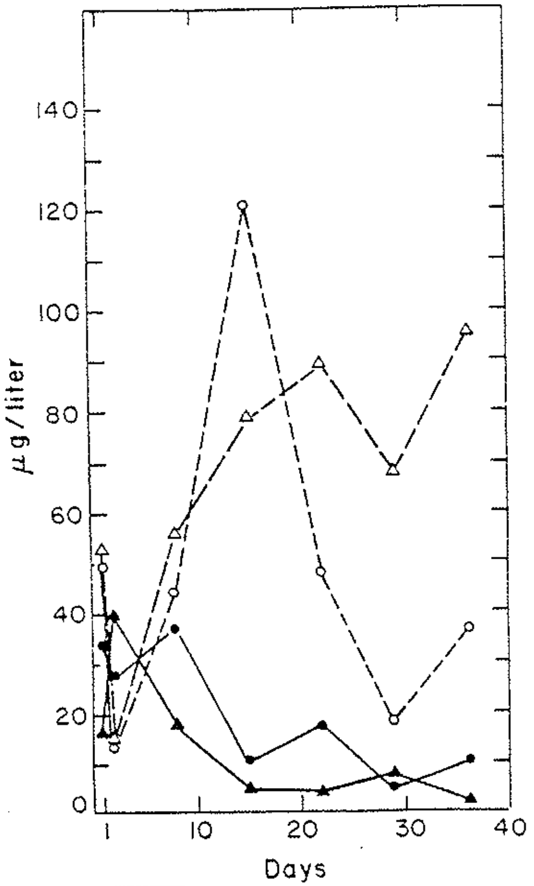
Legend:

- ▲——▲ Controls
- ●——● Controls with sediment
- △---△ Treatments
- ○---○ Treatments with sediment

Note: The experiment covered five weeks.

FIGURE 8

Levels of Dissolved Iron Measured During the Mosquito Lake Experiment



Legend:

▲——▲ Controls

●——● Controls with sediment

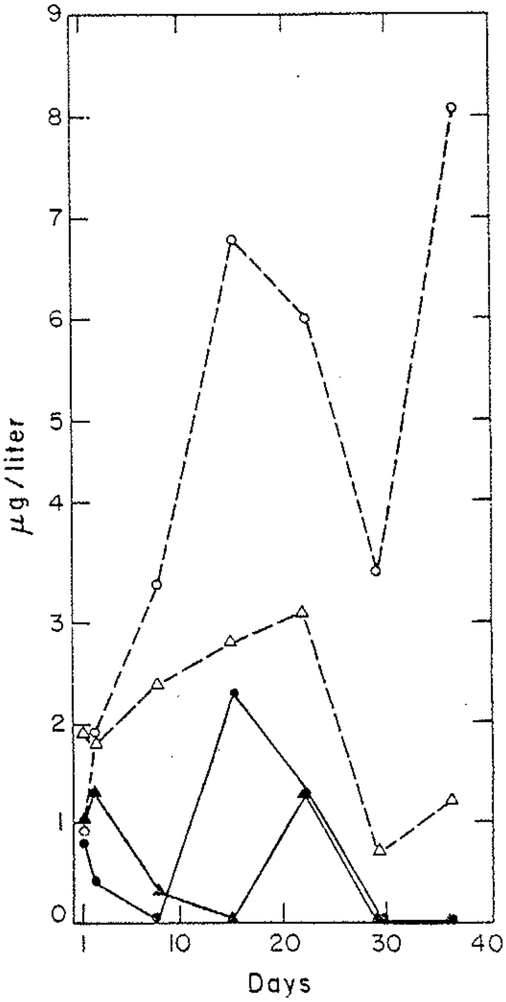
△- - -△ Treatments

○- - -○ Treatments with sediment

Note: The experiment covered five weeks.

FIGURE 9

Levels of Dissolved Manganese Measured During the Mosquito Lake Experiment



Legend:

▲——▲ Controls

●——● Controls with sediment

△- - -△ Treatments

○- - -○ Treatments with sediment

Note: The experiment covered five weeks.

ACKNOWLEDGEMENTS

The research leading to this report was supported in part by the United States Department of Interior under the Annual Cooperative Program of Public Law 95-467, Project A-081-CAL, and by the University of California Water Resources Center, Project UCAL-WRC-W-591. Contents of this publication do not necessarily reflect the views and policies of the Office of Water Policy, U. S. Department of Interior, nor does mention of trade names or commercial products constitute their endorsement or recommendation for use by the U.S. Government. The author would like to thank J. Oldfather, R. Bastasz, A. Hodgson, G. Winston-Harris, and C. Blanchard for their assistance during this study.

1. See the report by E. Barret and G. Brodin, "The Acidity of Scandinavian Precipitation," *Tellus,* 7: 251-257 (1955), for a discussion of some of the early data collected on acid rain occurrence in Scandinavia.

2. See, for example, U S Department of Interior, Office of Water Research Technology, C.L. Schofield, *Acid Snowmelt Effects on Water Quality and Fish Survival in the Adirondack Mountains of New York State,* Research Programs Technical Comprehensive Report No. A-072-NY. (1977).

3. For a complete discussion of possible effects of acid rain on forests, crops, and soils, see the symposium volume *Effects of Acid Precipitation on Terrestrial Ecosystems,* T.C. Hutchinson and M. Havas, eds. (New York: Plenum Press, 1980).

4. See, for example, J. McColl, *A Survey of Acid Precipitation in Northern California,* Final Report #A7-149-30 to the California Air Resources Board (February 19, 1980); and J.J. Morgan and H.M. Liljestrand, *Measurement and Interpretation of Acid Rainfall in the Los Angeles Basin,* Final Report to the California Air Resources Board (February 29, 1980).

5. The pH scale measures the acidity or alkalinity of solutions, in a range from 0-14, with decreasing numbers indicating increasing acidity, and larger numbers signifying higher alkalinity. Because the pH scale is logarithmic, each unit decrease corresponds to a ten-fold increase in acid content. Distilled water with a pH of 7 is considered neutral. Precipitation is often considered acid if its pH is below 5.6, the normal value for unpolluted precipitation in equilibrium with atmospheric carbon dioxide (CO_2).

6. See the forthcoming report, "Proceedings of the California Symposium on Acid Precipitation" (Sacramento: California Air Resources Board, 1982).

7. Buffering capacity is the ability of a lake to recover by neutralizing acid that enters the lake basin as rain, snowmelt or dry deposition. The normal pH of Sierra lakes is near neutrality, (pH7) but the lakes have a very low buffering capacity (alkalinity) of only 10-500 μeq/liter (micro-equivalents per liter). A lake's alkalinity is defined as the amount of material available to neutralize any added acid. A well-buffered system typically has an alkalinity greater than 1000 μeq/liter. Studies of the alkalinity of Sierra lakes by Professor J. Melack of U.C. Santa Barbara also demonstrate the low alkalinity of these systems. (See the *Proceeding of the American Water Resources Association, International Symposium on Hydrometeorology,* Denver, Colorado (June 13-17, 1982).

8. See, for example, D.S. Jeffries, C.M. Cox, and P.J. Dillon, "Depression of pH in Lakes and Streams in Central Ontario during Snowmelt." *J. Fish. Res. Board Can.* 36:640-646 (1979), for a discussion of this concentration effect in Canada. Similar observations in Norway are described in, M. Johannessen and A. Henriksen, "Chemistry of Snow Meltwater: Changes in Concentration During Melting," *Water Resources Research* 14(4):615-619 (August 1978).

9. These processes include the weathering of rocks and biological production, which can yield acid-neutralizing products.

10. See K. A. Tonnessen, "The Potential Effects of Acid Deposition on Aquatic Ecosystems of the Sierra Nevada, California," Ph.D. dissertation, Energy and Resources Group, U.C. Berkeley, 1983 (in preparation).

11. For a review of data on increases in trace-metal concentrations in acidified lakes, see the report of the National Research Council of Canada, *Acidification in Canadian Aquatic Environment: Scientific Criteria for Assessing the Effects of Acidic Deposition on Aquatic Ecosystems,* NRCC Report No. 18475, pp. 189-192 (1981).

12. Water samples were collected at mid-day at three stations in each lake (the shore, the mid-lake surface, and the maximum depth at which a standard black and white disk, called a secchi disk, can be seen by an observer). Some lakes were sampled in two consecutive years; others were studied once. Standard methods were used for all chemical measurements: the lake pH was measured using a Sargent-Welch pH meter with glass, combination electrode; alkalinity determinations were made by Gran titration with 0.01 $\underline{N}$ HCl. Trace-metal concentrations were measured by atomic-absorption spectrophotometry.

13. A μg/l (microgram per liter) is equal to a part per billion on a weight-of-metal per weight-of-water basis.

14. For a general discussion of the aluminum leaching phenomenon, see C.S. Cronan and C.L. Schofield, "Aluminum Leaching Response to Acid Precipitation: Effects on High-Elevation Watersheds in the Northeast," *Science,* 204:304-306 (April 20, 1979).

15. See two articles in D.S. Shriner, et al., *Atmospheric Sulfur Deposition Environmental Impact and Health Effects* (Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc., 1980). In this volume, stream acidification experiments in Hubbard Brook Experimental Forest are described in R.J. Hall and G. Likens, "Ecological Effects of Whole-Stream Acidification." Canadian experiments with lake acidification are described in D.W. Schindler, "Ecological Effects of Experimental Whole-Lake Acidification."

16. Points on the graphs of metal concentrations vs. time represent the mean ($\bar{X}$) of the replicate tanks. These values have standard deviations of 10 to 15 percent in most cases. Differences in the mean concentrations between treatments and controls are significant at the 99 percent confidence level.

17. Data on changes in zooplankton and phytoplankton populations are included in K. A. Tonnessen, "Potential for Aquatic Ecosystem Acidification in the Sierra Nevada, California," in the *Proc. Symp. Acid Precipitation: Aquatic Effects,* G. Hendrey, ed. (Ann Arbor, Michigan: Ann Arbor Science Publishers, 1983).

18. The similarity of precipitation composition on the western slope of the Colorado Rockies and that of the L.A. Basin is discussed in J. Harte, G.P. Lockett, and R.A. Schneider, "Acid Precipitation and Surface-Water Vulnerability on the Western Slope of the High Colorado Rockies" (submitted for publication to *Environ. Sci. Technol.)* Lawrence Berkeley Laboratory, Berkeley, CA.

19. Goods derived from healthy ecosystems include fish, lumber, and agricultural crops. Services include the regulation of air quality; the maintenance of water quality, storage, and flow; the moderation of climate; the maintenance of a genetic "library" for future generations; the cycling of essential nutrients within and between soil and water; and the breakdown of toxic wastes to harmless products. For a full discussion of these goods and services, along with an evaluation of the ways energy technologies can degrade them, see J. Harte and A. Jassby, "Energy Technologies and Natural Environments: the Search for Compatability," *Annual Review of Engergy,* 3: 101-146 (1978).

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—The Editors

The potential for acid precipitation damage to aquatic ecosystems of the Sierra Nevada, California (U.S.A.)

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Energy & Environment Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, U.S.A.

Within the United States acid precipitation is a recognized problem in the northeastern region of the country[1-2]. Recent evidence of acid precipitation in the western United States has been reported for locations within California[3-4] and Colorado[5]. Energy policies in these western states may result in the acceleration of acid-precipitation problems in these areas.

This research involves a study of the potential impacts of acid precipitation on aquatic systems within the state of California. Possible ecological consequences of such acid deposition are being investigated through a field sampling program and laboratory research using microcosm experiments to simulate lake system response to perturbation[6].

The experimental focus is on the relationship of acid inputs to lakes and increases in the levels of toxic metals in the water column. Population levels and diversity of phytoplankton and zooplankton species are the variables to be studied in the presence of lowered pH and increasing metals levels.

Field sampling of selected lakes located on the western slope of the Sierra Nevada in California will be continuing through fall, 1980. Data are being collected on the pH and metals levels (Al, Cd, Cu, Fe, Mn, Pb, Zn) in the water column of these lakes. Lake sediment samples are also being analyzed for metal content using atomic-absorption spectrophotometry.

Preliminary results of the field sampling indicate a pH gradient for lakes in the Sierra ranging from pH 7.6 to pH 5.8, with lower pH values being recorded for lakes at higher altitudes. Regional variability in metals levels in lake water is great, with high levels of aluminum being noted in a number of the lakes sampled (40-250 μg/1). The relationship of lowered pH of lake water and rising aluminum concentration has already been noted in the northeastern part of the U.S.[7]. This variable appears to be important in identifying lakes which may be adversely affected by acid precipitation. Further monitoring of aluminum levels in Sierra lakes may therefore provide valuable information on the extent to which these lakes are susceptible to damage.

The use of microcosms for evaluating acid-precipitation damage to aquatic systems has been documented elsewhere[8-9]. In this laboratory study 50-liter replicate systems, some with sediment and some without, were set up under controlled conditions (17°C, 12 h light – 12 h dark). The treatment systems received acid inputs sufficient to bring the system pH down to 4.0. The response of the perturbed systems was then tracked through time by measuring changes in (1) pH (figure 1), (2) metals concentrations in the water column (figure 2), (3) zooplankton population levels (figure 3), and (4) phytoplankton population levels (figure 4).

This is a small but representative subset of the data collected thus far. Similar trends in population levels through time were noted for other species of phytoplankton and zooplankton. Diversity of species through time increased significantly in the control systems while remaining at a low level in the systems which received acidic inputs.

From this experiment and other 4-liter experimental trials performed thus far, the following may be inferred: (1) the leaching response of metals in sediments and particulates to acid inputs is extremely variable over lakes and among metals measured in the experiments, (2) in the treatment systems large changes in biota (species and number) relative to control levels were induced by acid inputs.

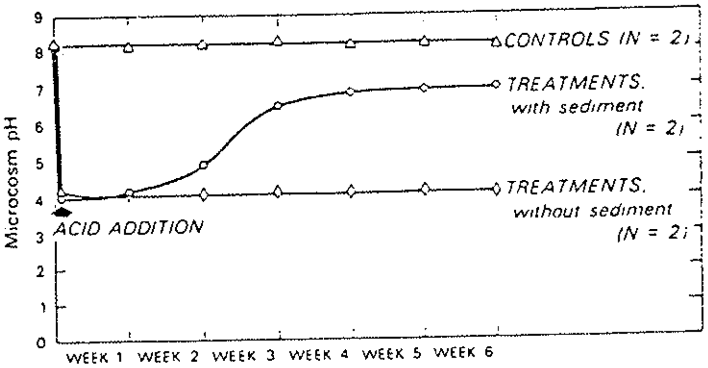

Figure 1. Changes in pH of the experimental systems through time.

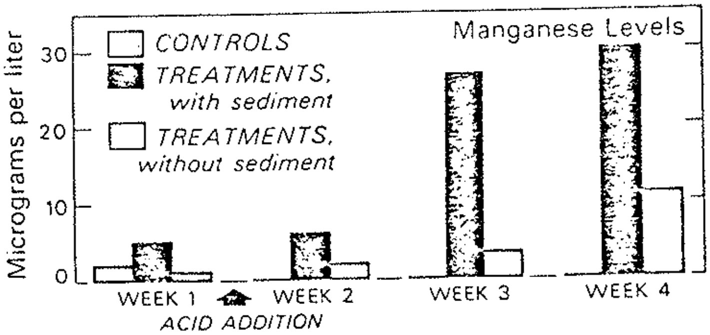

Figure 2. Changes in manganese levels during the four-week experiment.

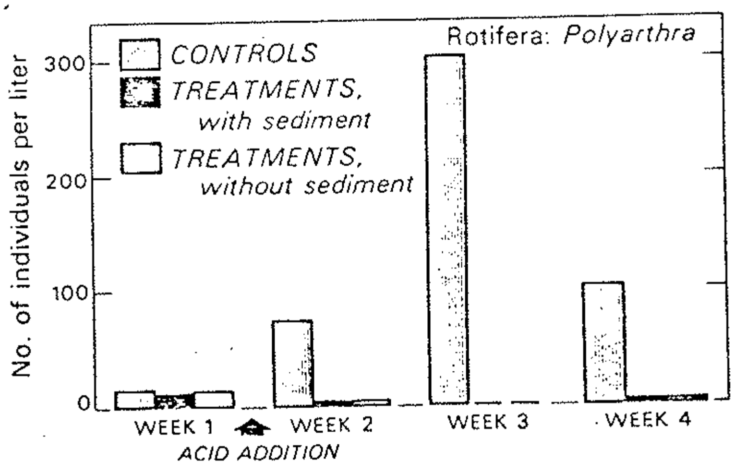

Figure 3. Changes in population levels of the rotifier, Polyarthra, through time.

Additional microcosm experiments are planned in an attempt to model both the changes in metals levels and responses of biota from different Sierra lakes under conditions of varying amounts of acid inputs to the experimental systems.

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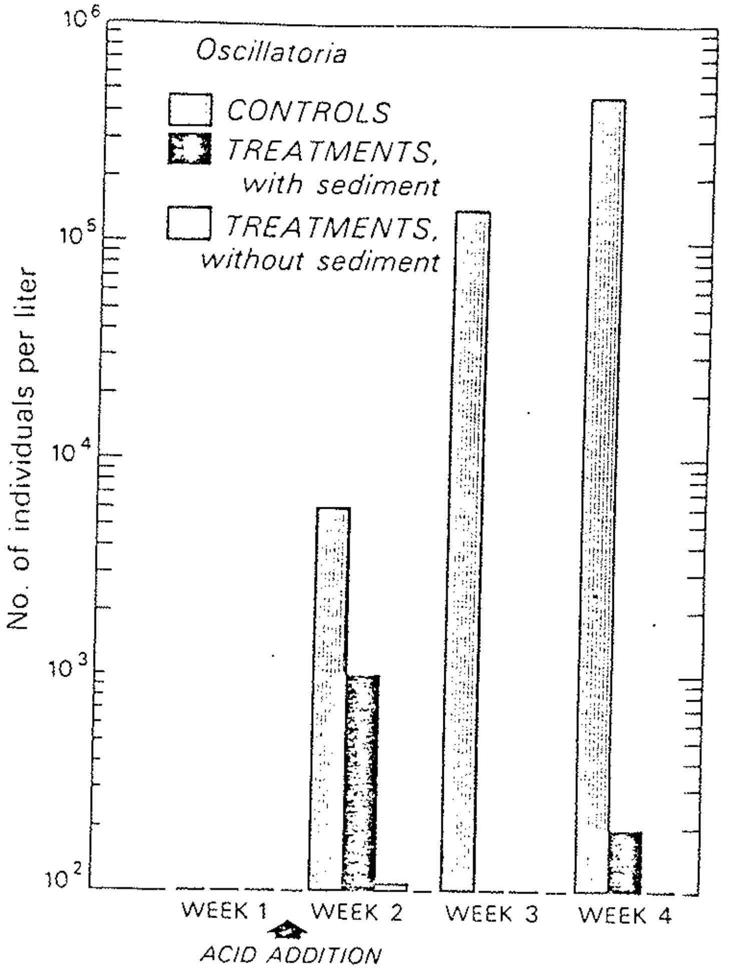

Figure 4. Changes in populations levels of the blue-green algae. Oscillatoria, through time.

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G. Hendrey, ed.
Ann Arbor Science
Woburn, MA (1983)

Potential for Aquatic Ecosystem Acidification in the Sierra Nevada, California

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Abstract

Acid deposition has been measured in California, including areas of the Sierra Nevada. This region is characterized by low-alkalinity, granite-based lakes which may be sensitive to such acid inputs, particularly during the snowmelt period. A lake survey and a series of laboratory microcosm experiments were designed to evaluate the current status of these lakes and the potential for chemical and biological changes due to increasing system acidification.

The survey established that lakes located in subalpine basins on the western slope of the Sierra have circumneutral pH's, low alkalinities (10 -500 μeq/l) and detectable levels of such metals as aluminum, iron and manganese. Microcosm experiments, using 18-liter tanks containing whole-lake water and littoral sediments, were valuable in identifying the behavior of trace metals and plankton populations following a pulsed acidification event which lowered system pH to 4.0. Although the response of the system pH to acid stress differed between the two experiments described (Mosquito Lake vs. Tenaya Lake), the effect of acidification on growth rates within individual phytoplankton and zooplankton taxa was similar. Microcosm experiments of this kind appear to be useful in determining changes in geochemical cycling and in identifying sensitive "indicator" taxa in acid-stressed aquatic systems.

INTRODUCTION

Numerous dilute, softwater lakes are located within alpine and subalpine basins in the Sierra Nevada of California. These lakes share many of the physical and chemical characteristics common to systems considered to be sensitive to acid deposition: small watershed areas, granitic basins, thin watershed soils and low-alkalinity waters. Recent studies indicate that acid precipitation is falling in this region of California[1,2]. This acid deposition appears to have its origin in the urban centers along the Pacific coast and in the Central Valley of California, with significant nitric acid contributions coming from mobile sources.[3]

The potential for adverse impacts to aquatic systems of the Sierra from such deposition is great. Much of the runoff into high-altitude lakes occurs during spring snowmelt, a situation which may serve to exacerbate the impact of acidic deposition on oligotrophic lakes.[4,5] Such seasonal depressions in lake-water acidity may result in the gradual depletion of water-column alkalinity and leaching of trace metals from soils and sediments. These chemical changes will be accompanied by biological changes, especially among populations of attached and planktonic algae and zooplankton.

Despite this potential for ecosystem damage to aquatic systems of the Sierra, continuous, baseline data on the chemistry and biology of these systems have not been collected. This study was designed to investigate the sensitivity of subalpine lakes located on the western slope between 1600-2600 m. Baseline data on lake-water chemistry were collected and controlled, laboratory microcosm experiments were run in an effort to measure the susceptibility of these ecosystems to acid deposition.

This research was designed to answer specific questions regarding lake acidification in the Sierra:

(1) are these western slope lakes sensitive to acid deposition and is there evidence that changes due to such deposition have already occurred?

(2) what influence do sediments have on changes in water chemistry which may occur following a pulsed acidification event (such as may occur during snowmelt)?

(3) what systematic changes in aquatic biota might be observed following a short-term acid stress?

(4) are laboratory microcosms useful tools for evaluating chemical and biological impacts of aquatic acidification?

METHODS

Field Study

A survey of the water quality of 40 western slope, subalpine lakes was conducted from 1979-1981 during the ice-free season. Lakes were sampled once at three stations per lake: shore, surface (midlake) and secchi-disc depth (midlake). Samples were collected from an inflatable boat using an acid-washed Van Dorn sampler. Measurement of pH was done immediately on two replicate samples per station using a Sargent Welch* model PBX pH meter and combination electrode, calibrated with standard buffers. Calibration using dilute acids was performed at regular intervals as a check on electrode accuracy.[6] The electrode was rinsed with sample water for 10 minutes before a pH value was recorded. Alkalinity determinations were performed in the field on replicate 100-ml samples titrated with 0.01 N HCl dispensed from a 2-ml micrometer buret and then evaluated using Gran methods.[7] One-liter samples were filtered through a 0.45 μm filter (Nucleopore)* and preserved with Ultrex* nitric acid (HNO_3) for laboratory analysis. Atomic-absorption spectrophotometry (graphite furnace) was used to determine concentrations of total and dissolved trace elements: aluminum (Al), cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), manganese (Mn) and zinc (Zn). Detection limits for these elements were 1.0 μg/l. Calcium (Ca) and magnesium (Mg) concentrations were measured using both flame and graphite-furnace atomic-absorption techniques (detection limits of 10.0 μg/l).

9

Microcosm Experiments

Microcosms were established in the laboratory using unfiltered water and sediments collected from two Sierra lakes: Mosquito Lake (2440 m), located in Stanislaus National Forest and Tenaya Lake (2480 m), located in Yosemite National Park. Each experiment was conducted in twelve 18-liter Nalgene* tanks: six control tanks (three with sediment, three without) and six treatment tanks (three with sediment, three without). Two control, distilled-water tanks were also set up and

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* Sargent Welch Scientific Co., 1617 Ball Rd., Anaheim, CA 92803.

* Nucleopore, 7035 Commerce Circle, Pleasanton, CA 94566.

* Ultrex: J.T. Baker Chemical Co., Phillipsburg, NJ 08865.

* Nalge Sybron Corp., P.O. Box 365, Rochester, NY 14602.

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sampled to test for environmental contamination. Sediment packages contained intact littoral sediments collected in glass petri plates (10 cm diameter). These microcosm systems were set up in a light- and temperature-controlled facility. Light levels were maintained at approximately 1/20 of natural ambient insolation. Light-dark regimes were designed to simulate conditions existing at the time of water collection (fall for Mosquito Lake, early summer for Tenaya Lake). Each tank was placed in a steel-jacketed outer tank, which was filled with cooling water. This allowed the microcosm water temperature to remain at the lake temperature measured in the field. Each tank was aerated using filtered air; this allowed for water agitation and aeration of both water and sediments.

In each of the two experiments (referred to as "Mosquito experiment" and "Tenaya experiment"), baseline biological and chemical data were collected in the field and in the laboratory: pH, alkalinity, levels of Ca, Mg, Al, Cd, Cu, Fe, Mn, Pb, Zn (total and dissolved) and phytoplankton and zooplankton populations. Following this initial sampling the pH of the treatment tanks was lowered to 4.0 by the addition of nitric acid (0.1 N HNO_3). This type of acid was chosen because of the prevalence of the NO_3^- anion in acidic deposition in California. Chemical and biotic samples were collected each week (six weeks for the Mosquito experiment and seven weeks for the Tenaya experiment). During the sampling procedure the sediment packages were removed from the tanks and the water stirred. An integrated water sample was taken using a glass tube. Filtered (0.45 µm Nucleopore) and unfiltered water samples were preserved in nitric acid (HNO_3) and analyzed by atomic-absorption spectrophotometry for cation concentrations. Alkalinity and pH were measured using techniques described under "Field Study". A 5-ml water sample was collected from each tank using an acid-washed pipette and 27 preserved in Lugol's solution for microscopic examination of phytoplankton. Zooplankton population estimates were based on a 1-liter sample filtered through a 64 μm mesh. These biotic samples were allowed to 71 settle in Wild plate chambers and then were observed under a Leitz microscope.* The entire chamber was counted when making population estimates of both zooplankton and phytoplankton.

RESULTS

Sierra Lake Chemistry

A subset of the data collected during the lake survey is presented in Figure 1. This graph of pH vs. alkalinity represents data collected from 26 California lakes during the summers of 1980-81. Two of these 72 lakes (designated by ☐) are large reservoirs; one is located in the Sierra foothills and the other in the San Francisco Bay Area hills. These two points may be compared with the data recorded for the small, subalpine, western slope lakes. These lakes have pH's in the circumneutral range (6.0-8.0) and are characterized by low alkalinities (<300 μeq/l). About half of these Sierra lakes had measured alkalinities below 100 μeq/l, a value characteristic of lakes sensitive to acid deposition. Each point in Figure 1 represents the average pH and alkalinity of three replicate surface-water samples per lake (pH ± 0.05; alkalinity ± 5.0 μeq/l). Little variability in pH or alkalinity was noted among

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* Leitz-Wetzlore, Midland, Ontario, Canada.

the three stations sampled in each lake.

A summary of lake-water quality for ten representative, granite-based Sierra lakes is presented in Table 1. Measurements were made on surface-water samples. Levels of calcium (0.2-1.9 mg/l) and magnesium (0.03-0.55 mg/l) were low and strongly correlated with alkalinity (r = 0.85 and r = 0.76 respectively for Ca and Mg). Concentrations of dissolved aluminum (4.9 - 30.9 μg/l), iron (2.2-50.6 μg/l) and manganese (1.1-10.4 μg/l) were measured in these surface-water samples. These represent average values, with a standard deviation of ± 10%. Concentrations of the other trace metals were below detection limits (1.0 μg/l) for most of the lakes sampled.

Experimental Results

Chemical Changes

Changes in microcosm pH are shown in Figures 2 and 3. Each point represents the mean pH of the three replicate tanks (± 0.1 pH units). During the Mosquito experiment the control tanks remained at a pH of between 6.7-7.0. Acidified systems with sediments showed an increase in pH from 4.0 to 5.2 at the end of the six-week experiment. Only a small pH change was observed in the treatment tanks without sediment following acidification. A more extreme result was recorded during the Tenaya experiment. The pH of the control tanks varied from 6.2 - 6.6 during the seven-week experimental period. The treatment tanks with sediment showed a pH increase from 4.0 - 4.2 in the first two weeks; only a slight increase in pH was detected in the acidified systems without sediment. In both experiments alkalinity remained relatively constant in the control microcosms: 60.0 μeq/l in the Mosquito experiment and 30.0 μeq/l in the Tenaya experiment. In both experiments treatment system alkalinity was exhausted and excess acidity was measured in the water column at pH = 4.0. A recovery of alkalinity was recorded only during the Mosquito experiment in the systems with sediment.

The largest changes in cation concentrations following acidification were observed for calcium (Ca) and magnesium (Mg) (see Figures 4-7). During the Mosquito experiment dissolved Ca concentrations increased in the acidified tanks, with the largest changes being measured in the systems with sediments (from 0.26±.02 to 0.81±.03 mg/l). Magnesium levels remained relatively constant in the treatment tanks without sediment. Increases in dissolved Mg from 0.11±.02 to 0.23±.02 mg/l were measured in the tanks containing sediment. Lower concentrations of Ca and Mg were measured in the Tenaya experiment than in the Mosquito experiment. The largest net increase in Ca concentration in the Tenaya systems was measured during the first week following acidification in both sets of treatment tanks (from 0.16±.02 at day 0 to 0.21±.03 mg/l at week 1). Variability within replicate tanks and the possibility of contamination during filtration must be considered when analyzing these data. This experimental variability makes it difficult to identify significant trends in either Ca or Mg concentrations following acidification during the Tenaya experiment.

Among the trace metals measured during these two experiments only aluminum (Al), manganese (Mn), and iron (Fe) significantly increased in the treatment tanks. The largest increases were observed for aluminum (see Figures 8-9). In the Mosquito experiment dissolved Al increased in both sets of treatment systems following acidification, with a five-fold increase occurring in the systems with sediment (from 12.0±2.5 to 61.3±4.3μg/l). Increases in Al concentrations in the acidified systems without sediment may be explained in terms of leaching of suspended particulates present in the whole-lake water used in the microcosms. During the Tenaya experiment even higher levels of dissolved Al were recorded in the treatment systems with sediment, with a maximum concentration of 70.6±3.4 μg/l recorded four weeks following acidification.

Significant increases in metal concentrations were recorded for Fe and Mn. In the Mosquito experiment, dissolved Fe increased in both the treatments with sediment (12.2±2.1 to 120.3±10.2 μg/l) and treatments without sediment (15.2±2.6 to 90.0±7.6 μg/l). Suspended particulates in the water column of the latter systems account for this increase. Fe levels also increased in the Tenaya experiment, although the maximum concentrations were less than those in the Mosquito experiment. The treatments with sediment showed increases from 7.2±3.2 to 18.8±4.2 μg/l; treatments without sediment had Fe increases of 7.6±3.2 to 19.7±5.6 μg/l. In both cases, peak Fe concentrations occurred two weeks after acidification.

Small but replicable increases in Mn concentrations were observed during both experiments. Dissolved Mn concentrations fluctuated from a low of 1.0±.06 μg/l to a high of 8.0±2.5 μg/l in Mosquito Lake systems with sediments. During the Tenaya experiment, Mn levels changed from an initial level of 2.5±1.2 μg/l to a peak of 4.7±1.6 μg/l. The treatments without sediment did not show such increases.

Biological Changes

The response of biological populations to microcosm acidification is expressed in terms of phytoplankton and zooplankton population changes through time. These population estimates are based on microscope counts and are expressed as numbers of individuals per liter for zooplankton. Each point graphed represents the mean of the populations sampled in the three replicate tanks. Standard errors of these zooplankton population estimates varied from 5-30%. Individuals were identified to genus in all cases and to species where possible.

Zooplankton population growth was negatively affected by acid treatment in both experiments. The largest number of zooplankton identified belonged to the group Rotifera. The negative effect of acidification on rotifers is shown in Figures 10 - 11. The pattern of response of these populations to acid treatment differed between the two experiments. In the Mosquito microcosms the number of individuals increased in the controls until week 4, when the populations were estimated at about 70±9 individuals per liter. Rotifer populations in the treatments decreased until week 6 when a slight increase was noted. During the Tenaya experiment the rate of increase of the control populations accelerated after week 4. An increase in the number of rotifers in the treatment systems with sediment was also observed after week 4, but the magnitude of that increase was less than in the controls. The population in the treatment systems without sediment remained low throughout the experiment.

A more extreme response of zooplankton populations to acidification was observed within a specific rotifer genus: (Keratella) (see Figure

12). This genus was represented in both experiments by two species: K. quadrata and K. cochlearis.

Larger numbers of taxa and individuals were observed within the phytoplankton. In the Mosquito experiment all major phytoplankton groups were represented. The response of these taxonomic groups to acidification is summarized in Table 2. Negative effects of acidification were observed within the green, blue-green and golden algae (especially the diatoms). The presence of sediments in the treatment systems, which resulted in an increase in pH during the experiment, appeared to mitigate this negative effect. While populations of dinoflagellates (principally Peridinium spp.) and cryptomonads decreased in the control tanks, an increase in populations of these groups was measured in the acidified systems. Figure 13 presents an example of the negative impact of acidification on phytoplankton (Chrysophyta: Bacillariophyceae and Chrysophyceae); the stimulation of growth rate due to acid treatment is shown in Figure 14 (Cryptophyta). Each point on these graphs represents the mean of the population estimates from three replicate tanks. Variability among tanks was greater than estimates of zooplankton populations; standard errors ranged from 7% - 60%.

Changes in phytoplankton populations during the Tenaya experiment are presented in Table 3. This experiment was initiated in early summer when phytoplankton populations in the lake were low. Consequently, populations of some taxa (Cyanophyta and Pyrrhophyta) were too small to be counted accurately given the sampling procedure used in these microcosms. The impact of acidification on populations during this experiment was quantitatively different from that observed during the Mosquito experiment. Among the chlorophytes (green algae) populations increased in all tanks, with a slower rate of growth occurring in the acidified systems. An increase in chrysophyte populations (including *Dinobryon* spp. and many species of diatoms) was characteristic of the controls; populations of these groups showed little change in the acidified systems (see Figure 15). Cryptomonads increased only in the treatment systems with sediment (see Figure 16). Although periphyton populations were not sampled during this experiment, it was observed that mats of filamentous green algae (principally *Mougeotia* sp.) formed in all treatment tanks following acidification.

DISCUSSION

Sierra Lake Sensitivity

Sensitive areas maps have been prepared in an attempt to pinpoint those regions where lakes may be particularly vulnerable to damage from acid deposition. Such maps were drawn based on a generalized description of bedrock geology[8] and have been refined to include additional diagnostic characteristics of watersheds.[9] In California, an area of sensitivity has been identified in the region of the Sierra Nevada. Other variables, in addition to bedrock geology, needed to be investigated to allow for an evaluation of lake sensitivity in this region of the country.

This study, along with other lake surveys in the subalpine and alpine regions of the Sierra,[2,10] has provided baseline data on lake-water quality. Although the lakes sampled were circumneutral in pH, their alkalinities were low (10-300 μeq/l). It has been established that in assessing lake susceptibility to acid deposition, alkalinity is a more useful measure than pH.[11] This survey has also identified characteristics of Sierra watersheds which are similar to those of sensitive systems located in other areas:[12,13] dilute, oligotrophic waters; small watershed areas; thin, acidic soils; large snow accumulations with a limited period during which melting occurs.

At present, there is no indication that these aquatic systems have been adversely affected by acid deposition. Elevated levels of major cations (Ca, Mg) and trace metals (Al, Mn, Fe), which may indicate progressive ecosystem acidification, have not been observed. It is most likely that chemical changes in Sierra lake water due to acidic deposition would occur during the spring thaw since most precipitation in this region falls as snow. Monitoring of snowpack chemistry and composition of meltwater needs to be carried out in these high-elevation systems so that possible changes can be detected.

Lake Water-Sediment Interactions

An important process to be considered during lake acidification is the role of sediments in maintaining the buffering capacity of lake water. As the system is titrated by acid inputs there are two possible sources of additional alkalinity: weathering reactions and leaching of lake sediments and watershed soils.

The two microcosm experiments described here allow for a comparison of the responses of different lake sediments to a similar acid stress. During both experiments the pH of the acid-treated systems without sediment remained relatively constant at 4.0-4.2; no buffering of the lake water was observed. During the Mosquito experiment the pH increase from 4.0 to 5.2 was the result of neutralization of excess acidity by sediments. This buffering of the lake water may be partially explained by ionic exchange or by weathering reactions:[14]

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{++} + 2HCO_3^-$$

$$MgCO_3 + H_2O + CO_2 \rightarrow Mg^{++} + 2HCO_3^-$$

This mechanism is supported by the observation that concentrations of dissolved calcium and magnesium increased in the systems with sediment following acidification. Such increases in basic cations in acidified lake water have also been reported in field situations.[15]

A different response of the experimental systems to acidification was observed during the Tenaya experiment. The treatment systems with sediment showed little change in pH and no recovery of alkalinity following acid addition. The lack of buffering materials in the sediments may help to explain this response. Little real change in calcium or magnesium concentrations was observed in these treatment systems when compared with the controls. Observed fluctuations among the systems in concentrations of dissolved Ca and Mg were most probably due to contamination of sample bottles or filtration apparatus.

The apparent difference in the ability of these experimental systems to recover alkalinity following an acid stress is the result of gross differences in sediment composition. Although both sediment samples were collected in the littoral zone of the lakes under study they were qualitatively different, particularly with respect to sediment grain size. The Mosquito Lake sediments were fine and silty in texture, while those sediments collected from Tenaya Lake were coarse and gravelly. Future work on characterizing the differences in Sierra lake sediments should include an investigation of cation exchange capacity and mineralogy of these sediments.

In watersheds of the Sierra Nevada it is possible that lake-water buffering by sediments could be a significant process.[2] The large percentage of precipitation falling as snow and accumulating in thick snowpacks may result in relatively little contact between acidic precipitation and basin soils. However, the process of sediment buffering of lake water might be less important during the snowmelt period because of high rates of flow through a lake which may be stratified.

Lake sediments may also serve as a reservoir of leachable trace metals. Increases in metal concentrations have been observed in acidified lakes[13] and in experimental lake cylinders.[16] These increases may be attributed to three sources: direct deposition, leaching from watershed soils or leaching from lake sediments. The metals most often measured at elevated concentrations under conditions of acidification are aluminum, manganese, iron and zinc. Three of these metals (Al, Mn, Fe) were observed to be present at significantly elevated concentrations in the acidified Sierra lake microcosms. The most important of these biologically is Al. Large increases in aluminum concentrations have been documented in lakes and streams affected by acid deposition.[17] Toxic effects of these elevated aluminum levels on fish have been observed in lakes located in Scandinavia and the northeastern U.S.[18]

Trace metal releases from sediments were observed in both microcosm experiments. During the Mosquito experiment dissolved Al increased in both sets of treatments following acidification, with a five-fold increase occurring in the systems with sediment. Increases in Al levels in the systems without sediment may be attributed to leaching from suspended particulates. Tenaya experiment microcosms showed the same type of response to acidification. In the systems with sediment levels of dissolved Al reached 70.0 μg/l. It is interesting to compare these results to _in situ_ cylinder experiments performed at Lake 233 in the Experimental Lakes Area of Canada. Acidification of these littoral systems to pH 5 resulted in an increase in Al from 2 to 10 μg/l, a five-fold increase in concentration.

The potential for increased loading of dissolved, inorganic aluminum in Sierra lake water during acidification is large. It has been demonstrated that under extreme episodes of acid stress (pH <4) that large contributions of Al may be expected from lake sediments. Acidic deposition, in the form of direct deposition or snowmelt, may also leach Al from basin soils. It is difficult to predict at this point which source would be more important because of variability in patterns of deposition, watershed area and lake-water residence time.

Biological Impacts of Acid Deposition

In chronically acidified aquatic systems (pH <5.0), attention has been focused on impacts on fish and macroinvertebrates. However, in regions like the Sierra Nevada, biological changes due to progressive acidification or during acid pulse events might be more readily observed among plankton populations. Biological indicators of acid stress may be identified within a particular zooplankton or phytoplankton group. Community level changes in species composition or biomass may occur during lake acidification. These possibilities were investigated for Sierra lakes using simplified species assemblages. Although the two lakes studied supported different plankton communities, certain similarities in response to acidification were noted.

In general, numbers of zooplankton species were low in the microcosms, a reflection of their abundance and patchiness in such oligotrophic lakes. Rotifers were most abundant in both experiments, the principal genus being Keratella. During both experiments numbers of rotifers in the control tanks increased, perhaps in response to a decreased predation rate. In contrast, populations in the acidified tanks either decreased through time or increased at a slower rate. Such changes in zooplankton numbers have been observed in natural systems undergoing acidification. Of particular importance are changes in species composition and size distribution of zooplankton.[19] Because of the limitations of these microcosms systems such community indices were not amenable to study. These laboratory simulations allowed for the identification of sensitive or "indicator" zooplankton taxa, whose populations may respond to either short- or long-term changes in system pH.

These experimental systems proved most useful in assessing phytoplankton response to a short-term acid pulse. Negative impacts of acidification were observed among the chrysophytes (Dinobryon sp. and diatom species). Cryptomonad populations increased in acidified systems during both experiments. In the Mosquito experiment Pyrrhophyta (dinoflagellates) populations were positively affected and Cyanophyta (blue-green algae) negatively affected by acid additions. Variable changes in chlorophyte (green algae) populations were observed in both sets of systems.

These experimental changes in phytoplankton populations were similar to those observed in acidified lakes,[20] in an artificially-acidified lake (Lake 223)[21] and in tube experiments.[22] In acidified Swedish lakes (pH 5) cryptomonads and dinoflagellates were dominant.[20] In the Experimental Lakes Area whole-lake acidification experiment, an increase in acidity favored Chlorophyta and had a negative impact on Chrysophyta.[21] In Canada, artificially acidified cylinders in Carlyle Lake showed similar community changes; chrysophytes decreased and dinoflagellates (especially *Peridinium* spp.) and cryptomonads became dominant.[22] Another striking similarity between these field observations and the Tenaya experiment was the development of littoral mats of filamentous algae (*Mougeotia* sp.) in acidified systems.

Other indices used to measure phytoplankton community changes, such as biomass or species diversity, have not shown consistent trends with acidification.[22] These parameters are also difficult to measure in microcosm systems due to problems of scale and sampling bias. However, these experimental systems have proved useful in the identification of acid-sensitive phytoplankton taxa and in the observation of community-level shifts in dominance which occur following pH depression.

Use of Microcosms

Investigations of aquatic effects of acid deposition have been conducted using three approaches: 1) comparisons among similar lakes in affected areas, 2) direct acidification of ecosystems or isolated parts of systems (cylinders, limnocorals, stream sections) and 3) acidification of laboratory systems under controlled conditions. During this investigation the latter approach was used for reasons of convenience, replicability and feasibility.[23]

This type of microcosm system has proven useful in studying certain biological and chemical variables which might be altered during short-term, pulsed acidification events. The magnitude of those changes observed in the laboratory might not prove to be realistic due to problems of scale. However, these data have suggested variables which might well be measured during any monitoring program designed to identify aquatic impacts of acidification in the Sierra Nevada.

The applicability of these data to field situations must be qualified. There are certain limitations on the use of microcosms which are generic to this experimental approach.[24,25] These include problems of scale, collection of a representative sample of the system to be studied, and the selection of a process or cycle which can be studied in the laboratory.

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Figure Captions

Figure 1:	Plot of pH vs alkalinity for 26 California lakes: o indicates subalpine, Sierra lakes, ☐ represents lower-elevation reservoirs.
Figure 2:	Changes in microcosm pH ($\bar{y}$; n=3) through time (Mosquito experiment).
Figure 3:	Changes in microcosm pH ($\bar{y}$; n=3) through time (Tenaya experiment).
Figure 4:	Concentrations of dissolved calcium (mg/l) in Mosquito Lake microcosms.
Figure 5:	Concentrations of dissolved magnesium (mg/l) in Mosquito Lake microcosms.
Figure 6:	Concentrations of dissolved calcium (mg/l) in Tenaya Lake microcosms.
Figure 7:	Concentrations of dissolved magnesium (mg/l) in Tenaya Lake microcosms.
Figure 8:	Concentrations of dissolved aluminum (μg/l) in Mosquito Lake microcosms.
Figure 9:	Concentrations of dissolved aluminum (μg/l) in Tenaya Lake microcosms.
Figure 10:	Changes in rotifer populations during the Mosquito experiment.
Figure 11:	Changes in rotifer populations during the Tenaya experiment.

Figure 12: Changes in the population of two species of Keratella (Rotifera) during the Mosquito experiment.

Figure 13: Changes in chrysophyte populations during the Mosquito experiment.

Figure 14: Changes in cryptomonad populations during the Mosquito experiment.

Figure 15: Changes in chrysophyte populations during the Tenaya experiment.

Figure 16: Changes in cryptomonad populations during the Tenaya experiment.

Table 1: Water Quality of Ten Lakes of The Sierra Nevada

	ALTITUDE (m)	pH	ALKALINITY μeq/1	Ca mg/1	Mg mg/1	Al μg/1	Fe μg/1	Mn μg/1
Woods Lake	2510	6.5	178.0	1.90	0.55	11.4	16.0	3.4
Tenaya Lake	2480	6.3	29.0	0.30	0.03	21.2	4.6	4.5
Mosquito Lake	2440	6.9	62.0	0.35	0.09	18.2	50.6	4.7
Kirkwood Lake	2340	7.1	104.0	0.76	0.24	5.4	29.5	0
Angora Lake	2270	6.6	41.8	0.20	0.06	30.9	12.9	1.3
Echo Lake	2260	6.7	56.0	0.35	0.09	4.9	2.2	3.4
Huntington Lake	2120	6.6	150.0	0.58	0.12	6.1	7.3	2.7
Haven Lake	2050	6.7	87.0	0.30	0.36	26.4	3.5	1.1
Forebay Lake	2000	6.6	128.0	0.60	0.15	14.8	5.0	10.4
Fuller Lake	1630	6.6	192.0	1.50	0.42	12.7	19.2	12.0

PHYTOPLANKTON TAXA	CONTROLS	CONTROLS WITH SEDIMENT	TREATMENTS	TREATMENTS WITH SEDIMENT
Chlorophyta (greens)	+	+	-	-
Chrysophyta (golden)	0	0	--	-
Cyanophyta (blue greens)	0	0	--	0
Pyrrhophyta (dinoflagellates)	-	-	0	++
Cryptophyta (cryptomonads)	--	--	++	++

Table 2: Mosquito Experiment:
Changes in populations of phytoplankton taxa over the six-week experimental period. Changes in numbers per 5-ml sample are designated as follows: ++, large increase; +, small increase (less than one order of magnitude; --, large decrease; -, small decrease; 0, no change.

PHYTOPLANKTON TAXA	CONTROLS	CONTROLS WITH SEDIMENTS	TREATMENTS	TREATMENTS WITH SEDIMENT
Chlorphyta (greens)	+	+	+	+
Chrysophyta (golden)	+	++	0	0
Cryptophyta (cryptomonads)	0	0	0	++

Table 3: Tenaya Experiment:
Changes in populations of phytoplankton taxa over the seven-week experimental period. Changes in numbers per 5-ml sample are designated as follows: ++, large increase; +, small increase (less than one order of magnitude); --, large decrease; -, small decrease; 0, no change. Cyanophyta (blue-greens) and Pyrrhophyta (dinoflagellates) populations were too low to be accurately counted.

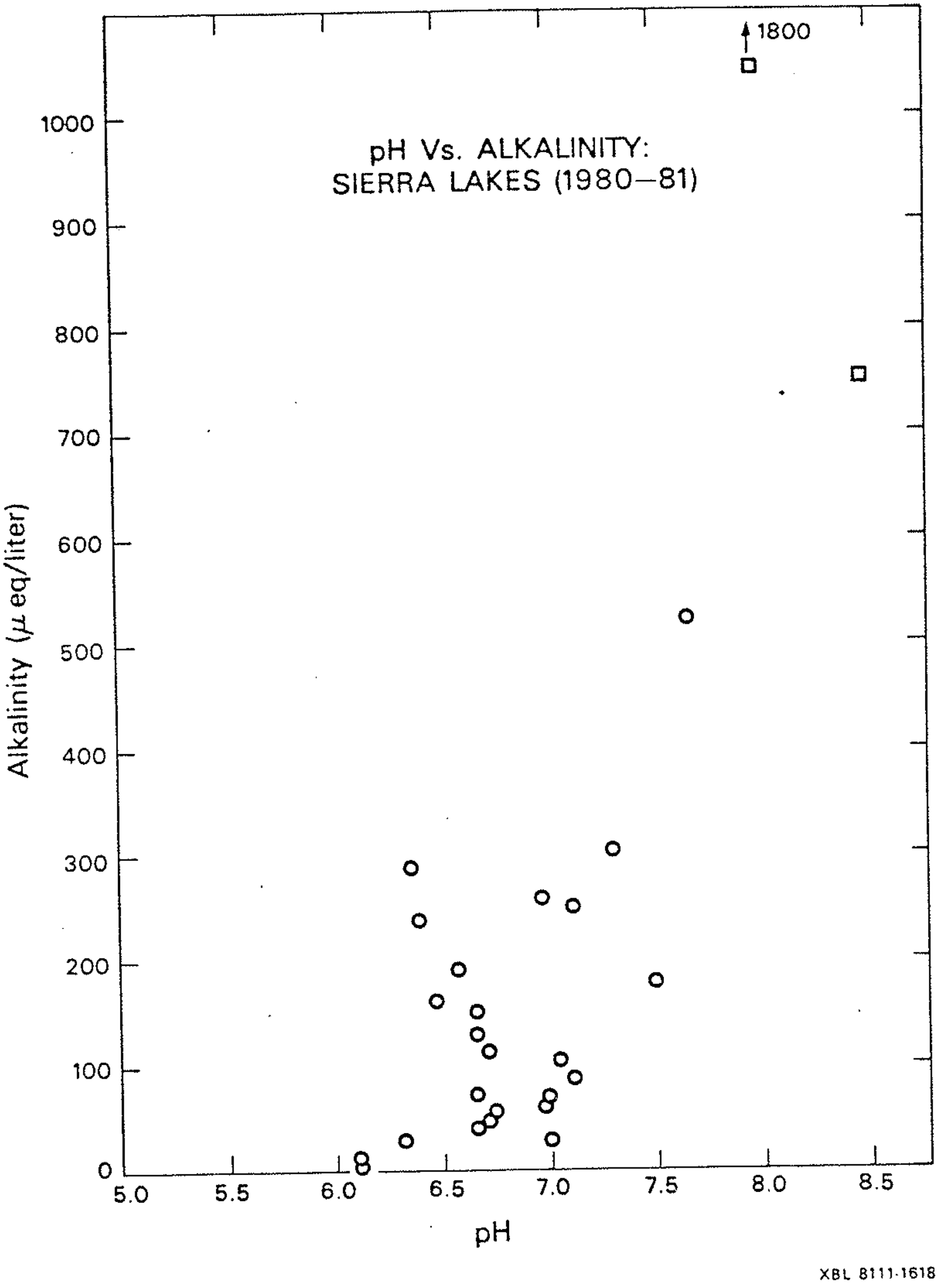
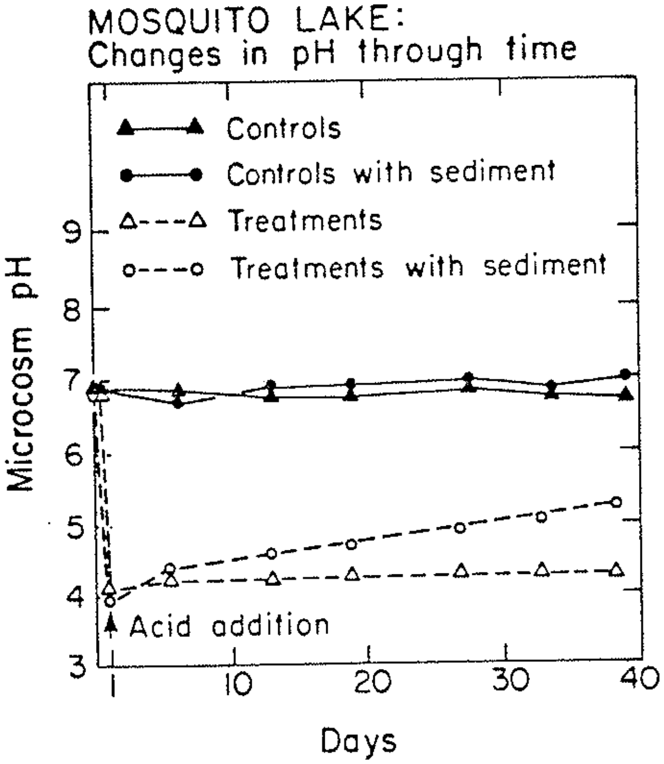

pH Vs. ALKALINITY:
SIERRA LAKES (1980–81)
1800
Alkalinity (μ eq/liter)
0
100
200
300
400
500
600
700
800
900
1000
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
pH
XBL 8111-1618

Figure 1



XBL 811-22A

Figure 2

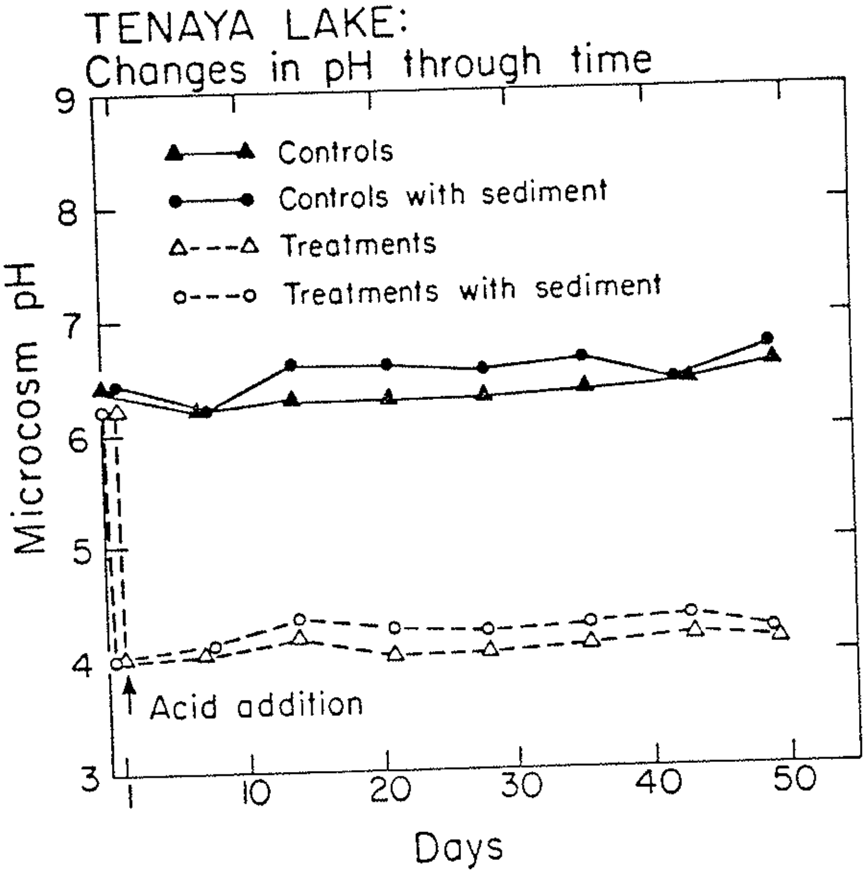


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Figure 3

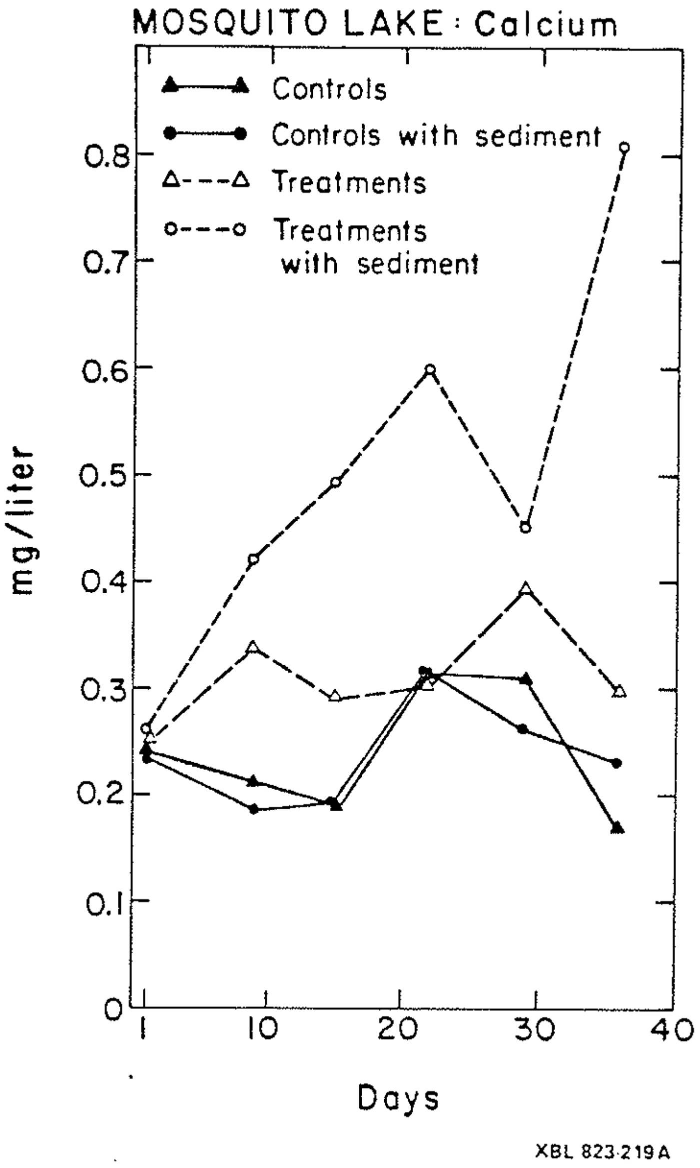
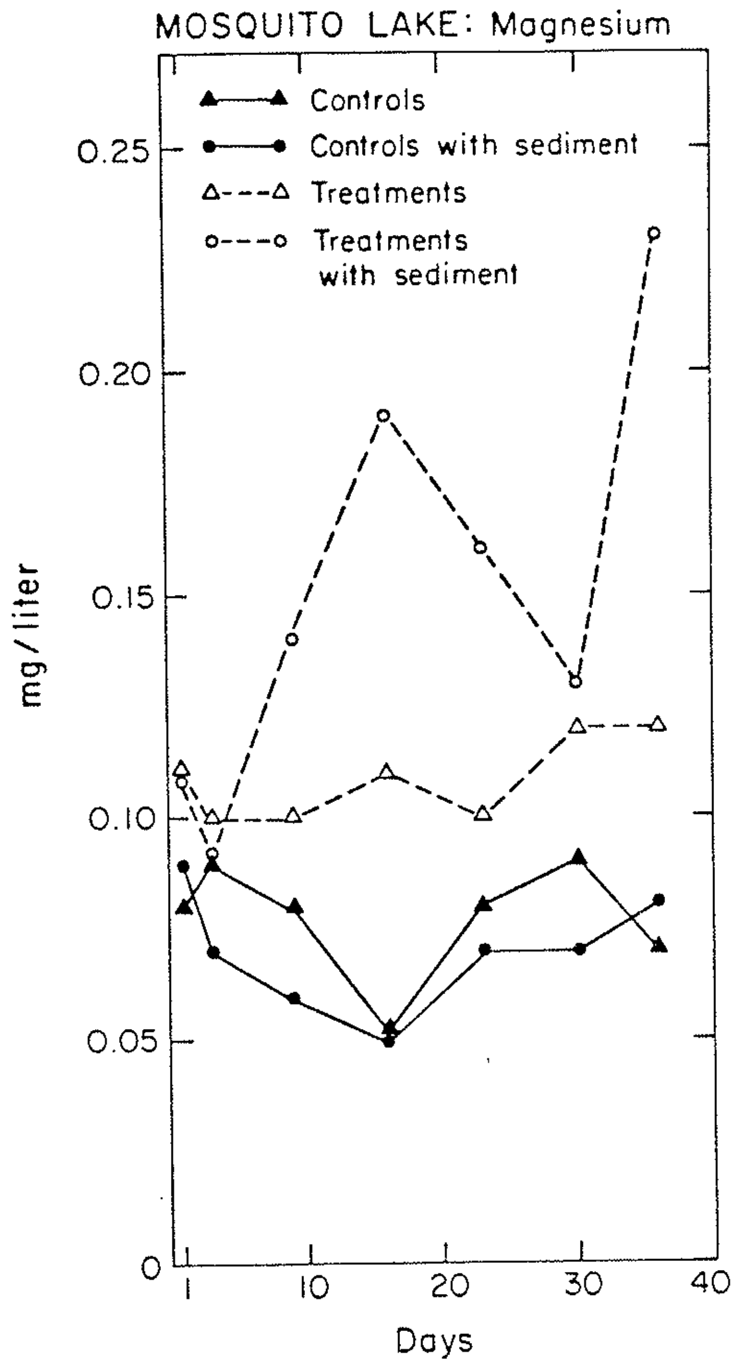
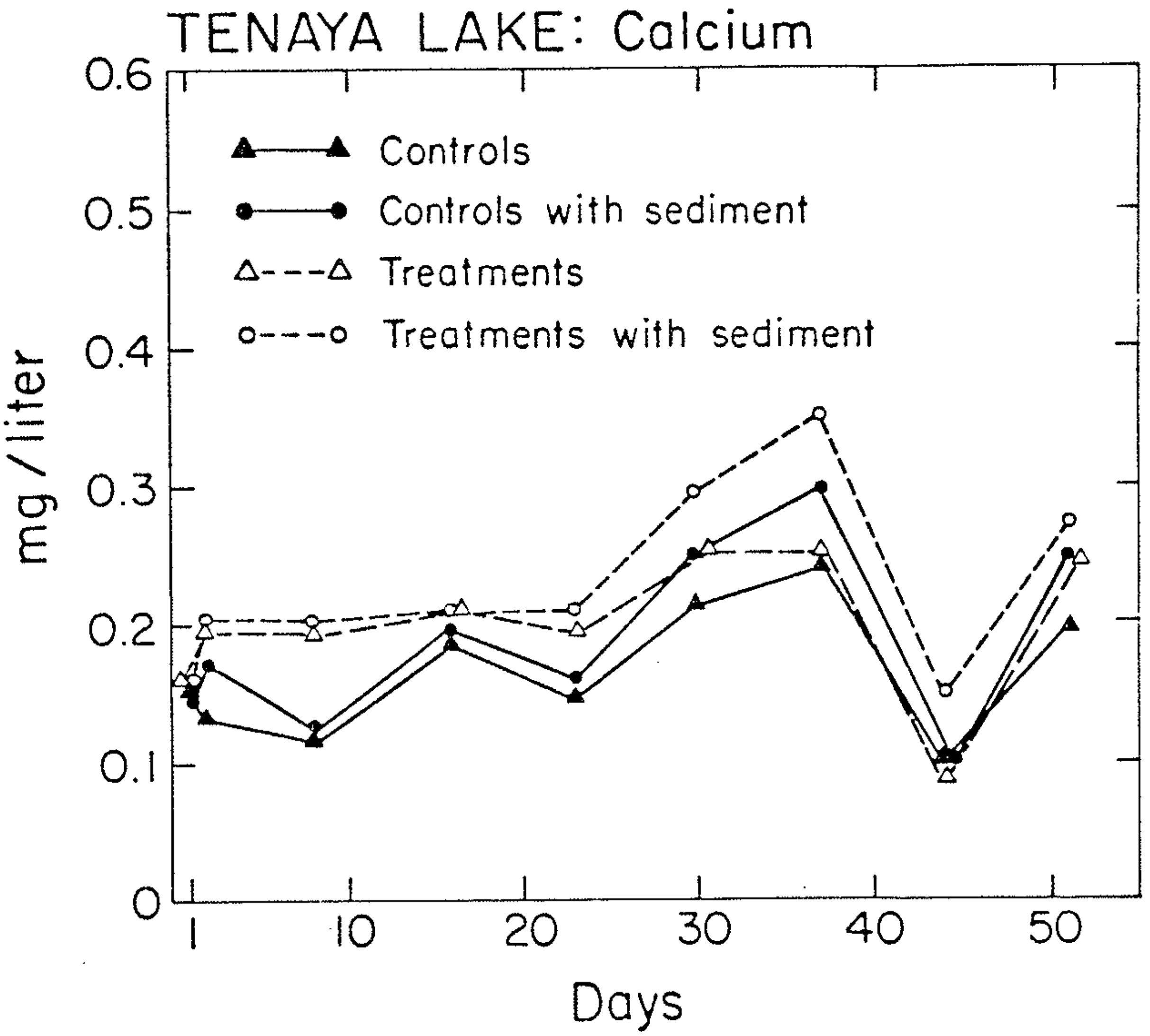

MOSQUITO LAKE: Calcium
Controls
Controls with sediment
Treatments
Treatments with sediment
mg/liter
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Days
1
10
20
30
40
XBL 823-219A

Figure 4



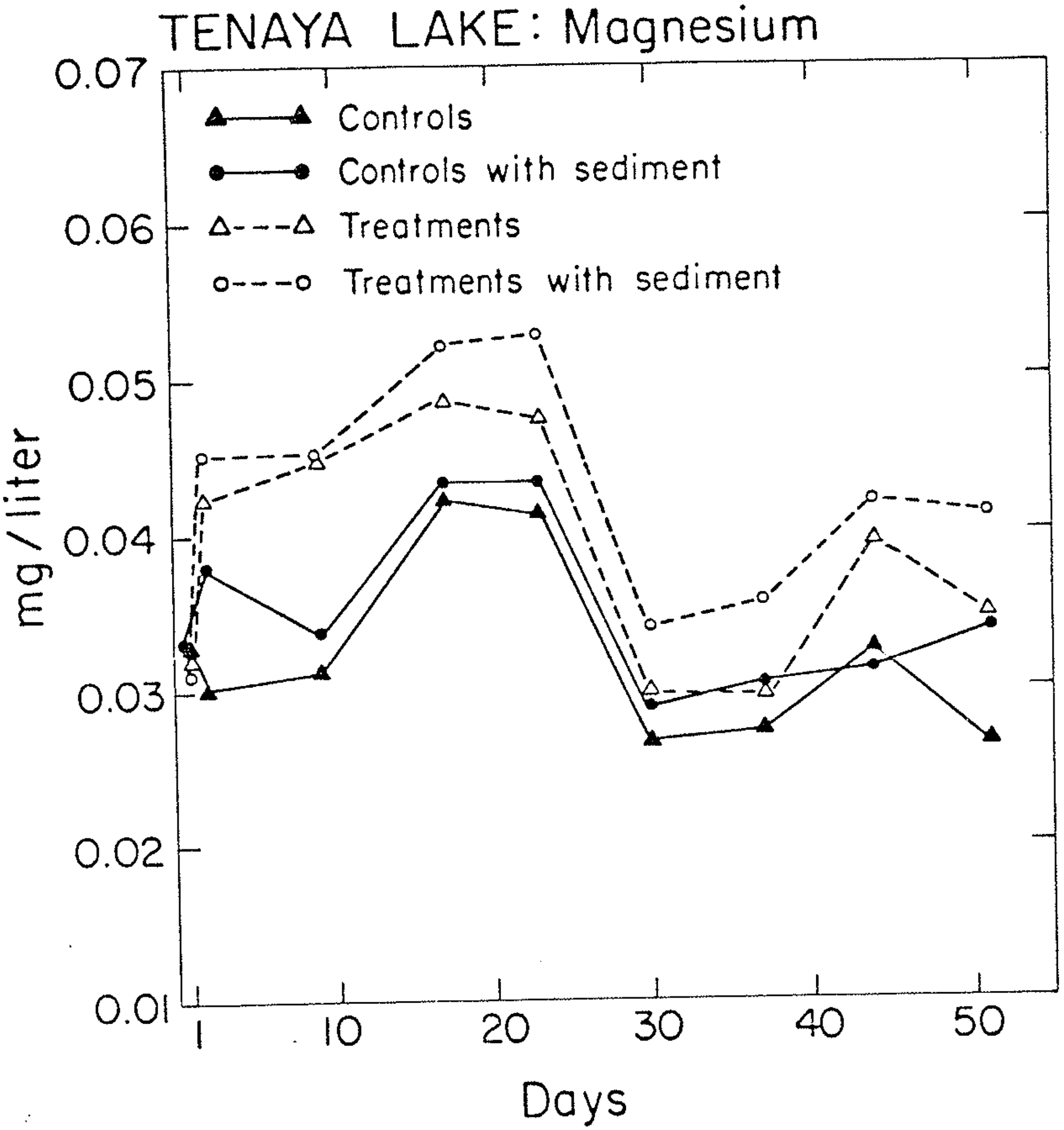
XBL 825-603

Figure 5



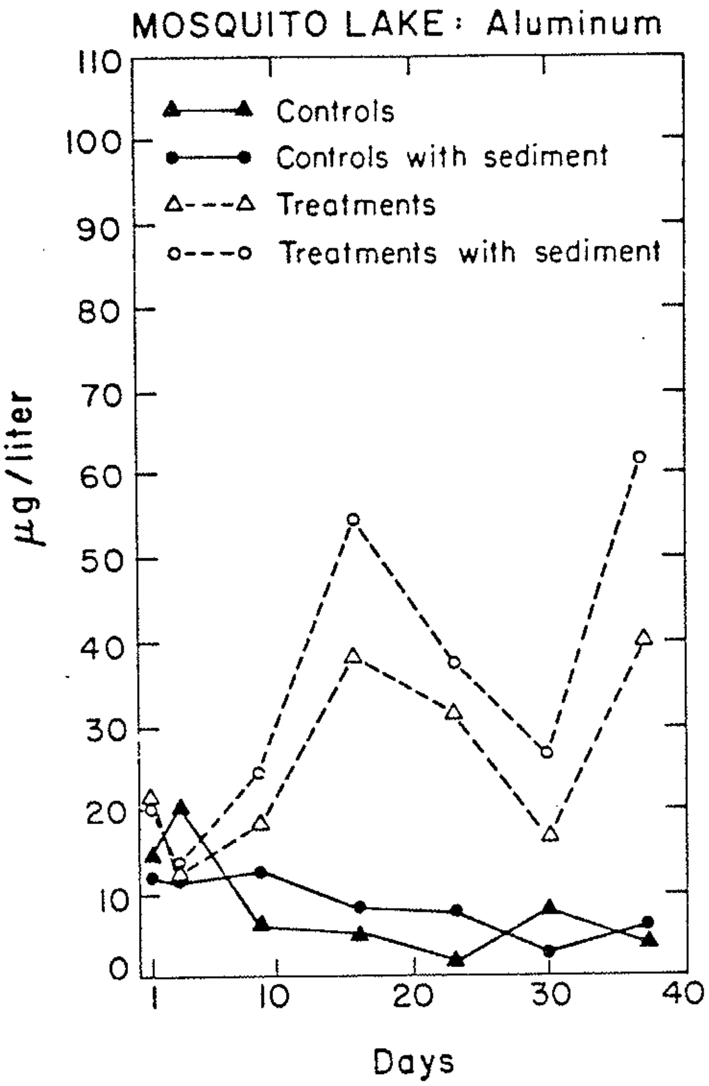
XBL 823-218 A

Figure 6



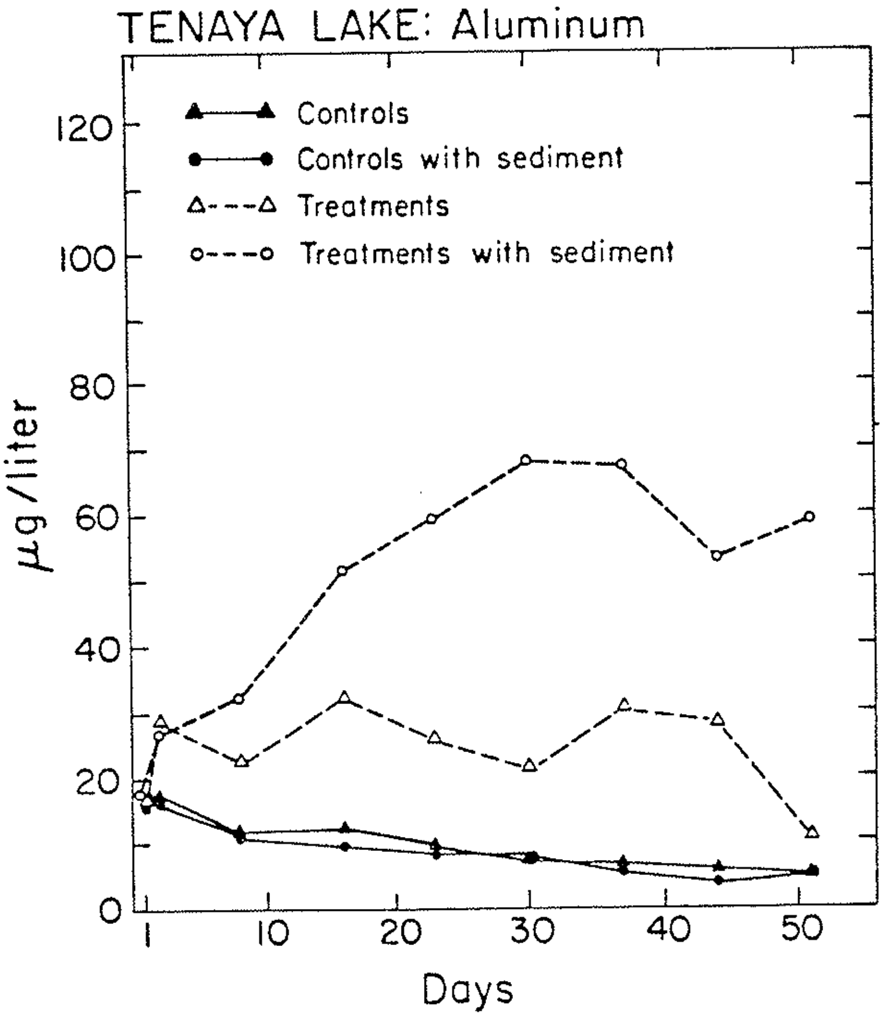
XBL 825-675

Figure 7



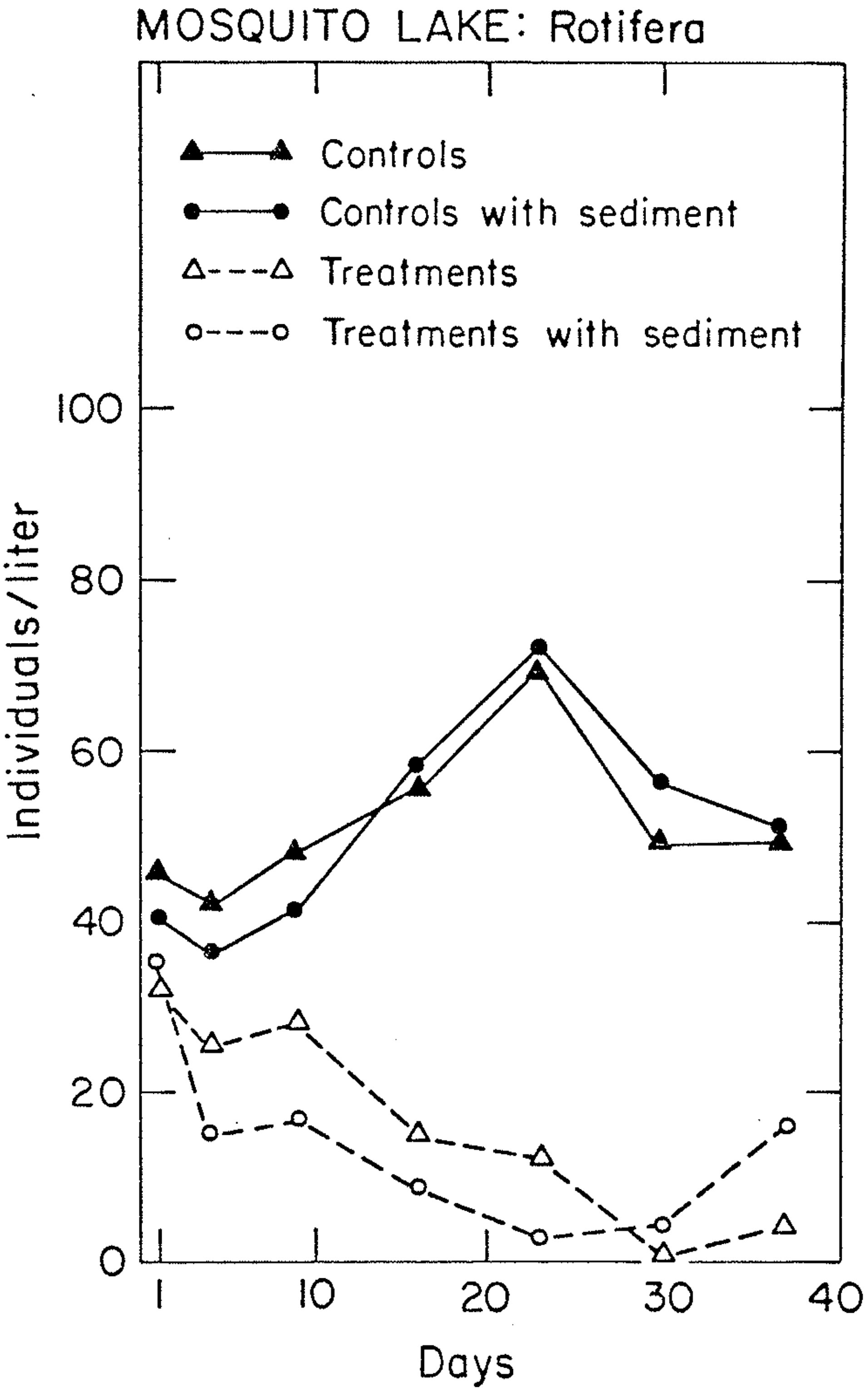
XBL 823-206 A

Figure 8



XBL 823-205 A

Figure 9



XBL 823-222A

Figure 10

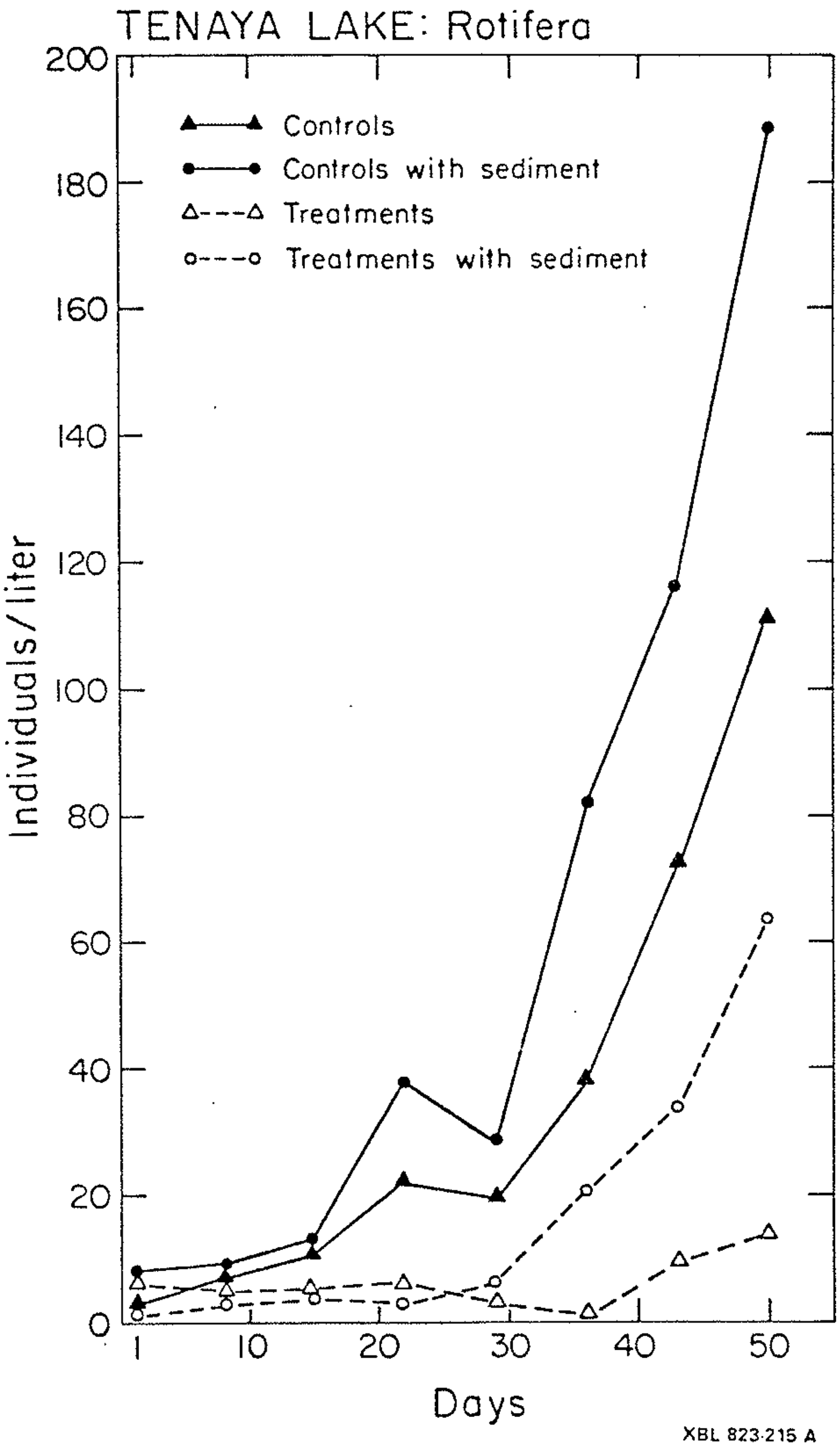

TENAYA LAKE: Rotifera
Controls
Controls with sediment
Treatments
Treatments with sediment
Individuals/liter
200
180
160
140
120
100
80
60
40
20
0
1
10
20
30
40
50
Days
XBL 823-215 A

Figure 11

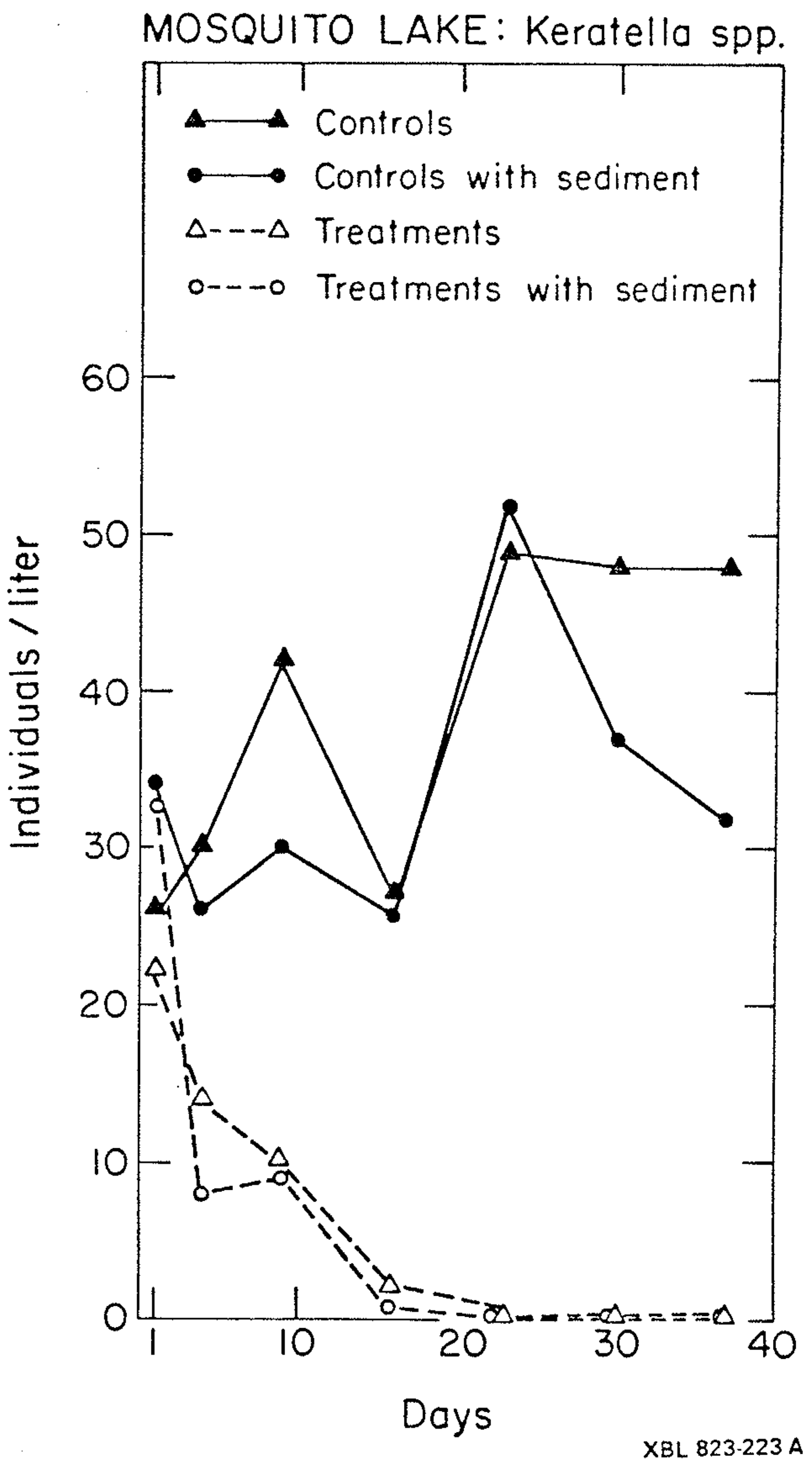
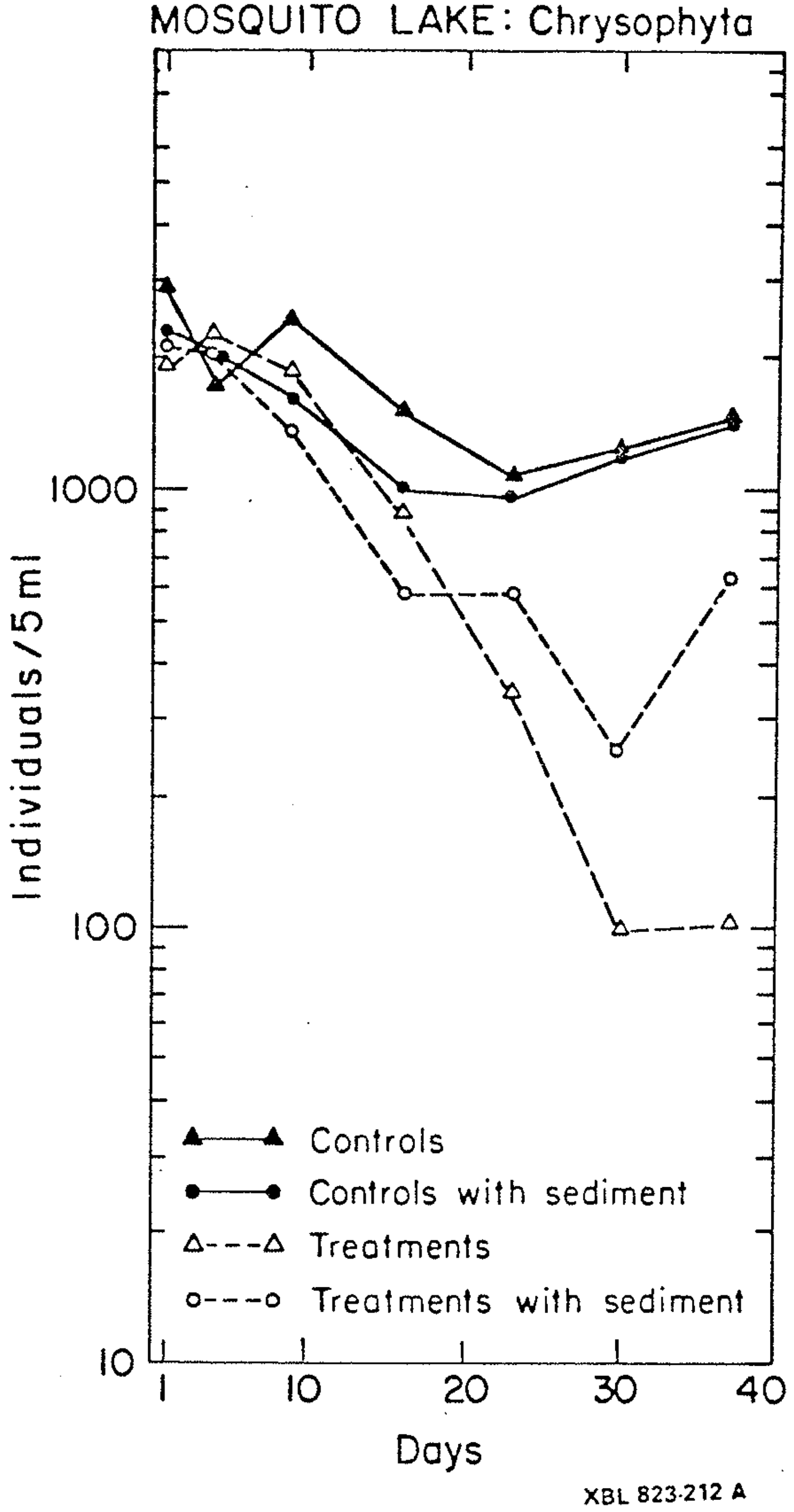
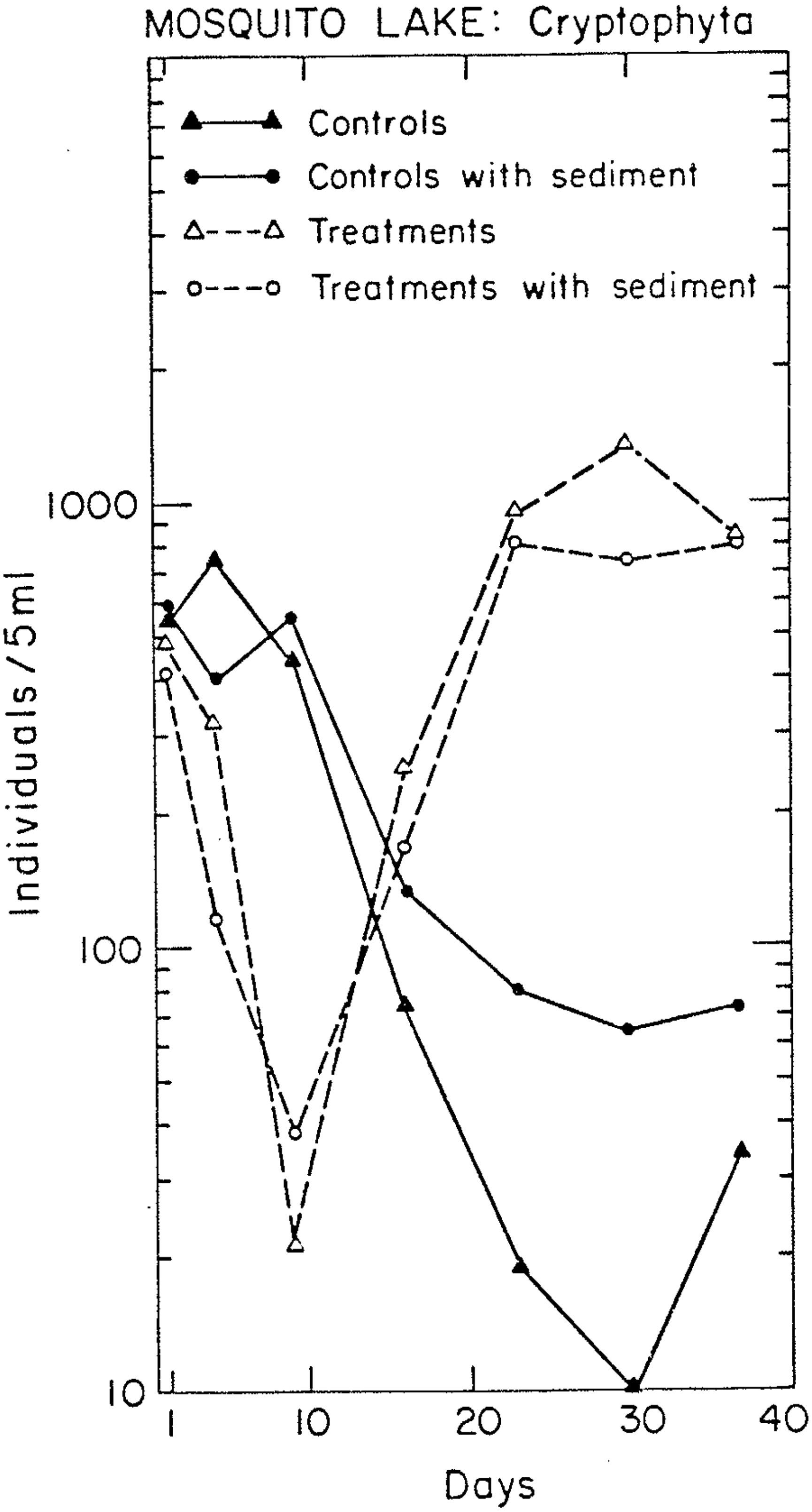

MOSQUITO LAKE: Keratella spp.
Controls
Controls with sediment
Treatments
Treatments with sediment
Individuals / liter
0
10
20
30
40
50
60
1
10
20
30
40
Days
XBL 823-223 A

Figure 12



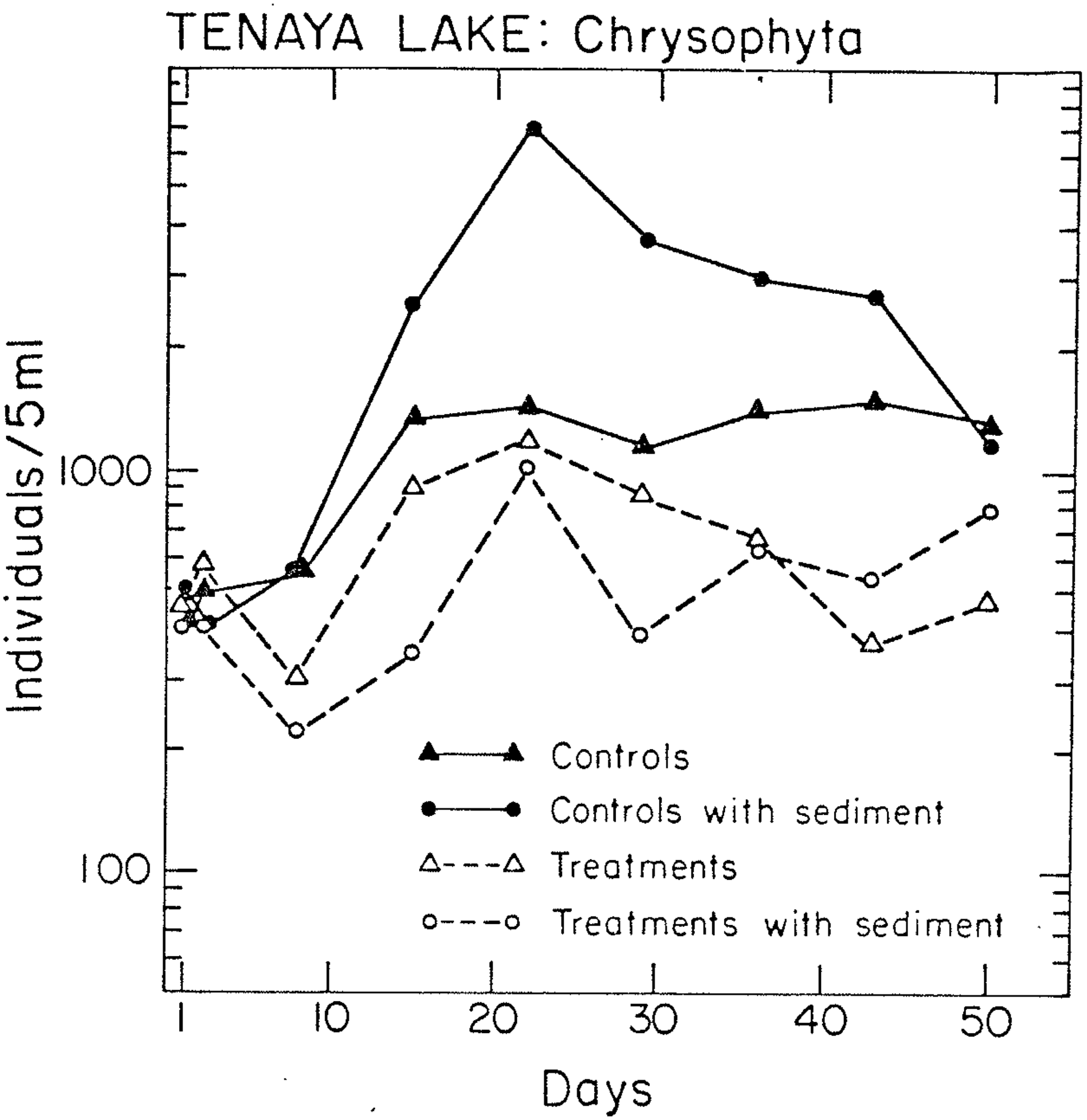
MOSQUITO LAKE: Chrysophyta
Individuals/5 ml
1000
100
10
1
10
20
30
40
Days
Controls
Controls with sediment
Treatments
Treatments with sediment
XBL 823-212 A

Figure 13



XBL 823-211 A

Figure 14



XBL 823-197 A

Figure 15

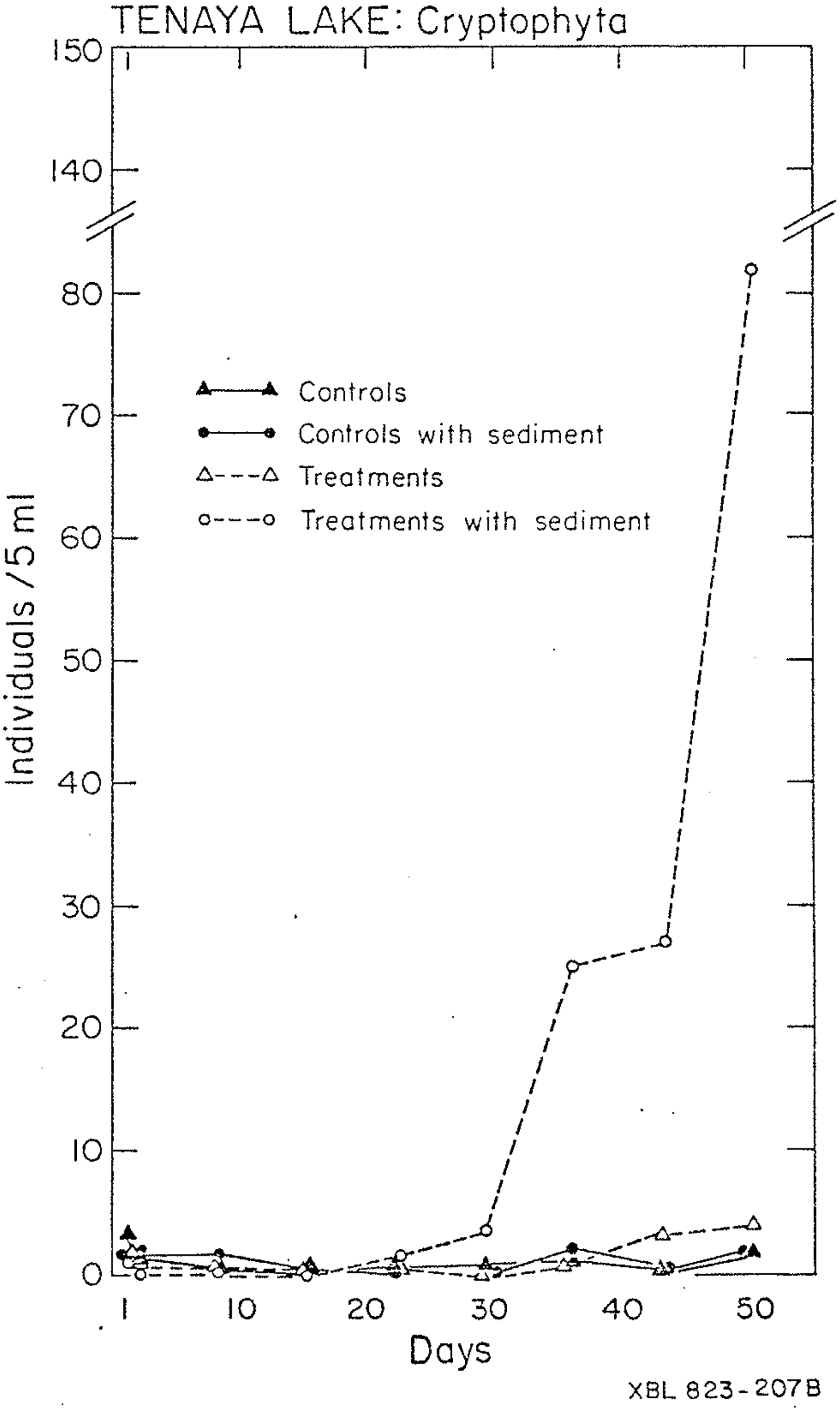

TENAYA LAKE: Cryptophyta
Individuals /5 ml
150
140
80
70
60
50
40
30
20
10
0
1
10
20
30
40
50
Days
Controls
Controls with sediment
Treatments
Treatments with sediment
XBL 823-207B

Figure 16